Radiochemical studies of ion-exchange

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Randle, K. (1966) Radiochemical studies of ion-exchange. Doctoral thesis, Durham University.

RADIOCHEMICAL STUDIES
OF ION-EXCHANGE

THESIS

presented in candidature for the degree of

DOCTOR OF PHILOSOPHY

in the

UNIVERSITY OF DURHAM

by

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MEMORANDUM

Part I of the work described in this thesis was carried out in the Londonderry Laboratory for Radiochemistry, Durham University, Durham, between October 1963 and October 1964 under the supervision of Mr. G. R. Martin, Reader in Radiochemistry. Part II was carried out partly in the Londonderry Laboratory for Radiochemistry, Durham University, Durham and partly in the University Chemical Laboratory, Canterbury, Kent, between October 1964 and December 1966 under the supervision of Dr. S. J. Lyle, Lecturer in Chemistry.

The thesis contains the results of some original research by the author and no part of the material presented has previously been submitted by the candidate for a degree in this or any other university. Where use has been made of the results and conclusions of other authors in the relevant studies, care has been taken to ensure that the source of the information is always clearly indicated, unless it is of such general nature that indication is impracticable.

K. Randle

ABSTRACT

The first part of the work described in this thesis deals with the preparation of uniformly thin sources suitable for the counting of weak β-emitting radioisotopes. The method developed involved the preparation of a thin sulphonated polystyrene layer supported on a thin VYNS film on which cations were deposited by ion-exchange. The β-counting efficiency of the sources in a 4 Π β-proportional counter was determined by coincidence counting. Autoradiography was used to determine the uniformity of the sources. Evaporated gold on the VYNS film support was found to promote the surface diffusion of mercury and investigations led to a procedure applicable to the measurement of the counting efficiency of β-emitting mercury isotopes; a method for the calibration of a proportional counter used in the determination of the $Tl^{203}(n,p)Hg^{203}$ cross-section was thereby evolved.

In Part II preliminary experiments were directed towards finding a suitable "liquid ion-exchanger" for an investigation of ion-exchange behaviour, particularly at high electrolyte concentrations; mono-(2-ethylhexyl) phosphoric acid (H_2MEHP) in toluene was eventually selected.

The distribution of Y^{91}, $Eu^{152 + 154}$, Gd^{153}, Ce^{144} and Am^{241} between H_2MEHP and various aqueous electrolyte systems was studied and separation factors calculated from the distribution coefficients. A study of the effect of mixing H_2MEHP with di-(2-ethylhexyl)-(HDEHP) and tri-n-butyl esters of phosphoric acid showed the presence of a synergistic effect.

Investigations were carried out in order to determine why H_2MEHP behaved differently from di- and tri-alkyl phosphoric acid esters. An estimate of the degree of polymerisation of H_2MEHP in toluene was made from the distribution of Y^{91} between aqueous solutions loaded with yttrium ions and H_2MEHP; this revealed a significant difference between the degree of polymerisation of the mono- and di-alkyl esters. Other experiments on the extraction of water and mineral acids coupled with infra-red studies of the ester phases revealed further differences between the two esters. The data thus obtained permitted the construction of a model to explain salient features in the behaviour of H_2MEHP in toluene as an extractant.

PART I

SURFACE ION-EXCHANGE IN THE PREPARATION OF THIN, UNIFORM RADIOACTIVE SOURCES

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CHAPTER I

INTRODUCTION

The ability to determine the absolute disintegration rate of radionuclides is important in several types of experiments. This is particularly true of experiments designed to measure nuclear constants and reaction cross-sections. Absolute disintegration rates may also be required in the study of the efficiency of radiation to produce ionisation or to initiate secondary reactions. Neutron fluxes may be monitored from a knowledge of the disintegration rate of radioactive nuclides. Since neutrons are non-ionising in their interaction with matter, absolute standardization of such sources cannot be carried out directly. However, if a neutron source is surrounded by a suitable substance which captures neutrons to produce a radioactive nuclide, when this activity has built up to equilibrium the number of atoms disintegrating per unit time is equal to the number of neutrons captured. The induced activity may then be equated to the neutron flux provided that other relevant data are available(1). It is also possible to determine the decay constant of long lived isotopes by using the relationship

$$^{dN}/_{dt} = N\lambda$$

where N equals the number of atoms of a given mass and λ is the decay constant. N may be found from mass spectrometric studies and if $^{dN}/_{dt}$ can be determined absolutely, then λ can be calculated.(2) Knowledge of the absolute disintegration rate of a source is also of importance in radiobiology where doses of radiation administered to patients apparently must often be accurately known.

The need for absolute methods of measurement was recognised very early in the history of radioactive techniques and in 1910 the Congress of Radiology and Electricity, held in Brussels, arranged for the preparation of international standards of radioactivity. Since then a large number of methods of standardizing radioactive materials have been developed and several methods are in current use in various laboratories throughout the world. The actual method adopted may be influenced by the type of radiation emitted by the nuclide under observation, although some methods are of greater applicability than others. Of the methods currently used probably the most important are (a) defined solid angle counting, (b) calorimetry, (c) 'loss of charge methods', (d) ionisation chambers, (e) 4Π and coincidence methods. Each of these counting methods has its advantages and disadvantages and often, for intercalibration purposes, several different methods are used in the standardization of a given nuclide.

Formerly, defined solid angle detectors were one of the principle means of determining disintegration rates,(3,4,5) though their use in recent years has greatly decreased, especially for the standardization of β-emitting nuclides. The principal of the method is that a source is placed at a given distance from a counter such that it subtends a well-defined solid angle, Ω, at the counter window. If particles are emitted isotropically at a rate, N_0, per unit time, then the counting rate should be

$$N = \frac{N_0 \; \epsilon \; \Omega}{4\Pi}$$

where ϵ is the intrinsic efficiency of the detector for a given type of radiation. A standardised arrangement is used in practice.

The method, however, suffers from inherent uncertainties introduced by the many corrections which must be applied; they include (i) an integration over the source area in order to obtain the effective solid angle if the source is not sufficiently far from the detector, (ii) absorption in the counter window and the air, (iii) scattering and absorption by the source material, and (iv) scattering by the source backing. The correction for absorption in the counter window and the air is made by extrapolation of the observed absorption curve to zero absorber thickness, although this is not valid if very soft radiation is present. The use of a windowless, demountable counter, which may be evacuated and then filled with counting gas at low pressure eliminates window absorption and reduces air absorption.(6) The finite source thickness causes self-absorption and also scattering of particles. Scattering is greater for obliquely emitted particles than for ones emitted normal to the source plane and this tends to increase the number leaving perpendicular to the source.(7) This forward scattering compensates and may outweigh absorption effects. The source backing tends to increase the counting rate. The value depends on the atomic number and the thickness of the backing, but reaches a saturation value at a given thickness depending on Z. The correction is usually estimated empirically using standard source mounting procedures.(8) For β-emitters, all these corrections are dependent on the shape of the β-spectrum and they are different for positrons and negatrons. Thus, the whole procedure is subject to considerable doubt. However, in the standardization of β-emitters, intercomparisons indicate that this method gives an overall accuracy of approximately ±5% for β-particles of energy greater than 1 MeV.

Calorimetric methods for determining disintegration rates are amongst the oldest methods of standardization, and were used by the earliest workers in the field of radioactivity. Thus CURIE and LABORDE(9) in 1903 used a Bunsen ice calorimeter to determine the energy release from radium. The method involves the determination of the rate at which energy is liberated by a radioactive source. If the energy release is determined calorimetrically then the ratio of this energy, E, to the average energy released per disintegration, $\bar{e}$, gives the disintegration rate N, according to the relation

$$N = {}^{E}/_{\bar{e}}$$

For β-emitters, $\bar{e}$, may be determined accurately from a knowledge of the decay scheme, the β-spectrum and the absorption of energy in the apparatus. Calorimeters have been designed to measure the rate of energy dissipation by α-emitters,(10) β-emitters(11) and more recently γ-emitters.(12) These methods are particularly useful for low energy β-emitters.

The measurements are performed (a) under isothermal conditions where the calorimeter remains at a constant temperature, and a change of state (usually the evaporation of a liquid) is measured, or (b) under adiabatic conditions, where a change of temperature is recorded.

The first isothermal measurements were made by CURIE and DEWAR,(13) using the evaporation of liquid nitrogen and liquid hydrogen to measure the heat dissipated by α- and β-particles from radium.

Microcalorimetric techniques have increased the sensitivity of the method, which has been used to determine the disintegration rate of P^{32}, using the evaporation of liquid nitrogen and a source of 24mc. Allowing for a Bremsstrahlung correction, the results agree within ± 1.5% of those obtained by counting methods.(14) The absolute disintegration of tritium has also been measured in this way, again using the evaporation of liquid nitrogen.(15) CANNON and JENKS(16) have determined the disintegration rate of Au^{198}, though there was some doubt as to the disintegration scheme. The method has been improved by the use of liquid helium in place of nitrogen. Using lead and heavy alloy calorimeters, MYERS determined the disintegration rate of a 2-curie source of Co^{60} with an estimated error of less than 1%.(17)

The adiabatic method is sometimes advantageous where one has a very low heat input, since it is possible to control the external conditions with greater accuracy.

LECOIN(18) has described an apparatus for adiabatic measurements. Here the calorimeter is suspended inside a large sealed, metal sphere, which is in turn immersed in water. The temperature of the bath oscillates above and below that of the calorimeter in a regular, cyclic fashion, and the temperature difference between the calorimeter and the container is measured with a thermocouple connected to the calorimeter and its container walls. This method was also used by SANIELEVICI and NAGL.(19) BAYLEY(20) has determined the disintegration rate of P^{32}. In his work a differential calorimeter was used, one unit containing the source and the other heated externally; their thermal balance enabled the disintegration rate to be found. Using 116mc of P^{32} an accuracy within ± 2% of counting methods was claimed. A differential calorimeter has also been used to measure γ-emitters.(21)

The main disadvantage of these methods is that large sources are required for accurate work, owing to the small rate of energy dissipation. Their principle use is in the determination of either N or $\bar{e}$, when one or the other is known from other methods.

'Loss of charge methods' are based on the fact that a β-particle is merely a high velocity electron, carrying a negative electronic charge of 1.602 x 10^{-19} coulomb. Thus, as a source emits electrons so it loses charge and by measuring the loss of charge the disintegration rate can be found. The main difficulty is in preventing the large number of secondary electrons emitted along with the β-particles from being counted. Once again the method is of long standing and has been known since 1903, though it has never been widely adopted for standardizing sources.

FAILLA et al.(22) used this method to determine the disintegration rate of a source of P^{32}. The source was supported on a thin aluminium foil inside an evacuated chamber, to prevent any charge being formed due to air ionisation. The current was measured by a null method with a Lindermann electrometer. A grid was used to repel secondary electrons back to the source. The accuracy was estimated at ± 5% for a 0.1mc of P^{32}. A similar procedure was adopted by CLARKE.(23)

An interesting modification of this procedure was used by GROSS and FAILLA(24) and later by ENGELMANN(25) to determine disintegration rates. It involved the use of two plain electrodes mounted parallel to and close beside one another in a vacuum container. The source was put on one of the electrodes and back-scattering from this electrode was compensated for by reflections from the other. A magnetic or electric field was used to eliminate secondary electrons. For sources of Sr^{90} - Y^{90}(0.1mc) and P^{32}(50-90μc), ENGELMANN found that the results agreed well with 4Π measurements. When S^{32} was used, however, the results were found to be affected by the atomic number of the electrode material, which had thus to be carefully chosen. This method has also been investigated by KEENE.(26) Again the method suffers from the large sources that are required for reliable measurements.

Ionisation chambers are rarely used as primary methods for standardizing sources. They are based on the observation that radiation, on passing through a gas, produces ionisation within that gas. Continuous current ionisation chambers are used, in which all the charges produced by the radiation in a given gas volume are collected by two electrodes. The resulting current, assuming equilibrium conditions, is equal to the rate of production of the charge by ionisation. Thus, if the efficiency of ionisation of the radiation is known, the disintegration rate can be found. Absolute determinations of dose rate, that is quantity of radiation, has been measured,(27) and by applying the methods of MARINELLI et al.(28) the disintegration rate may be determined.

For β-particles, ionisation methods can be used when a uniformly distributed source is employed. The method depends on the fact that the distribution of fast electrons in a medium is not disturbed by the introduction of a small cavity into it.(29) In practice the source is usually a solution with an air cavity in the form of an ionisation chamber in it. The charge collected by the ionisation chamber is then proportional to the energy dissipated, which is in turn proportional to the disintegration rate and the energy of the β-particles. A modification of this method was used by LOEVINGER,(30) who measured the rate of ionisation at the boundary of a semi-infinite radioactive medium rather than in a cavity within the medium.

For nuclides emitting γ-rays according to a known disintegration scheme this method offers an easy way of standardising a source. Here ionisation chambers of finite volume with air-equivalent walls are used so that the flow of radiation is not affected by the cavity.(31) Activities of a few millicuries are necessary for reliable results with γ-chambers. The whole field has been reviewed by GRAY.(32)

A 4Π solid-angle slit ionisation chamber has been developed.(33) It consists of two concentric aluminium spheres, with the inner sphere as collecting electrode and the source at its centre. An error within 7 to 8% for sources ranging from 10^{-4} to 10c is claimed for this chamber.(34)

To-day, by far the most widely used method for the standardisation of sources is that of 4Π-counting, especially 4Π, β-gas counting, which is particularly useful for β-emitters with maximum energy greater than 300 KeV.(35)

Systems which achieve a geometry of 4Π steradians can be produced in a number of ways. Thus, one may have a gaseous source as part of the gas filling of a counter. Alternatively, the source may be dispersed in a phosphor of a scintillation unit, or sandwiched between two solid phosphors. Finally it may be achieved by placing the source between two 2Π proportional counters. It is this latter method which has been used in the present work and the one which has received most attention to date.(36,37,38,39)

The basis of 4Π β-proportional (or Geiger) counting is that since a 4Π geometry is used if the counter system can be made to respond to every particle leaving the source then the counting rate will correspond to the disintegration rate. This will be true even though secondary radiations accompany the primary disintegration provided that the time interval between the primary and secondary radiations is within the resolving time of the apparatus. This latter condition is relatively easy to apply using the associated electronic equipment.

In principle, therefore, this is the simplest method for the absolute counting of β-and α-emitters and can be used for electron capture nuclides provided that certain additional information is available.

The first gas counter which approached 4Π geometry was that of SIMPSON.(40) This was a Geiger-Muller (G-M) counter, and had a short plateau, high background count and operated only at high voltages. The first true 4Π counter was designed by L. MEYER-SHUTZMEISTER and reported by HAXEL and HOUTERMANS.(41) Later a 4Π G-M counter was described operating with an argon-alcohol filling and giving a much reduced background;(42) several other 4Π G-M counters followed.(6,43,44) The first 4Π proportional counter was reported by BORKOWSKI(45) and a cylindrical 4Π counter was described by CHARPAK and SUZOR.(46) Later, more detailed investigations revealed the inherent difficulties in the method, particularly with respect to absorption of particles in the source mount and in the source itself.(36,37,38,39,47,48,49,50) Various source backings and improved methods of source preparation were discussed by LE GALLIC(51) and MARTINSSON.(52) Later, a method of eliminating self-absorption by weak β-particles was developed.(53)

There are two important considerations to be taken into account when using this method to determine disintegration rates. The first is to produce a system which responds to every charged particle entering the sensitive volume of the counter and secondly to prepare the active sample in such a way that every particle emitted does in fact enter the sensitive volume of the counter. It has been shown that a plot of counting rate against applied counter voltage shows a long plateau region for α and β-particles of widely varying energy, indicating a response probability of the counter, i.e. the probability that a particle entering the counter triggers the recorder, close to unity.(36,54,55) Other variables, such as the discriminator bias, source location, counter gas purity, field strength at the source and the counting rate can also be shown to be adjustable to give a response probability of unity(36,55,56) even for activities emitting only very weak particles such as Ni^{63} and S^{35} and for source diameters up to at least one centimetre.

The other consideration, and by far the most important for most practical counting systems, is that of absorption of the radiation in the source mount and self-absorption of the source. The object is to ensure that as high a proportion of the radiation as possible enters the counter system and to be able to estimate the fraction that does not emerge from the source and its support.

With present techniques the problem of absorption in the source support is the lesser of the two. Several methods have been published for the fabrication of thin, organic films capable of supporting a radioactive source.(47,49,55,57,58,59,60,61) However, by far the most widely used source support is a film of VYNS (a polyvinylchloride-acetate copolymer) which can be safely used even down to a thickness of 3 or 4μgm/cm².(58) If required, thicker films are readily prepared from several layers of film.

These organic films suffer from the disadvantage that they are non-conducting, and although SELIGER and CAVALLO(48) originally claimed that such films produced no loss in efficiency, it is now generally accepted that for reliable results the films must be made conducting, a view later confirmed by the first mentioned of the above authors.(49)

The source mounts are usually made conducting by the evaporation of a thin layer of a suitable metal on to the film. The metal usually employed is gold, although metals of the platinum group, and particularly palladium, have been recommended, since these absorb less infra-red radiation and are thus less liable to cause rupture of the film during heat-drying of a source.(62) There is some disagreement concerning the thickness of gold required for reliable results and estimates vary from 5 to 30μgm/cm^2.(47,61,62) The majority of workers appear to consider that between 5 and 10μgm/cm^2 is adequate.(36,55,62)

Absorption in these films (with a total thickness between 10 and 30μgm/cm^2) has been shown to be very small even for very soft β-particles.(37) However, in the most accurate work a correction must be made for absorption in the source support. Three procedures have been suggested for determining this correction:

(i) the "sandwich" procedure, used by HAWKINGS et al(47) where the counting rate is determined with and without a film over the source identical to the support, the reduced count in the former case being used to correct the absorption in the latter;

(ii) a mathematical relationship based on 2Π, 4Π single and sandwiched film counting rates(48,49,63)

(iii) the "absorption curve method", whereby the counting rate is determined for progressively thicker source supports, and the resulting curve extrapolated back to zero support thickness.(37)

SMITH(50) found that the sandwich procedure gave unreliable results with weak β-emitters such as S^{35}, though it is reasonably good for more energetic β-particles. Both the first two methods were thoroughly investigated by PATE and YAFFE.(37,38) Their results confirmed those of SMITH as to the unreliability of the sandwich procedure, concluding that this was due to back-scattering effects in the film.(38) The mathematical calculations do not allow for this either. The absorption curve method was shown to be accurate provided sufficiently thin films were used to obtain initial counting rates.

This arises from the shape of the curve, which shows a sharp initial fall. Extrapolation from thick films ignores this with consequent erroneous results.(50)

The major problem in determining disintegration rates lies in self-absorption. The solution to this problem may be sought in two ways, namely by obtaining a suitable absorption curve and extrapolating to zero source thickness(53) or by eliminating self absorption altogether.

The simplest method of source preparation involves the evaporation of a suitable aliquot part of active solution on to the support.(6,47) In principle, if the area of the source is kept constant but the amount of carrier continually reduced it should be possible to extrapolate to zero source weight.(47) Unfortunately, evaporation of a liquid drop produces aggregation of crystals and as the mass is decreased these aggregates reach a limiting size beyond which further reduction of source weight merely reduces the number of aggregates but not their size.(39) Some improvement is obtained by the use of various wetting agents such as insulin (35,39,51,64) Cetavlon-Acetone-ethanol mixture,(51) teepol(51) and long chain hydrocarbons such as

"Tween 20"(51,52) and "Span 20",(51) though aggregation is still not completely prevented by these means. MARTINSSON(52) states that supports of very thin aluminium films are superior to plastic films in this respect since a more even deposit is obtained. The wetting agent itself, however, contributes to the source weight, which partially off-sets its usefulness. The use of colloidal silica has also been described ("Ludox" SM)(65) although this gives only marginally better results than insulin in many cases. Care has also to be taken in this method to prevent gelation of the silica.

A far better method of source preparation is that based on the "ion ejection" procedure of CARSWELL and MILSTEAD.(66) This involves applying a large potential between a fine capillary, containing the source solution, and the source mount. This causes the production of a fine spray of solution which under suitable conditions loses its solvent by evaporation before it reaches the support. Using this method, MERRITT et al(65) obtained a source of Cs^{134} which emits a β-particle of maximum energy 86 keV with only approximately 7% self absorption compared to some 21% for an insulin treated source.

A more limited technique, but one which appears to be superior to insulin-wetting, is to precipitate the element as its hydroxide using ammonia(65) or, as in the case of mercury, as its sulphide using hydrogen sulphide.

One of the most promising methods for producing thin uniform sources to date is that investigated first by PATE and YAFFE.(39) This involves vacuum distillation of a solid source material directly on to the film. The method was used much earlier to prepare 4Π sources,(41,44) and its use for preparing sources for β-spectrometry has been discussed by PARKER et al.(67) The method was later extended by YAFFE and FISHMAN(68) who distilled suitable organic substances of several elements on to VYNS films. Although the method is an improvement on most other existing procedures, self absorption corrections still have to be applied and calibration curves have to be constructed for each nuclide used, as it was shown that experimental and theoretical absorption curves were not identical.(68)

If a nuclide emits a γ-ray in coincidence with the β-particle then the difficulties associated with the extrapolation of an absorption curve do not arise, since self absorption may be determined directly by the 4Πβ-γ coincidence techniques.(65,59) Although only normally used for nuclides with relatively simple decay schemes it was shown that it could be applied when the decay schemes are very complex and/or uncertain, provided one β-cascade is known.(70)

By combining a β-γ "tracer" with a pure β-emitter the self absorption errors in determining the disintegrations rate of the latter may be eliminated. This technique was first used by CAMPION et al.(53,71) Intimate mixing of "tracer" and the pure β-emitter is necessary in this method and was achieved by CAMPION by incorporating both nuclides in the same complex. The method was later extended to nuclides which could not readily be incorporated into such a compound, but which could be intimately mixed in a colloidal solution of silica or graphite.(72)

γ-γ coincidence may also be used for determining disintegration rates(60) and the use of a single scintillator coupled to two photomultipliers for coincidence measurements has been described.

A different approach to 4Π counting is that of scintillation counting in its various forms. Liquid scintillation counting has been used to standardize both α- and β-emitters as first described by BELCHER.(73) In general the active substance is dissolved in the liquid scintillator which entails virtually no source preparation and also means that absorption effects are negligible. It was first shown to yield disintegration rates for α-emitters(74,75) and the method was later used by STEYN and STRELOW(2) to determine the half life of U^{238}. STEYN(76) showed that fairly energetic β-particles could also be standardised by this method and compared his results with those obtained by other methods and found good agreement. This was also shown to be the case by other workers.(77,78,79) A thorough comparison of this method and that of 4Π,β-counting was made by STEYN.(80)

Solid scintillators have also been used for 4Π-counting. Here, the source is deposited directly on to the crystal or on a thin foil, sandwiched between two scintillators.(81,82) This method has been used to standardize certain electron capture nuclides.(83) Thus ALLEN(84) described an arrangement for measuring the K X-rays from Cs^{131}, using a NaI(Tl) crystal as a scintillator, since absorption of these K X-rays is approximately 100% in crystals of suitable geometry.

Gaseous samples of low energy β-emitters may be standardized by adding them to the counting gas of a G-M or proportional counter, and this method is particularly useful for counting tritium and C^{14}. If the substance can be introduced into the counter tube directly as a gas then, at least in principle, it may be counted with 100% efficiency, since there are no absorption effects. Associated with the method are a number of problems, such as compatability of the gaseous substance with the gas filling of the counter; the difficulty of obtaining an effective volume identical to the actual volume of the counter and gas absorption on the counter walls. In addition, a solid or liquid must be converted to a suitable gaseous form.(83) These problems have been thoroughly investigated by several workers.(55,85,86) MANN et al(87) have described an arrangement of two counters of different lengths to obviate the problem of counter volumes.

The starting point of the present work was a paper by BJÖRNHOLM and LEDERER(88) in which they described the preparation of a thin layer of cation-exchanger by the action of sulphuric acid on polystyrene sheet. By exchanging thorium and radium for the hydrogen ions of the sulphonic acid groups on the polystyrene they prepared sources suitable for α-counting. By sulphonating a small area of a thin polystyrene film supported on a VYNS backing, a suitable cation-exchange film was produced. This was then used for preparing sources of several weak β-emitters. Such sources have negligible weight and therefore little self-absorption and would be expected to be more efficient than sources prepared on insulin-treated VYNS films. Autoradiographs were taken of the sources prepared by the present technique and those prepared on insulin-treated VYNS. Mercury sources presented problems due to the mobility of this metal along gold-coated surfaces and measurements, including autoradiography, were made on the rate of surface diffusion.

An attempt was also made to introduce solutions of cation exchange resins into a VYNS solution to produce a single film containing cation exchange groups, which would have some advantages over sulphonated polystyrene films.

Using the above method of source preparation to aid in the calibration of a proportional counter, the $Tl^{203}(n,p)Hg^{203}$ cross-section was measured.

CHAPTER II

GENERAL THEORY AND EXPERIMENTAL METHODS

Theoretical treatment of absorption

The absorption of β-particles emitted by a radioactive sample is due to two effects, (a) absorption of the radiation in the source mount and (b) self-absorption.

(a) An expression for the absorption of β-radiation in the source mount may be deduced in the following way if one assumes an exponential decrease of radiation intensity with increasing support thickness.

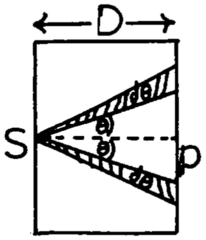


fig. 1

Assume a source mount of thickness D, and let particles be emitted in a cone of thickness $d\theta$ subtending an angle θ at the source, S. The area that this cone generates, A_c, is given by

$$A_c = 2\Pi \, pD\sec\theta d\theta$$

but $$p = D\tan\theta$$

$$A = 2\Pi\ D\tan\theta D\sec\theta d\theta$$

$$= 2\Pi\ D^2\sin\theta\sec^2\theta d\theta$$

However, the total area, A_t, is

$$A_t = 4\Pi\ D^2\sec^2\theta$$

Thus, the fraction of the total particles emitted from S into the annulus generated by the shaded segment in fig. 1 is given by the ratio of these two areas; that is

$$\frac{2\Pi\ D^2\sin\theta\sec^2\theta d\theta}{4\Pi\ D^2\sec^2\theta}$$

$$= \tfrac{1}{2}\sin\theta d\theta$$

If N-particles are emitted from the source in unit time, then the number emitted into the segment is given by

$$N\sin\theta d\theta$$

The absorption, f_a, of a particle leaving a point source at an angle θ is taken to be$^{(68)}$

$$f_a = e^{-\mu D\sec\theta}$$

where μ is the absorption coefficient.

Thus the number of particles, E, leaving the film will be

$$\frac{N}{2} \int_{0}^{\Pi/2} e^{-\mu D \sec\theta} \sin\theta d\theta$$

Putting $\cos\theta = x$

$$E = -\frac{N}{2} \int_{1}^{0} e^{-\frac{\mu d}{x}} dx$$

Putting $\frac{1}{x} = y$

$$E = \int_{1}^{a} \frac{1}{y^2} e^{-\mu D y} dy$$

Values for this integral are obtained from published tables(89).

(b) Various relationships have been derived to describe the self-absorption(90,91,92). Probably the most useful is that derived by GORA and HICKEY(93), who used a rigorous integration procedure, starting with the integral

$$a_{\alpha,D} = \frac{1}{\Omega\alpha} \int_{0}^{\alpha} \frac{a_o \cos\theta}{\mu D} \left(1 - e^{-\frac{\mu D}{\cos\theta}}\right) d\,\Omega$$

where $a_{\alpha,D}$ = specific activity observed

a_o = true specific activity

μ = absorption coefficient

D = thickness of the source

Ω = $2 \ (1 - \cos\alpha)$

α = solid angle over which radiation from a point source is detected

θ = angle of observation to the normal i.e. angle subtended by the counter at the source.

This equation takes into effect the counter geometry, which must be so if μ is to have any real meaning$^{(93)}$.

Using the above equation they obtained limiting cases of the self-absorption factor, f, for (a) a narrow angle counting assembly and (b) for a counting assembly of 2Π steradian geometry.

For case (a),

$$f(\alpha, \mu D) = \frac{1}{\mu D}$$

For case (b),

$$f(\frac{\Pi}{2}, \mu D) = \frac{1}{2\mu D}$$

YAFFE and FISHMAN$^{(68)}$ have shown that an identical expression holds for 4Π geometry as for 2Π geometry.

Coincidence Theory

(i) The basic formula for the determination of the efficiency of a β-counter by the coincidence method is easily derived. Consider a point source emitting a β- and a γ-ray successively, and suppose that there are N_o disintegrations per unit time interval. If the two detectors are set so that the one detecting particles is sensitive only to β-particles and the γ detector only sensitive to γ-rays, then the count rate in each detector,

n_β and n_γ, will be

$$n_\beta = N_o \epsilon_\beta \qquad - (1)$$

$$n = N_o \epsilon_\gamma \qquad - (2)$$

where ϵ_β and ϵ_γ are the respective efficiencies of the β- and γ -detectors.

The probability of detecting a coincidence count i.e. of detecting both a β-particle and a γ-ray at the same time is the product of these two efficiencies, $\epsilon_\beta \epsilon_\gamma$. Thus the coincident count, n_c, is given by

$$n_c = N_o \epsilon_\beta \epsilon_\gamma \qquad - (3)$$

It therefore follows that

$$\beta = \frac{n_c}{n_\gamma} \qquad - (4)$$

and

$$N_o = \frac{n_\beta n_\gamma}{n_c} \qquad - (5)$$

Thus the determination of the count rate in the gamma-counter and the number of coincidences serves to define the efficiency of the beta-counter.

This is a somewhat idealised situation and in general a number of corrections must be applied, though for the experimental arrangement used in this work these corrections were usually very small or negligible. The following corrections were considered, however:

(i) Correction for the finite size of the source. Putman(94) has shown that the method is valid for a distributed source provided that one of the detectors is equally sensitive to all parts of the source, which is approximately true for a 4Π counter, and a correction was not made in this work.

(ii) It is rarely possible to achieve a system in which both detectors are sensitive to only a unique type of radiation. In general the β-counter will be sensitive to γ-radiation and following the line of argument put forward by Campion(95), one may arrive at a correction for this factor.

For a simple decay scheme, the count rate in the 4Π counter is given by

$$n_\beta = N_o \; [\, \epsilon_\beta + (1 - \epsilon_\beta)(\epsilon_\beta)_\gamma \,] \qquad - (6)$$

where $(\epsilon_\beta)_\gamma$ is the efficiency of the 4Π counter for γ-rays, and $(1 - \epsilon_\beta)$ represents that fraction of β-particles not detected by the 4Π counter but which are accompanied by γ-rays which may be recorded as separate counts in the 4Π counter. Thus combining equations (5) and (6) one obtains

$$\frac{n_\beta n_\gamma}{n_c} = N_o \; [\, 1 + \frac{(1 - \epsilon_\beta)(\epsilon_\beta)_\gamma}{\epsilon_\beta} \,] \qquad - (7)$$

It is seen that if $(\epsilon_\beta)_\gamma$ is very small and ϵ_β very large, that is β-efficiency approaches unity, equation (7) approximates to the simple form of equation (5). If more than one γ-ray is emitted in coincidence, however, it is possible that a γ-ray be detected in each counter without the β-ray being detected, giving a coincidence detection probability, ϵ_c. The correction for this is given by the following expression

$$\frac{n_\beta n_\gamma}{n_c} = N_o \left\{ 1 + \frac{(1 - \epsilon_\beta)\,[(\epsilon_\beta)_\gamma\,\epsilon_o - \epsilon_c]}{\epsilon_\beta\,\epsilon_\gamma + (1 - \epsilon_\beta)\epsilon_c} \right\} \quad - (8)$$

$(\epsilon_\beta)_\gamma$ and ϵ_c are always very small and so if ϵ_β is approximately 1, then again this correction becomes negligible, and was assumed to be so in this work.

The β-sensitivity of the γ-counter is rendered negligible in the experimental arrangement used (see page 40) as β-particles are prevented from entering the scintillation counter. The associated Bremsstrahlung may be neglected.

(iii) A correction may be necessary for the angular correlation between the β-particles and γ-rays, although with a 4Π counter of nearly 100% counting efficiency, this correction is also negligible.

(iv) There are also corrections to be applied for random coincidences due to the finite resolving time of the coincidence mixer. Thus if τ is the resolving time, c_1 and c_2 are the single counting rates of the two counters, then the probability, p, that a pulse counted in one counter is accompanied by a non-coincident pulse in the second counter with $\pm\tau$ is given by

$$p \approx 2\tau c_1 c_2 \qquad - (9)$$

If the background coincidence value is b_c, then the total number of coincidences measured, m_c, is

$$m_c = c_{12} + 2\tau c_1 c_2 + b_c \qquad - (10)$$

where c_{12} represents the true coincidences. This correction is by far the most important of those considered in the work reported here and due allowance for it was always made in the present work.

Experimental methods

The Preparation of VYNS and Polystyrene Films

The source supports used in this work consisted mainly of thin VYNS films, produced by a method based on that described by Pate and Yaffe(58).

A stock solution of 11% by volume of VYNS in cyclohexanone was prepared and kept in a glass-stoppered bottle. A small volume of this solution was poured into a petri dish and the long edge of a 3 ins microscope slide dipped into the solution. This edge was then placed on the surface of water contained in a tank, causing a film of VYNS to spread on the surface of the water. The edges of the film were taken between the middle finger and thumb, and by drawing the hand away from the slide a fairly uniform, thin film could be drawn out. The thickness of the film was controlled by the rate at which the hand was drawn down the tank, the latter being tilted at a slight angle.

Ideally, a completely uniform film can be produced in this way, though in most cases the thickness varied slightly from area to area, but only those portions of the film of the required thickness were used. The thickness of the film was determined by observing its colour in transmitted daylight. In general, films of superficial density of 5 to 15 μ gm/cm^2 were used. They were greyish-white to very pale yellow in colour.

Aluminium rings of 2.6 cm internal diameter and 3.7 cm outer diameter were then carefully placed on top of selected portions of the film, the excess film around the rings was then broken away and the ring lifted from the water. Rings were removed in such a manner that practically no water adhered to them and thus suspended solids in the water of the tank were not deposited on the films when they were dried.

Polystyrene films were produced in a similar way. Cyclohexanone was again a suitable solvent, and 22% by weight of polystyrene in cyclohexanone was found to be a suitable concentration. Colourless films (thicker ones wrinkled too much on drying) estimated to be less than 5 μ gm/cm thick were used. Having produced a film on the surface of the water, an aluminium ring with a VYNS film on it was very carefully placed on the polystyrene film so that the VYNS film adhered to the polystyrene. Having trimmed away the edges, the films were lifted from the water and stood vertically to dry. This also allowed any air pockets trapped between the two films to escape; air pockets were however rarely formed.

Initially, having formed the polystyrene layer, the film was sulphonated and finally coated with gold. Later, however, this procedure was modified, and the VYNS film was coated with gold before depositing the polystyrene film on it. This eliminated the possibility of gold being deposited on the sulphonated area. The VYNS films were coated with a conducting layer of gold on the side opposite to that on which the polystyrene film was to lie. Several films were coated at once by supporting them on a hemispherical wire frame having a heated tungsten wire loop carrying the molten gold at its centre.

After formation the polystyrene film was sulphonated. Several sulphonating agents were tried; these ranged from a 7% oleum solution (7% $^{w}/w$) sulphur trioxide in concentrated sulphuric acid) to a 90% aqueous solution of sulphuric acid. From preliminary experiments by DOWNING(96) it was concluded that stronger oleum solutions produced so much heating during the subsequent washings with water that the films very often ruptured. The sulphonation time was also varied, from 2 to 60 minutes, so that optimum sulphonation conditions could be determined.

Sulphonation of the polystyrene film was carried out by applying a few drops of one of the sulphonating solutions to the film, using a 10 ml. capacity polythene bottle with the top drawn out into a capillary. The solution covered an area of about 1 sq.cm. The solution was allowed to remain in contact with the film for a known time, after which it was removed with the aid of a micropipette apparatus, shown in fig. 2. An allowance was made for the time (approximately 20 seconds) taken to remove the drop completely.

