THE EXTRACTION OF QUATERNARY SALTS FROM WATER INTO APROTIC SOLVENTS

A thesis submitted in fulfilment of the requirements for admission to the Degree of

Doctor of Philosophy

by

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SUMMARY

This thesis deals with the extraction of quaternary salts from water into four organic solvents, chloroform, dichloromethane, 1,2-dichloroethane and 2,2'-dichlorodiethylether. In all, some seventeen different quaternary ammonium, phosphonium and arsonium cations and some eighteen different anions were studied.

The extraction of the quaternary salts was studied over a range of concentration, and over a range of cation concentration with the anion concentration constant and the results have been interpreted as indicating that only ion pairs and dissociated ions are present in the organic phase. The extraction over a range of chloride and bromide concentration with the cation concentration constant have also been investigated. The results obtained using hydrochloric acid as the source of chloride ions were anomalous. Possible explanations for this behaviour were examined and it was postulated that ion pair formation in the hydrochloric acid solution was the reason for the anomaly.

The extraction of quaternary salts under conditions where ion pairs are the only important species present in all four solvents has been investigated. The results obtained are discussed in terms of the cation size, the properties of the anion and the properties of the organic solvent. In general it was found that extraction increased with increasing cation size although the effect of substitution at various positions on the cation was found to be very important.

The nature of the anion was found to be the most important factor governing the amount of extraction, and a very good correlation between the enthalpy of hydration of the anion and the percentage extraction of the quaternary salt was observed.

The four organic solvents used showed relatively small differences in their extracting power in view of the large differences in their dielectric constants. Reasons for this behaviour are discussed in terms of specific interactions between the solvent molecules and the ion pairs.

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SECTION 1

PREFACE

Section 1 Preface

This thesis is a result of an investigation of the extraction of a number of quaternary ammonium, phosphonium and arsonium salts into four different aprotic solvents. In all, some seventeen different cations and some eighteen different anions have been investigated. This work was complemented by some work carried out in this School by Miss E. Guymer on the influence of cation size on the extraction of the permanganate ion.

Quaternary ammonium, phosphonium and arsonium salts have been widely used in analytical chemistry to extract anions into various organic solvents, but very little work has been reported on the factors which affect the extraction. The present investigation was therefore started with the object of elucidating the effect of the nature and properties of the cations and anions on the extraction of these salts. The effect of the properties of the organic solvent on the extraction has also been investigated for the four different solvents, chloroform, dichloromethane, 1,2-dichloroethane and 2,2'-dichloro-diethylether.

The thesis is divided into seven sections, these sections are further divided into subsections; this short preface is the first of these sections. Section 2 is a survey of the literature on the extraction of quaternary salts. In any field, particularly one as large as solvent extraction, it is almost impossible to thoroughly review the published literature, and the papers mentioned in Section 2 are in general those which are referred to in later sections in discussions of the results presented in those sections. Section 3 is devoted to

a development of the theory of the distribution of the quaternary salts under the conditions used in the experiments described in Sections 4 and 5. In Section 4 results are presented of the extraction of some quaternary salts as the concentration of the anion and/or the cation is changed. From these results conclusions are drawn regarding the state of aggregation of the quaternary salt in the organic solvent. Section 5 contains the results of the distribution of a large number of quaternary salts at a constant initial concentration of quaternary salt in the aqueous phase. Both Sections 4 and 5 contain some discussion of the results obtained during the course of this work but this discussion is amplified and extended in Section 6. Section 7 contains details of the experimental procedures and preparative methods used during the course of this work.

The results are collected together in an Appendix of some thirty two tables. This was thought advisable as some tables are referred to in several different places in the text; in some cases, however, results from several different tables have been presented again in tabular form in the text for ease of comparison. All the figures are bound as closely as possible to the page of the text where the first reference to the figure appears, and all the figures are accompanied by a statement of the tables where the numerical values used in constructing the figures may be found.

All results other than original work carried out by the author whilst preparing for this dissertation, have been acknowledged by the assignment of a reference number. These references include acknowledgement to the author's B.Sc honours thesis whenever results have been taken from this source.

Some of the work on the preparation and the infrared and ultraviolet spectra of the quaternary arsonium compounds has been accepted for publication in the Australian Journal of Chemistry. The results on the ultraviolet spectra of these compounds presented in that paper are taken from the author's B.Sc Honours thesis and the results presented in Section 7.1 are new measurements of the spectra of these compounds dissolved in a different solvent.

Themajority of the results contained in this thesis are being prepared for publication in a series of papers under the general title "The distribution of salts of large cations between water and organic solvents".

Abbreviations

The following abbreviations have been used in this thesis:

Ph_4As^+	tetraphenylarsonium cation
Ph_4P^+	tetraphenylphosphonium cation
Ph_3S^+	Triphenylsulphonium cation
Ph_4Sb^+	tetraphenylstibonium cation
$n\text{-}Bu_4N^+$	tetrabutylammonium cation
$n\text{-}Pr_4N^+$	tetra-n-propylammonium cation
$n\text{-}Hexyl_4N^+$	tetra-n-hexylammonium cation
$BzEt_3N^+$	benzyl triethylammonium cation
Ph_3AmP^+	triphenyl-n-amylphosphonium cation
$Ph_3n\text{-}PrP^+$	triphenyl-n-propylphosphonium cation
$Ph_3iso\text{-}PrP^+$	triphenyl-iso-propylphosphonium cation
Ph_3EtP^+	triphenylethylphosphonium cation
Ph_3AllP^+	triphenylallylphosphonium cation
Ph_3MeP^+	triphenylmethylphosphonium cation
Ph_3MeAs^+	triphenylmethylarsonium cation
$Ph_2Me_2As^+$	diphenyldimethylarsonium cation
$PhMe_3As^+$	phenyltrimethylarsonium cation
$2\text{-}BrCH_2BzPh_3P^+$	2-bromomethylbenzyltriphenyl-phosphonium cation
$3\text{-}BrCH_2BzPh_3P^+$	3-bromomethylbenzyltriphenyl-phosphonium cation
$PhMe_3N^+$	phenyltrimethylammonium cation
$BzCeMe_2N^+$	benzylhexadecyldimethylammonium cation
$BzEt_3N^+$	benzyltriethylammonium cation

SECTION 2

INTRODUCTION

Section 2.1 Factors Influencing the Extraction of Quaternary Salts

The extraction of inorganic compounds from aqueous solution into an organic solvent of low dielectric constant is probably dependent on the prior formation in the aqueous solution of an uncharged species. This may be brought about in a number of different ways and several authors have classified various extraction systems on the basis of how these neutral species are formed (1), (2), (3). Irving and Williams (4) have however, classified various systems according to the extent to which simple mathematical treatments based on the assumption of constancy of partition coefficients can be applied, and Marcus (5) has classified extraction systems according to the reactions involved and the nature of the solute-solvent interactions. Quaternary salts exist in the organic phase as ion association aggregates, held together by the physical forces of attraction of oppositely charged species. Such an extraction system is classified as an ion association type system (1), or as coordinately unsolvated salts (2), or as an ion exchange system (3).

There are a number of factors which have been shown to be important in affecting the amount of extraction of quaternary salts into the organic solvent. The nature of the species in the organic phase will be of importance. The formation of the ion association compound may be represented by:

$$R_4P^+ + X^- \rightleftharpoons (R_4P^+, X^-)$$

The existence and behaviour of such compounds was predicted by Bjerrum; confirmation and amplification of the theory has come largely from conductivity measurements in non-aqueous solvents.

This work has been summarized in a review by Kraus (6). The ion pair complex once formed may polymerise to higher aggregates in the organic solvent

$$2\,(R_4P^+,X^-) \rightleftharpoons (R_4P^+,X^-)_2$$

In extraction systems polymerisation will tend to reduce the activity of the extractable species in the organic phase and the overall extraction equilibrium will be shifted in favour of higher distribution ratios. Such polymerisation may occur at quite low concentrations in solvents of low dielectric constant, e.g. certain large quaternary ammonium salts polymerise in benzene at concentrations about 5×10^{-6}M (7).

The size and shape of the quaternary ammonium ions has been shown to be important by Wilson et al. (8) who investigated the extraction of metal ions as halide complexes into 1,2-dichloroethane. The effects of concentration of the metal ion, contacting time and type of halide were also discussed. Good et al. (9) have also investigated the extraction of metal ions as anionic complexes from aqueous halide solutions into chloroform, trichloroethylene and toluene, with quaternary ammonium ions. The extraction efficiency increased with the number of carbon atoms in the quaternary ammonium ion, and was found to be very poor if the number of carbon atoms in the cation was less than eighteen. Extraction was favoured if the quaternary ammonium ion had relatively short bulky aliphatic groups rather than a long chain with smaller groups.

Similar systems have been studied by Senise (10) who has investigated the extractability of fourteen metal ions from chloride, bromide,

iodide, thiocyanate and azide solutions with a series of phosphonium salts. Senise varied the n-alkyl group in a series of triphenyl-n-alkylphosphonium salts from methyl to n-octadecyl and studied the effect of this variation on the extraction of a number of metals as their thiocyanato complexes. There was a steady increase in the extractability of the complexes as the length of the alkyl chain increased from one to seven carbon atoms. With seven carbon atoms in the alkyl chain a high value of the distribution ratio was reached and this remained constant or decreased slightly on further increasing the n-alkyl chain length.