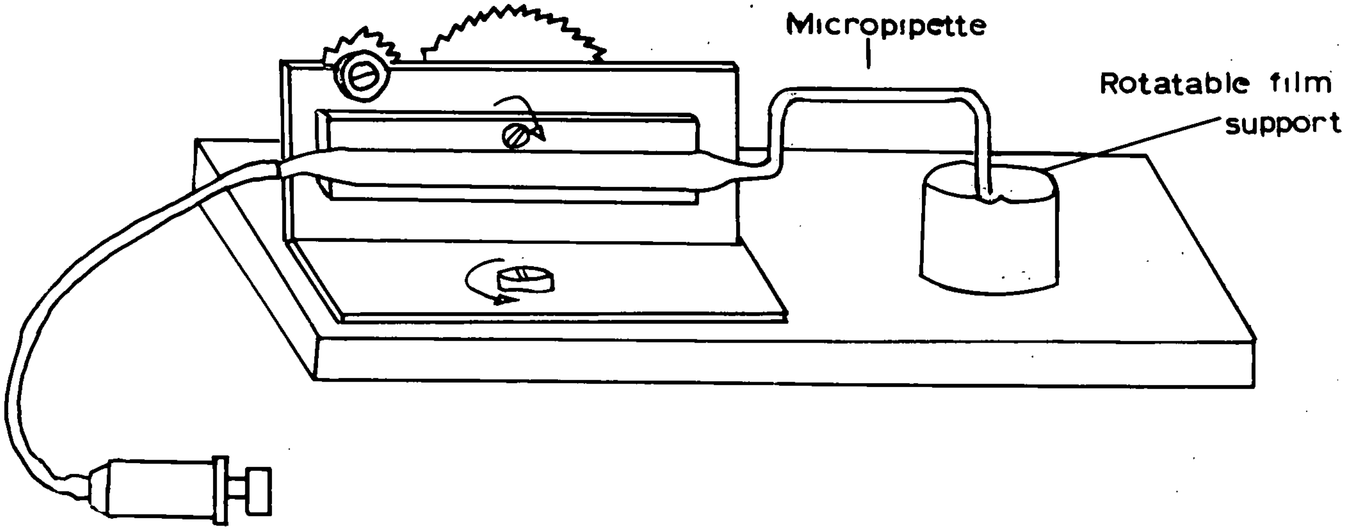


Fig.2. Apparatus used for washing 4π sources.

The sulphonated area was then "washed" with successively weaker solutions of sulphuric acid, each solution being applied to the area from a polythene bottle and removed with the aid of the micropipette. After washing with 90% aqueous acid the film could be washed with water. Water applied directly to stronger solutions of acid produced sufficient heat and swelling to damage the films.

In the early experiments the films were finally washed under the tap and dried under an infra-red lamp. Later, however, it was found safer to dry the films in air, since there was then less possibility of the films breaking.

The strengths of oleum sulphonating agents were determined by Karl Fischer titration(97), using a solvent mixture of pyridine and dioxane (1:1 $^{v}/v$) and carrying out a blank using concentrated sulphuric acid. In this way the sulphur trioxide content of the oleum solution was determined. For the designated "7% oleum solution" a value of 7.4% sulphur trioxide was found, compared to the calculated value of 7.5%.

Counting equipment

The radioactive samples were counted in a 4Π counter and the β-particle counting efficiency of the sources checked by a β-γ coincidence method, using a 4Π counter in conjunction with a γ-scintillation counter.

(a) The 4Π counter

This was of the pill-box type, and is shown in fig. 3. It was a gas-flow proportional counter and consisted of two cylindrical, brass chambers. Brass was preferred to aluminium as there is less contribution from the former to the background count. Each half carried a very thin anode wire (0.001" thick) and the source formed a partition between the two chambers so that it was equidistant from each anode.

The gas was a standard commercial mixture of 90% argon and 10% methane, which was dried before entering the counter by passing it through columns of silica gel and "Anhydrone". Having passed through a glass wool filter to remove any dust it entered the counter through a reducing valve and flow-meter. The gas was supplied to the counter at slightly above atmospheric pressure, and at a constant flow rate although slight variations in the latter did not affect the counting rate. A block diagram of the apparatus is shown in fig. 7 with a 4Π counter in place of the proportional counter depicted in that diagram.

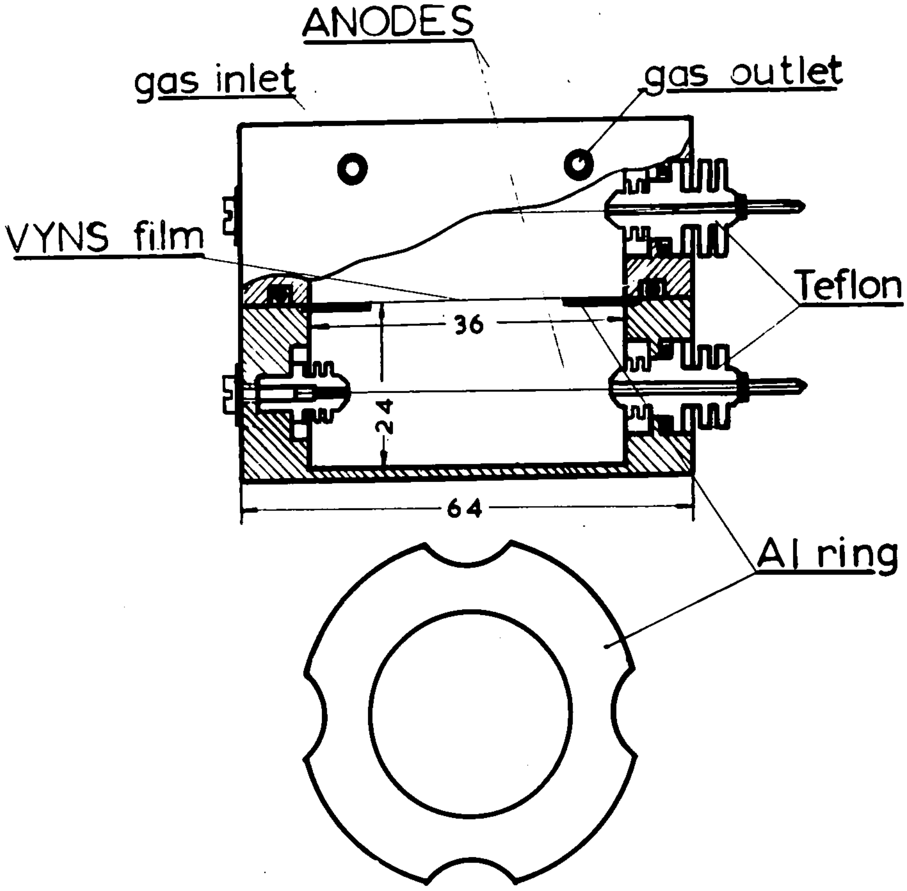


Fig 3. 4π Counter

The counter normally had a plateau 200-300 volts long, and the normal working voltage was 1800v. The counter, enclosed in a lead castle, had a background count of 40-50 counts per minute (c.p.m.).

Pulses from the counter were externally amplified by a factor of approximately 10^6 and they were then fed into the scaler which was operated with a paralysis time of 50 μsecs. and a 15v bias which was well above the electronic noise level.

In humid weather the insulation on the counter showed some tendency to break down, but this was alleviated by placing some granules of silica gel in the lead castle and by carefully drying the chambers of the counter with hot air.

(b) The scintillation counter

(i) The scintillation counter used in the work described here was a commercial one, type 12/DM-2/12, obtained from Nuclear Enterprises (G.B.) Ltd. It consisted of a 3" x 3" sodium iodide (thallium activated) crystal connected to an E.M.I. type photomultiplier, as shown in Fig. 4 . The crystal was enclosed in an aluminium can, having an entrance window 0.032" thick. A pulse height analyser used

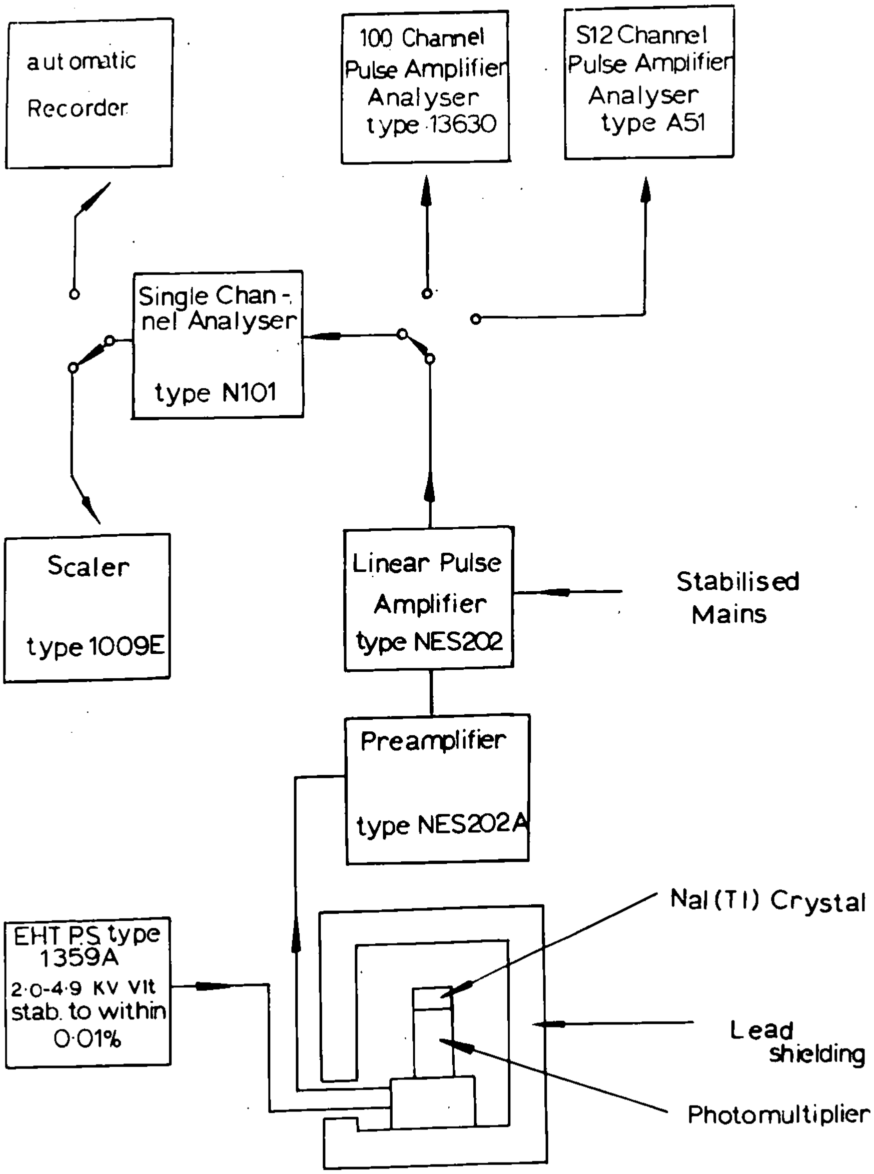


Fig 4. Block diagram of the circuits used for scintillation counting.

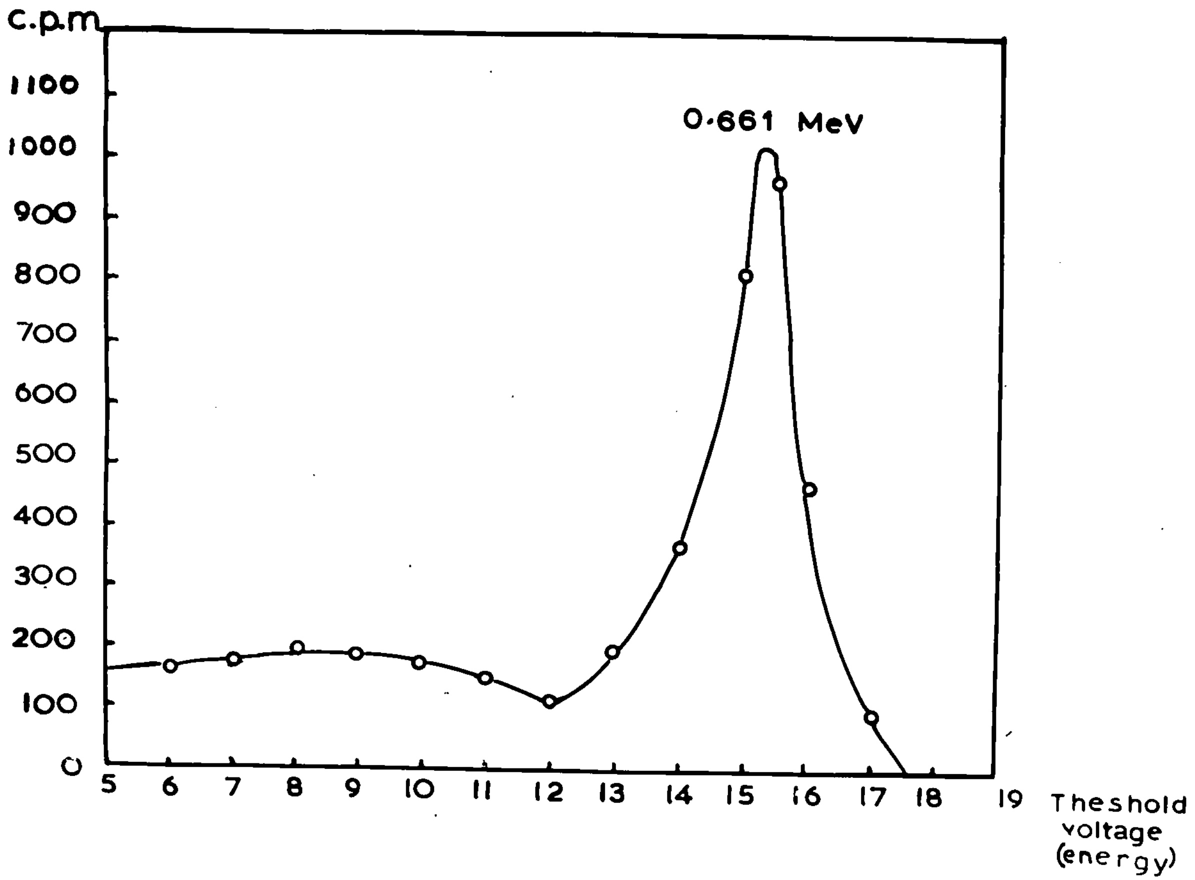


Fig.5. γ-ray Spectrum of Cs^{137}

in conjunction with the photomultiplier wasprovided with a continuously variable channel width and threshold voltage selector, both of which could be varied from 0 to 100v.

(ii) The spectrum of a γ-emitter was obtained by selecting a narrow channel width (usually 1 volt) and determining the count rate as the threshold voltage was slowly increased from a minimum value, which was just above the electronic noise level of the apparatus, to a value where the counting rate had dropped virtually to the background level. The spectrum was then determined by plotting the counting rate against the threshold voltage, after subtracting the background count appropriate to each voltage setting. A typical spectrum, obtained for Cs^{137}, is shown in fig.5

The principal peak is the photopeak, and in γ-ray counting the threshold voltage and channel width were selected to include most of this peak, thus giving as high a counting efficiency as possible. Nuclides emitting several γ-rays have an equivalent number of photopeaks, and by selecting a suitable threshold voltage and channel width, it was possible to count those pulses arising from any given γ-transition.

(c) Coincidence counting

For β-γ coincidence counting the β-detector was a 4Π counter containing the source and the γ-detector was a scintillation counter, on top of which the 4Π counter was placed. The two counters were enclosed in a single lead castle.

The electronic apparatus was essentially similar to that described earlier for the 4Π and scintillation counters singly. However, when these were used in a coincidence set-up, the pulses from the separate circuits were fed into a three-channel coincidence unit and thence to three scalers, in order to record β-, γ- and coincident β-γ events separately. The coincidence unit had two coincidence mixers, one of maximum resolving time 2 μsecs. and the other 4 μsecs. The unit was always operated such that the maximum resolving time was 4 μseconds.

Each input channel of the unit was provided with a variable delay, which allowed for differences in the rise time of the pulses in the different channels. It was necessary to set these delays to obtain coincidence counts. With a suitable source in the counter, the coincidence resolving time was set at a low value (0.5 μsec.) and keeping the delay time in the γ-circuit at zero, the delay in the β-circuit was varied from about 0.5 μsec.

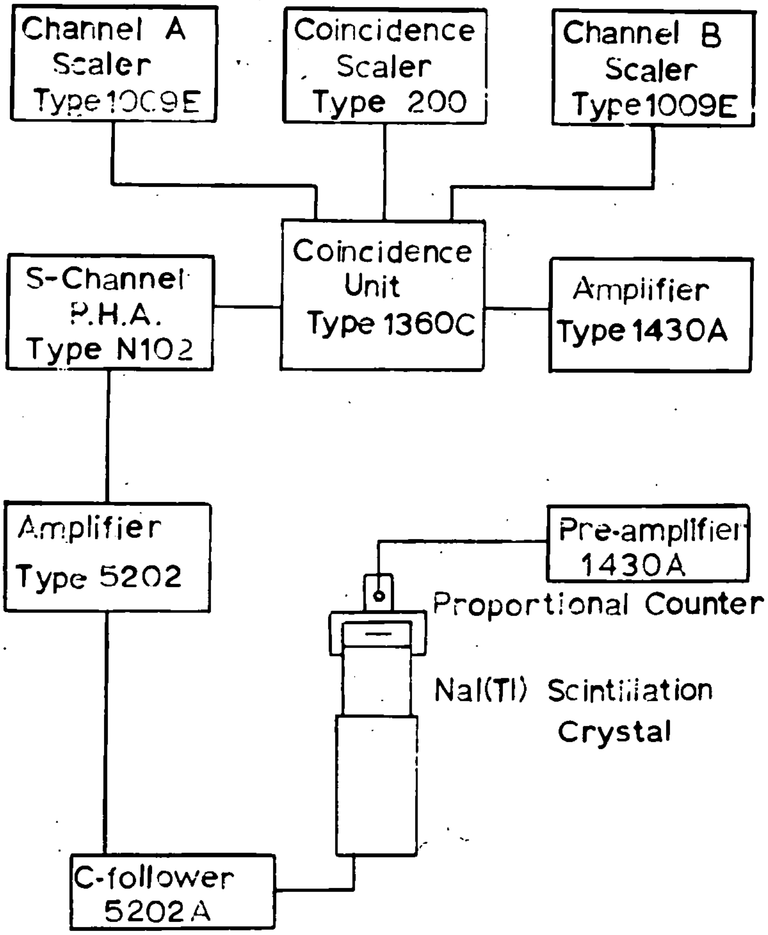


Fig.6. Block diagram of coincidence circuit.

to 1.0 μsec., and the number of coincidence counts at each setting noted. The delay time which gave the maximum number of coincident counts was the correct setting.

The optimum coincident resolving time was determined in exactly the same way, except that the delay time was now kept constant (at the value found to give the maximum coincident count rate) and the resolving time was varied from 0.5 to 4 μsec. Again, the setting which gave the maximum number of coincident counts was the correct one. The electronic circuit is shown in fig. 6 .

The actual coincidence resolving time was determined as follows. Two independent sources were counted by means of the two counters. One source was placed inside the 4Π counter whilst the second source was placed on an aluminium tray on top of the scintillation counter. The two counters were placed in separate lead castles, some three feet apart in a horizontal plate, so that no coincident or scattered radiation could reach both counters. The coincident counting rate was then determined. This rate was due only to the finite resolving time and to a background produced by cosmic rays, the latter being very small with the above arrangement . Knowing the individual β-particle and γ-ray counts, the resolving time may be determined (cf P31) With a nominal resolving time of 2 μsecs. the following results were obtained (with sources containing Sc^{46}).

Corr. β-counts (c.p.m.)	Corr. γ-counts (c.p.m.)	Corr. Coincidence counts(c.p.m.)	2τ(μsec)
50327	6108	22.0	4.294
49699	6147	19.1	3.751
49855	7130	22.4	3.781
49186	7124	22.7	3.855
44572	9546	28.9	4.075
44304	9565	27.3	3.837

The mean value for 2τ is 3.93 μsecs. where τ is the resolving time.

For the cross-section measurements the activity from Hg^{203} was measured by means of an end-window proportional counter and that from Mn^{56} in a halogen-quenched Geiger-Muller liquid counter of the annular type.

(d) The end window proportional counter

This was of the type shown in the block diagram of Fig. 7. The window consisted of several layers of VYNS to give a total thickness of about 80μgm/cm². The

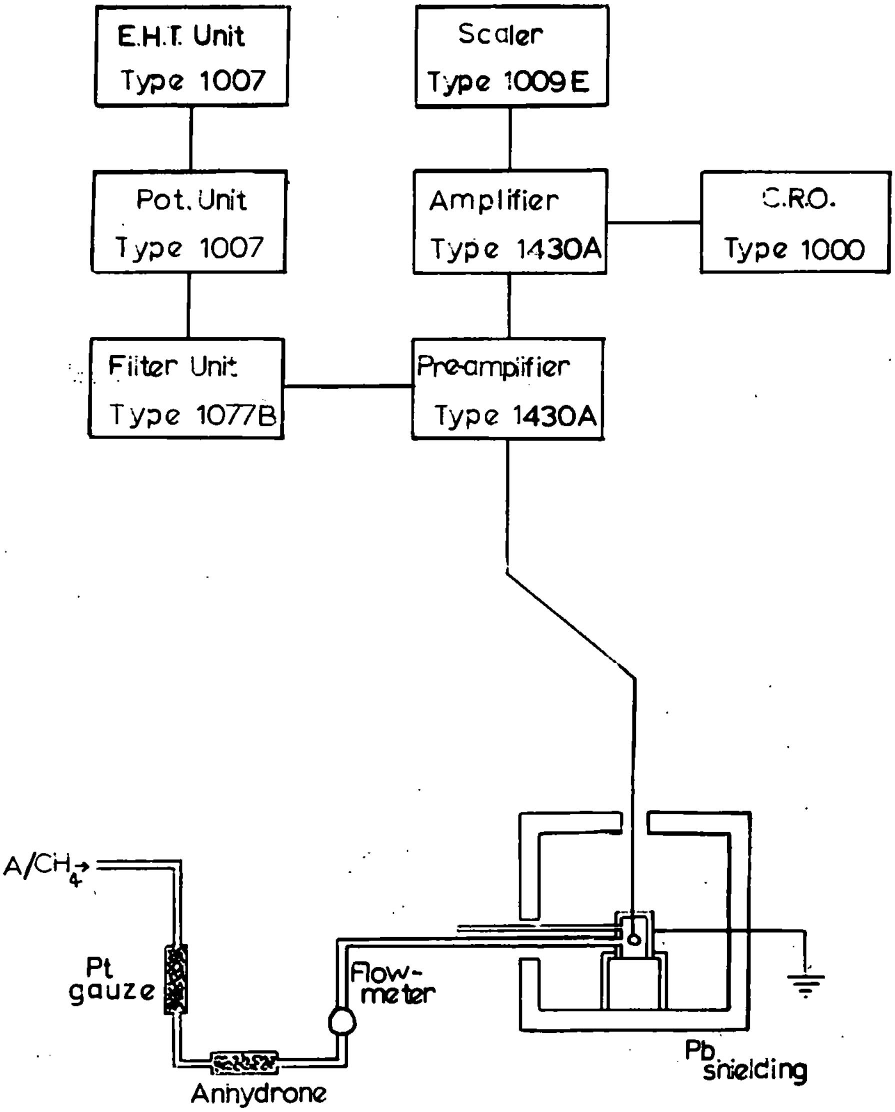


Fig.7 Block diagram of proportional counter electronic and gas flow circuits.

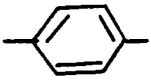
anode consisted of constantan wire (0.001" in diameter) formed in to a loop and suspended from a nickel tube 5/8" from the window. The gas was a standard mixture of 90% argon and 10% methane, dried as previously described. A flow rate of 0.75 cc/minute was maintained. Under these conditions a plateau some 200 - 300 v. long was obtained and the counter was normally operated at 1850v. Sources were counted in an aluminium planchet placed in the top shelf of the counter assembly. A background count of 10 - 11 c.p.m. was obtained with the counter inside a lead castle; the counter efficiency was checked periodically with a Radium D, E, F source.

(e) The halogen-quenched liquid counter

The counter was a 20th Century Electronics model, type M6H, having a capacity of 10 ml. It was operated in conjunction with a probe unit which provided both the paralysis time and the bias voltage. The paralysis time was 500 μsecs. (checked by means of a double beam oscilloscope) which limited counting rates to about 1 to 2 x 10^4 c.p.m. The counter was normally operated at 420v., with a threshold at 350v. and a plateau about 140v. long.

It was supported in a lead castle, electrical contact being made through a pool of mercury. The background count was usually about 14 c.p.m. The efficiency was checked periodically with a standard Cs^{137} source.

Calculations

An estimate may be made of the counting rate to be expected from a source in which total sulphonation of the polystyrene occurs. For a polystyrene film 5 μgm./cm^2 thick and a sulphonated area of 1 sq. cm., the amount of polystyrene sulphonated is 5 μgm. The molecular weight of each  $-CH-CH_2-$ group is 104. Assuming that there is one $-SO_3H$ group per benzene ring, then the number of gram-equivalents of polystyrene units and hence the number of gram-equivalents of replaceable hydrogen, G_H, is

$$G_H = \frac{5 \times 10^{-6}}{104} \sim 5 \times 10^{-8} \text{ gm. equivalents} = 3 \times 10^{16} \text{ atoms}$$

Assuming complete exchange of Tl^+ for H^+, there will be 5×10^{-8} gm. equivalents of thallium on the source. In the solutions used, the ratio of active to total thallium was 9.8×10^{-7}. Thus the source will contain $5 \times 10^{-8} \times 9.8 \times 10^{-7}$ gm. equivalents of active thallium i.e. 4.9×10^{-4} gm. equivalents. 1 gm. equivalent of Tl^{204} gives 8×10^{16} d.p.m. Thus the activity of the source will be $4.9 \times 10^{-14} \times 8 \times 10^{16}$ d.p.m. $\sim$ 4000 d.p.m.

CHAPTER III

THE β-COUNTING EFFICIENCY OF SOURCES PREPARED BY THE ION-EXCHANGE METHOD

Preliminary investigations

Preliminary investigations of the suitability of the method for source preparation were carried out using Tl^{204} which has a half-life of 3.9*y* and decays by the emission of a single, relatively energetic β-particle (maximum energy, E_{max} = 0.77MeV). The source solutions used had activities of approximately 4 μc/gm. of solution, each gm. of solution containing approximately 100 μgm. Tl.

One drop of active solution was applied to the sulphonated area, which had previously been wetted with water. The solution was confined to the sulphonated area owing to the hydrophobic nature of the untreated polystyrene film. In the early experiments the drop of active solution was applied from a small polythene bottle, the top of which had been drawn out into a fine capillary. The actual weight of solution applied varied from 8 to 20 mg. The active solution was allowed to remain in contact with the sulphonated area for 1 to 2 hours to ensure good exchange between the thallium and the hydrogen ion of the sulphonic acid groups. At the end of that time excess active solution was sucked off with the micropipette. A little water was then spread over the source area and then sucked off again. Finally the films were dipped, edge on, ten times in distilled water and then ten to fifteen times in 600 ml. of distilled water to remove final traces of surplus activity. The films were then dried prior to counting.

The results obtained from these early experiments were very erratic. It was possible that equilibrium had not been established between the thallium and the hydrogen ions, although extending the time of contact produced no better results. However, a more likely explanation was that during the washing of the films under the tap immediately after sulphonation, metal ions in the water and especially Ca^{2+}, may have partly exchanged with the hydrogen ions, thus hindering the uptake of thallium ions. This was checked by sulphonating several films and then washing half of them under the tap whilst the other half were washed by repeatedly dipping them in de-ionised water. After drying, a sample of Tl^{204} was applied and the films then washed, dried as previously described and then counted.

The results are shown below in Table I:

TABLE I - A comparison of the washing procedure on the observed counting rate

Time of Sulphonation	Final Washing Procedure after Sulphonation	Weight of Active Solution Applied	Counting Rate
5 mins.	Film washed under tap.	~ 20 mg.	9822
5 mins.	Film washed in de-ionised water.	~ 16 mg.	11915
10 mins.	Film washed under tap.	16.3 mg.	3951
10 mins.	Film washed in de-ionised water.	15.7 mg.	12312
20 mins.	Film washed under tap.	14.6 mg.	4047
20 mins.	Film washed in de-ionised water.	17.7 mg.	15051

There thus appears to be a significant difference between those films washed under the tap and those washed in de-ionised water; for all later experiments films were washed only in de-ionised water.

The results of varying the sulphonation time are shown in Table II, where the variation of counting rate with sulphonation time is shown.

TABLE II - The effect of varying the time of sulphonation

Sulphonating agent	Time of sulphonation (minutes)					
	2	5	10	15	20	60
7.5% Oleum	170	260	1677	2504	3052	2339
Conc. Sulphuric Acid	-	250	775	588	2060	2275
90% Aqueous H_2SO_4	-	169	1420	2657	2100	2210

It would appear that for any given sulphonating agent the amount of sulphonation increases with the length of the sulphonation time up to 20 mins., after which time no further sulphonation of the polystyrene occurs, even for periods of up to one hour. Also, it is seen that there is little difference between the final constant activity of sources prepared from the various sulphonating agents, indicating that a saturation sulphonation occurs after about 20 minutes. This would seem to indicate that the polystyrene is probably fully sulphonated, since calculations showed that activities observed after 20 minutes are roughly the same as those calculated for a completely sulphonated film using this particular sample of Tl.

The results were still somewhat variable and the probable explanation, namely re-distribution of activity during the washing, came from work carried out later with Sc^{46} sources.

On the basis of these results it appeared that concentrated sulphuric acid applied for 20 minutes would provide the optimum conditions for the sulphonation of the polystyrene films.

The efficiencies of sources of specific nuclides

(i) Sources of Mn^{54}

Mn^{54} decays by K-capture with the subsequent emission of Auger electrons of approximately 55 keV in energy. These are in coincidence with a single γ-ray of 0.84 MeV energy. It is thus equivalent to a very weak β-emitter and should therefore provide an excellent test of the usefulness of the above method of source preparation.

Twelve sources in all were prepared: six by evaporation of a Mn^{54} solution on VYNS previously treated with insulin and six on sulphonated polystyrene. After drying, all these sources were counted by the coincidence method.

The sources prepared on sulphonated polystyrene were found to have very low activity, and it was impossible to obtain any reliable efficiency data from them since the coincident rate was too low.

This indicated that very little manganese had exchanged with the sulphonic acid groups, though the reason for this was not quite clear. No further measurements were made with this nuclide.

(ii) Sources of Sc^{46}

Sc^{46} is not quite as suitable as Mn^{54} since it is a β-emitter with a β-particle of maximum energy 0.36 MeV. It is consequently less vulnerable to self-absorption than Mn^{54}. Even so, self-absorption in sources of 2 $\mu gm/cm^2$ mean superficial density prepared by the colloidal silica technique is 2.8 ± 0.4%, whilst for those prepared by evaporation on insulin films of the same superficial density it is 5.3 ± 1.7%(65).

As with Mn^{54}, sources were prepared both by evaporation of a known weight of Sc^{46} solution on to sulphonated polystyrene films previously treated with insulin, using a source solution of activity approximately 2 $\mu c/ml$. Sources were also prepared by the present ion exchange technique, here using a source solution of approximately 88 $\mu c/ml$. activity. In this way a direct comparison between the two techniques was possible.

The sources were then counted by the β-γ coincidence method. Sc^{46} decays by the emission of a single β-particle followed by the coincident emission of two γ-rays, both of which are emitted within 10^{-11} sec. of each other. Thus it was necessary for the γ-counting to select a threshold voltage and channel width to include the photopeaks of both of these γ-rays.

The results for three films prepared by the evaporation method and for six prepared by ion-exchange are presented in Table III.

Sources prepared by evaporation and with a low mean superficial density are relatively efficient, although the efficiency drops rapidly as the source weight is increased.

The efficiencies of sources prepared by the ion-exchange method are, however, very poor and entirely unexpected. The explanation for these low counting efficiencies was found to be the method of washing the sources. The final washing of the source entailed dipping the films several times into a beaker of water. It was possible that during this operation some of the active material would be washed off the sulphonated

TABLE III - The β-counting efficiency of Sc^{46} sources

Film	Method of source preparation	Weight of source solution added (mg)	Corrected β-counts (c.p.m.)	Corrected γ-counts (c.p.m.)	Corrected coincidence counts (c.p.m.)	β-counting efficiency
X 13	Evaporation on sulphonated polystyrene	22.4	54553±225	4390±66	3491±20	80±2%
X 14	" "	~ 17	39004±198	3311±58	2704±14	82±1%
X 15	" "	~ 13	38275±197	2422±49	2272±16	94±1%
1	Ion-exchange on sulphonated polystyrene	~ 6	6740±82	487±22	409±7	84±1%
3	" "	~ 8	14233±119	972±31	891±10	92±1%
5	" "	~ 6	6758±82	555±24	426±7	78±1%
7	" "	~ 5	24023±155	1825±43	1549±39	85±1%
9	" "	~ 7	23142±152	1831±43	1411±38	77±1%
11	" "	~ 7	13653±117	1104±33	876±30	79±1%

region and become deposited on the aluminium ring. This activity would contribute to the overall counting rate but the efficiency of counting these β-particles would be considerably less than that of β-particles emitted from the sulphonated area. The effect on the γ-rays would be less marked owing to their greater penetrating power. Thus the overall counting efficiency would be considerably reduced. This was checked by taking the two sources which gave the lowest counting efficiencies (films 9 and 11) and the plastic films were very carefully detached from the aluminium rings with the aid of a disc coated with cyclohexanone. The aluminium rings, free from all surplus film, were then counted in the 4Π counter. The results are tabulated below:

TABLE IV - Radioactivity on the aluminium rings.

Source	β-Counting Rate (c.p.m.)
Background	51
Aluminium Ring, 9	5835
Aluminium Ring, 11	2509

Thus it appeared that considerable activity had been deposited on these rings, quite sufficient to explain the low efficiencies found for these sources. It was verified that no activity was present on the rings from the evaporated sources and that only slight activity was present on the ring from the most efficient source prepared by the new technique (film 3).

Estimates were made of the counting efficiencies of films 9 and 11, correcting for activity on the ring and they were found to be close to 100%.

Thus it appeared that washing the films by dipping them in water was unsatisfactory for general purposes.

Some further experiments were now carried out to determine the uniformity of the sources produced by the technique described and to compare them with sources prepared by evaporation, where marked agglomeration of activity was known to occur. Autoradiography with the dual advantages of simplicity of operation and cheapness of materials required compared with other possible methods was used for this purpose. Pieces of Ilford

X-ray film approximately 5 cm. square were used to record the autoradiographs. The film was placed in the bottom of a light-tight box and one of the sources placed on top of it, the operation being carried out in the dark. The lid of the box was replaced and the film exposed for 35 hours, after which time it was removed and developed in Ilford 1D-B-19 developer at 68°F for 5 minutes. The same source was then exposed for 100 hours and developed for 7 minutes. This gave the negative 10b, fig. 8.

From fig. 8 it can be seen that apart from the source area, the outline of the aluminium ring is also visible, and the dark areas on the ring indicate areas of activity. This provides further evidence for the contamination of the rings. However, the source area itself is of uniform density, indicating uniform distribution of activity, without any local aggregations and in this respect it is superior to sources prepared

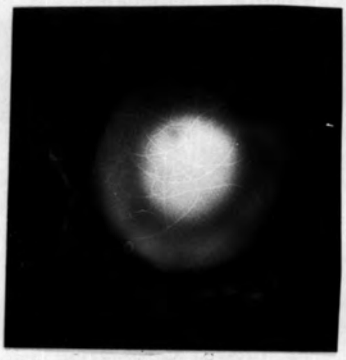


Fig. 8

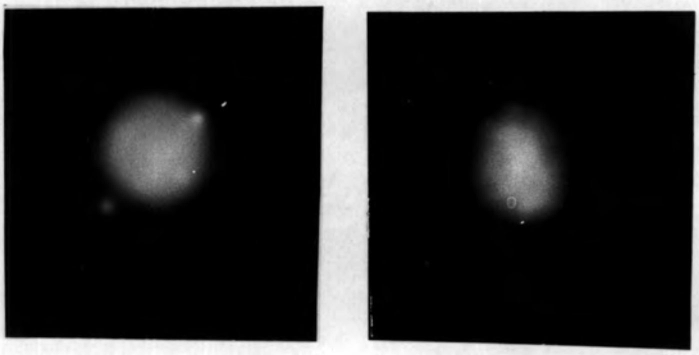


Fig. 9(a)

Fig. 9(b)

Autoradiographs of Sc^{46} sources.

by evaporation.

A modified washing technique was devised. Two micropipettes were clipped together in large "Terry" clips. One of these pipettes (designated the "water pipette") was used to perform the initial wetting of the sulphonated area. After deposition of the active solution and allowing sufficient time for exchange, the second pipette (designated the "solution pipette") was used to suck off the bulk of the surplus solution. More water was then put on the film from the water pipette and removed by the solution pipette. This procedure was repeated some 25 times, when it was assumed that all excess activity was removed. This assumption was verified by counting the source after 25 washings and again after a further 25 washings. The two counting rates were found to be the same.

The results obtained for four films are presented in Table V.

TABLE V The β-counting efficiency of Sc^{46} sources

Film	Corrected β-counts	Corrected -counts	Corrected coincidence counts	β-efficiency
	c.p.m.	c.p.m.	c.p.m.	
22	19161	1363	1269	93 ± 2%
23	10055	709	668	94 ± 2%
24	8468	594	575	97 ± 1%
25	8670	615	597	97 ± 1%

($2\tau = 4.141\ \mu$ secs)

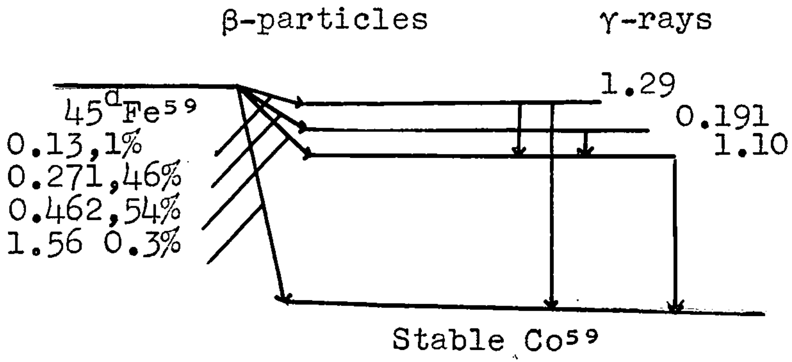
The slightly low efficiencies of films 22 and 23 may be due to inadequate washing.

Autoradiographs were then prepared from these films, using exposure times of approximately 100 hours and developing the films for 7 mins. Examples are shown in fig.9(a). Two sources were also prepared by evaporation on insulin treated VYNS and labelled B and C. After determining the efficiency of these sources (91% and 92% for B and C respectively) autoradiographs were prepared, using an exposure time of 40 hours. One of these is illustrated in fig. 9(b). They clearly show the marked non-uniformity of such sources; some local aggregations of activity and some areas almost free of activity are evident.

(iii) Sources of Fe^{59}

Fe^{59} emits weaker β-particles than Sc^{46} and the effects of self-absorption are therefore expected to be more important for this isotope than for Sc^{46}.

It has a conveniently long half-life (45 days) and should undergo exchange with hydrogen even more readily than scandium. The β-particle has an end-point energy of 0.27 MeV. A disadvantage of Fe^{59}, however, is that it has a somewhat complex decay scheme, shown below(98).



The 0.271 MeV β-particle constitutes 46% of the total β-particle emission and is accompanied by a γ-ray of energy 1.29 MeV. For the purposes of this experiment, coincidences were counted between the 0.271 MeV β-particles and the 1.29 MeV γ-rays.

A γ-ray spectrum of Fe^{59} was first plotted and the position of the 1.29 MeV γ-ray determined. A suitable threshold voltage and channel width were chosen so that (a) only γ-rays of this energy were counted and (b) the only coincidences counted were those between this γ-ray and the 0.271 MeV β-particle.

A source of Fe^{59} was available consisting of 0.8 ml of $FeCl_3$ in 0.1N hydrochloric acid, and with a specific activity of approximately 0.6 μc/μgm. This solution, R1, was used to prepare sources by the ion-exchange method. On diluting an aliquot of this solution ten times solution, R2, was obtained; it was used to prepare sources by evaporation on insulin treated VYNS films.

An attempt was made to determine directly the total thickness of the source support. A gold coated film of VYNS plus polystyrene on an aluminium ring was first weighed, using an analytical balance. The film was then removed from the ring as completely as possible and the ring re-weighed. The difference in the two weights gave a value for the weight of the gold-coated films. Knowing the area of the film the superficial density could be calculated. A typical result is given below.

Weight of aluminium ring + gold-coated films = 1.12476 g.

Weight of aluminium ring alone = 1.12462 g.

∴ Weight of gold-coated films = 0.00014 g.

Inside radius of ring = 1.27 cm.

Area of film $= \Pi r^2 = 3.142 \times (1.27)^2$ cm^2

$= \underline{5.068 \text{ cm}^2}$

∴ Superficial density of the film $= \frac{140}{5.068}$ μgm /cm^2

$= \underline{27.6 \ \mu\text{gm /cm}^2}$

As there was no reason to suppose that this was not a typical film it confirmed the earlier assumption that absorption of β-particles in the source support would be almost negligible.

A final modification was now made to the washing procedure, and this was used in all further experiments. It was desirable to make the washing as automatic as possible, since it was a rather tedious operation. A single micro-pipette was now used but was connected to a water pump through a "suck-back" trap (see diagram, fig. 10). A 50 ml burette was then placed so that its tip was about two millimetres from the centre of a film which rested on a support. The tip of the pipette was adjusted so that it was approximately 1 mm. above the surface of the film, and over the source area. The burette contained de-ionised water which was allowed to drip slowly on to the source. At the same time very gentle suction was applied to the pipette by the pump,

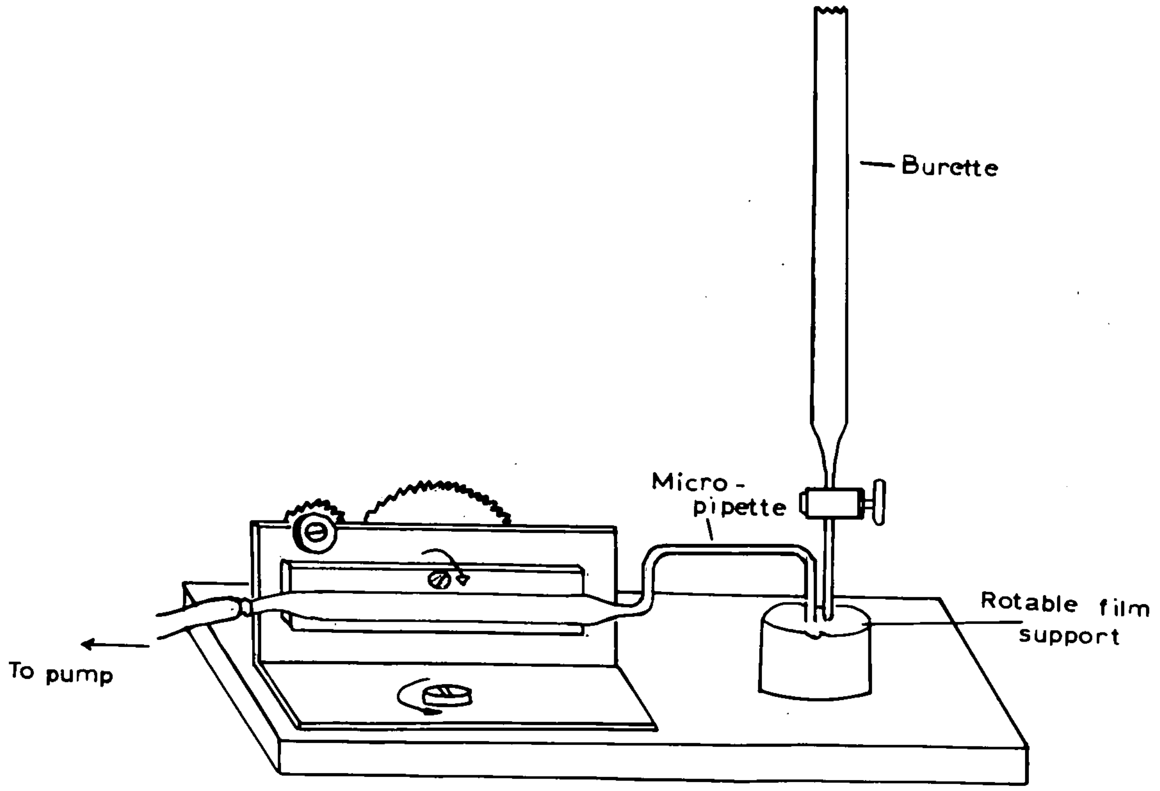


Fig 10. Modified apparatus for washing 4π Sources.

which thus removed surplus water. The source was thereby continually washed while remaining covered with some 100 μl of water. The film was continually rotated on the support during the washing operation and this enabled the entire source area to be quickly but efficiently washed. The source was eventually sucked as dry as possible with the aid of the pipette and then allowed to dry at room temperature.

The results obtained for a set of sources prepared in the above manner are presented below in Table VI. The high efficiencies which could now be obtained by the ion-exchange method, observing all the necessary precautions in source preparation are thus demonstrated. It should be pointed out that corrections were not applied to the coincidence count rate to allow for the γ-efficiency of the 4Π counter (estimated to be very small) or to allow for the possibility of one γ-ray being detected in both counters when the β- particle was missed. Such

TABLE VI - The β-counting e

Film	Method of source preparation	Corrected β-cou c.p.m.
FC	Evaporation of 11.1 mg. of active solution onto VYNS.	30318 ± 55
FD	Evaporation of 10.0 mg. of active solution onto VYNS.	25815 ± 48
F13	Ion-exchange	9649 ± 11
F14	"	7414 ± 22
AS1	"	12540 ± 24
BS2	"	8392 ± 16
BS3	"	8259 ± 18
CS4	"	4494 ± 11
CS7	"	4243 ± 19
DS8	"	7414 ± 22

corrections were assumed to be negligible. The efficiencies for sources prepared by evaporation of a given weight of solution on to insulin treated VYNS show that they are considerably less than for sources prepared by the new technique.

(iv) Sources of Co^{60}

Co^{60}, like Sc^{46}, emits a single β-particle but two coincident γ-rays. Thus a suitable threshold voltage and channel width must be set on the pulse height analyser to include both these γ-rays. Typically the channel width was 16-18 volts with an E.H.T. of 800 volts and an overall amplification of 3. The β-particle has $E_{max} = 0.318$(99), which is slightly more energetic than the weak β-particle from Fe^{59}.

Several sources were prepared using the washing procedure described earlier for Fe^{59} sources.

The results for the efficiency of sources of Co^{60} are shown in Table VII. Even with the modified washing procedure occasionally some films have a low counting efficiency. This may possibly be due to activity being transferred by splashing on to the outer parts of the

TABLE VII - The β-counting efficiency of Co^{60} sources

Film	Corrected β-counts c.p.m.	Corrected γ-counts c.p.m.	Corrected coincidence counts c.p.m.	β-counting efficiency
A03	6587 ± 24	373 ± 7	354 ± 5	95 ± 2%
A04	9802 ± 19	435 ± 6	408 ± 4	94 ± 3%
B07	3172 ± 12	164 ± 5	159 ± 3	97 ± 4%
B08	2283 ± 11	130 ± 4	127 ± 3	98 ± 4%
C09	4908 ± 16	264 ± 4	250 ± 4	95 ± 3%

film during the washing. The rings, however, were not found to be contaminated.

(v) Sources of Hg^{203}

Hg^{203} ($t_{\frac{1}{2}}$, 48 days) emits a weak β-particle (E_{max} = 0.208 MeV), accompanied by a single γ-ray (E_{γ} = 0.28 MeV). This nuclide should therefore provide a suitable test for the method of source preparation. For evaporated sources, self-absorption usually amounts to 15 - 20%, although some distillation methods have given better results(68).

Experimental

A source of Hg^{203} was available; it consisted of 1 ml. of Hg_2Cl_2, with a specific activity of lmc/mg. of mercury. However, such a solution proved useless for source preparation by the ion exchange method, presumably due to the fact that the mercury was not in a cationic form in this solution. It was, therefore, necessary to prepare a cationic form of mercury, the nitrate being chosen. The method involved reduction of the mercurous salt to metallic mercury with hydrazine hydrate and the subsequent dissolution of the mercury in nitric acid. This solution was finally evaporated to dryness and the resulting solid taken up in 1.5 ml of 0.5 N nitric acid to give the stock solution of Hg^{203}.

(a) Counting of sources

Initially considerable difficulty was encountered in determining the efficiencies of sources containing Hg^{203}. The first sources prepared had very low efficiencies and the 4Π counter was found to be contaminated after counting them. The mercury was found to diffuse from the source area on to the aluminium rings. Counting the aluminium rings after removal of the film and also autoradiography provided the evidence and the latter experiments proved that given sufficient time all of the activity eventually found its way to the aluminium rings. This phenomenon has been noted by other workers(72) and suitable precautions taken to prevent it.

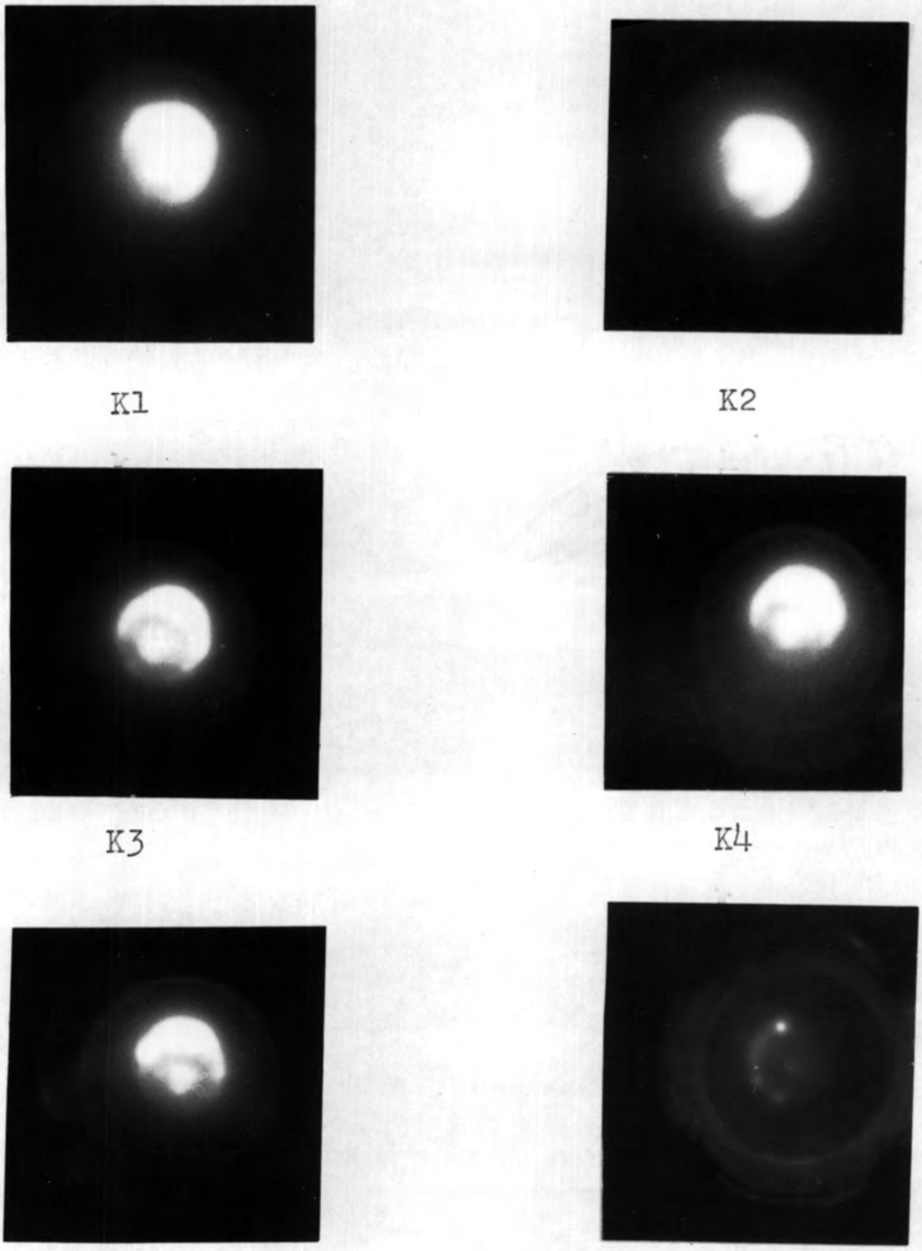
(b) Diffusion experiments

Although there are some references in the literature to the surface diffusion of mercury on various metals(100,101,102) little work has been done on the surface diffusion of mercury on gold. Because of the effects observed in the preparation of Hg^{203} sources some diffusion experiments were conducted in which Hg^{203} was put on strips of "Melinex" film, both coated and uncoated with gold, and the distribution of mercury as a function of time was determined with the aid of a Geiger counter. These experiments confirmed that diffusion was occurring along the gold surface and that uncoated films showed negligible diffusion.

In another series of experiments the diffusion was followed by autoradiography. A very active source (approximately 10^6 dpm) was evaporated on to a gold-coated VYNS film. The high activity allowed short exposures (about 2 hours) to be used, so that the diffusion could be followed at intervals of only a few hours after source preparation. In all six exposures were taken over a period of 18 days. Experimental details are summarised in Table VIII and the corresponding autoradiographs (K1 to K6) are shown in Fig.11.

TABLE VIII - Diffusion of mercury along a thin evaporated gold film

Number of film	Exposure time			Time since source prepared
	Start	Finish	Total time	
Source put on film at approximately 10.15 on 27.7.64.				
K1	10.25 (27.7.64)	12.45	2 hrs. 20 mins.	2 hrs. 35mins.
K2	13.00 (")	15.45	2 hrs. 40 mins.	4 hrs. 15mins.
K3	18.00 (")	20.15	2 hrs. 15 mins.	9 hrs.
K4	9.30 (28.7.64)	12.00	2 hrs. 30 mins.	1 day
K5	9.30 (29.7.64)	12.30	3 hrs.	2 days
K6	9.30 (14.8.64)	12.30	3 hrs.	18 days



K1 K2

K3 K4

K5 K6

Fig. 11: Autoradiographs illustrating the diffusion of mercury on gold.

The most significant evidence derived from autoradiographs is that diffusion occurs very rapidly and that after only four hours a substantial amount of activity has already reached the aluminium ring. After about one day the activity is spread fairly uniformly over the whole film. After 18 days most of the activity is on the ring, with only a small fraction still remaining on the original sulphonated area.

(c) Modified procedure for the preparation of sources of Hg^{203}

Owing to the diffusion process, presumably by mercury in the elemental form, it was necessary to prevent activity spreading from the sulphonated area; this was done by forming a suitable stable mercury compound on the film.

From the point of view of stability, the two most promising mercurous derivatives are the cyanide and the sulphide. The cyanide was tried initially but it was abandoned because of problems arising from the high toxicity of hydrogen cyanide. Thus, the sulphide was used. The procedure consisted of preparing a source of Hg^{203} in the usual way, but on supports not yet coated with gold. Whilst the source area was still wet, the film was placed in an empty desiccator, which was then evacuated. A Kipp's generator was then attached to the desiccator which was filled with hydrogen sulphide. The films were left for several hours in this hydrogen sulphide atmosphere and then removed, gold-coated and finally counted in the usual way. Experiments showed that activity was not deposited on the aluminium ring after sources had been treated in this manner even several days after source preparation.

The results are tabulated in Table IX. It is seen that sources in general have efficiencies of about 90%. This is rather low and might indicate that some diffusion may still be occurring, although as pointed out earlier, no activity actually reached the ring.

The preparation of sources on films prepared from solutions of ion-exchange resins

One of the disadvantages of films prepared by the sulphonation of polystyrene is the limited amount of activity which could be put on such a film, presumably due to the limited number of exchange sites produced by the sulphonation techniques. If, however, films could be prepared which had exchange groups throughout the whole film, then much more active sources could be

TABLE IX - The β-counting efficiency of Hg^{203} sources

Film	Corrected β-counts c.p.m.	Corrected γ-counts c.p.m.	Corrected coincidence counts c.p.m.	β-counting efficiency
G2	40630 ± 64	3917 ± 20	3391 ± 18	87 ± 1%
G4	23740 ± 41	2233 ± 13	1956 ± 12	88 ± 1%
G10	18250 ± 42	1747 ± 13	1561 ± 12	89 ± 1%
Z1	14092 ± 31	1303 ± 12	1161 ± 9	89 ± 1%
G11	21464 ± 42	1995 ± 14	1724 ± 12	86 ± 1%
G14	31091 ± 52	2935 ± 17	2555 ± 15	87 ± 1%

prepared and a higher percentage of the original activity would be retained on the film.

A possible method of obtaining such sources would be to prepare a solution of an ion-exchange resin and to mix this with VYNS solution, the mixture then being used for preparing films, which would require no further treatment apart from gold-coating. In practice, however, difficulties were encountered in dissolving the resins. This was perhaps not unexpected since one of the desirable properties of an ion-exchange resin is its insolubility in solvent systems that are liable to be met with in practice. Limited solubility was, however, found for some solvent systems.

Experimental

Zeo-Karb-225, cation exchange resin of 2% cross-linking was selected for study, since from a solubility point of view a low resin cross-linking is desirable. Solvents which were tried for this resin included acetone, benzene, xylene, toluene, diphenyl ether, nitrobenzene, chloroform, amyl acetate, ethyl acetate, cyclohexanone and various mixtures of them. None proved satisfactory; even refluxing the resin for two days with toluene did not produce significant dissolution.

Subsequently it was found possible to dissolve a small amount of resin in a solvent mixture of formic acid and amyl acetate. About 5 g. of resin were added to 50 ml. of the solvent mixture (95% $^{V}/_{V}$ formic acid) and the solution refluxed for about 5 hours. At the end of this time an estimated 0.3 g. of resin were in solution.

After cooling, 2 ml. of this solution were dissolved in 20 ml. of dilute VYNS solution and the mixture thoroughly stirred for 5 minutes. Films could then be prepared from this solution in the normal way although they had to be at least 15 $\mu gm/cm^2$ thick, as thinner films invariably broke. Radioactive sources were then prepared on these films by the procedure described earlier. More concentrated solutions of resin in VYNS could not be used, since it was found impossible to prepare films from such solutions. Tl^{204} was used to prepare the sources. A little insulin was applied to make the surface hydrophilic, although this was always washed off later. Film thickness was estimated from the colour of the film in transmitted light. They appeared to be as stable as normal VYNS films.

The results for several films are presented in Table X. Included in this Table are estimates for the capacity of the films, that is the number of equivalents of exchangeable hydrogen per sq. cm., and for the specific capacity, that is the number of equivalents of exchangeable hydrogen per gram of film. These values were obtained using an estimated ratio of active to total thallium in the source solution. A value of 9.8×10^{-7}:1 was used for this ratio in the present calculation.

Neglecting the two obviously low results, a mean value of 0.67 ± 0.08 m equivalents/gram is found for the specific capacity, which is about 10% of the capacity of the original resin.

Difficulties in source preparation and lack of time prevented further investigation of this method of source preparation.

TABLE X - The preparation

res

Film	Thickness (μgms/cm^2)	Wt. of source solution (mgs.)	Area (
PM	41 ± 5	35.6	~
PN	35 ± 4	17.2	~
PO	39 ± 5	12.6	~
PP	34 ± 4	32.6	~
F1	31 ± 4	21.1	~
F2	30 ± 4	20.6	~
F4	40 ± 5	21.6	~
F6	33 ± 4	24.2	~

CHAPTER IV

THE DETERMINATION OF THE Tl^{203}(n.p.) Hg^{203} CROSS SECTION

Equipment and general considerations

(a) The neutron generator

Neutrons of 14.7 MeV were produced by the Cockroft-Walton type of accelerator, built in The Londonderry Laboratory for Radiochemistry, Durham, by G.R. and E.B.M. Martin(103). A beam of deuterons impinging on a tritium target produce neutrons according to the reaction $H^3(d, n)He^4$, ($Q = + 17.58$ MeV).

The targets consisted of about 1 curie of tritium adsorbed on a thin film of titanium (about 300 μgm/cm^2 thick) which was evaporated on to a thin copper disc. The disc was attached to the inside of the thin brass top of the water-cooled target block which formed the end of the beam-tube of the accelerator, as shown in fig.12. Deuterons of 140 keV were used for bombardment and the beam at the target occupied about 1 cm^2. Samples were placed close to the target block for irradiation. A moveable molybdenum disc was used to protect the target from the deuteron beam until the neutron flux was required.

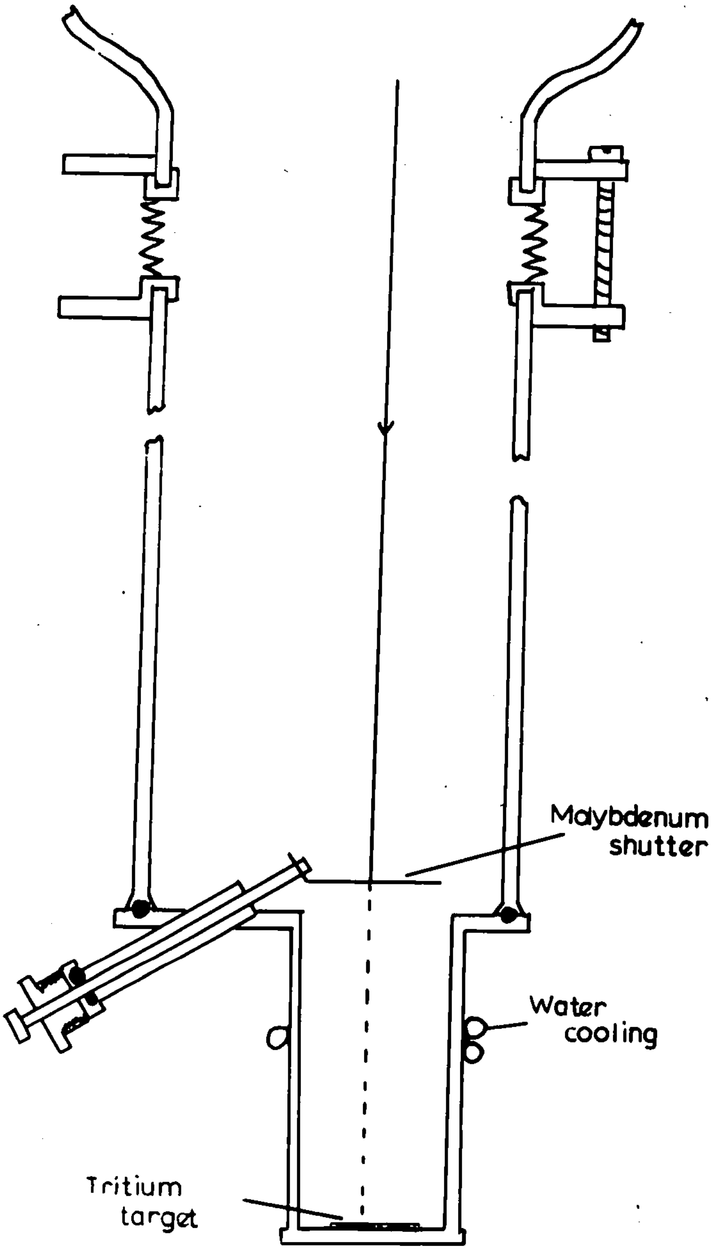


Fig.12 The target assembly

While the energy of the incident deuterons varied according to the depth of penetration of the tritium target, over 80% of the neutrons were generated by deuterons of energy between 80 and 130 keV(104). Similarly, due to the angular spread of neutrons, their energies vary from 14.5 to 14.9 MeV, with a mean of 14.7 MeV.

The neutron flux was monitored by means of a proton-recoil scintillation counter. This provided a measure of the variation in the flux, a knowledge of which was essential for cross section calculations. Monitor readings were taken at intervals depending on the length of irradiation. For a two hour irradiation they were usually at 10 minute intervals.

(b) Calibration of the counters

The only nuclide counted in the liquid counter was Mn^{56}, and the counter was calibrated for it by counting 10 ml portions of solution which had previously been standardised by the 4Π counting method. In the present work only 0.1 g of iron were dissolved and the counter was calibrated for this concentration(105). The efficiency of the liquid counter $\left(\frac{\text{observed counting rate}}{\text{absolute disintegration rate}}\right)$ used in all the determinations of cross-section was 8.3%.

The efficiency of the proportional counter was calculated directly for Hg^{203} and not by interpolation methods usually employed.

Several 4Π sources of Hg^{203} were prepared by the ion exchange method, with fairly high activities (1.3 to 2 x 10^4 c.p.m.). These sources were counted by the coincidence method and the absolute disintegration rate thus determined.

The films were then very carefully removed from the aluminium rings using a glass rod drawn out into a fine point at one end. The film was then placed in a 5 ml round-bottomed flask and refluxed for one hour with 1.2 ml of fuming nitric acid and a drop of perchloric acid (S.G. 1.70) in order to dissolve the film and the source. The cooled solution was then transferred to a 25 ml volumetric flask. The round-bottomed flask was washed out twice with 2 drops of nitric acid and the washings added to the volumetric flask. 6 ml of standard mercury carrier solution containing approximately 7 mg of mercury were added to the round-bottomed flask in two portions and these solutions transferred to the flask. Finally, the round-bottomed flask was rinsed two or three times with distilled water and the washings also transferred to the volumetric flask, which was then made up to the mark with distilled water.

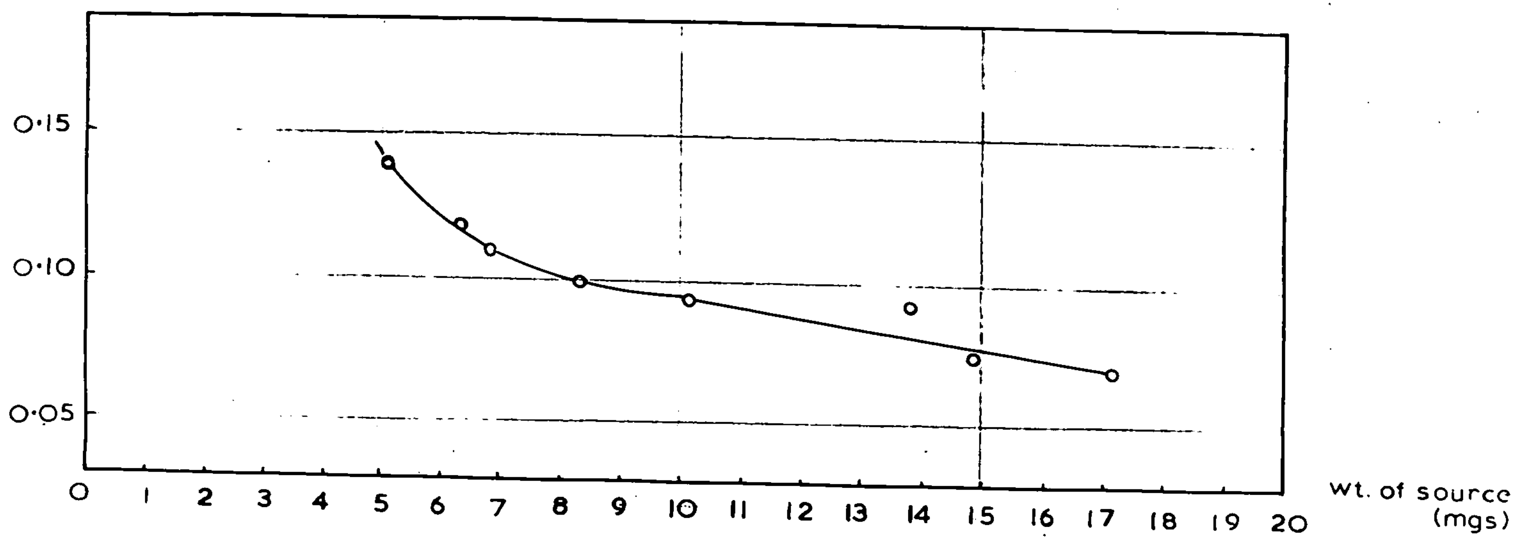


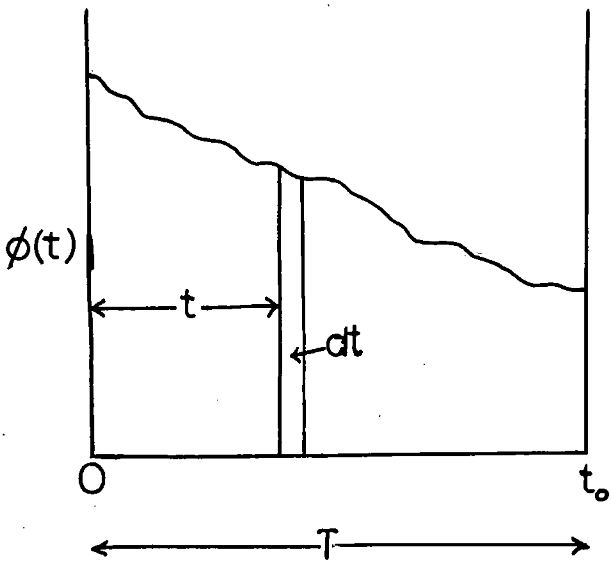
Fig13. Self-absorption curve for Hg^{203}

Aliquot portions of this solution were taken and sources of mercury periodate prepared as described later (page 79). These sources of known weight were then counted by means of the proportional counter and their efficiency thus determined. A plot of self-absorption against source weight was obtained; it is shown in fig. 13.

(c) Methods of calculation

The cross-section was measured relative to the reference reaction $Fe^{56}(n,p)Mn^{56}$, assuming that both the source and the reference had been exposed to the same neutron flux.

Since the neutron generator does not produce a steady flux of neutrons, allowance must be made for this.



Variation of neutron flux with time during the course of an irradiation.

The neutron flux is not constant but varies with the time, as illustrated in the fig. above and therefore, the calculation of product yield at the end of irradiation is necessarily somewhat more elaborate than it would be in the absence of this factor. A stable nuclide, A, is activated during the irradiation of duration time, T, to produce a radioactive nuclide, B. This nuclide subsequently decays to a stable nuclide, at a rate depending on its disintegration constant, λ.

Thus $$A \xrightarrow{(n,x)} B \xrightarrow[\lambda]{\beta} \text{stable}$$

Nuclide, B, is produced throughout the irradiation at a rate given by the expression

$$\frac{dN_B}{dt} = N_A.\sigma_{AB}\phi(t)$$

where $\frac{dN_B}{dt}$ is the rate of production of B.

N_A is the number of nuclei of A exposed to the neutron flux.

σ_{AB} is the cross-section for the reaction A(n,x)B.

$\phi(t)$ is the neutron flux as a function of time.

During the short interval, dt, the number of nuclei of B produced is

$$dN_B = N_A\sigma_{AB}\phi(t)dt$$

These decay exponentially, so that the number remaining at the end of the irradiation, time to, is given by

$$dN_B(to) = N_A\sigma_{AB}\phi(t)e^{-\lambda(T-t)}dt$$

The absolute neutron flux is not known,but its variation is proportional to the variation in the counting rate of the monitor, I(t),

$$\text{i.e. } \phi(t) = {}^{I(t)}/_{P}$$

where P is the factor relating flux at the counting position to the counting rate of the monitor.

$$\text{Thus} \quad N_B(to) = \frac{N_A\sigma_{AB}}{P}\int_{t=o}^{t=to} I(t)e^{-\lambda(T-t)}dt$$

This integral may be replaced by the summation

$$\Sigma(Ie^{-\lambda(T-t)})t \quad - \text{(abbreviated to } S_2\text{)}$$

as long as t is small compared to the half-life of nuclide B.

$$\text{Then} \quad N_B(to) = \frac{N_A\sigma_{AB}S_2}{P}$$

If $$Ar \longrightarrow Br \xrightarrow[\lambda r]{\beta} \text{stable}$$

represents the reference reaction,

$$\frac{N_B(to)}{N_{Br}(to)} = \frac{N_A \sigma_{AB} S_2}{N_{AR} \sigma_{ABr} S_{2r}}$$

the unknown factor, P, cancels between the two expressions, provided that the sample and reference are exposed to the same flux.

As stated, the activities of resultant nuclides at time to, are determined by extrapolation of their decay curves.

Then since $$\frac{A_A(B)}{A_A(Br)} = \frac{C_B \lambda N_A \sigma_{AB} S_2}{C_{Br} \lambda_r N_{AB} \sigma_{ABr} S_{Br}}$$

where C_{Br} and C_B are the detection coefficients for the respective nuclides.

In practice, since the mercury activity produced by the reaction $Tl^{203}(n,p)Hg^{203}$ was so small, the activity of the mercury immediately at the end of the irradiation was determined by calculation and not by extrapolation of a decay curve back to this time.

EXPERIMENTAL

Homogeneous mixtures of thallous nitrate and iron granules were irradiated. The half-life of the Hg^{203} produced from the thallium is 49 days.

Preparation and standardisation of the mercury carrier solution

The carrier solution was prepared from AR mercurous nitrate ($Hg_2(NO_3)_2.2H_2O$); it contained approximately 8 mg. of mercury per ml.

The solution was standardised against AR potassium iodate in an Andrews titration, observing the colour change in chloroform for end-point detection. It was also standardised against potassium dichromate, and the two methods were in good agreement.