Senise has also studied the differences in the extraction of these metal complexes with triphenyl-n-propylphosphonium and triphenyl-iso-propylphosphonium cations. In about 15% of the different systems studied, extraction occurred from solutions containing $Ph_3n\text{-}PrP^+$ but not from solutions containing $Ph_3iso\text{-}PrP^+$. This behaviour did not occur with all the solvents tested; it was not observed using chloroform as the organic solvent but it was observed using a variety of alcohols, esters and ketones. Such differences were not observed with isomerism of butyl and amyl groups or upon changing phenyl to alkyl groups, but still keeping at least one n-propyl or iso-propyl group in the phosphonium cation.

A number of Russian workers have examined the effects of structural and other factors on the extraction of small concentrations of triphenylmethane dyes in the presence of relatively large concentrations of anion in the aqueous phase. Unfortunately many of these papers have been seen in abstract form only. Yatsimirskii (11) has reported that the best extraction of ionic compounds from aqueous

solution is attained in the presence of minimum ionic charge and at a definite relationship between the radii of the cation and the anion and in the presence of hydrophobic groups on one or both ions.

The effect of structural factors, dielectric constant of the organic solvent and ionisation of the ion pairs in the organic solvent on the extraction of a number of triphenylmethane dyes into chloroform and iso-amyl alcohol has been investigated in a series of papers by Krasnov et al. (12) (13) (14) (15) (16) (17) (18). The anions studied were chloride, bromide, iodide, nitrate, perchlorate, thiocyante and sulphate; the aqueous phase was adjusted to constant ionic strength by the introduction of a salt of the same anion being extracted by the cation. At constant temperature, for a given cation, the distribution was found to increase with increasing radii of the halide anions, but the effect of the nature of the anion was also shown to be important. The distribution ratio for thiocyanate was higher than that of bromide, even though these ions have approximately the same radius. This increase in the distribution ratio was attributed to unshared pairs of electrons on the nitrogen atom of the thiocyanate ion which are capable of forming hydrogen bonds with solvent molecules. The extraction of cations with the same anion increased with increasing size of the cation, and also with increasing substitution of methyl groups on the phenyl rings (15). It was also found that the extraction decreased slightly with increasing temperature (13), (18).

Diamond and co-workers (2), (19), (20), (21), (22) in particular have emphasised the idea that a large number of extraction systems

are best described in terms of a competition between water and the organic solution for solvation of the various species present in solution. In the extraction of quaternary salts the competition is between the hydration of the cation and anion in the aqueous phase and the total solvation energy of the ion pair in the organic phase.

Ionin and Kurina (23) have studied the extraction of ferric chloride from hydrochloric acid solution into di-iso-propyl ether and have derived an equation which establishes the dependence of the distribution ratio on the activity of the ions in the aqueous and organic phase and to the differences in the solvation energies between the two phases.

The extraction of a given anion from aqueous solution will, of course, depend on the presence of any other anions present in solution. Tribalat has studied the distribution of Ph_4AsCl and Ph_4PCl between water and chloroform in the presence of perrhenate (24), (25) and pertechnetate anions (26), (27). From a simplified theory it was predicted, and then shown experimentally, that the distribution ratio for the pertechnetate ion was solely a function of the concentration of the tetraphenylarsonium cation; in the presence of excess chloride ions the distribution ratio was found to be proportional to the concentration of the arsonium cation and inversely proportional to the concentration of the chloride ions (24). Tetraphenylphosphonium chloride was shown to exist as ion pairs in chloroform up to a concentration of about 10^{-3}M; at higher concentrations dimerisation of the ion pairs in the chloroform occurred. No further polymerisation of the ion pairs in the organic phase

was observed up to organic phase concentrations of about 0.3M (25).

Bock et al. have studied the extraction of a large number of salts of the Ph_4As^+ (28), Ph_4P^+ (29) and Ph_3S^+ (30) cations into chloroform from aqueous solution. The ratio of cation to anion concentration added initially to the aqueous phase was 2:1 and the distribution was studied by measuring the anion concentration in both phases. It was found that the singly charged anions I^-, NCS^-, ClO_3^-, ClO_4^-, MnO_4^-, ReO_4^- and NO_3^- were extracted almost quantitatively by chloroform with Ph_4As^+ and Ph_4P^+, the anions Cl^-, Br^-, BrO_3^- and NO_2^- were extracted but not quantitatively, while the anions $SO_4^=$, PO_4^{-3}, IO_3^-, F^-, OH^- were not extracted at all. The Ph_3S^+ cation was found to be a poorer extracting agent than the Ph_4As^+ or Ph_4P^+ cations. The extraction of anions with these cations was found to be nearly independent of the pH of the aqueous phase except for the dichromate anion. The extraction of Cr(VI) into chloroform with triphenyltetrazolium, tetraphenylarsonium and triphenyl-n-propylphosphonium cations has been studied in some detail (31). It was found that under the conditions used Cr(VI) extracted as the ion pair (Ph_4As^+, $HCrO_4^-$) and that species such as $Cr_2O_7^=$ were not extracted. The extraction of salts of Ph_4As^+ into chloroform has also been investigated by Alimarin and Perezhogin (32) and they give the order of extractability of the anions into $CHCl_3$ as

$$MnO_4^- > TcO_4^- > ReO_4^- > ClO_4^- > (I^- \sim NCS^- \sim HCrO_4^-) > NO_3^- > Br^- > Cl^-$$

Anions such as $AuCl_4^-$, $TlCl_4^-$, $FeCl_4^-$, $GaCl_4^-$ and $SbCl_6^-$ were also extracted from HCl solutions.

The extraction of tetraphenylstibonium salts from water into organic solvents was first reported by Moffett et al. (33) who separated

fluoride from sulphate ions by extraction of tetraphenylstibonium fluoride into carbon tetrachloride. They reported that the solubility of the tetraphenylstibonium salts in carbon tetrachloride decreased in the order

$$F^- > Cl^- > Br^- > SO_4^= > NO_3^- >> ClO_4^- .$$

Bowen and Rood (34) have studied the distribution of Ph_4SbF between water and CCl_4 in more detail. The extraction is strongly pH dependent and also shows a variation with the salts used to adjust the ionic strength of the aqueous phase. The distribution ratio decreased below pH 3 and this was explained by the association of F^- with H^+ to form HF which decreases the amount of extractable fluoride ion in the aqueous phase.

The distribution ratio also decreased above pH 3 and this was explained by the association of the cation with hydroxide ion. Bock and Grallath (35) have recently studied the extraction into chloroform of a number of different anions by the Ph_4Sb^+ cation using a twofold excess of cation to anion and observed a number of important differences between Ph_4As^+ and Ph_4Sb^+. The extraction of the anions was pH dependent and this was explained by the fact that Ph_4SbOH is extracted and there is therefore a competition set up between the anions and the hydroxide ion which favours the hydroxide as the pH is raised.

Smulek (36) has briefly reported the extraction of $FeCl_4^-$ from 8M HCl solution into chlorobenzene and toluene using Ph_4SbCl as the extractant and has compared the results with those obtained using tetrabutylammonium chloride. The extraction coefficients for the two extractants are very similar in chlorobenzene but they differ

significantly in benzene.

The solvent used to extract the ion pairs from the aqueous solution has been shown to influence the amount of extraction of quaternary salts. Hála et al. (31) have found that the extraction of Cr(Vl) from aqueous solution by triphenyltetrazolium chloride into various organic solvents decreased in the following order:-

n-hexanol > nitrobenzene > chloroform > butyl acetate > (trichloroethylene ~ benzene ~ carbon tetrachloride) > tetrachloroethylene > cyclohexane.

Smulek (36) in a study of the extraction of the $FeCl_4^-$ anion with $n\text{-}Bu_4N^+$ found the extraction decreased in the order:-

nitrobenzene > o-dichlorobenzene > chlorobenzene > chloroform > ethyl iodide > bromoform > benzene > toluene > o-xylene > carbon tetrachloride > n-heptane.

These orders are roughly the order of decreasing dielectric constant of the organic solvent. Diamond and Tuck (2) have explained this order by attributing it to the solvation of the quaternary salt in the organic phase; the greater the solvation energy in the organic phase the better the extraction. The solvation energy of the ion pair in the organic phase should be greater the higher the dielectric constant of the organic phase and so the observed order is expected.

Smulek (36) has pointed out that the ion pair in the organic phase has a large dipole moment and that between the ion pair and the organic solvent an electrostatic dipole-dipole interaction will be predominent. He has shown that there is a good correlation between the extraction of the ion pair and the dipole moment of the organic solvent.

Section 2.2 The extraction of Metal Complexes with Quaternary Salts

Quaternary ammonium, phosphonium and arsonium salts have been widely used to extract metal complexes from aqueous solution. More than fifty elements have been found to extract under certain conditions and the quaternary salts have been widely used in analysis (38). Any metal which is capable of forming an anionic complex with only one or two negative charges ought to be extracted by quaternary cations. A number of general investigations on the extractability of metal ions from aqueous media have been reported and will be discussed below. A number of papers have appeared on the extraction of a smaller number of metal ions under varying conditions and some of these will be mentioned below and discussed more fully in Sections 4.3 and 4.4.