Separation of mercury from thallium

Usually 2 gm. of thallous nitrate and 0.5 gm. of iron were irradiated. After removal of the iron granules with an electromagnet the thallous nitrate was weighed and then dissolved in about 50 ml of water. Two millilitres of carrier solution were added followed by 10 ml of concentrated ammonium hydroxide together with 2 drops of hydrazine hydrate (a solution of 50% w/w hydrazine hydrate in water). The solution was stirred for two minutes to precipitate the mercury which was separated by centrifugation. The precipitate was washed twice with water and three times with ether and then dissolved in approximately 20 ml of concentrated nitric acid. The resulting solution was transferred to an evaporating basin and evaporated to dryness. The residual mercurous nitrate was dissolved in 150 ml of 0.1 N sulphuric acid and the solution heated to boiling. Finally, a solution of 2 g of sodium periodate in 50 ml water were slowly added with constant stirring to the boiling solution. The precipitate was collected on a previously weighed glass fibre filter disc supported on sintered polythene in a demountable filter stick.

The chemical yield was determined by direct weighing and after setting aside for several hours before counting to allow all extraneous activities to decay away the source was counted by means of the proportional counter. Owing to the very low initial activity, the decay of Hg^{203} could not be followed.

The iron granules (supplied by the Bureau of Analytical Samples Ltd., with a guaranteed purity of at least 99.8%) were weighed, but owing to the high activity induced in the iron, only 0.1 g of iron was used for

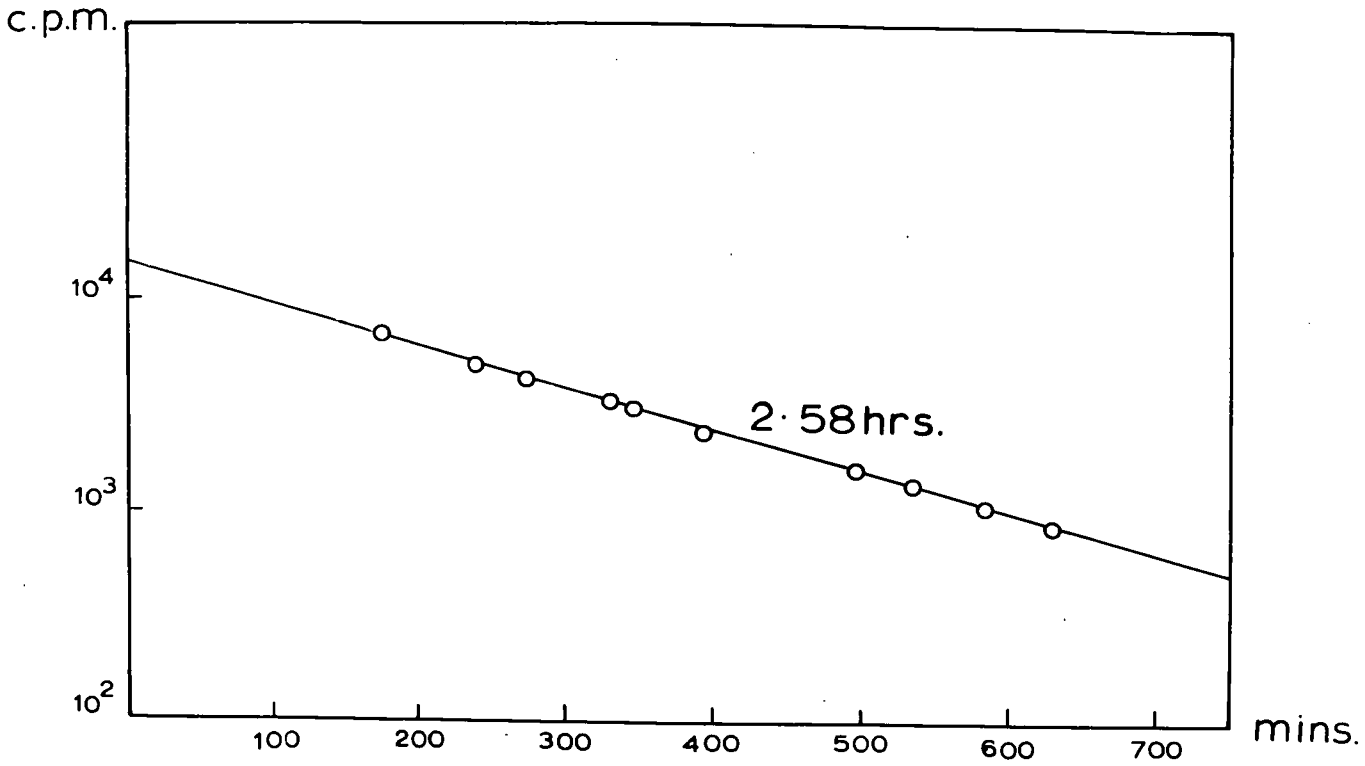


Fig 14. Decay of Mn^{56} induced in the iron monitor.

preparing active solutions. The iron was dissolved in 10 ml of the standard acid mixture (1:1 $^{v}/_{v}$ 5N nitric acid : 5N sulphuric acid with a little manganese carrier present) and made up to 12 ml in a volumetric flask. A 10 ml aliquot was then taken for counting and the decay followed over several half-lives. A typical decay curve is shown in fig.14.

The solid thallous nitrate used was analysed by means of an Andrews titration using KIO_3. The mean of several values gave 74.7 ± 0.5% by weight.

Results and discussion

The results are presented in Table XI.

The value obtained in the present work for the $Tl^{203}(n,p)Hg^{203}$ cross section, 1.82 ± 0.30 mb, is to be compared with the only other reported value of 30 ± 10 mb(106). The latter value, however, was obtained by an indirect method and is possibly in considerable error.

The measurement of the $Tl^{203}(n,p)$ Hg^{203} cross section suffers from the very low counting rates obtained for Hg^{203}. This was due to the inadequate neutron flux available at the time. The value obtained should therefore be taken only as a rough measure of this cross section which has subsequently been measured using a much higher neutron flux(107) giving a result differing only from that obtained in this work by a factor of about 2.

TABLE XI - Results for the $Tl^{203}(n,p)Hg^{203}$ cross section

	SAMPLE REACTION				REFERENCE REACTION				
Irradiation No.	No. of target nuclei	A_0 observed c.p.m.	A_0 correct d.p.m.	S x 10^5	No. of target nuclei	A_0 observed c.p.m.	A_0 correct d.p.m.	S x 10^5	Measured cross section mb
1	1.285×10^{21}	5.1	1.21×10^{2}	1.89	4.585×10^{21}	7.68×10^{4}	1.11×10^{6}	1.41	1.54
5	1.474×10^{21}	4.8	9.71×10	1.43	8.303×10^{20}	1.29×10^{4}	1.87×10^{5}	1.03	1.09
7	1.323×10^{21}	7.0	1.15×10^{2}	1.95	1.007×10^{21}	1.22×10^{4}	1.76×10^{5}	1.49	2.01
8	1.373×10^{21}	4.1	7.53×10	3.26	1.009×10^{21}	6.09×10^{4}	8.81×10^{5}	2.57	2.63

$\sigma_{Fe^{56}(n,p)Mn^{56}}$ = 124 mb. $t_{\frac{1}{2}}\,Hg^{203}$ = 47d.

$t_{\frac{1}{2}}Mn^{56}$ = 2.58 hrs.

$C_{Mn^{56}}$ ⇒ 0.83 (0.79 for irradiation 1)

Mean Value for cross section =

1.82 ± 0.30 mb

CHAPTER V

DISCUSSION

In general the present work has shown that the ion exchange method of source preparation is superior to sources prepared by wetting a VYNS film with insulin. The results for Hg^{203} sources are a little anomalous and this was shown to be connected with the high mobility of mercury.

Autoradiographs taken of several sources show the high uniformity of sources prepared by the ion exchange method. This is to be compared with sources prepared on insulin-wettled films, which show local aggregations of activity due to localised crystal growth. Thus, whatever absorption may be taking place in the source should be uniform throughout the source in the former case, and not variable as with insulin-treated films. This should make absorption corrections more reliable.

Problems arising from the non-conductivity of organic films do not appear if the support itself is conducting. Some workers prefer to use thin aluminium foils as source supports(52) though these have the disadvantage that foils of not much less than $200\mu gm/cm^2$ can be used, thereby producing significant absorption. Recently a method has been described for preparing very thin films of carbon(108), and these may prove useful in 4Π counting, but they do not appear to have received much attention to date. Thin films of aluminium oxide may also be prepared(109) and while non-conducting they have the advantage of being resistant up to 2000° and they can therefore be safely used for vacuum deposition of source material(67)

Due to the difficulty of preparing solutions of ion exchange resins their incorporation in VYNS films to produce single films with suitable ion exchange properties does not offer much prospect of success. However, there are now various liquid ion exchange materials available and these may well be dissolved in a cyclohexanone solution of VYNS to produce the desired single cation exchange films. One such material is dinonylnaphthalenesulphonic acid (DNNS) which has been shown to possess cation exchange properties similar to the sulphonic cation exchange resins(110,111,112). Undoubtedly, mixed films of VYNS and DNNS could be readily prepared and may well be worthy of further investigation.

One problem associated with the calibration of I^{131} sources is the volatility of iodine which may be produced by oxidation in the source material, especially when heat-drying techniques are employed. An alternative method suggested by the present work would be to prepare a cation-exchange film in the silver form by replacement of hydrogen ions with silver ions. On subsequent treatment of this film with active iodide solution, iodide ions would be well distributed and tightly held by the silver ions. Thus, the possibility of a convenient and reliable standardisation of I^{131} is offered by this method.

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PART II

ION-EXCHANGE IN LIQUID-LIQUID EXTRACTION

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CHAPTER I

INTRODUCTION

The phenomenon of ion-exchange, like that of several others which have assumed prominence in various branches of science in recent years, has a long history although the principles underlying it have only recently began to be properly understood. There is a reference to what is assumed to be an ion-exchange process in the Bible and it is probable that the ancient Greeks were aware of this process.(1) It is also of interest to note that ion-exchange plays an important role in several functions of living organisms.(2)

However, no real use of ion-exchangers was made until the rediscovery of cation exchange in soils by WAY (3) and THOMPSON (4) in the middle of the last century. This led to investigations of the materials responsible for the ion - exchange process and to attempts to synthesise materials having similar properties.(5) Little progress was made in this direction until 1935, when the first synthetic organic exchangers were prepared.(6) From this point onwards ion-exchange resins began to be investigated systematically for the first time. By the beginning of the last decade the broad features of the ion-exchange process were known and some tentative theories had been put forward to explain the observed results. (7,8,9) However, these theories were very inadequate, but further refined experimental studies allowed the devlopment of more detailed and useful models of ion-exchange systems. (10,11,12,13,14,15,16,17,18,19,20, 21,22,23)

Virtually all of the ion-exchange systems studied in the period up to 1950 were concerned with dilute external aqueous solutions and even after this date the vast amjority of measurements were still made under these conditions. The models which have been developed are usually adequate to explain the observed behaviour of these dilute external solutions. However, when work was extended to more concentrated external solutions theoretical studies became more complex since several new factors, which could be neglected when more dilute solutions were used, had to be taken into account.(10,22)

This first became apparent from some observations of SAMUELSON (24) who found that on attempting to elute Fe(III) from a cation-exchange resin with increasing concentrations of hydrochloric acid the Fe(III) became less strongly adsorbed as the acid strength increased up to 4M hydrochloric acid but that beyond this acidity the iron was increasingly strongly adsorbed. This behaviour was repeated with several elements.

These observations were confirmed by KRAUS and NELSON (25) who made measurements in both hydrochloric acid and lithium chloride, which revealed that the anomolous adsorption at high external electrolyte concentrations was more marked with lithium chloride than with hydrochloric acid. The marked difference between these two electrolytes had been noted earlier. (26) Indium (III) was also shown to exhibit behaviour similar to Fe(III) from solutions of several alkali metal halides (27) but not from hydrochloric acid. (28) This and other work (25,29,30) indicated that the difference between hydrochloric acid and lithium chloride was not specific to this system but that such a difference was general in the system HX - MX (X being a halide and M an alkali or alkaline earth cation) and various suggestions were put forward to explain this difference.(26,31,32,33)

Besides the large differences between alkali metal halides and the corresponding hydrohalic acids it was found that perchloric acid usually had a much more pronounced affect on the anomolous adsorption behaviour of cations at high acid concentrations than did hydrochloric acid.(28,29,34,35,36,37) The work of CHOPPIN and DINIUS (36) indicated that this was a particular example of a more general effect. It was shown that the anion of the acid had a very considerable effect on adsorption behaviour of cations at high acid concentrations, a conclusion verified by WHITNEY and DIAMOND.(29,35) The influence of the anion on extraction behaviour had already been observed in the extraction of indium from alkali metal halides.(27) It therefore became apparent that both the cation and the anion of the supporting electrolyte solution exerted appreciable influence on the distribution of a metal between such solutions and ion-exchange resins.

During the period following the initial production of several transuranic elements separation procedures were developed which mainly relied on the differences in behaviour of these elements at high hydrochloric acid concentrations. Thus americuim and curium were separated on a cation - exchange resin by elution with 12M hydrochloric acid (38) and this was later extended to the separation of other transuranic elements.(39) The separation of the actinides from the lantharides was found to be comparatively easy at high hydrochloric acid concentrations owing to the completely different behaviour exhibited by the two groups at high acid concentrations. The distribution coefficients of all the lanthanides, after reaching a minimum value between 4 and 7 M hydrochloric acid, increase as the acid concentration is increased beyond 7M. The actinides on the other hand do not show such an increase in distribution coefficient, which remain at low values in concentrated acid.(28,40,41) This behaviour was considered to be due to the greater complexing power of the actinides compared to the lanthanides, a conclusion evidently supported by the behaviour of the lanthanides and actinides in ammonium thiocyanate.(42)

Metals of the alkaline earth series were first studied at high acid concentrations by DIAMOND.(43) Using an aqueous phase of hydrochloric acid he found that distribution values for calcium, strontium and barium as a function of acid concentration passed through minima. This was not the case for radium or magnesium (28,34) where the distribution coefficient showe a continuous decrease. Calcium and strontium exhibit the same behaviour in perchloric(28,35) and nitric acids(35) as in hydrochloric acid. Barium on the other hand no longer exhibits a minimum in either perchloric (28,35) or nitric acid.(35) The explanation offered for these observations depends on differences in cation - anion interactions in both phases.(35) In perchloric acid there is a reversal in the elution order of the heavier alkaline earths from the normal dilute solution sequence Ca $\triangleright$ Sr $\triangleright$ Ba $\triangleright$ Ra to Ra $\triangleright$ Ba $\triangleright$ Sr $\triangleright$ Ca in concentrated perchloric acid. The behaviour of beryllium in perchloric acid is unusual in that there is no minimum in the distribution curve as might have been expected by comparison with calcium and strontium.(28,43) This is attributed to the very high hydration number of the Be^{2+} ion.

There have also been quite extensive studies of the alkali metals in recent years.(25,28,29,43,44,45) They show negligible adsorption from concentrated hydrochloric and perchloric acid but like the elements of the alkaline earth series there is a reversal of the dilute solution elution order (Cs $\triangleright$ Rb $\triangleright$ K $\triangleright$ Na $\triangleright$ Li) in concentrated acids (Li $\triangleright$ Na $\triangleright$ K $\triangleright$ Rb $\triangleright$ Cs). This reversal of the elution sequences has also been observed in concentrated lithium chloride solutions.(44,45)

One of the principle differences in using ion - exchangers in concentrated rather than in dilute solutions is that in the former the exchanger adsorbs considerable amounts of non - exchange electrolyte which introduces a factor not encountered to a significant extent in dilute solutions. Thus using an 8% cross-linked sulphonic acid resin and an external solution 13•5M in lithium chloride, the resin phase is approximately 8•7M in lithium chloride.(44) Less data is available on the adsorption of other electrolytes at high external concentrations but the molarity of hydrochloric acid inside a 10% cross-linked sulphonated polystyrene resin is about 0•3M with an external hydrochloric acid concentration of 2•3M (46) and 1•3M when the external acid concentration is 4•4M.(47)

Slightly higher values are found for the adsorption of potassium chloride and acetate. (48) That the uptake of electrolyte is an important factor in determining distribution behaviour is shown by the fact that for certain synthetic zeolite exchangers, which are highly resistant to electrolyte intrusion, no reversal of the alkali metal elution sequence was found at high electrolyte concentrations.(49,50)

Most of the theories proposed to explain distribution data in concentrated solutions place considerable emphasis on the interaction between the exchanging cations and the fixed anionic groups on the resin matrix. (10,11,14,51) Thus a polymeric diallyl phosphate resin showed marked selectivity for Be^{2+} and $UO_2{}^{2+}$ ions in marked contrast to sulphonic acid resins and liquid sulphonic acid exchangers which have low affinity for these cations compared with other divalent species.(52,53) It has also been observed that dibasic phosphorylated resins give the normal adsorption sequence for alkali metals under acidic conditions (Cs $\triangleright$ Rb $\triangleright$ K $\triangleright$ Na $\triangleright$ Li) and the reversed sequence under alkaline conditions. (54, 55)

Russian workers have also observed the normal sequence under acidic conditions.(56,57) Reversal of the normal sequence was also found with carboxylic acid resins.(29, 58) These reversals are connected with the polarizability of the resin functional group as first pointed out by BREGMAN.(54) Mono-alkyl phosphoric acid esters have also been shown to have markedly different properties to sulphonic acid exchangers for certain cations.(59)

Outline of the present work

By and large the data on exchanger systems have been obtained using ion-exchange resins. Since these are solids information on processes occuring within the exchanger itself is difficult to obtain because of or lack of methods for the complete separation of the phases. Liquid exchangers offer much better prospects in this respect. Some observations have been made with dinonylnaphthalene sulphonic acid, a liquid sulphonic acid with properties very similar to those of sulphonic acid resins.(30,60,61,62) Mono-(2-ethylhexyl) phosphoric acid also behaves in an analogous manner to ion-exchange resins .(59)

An important point of nomenclature arises here. Many organic substances extract metals from solution and in the literature they are often referred to as liquid ion- exchangers(63) or it is inferred that they are liquid cation- exchangers.(64,65) A rigorous definition of a "liquid ion - exchanger" is difficult but one which has been proposed is the following:(66)

"liquid ion-exchange refers to those liquid -liquid extraction systems that operate, at least formally, by interchange of ions at the interface between an aqueous solution and an imiscible solvent with negligible distribution of the extracting agent to the aqueous phase". A further point arises that although a large number of substances may be denoted as liquid ion-exchangers using the above definition they may frequently show completely different behaviour under certain conditions. This may be illustrated by reference to the phosphate esters where the mono-alkyl esters are analogous to the corresponding ion-exchange resins under all conditions whereas the di-alkylphosphate esters exhibit very different behaviour from both the mono-alkyl esters and the corresponding resins at high electrolyte concentrations.

It was the purpose of the present work to investigate various potential "liquid cation - exchangers" and evaluate their usefulness with regard to extending our knowledge of ion-exchange processes. From these preliminary investigations a mono-alkylphosphate ester was selected as the most promising in this respect.

Distribution studies with radioactive tracers together with investigations of the effect of changing the composition of the organic phase and "loading" the aqueous phase with carrier were made. From these and studies of the extraction of water and electrolytes by the ester it was hoped to gain some insight into the exchange processes occuring from strong aqueous electrolyte systems.

CHAPTER II

EQUILIBRATION METHODS AND EQUIPMENT USED IN THE EXPERIMENTAL WORK

Introduction

The present chapter deals with the general procedures adopted for equilibrations involving both solid and liquid ion-exchanger systems. The preparation of the exchanger and stock electrolyte solutions is discussed together with the method of calculating distribution coefficients. There is also a brief outline of the radiochemical methods of measurement employed in the course of the distribution studies.

(A) Ion-exchange resins

(i) The distribution coefficient of a metal was determined by the batch equilibration technique in which a known weight of resin was agitated with known volumes of solution containing the labelled metal ion. Agitation was continued until there was no significant change in the activity of the aqueous phase with time. Usually 12 hours was sufficient for equilibration, though occasionally 1 to 2 days were required for the strongest solutions. By counting aliquot portions of the aqueous phase before and after equilibration the distribution coefficient, K_d, was calculated from the relation

$$K_d = \frac{\text{Volume of aqueous phase}(V_a)}{\text{Weight of resin taken }(W_m)} \times \frac{\text{Initial activity }(C_1) - \text{Equilibrium activity }(C_2)}{\text{Equilibrium activity }(C_2)}$$

The activity was expressed as counts per minute (c.p.m.).

(ii) Preparation of the resin

The resin was supplied in the sodium form and occasionally it was required in the hydrogen - or lithium form. A batch of about 100 g of resin was slurried into a large column with distilled water. It was then washed with about 15 column volumes of 2M hydrochloric acid, which removed any iron; this also converted it to the hydrogen form. Excess acid was washed out with distilled water. Resin "fines" were removed by decanting a partially settled slurry of the resin. If the lithium form was required a batch of the hydrogen form was loaded into the column and treated with 2M lithium chloride solution until the effluent was free of hydrogen ions. The resin bed was finally washed with 3 or 4 column volumes of distilled water to remove excess electrolyte. Before using the resins in distribution experiments they were dried in an oven at approximately 80°C until the beads did not stick together. This operation required about 24 hours; the resin was finally stored in dry, screw-top glass jars.

(iii) Preparation of stock solutions

Stock solutions of a given salt were prepared by dissolving the requisite amounts of the salt in distilled water. The stock solutions were prepared in such a way that appropriate aliquot portions on dilution to a given volume gave solutions of the required salt concentration. The majority of the salts used were not sufficiently stoichiometric in composition to allow accurate concentrations to be prepared by direct weighing methods. Solutions of approximately the required strength were prepared and then standardised by appropriate titration procedures. For bromides and chlorides the method of Mohr was used. Stock acid solutions were standardised against alkali.

The active solutions were prepared by pipetting aliquot portions of stock solutions into volumetric flasks and adding 0.5 to 1 ml of tracer solution so that after making the volume up to the mark a 10 ml portion of the solution gave approximately 10^4 c.p.m. in a G-M liquid counter. The amount of tracer added depended on the concentration of solution since the absorption of β -particles increases with the density (and hence with the concentration) of the solution.(27) When salt solutions were used sufficient of the corresponding acid was added to prevent hydrolysis of the tracer metal.

(iv) Counting equipment.

The tracer chosen for the ion-exchange studies was In^{114}, which emits a fairly energetic β-particle and has a half-life of 50 days. The activity was counted in a G-M liquid counter, whose function has already been described in Part I of this work. (Page 43).

(v) Procedure for equilibrations.

Known amounts of resin (usually 0.500 g.) were weighed into polythene capsules having an opening (4 mm diam.) on a short neck at one end. Fifteen ml of active solution were then pippetted into the capsules, which were sealed by warming the neck at the open end of the capsule in a bunsen flame until the polythene softened. The sides of the neck were then pressed firmly together with the aid of a pair of tweezers. The tip was then warmed in the bunsen flame in order to complete the seal which was tested by inverting the capsule and squeezing it gently. If any liquid seeped through the capsule was discarded.

The capsules were clamped on to a rotating wheel inside a constant temperature water bath. The wheel could accommodate 16 capsules at a time and equilibrations were continued for the required (predetermined) length of time. The temperature was 25 ± 1°C.

At the end of the equilibration the capsules were removed from the bath. The tip was removed with a razor blade and the aqueous phase squeezed into a centrifuge tube. In this way only a small fraction of the resin was transferred, The solution was centrifuged for about 5 minutes and then an aliquot portion of the solution carefully removed for counting.

B. Liquid-liquid systems.

(i) Preparation of solutions of the "liquid exchanger".

All measurements in this work were carried out using toluene as the organic diluent. Solutions were usually prepared by weighing out an appropriate amount of the "liquid exchanger" into a volumetric flask and making the volume up to the mark with AR grade toluene. When a series of solutions of different concentrations were required a stock solution of the "exchanger" was prepared and the other solutions prepared from this by dilution.

(ii) Procedure for equilibra tions.

In all cases a pre-equilibration of the phases was carried out by shaking suitable volumes of the organic and inactive aqueous phase together. Portions of the equilibrated organic phase were then removed for equilibration with the active aqueous solution.

Solutions were shaken in stoppered volumetric flasks using a mechanical shaker of the vibratory type, which provided adequate mixing of the two phases. After equilibration the solution was centrifuged and then aliquot portions of the appropriate phase removed either for further equilibrations or for counting. The solutions were maintained at room temperature (21 ± 2$^{\circ C}$) throughout.

If the distribution coefficient was very small ($< 2 \times 10^{-1}$) then a modified procedure was used. A small value of K_d means that the final counting rate of the aqueous phase will not differ very much from the initial counting rate i.e. one is determining a small difference between two large quantities. This was overcome using a back-extraction technique in which the pregnant organic phase was further equilibrated with a second barren aqueous phase, identical to the aqueous phase used in the pre-equilibration step. Since the K_d value was very small from the definition of K_d (see section (iv)), virtually all of the activity transferred to the aqueous phase, which on counting then gave directly a reasonable measure of C_1-C_2 in section (iv).

(iii) Radiochemical measurements

All tracers used in this work were obtained from the Radiochemical Centre, Amersham, Bucks.

The majority of distribution measurements were made using carrier-free Y^{91} which is conveniently counted in a G-M liquid counter. Later some measurements were made with carrier-free Ce^{144}, Gd^{153} (containing 1.4×10^{-3} μgm of gadolinium per ml of solution used in equilibrations) $Eu^{152+154}$ (containing 6×10^{-2} μgm of europium per ml of solution used in equilibrations), and Am^{241}. Ce^{144} in equilibruim with the Pr^{144} daughter may also be counted in a liquid counter but Gd^{153}, $Eu^{152+154}$ and Am^{241} decay giving rise to γ-rays suitable for scintillation counting. The solutions for γ-counting (usually 5 ml) were contained in snap-top polythene vials. They were counted using a NaI(Tl) well-type crystal manufactured by Nuclear Enterprises (GB) Ltd. - Type $7F_8$. The crystal was ¾" in diameter and 2" high. The associated electrical eqipment was similar to that already described in Part I of this work (P. 38). The γ- spectra for these nuclides was plotted and suitable photopeaks selected for γ -ray counting. Since the peak position drifted somewhat a periodic check was made on bias voltage settings, adjustments were made where necessary to ensure reproducible counting rates for a standard source of the given nuclide.

(iv) Calculation of the distribution coefficient

The distribution coefficient, K_d, is defined in these systems in an analogous way to that in the liquid-resin system; the weight of resin used is replaced by the volume of organic phase equilibrated. Thus

$$K_d = \frac{\text{Vol. of aqueous phase (ml)}}{\text{Vol. of organic phase (ml)}} \times \frac{\text{Initial counting rate } (C_1) - \text{final counting rate } (C_2)}{\text{final counting rate } (C_2)}$$

As before counting rates in the aqueous phase, are applied to the formula to compute K_d.

CHAPTER III

PRELIMINARY INVESTIGATIONS WITH ION-EXCHANGE RESINS AND POTENTIAL "LIQUID ION-EXCHANGERS"

Introduction

Ion-exchange behaviour as a function of the external electrolyte concentration was observed with a commercial polystyrene based resin in several salt forms and shown to be in reasonably good agreement with published data. A series of potential "liquid exchanger" systems were then investigated in order to determine their ion-exchange characteristics. Both solid (stearic acid, cetyl sulphonic acid and lauryl acid phosphate) and liquid (nonyl acid phosphate, mono-2-(ethylhexyl) phosphoric acid and dinonylnapthalene sulphonic acid) substances dissolved in a suitable diluent were used. The preparation and attempted purification of some of these substances is discussed. On the basis of the results obtained with these "liquid exchangers", mono-2-ethylhexyl phosphoric acid was selected for more detailed investigations.

Experimental

a) Ion-exchange resins

Earlier work on the adsorption of metal cations from strong electrolyte solutions indicated the importance of both the cation and the anion of the electrolyte in determining the extent of the distribution.(25,27,29,30,35,45) Much of the work was carried out using Dowex-50 cation-exchange resins. It was thought desirable to check that similar results could be obtained with Zeo-Karb-225 cation-exchange resins, which would eliminate the possibility of the effects observed being due to resin impurities. The effect of changing the cation form of the resin was also studied.

In^{114} was chosen as the tracer for these studies as there is published data for the sorption of this metal on cation-exchange resins.(27)

The resin used was "Chromatographic Grade" Zeo-Zarb-225, 100 to 200 mesh having 8% DVB content. The different cation forms of the resin were prepared as previously described (Chapter II). Samples of 0.50 g of resin were equilibrated with 15 ml of aqueous solution containing the tracer using the procedure already outlined and log K_d plotted against the molarity of the external aqueous electrolyte solution. The results are presented graphically in fig. 1 (a), (b) and (c).

The data in fig. 1 (a) show similarities to that obtained in earlier work with In^{114} and sodium bromide solutions.(27) However, the minimum value found for the distribution coefficient in this work is at a lower sodium bromide concentration than that found by IRVING(27) and it is also less broad. The increase

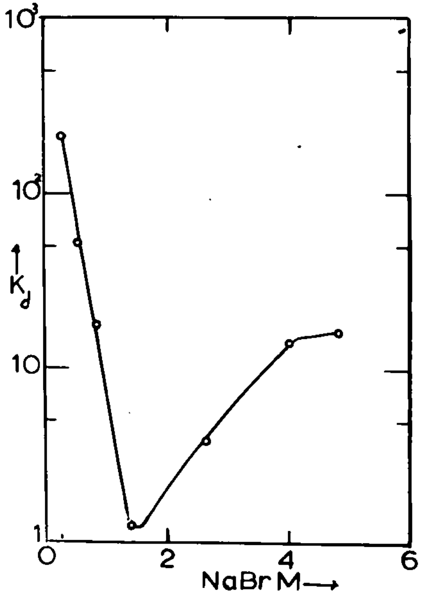

Fig.1(a) Distribution of In^{114} between NaBr and 8% Zeo-Karb-225 resin(H^+form)

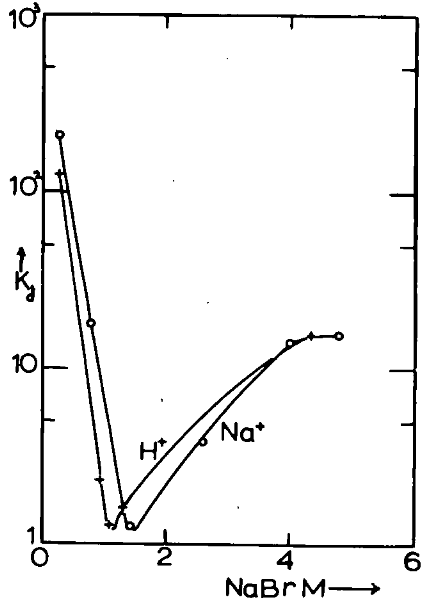

Fig.1(b) Distribution of In^{114} between NaBr and 8% Zeo-Karb-225(Na^+ and H^+ forms)

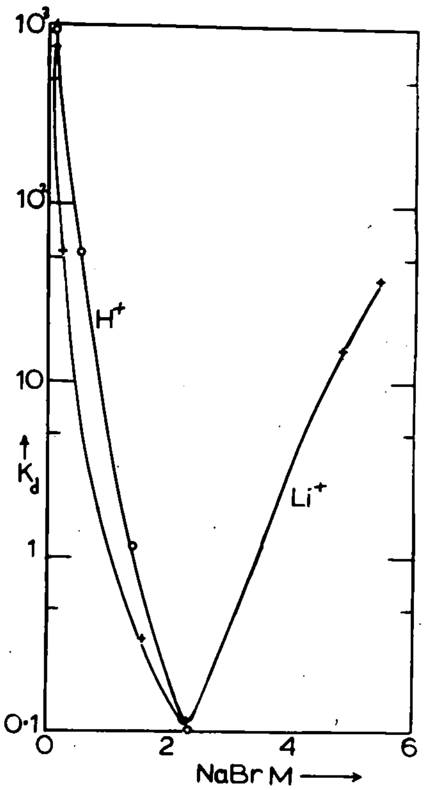

Fig.1(c) Distribution of In^{114} between LiBr and Zeo-Karb-225(H^+ and Li^+ forms) in the distribution coefficient after this point is also less marked. These differences may be due to differences in the resin used in the two cases.

On changing from the hydrogen form to the sodium form of the resin little difference in the shape of the distribution curve was found, though the minimum value for the sodium form was displaced to slightly higher sodium bromide concentration.

When lithium bromide was used as the electrolyte the distribution coefficients were higher than inequivalent concentrations of sodium bromide, which is in agreement with previous observations that distribution values are higher from lithium salts than from the corresponding sodium or hydrogen salts. (25,27,29)

(b) Stearic acid.

The preliminary experiments with ion-exchange resin confirmed the form of distribution curve found by earlier workers. In order to investigate further those factors which may be of importance in determining the exact form of the distribution curve over a wide electrolyte concentration range, other possible exchange systems than resins were considered. The main disadvantage of an ion-exchange resin is that it is difficult to investigate phenomena occurring within the resin itself due to the very nature of these substances. A much more convenient exchange system would be one in a liquid form. Measurements can then be carried out more easily and with greater scope for exploration of relevant properties.

One such exchanger with which some experiments have been carried out is dinonylnaphthalene sulphonic acid(29,30,61,62). At the time that this work was commenced a sample of this material was not immediately available, in the laboratory, so that work was initially directed towards finding other suitable ion-exchangers.

Stearic acid was the first substance selected for investigation. It was thought that it might act as an ion-exchanger since resin exchangers with carboxylic instead of sulphonic acid groups were already known. Fatty acids have been shown to be capable of extracting certain metal ions from mineral acid solutions,(68) and stearic acid is a typical, readily available long chain fatty acid.

Initially there was some difficulty in finding a suitable solvent for stearic acid. It was virtually insoluble in benzene and toluene and although it dissolved in carbon tetrachloride to some extent it tended to precipitate out on standing. Eventually a 1:1 mixture of carbon tetrachloride and chloroform was found to be satisfactory. A 0.2M solution of stearic acid in this solvent mixture was prepared. Distribution measurements with Y^{91} as the radioactive tracer were conducted using aqueous phases of perchloric acid and lithium bromide (0.02M in hydrobromic acid) containing the Y^{91}. In neither case was any significant extraction of yttrium into the stearic acid found to be occurring. This was true even for the most dilute aqueous solutions used (approximately 0.2M). It therefore appeared that stearic acid was not behaving as a liquid exchanger and no further measurements were made with this substance.

(c) Cetyl sulphonic acid.

Cetyl sulphonic acid (CSA) was selected for investigation since it was thought that it might behave similarly to dinonylnaphthalene sulphonic acid. This particular acid was chosen in consequence of its large hydrocarbon chain which should endow it with negligible solubility in the aqueous phase. It was also relatively easy to prepare.

The preparation was based on the method of MURRAY (69), in which 24 g of cetyl iodide were slowly added to a boiling solution of KSH. The resulting mercaptandisulphide was then carefully oxidised to the sulphonic acid using fuming nitric acid. The resulting solution was evaporated to half its original volume and the acid formed recrystallised from 50% aqueous methanol and stored in a desiccator.

A 0.025M solution of the soap was prepared in toluene, and initially distribution measurements were carried out with Y^{91} from hydrochloric acid solutions. It was found that these solutions readily emulsified and the emulsion could not be broken down either by centrifugation or the addition of chemicals.

In later experiments a 0.0025M solution of CSA in toluene was used with perchloric acid as the aqueous phase instead of hydrochloric acid. Emulsions still formed after equilibrating the two phases, though these could be partially broken down by centrifuging the solutions for several minutes. However, the results indicated that little distribution of activity was occurring.

Some further equilibrations were carried out with a solution of CSA in "hexone" (methyl iso-butyl ketone) and aqueous solutions of perchloric acid, sodium perchlorate and lithium bromide. Some exchange was found to occur in these systems though this was later shown to be due entirely to extraction by the hexone solvent.

The results suggest that CSA has only negligible ion-exchange properties and no further investigations were carried out.

(d) Lauryl acid phosphate.

A considerable amount of data on the extraction of metal ion into phosphate esters has been published. Much of this work has been carried out using the di-esters, particularly di-butyl and di-ethylhexyl phosphoric acid esters.

A sample of "lauryl acid phosphate" (LAP) was available (Albright & Wilson Mfg. Co. Ltd.) and this was now investigated as a possible ion-exchanger. Although the composition of the material was unknown, the manufacturers stated that it consisted mainly of a mixture of mono- and di- lauryl phosphoric and esters. Initially no attempt was made to separate these esters.

A solution containing 53 g of ester per litre of toluene was prepared. Using Y^{91} as tracer, distribution measurements were carried out usingaqueous phases of perchloric acid and lithium bromide.

Equilibrations with dilute solutions of these two electrolytes and the LAP solution gave rise to stable not-readily-dispersed emulsions, although aqueous solutions of either electrolyte greater than 2M in concentration did not produce emulsions. The distribution data indicated high K_d values especially from the most concentrated solutions employed (5M LiBr and 11M $HClO_4$)

TABLE I. Extraction of Y^{91} from perchloric acid and lithium Bromide into a toluene solution of LAP (53g LAP/l).

Aqueous Phase	Molarity	K_d
$HClO_4$	3.74	2.50
	10.76	6.00
LiBr	2.01M	1.92
	5.11M	6.30

When sodium perchlorate was substituted for perchloric acid emulsification problems were increased to such an extent that worthwhile distribution measurements could not be made.

In order to try and reduce emulsification a more dilute solution of LAP in toluene was prepared; it contained 13.3 g LAP per litre. Emulsification still occurred, especially when salts rather than acids constituted the aqueous phase. Sodium chloride, sodium bromide, ammonium chloride and ammonium nitrate were all tried but none proved to be of any general use because of the emulsions formed with the organic phase, even when concentrated aqueous salt solutions were used.

The high distribution coefficients from concentrated solutions of perchloric acid and lithium bromide indicated that phosphate esters of this type might be good liquid ion-exchangers, though their usefulness was obviously seriously limited by the formation of emulsions with the majority of the aqueous solutions used. Thus although no further expe riments were carried out with LAP, it was considered worthwhile investigating other phosphate esters.

(e) Nonyl acid phosphate.

Nonyl acid phosphate (NAP) like the lauryl ester, was supplied by Albright and Wilson Mfg. Co. Ltd. as a mixture of mainly the mobo- and di-esters. Some preliminary experiments were carried out on this crude material concurrently with those on LAP.

A solution of approximately 11.3 g NAP per litre was prepared in toluene, and this solution was used in equilibrations with perchloric acid. Equal volumes of each phase were shaken together for about an hour and the solutions then centrifuged. There was little sign of emulsification. The pre-equilibrated organic layer was then equilibrated with the active aqeuous phase, using Y^{91} as tracer. After equilibration and centrifuging the solutions, the lower aqueous phase was re-counted. The results obtained are given in Table II.

TABLE II. Extraction of Y^{91} from perchloric acid into a toluene solution of NAP (11.3 g NAP/1)

Concentration of Perchloric Acid.	K_d
0.373 M	295
3.73 M	0.63
10.82 M	69.7

The above results showed that a minimum recurs in K_d plotted as a function of the perchloric acid concentration, as was found for ion-exchange resins. Moreover, the increase in K_d beyond the minimum value appears to be quite marked pointing to NAP having properties similar to an ion-exchange resin.

When sodium perchlorate and sodium bromide replaced perchloric acid some difficulty was encountered over emulsification but only when dilute salt phases were used (0.2M or less of $NaClO_4$ and NaBr). The more concentrated solutions proved completely successful in this respect. The K_d values obtained for these solutions were very high at all the aqueous phase concentrations investigated and virtually all the activity transferred into the organic phase. This same behaviour was found when ammonium chloride and nitrate were equilibrated with the NAP solution and this is to be contrasted with the behaviour in the perchloric acid system.

These results seemed to indicate that on changing the cation from hydrogen to an alkali metal or ammonium ion the exchange behaviour was markedly altered. In order to investigate this more thoroughly a series of solutions of mixed sodium chloride and hydrochloric acid were prepared in which the chloride concentration was held constant (at 4.50 M) but in which the sodium ions were gradually replaced by hydrogen ions. The K_d values for these solutions were then determined, and are presented in Table III.

TABLE III Extraction of Y^{91} from HCl-NaCl solutions into NAP in toluene (11.3 g/l) with a constant chloride concentration of 4.50 M.

Concentration of Hydrogen Ions	K_d
0.048 M	74.7
0.47 M	6.8
0.94 M	2.0
1.88 M	0.52
2.82 M	0.25
4.50 M	0.01

These results indicate the importance of the cation on the distribution coefficient of Y^{91}. The value of K_d when the concentration of hydrogen ions is the same as that of sodium ions is only about 0.005 of the value for almost pure sodium chloride.

An attempt to determine the composition of the NAP was now made. First the mean equivalent weight was measured using a standard sodium hydroxide solution; a value of 157 was obtained (the pure mono-ester would have an equivalent weight of 112.5 while that of the di-ester would be 351). A more detailed titration was used in order to try and determine the composition of the sample.

The manufacturers stated that the sample consisted almost entirely of either mono- or di-phosphate esters together with a small fraction of free phosphoric acid. Initially a mixed indicator method was used, based on one developed in the research department of Messrs. Albright and Wilson Mfg. Co. Ltd.(70) The table below indicates the composition of the indicator.

TABLE IV. Composition of an indicator for titration of NAP against sodium Hydroxide.

Reagent	Weight	Solvent	Volume
Methyl Red	0.125 g	ethyl alcohol	150 ml
		water	50 ml
Bromocresol Green	1.35 g	ethyl alcohol	200 ml
		water	50 ml
p-Nitrophenol	4.30 g	ethyl alcohol	200 ml
Phenolphthalene	16.80 g	ethyl alcohol	200 ml

The above solutions were mixed together and standardised by adding a drop to a solution of 3 g of mono-sodium acid phosphate in 100 ml of water and adjusting the pH to 4.5. The indicator should be decolourised in this solution and necessary adjustments were made to the composition until this behaviour was achieved. The phosphate solution was then titrated potentiometrically with 1.0 M sodium hydroxide to a pH of 8.55. One drop of indicator should have given a grey tint at the above pH and again the composition was adjusted until this colour was obtained. (Occasionally this necessitated checking the colour obtained at pH4.5.). In practice it was found difficult to prepare an indicator solution which would give the required response at the above mentioned pH values.

About 0.5 g of the ester were accurately weighed out and dissolved in a mixture of 70 ml of ethanol and 30 ml of water. The solution was titrated against 0.1N potassium hydroxide in a mixture of 70% ethanol and 30% water by volume, until the indicator was decolourised. This was the first end-point. Next 7.2 g of sodium chloride were added (to bring the pH closer to 7) and the titration continued to the second end-point (at pH 9.5). Calcium chloride was then added and the titration continued to a third end-point, at which the solution assumed a red colour. The three end-points represent successive replacements of the hydrogen atoms in the esters and phosphoric acid by potassium ions. From the various titres it is possible to calculate the percentage of each substance present. In practice, however, there was some difficulty in determining the second end-point even potentiometrically. Thus the results obtained were somewhat imprecise; the sample contained about 40% of the di-ester, approximately 50% of mono-ester and about 2% phosphoric acid (the balance was probably nonyl alcohol).

A separation of the esters was now attempted. The procedure used was similar to that described by PEPPARD(71), for the separation of ethylhexyl phosphate esters.

Approximately 300 g of the mixed esters were taken for purification. After hydrolysis with 6M hydrochloric acid the esters were converted to the sodium salts by the addition of a slight excess of 1M sodium hydroxide. On addition of ether two layers were produced, the upper ethereal phase containing most of the di-ester, the lower aqueous phase the major portion of the mono-ester. The two phases were separated and each subjected to a number of further purification steps in order to obtain pure samples of each of the esters. Considerable problems were encountered in many of these stages due to emulsification of the phases present and the resulting yields of the pure esters were very poor. The separation was repeated, with modifications, a number of times but always with poor yields of the pure esters.

Because of the difficulties encountered in the separation of the esters by solvent extraction procedures, other possible methods of separation were considered.

An anion-exchange method was examined. De-Acidite FF (chloride form) having a particle size in the 100 to 200-mesh range and 7 to 9% cross linked was used. Ten g of moist resin were slurried into a tube to give a resin column about 38 cm. long. The column was washed first with 100 ml of distilled water followed by 50 ml of a 70:30 (v/v) solution of alcohol and water. Initially a sample of NAP was converted to the sodium salt which dissolved in the alcohol/water mixture. This could not be adsorbed in a narrow band on the column and therefore the acid itself was used in subsequent experiments. About 0.2 g of the acid were dissolved in 2 ml of the ethanol/water mixture and adsorbed on the top of the resin column which was eluted with the ethanol/water solution. The flow rate was 0.2 ml per minute. Three ml fractions were collected and analysed for phosphate by the method of RIEMAN III.(72) in which the phosphate was determined spectrophotometrically as the vanadomolybdate, measuring the absorbance at 400 mμ(73).

A preliminary semi-quantitative determination of the phosphate present in the fractions was carried out by spotting small amounts of each fraction on a Whatman No.1 filter paper and spraying the paper with an alkaline solution of "universal" indicator.(74) The first results indicated very poor separation of the esters. However, on eluting at pH 10 a separation was affected; as the data presented in fig. 2 indicate. As a means of separating esters on a large scale, however, the method did not seem to offer very good prospects, since loading factors had to be very

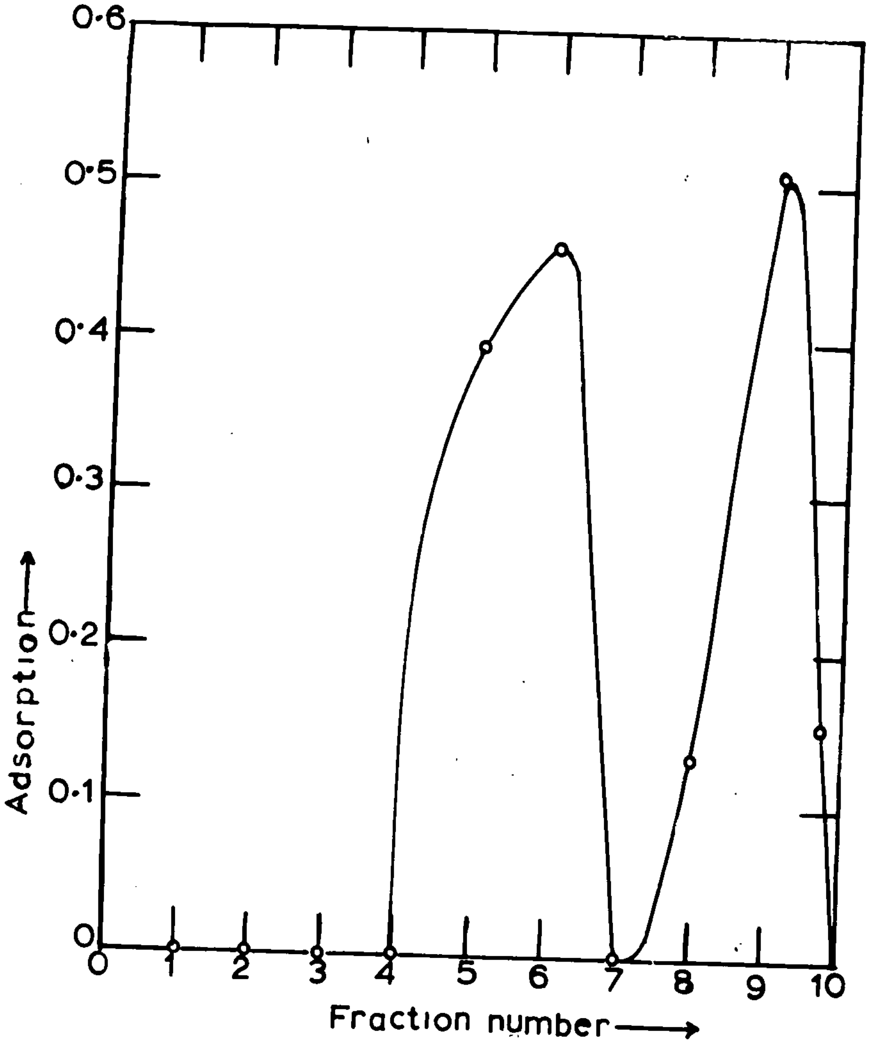

Fig. 2 Separation of NAP esters on an anion-exchange column

small to effect an adequate separation. Other means of separating the esters were therefore considered.

Another possibility was that based on the principle of "ion-exclusion".(75) A column of Zeo-Karb-225 resin in the hydrogen form (8% DVB content and 100 to 200 mesh range), 102 cms. long and with a cross-section of 1.6 cm^2, was prepared. Three g of the acidic ester were loaded on to the column in 2 ml of the ethanol/water mixture. On adsorption on the resin the column was eluted with ethanol/water, using a flow rate of about 0.5 ml per minute. The first 36 ml of elvant were discarded and 15 ml fractions (12 in all) were collected. The fractions were analysed spectrophotometrically as previously described. These results indicated that the ester passed rapidly through the column without any separation being effected and the method was abandoned.

A satisfactory method was not found for the separation of the esters in this mixture. But a few more distribution measurements were made on the mixed esters. A solution of NAP in toluene was prepared and the distribution of Y^{91} determined between this and solutions of perchloric acid, hydrochloric acid and lithium bromide. The results are shown in Table V.

TABLE V. Extraction of Y^{91} into NAP solution (26 g NAP/1) from $HClO_4$, HCl and LiBr.

Aqueous Phase	Concentration	K_d
$HClO_4$	0.36 M	388
	3.60 M	0.4
	10.20 M	15
HCl	0.48 M	399
	4.80 M	0.2
	10.60 M	0.3
LiBr	0.27 M	5.45×10^3
	2.70 M	7.05×10^3
	5.88 M	2.29×10^4

Distribution coefficients were then determined in more detail for the perchloric acid solutions using a more dilute solution of NAP. Duplicate and frequently triplicate measurements were made at each acid concentration. The results are given in Table VI.

TABLE VI. The Extraction of Y^{91} into NAP in toluene (10.87 g/l) from perchloric acid.

Concentration of Perchloric Acid	K_d
0.36 M	200 ± 20
2.90 M	0.55 ± 0.03
3.24 M	0.34 ± 0.02
3.60 M	0.24 ± 0.01
3.96 M	0.39 ± 0.03
6.48 M	2.65 ± 0.02
8.35 M	3.09 ± 0.07
9.28 M	4.37 ± 0.03
10.21 M	21 ± 1

Finally the HCl- and LiBr- NAP systems were examined in more detail and K_d values found at suitable concentrations throughout the range of electrolyte concentrations used. The results are presented in Tables VII and VIII.

TABLE VII. Extraction of Y^{91} into NAP in toluene (10.87 g/1) from hydrochloric acid.

Concentration of Hydrochloric Acid.	K_d
0.48 M	70 ± 2
2.04 M	0.57 ± 0.03
4.08 M	0.14 ± 0.02
4.80 M	0.1
5.52 M	0.1
7.20 M	0.1
9.00 M	0.20 ± 0.02
10.60 M	0.30

TABLE VIII. Extraction of Y^{91} NAP in toluene (10.87 g/1) from lithium bromide (each solution 0.05M in hydrobromic acid.

Concentration of Lithium Bromide	K_d
0.27 M	$1.47 \pm 0.04 \times 10^3$
2.70 M	$3.64 \pm 0.02 \times 10^3$
5.88 M	$1.56 \pm 0.03 \times 10^3$

The data contained in Tables VI to VIII show that the mixed esters of NAP exhibit exchange behaviour which is closely analogous to that observed in cation-exchange resins.(25, 27,29,30,35) Such a system is therefore promising as a liquid ion exchanger. The main obstacle to using NAP is that the esters could not be easily separated and it is obviously desirable to carry out distributions on the pure ester rather than a mixture. The extensive work already carried out with di-esters indicate that these do not show the behaviour just noted (77,81,82) and it is therefore reasonable to assume that it is the mono-ester which is responsible for the form of distribution observed. Because a pure sample of the mono-ester could not be obtained by separation methods in sufficient quantity other alkyl esters were considered.

(f) Mono-(2-ethylhexyl) phosphoric acid

Investigations by PEPPARD et al (59) had shown that mono-(2-ethylhexyl)phosphoric acid exhibited exchange behaviour closely similar to that already observed in ion-exchange resins. It therefore offered the prospect of being a suitable material with which to study ion-exchange behaviour and some preliminary experiments were carried out. Previously mono-(2-ethylhexyl) phosphoric acid (H_2MEHP) had been obtained by separating it from a commercial mixture of the 2-ethylhexyl esters.(71) Such a mixture was no longer available and this necessitated the synthesis of the monoester. The preparation was similar to that described by GAMRATH and CRAVER.(76) Forty-six g of phosphoryl chloride were cooled to 15°C and 39 g of 2-ethylhexanol, previously cooled to 15°C, slowly added, with continuous stirring at such a rate that the temperature was maintained at 15°C. The reaction vessel consisted of a round-bottomed, four necked flask. After the complete addition of the alcohol stirring was continued for one hour, with the temperature maintained at 15°C. After this time the temperature was allowed to rise to 25°C. and the stirring continued for a further hour. The hydrogen chloride formed in the reaction was removed under suction by a water-pump. The main reaction product is 2-ethylhexylphosphoryl dichloride, formed according to the equation.

$$C_8H_{17}OH + POCl_3 \longrightarrow (C_8H_{17}O)PCl_2 + HCl$$

The flask containing the dichloride was set aside overnight, after which the 2-ethylhexyl phosphoryl dichloride was hydrolysed to H_2MEHP. Hydrolysis was effected by the addition of water. Since considerable heat is evolved during this process the solution was cooled externally by ice and the water added very slowly, with efficient stirring. The solution was set aside for 2 hours after which time the cooled mixture was transferred to a separating funnel. The lower aqueous layer was run off and discarded. The ester layer was then purified by the method of PEPPARD et al(71) (cf. P.33). The yield of mono-ester was only about 15% of the theoretical yield. A further portion of the ester was prepared in slightly better yield, and the two portions combined. This produced sufficient H_2MEHP to allow a series of preliminary investigations to be carried out.

The equivalent weight of the ester was determined by titration with aqueous sodium hydroxide. A known weight of the ester (about 0.2 g) was dissolved in at least 75 ml of ethanol, and titrated against standard 0.1N NaOH, using phenolphthalein or thymol blue as indicator. The equivalent weight so determined was 105.4 compared to the theoretical value of 105.1. The ester was on this basis considered to be of satisfactory purity. Later the ester was further characterised by determining its refractive index (cf. P 57).

Distribution Measurements with H_2MEHP.

A 0.0335 M solution of H_2MEHP in toluene was prepared and used in preliminary distribution measurements with hydrochloric acid, perchloric acid and lithium bromide. Preequilibrations were carried out in all cases. With the most dilute lithium bromide solution (0.18M) emulsification occurred. PEPPARD (77) has noted that a gel-like substance is formed when solutions of H_2MEHP are shaken with water. The gel is broken down by the addition of mineral acid. It is not altogether surprising, therefore, that dilute lithium bromide solutions should emulsify with H_2MEHP. This prevented distribution measurements from being carried out in dilute salt solutions. The K_d values obtained in concentrated hydrochloric acid solutions were determined by counting the aqueous phase before and after equilibration with H_2MEHP. The two count rates differed by 1% or less, and thus the K_d value so obtained can be taken only as a rough approximation at this stage. As was found with NAP, K_d values in the LiBr-phosphate system were very high at all concentrations of bromide (even though a value at dilute solutions was not available there is no reason to suppose that it would be significantly different from those obtained at high concentrations). Values of K_d for three representative concentrations of $HClO_4$, HCl and LiBr (2 values) are recorded in Table IX.

TABLE IX. Extraction of Y^{91} from $HClO_4$, HCl and LiBr into 0.0335M H_2MEHP

Aqueous Phase	Concentration	K_d
HCl	0.48	2.52
	4.80	0.01
	10.60	0.01
$HClO_4$	0.37 M	7.37
	3.74 M	0.07
	10.74 M	11.83
LiBr	0.18 M	-
	1.80 M	320
	3.96 M	310

These results indicated that H_2MEHP would be a suitable liquid ion-exchanger and it was proposed to carry out more detailed investigations of ion-exchange behaviour using this material at a later stage.

(g) Dinonyl naphthalene sulphonic acid.

In the course of the exploratory work a sample of dinonylnaphthalene sulphonic acid (HDNNS) became available. It was supplied by R.T. Vanderbilt and Co., Inc., Park Ave., New York, 17, as a 36% solution of the acid in heptane. A comparison of distribution measurements obtained with this substance and those obtained using H_2MEHP seemed worth investigating. Any differences in exchange behaviour between the two types of exchanger could provide information concerning the factors which are of importance in determining ion-exchange behaviour.

Toluene has been used as a diluent in the H_2MEHP studies, and published data have shown the effect of the diluent on distribution values.(78, 79, 80, 81, 82) Therefore in order to make a direct comparison between data obtained in the two systems an attempt was made to prepare a toluene solution of HDNNS. Approximately 40 ml of the HDNNS in heptane was placed in a two-necked, 250 ml round-bottomed flask. One neck carried an air-leak while the other was connected to a water-pump. The solution was pumped at room-temperature for about 6 hours after which time no odour of heptane was detected and the residue was a dark-brown, very viscous fluid. This was assumed to be a pure sample of HDNNS. The yield was about 20 g and 14.5 g were dissolved in 500 ml of AR toluene to give a stock solution of HDNNS. Distribution data for Y^{91} were determined for the systems HDNNS-HCl, HDNNS-$HClO_4$ and HDNNS-LiBr. The results are presented in Table X.

TABLE X. The distribution of Y^{91} between HCl, $HClO_4$, LiBr and toluene solutions of HDNNS (29.08 g/l)

Aqueous Phase	Concentration	K_d
HCl	0.48	16
	4.80	0.29
	10.60	0.1
$HClO_4$	0.36	50.4
	3.60	0.33 ± 0.01
	10.30	0.53 ± 0.02
LiBr	0.18	796
	1.80	3.0
	3.96	0.5
	7.22	0.15 ± 0.02

Previous investigators, using Fe^{59} as tracer, had found distinct minima in the plots of log K_d against electrolyte concentration for both perchloric acid and lithium bromide, with a marked rise in K_d after this minimum value(29,60). Similar minima would be expected in the distribution of Y^{91}. There was no adequate explanation for the discrepancy but possible desulphonation of the acid during the evaporation of the n-heptane may have been a contributing factor, even though mild distillation conditions were employed.

Consequential to this work distribution measurements were made using the original stock heptane solution of HDNNS diluted with petroleum ether (boiling range 80 to 100°C). An approximately 0.1M solution was initially prepared. Distribution measurements were carried out using equal volumes of this solution and perchloric acid solutions containing Y^{91} as tracer, and the results tabulated below.

TABLE XI. Extraction of Y^{91} from perchloric acid into 0.10M HDNNS

Concentration of perchloric Acid.	K_d
0.36 M	117
2.88 M	0.44
3.60 M	0.31
5.40 M	0.23
8.42 M	1.30
10.53 M	5.98

Discussion of results

The preliminary investigations outlined in the preceding pages indicated that solutions of monophosphate esters and HDNNS were behaving in a manner closely resembling that of cation-exchange resin, exemplified in the present work by Zeo - Karb - 225. This being the case it would be justifiable to apply the term "liquid ion - exchanger" to these substances. The problem of emulsification encountered with the phosphate esters when used with dilute solutions tended to limit to some extent the useful range of electrolyte concentrations over which distribution measurements could be made. This aspect was appreciably less serious with a purified sample of H_2 MEHP than for the mixed commercial esters (NAP, LAP) used earlier. The emulsification problem did not arise in the case of HDNNS, which however consists of an ill - defined chemical substance or substances whose performance may vary from batch to batch. On the basis of this consideration and the distribution data, H_2 MEHP was selected for more detailed investigations.

CHAPTER IV.

A STUDY OF MONO-(2-ETHYLHEXYL) PHOSPHORIC ACID IN LIQUID-LIQUID EXTRACTION.

Introduction

More detailed investigations of the extraction behaviour of H_2MEHP are reported in this chapter. After a preliminary discussion of the validity of the assumption of negligible transfer of the ester into the aqueous phase there follows a number of distribution measurements for Y^{91} between H_2MEHP and several aqueous systems. Included in this section are distribution measurements for $Eu^{152+154}$ and Am^{241} between H_2MEHP and hydrochloric acid. Measurements were made to determine the effect of HDEHP on the extraction behaviour of H_2MEHP and these were later supplemented by more extensive investigations of the HDEHP-H_2MEHP system with aqueous phases of various compositions. The effect of varying the aqueous to organic phase ratio on the distribution of Y^{91} was also determined. There is also a brief discussion of the variation of K_d values as the aqueous yttrium concentration is increased and information about the interaction of yttrium with the ester that this yields. Finally separation factors for Y, Ce, Gd and Eu are calculated from measured distribution coefficients in several H_2MEHP- aqueous systems. The results are compared with those determined for HDEHP and mineral acid solutions.

Transfer of the phosphate ester into the aqueous phase.

All distribution measurements made in systems such as those discussed in the present work depend for their validity on the assumption that there is negligible transfer of undissociated extracting reagent into the aqueous phase. In order to make a semi-quantitative check on this assumption the following procedure was adopted. Twenty ml of a 0.1M H_2MEHP solution or 0.1M di-(2-ethylhexyl) phosphoric acid (HDEHP) were equilibrated with the same volume of aqueous phase. After centrifuging 15 ml of the aqueous phase were pipetted into a 250 ml beaker and the solution partially neutralised by the addition of 3M sodium hydroxide. This solution was then shaken with 30 ml of diethyl ether for 3 minutes, after which time the ether phase was separated and poured into a previously weighed 50 ml beaker. A second extraction was performed on the aqueous phase using 25 ml of ether and this ether extract added to the beaker, having evaporated the majority of the original solution. The solution was then evaporated to dryness and after cooling, the beaker was re-weighed. This gave an estimate of the amount of substance being extracted into the aqueous phase. Blank runs were also carried out in which 20 ml of toluene alone were equilibrated with the aqueous solution. The results are shown in Table XII.

TABLE XII Determination of the amount of substances extractable from the organic into the aqueous phase.

Aqueous phase	Organic phase	Weight of Residue
9.33M $HClO_4$	0.1M H_2MEHP	0.1330 g
	Toluene	0.2742 g 0.1387 g
0.50M $HClO_4$	0.1M H_2MEHP	0.0955 g 0.1117 g
0.5M $HClO_4$	Toluene	0.0907 g
9.33M $HClO_4$	0.1M HDEHP	0.1327 g 0.1583 g
9.33M $HClO_4$	Toluene	0.2742 g 0.1387 g
0.50M $HClO_4$	0.1M HDEHP	0.0965 g
	Toluene	0.0955 g 0.1117 g

Thus there is no evidence for any extraction of either H_2MEHP or HDEHP into the aqueous phases used in this experiment.

The purity of the toluene used and any possible effects that this may have on K_d values was checked by carrying out distribution measurements with 0.1M H_2MEHP in "as received" AR toluene and AR toluene which had been redistilled. No difference in K_d values was found between the two solutions. A residue was not obtained when AR toluene was evaporated.

Preparation, purification and characterisation of the ester.

Before any distribution measurements were made further batches of the ester were prepared. For each batch the ratio of phosphoryl chloride to ethylhexanol was increased from a 1:1 molar ratio of about 1.2:1 in order to try and increase the yield of mono-ester with respect to di-ester. Thus 230 g of phosphoryl chloride were reacted with 160 g of 2-ethylhexanol and the mono-ester so produced was purified by the methods outlined earlier. The samples of mono-ester obtained from each preparation were combined and passed through another purification cycle. The resulting ester had an equivalent weight of 106.2. The purity of this ester was checked by using it to determine K_d for yttrium and comparing the values with those obtained for the previously prepared sample of ester. The values with the newly prepared ester were almost identical with those obtained with the original ester at high acid concentrations but about 10% lower at low acid concentrations. Because of this latter discrepancy the ester was passed through yet another purification cycle, with petroleum ether (boiling range 60 to 80°C) replacing benzene in the extraction process. Distribution measurements were then made using the refined ester; the values obtained were identical with those obtained before the last purification step. Thus although the K_d values obtained with the new batch of ester were slightly lower under certain conditions than those obtained with the original sample, the fact that the additional purification step did not result in a change in distribution values was taken to indicate that the ester was sufficiently pure. Comparison of K_d values for this new batch of resin and those published by PEPPARD (59) indicate good agreement, as shown below in Table XIII.

TABLE XIII. Comparison of K_d values for Y^{91} (0.48M H_2MEHP) in hydrochloric acid.

Concentration of hydrochloric acid	K_d (Present Work)	K_d (PEPPARD (59))
2M	0.86	0.8
3M	0.20	0.3
10.6M	1.20	1.10

As a further check on purity thin-layers chromatograms of the esters were prepared in order to try and detect any possible impurities present. Thin-layer chromatography (TLC) has assumed increasing importance in analytical work in the last few years.(84, 85, 86, 87) But it has received little attention in the field of organophosphorus acids. The work of STANLEY (88) indicated that mono- and di-phosphoric acid esters might be separated by TLC but that detection may be difficult in some cases.

Apparatus used in this work was supplied by the Shandon Scientific Co.Ltd. (London). Plates, 20 cms x 10 cms., were prepared from silica gel containing 13% plaster of paris (B.D.H.) as binder. Twenty-four g of the silica gel were ground with 48 ml of water in a mortar and the resulting slurry poured into the "applicator" which was drawn along the glass plates to form a layer 0.25 cm thick (the plates were held flat on a special air-bed supplied as part of the equipment). After drying on air for 5 minutes the plates were heated in an oven for 2 hours at 110°C in order to activate the gel.

Solutions containing approximately 1 mg/ml of ester in benzene were prepared from the original ester and from the new batches of ester which had been prepared. A sample of 10 μl of each of these solutions was spotted on to the plates some 3 cm from one end. A line was drawn across the plate 10 cm from the starting line to note the end of solvent travel. Spots were kept near the centre of the plates to avoid "edge effects".(89,90)

The solvent system used was a mixture of n-propanol, n-butanol and 2N ammonia solution (50:20:30 v/v)(88); a portion was placed in the developing tank to a depth of about 1 cm and given about 2 hours to saturate the atomsphere of the tank. After this time the plates were placed in the tank. The ascending development method was used. The time taken for the solvent front to travel 10 cms (the development time) was in the region of 3 hours. The plates were then dried in an oven at 110°C for 1.5 hours and after cooling they were sprayed with the chromogenic reagent.

Two reagents were tried initially (a) alkaline potassium permanganate and (b) ferric chloride - sulphosalicylic acid (FSSA). There were prepared as set out below.

(a) Solutions of 1% potassium permanganate and 2% sodium carbonate were mixed before use.

(b) (i) 0.1 g $FeCl_3;6H_2O$ dissolved in 1 ml 1N hydrochloric acid and the solutions diluted to 100 ml with 80% ethanol/20% (v/v) water mixture.

(ii) 1 g of sulphosalicylic acid (B.D.H.) in 100 ml of 80% ethanol. The plate was sprayed first with (i), then with (ii). FSSA was tried first, but the results were unsatisfactory. Using alkaline permanganate spots were detected, and since these all had the same R_f value (0.47-0.5), it was assumed that they corresponded to the mono-ester. However, when pure di-ester was used a spot could not be detected after development. This was further checked by taking a prepared mixture of mono-ester (using the original sample) and di-ester and developing these. As before spots with an R_f value of 0.5 could be detected but no other spots. Later the FSSA reagent was tried again, this time spraying very lightly with ferric chloride solution. On spraying with (ii), spots representing H_2MEHP were revealed, white against a pink background. Once again, however, spots corresponding to the di-ester were not observed. Finally alkaline (Universal Indicator) solution was tried, but with no more success than the other reagents.

Thus the evidence from TLC is inconclusive, and in the absence of further means of characterisation it was proposed to use the newly prepared ester as it was for distribution studies.

Molecular Weight determined for H_2MEHP = 212.8 ± 0.3
(theoretical = 210.3)

Refractive Index = 1.4418 ± 0.0002.

The refractive index was measured using an Abbe refractometer.

(a) Distribution of Y^{91} between 0.034 M H_2MEHP and mineral acid solutions.

A 0.034 M solution of H_2MEHP in toluene was prepared.

Equilibrations were carried out in the manner previously described (P.16). Some preliminary measurements indicated acid concentrations where K_d values were very small. These points were then determined more accurately by extracting the activity from the equilibrated organic phase into a second blank aqueous solution. Measurements in the region of the minimum in the log K_d against concentration plot for perchloric acid were made in triplicate. Values at other concentrations were usually duplicated but occasionally only single measurements were made. A similar policy concerning measurements was adopted for the hydrobromic acid system.

The results for the $H_2MEHP-HClO_4$ and - HBr systems are shown in fig. 3 (a) and (b) and fig. 4 respectively. The pronounced minimum observed earlier (P.43) is very evident as is the marked increase in K_d beyond this region. The minimum is broad in contrast to the much sharper minima found when sulphonic acid resins$^{(28)}$ or HDNNS $^{(30,60)}$ are used as second phases. With H_2MEHP the minimum extends from about 3.5 to 7.0M $HClO_4$. KRAUS and NELSON$^{(28)}$ found a minimum value with ion-exchange resins at about 4M $HClO_4$. With HDNNS the data from the present work were not sufficiently detailed to define the minimum region precisely but it was between 4 and 5.5M $HClO_4$.

With hydrobromic acid a minimum was not found for the range of acid concentrations investigated. It is, however, quite probable that this system would show a minimum if higher acid concentrations has been used. DIAMOND $^{(29)}$ maintains that the minimum in a bromide system should occur at higher concentrations than in the corresponding perchlorate system. Since the minimum for the latter is already between 4 and 7M in perchloric acid that for hydrobromic acid would be expected to be at still higher concentrations which are not readily attainable in practice.