Maeck et al. (37) have studied the extraction of fifty seven metal ions with three quaternary ammonium ions n-Pr_4N^+, n-Bu_4N^+ and n-$Hexyl_4N^+$ into methyl-iso-butylketone from HNO_3, H_2SO_4, HF, HCl and NaOH solutions at acid or alkali concentrations up to 5M. It was found that very few ions extracted from NaOH, H_2SO_4 or HF solutions. From HCl and HNO_3 solutions there was no significant extraction of any anion known to have more than a single negative charge.

The extraction of over fifty elements into chloroform using benzyltriethylammonium thiocyanate from ammonium thiocyanate solution (0.1M to 7M) (38) and tetraphenylarsonium chloride from hydrochloric acid (0.5 to 12M) solution (39) has been reported. Those elements which form anionic complexes with chloride or thiocyanate ions were extracted into chloroform. Monovalent anionic species or complexes

such as TcO_4^- $FeCl_4^-$ and $AuCl_4^-$ were found to be extracted better than di- or trivalent anionic species such as $ZnCl_4^=$, $CdCl_4^=$ and $AgCl_3^{-2}$. In general it was found that extraction of a particular metal was better using Ph_4AsCl than $BzEt_3NNCS$ as the extractant.

Seeley and Crouse (40) have investigated the extraction into diethylbenzene of sixty three metal ions from both hydrochloric acid and acidified lithium chloride solutions with primary, secondary, tertiary and quaternary ammonium chlorides. The quaternary ammonium cation used was Aliquat 336 which is a mixture of methyltri-n-octylammonium and methyltri-n-decylammonium chlorides. The extraction coefficients were usually higher from lithium chloride than from hydrochloric acid solutions. With most metals the extractive power of the amine salt decreased in the order

Quaternary > tertiary > secondary > primary.

With Aliquat 336 and Co (II), Fe (III), Cu (II), Zn (II), Mn (II), Cd (II), In (III), Sb (III) and V (IV) ions it was found that extraction of the metal from HCl solutions increased with increasing HCl concentration, passed through a maximum and then decreased at higher HCl concentrations, whereas the extraction from LiCl solutions increased steadily with increasing LiCl concentration. This effect will be discussed in more detail in Section 4.3. The extraction of Pb (II), Cd (II), Cu (II), Co (II), Zn (II) and Fe (III) from HCl, HBr and HI solutions into xylene using trioctylmethylammonium salts has been reported (41). The extractability of Pb (II), Cd (II), Cu (II), and Co (II) increased in the order HCl < HBr < HI and were interpreted, in the case of lead, in

terms of thestability constants of the lead halide complexes. Extractability of Zn (II) and Fe (III) decreased in the order HCl > HBr > HI.

The extraction of metal complexes other than halide or thiocyanate complexes using quaternary salts has been little studied. Nitrato complexes of cerium, (42), plutonium, (43), uranium, (44), (45), (46), americium, curium, californium and einsteinium (47) have been extracted from aqueous solution by quaternary ammonium salts. Uranium has been extracted into chloroform as the uranyl tribenzoate ion with tetraphenylphosphonium chloride as the extractant (48). Silver and gold have been extracted from dilute aqueous cyanide solution using quaternary ammonium hydroxides (49).

The extraction of trivalent actinides and lanthanides as ethylenediaminetetraacetato or hydroxyethylenediaminetriacetato acid complexes into methyl-iso-butylketone by primary, secondary, tertiary and quaternary amines has been reported (50) (51) (106). In view of the ability of these chelates to form complexes with a wide variety of metal ions, a much larger number of metal ions should be capable of being extracted as ethylenediaminetetraacetato complexes than has been reported so far.

Section 2.3 Extraction of Acids by High Molecular Weight Amines

The extraction of acids by high molecular weight amines has been the subject of a large number of papers since it was first reported by Smith and Page (52) and has been reviewed several times (53) (54) (5). Work on extraction with amines has been confined to extraction from acid solution and under such conditions the amine is converted into a salt

$$R_3N + H^+ + X^- \rightleftharpoons R_3NH^+ + X^-$$

which will exist as ion pairs or higher aggregates in the organic solvent. This similarity of extraction mechanism between amines and quaternary salts means that many of the factors discussed in Section 2.1 as affecting quaternary salt extraction also apply to amine salt extraction, although some special factors affecting the latter have been observed.

The extraction of amine salts into an organic solvent is often accompanied by the extraction of acid in excess of the 1:1 ratio required for the formation of the amine salt.

In the case of hydrochloric acid infrared data supports the formation of a species $R_3NH^+ \ HCl_2^-$ in the organic phase (55). However, the explanation that at least some of the excess acid simply dissolves in the amine salt-organic solvent system is highly probable. The presence of the amine salt in the organic phase has a marked effect on the nature of the phase. The dielectric constant of solutions of trilaurylammonium bromide in benzene and cyclohexane increases markedly as the concentration of the salt increases (56). Water is also extracted into the organic solvent with these salts.

Bucher and Diamond (19) have found that water is extracted into benzene with trilaurylammonium perchlorate but conclude that the water does not significantly affect the aggregation of the salts in the organic phase (56) (19).

The aggregation of the amine salt in the organic phase has been studied in much more detail than in quaternary salt systems. Most of the recent work seems to support the conclusion that aggregation in the organic phase is less extensive than was at first thought. Tridodecylammonium chloride in benzene exists as monomers and dimers over the concentration range 0.001 to 0.18M while with tridodecylammonium nitrate over the same concentration range trimers are also postulated (58). Similar results have been obtained for trihexylammonium nitrate in benzene where dimers and trimers are postulated (59). The association of trilaurylammonium salts in a number of different solvents has been investigated. Association was found to increase in the order $C_6H_5NO_2 < CHCl_3 < C_6H_6 < CCl_4 <$ cyclohexane (56). In nitrobenzene the ion pairs were dissociated to the free ions at low concentrations; no association beyond the ion pair was observed in chloroform up to 0.1M concentration, but higher aggregates were observed in the other solvents. This difference in behaviour from one organic solvent to another has been explained by interactions between the organic solvents and the ammonium salts (56).

In general the extraction of amine salts into organic solvents does not seem to depend on the dielectric constant of the organic solvent. Good and Bryan (60) found that the extraction of $CoCl_4^{=}$

by amines into various solvents decreased in the order

benzene > 1-bromo-2-chloroethane > bromocyclohexane > nitrobenzene > 1-bromo-3-chloropropane > anisole > 1,2-dichloroethane > bromochloromethane > trichloroethylene > chloroform > bromoform.

This order shows little relationship to the dielectric constant of the solvents. Recently the extraction of $Co(NCS)_4^=$ by tri-n-octylamine has been reported and it was found that with the exception of chloroform and nitrobenzene the smaller the value of the dielectric constant the greater the extraction of $Co(NCS)_4^=$ (130). However, Diamond et al. (19), (56) have studied the extraction of anions by trilaurylamine into a number of different solvents, and have found that the extraction of the various salts into the organic solvents increases as dielectric constant of the organic solvent increases. Nuclear magnetic resonance and infrared studies have been interpreted as indicating a tendency towards hydrogen bond formation between the proton of the cation R_3NH^+ and the anion of the amine salt (61) (62) (63). The low extraction of $CoCl_4^=$ into chloroform has been ascribed to a competition between $CHCl_3$ and $CoCl_4^=$ for the amine (60). Species such as $R_3NH^+Cl^- \cdots HCCl_3$ (61) or $R_3N \cdots HCCl_3$ (62) have been postulated.

SECTION 3

THEORY OF THE DISTRIBUTION OF QUATERNARY SALTS

Section 3.1 Definition of Terms.

The extraction of a solute from an aqueous solution is expressed by the distribution or partition coefficient K_D. This quantity is independent of the concentration of the solute only in an ideal case where the two phases are completely immiscible and when interactions between the solute and solvent and dissociation or association of the solute in either phase are non-existent. These conditions are never achieved in practice, although some systems do approach this behaviour. Since generally we are more concerned with the stoichiometric distribution of the solute of interest between the phases it is usual to describe the distribution by means of the distribution ratio D. This is the stoichiometric ratio including all species of the solute in the respective phases

$$D = \frac{\text{total concentration of solute in the organic phase}}{\text{total concentration of solute in the aqueous phase}}$$

If we are aware of all the significant interactions of the distributing species, we may arrive at an expression for D as a function of the experimental parameters.

Of even more practical importance than D is the percentage extraction %E. By definition

$$\%E = \frac{100\ D}{D + \frac{V_{aq}}{V_{org}}}$$

where D is the distribution ratio, V_{aq} is the volume of the aqueous phase, and V_{org} is the volume of the organic phase.

The percentage extraction is a more practical term, since with equal

volumes of both phases widely differing values of D from 99 to ∞ actually correspond to a variation in the percentage extraction of from 99% to 100%.

Section 3.2 Extraction of R_4PX over a range of cation concentration with the total anion concentration constant

The model used in the discussion in this section and in Section 3.3 is that of a cation R_4P^+ (where R may be either an alkyl or an aryl group and P may be replaced by either N or As), extracting into an organic solvent along with a univalent anion X^-. In the expressions for the equilibrium constants K and distribution ratio D the charges on the ions have been omitted for the sake of clarity. The subscript o is used to distinguish the species in the organic phase from those in the aqueous phase. Activities have been replaced by concentrations throughout this Section.