Distribution measurements were also made for a hydrochloric acid system. A more concentrated solution of

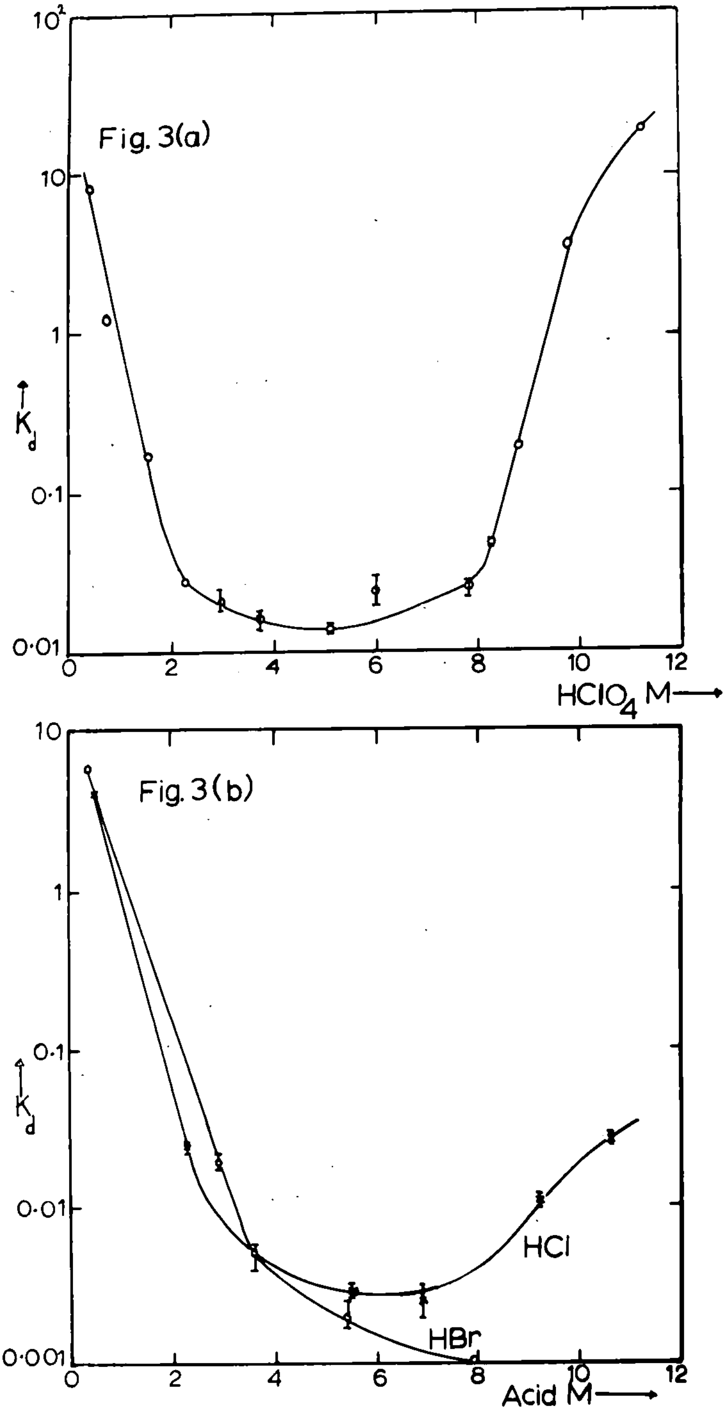

Fig. 3 Distribution of Y^{91} between 0·035M H_2MEHP and mineral acids.
(a) $HClO_4$ (b) HCl and HBr

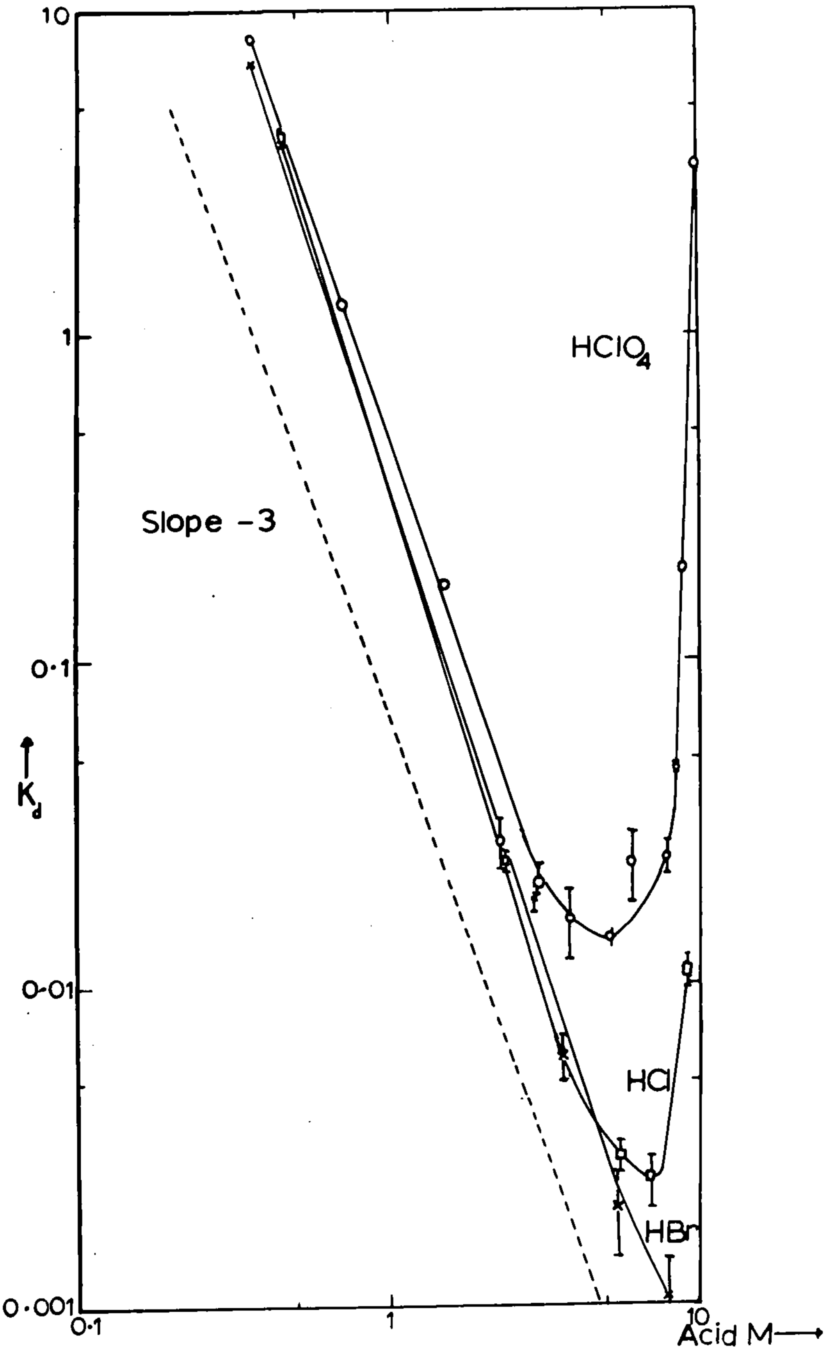

Fig.4 Distribution of Y^{91} between 0·035M H_2MEHP and mineral acids.

H_2MEHP was at first used for these measurements as the earlier work had indicated a very shallow minimum with 0.035M H_2MEHP and accurate measurements were difficult. Thus the appropriate distribution measurements were made with a 0.235M solution of H_2MEHP in toluene. The results are tabulated below.

TABLE XIV. Distribution of Y^{91} between hydrochloric acid and 0.235M H_2MEHP

Concentration of Hydrochloric Acid	K_d
0.47 M	27.9
2.34 M	0.231
4.68 M	0.058
5.62 M	0.044
7.96 M	0.072
10.30 M	0.313

The form of the distribution of Y^{91} in this system is very similar to that found by PEPPARD(59) using a 0.48M solution of H_2MEHP. The minimum lies between 5 and 7M in hydrochloric acid; this is perhaps a little lower than would have been expected from the measurements in perchloric and hydrobromic acid.

On the basis of these results a further set of distribution measurements were undertaken but now using 0.035M H_2MEHP, so that the results could be compared directly with measurements made earlier with perchloric and hydrobromic acids. Since the measurements made with 0.235M H_2MEHP had indicated the expected minimum in the plot of log K_d against hydrochloric acid concentration it was hoped that more careful determinations with the weaker ester solution would also reveal such a minimum. The results are shown in fig. 3 (b) and fig. 4, where log K_d is plotted against log acid concentration. A definite minimum is shown in the plot and at the same acid concentrations as with the more concentrated ester solution. In the dilute acid region (up to at least 1.5M HCl) the plot has the expected slope of -3.

A plot of log K_d against log activity coefficient of perchloric acid was made; it is shown in fig. 5 (a). Activity coefficient data were taken from published values.(91) Only data for the high acid region were available. The plot is of similar form to that of log K_d against perchloric acid concentration. A more revealing plot is that of log K_d against water activity for the perchloric acid solution,(91) and shown in fig. 5 (b). The curve has a very broad minimum but rises sharply at both very low and very high water

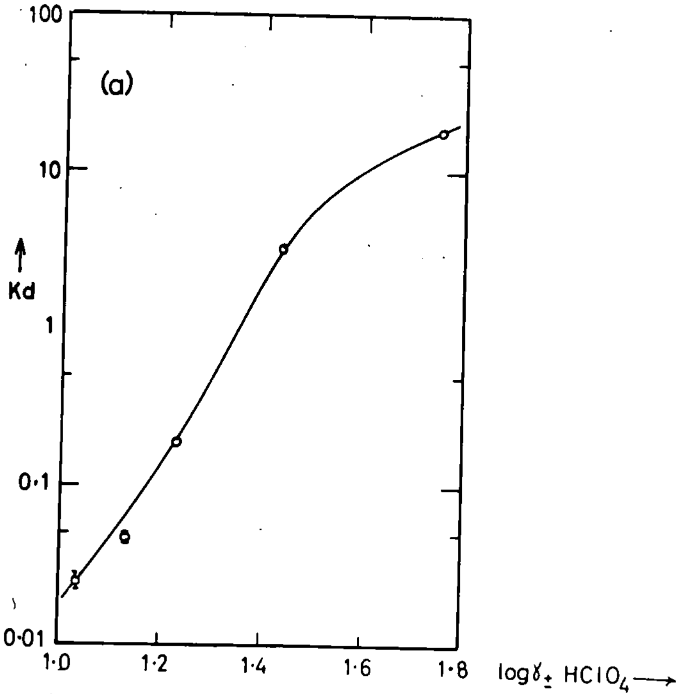

Fig. 5(a) K_d as a function of $\gamma_{\pm HClO_4}$(aqueous)

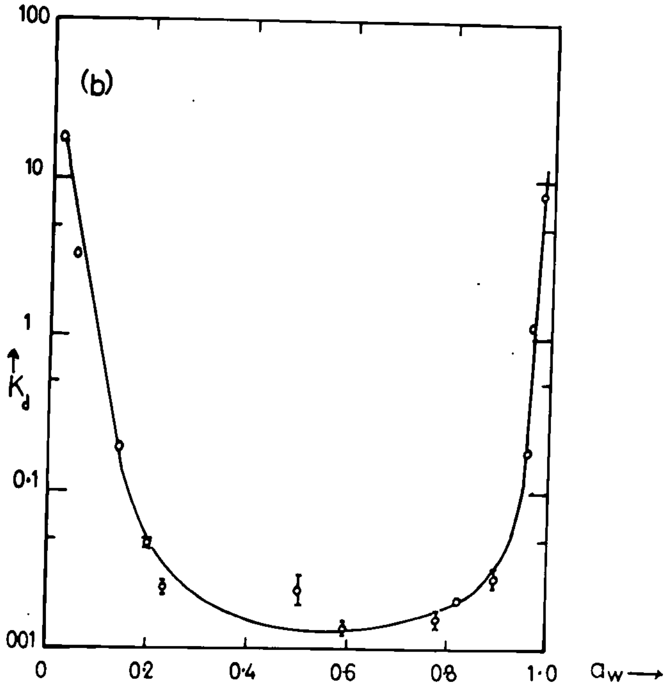

Fig. 5(b) K_d as a function of the water activity of aq. $HClO_4$

activities. Thus in such regions the K_d values are very sensitive to water activity whilst throughout most of the acid range K_d is very insensitive to water activity. The rapid fall of K_d with small variations of water activity at the low acid concentrations (high water activity) is probably not of great significance. The decrease of K_d with log acid concentration in the region 0 to 1.5 M $HClO_4$ (a straight line of slope -3 is obtained) follows directly from the mass-action law for increasing hydrogen ion concentration. The steep increase of K_d with change in water activity at the high acid concentrations probably reflects the importance of "ion association" of the type defined by DIAMOND,(29) which becomes of increasing importance as the water available for the hydration of the cations present decreases. There is insufficient data concerning the dielectric constant values of perchloric acid solutions to allow for any attempt to correlate distribution values with the dielectric constant of the solution.

The distribution of $Eu^{152+154}$ and Am^{241} between hydrochloric acid and 0.110MH_2MEHP.

Distribution measurements with europium and americium have been made between hydrochloric acid and H_2MEHP.(59) The results were compared with those found for styrene-based sulphonic acid resins. The behaviour of americium was apparently very different in the two systems and therefore it was decided to check the behaviour of both americium and europium in the hydrochloric acid - H_2MEHP system. A 0.11M solution of H_2MEHP in toluene was used for these measurements.

The radiochemical purity of the Am^{241} was checked in two ways. The first was by means of γ-ray spectroscopy. The principle daughters resulting from the decay of Am^{241} are Np^{237} and Pa^{233} both of which are γ-emitters. Np^{237} emits several weak γ-rays (all with energies less than 200 KeV) plus a 312 keV γ-ray which is due to Pa^{233} present. Pa^{233} itself emits four principle γ-rays of energies 107 keV, 300 keV, 312 keV and 400 keV. Thus if either Np^{237} or Pa^{233} are present a γ-peak at 300 to 312 keV should be observed. No such peak was found. This was confirmed by solvent extraction data. Protoactinium is readily extracted into a chloroform solution of n-benzoyl-n-phenylhydroxylamine (BPHA) from hydrochloric acid solutions greater than 10M(92). Thus 10 ml of a 1% solution of BPHA were shaken with a similar volume of 10.6 M HCl containing Am^{241} for about 20 minutes. After centrifuging 5 ml of the organic phase were removed for counting. Activity attributable to Pa^{233} was not observed, and it was therefore concluded that the americium used in these experiments was not contaminated with either neptunium or protactinium activities.

The Am^{241} activity was counted in a crystal scintillation set-up using the 60 keV γ-ray. For $Eu^{152+154}$ the γ-rays in the energy region 1.00 to 1.28 MeV were counted. The results are plotted in fig. 6. The behaviour of both elements is very similar to that already observed.(59) The most significant points about the americium plot are the rise in K_d values between 8 and 10M HCl and the fact that the K_d value at 11.3 M HCl is less than that at 10.6M HCl. The presence of a minimum in the americium plot is in marked contrast to its behaviour when ion-exchange resins of the sulphonic acid-type are used.(28)

(b) Effect of the addition of HDEHP to H_2MEHP.

A series of distribution measurements were made in which varying amounts of HDEHP were added to a constant concentration of H_2MEHP. A 0.017M solution of H_2MEHP was used and HDEHP solutions ranging in concentration from 0.017M to 0.093M were added and distribution measurements made from perchloric acid. K_d values are plotted in fig. 7. From this it is seen that in the high acid region for a given acid concentration the K_d values for the various phosphate mixtures are very similar. This is not the case in the low acid region. The position of pure H_2MEHP appears to

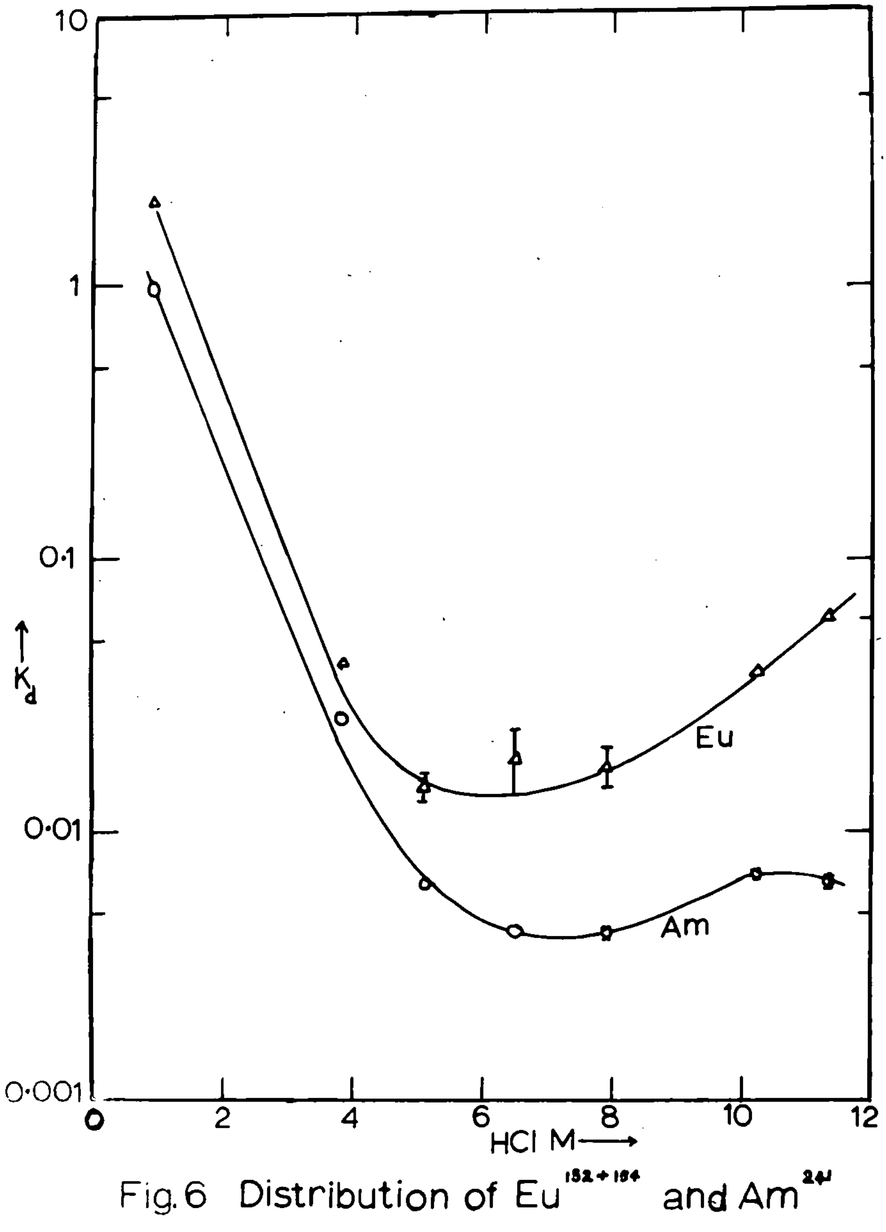

Fig. 6 Distribution of $Eu^{152+154}$ and Am^{241} between 0·110M H_2MEHP and HCl

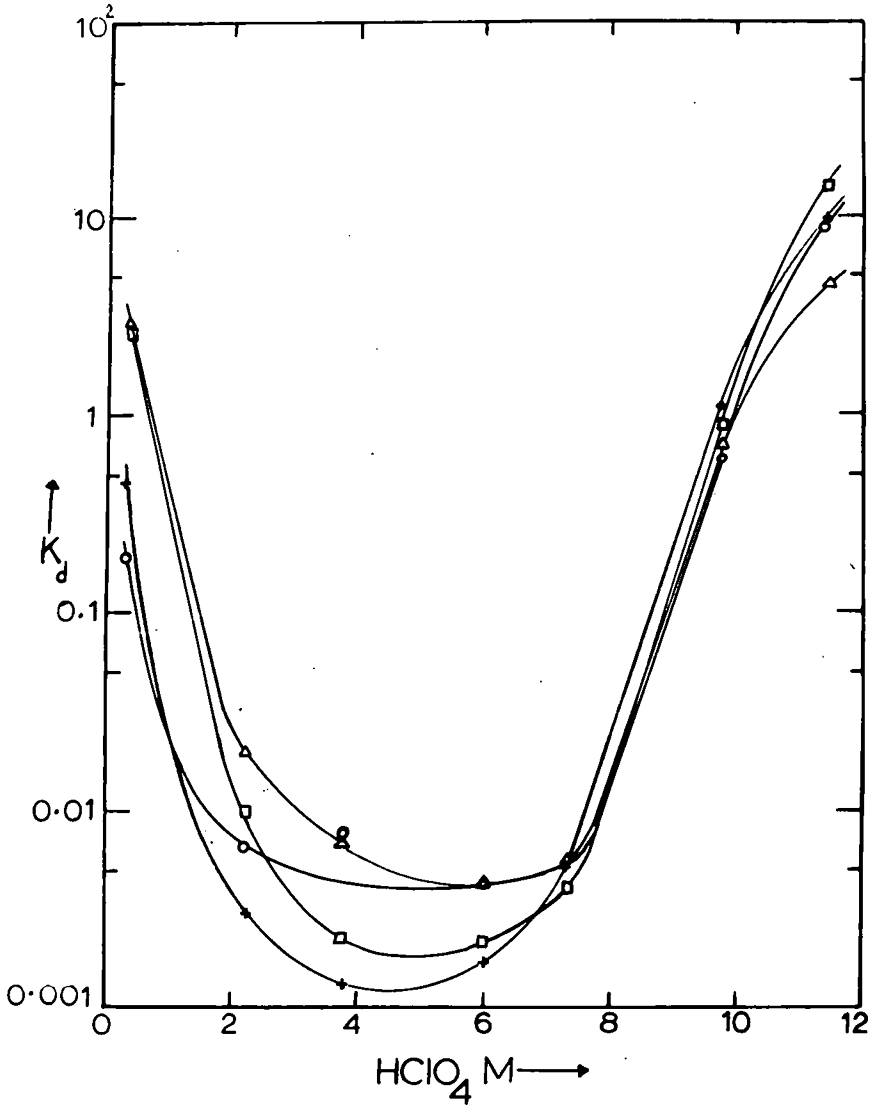

Fig. 7 Variation of K_d with addition of HDEHP to H_2MEHP (in $HClO_4$)

△ 0·017 M H_2MEHP

○ " + 0·017 M HDEHP

+ " + 0·033 M "

□ " + 0·093 M "

be anomolous in this region.

(c) Effect of varying the aqueous to organic phase ratio.

Two sets of experiments were carried out in one of which the aqueous to organic phase ratio was 0.5 whilst in the other it was 3. Initially the aqueous phase was perchloric acid but later sodium perchlorate was also used. A 0.035M solution of H_2MEHP was prepared and distribution measurements made as described earlier. A plot of log K_d against perchloric acid concentration is shown in fig.8 (a). The most significant point that arises from these measurements is the complete absence of a minimum in the curve when an aqueous to organic phase ratio of 3 was used. In fact K_d values at perchloric acid concentrations less than about 7M are extremely small, less than 10^{-4}. This was checked by equilibrating the pregnant organic phase with a fresh aqueous solution and counting the latter. The count rate differed from the background count rate by only one or two c.p.m. When the aqueous to organic phase ratio is 0.5 then the "normal" distribution curve is obtained with a broad minimum between 3.5 and 7M perchloric acid.

A similar set of measurements were then made with sodium perchlorate in place of perchloric acid. The results are shown in fig. 8 (b). As with the perchloric acid

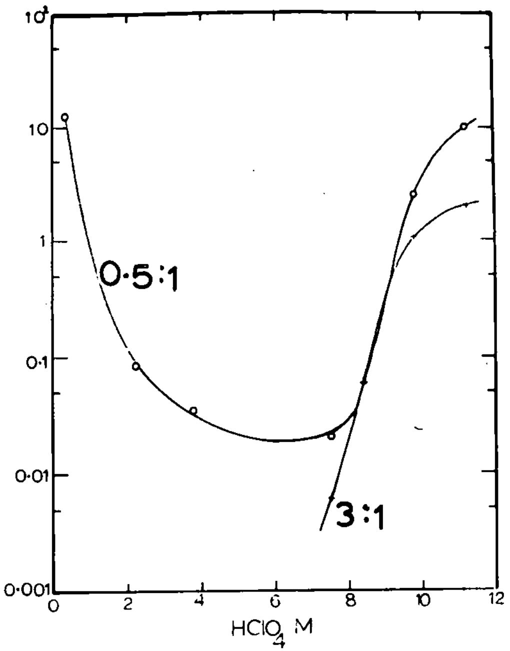

Fig.8(a) Effect of varying the phase ratio on the distribution of Y^{III} between 0·035M H_2MEHP and $HClO_4$

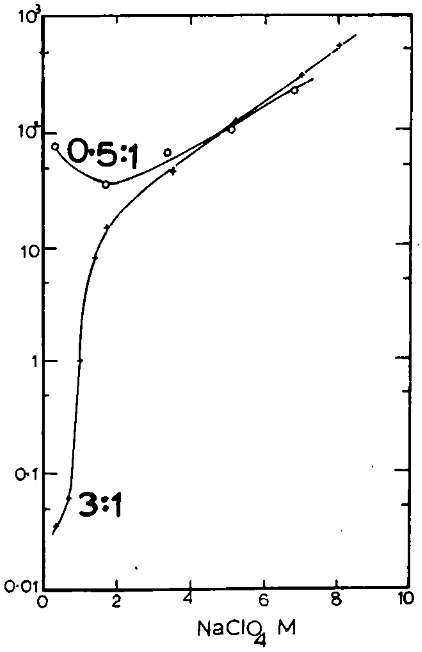

Fig.8(b) Effect of varying the phase ratio on the distribution of Y^{III} between 0·035M H_2MEHP and $NaClO_4$(0·1M$HClO_4$)

measurements, with an aqueous to organic phase ratio of 3, K_d values are very low at low salt concentrations in complete contrast to what might be expected, for the earlier results indicated high K_d values at low electrolyte concentrations. For a phase ratio of 0.5 a minimum is found. It is to be observed that in both sets of measurements the two curves corresponding to the two phase ratios approximate quite closely at high aqueous concentrations and it is only at the lower concentrations that they show such a marked difference. At these low concentrations a considerable amount of water extracts into the organic phase (P. 83). Extraction of water has been shown to considerably modify the structure of H_2MEHP by producing extensive polymerisation.(77,98) It is possible that when the aqueous phase is in a large excess compared with the organic phase the amount of water extracted is such that polymers may be built up in which hydrogen atoms are so tightly bound that exchange with other cations is less favoured and thus K_d values are very low.

(d) The effect of H_2MEHP concentration on the extraction of Y^{91} from perchloric acid.

(i) Distribution coefficients in 9.76M perchloric acid.

A series of solutions of H_2MEHP in toluene ranging in concentration from 0.0118 to 0.650M were prepared and these solutions equilibrated with 9.76M $HClO_4$. The results are plotted as log K_d against log molarity of H_2MEHP in fig. 9 (a). The slope of this plot is 1.5.

(ii) Distribution coefficients in 0.5 and 0.7M perchloric acid.

Similar sets of distribution measurements were made at two low acid concentrations and over a slightly longer range of ester concentrations. The results are plotted in fig. 9 (b) and (c). The most significant point about these plots is the distinct break in the curve at a concentration between about 0.03 and 0.04M H_2MEHP. At ester concentrations in excess of these values the plot is a straight line of slope approximately unity. However, at lower concentrations the K_d values fall away rapidly with decreasing H_2MEHP molarity.

A first-power dependence on reagent concentration has been observed by PEPPARD et al for promethium from 0.5 and 1.0M $HClO_4$(77) and for europium from 0.25M HCl.(94) In the former case there appears to be a constant slope of 1 throughout the range of ester concentrations studied although data only extend down to about 0.05M H_2MEHP in the studies with 0.5M acid. The break observed in the plots from the present work with the more dilute acid may be attributable to changes in the ester structure as polymerisation of H_2MEHP has been shown to be strongly

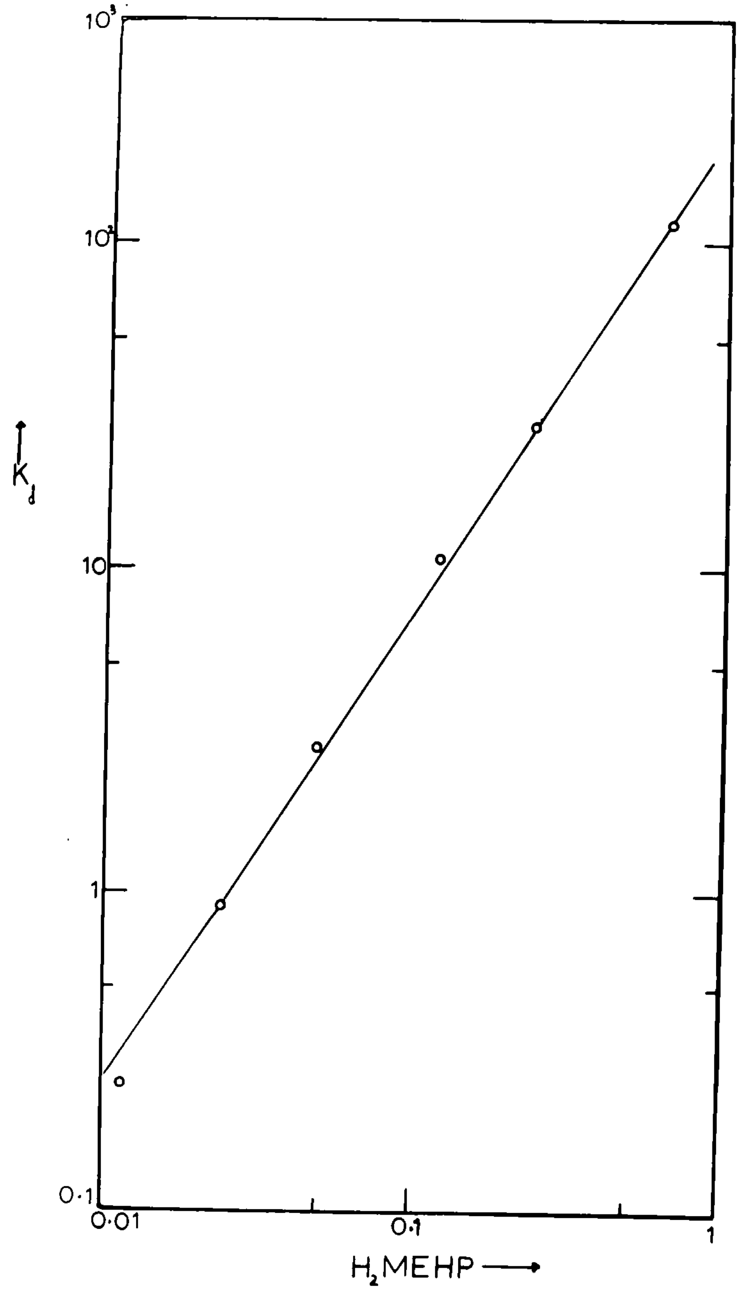

Fig. 9(a) Distribution of Y^{91} from 9·73M $HClO_4$ as a function of H_2MEHP concentration

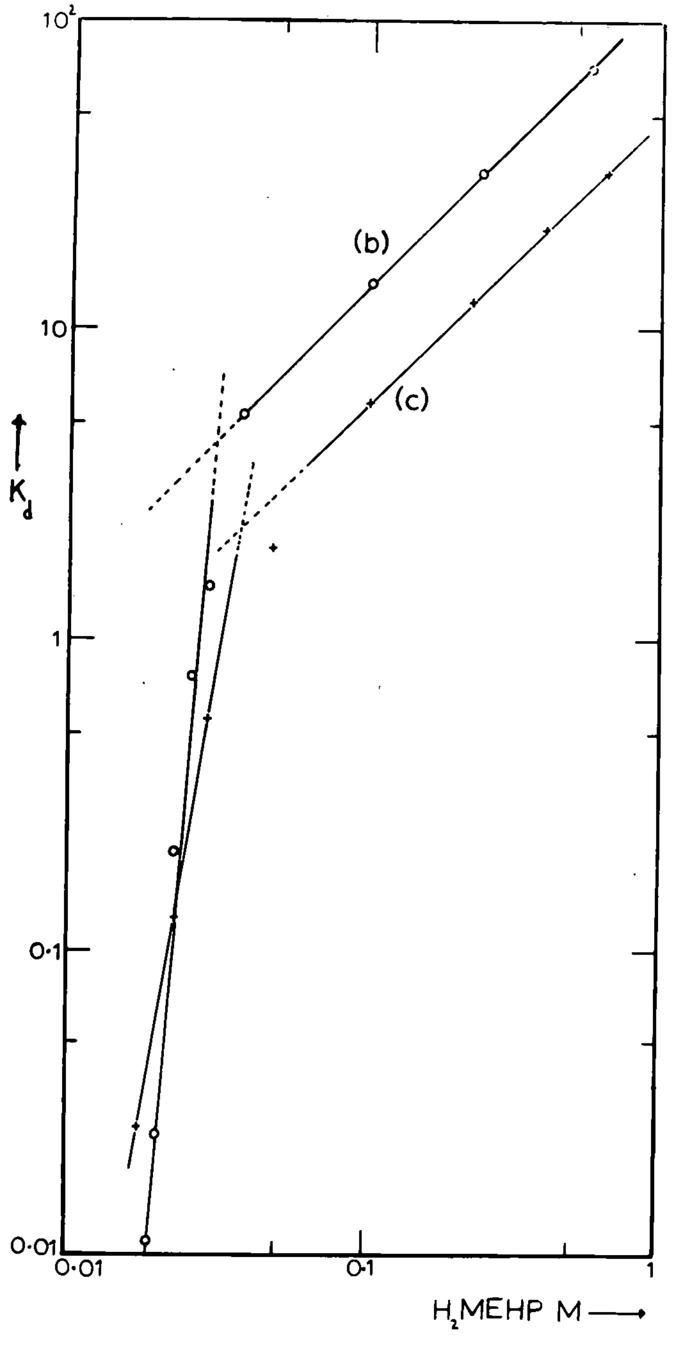

Fig. 9(b) & (c) Distribution of Y^{3+} from 0·50(b) and 0·70 M(c) $HClO_4$ as a function of H_2MEHP concentration

concentration dependent.(93) There is also the effect of water on the structure of H_2MEHP to be considered. It is possible that these two effects may produce a significant change in the structure of the ester at the concentrations mentioned. A significant change in the water taken up by the organic phase may also occur at the transitions although this was not tested.

That there is no break in the curve plotted at 9.76M $HClO_4$ may be explained on the above basis by assuming that so little water (see later, P. 83) is extracted at this high acid concentration that there will not be significant changes of structure attributable to this substance.

(e) Distribution studies with H_2MEHP and HDEHP mixtures of constant total ester concentration.

A series of distribution measurements were carried out on mixtures of H_2MEHP and HDEHP, in which total ester concentration (H_2MEHP + HDEHP) was kept constant but the mole fraction of HDEHP was varied. Measurements were made using an aqueous phase of 9.76M $HClO_4$. Stock solutions of both H_2MEHP and HDEHP were prepared, such that a 35 ml aliquot portion of either when diluted to 50 ml gave a solution 0.0700 M in either HDEHP or H_2MEHP. Other concentrations were prepared by taking the appropriate aliquot portion for a dilution to 50 ml.

When this required taking less than a 5 ml portion the required volume was doubled and the dilution made up to 100 ml. Three sets of measurements in all were carried out, with total ester concentrations of 0.0175, 0.0700 and 0.175M. The results for these measurements are plotted in fig. 10 (a) Here K_d is plotted against mole fraction of HDEHP. A plot of log K_d against log mole fraction of HDEHP is also shown in fig. 10 (b).

The plots in fig. 10 (a) all have a very similar shape except that the maximum is progressively shifted to a higher HDEHP mole fraction as the total concentration of ester is increased. In addition they all show a point of inflexion when the mole fraction of HDEHP is approximately 0.9, after which point the line becomes almost horizontal with the abscissa.

In fig. 10 (b) where log K_d is plotted against log mole fraction, there is an approximately constant factor between the ratio of log K_d values and of total ester molarities for chosen mole fractions.

(f) The effect of HDEHP on the distribution of Y^{91} between 0.075M H_2MEHP and perchloric acid.

Suitable stock solutions of H_2MEHP and HDEHP were prepared. The HDEHP used was supplied by Messrs. Albright &

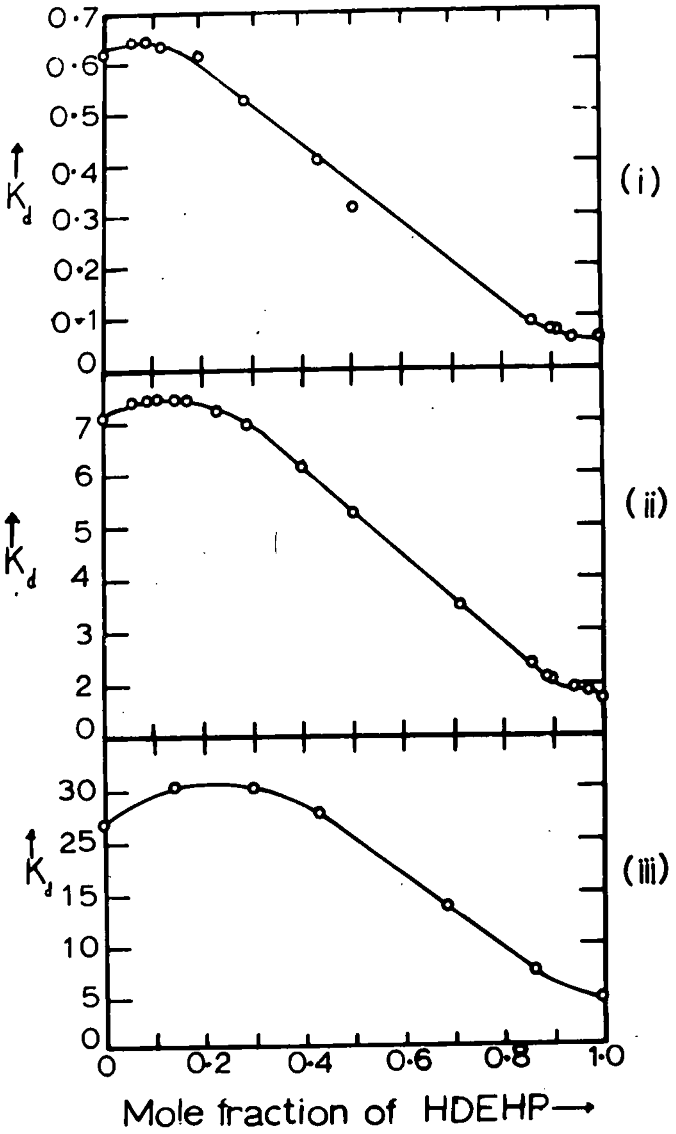

Fig.10(a) Variation of K_d with mole fraction of HDEHP at 9·76M $HClO_4$

(i) Total ester concentration = 0·0175 M

(ii) " " " = 0·070 M

(iii) " " " = 0·175 M

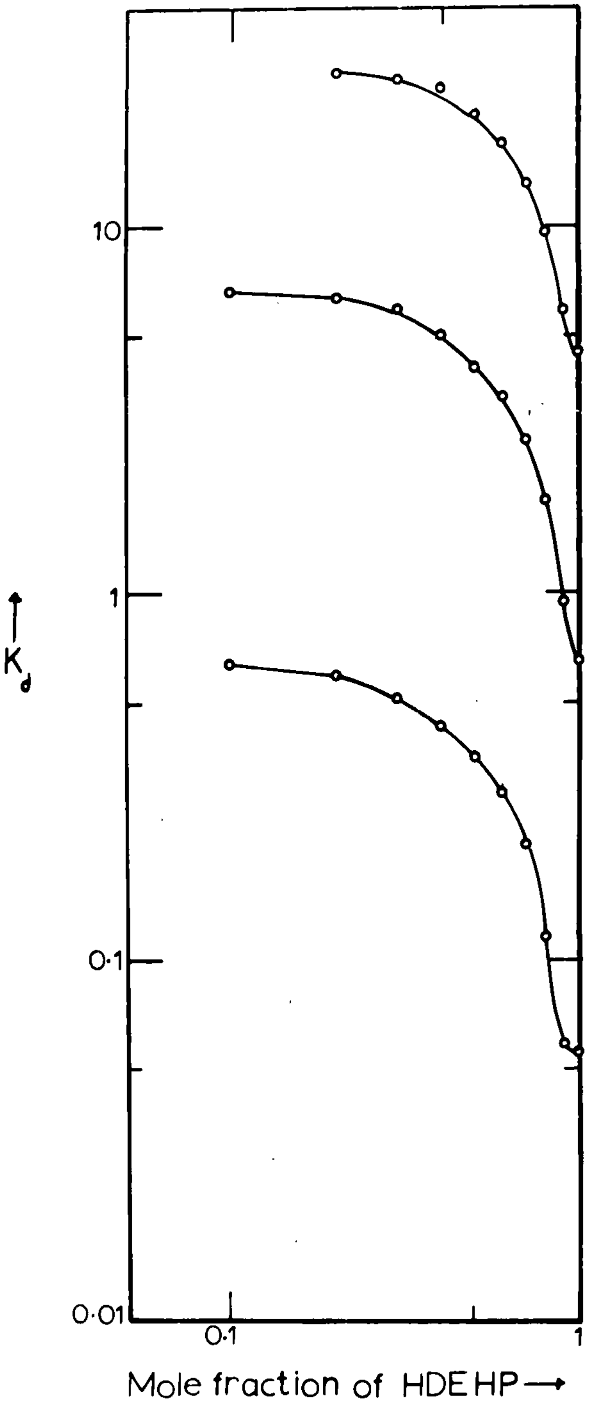

Fig.10(b) Variation of K_d with mole fraction of HDEHP at 9·76 M $HClO_4$

Wilson; it was purified by the method of SCHMITT and BLAKE.(95) Solutions were prepared in either 50 or 100 ml volumetric flasks, and either 15 or 30 ml respectively of 0.250M H_2MEHP pipetted into the flasks to give a 0.075M H_2MEHP solution on dilution. Stock solutions of HDEHP were 0.025M, 0.10M and 0.70M, and appropriate aliquot portions were added to the H_2MEHP solutions and the volumes made up to the mark with toluene.

Results of distribution measurements are given in fig.11, where log K_d is plotted against the ratio of the molarity of HDEHP to H_2MEHP(r). The results relate to two perchloric acid concentrations, 0.25M and 9.76M. Both curves have similar features, namely a steep initial rise followed by a much more gradual increase of slope. This levelling off is more pronounced at the low than the high perchloric acid concentrations. The point at which the slope of both plots becomes constant is where r is approximately unity. In neither case is there any evidence for a reversal in the direction of the slope over the range of ester concentrations considered. This is in marked contrast with the behaviour of solutions of H_2MEHP and tributyl phosphate (TBP) in 0.25M HCl (94) where the curve shows the same initial rise with increasing r values until a maximum is reached at r = 0.2 to 0.3. Beyond this

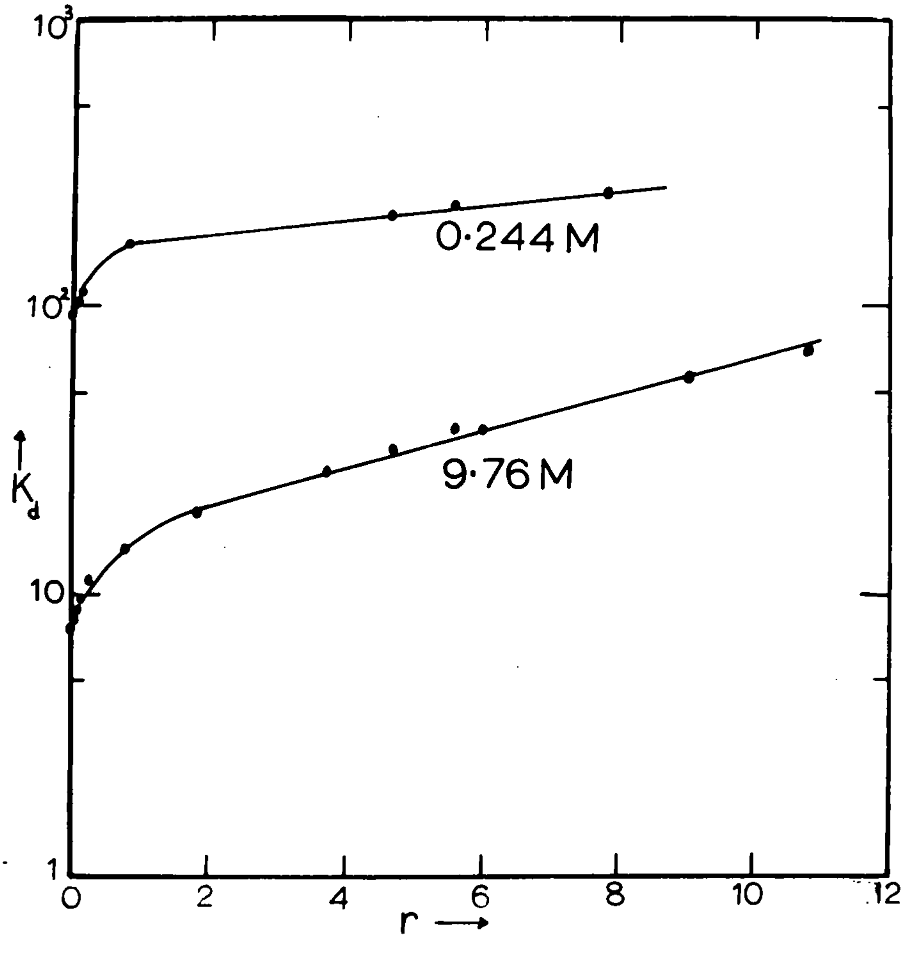

Fig.11 K_d as a function of r at 0·244 and 9·76 M $HClO_4$ (H_2MEHP=0·075M) r the curve shows a pronounced negative slope. Thus the addition of small amounts of TBP to H_2MEHP produces a positive synergistic effect whilst larger quantities produce a negative effect. This may be explained if one assumes the formation of an adduct between H_2MEHP and TBP which has greater extracting powers than H_2MEHP alone. It has been shown that in the absence of water TBP and H_2MEHP interact in the ratio of 1:3 by formula weight. (96) Thus the adduct is formulated as $(H_2MEHP)_6(TBP)_2$ and it is this substance which produces positive synergism. Addition of further TBP causes the formation of an adduct postulated as $(H_2MEHP)_2$ (TBP). This formulation follows from the consideration that TBP resembles acetone in that it can accept but not contribute a hydrogen atom in hydrogen bond formation. On this basis it is postulated that the antisynergistic adduct contains a dimeric unit of H_2MEHP and a molecule of TBP. Its antisynergistic behaviour is postulated by PEPPARD to arise from the inactivation of all the theoretically ionisable hydrogen atoms in the H_2 MEHP molecule.

When HDEHP is added to H_2MEHP then only positive synergism is displayed throughout the experimental concentration range, which extended to values of r in excess of 10. Since pure HDEHP is a much poorer extractant than H_2MEHP at both acid concentrations studied, there is presumably a range of concentrations of HDEHP in which the system will show antisynergistic behaviour, and thus the curve would show a maximum followed by a downward trend, similar to the plots obtained with TBP. There is no evidence, however for this from the present work. It is possible in this instance that synergism is brought about by the formation of an adduct similar to that postulated for the positive synergistic form with TBP. That is an adduct of H_2MEHP containing two molecules of HDEHP. Since HDEHP is known to be solely dimeric in toluene it may be postulated that 2 molecules of HDEHP become attached to the H_2,EHP structure and the resultant adduct displays positive synergistic behaviour.

The behaviour of TBP (supplied by BDH) with H_2MEHP was checked by repeating a set of experiments similar to those used by PEPPARD et al.(94) Distribution measurements were conducted using purified TBP - H_2MEHP mixtures and 0.250 M HCl. The results plotted in fig. 12 were essentially similar to those obtained by PEPPARD, indicating that the H_2MEHP was behaving

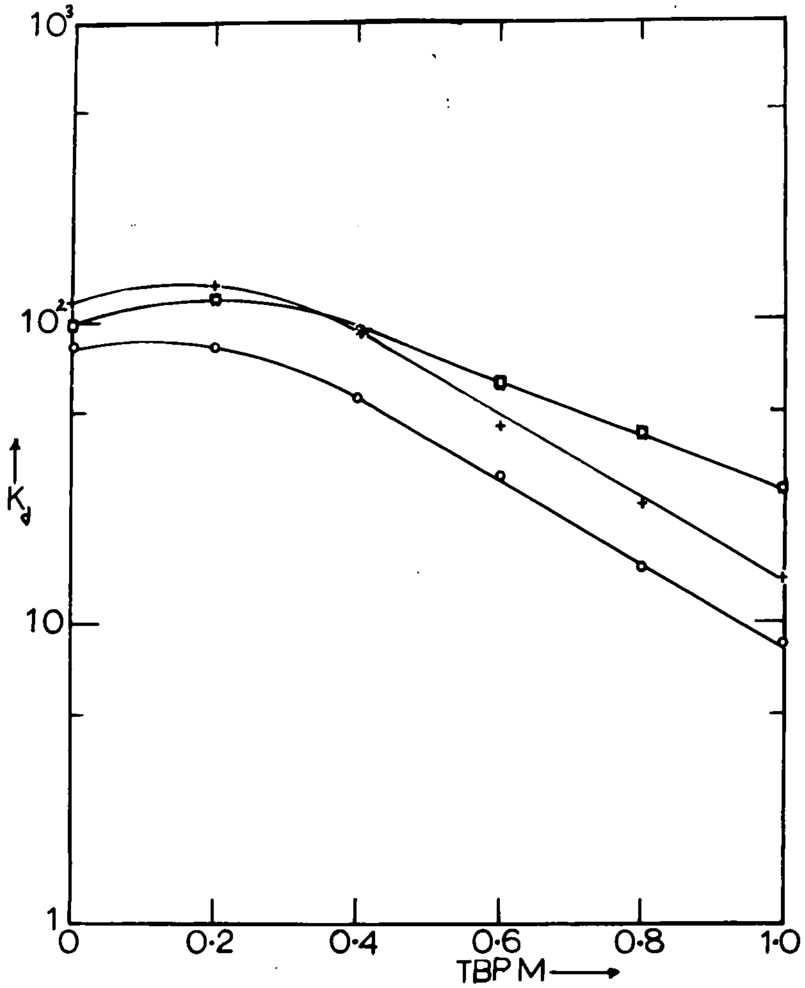

Fig.12 Variation of K_d with molarity of TBP in the 0·10M H_2MEHP(toluene) vs. 0·25M HCl system(○ this work, ▫ Peppard) and 0·25M $HClO_4$(+)

in the manner expected. Exactly the same distribution pattern was found for 0.25M $HClO_4$ as shown in Fig. 12

(g) Effect of yttrium 'loading' on distribution values.

The effect of increasing the concentration of yttrium in the aqueous phase on the distribution of Y^{91} into 0.035M H_2MEHP was investigated. Yttrium oxide of 99.9% was obtained from Koch-Light Laboratories. Approximately 2g were heated strongly in a platinum crucible for 15 minutes in order to convert any carbonate or hydroxied present to the oxide. The crucible was then cooled in an evacuated desiccator.

Stock solutions of yttrium perchlorate were prepared by weighing out appropriate amounts of the oxide into volumetric flasks. Sufficient perchloride acid (specific gravity 1.54) was then added to the oxide such that after making up the solution to the mark with water 20 ml of the solution on dilution to 450 ml would be 0.37M in perchloric acid. Thus after dissolving the oxide in the perchloric acid (which frequently required shaking the contents for some time), the volume was made up to the mark with distilled water. Twenty ml of this solution were then pipetted into a 50 ml volumetric flask and sufficient active yttrium tracer added to give a counting rate of approximately 10^4 c.p.m. when 10 ml were counted in the G-M liquid counter. Later when aliquot portions other than 20 ml were required to give a solution of the required yttrium concentration the appropriate volume of perchloric acid was also added to achieve a final perchloric acid strength of 0.37M on making up to the 50 ml mark. The stock solutions prepared were 2.012 x 10^{-4}M, 2.002 x 10^{-3}M, 2.002 x 10^{-2}M and 8.22 x 10^{-2}M in yttrium perchlorate. Distribution measurements were made and these are recorded in fig.13 in which log K_d is plotted against log yttrium concentration in the organic phase. The concentration of yttrium in the organic phase was obtained from the equation:

$$K_d = \frac{\text{Concentration of yttrium in the organic phase}}{\text{Initial concentration of yttrium in the aqueous phase} - \text{conc. of yttrium in the organic phase.}}$$

The initial portion of the plot is virtually a straight line parallel to the abscissa. It may be postulated that in this region the concentration of yttrium is sufficiently small for one yttrium ion to be associated with one ester polymer grouping only, and thus the K_d values should be relatively independent of the yttrium concentration. The

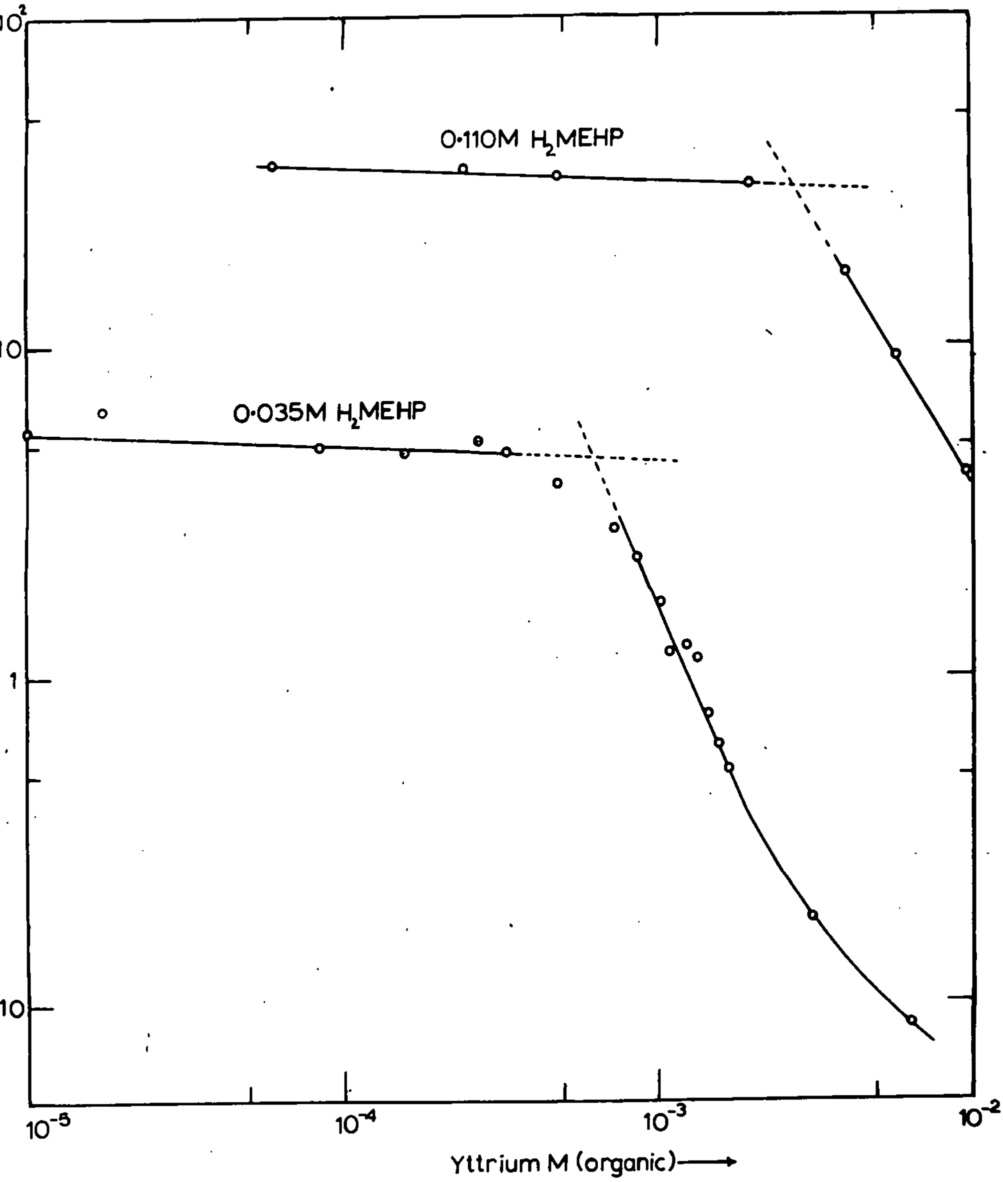

Fig.13 K_d as a function of the yttrium concentration in the organic phase sudden change in slope at an yttrium concentration of 6.2×10^{-4}M may represent the point where this condition no longer applies and that further increases in yttrium concentration force the polymers to take up more than a single yttrium ion. At this yttrium concentration the ratio of the ester concentration (0.035M) to the yttrium concentration (6.2×10^{-4}M) is about 57. Thus for very light 'loading' with yttrium apparently one yttrium ion is associated with a polymer of about 50 to 60 H_2MEHP units.

These results prompted further investigation with different concentrations of H_2MEHP. Using a 0.0071M solution of H_2MEHP no reliable results could be obtained owing to the very small amount of yttrium distributing into the organic phase, which is in accord with earlier observations on the dependence of K_d with H_2MEHP concentration. For a solution of 0.110M H_2MEHP a plot of log K_d against log of yttrium concentration in the organic phase was very similar to that obtained with the more dilute ester solution. The sudden change in slope occurs at an yttrium concentration of about 2.19×10^{-4}M corresponding to an H_2MEHP: yttrium concentration of approximately 50. Less detailed experiments with ester concentrations intermediate between 0.035 and 0.110M also indicated sudden changes of slope but there was insufficient data to determine this region accurately.

(h) Determination of separation factors for Y, Ce, Gd and Eu.

A measure of the efficiency of an extraction system in separating a pair of elements is given by the quantity known as the separation factor. The separation factor, D, for a given pair of elements, A and B, may be defined by:

$$D = \frac{K_d(A)}{K_d(B)}$$

The separation of elements in the lanthanide series is usually very difficult and this applies even more so to adjacent pairs of elements, such as europium and gadolinium, in the series. Thus a good indication of the usefulness of an extraction system for the separation, of the lanthanides, is the separation factor for adjacent pairs of elements. Some work has already been carried out in this respect using HDEHP as the extracting agent,(98) and reasonably good separation factors were found. There is, however, little information on separation factors for H_2MEHP.

Separation factors were calculated from measured distribution values of the four lanthanides listed earlier, using 0.035 and 0.11M solutions of H_2MEHP in toluene and aqueous solutions of 0.12 and 9.76M $HClO_4$, 12M HNO_3 and 7.2M LiBr (0.05M in HBr). Distribution measurements were also made using 0.035 and 0.20M HDEHP in toluene and 0.12M $HClO_4$. When 12M HNO_3 was used as the aqueous phase it was found that the organic phase was attacked by the nitric acid, K_d values were low, and separation factors very poor. The results for this system are not included in the tables annexed. K_d values and separation factors are shown in Tables XV to XVII.

It is observed that in general separation factors for the HDEHP-mineral acid system are much larger than for the various H_2 MEHP-aqueous systems. For the H_2MEHP systems the greatest separation factors are found in the H_2MEHP-7.2M (LiBr) (0.05M HBr) system although even here they are inferior to those in the HDEHP-perchloric acid system. An interesting point with H_2MEHP and concentrated solutions in the inversion of the Y/Eu and Y/Gd separation factors compared with those in dilute solutions. It is most pronounced when 7.2M LiBr is used as the aqueous phase. This inversion has previously been noted for yttrium and europium.(59) The values found in the

TABLE XV. K_d values and separation factors for Y, Ce, Gd & Eu with the H_2MEHP (0.035 and 0.110M)-0.12M $HClO_4$ system

		K_d			
Organic Phase	No of Measurements	Y	Ce	Gd	Eu
0.110M H_2MEHP	3	780±75	673±18	1290±20	2160±45
0.035M H_2MEHP	3	160± 5	115±2	177±5	225±3

Separation Factors

EUROPIUM	GADOLINIUM	YTTRIUM	
2.9±0.3	2.00±0.08	1.3±0.1.	CERIUM
	0.7 ±0.2	0.45±0.08	EUROPIUM
		0.64±0.03	GADOLINIUM

TABLE XVI K_d values and separation factors for Y,Ce,Gd & Eu with the H_2MEHP (0.035 and 0.110M) - 9.76M $HClO_4$ system

Organic Phase	No of Measurements	K_d			
		Y	Ce	Gd	Eu
0.110M H_2MEHP	3	15.0±0.5	4.1±0.1	8.6±0.1	9.9±0.1
0.035M H_2MEHP	3	1.56±0.02	0.56±0.01	1.01±0.01	1.05±0.02

Separation Factors

EUROPIUM	GADOLINIUM	YTTRIUM	
2.3±0.2	2.1±0.1	3.4±0.3	CERIUM
	0.91±0.06	1.51±0.02	EUROPIUM
		1.6 ±0.1	GADOLINIUM

TABLE XVII. K_d values and separation factors for Y,Ce,Gd, & Eu with the H_2MEHP (0.11M)-7.2M LiBr (0.05M HBr) system

K_d values (Mean of 2 measurements)

Y	Ce	Gd	Eu
108±3	16.6±0.2	45 ± 1	51 ± 1

Separation Factors

EUROPIUM	GADOLINIUM	YTTRIUM	
3.07	2.71	6.51	CERIUM
	0.89	2.12	EUROPIUM
		2.40	GADOLINIUM

TABLE XVIII. K_d values and separation factors for Y, Ce, Gd, & Eu with the HDEHP (0.2M)-0.12M $HClO_4$ system

K_d values (Mean of 2 measurements)

Y	Ce	Gd	Eu
47±2	0.033±0.001	1.50±0.05	1.01±0.02

Separation Factors (this work)

	EUROPIUM	GADOLINIUM	YTTRIUM
CERIUM	30.6	45.5	1.42×10^{3}
EUROPIUM		1.49	46.2
GADOLINIUM			31.1

Separation Factors PIERCE & PECK (98)

	EUROPIUM	GADOLINIUM	YTTRIUM
CERIUM	35.4	50.7	1.68×10^{3}
EUROPIUM		1,43	47.4
GADOLINIUM			33.2

The standard deviations quoted simply record the spread of experimental results. When difference concentrations of H_2MEHP were used results for the two concentrations in a given system were in good agreement.

TABLE XIX. K_d values and separation factors for Am and Eu with the H_2MEHP (0.110M) - HCl system.

Aqueous HCl molarity	K_d		$D(\frac{Eu}{Am})$
	Am	Eu	
0.92	0.97	2.01 (1)	2.07
3.81	0.0260	0.0415 (1)	1.60
5.10	0.00639	0.0145±0.003(3)	2.27
6.50	0.00423	0.0185±0.005(3)	4.37
7.89	0.00416±0.0001 (3)	0.0185±0.003(3)	4.45
10.20	0.00691±0.00002(3)	0.0385 (2)	5.57
11.37	0.00638±0.00006(3)	0.0604 (2)	9.47

(numbers in parentheses represent number of determinations made).

present work for the separation factors in the HDEHP-perchloric acid system are seen to agree reasonably well with those found by PIERCE and PECK.(98) From the above K_d values for europium and americium these elements are most easily separated in concentrated HCl. The corresponding separation factor for HDEHP-HCl is approximately 22.(97)

Thus it would seem that H_2MEHP and strong electrolyte solutions do not offer any advantages over HDEHP with dilute acids for the separation of the lanthanides. It may well be of interest to determine separation factors in mixtures of HDEHP and H_2MEHP in both dilute and concentrated aqueous electrolytes.

CHAPTER V

THE EXTRACTION OF ELECTROLYTES AND WATER BY H_2MEHP AND HDEHP

Introduction

The extraction of hydrochloric and perchloric acids into the organic phase was determined by suitable titration procedures. An apparatus suitable for carrying out Karl Fischer titrations was developed for the determination of the water content of the esters. These studies were extended by the use of infra-red spectral data and a qualitative correlation made between the two sets of data.

(a) The uptake of electrolytic components by H_2MEHP and HDEHP

Titration methods were used to determine the distribution of hydrochloric and perchloric acids between an aqueous solution of these acids and the organic phase. In practice 20 or 25ml (occasionally 60 and 110ml) of each phase were shaken together until equilibrium was reached. After centrifuging suitable aliquot portions were removed by pipette and equilibrated with equal volumes of 0.16M nitric acid. In this way acid extracted by the ester in the original equilibration was transferred to the nitric acid. Water cannot be used in place of nitric acid because of the emulsification problems this introduces as mentioned earlier. The aqucous phase was then titrated againstt standard alkali to determine the acid transfer. In the determination of hydrochloric acid titrations with silver nitrate were also used, with good agreement between the two types of titration as indicated in Table XX.

TABLE XX Determination of HCl transfer by silver nitrate and alkali titration methods.

	Molarity of HCl in the organic phase	
Aqueous HCl molarity	Silver nitrate titration	Alkali titration
8.93	8.5×10^{-3}	8.3×10^{-3}
10.18	16.9×10^{-3}	18.8×10^{-3}
11.16	19.6×10^{-3}	19.7×10^{-3}

Blank titrations were carried out to determine the amount of acid taken up by toluene alone. This correction was negligible for perchloric acid solutions at all the concentrations studied but an appreciable correction was necessary for hydrochloric acid. A "nitric acid blank" was also determined by shaking appropiate volumes of the virgin ester phase with the dilute nitric acid and then titrating this against standard alkali. This titre plus the toluene blank were subtracted from the titres for the equilibrated nitric acid phase in order to determine the amount of acid extracted by the ester itself. For some measurements with HDEHP the equilibrated organic phase, after dilution with alcohol, was titrated directly against standard alkali. The values obtained by this procedure and those from equilibrating the organic phase with nitric acid were found to be in good agreement.

An attempt was made to determine the concentration of perchlorate anion in the organic phase by the method of IRVING(99,100), in which a strongly coloured liquid anion exchanger is equilibrated with an aqueous solution of the perchlorate resulting in transfer of perchlorate ion to the organic phase and an equivalent transfer of coloured anion into the aqueous phase. The optical density of the aqueous phase is determined spectrophotometrically. Hexadecyltrimethylammonium erdmannate(101), was used as the liquid anion - exchanger but reproducible results could not be obtained, possibly due to the instability of the reagents employed.

(b) Extraction of water

The data on water extraction were determined by means of Karl Fischer titrations(102). The apparatus used is shown in fig. 14 A single stream of nitrogen, dried by passing it through the towers of anhydrone and finally through a solution of the Karl Fischer (KF) reagent, was used both to stir the solution in the reaction vessel and to fill the automatic burette. Thus by turning the three - way tap, A, to position 1, the nitrogen was used to force KF reagent from the reservoir, C, into the burette. Excess pressure in the system was released by momentarily opening tap, B. With tap, A, in position 2, the nitrogen bubbled through the reaction vessel.

Initially the end point of the titration was determined with the aid of a pair of platinum electrodes using the "dead stop" technique. Later, however, a visual end point, utilising the change in colour of the KF reagent itself, was found to be sufficiently accurate.

All reagents for the KF titrations were supplied by B.D.H. The reagent was standardised before a given set of measurements against a standard solution of methanol

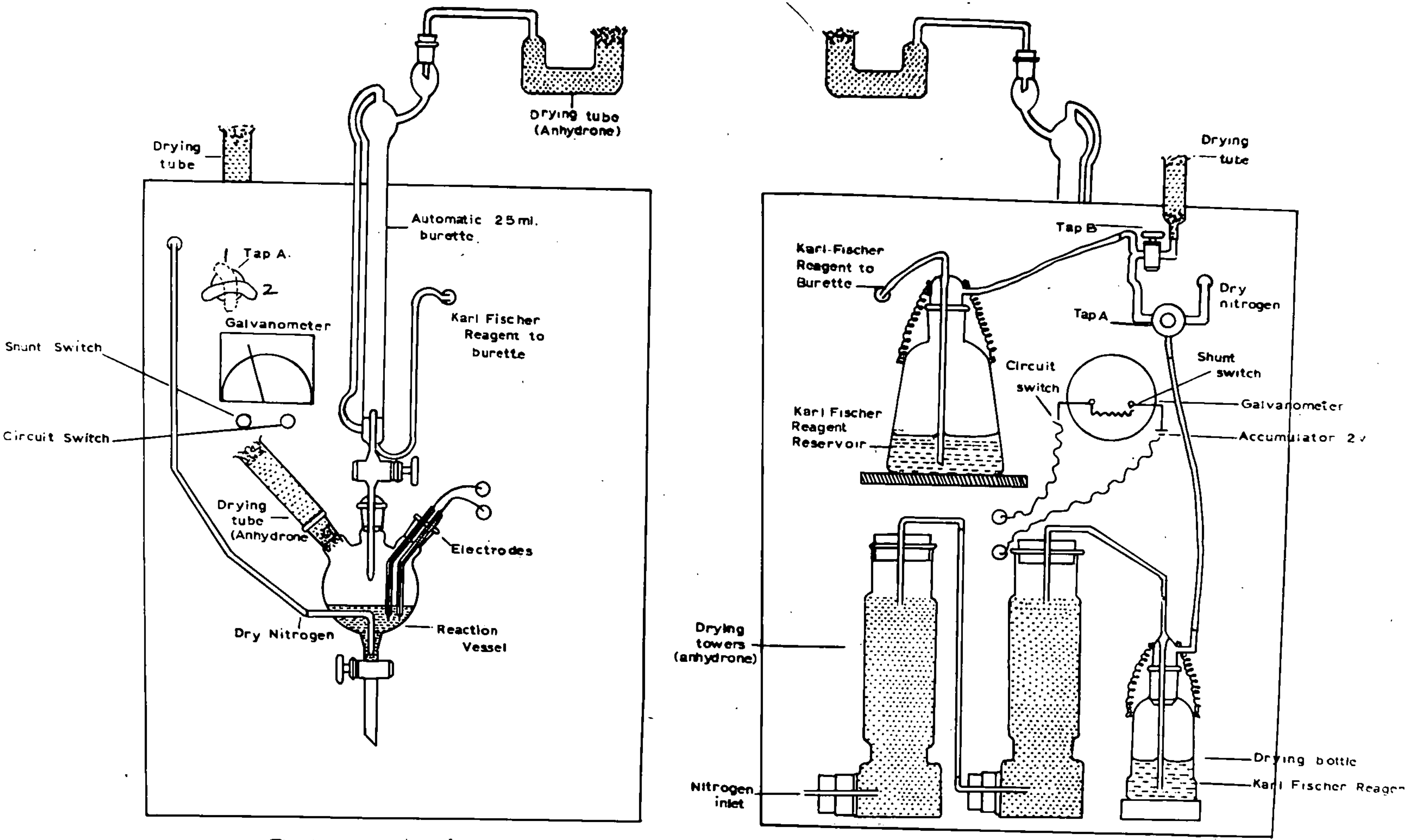

Fig.**14** Diagram of the apparatus used in the determination of water by Titration with Karl Fischer Reagent.

containing 5mg. of water per ml. Titrations were carried out to correct for adsorbed moisture in the reaction vessel and by titrating a sample of anhydrous methanol a correction could be made for the reagent consumed by the methanol in the water standard.

In general 15ml portions of the equilibrated organic phase were titrated against the Fischer reagent and it was shown that the esters did not interfere with the reagent. Before titrating a sample 25ml of anhydrous methanol were pipetted into the reaction vessel and titrated against the reagent to the end-point. This then provided a suitable solvent for the ester solutions. It was found that three or four samples could be titrated successively without the need to empty the reaction vessel. This minimised the amount of moisture entering the vessel. The contents of the vessel were exposed to the atmosphere for the shortest time possible to minimise absorption of extraneous water.

The extraction data were determined for 0.110M solutions of the esters. It was found that the amount of acid extracted was directly proportional to the concentration of the ester but that the relationship between concentration of ester solution and the amount of water extracted was more complicated (a threefold decrease in ester concentration resulted in a fivefold decrease in the amount of water extracted). A non-linear dependence between ester concentration and water extracted has also been observed in the TBP-nitric acid system(103).

The water and acid extraction data are recorded below in Tables XXI, XXII, XXIII, XXIV, and a plot of concentration of water in the H_2MEHP against the water activity of the aqueous phase is shown in fig. 15.

Discussion of results

One of the most significant differences between the two esters is in the amount of water that they extract. From dilute solutions H_2MEHP extracts 15 to 20 times the amount extracted by HDEHP for equivalent concentrations. It is also seen from Table XXI that the water extracted from hydrochloric acid solutions decreases with increasing acid concentration but levels off at an acid concentration between 8 and 9M. On the other hand there is a minimum in the water extracted from perchloric acid solutions between 8 and 9M $HClO_4$. HDEHP shows

TABLE XXI. Distribution of hydrochloric acid and water between aqueous and 0.110M H_2 MEHP phases

Aqueous Phase		Organic Phase	
HCl Concentration (M)	HCl extracted by toluene alone (M)	HCl extracted by H_2 MEHP (M)	Water concentration (M)
0.22	0	0	2.77×10^{-1}
1.16	0	0	2.52×10^{-1}
2.32	0	0	1.82×10^{-1}
3.48	0	0	1.42×10^{-1}
4.49	very small	2.65×10^{-3}	9.87×10^{-2}
6.70	1.42×10^{-3}	5.40×10^{-3}	6.07×10^{-2}
7.85	4.40×10^{-3}	7.46×10^{-3}	4.74×10^{-2}
8.93	5.32×10^{-3}	9.06×10^{-3}	3.60×10^{-2}
9.98	2.03×10^{-2}	1.36×10^{-2}	3.54×10^{-2}
11.12	4.72×10^{-2}	1.96×10^{-2}	3.74×10^{-2}

TABLE XXII Distribution of perchloric acid and water between aqueous and 0.110M H_2MEHP phases

Aqueous Phase	Organic Phase	
$HClO_4$ concentration (M)	$HClO_4$ concentration (M)	Water concentration (M)
0.19	0	3.02×10^{-1}
0.93	0	2.37×10^{-1}
1.86	0	1.82×10^{-1}
4.88	6.4×10^{-4}	6.60×10^{-2}
7.32	2.15×10^{-3}	8.67×10^{-2}
8.54	8.51×10^{-3}	3.33×10^{-3}
9.76	2.82×10^{-2}	1.40×10^{-2}
10.98	5.47×10^{-2}	1.73×10^{-2}

TABLE XXIII Distribution of hydrochloric acid and water between aqueous and 0.110M HDEHP phases

Aqueous Phase	Organic Phase		
HCl Concentration (M)	HCl extracted by toluene alone (M)	HCl extracted by HDEHP (M)	Water concentration (M)
0.22	0	0	1.80×10^{-2}
1.16	0	0	1.67×10^{-2}
4.49	very small	very small	-
6.70	1.42×10^{-3}	very small	2.00×10^{-3}
7.85	4.40×10^{-3}	1×10^{-4}	2.00×10^{-4}
8.93	5.32×10^{-3}	8.29×10^{-3}	0
9.98	2.03×10^{-2}	1.78×10^{-2}	0
11.12	4.72×10^{-2}	3.03×10^{-2}	0

TABLE XXIV Distribution of perchloric acid and water between aqueous and 0.110M HDEHP phases

Aqueous Phase	Organic Phase	
$HClO_4$ concentration	$HClO_4$ concentration	Water concentration
0.19	0	1.80×10^{-2}
0.95	0	1.93×10^{-2}
1.86	0	1.93×10^{-2}
4.88	4.5×10^{-4}	6.67×10^{-3}
7.32	2.38×10^{-3}	0
8.54	1.28×10^{-2}	2.00×10^{-3}
9.76	3.50×10^{-2}	4.00×10^{-3}
10.98	4.53×10^{-2}	-

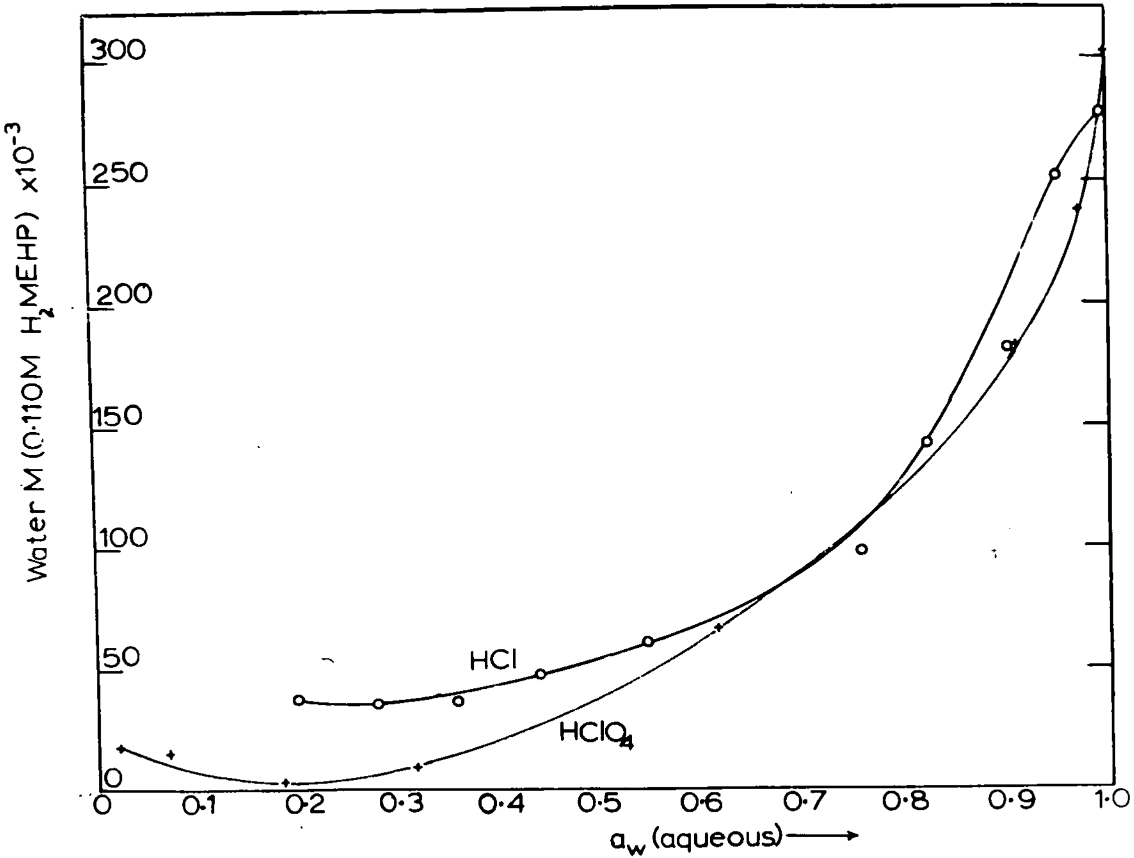

Fig.15 Molarity of water in 0·110M H_2MEHP as a function of the water activity of the aqueous phase

parallel behaviour in the two systems although the minimum in perchloric acid is less marked. The presence of a mimimum at high acid concentrations is also shown in the TBP - HNO_3 - H_2O system at about 9M in HNO_3 (103,104,105,106,107).