The extraction of the salt R_4PX into the organic phase from an aqueous solution which contains a constant excess of a salt containing the anion X^- may be described by the following reactions.

(a) Association of the Salt $R_4P^+X^-$ in the aqueous phase

$$R_4P^+ + X^- \rightleftharpoons (R_4P^+, X^-)$$

$$K_a = \frac{[R_4PX]}{[R_4P][X]} \qquad (1)$$

(b) Extraction of the ion pair (R_4P^+, X^-) into the organic phase

$$(R_4P^+, X^-) \rightleftharpoons (R_4P^+, X^-)_o$$

$$K_b = \frac{[R_4PX]_o}{[R_4PX]} \qquad (2)$$

(c) Dissociation of the ion pair (R_4P^+, X^-) in the organic phase

$$(R_4P^+X^-)_o \rightleftharpoons (R_4P^+)_o + (X^-)_o$$

$$K_c = \frac{[R_4P]_o [X]_o}{[R_4PX]_o} \qquad (3)$$

(d) Association of the ion pair (R_4P^+,X^-) in the organic phase

$$2\,(R_4P^+X^-)_o \rightleftharpoons (\,(R_4P^+,X^-)_2)_o$$

$$K_d = \frac{\left[(R_4PX)_2\right]_o}{\left[R_4PX\right]^2_o} \qquad \text{——— (4)}$$

It is possible to envisage association of the ion pair to higher aggregates than the dimer but in the solvents and at the concentrations used this is unlikely, and so has been neglected. No association of ion pairs to higher aggregates in the aqueous solution is likely and so this has also been neglected. Triple ions such as $(\,(R_4P^+)_2,X^-\,)^+$ which have been postulated as a result of conductivity studies on quaternary ammonium salts in organic solvents (6) have been ignored. It will be shown that under the conditions used in this work, it is not necessary to postulate any aggregates higher than ion pairs to completely explain the observed distribution behaviour.

The distribution ratio D of the salt R_4PX is given by the expression

$$D = \frac{\text{Total concentration of } R_4PX \text{ in the organic phase}}{\text{Total concentration of } R_4PX \text{ in the aqueous phase}}$$

$$= \frac{\left[R_4P\right]_o + \left[R_4PX\right]_o + 2\left[(R_4PX)_2\right]_o}{\left[R_4P\right] + \left[R_4PX\right]}$$

The concentration of the ionpair (R_4P^+,X^-) in the aqueous phase will usually be very small compared to $\left[R_4P^+\right]$ and so may be neglected.

Therefore $$D = \frac{\left[R_4P\right]_o + \left[R_4PX\right]_o + 2\left[(R_4PX)_2\right]_o}{\left[R_4P\right]}$$

From equations (1), (2), (3) and (4) we obtain by substitution

$$D = K_aK_b\left[X\right]\left\{1 + \frac{K_c}{\left[X\right]_o} + 2\,K_bK_d\left[R_4PX\right]\right\} \text{—— (5)}$$

Kraus (6) has shown that if the dielectric constant of the organic solvent is between 3 and 5 as is the case with chloroform, then for ion pairs with an inter-ion distance of 5 to 7$\overset{o}{A}$, K_c the equilibrium constant for the dissociation of the ion pair in the organic solvent lies between 10^{-11} and 10^{-14} and so even for low concentrations of $[X]_o$ e.g. 10^{-7}M the value of $\frac{K_c}{[X]_o}$ will be small.

The term $2K_bK_d[R_4PX]$ in equation (5) will also be small if association of ion pairs in the organic phase can be ignored. The evidence suggests that in chloroform association of ion pairs does not take place, (see Section 4) and so equation (5) simplifies to

$$D = K_aK_b[X] \qquad (6)$$

$$= \text{Constant if } [X] \text{ is constant}$$

For solvents whose dielectric constants are about 10, as is the case for the solvents dichloromethane and 1,2-dichloroethane, then K_c for the same inter-ion distance is about 10^{-4} to 10^{-2} and the value of $\frac{K_c}{[X]_o}$ will not be negligible and the expression for the distribution ratio becomes

$$D = K_aK_b[X]\left\{1 + \frac{K_c}{[X]_o}\right\} \qquad (7)$$

and the value of D will be expected to change with the concentration of R_4P^+. The association of ion pairs to higher aggregates has again been neglected.

If the salt is completely dissociated in the organic phase then equation (7) predicts that the value of D determined at different total concentrations of the quaternary cation will be inversely proportional to the concentration of the quaternary salt in the organic phase.

Section 3.3 Extraction of the salt R_4PX from aqueous sulphate media

Most of the extractions described in this thesis were from aqueous solutions whose ionic strength was adjusted with sodium sulphate. The extraction of the salt $R_4P\,X$ into an organic solvent from aqueous sulphate media may be described by the equations (1) to (4) in Section 3.2 and by

(e) Association of the salt $(R_4P)_2SO_4$ in the aqueous phase

$$2\,R_4P^+ + SO_4^= \rightleftharpoons ((R_4P^+)_2SO_4^=)$$

$$K_e = \frac{[(R_4P)_2SO_4]}{[R_4P]^2\,[SO_4]} \qquad (8)$$

(f) Extraction of the ion pair $((R_4P)_2SO_4^=)$ into the organic solvent

$$((R_4P^+)_2SO_4^=) \rightleftharpoons ((R_4P^+)_2SO_4^=)_o$$

$$K_f = \frac{[(R_4P)_2SO_4]_o}{[(R_4P)_2SO_4]} \qquad (9)$$

(g) Association of the ion pairs $(R_4PX)_o$ and $((R_4P)_2SO_4)_o$ in the organic phase

$$(R_4P^+X^-)_o + ((R_4P^+)_2SO_4^=)_o \rightleftharpoons ((R_4P^+)_3SO_4^=X^-)_o$$

$$K_g = \frac{[(R_4P)_3SO_4X]_o}{[R_4PX]_o\,[(R_4P)_2SO_4)]_o} \qquad (10)$$

Species similar to the mixed dimer above have been postulated by Scibona et al. (64) in the extraction of ReO_4^- by tertiary amines. The total amount of $(R_4P)_2SO_4$ in the organic phase will not be large as $SO_4^=$ does not extract well and so association and dissociation of $(R_4P)_2SO_4$ in the organic phase will not be considered.

The distribution ratio for the salt R_4PX is given by

$$D = \frac{\text{Total concentration of X in the organic phase}}{\text{Total concentration of X in the aqueous phase}}$$

As before $[R_4PX]$ is negligible compared with $[X]$

$$D = \frac{[X]_o + [R_4PX]_o + 2[(R_4PX)_2]_o + [(R_4P)_3SO_4X]_o}{[X]}$$

Substitution from equations (1), (2), (4), (8), (9) and (10) we obtain

$$D = \frac{[X]_o}{[X]} + \frac{K_a K_b [(R_4P)_2SO_4)]_o^{\frac{1}{2}}}{K_e^{\frac{1}{2}} K_f^{\frac{1}{2}} [SO_4]^{\frac{1}{2}}} + \frac{2K_a^2 K_b^2 K_d [(R_4P)_2SO_4]_o [X]}{K_e K_f [SO_4]}$$

$$+ \frac{K_a K_b K_g [(R_4P)_2SO_4]_o^{3/2}}{K_e^{\frac{1}{2}} K_f^{\frac{1}{2}} [SO_4]^{\frac{1}{2}}} \quad \text{——— (11)}$$

Now on the basis of equation (6) Section 3.2 the distribution ratio of a salt $(R_4P)_2SO_4$ extracting into an organic solvent from aqueous solution containing a large excess of sulphate ions should be independent of the initial concentration of R_4P^+ ion in the aqueous phase. This has been confirmed experimentally for the distribution of $(Ph_4As)_2SO_4$ between water and chloroform (Table 2). Therefore

$$[(R_4P)_2SO_4]_o \propto \text{initial } [R_4P^+]$$

or

$$[(R_4P)_2SO_4]_o = k[R_4P^+]_T \quad \text{— (12)}$$

where $[R_4P^+]_T$ represents the initial concentration of the R_4P^+ ion in the aqueous phase and k is a constant.

Substituting equation (12) in equation (11)

$$D = \frac{[X]_o}{[X]} + \frac{K_a K_b k^{\frac{1}{2}} [R_4P]_T^{\frac{1}{2}}}{K_e^{\frac{1}{2}} K_f^{\frac{1}{2}} [SO_4]^{\frac{1}{2}}} + \frac{2K_a^2 K_b^2 K_d k [R_4P]_T [X]}{K_e K_f [SO_4]}$$

$$+ \frac{K_a K_b K_g k^{3/2} [R_4P]_T^{3/2}}{K_e^{\frac{1}{2}} K_f^{\frac{1}{2}} [SO_4]^{\frac{1}{2}}} \quad \text{——————} \quad (13)$$

If we can again assume that no dimerisation or dissociation of ion pairs takes place in the organic phase, equation (13) simplifies to

$$D = \frac{K_a K_b k^{\frac{1}{2}} [R_4P]_T^{\frac{1}{2}}}{K_e^{\frac{1}{2}} K_f^{\frac{1}{2}} [SO_4]^{\frac{1}{2}}}$$

$$= K [R_4P]_T^{\frac{1}{2}} \quad \text{——————} \quad (14)$$

where $$K = \frac{K_a K_b k^{\frac{1}{2}}}{K_e^{\frac{1}{2}} K_f^{\frac{1}{2}} [SO_4]^{\frac{1}{2}}}$$

If no association or dissociation of the ion pairs occurs in the organic phase then a plot of log D against log $[R_4P]_T$ should be a straight line with a slope of 0.5. At very low concentrations of the reagent in the organic phase or if the organic phase has a high dielectric constant then dissociation of the ion pairs may become significant and the term $\frac{[X]_o}{[X]}$ may no longer be ignored.

In this case

$$D = \frac{[X]_o}{[X]} + K [R_4P]_T^{\frac{1}{2}} \quad \text{——————} \quad (15)$$

However, if both association and dissociation of the ion pairs occurs in the organic phase then equation (13) is the one which governs the behaviour of the distribution ratio over a range of concentration.

The model which has been proposed to derive the above equations has been used throughout this thesis as a basis for discussion. However, it should be pointed out that models which assume that (a) free ions extract into the organic solvent and these ions then associate to ion pairs or higher aggregates in the organic solvent, or that (b) the ion pairs are formed at the interface of the two solvents, lead to equations which are formally similar to those derived above. It is not possible to distinguish between these three possibilities with equilibrium studies. Kinetic studies on solvent extraction systems are not numerous and none appear to have been made on the extraction of quaternary salts. The model used was chosen because although quaternary salts are strong electrolytes in aqueous solution there is evidence that ion pairing in aqueous solution does occur to a small extent when both cation and anion are large (76) (77).

The theory in Section 3.2 is an extension of the theory developed in a paper by Krasnov et al. (18). The theoretical treatment of the extraction of quaternary salts from aqueous sulphate media, developed in this section, has not been reported previously.

SECTION 4

EXTRACTION OF QUATERNARY SALTS OVER A RANGE OF CONCENTRATION OF CATION & ANION

Section 4.1 Introduction

Before discussing the results obtained in this work, it will be helpful to briefly describe how the distribution of the quaternary salts was measured. This is described in detail in Section 7.3. All the quaternary cations studied contain at least one aromatic ring and the concentration of the cation in the aqueous phase was determined by measuring the absorption at about 260mμ due to the presence of the aromatic ring. The concentration of the quaternary salt added to the system originally was known, so by determining the concentration in the aqueous phase it was possible to calculate the distribution ratio from material balance considerations. This method of determining the cation concentration has been used to determine the solubility of some tetraphenylarsonium salts (65). Most previous investigators who have studied the distribution of quaternary salts have measured the concentration of the anion in one or both phases. The method of measuring the distribution ratio used in this work has been checked by two independent methods which determined the anion concentration in both phases (Section 7.4).

Section 4.2 Extraction of quaternary salts over a range of cation concentration with the anion concentration constant

The results of the distribution of triphenylmethylarsonium chloride between three organic solvents chloroform, 1,2-dichloroethane and 2,2'-dichlorodiethylether and an aqueous solution of KCl (0.5M) over a range of concentration of $Ph_3MeAsCl$ are presented in Table 1 and are shown graphically in Figure 1. This situation has been treated theoretically in Section 3.2 and the equation derived by this treatment (equation 6) predicts that if there is no dissociation or association of the ion pairs of $Ph_3MeAsCl$ in the organic solvent then the distribution ratios over a range of cation concentration will be constant. If the ion pair dissociates in the organic phase then the distribution ratio would be expected to increase above the value observed when the ion pair is not dissociated. Kraus and co-workers (6) have studied the behaviour of ion pairs of quaternary salts in organic solvents and have discovered that the dissociation of ion pairs is favoured by a high dielectric constant of the organic solvent and by low concentrations of the quaternary salt. In solvents of low dielectric constant and/or at high concentrations of the quaternary salt, association of ion pairs to ion quadrapoles or higher aggregates is likely to occur and the theory developed in Section 3 predicts that under these conditions the distribution ratio will again increase above the value observed for the ion pair.

Fig. 1 shows that the distribution of triphenylmethylarsonium chloride between chloroform and 0.5M KCl solution is independent of

Figure 1

Extraction of $Ph_3MeAsCl$ into different solvents over a range of concentration of Ph_3MeAs^+

Concentration KCl = 0.5M

Temperature 25°C

Plot of Log D against Log $\left[Ph_3MeAs^+\right]$ initially in aqueous phase.

○ $(C_2H_4Cl)_2O$

Figure 1

● $C_2H_4Cl_2$

● $CHCl_3$

Figure drawn from results in Table I.

Figure 1

Extraction of $Ph_3MeAsCl$ into different solvents over a range of concentration of Ph_3MeAs^+

Concentration KCl = 0.5M

Temperature 25°C

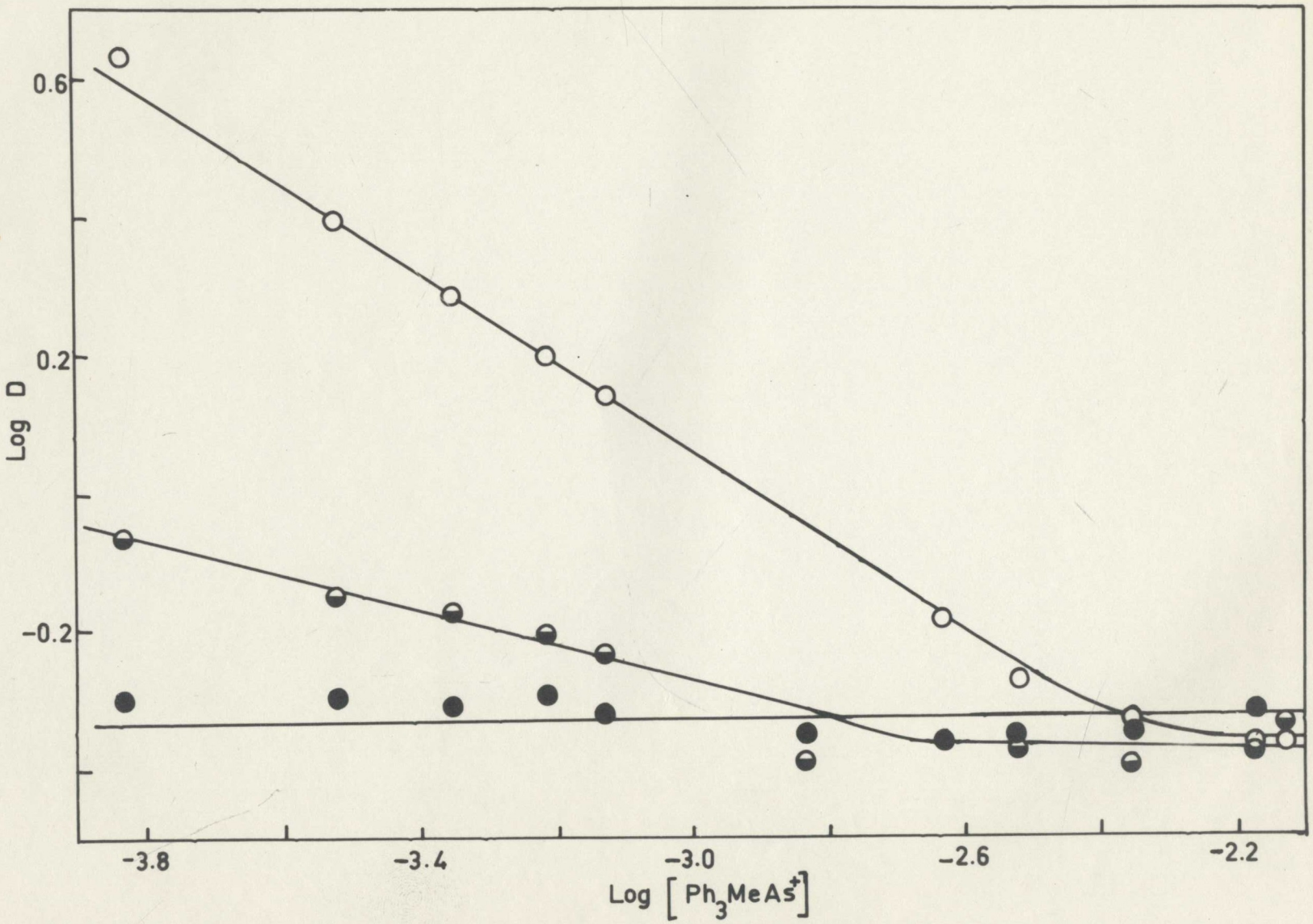
Plot of log D against log $[Ph_3MeAs^+]$ initially in aqueous phase.

○ $(C_2H_4Cl)_2O$

◒ $C_2H_4Cl_2$

● $CHCl_3$

Figure drawn from results in Table 1.


0.6
0.2
-0.2
Log D
-3.8
-3.4
-3.0
-2.6
-2.2
Log [Ph3MeAs+]

the initial concentration of triphenylmethylarsonium chloride over a range 3×10^{-4}M to 7.5×10^{-3}M. Below an initial concentration of 3×10^{-4}M (a concentration of 1×10^{-4}M in the chloroform) the distribution ratio increases (see Table 1), implying that below this concentration dissociation of the ion pairs of triphenylmethylarsonium chloride is occurring in the chloroform.