From the acid extraction data it is seen that no measurable uptake of hydrochloric acid occurs until an aqueous concentration between 4 and 5M is reached with H_2MEHP as extractant. The amount then slowly but steadily increases to a value of about 0.02M in the organic phase at 11.12M HCl. Extraction of perchloric acid is similar but the amount extracted rises sharply with increasing aqueous acid concentration, reaching a value of about 0.05M from 10.98M $HClO_4$. It is of interest to note that toluene itself extracts considerable amounts of hydrochloric acid where it probably exists as undissociated HCl molecules. PEPPARD(104) investigating the system HDEHP - HNO_3 - H_2O found that considerable nitric acid extracted into the organic phase from strong aqueous nitric acid.

(c) Infra-red spectra

Infra-red spectra were determined for three different concentrations of H_2MEHP (0.024, 0.073, 0.110 and 0.57M) and for two of the solutions after equilibration with 0.50M perchloric acid. A series of spectra were also obtained of 0.110M H_2MEHP equilibrated with increasing concentrations of perchloric acid. All the measurements were made with a Unicam SP 200 infra-red spectrophotometer, using liquid smears between sodium chloride plates. The H_2MEHP was in solution in toluene which necessitated using a toluene reference cell. This unfortunately reduced the sensitivity of the measurements. Examples of the spectra obtained are shown in fig. 16 and fig. 17. Table XXV lists the absorption maxima and the tentative assignment of some of these bands.

The vibrations in the region 1020 to 1050 cm^{-1} may almost certainly be assigned to stretching in the (P - O) — alkyl system.(108, 109) The band at 1050 cm^{-1} is particularly intense and is characteristic of alkyl phosphates.(71)

The strong bands at 1150 and 1185 cm^{-1} are tentatively assigned to phosphoryl absorptions.(109,110)

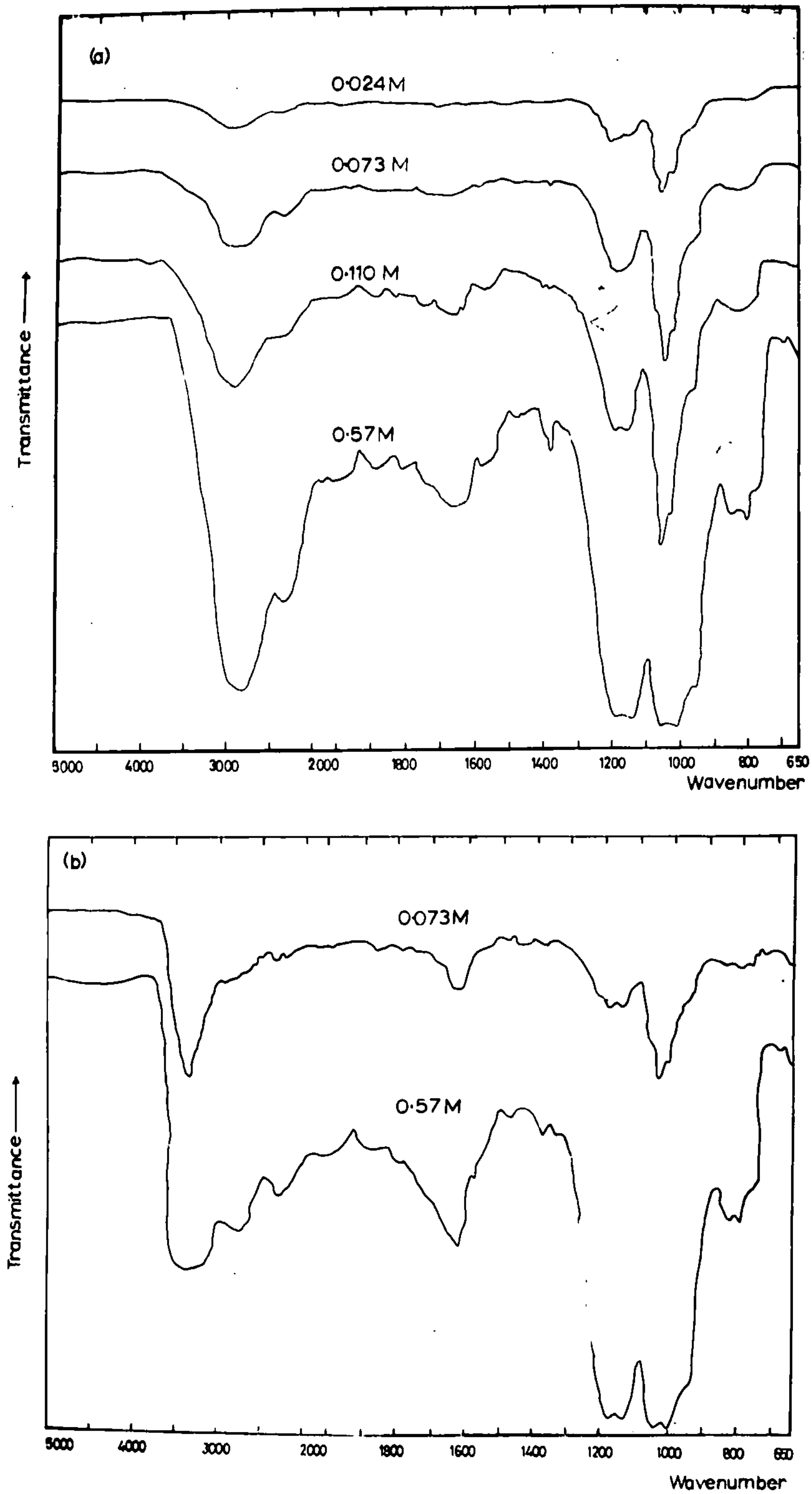

Fig.16 I-R spectra
(a) various concentrations of H_2MEHP in toluene
(b) 0·073 and 0·57 M H_2MEHP after equilibration with 0·50M $HClO_4$

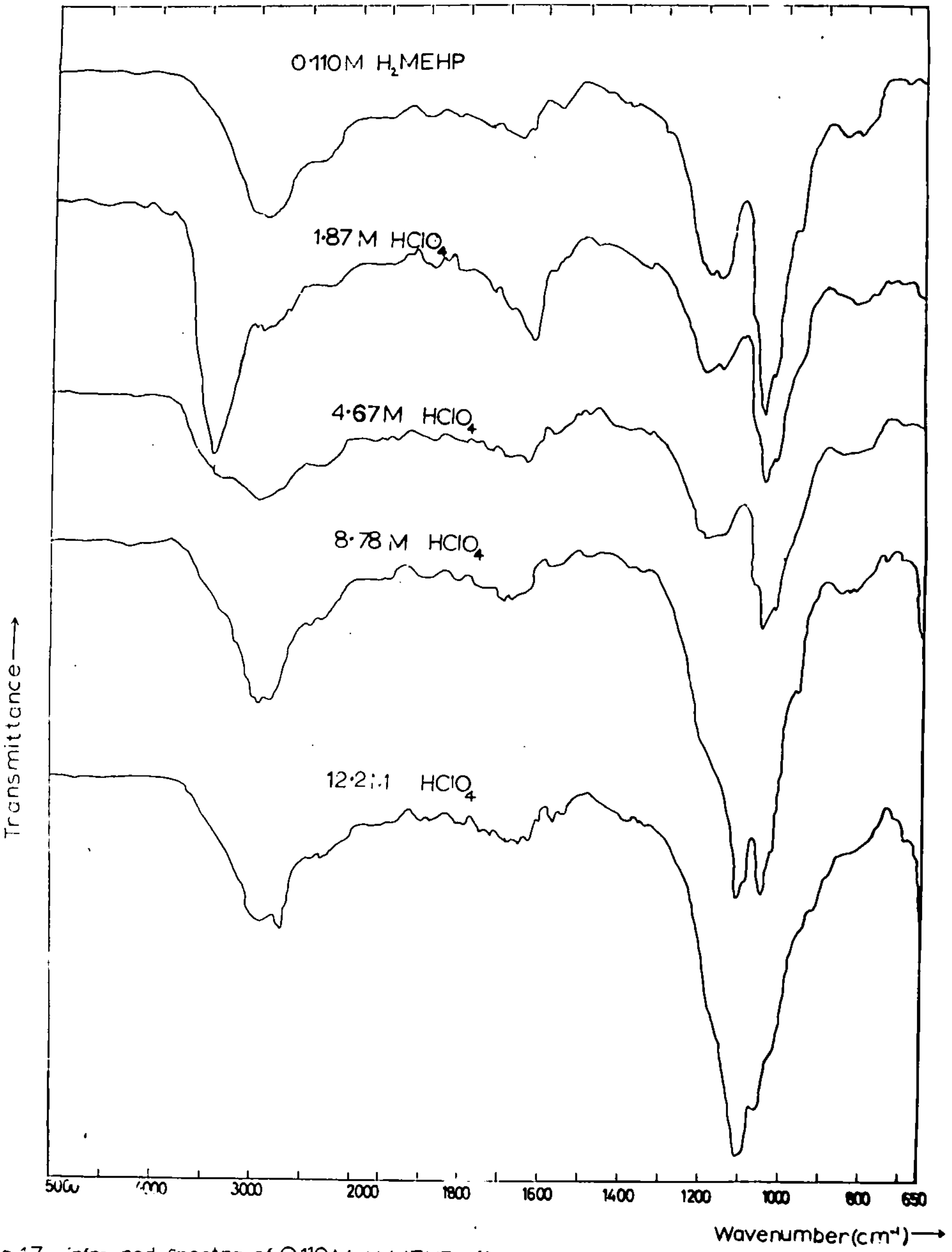

Fig.17 infra-red spectra of 0·110 M H_2MEHP after equilibration with several $HClO_4$ solutions

TABLE XXV Absorption maxima for H_2MEHP in dry toluene and postulated assignments

Absorption Maxima (cm^{-1})	Assignment
695 (vw)	
810 (vw)	
850 (vw)	
960 (sh)	
1020 (sh)	(P-O) - alkyl vibrations
1050 (vs)	
1150 (vs)	Bonded P → O stretching
1185 (vs)	
1380 (m)	CH_3 symmetrical deformation
1475 (vw)	
1660 (m) broad	OH combination overtone ?
1810 (w)	
1880 (w)	
2370 (m)	Combination frequency of OH stretching
2750 (vs) broad	Bonded O - H stretching

Abbreviations; (w) weak; (m) medium; (s) strong; (v) very; (sh) shoulder.

This band appears at 1225 cm^{-1} in HDEHP.(71,111) The appearance of several bands in this region may represent different types of hydrogen - bonding to the P ═ 0 group.(110) The region between 1400 and 2500 cm^{-1} is not very useful for characterising this ester and only one or two very tentative assignments were attempted.

The bands at 2750 and 2370 cm^{-1} are assigned to 0 - H vibrations. Originally both were assigned to fundamental modes (112,113) but they may be both attributed to combination frequencies connected with strong hydrogen - bonding,(114) although THOMAS (115,116) believes the 2700 cm^{-1} band is a hydrogen - bonded stretching frequency and the 2300 cm^{-1} band is a combination band. The broadness of these bands indicates that they are not pure vibrations, Their position, however, indicates strong hydrogen - bonding. On deuteration both these bands were moved to lower frequencies.

On equilibration with 0.50M perchloric acid two new bands appear,in the spectrum, one at about 3400 cm^{-1} and another at about 1630 cm^{-1}. That at 3400 cm^{-1} is almost certainly assignable to a water 0 - H stretching mode.

In pure water this band appears at 3445 cm^{-1} (117) and the shift to slightly lower frequencies may be due to hydrogen - bonding. The band at 1630 cm^{-1} is tentatively assigned to the H - O - H bonding frequency since for pure water this appears at 1627 cm^{-1}. (118)

For the spectra of H_2 MEHP shaken with different concentrations of perchloric acid one or two interesting points arise. In the first place only the two most dilute solutions (1.87 and 4.67 M. perchloric acid) show evidence of bands due to water, at 3400 and 1630 cm^{-1}. Secondly there appears to be a shift in the P ⟶ O stretching frequency from 1185 cm^{-1} in pure H_2 MEHP to about 1110 cm^{-1} in 12.2M perchloric acid. A similar shift was found by PEPPARD and FERRARO (104) for the HDEHP - HNO_3 system. In the present case it may well represent hydrogen - bonding of $HClO_4$ to the P ⟶ O group.

CHAPTER VI

DISCUSSION

In order to examine some aspects of ion-exchange quantitatively consider the exchange of the ions A^{z+} and B^{+}. The exchange reaction may be written

$$A^{z+} + \bar{B} \rightleftharpoons \bar{A} + zB^{+}$$

where a bar above a symbol represents a species in the resin phase. The molal selectivity coefficient, K_B^A, may be defined as follows

$$K_B^A = \frac{\bar{m}_A m_B{}^z}{m_A \bar{m}_B{}^z} \qquad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where m represents the molality of a species. From thermodynamic considerations and neglecting sorption of electrolytes and the swelling property of the exchanger the equilibrium constant, K_T, for the above reaction is(64)

$$K_T = \frac{\bar{a}_A a_B{}^z}{a_A \bar{a}_B{}^z} \qquad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

where a represents the activity of a given species. Combining (1) and (2), K_T is

$$K_T = K_B^A \left(\frac{\bar{\gamma}_A}{\gamma_A}\right)\left(\frac{\gamma_B}{\bar{\gamma}_B}\right)^z \qquad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where γ is the activity coefficient. Assuming the same reference and standard states for both the ion-exchanger and the external solution, K_T is close to unity

$$\therefore\ K_B^A = \frac{\gamma_A \bar{\gamma}_B^{\,z}}{\bar{\gamma}_A \gamma_B^{\,z}} = \frac{\bar{m}_A m_B^{\,z}}{m_A \bar{m}_B^{\,z}} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

The distribution coefficient, K_d, is defined as

$$K_d = \frac{\bar{m}_A}{m_A}$$

Thus (4) becomes$^{(28)}$

$$\log K_d = -z \log m_B + z \log \bar{m}_B - \log \Gamma_{A/B}$$

where $\Gamma_{A/B} = \dfrac{\gamma_A \bar{\gamma}_B^{\,z}}{\bar{\gamma}_A \gamma_B^{\,z}}$

$$\frac{d \log K_d}{d \log m_B} = -z + z \frac{d \log \bar{m}_B}{d \log m_B} - \frac{d \log \Gamma_{A/B}}{d \log m_B} \quad \ldots\ldots \quad (5)$$

If A is in tracer quantities then for dilute solutions $\Gamma_{A/B}$ is constant, $\bar{m}_A \ll \bar{m}_B$ and $\bar{m}_B$ is approximately constant. Under these conditions (5) reduces to

$$\frac{d \log K_d}{d \log m_B} = -z \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

From equation (6) a plot of log K_d against log of the external electrolyte concentration, m_B, should be a straight line of slope $-z$, as long as the above conditions apply. That this is indeed the case for Y^{3+}, in perchloric and hydrochloric acid acids using H_2 MEHP as the exchanger is shown by the plots in fig. 4 and Eu and Am were also shown to have slopes of -3 for solutions of less than about 2M. The minima and subsequent increase in K_d are not predicted from this simplified form of the equation but extension of the equation to allow for electrolyte invasion leads to the conclusion that distribution coefficients at high external solution concentrations are determined largely by the ratio of the activity coefficients of the electrolyte in the external solution and the exchanger phase.(28) These quantities, however, cannot be determined experimentally at present and thus a quantitative discussion is not possible. It was shown by BAUMAN and ARGERSINGER (119) that the adsorption of non-exhcnage electrolyte from dilute solutions was so small that its effect on K_d values could be ignored.

Originally the increase in K_d at high electrolyte concentrations was thought to be due to the uptake of negatively charged species (24,25, 27,) and indeed such species were shown to be present in the exchanger (30,) SAMUELSON (120) suggested that the negatively charged ions were adsorbed through interactions with the aromatic matrix of resins since he found very little adsorption of Fe (III) from 12M HCl using a non-aromatic, methacrylic acid - type of exchanger. Negatively charged species may well be adsorbed by the resin but more extensive work has shown that the formation of these is not a necessary condition for the observed behaviour. Many elements show marked adsorption from strong $HClO_4$ (28,34,35,36,37) in which complexing is very slight (121,122,123,124) and the formation of negatively charged species extremely improbable. The observation of SAMUELSON is difficult to account for but appears to be erroneous since "anomolous" behaviour has been observed in non-aromatic-type phosphate resins(52,53) and in the present work with H_2 MEHP.

The lack of experimental data has meant that more qualitative approaches have had to be made in order to attempt some explanation of adsorption from concentrated solutions. One of the most detailed of such approaches has been made by DIAMOND.(29,35,43,60) This involves consideration of the possible 'solvation' interactions in both the aqueous and the exchanger phases and their effect upon the distribution of an ion. In effect, therefore, it is a qualitative discussion of differences on activity of an ion in the aqueous and organic phases which was previously alluded to as accounting for the observed distribution behaviour in concentrated electrolytic solutions.(28)

In dilute external solutions hydration of the cations is far more important than cation-anion interactions even though such interactions exist.(125) There is much less water available in the resin phase(126) but the anion concentration is greater. This, together with the low dielectric constant of this phase,(127) mean that cation-anion interactions are more important but even so crystallographically smaller ions prefer the aqueous phase and force the larger cations into the exchanger. For the alkali metals for example, this leads to the distribution sequences $Cs^{+} \rhd Rb^{+} \rhd K+ \rhd N9+ \rhd Li+$, a sequence observed by several workers.(13,128,129,130)

In concentrated solutions on the other hand there is a much lower water activity, an increase in cation-anion interactions and thirdly electrolyte invasion of the exchanger. The cation-anion interactions are rather ephemeral but are enhanced by the low water activity and a decrease in the dielectric constant of the external solution.(131,132) Anions may become bound to highly polarised water molecules in the primary hydration sphere of the cation, so-called "localised hydrolysis" (133,134) and there are significant changes in the water structure. (135) The water activity in the exchanger is even lower and solvation of cations by the fixed anionic groups assumes primary importance. The overall effect is to force the crystallographically smaller cations, that is those with the highest charge density, into the exchanger. Since the Donnan potential (136) is unable to prevent invasion of non-exchange electrolyte this provides, to a first approximation, the exchanger with new "resin sites". This has the effect of increasing the K_d values of all the cations present. Such reasoning has been applied to account for the inversions in distribution values for the exchange of tetraalkylammonium ions with alkali cations (137) and also to account for the distribution behaviour of halide anions between an anion-exchanger and concentrated solutions.(138)

The present studies with H_2 MEHP support many of the above conclusions. Thus for the distribution of between H_2 MEHP and HCl and $HClO_4$ solutions the minimum in HCl is at a higher external concentration than with $HClO_4$, reflecting the stronger aqueous yttrium-chloride interactions compared to the corresponding yttrium-perchlorate interactions. The minimum for yttrium in hydrochloric acid found from this work and that reported by PEPPARD (59) is at a slightly higher external acid concentration than that found for sulphonate resins.(28) This may be attributable to differences in the amount of non-exchange acid entering the two exchangers. Measurable amounts of hydrochloric acid are only extracted into H_2 MEHP when the external concentration is 4 to 5M (see p.83) and even in concentrated solutions the amount adsorbed is much less than for resin exchangers.(46,47) There are thus less additional exchange sites in H_2 MEHP and this may counteract the effect of greater polarisability (54) and stronger basicity of the phosphate compared with the sulphonate groups (139) both of which favour exchange of the yttrium. This comparatively low exchanger invasion by the electrolyte may also explain the broad minimum observed in the distribution of Y^{91} into H_2 MEHP from $HClO_4$. The data on p.83 indicate that adsorption of $HClO_4$ by H_2 MEHP only becomes important at about 8M external $HClO_4$ so that in the minimum region between 4 and 7M $HClO_4$ the competition between water in the external and phosphate ions in the organic phase to solvate the Y^{3+} cation may be roughly equal resulting in relatively constant K_d values in this region, beyond this point both electrolyte invasion and K_d values increase rapidly.

The behaviour of Am (III) in HCl is seen to be completely different with H_2 MEHP than with sulphonic acid resins. In the latter case there is no minimum or rise in K_d values with increasing acid concentration(28) as found when using H_2 MEHP. On the other hand Eu (III) which normally shows similar behaviour to Am(III) in aqueous solutions exhibits a minimum in both systems. This difference is ascribed to differences in complexing ability of these two ions.(140) Americuim tends to form chloride complexes in HCl and these are sufficiently strong to prevent exchange with sulphonic acid resins containing the weakly basic sulphonate ion. With H_2 MEHP, however, which contains the much more polarisable and basic phosphate grouping and at acid concentrations below about 10.5M, interactions between Am(III) and the phosphate anion are more important than between Am(III) and chloride anions, as observed with some other cations.(55,141) This accounts for the increase in K_d values after the minimum value. Between 10.6 and 11.2M acid concentration K_d values decrease slightly presumably due to a sufficient decrease in water activity to cause aqueous chloride complexing to exceed that due to the phosphate anion with a consequent reduction in K_d. It is interesting to note that in strong $HClO_4$, where such aqueous "complexing" is much less important, the K_d values for Am(III) and Eu(III) are almost identical using a sulphonic acid-type resin,(36) whereas in HCl K_d values for Eu(III) are greater than for Am(III). The K_d values for both ions in HCl are also less than the corresponding ones in $HClO_4$(36) which is probably partly due to association of the acid in the organic phase(33) and may even lead to the formation of HCl_2^- ions.(142) This effect is smaller for $HClO_4$ since it is a stronger acid than HCl.

The importance of the interactions between cations and the fixed anionic group of the exchanger is demonstrated particularly clearly from studies with carboxylic acid - type resins.(29,142,143) The carboxylate group competes much more successfully with water to solvate the cations and even though the usual alkali metal sequence is retained in dilute acids (29) the smaller cations have much higher K_d values relative to the larger Rb+ and Cs+ ions. With ammonium chloride solutions(58) the sequence is reversed for all aqueous concentrations studied.

Although the effect of diluent on the extraction characteristics of H_2 MEHP was not investigated in the present work (all studies were conducted with toluene as diluent) it has been found that the diluent has a marked effect on K_d values when using di-butylphosphoric acid (DBP)(144,145,146,147,148) and TBP (149,150,151,152,153,154) BAES (81) has suggested that interactions with the polar core of the extracting complex is the dominant solvent effect. For aromatic diluents the dielectric constant and the π - electron system of the diluent have been suggested as the most important influences on the extractant.(155) However, PUSHLENKOV (156) found no correlation between extracting ability of TBP solutions and the dielectric constant of the diluent and SIEKIERSKI (154) believes that the activity of the TBP may be connected with the Hildebrand solubility parameter.(157)

Of obvious importance is the completely different behaviour shown by HDEHP and H_2 MEHP at high electrolyte concentrations. A plot of log K_d against acid concentration for yttrium in the former ester is a straight line of slope $\simeq 3$ at all acid concentrations up to at least 6M.(98) This would indicate that no significant changes in the organic phase are occuring in this region so that whatever mechanism is responsible for distribution values in dilute solutions this same mechanism is still operative at much higher concentrations. One significant difference between the two esters is in their degree of polymerisation. In dry toluene H_2 MEHP is known to form only hexamers.(93) However, on the addition of water polymerisation becomes much greater. Evidence from the metal loading experiments using the argument on p.73 suggests that polymers of perhaps 50 to 60 H_2 MEHP units are formed. These polymers almost certainly contain water and it was found experimentally that after equilibrating a toluene solution of the ester with dilute acids there were some 5 water molecules per "dimer" of ester; very little electrolyte was taken up from these solutions. A possible structure for the polymer is shown in Fig. 18. The positioning of the water molecules is only very tentative but three-dimensional models indicate that they could be accommodated in the structure as shown. Such models also show that the phosphate groups are partially shielded from the diluent by the extensive, branched alkyl groups. The water molecules may well be important in holding such a structure together. The experimental data also show that about one molecule of acid per dimer is taken up from strong acid solutions. The infra-red spectral data indicate that some at least of the adsorbed electrolyte is bonded to the P ⟶ O grouping in the esters, although all the adsorbed electrolyte is not necessarily bound in this way.

HDEHP on the other hand is known only to form dimers in toluene and with trace amounts of exchanging cation. (71)

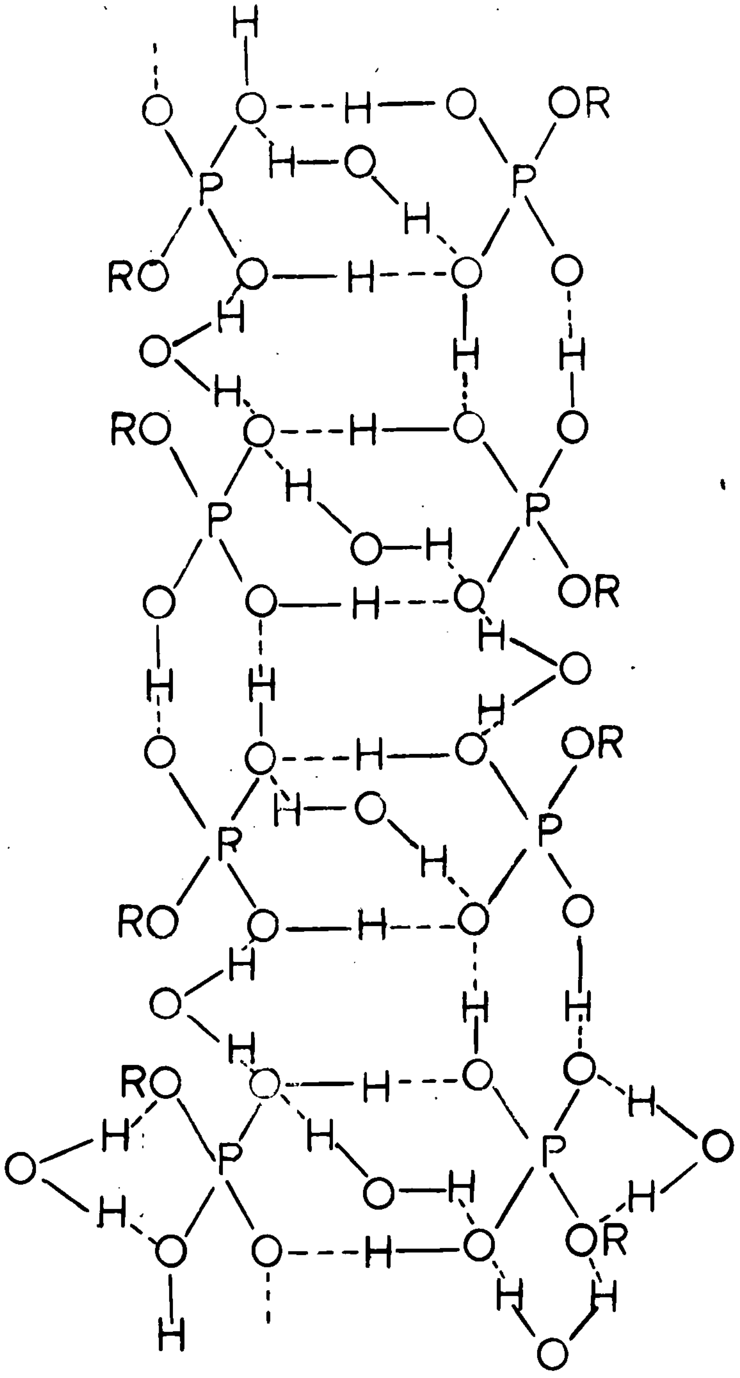

Fig.18 Proposed structure of H_2MEHP (all water molecules not shown)

Such a structure is much more open than the large H_2 MEHP polymers and since it can only take up water by bridges across the dimers water uptake would be expected to be much lower than for H_2 MEHP, as was found in the present work. Although HDEHP was found to adsorb as much non-exchange electrolyte as H_2 MEHP in this case all of it would be expected to be bound to the $P \longrightarrow 0$ groups.

From considerations of the proposed structure of H_2 MEHP and assuming that the diluent exerts its effect by interaction with the polar core of the extractant, as proposed by BÆES (81) it is possible that the diluent would have little effect on K_d values in H_2 MEHP because of the effective shielding of the polar groups by the alkyl groups attached to them.

The proposed structure of H_2 MEHP would allow the dispersion of electrolyte within its core as DIAMOND(33) proposes for conventional ion-exchangers whereas for HDEHP no such freedom can exist in a non-polar solvent. This restriction on free electrolyte may therefore be regarded as playing a significant role in determining the difference in behaviour.

It has already been shown that for yttrium log K_d

varies inversely as the third power of the hydrogen ion concentration and (for concentrations greater than about 0.04M) directly as the first power of the H_2 MEHP concentration. Thus if there are nH_2 MEHP monomers per polymer we may write the following equation

$$Y^{3+} + (H_2\ \mathrm{MEHP})_n \rightleftharpoons Y\left\{H_{n-3}(\mathrm{HMEHP})_n\right\} + 3H^+$$

The equilibrium constant, K, for this reaction is given by

$$K = \frac{[Y\{H_{n-3}(\mathrm{HMEHP})_n\}][H^+]^3}{[Y^{3+}][H_2\mathrm{MEHP}]_n} \qquad \ldots\ldots\ldots\ (1)$$

where square brackets represent concentration of a given species.

By definition,

$$K_d = \frac{[Y\{H_{n-3}(\mathrm{HMEHP})_n\}]}{[Y^{3+}]} \qquad \ldots\ldots\ldots\ldots\ (2)$$

Thus substituting in equation (1)

$$K = \frac{K_d[H^+]^3}{[H_2\mathrm{MEHP}]_n} \qquad \ldots\ldots\ldots\ldots\ (3)$$

If T_m = the total yttrium metal ion concentration
and T_{HMP} = the total ester concentration measured in
$(H_2\ MEHP)_n$ molecular units

$$\text{then } T_m = [Y^{3+}] + [Y\{H_{n-3}(HMEHP)_n\}] \quad \ldots\ldots\ (4)$$

$$\text{and } T_{HMP} = [H_2\ MEHP]_n + [Y\{H_{n-3}(HMEHP)_n\}] \quad \ldots\ldots\ (5)$$

On subtracting (4) from (5) we have

$$T_{HMP} - T_m = [H_2\ MEHP]_n - [Y^{3+}]$$

$$\therefore [H_2\ MEHP]_n = (T_{HMP} - T_m + [Y^{3+}])$$

Substituting this value into equation (3)

$$K = \frac{K_d\ [H+]^3}{(T_{HMP}-T_m+[Y^{3+}])}$$

$$\therefore K_d = \frac{K\ (T_{HMP} - T_m + [Y^{3+}])}{[H^+]^3}$$

and

$$\log K_d = \log K - 3 \log[H^+] + \log (T_{HMP} - T_m + [Y^{3+}]) \quad \ldots (6)$$

Since under the conditions of the experiment $[H^+]$ is constant we may replace $\log K - 3 \log[H^+]$ by log C.

Thus (6) may be written as

$$\log K_d = \log C + \log (T_{HMP} - T_m + [Y^{3+}])$$

or

$$\log K_d = \log C + \log (T_{HMP} - (T_m - [Y^{3+}])) \quad \ldots (7)$$

Now $T_m - [Y^{3+}]$ represents the metal concentration in the organic phase i.e., $[Y\{H_{n-3} (HMEHP)_n\}]$

$$\therefore \log K_d = \log C + \log (T_{HMP} - [Y\{H_{n-3}(HMEHP)_n\}]) \quad ..(8)$$

For low yttrium loading $T_{HMP} >> [Y\{H_{n-3}(HMEHP)_n\}]$

and so a plot of log K_d against log yttrium concentration of the organic phase at constant perchloric acid concentration should be relatively constant or decrease only slightly. This was observed experimentally (cf.p.73). As the organic phase is loaded with yttrium the right-hand side of (8) decreases. When $[Y\{H_{n-3} (HMEHP)_n\}]$ exceeds T_{HMP} equation (8) is no longer applicable: in order to take up more Y^{3+} a change in the structure of the H_2 MEHP polymer units must occur, and this would perhaps be expected to lead (see fig. 18) to decreasing K_d with increasing Y^{3+} on mass-action and energetic grounds. Further knowing n, T_{HMP}, $[Y\{H_{n-3}\ (HMEHP)_n]$ and the hydrogen ion concentration in the aqueous phase, equation (8) can be used to estimate K, the equilibrium constant. Using a value of n = 50 and 0.373 for $[H+]_{aq}$ K was found to be $4.5 \pm 0.1 \times 10^2$ $Mol.^2$ $litre^{-2}$

When log K_d was plotted against H_2MEHP at 0.50 and 0.70M aqueous $HClO_4$ a sharp break was observed at a concentration of about 0.03 to 0.04M. Below this concentration range K_d values decreased rapidly. It was also found from experiment carried out with 0.035 and 0.110M H_2 MEHP to determine water and electrolyte extraction that the amount of electrolyte adsorbed was directly proportional to the H_2 MEHP concentration whilst the amount of water imbibed varied more steeply with the ester concentration. Thus it is possible that the break in the plot represents a point where the amount of water adsorbed by the ester is insufficient to maintain the large polymer structure and at low ester concentrations there is a rapid decrease of polymer size with consequent lower distribution values.

The reason for the apparent synergistic effect of HDEHP on H_2 MEHP is not altogether clear. It has been shown that in dry toluene H_2 MEHP exists as hexamers and that TBP, which also produces a synergistic effect, did so through the formation of adducts of the type $(H_2MEHP)_6(TBP)_2$.(94) It is possible that HDEHP may also form such adducts as discussed earlier.

Thus it may be concluded with some justification that H_2 MEHP is a liquid ion-exchanger with properties analogous to conventional exchange resins. HDEHP on the other hand is apparently best considered to be similar in behaviour to chelating extractants such as thenoyl trifluoroacetone or cupferron than to exchange resins.

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ACKNOWLEDGEMENTS

I wish to record my thanks to the following:

Dr. S. J. Lyle for his supervision and interest throughout the course of this work.

Professor G. R. Martin under whose supervision part of this work was done.

Mr. A. J. Fassam who recorded the infra-red spectra and gave other technical assistance.

Mr. R. J. Oliver for running the neutron generator and for general technical assistance.

The Science Research Council for the award of a Research Studentship, during the tenure of which this work was undertaken..