Mueller and Diamond (56) found that trilaurylammonium bromide exists as ion pairs in chloroform over the concentration range 10^{-6}M to 10^{-1}M. The ability of the ion pairs of trilaurylammonium bromide to exist at lower concentrations in chloroform without dissociation may be due to the fact that in ion pairs of salts like trilaurylammonium bromide the halide ion is hydrogen bonded to the cation (63). Evidence has recently been reported that the ions of phosphonium salts of the type $Ph_3PCH_2R^+A^-$, where the group R may be a large number of different groups and A^- is a chloride, bromide or iodide ion, are held together in solution, and in the solid, by a hydrogen bond between the α methylene hydrogen and the halide ions (66). Such an interaction was not observed with the BPh_4^- anion which cannot form hydrogen bonds. If this type of hydrogen bonding, between an anion and a hydrogen bonded to a carbon atom occurs with triphenylmethylarsonium chloride, it would be expected to be weaker than the hydrogen bonding between the bromide ion and the hydrogen attached to the nitrogen in trilaurylammonium bromide. This means that ion pairs of trilaurylammonium bromide will exist without dissociation at much lower concentrations than is possible

for triphenylmethylarsonium chloride.

The distribution ratios for the extraction of tetraphenylarsonium sulphate from sodium sulphate solution(0.03M) into chloroform, over a range of concentration of the tetraphenylarsonium cation are given in Table 2. No dissociation at a concentration of 2×10^{-5}M is indicated by the distribution measurements. The higher charge on the sulphate ion would be expected to result in stronger electrostatic bonding of the anion and cations in the ion association complex and so dissociation will occur at lower concentrations.

The dissociation of ion pairs, at higher concentrations, in solvents with a higher dielectric constant than chloroform ($\epsilon = 4.8$) is clearly shown in Figure 1. In 1,2-dichloroethane ($\epsilon = 10.4$) dissociation of the ion pairs occurs at concentrations of triphenylmethylarsonium chloride below 2×10^{-4}M. In 2,2'-dichlorodiethylether ($\epsilon = 21.2$) dissociation of the ion pairs occurs at a concentration of about 2×10^{-3}M in the organic phase. If the quaternary salt were completely dissociated in the organic phase, then equation (7) (Section 3.2) predicts that the distribution ratio is inversely proportional to the concentration of the quaternary salt in the organic solvent. No such relationship was observed in the concentration range studied in the present work with any of the organic solvents.

The distribution of fuchsin chloride between iso-amyl alcohol ($\epsilon = 14.7$) and water has been shown (18) to obey equation (7) when the concentration of the cation was varied over the concentration range 3×10^{-6}M to 3×10^{-5}M. This upper concentration is just above the lowest concentration studied in the course of this work.

Section 4.3 Extraction of quaternary salts at constant cation concentration and varying anion concentration

The theory presented in Section 3.2 (equation 6) predicts that the distribution ratio of a quaternary salt which exists in the organic solvent only as ion pairs should be proportional to the concentration of the anion in the aqueous phase. In Tables 3, 4, 5, 6 and 7 the results for the distribution of Ph_3MeAs^+, Ph_4As^+ and Ph_3AmP^+ (concentration 5×10^{-3}M) over a range of concentration of chloride and bromide ions are presented.

Figure 2 shows that the distribution ratios of triphenylmethylarsonium chloride, triphenylmethylarsonium bromide, tetraphenylarsonium chloride and triphenyl-n-amylphosphonium chloride over a range of halide concentration from 5×10^{-3}M to 1M are directly proportional to the halide ion concentration. The results for triphenyl-n-amylphosphonium bromide and tetraphenylarsonium bromide also plotted in Figure 2 show a linear relationship between D and the bromide concentration over a small concentration range. At higher bromide concentrations, this linear relationship breaks down (see below). The distribution of tetraphenylarsonium chloride between chloroform and water over a range of chloride concentration has been reported recently (32), and the distribution was found to be proportional to the chloride concentration over the concentration range 0.045M to 0.9M. The concentration of the tetraphenylarsonium cation was 5×10^{-4}M. The slope of the plot of the distribution ratio D against the chloride ion concentration was reported to be 30, in very good agreement with the slope of 32 in Figure 2. In Figures 3 and 4, log D for these same salts is plotted against the logarithm of the halide ion concentration. Figure 3 also contains the results for the

Figure 2

Distribution of quaternary salts over a range of anion concentration

Distribution between chloroform and water

KCl or KBr used to adjust the anion concentration

Plot of D against [Halide]

[Cation] = 5×10^{-3}M

Temperature 25°C

Figure 2

● Ph_3AmPBr

◒ Ph_4AsBr

⊙ Ph_3AmPCl

◍ Ph_4AsCl

□ $Ph_3MeAsBr$

◒ $Ph_3MeAsCl$

Data taken from Tables 3, 6 and 7.

Figure 2

Distribution of quaternary salts over a range of anion concentration

Distribution between chloroform and water

KCl or KBr used to adjust the anion concentration

Plot of D against $[\text{Halide}]$

$[\text{Cation}] = 5 \times 10^{-3}\text{M}$

Temperature 25°C

◑ Ph_3AmPBr

◒ Ph_4AsBr

⊙ Ph_3AmPCl

● Ph_4AsCl

□ $Ph_3MeAsBr$

◒ $Ph_3MeAsCl$

Data taken from Tables 3, 6 and 7.

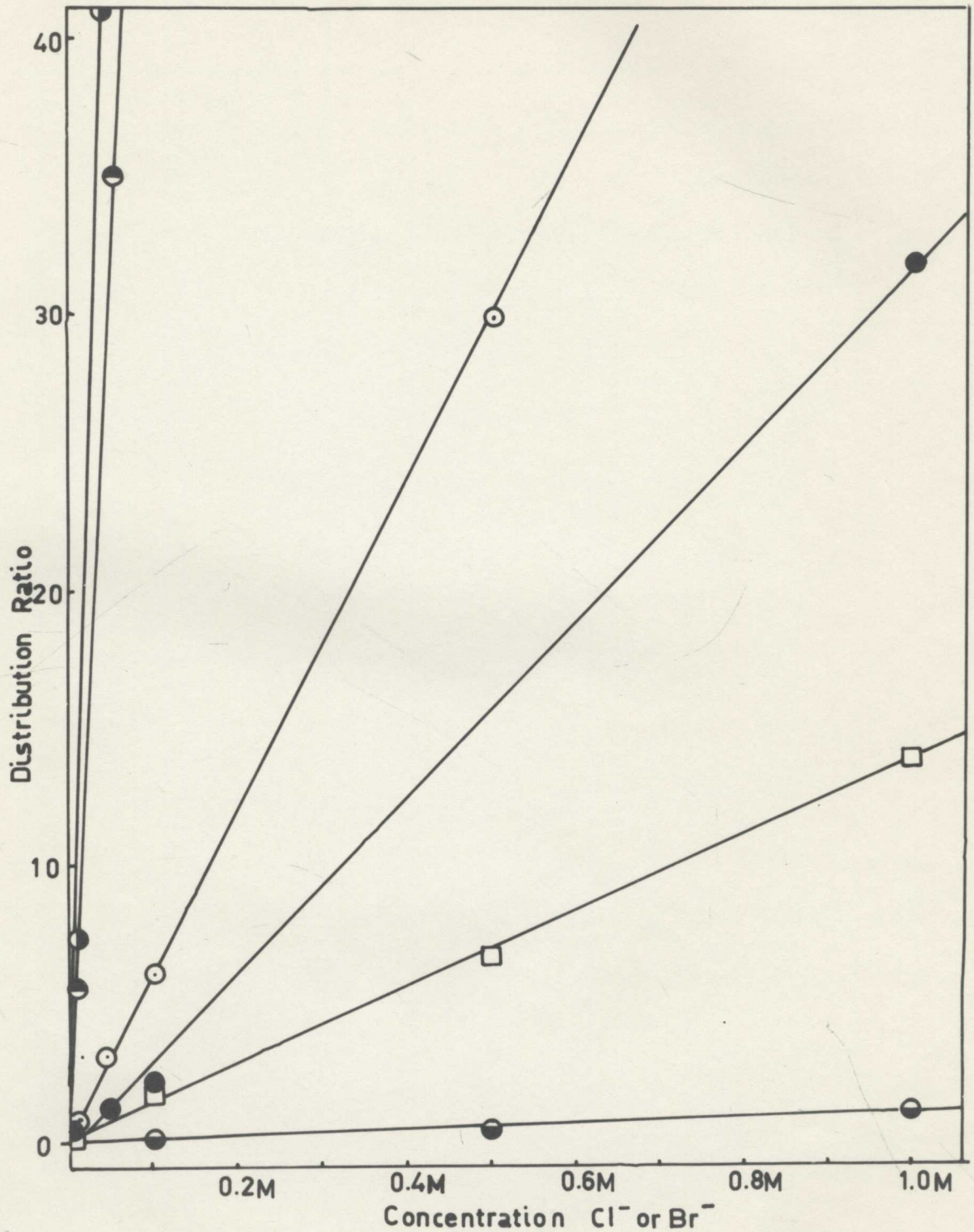

40
30
20
10
0
Distribution Ratio
0.2M
0.4M
0.6M
0.8M
1.0M
Concentration Cl⁻ or Br⁻

Figure 3

Distribution of quaternary salts over a range of anion concentration.

Distribution between chloroform, dichloromethane, 1,2-dichloroethane and water

Plot of log D against log $[Cl^-]$

Temperature 25°C

$[Cation] = 5 \times 10^{-3} M$

● Ph_3AmCl between $CHCl_3$ and water

■ Ph_4AsCl between $CHCl_3$ and water

⊙ $Ph_3MeAsCl$ between $CHCl_3$ and water

◒ $Ph_3MeAsCl$ between CH_2Cl_2 and water

◓ $Ph_3MeAsCl$ between $C_2H_4Cl_2$ and water

Data taken from Tables 3, 4, 5 and 6.

Figure 3

Figure 3

Distribution of quaternary salts over a range of anion concentration.

Distribution between chloroform, dichloromethane, 1,2-dichloroethane and water

Plot of log D against log $[Cl^-]$

Temperature 25°C

$[Cation] = 5 \times 10^{-3}M$

◑ Ph_3AmPCl between $CHCl_3$ and water

■ Ph_4AsCl between $CHCl_3$ and water

⊙ $Ph_3MeAsCl$ between $CHCl_3$ and water

◒ $Ph_3MeAsCl$ between CH_2Cl_2 and water

● $Ph_3MeAsCl$ between $C_2H_4Cl_2$ and water

Data taken from Tables 3, 4, 5 and 6.

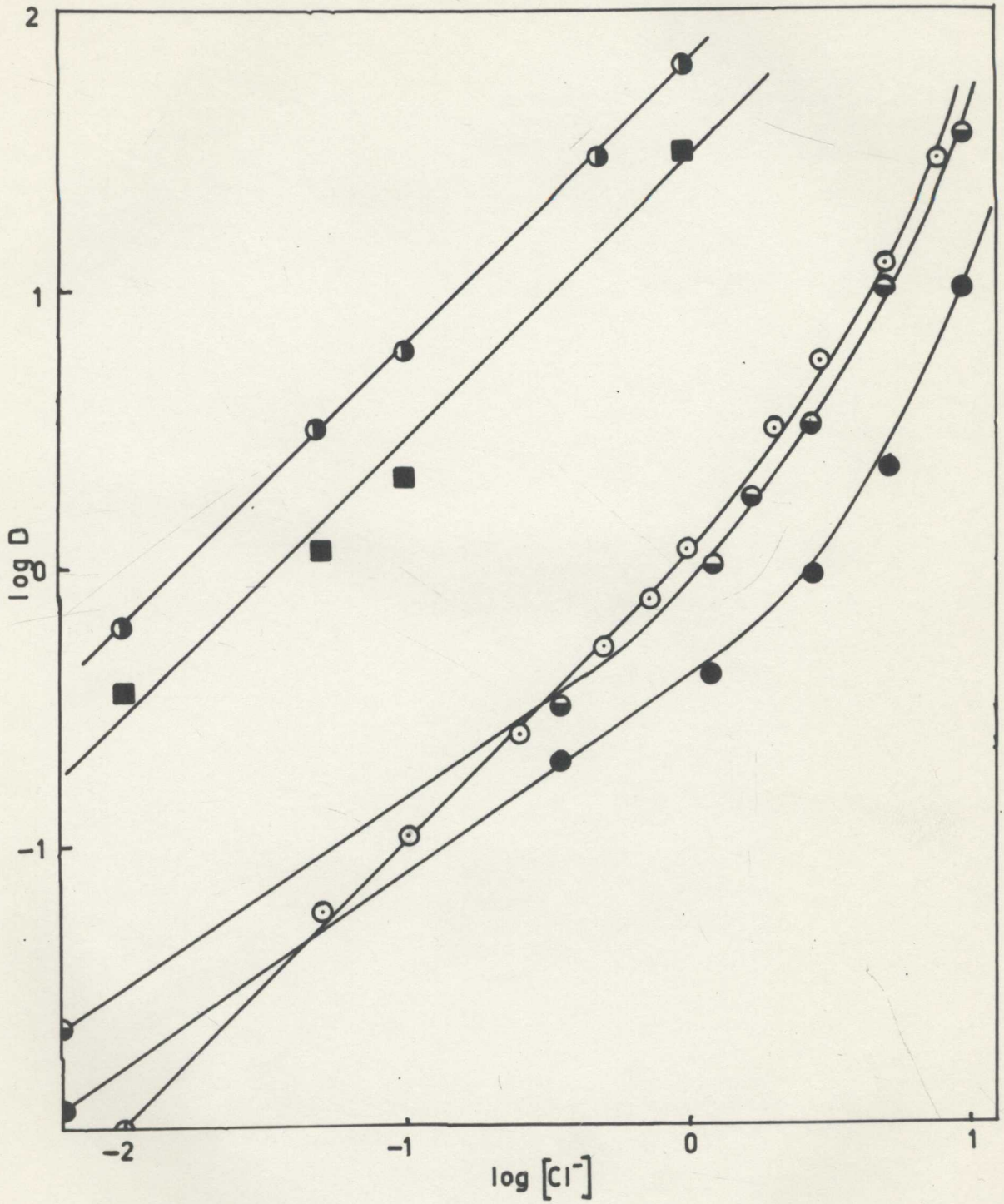

2
1
0
−1
log D
−2
−1
0
1
log [Cl⁻]

Figure 4

Distribution of quaternary salts over a range of anion concentration.

Distribution between chloroform and water.

Plot of log D against log $[Br^-]$

$[Cation] = 5 \times 10^{-3} M$

● Ph_3AmPBr at 25°C

○ Ph_4AsBr at 25°C

◉ Ph_3AmPBr at 35°C

⊠ $Ph_3MeAsBr$ at 25°C

Data from Table 7.

Figure 4

Figure 4

Distribution of quaternary salts over a range of anion concentration.

Distribution between chloroform and water.

Plot of log D against log $[\bar{Br}]$

$[Cation] = 5 \times 10^{-3} M$

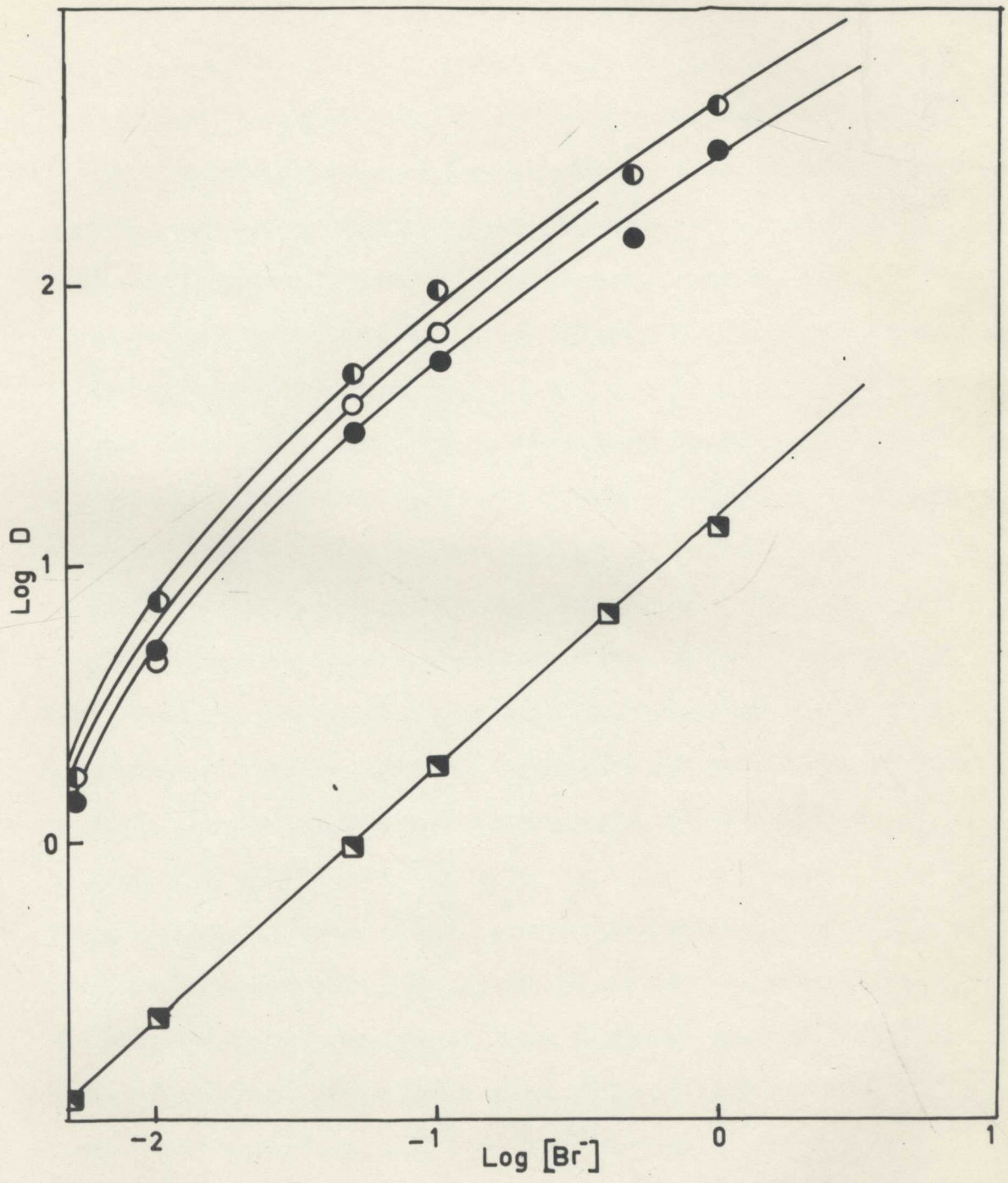
◐ Ph_3AmPBr at 25°C

○ Ph_4AsBr at 25°C

● Ph_3AmPBr at 35°C

◪ $Ph_3MeAsBr$ at 25°C

Data from Table 7.


Log D
2
1
0
−2
−1
0
1
Log [Br⁻]

distribution of $Ph_3MeAsCl$ between dichloromethane, 1,2-dichloroethane and water. With the exception of Ph_4AsBr and Ph_3AmPBr it is seen that there is a linear relationship between log D and the logarithm of the halide concentration up to a halide concentration of 1.0M. Triphenylmethylarsonium chloride is the only salt whose distribution has been studied at concentrations above 3M. Above 1M chloride the distribution ratios increased above the value predicted by the linear relationship between D and the chloride concentration (Figure 3). This increase may be due to activity effects in the aqueous phase at these high concentrations.

Scibona et al. (67) have observed the extraction of lithium chloride and lithium bromide from water into benzene solutions of quaternary ammonium compounds when the concentration of lithium chloride was above 1M. If extraction of the salt used to adjust the chloride concentration occurs above 1M concentrations in the systems studied here, then the properties of the organic solvents are likely to be changed significantly, and the distribution behaviour would also be altered. However, qualitative measurements indicate that no extraction of KCl occurs.

The anomalous behaviour of tetraphenylarsonium bromide and triphenyl-n-amylphosphonium bromide (Fig. 4) may be due to the errors in the high distribution ratios observed in these systems. The accuracy with which distribution ratios above about 20 could be measured is not high. (See the discussion of errors in Section 7.3.) The effect however, seems to be real, as the errors involved are thought to be too small to explain the observed deviation and no really satisfactory explanation is known. Association of ion pairs in the organic phase as the concentration of the quaternary bromides increases would be

expected to increase the distribution ratios above the value predicted by the expected linear relationship, whereas a decrease is observed. The lower distribution ratios of Ph_3AmPBr at 35° compared to the results obtained at 25° are worthy of note. (Figure 4 and Table 7). The distribution of quaternary salts over a range of temperatures is discussed more fully in Section 5.5.

All the results discussed so far for the distribution of the arsonium and phosphonium salts over a range of chloride concentration were made using potassium chloride or sodium chloride as the source of chloride ion. The results obtained using LiCl and CsCl as the source of chloride ion are also presented in Table 3. There was no significant difference between the four salts over the whole range of concentration studied; KCl and NaCl were used up to concentrations of 3M, CsCl up to 5M and LiCl up to concentrations of 10M. However, the use of HCl as the source of chloride ions resulted in a very significant difference in the distribution behaviour of the triphenylmethylarsonium cation. There was no difference in the extraction of $Ph_3MeAsCl$ into chloroform, dichloromethane or 1,2-dichloroethane up to concentrations of about 0.4M KCl or HCl. Above this concentration, the distribution ratios from HCl solutions increased more slowly with increasing chloride concentration than was the case for KCl solutions; reached a maximum between 1.5M and 2M HCl and then decreased as the HCl concentration increased still further. (See Figures 5 and 6). Similar behaviour has been reported for the distribution of Ph_4AsCl between HCl solution and chloroform (32); the maximum was reached at a HCl concentration of 2.5M.

A decrease in the distribution ratio with increasing HCl concentrations has been reported by a number of different authors (8) (9) in their

Figure 5

Distribution of quaternary salts over a range of anion concentration.

Distribution of $Ph_3MeAsCl$ between chloroform and chloride solutions.

Plot of log D against log $[Cl^-]$

Temperature 25°C

$[Ph_3MeAs^+] = 5 \times 10^{-3}M$

○ LiCl as chloride source

□ HCl as chloride source

Figure 5

Data taken from Table 3.

Figure 5

Distribution of quaternary salts over a range of anion concentration.

Distribution of $Ph_3MeAsCl$ between chloroform and chloride solutions.

Plot of log D against log $[Cl^-]$

Temperature 25°C

$[Ph_3MeAs^+] = 5 \times 10^{-3}M$

○ LiCl as chloride source

□ HCl as chloride source

Data taken from Table 3.

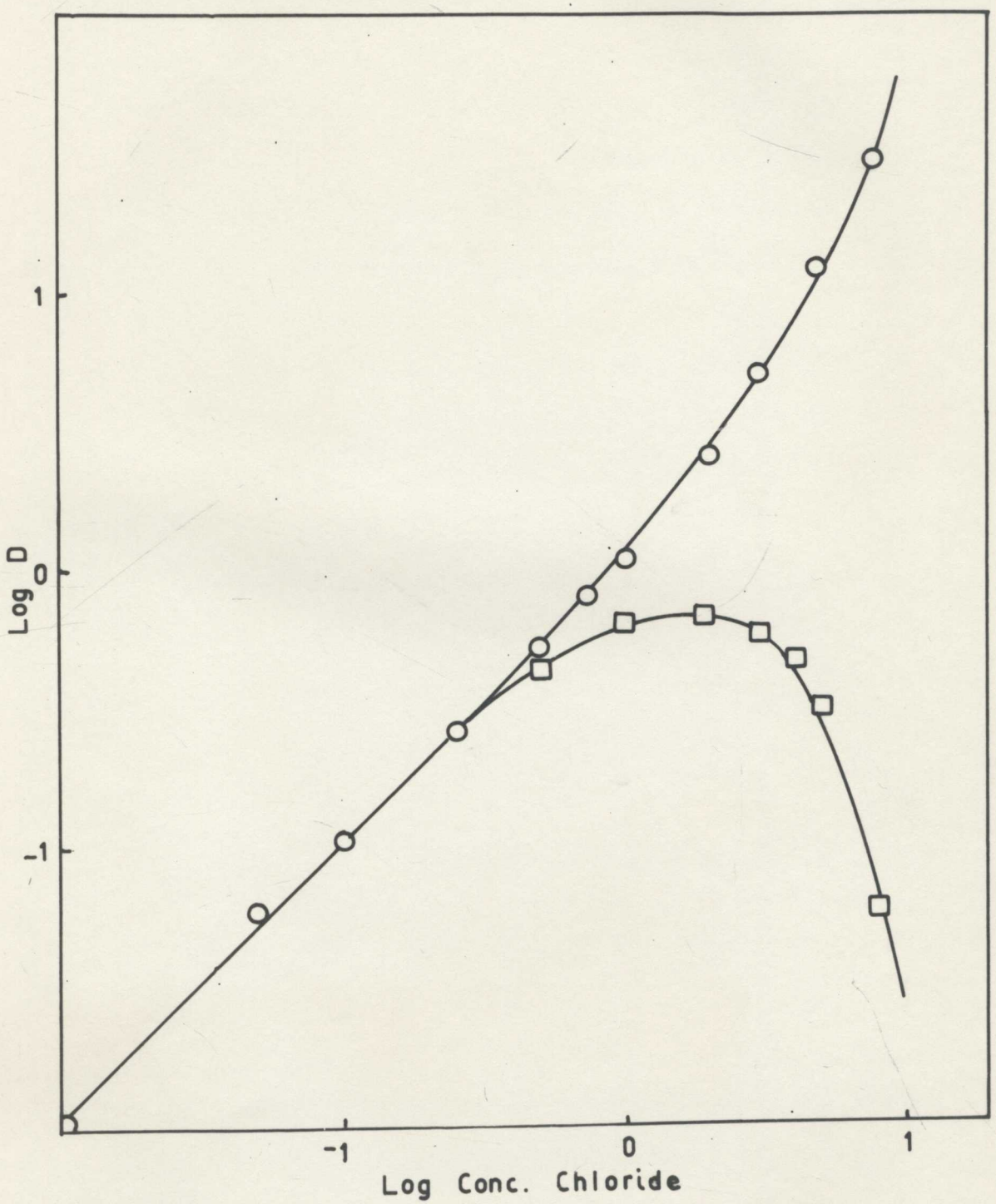

1
0
-1
Log D
-1
0
1
Log Conc. Chloride

Figure 6

Distribution of quaternary salts over a range of anion concentration.

Distribution of $Ph_3MeAsCl$ between dichloromethane, 1,2-dichloroethane and chloride solutions.

Plot of log D against log $[Cl^-]$

Temperature 25°C

$[Ph_3MeAs^+] = 5 \times 10^{-3}M$

Figure 6

● CH_2Cl_2 with LiCl

□ CH_2Cl_2 with HCl

○ $C_2H_4Cl_2$ with LiCl

◐ $C_2H_4Cl_2$ with HCl

Data taken from Tables 4 and 5.

Figure 6

Distribution of quaternary salts over a range of anion concentration.

Distribution of $Ph_3MeAsCl$ between dichloromethane, 1,2-dichloroethane and chloride solutions.

Plot of log D against log $[Cl^-]$

Temperature 25°C

$[Ph_3MeAs^+] = 5 \times 10^{-3}M$

Figure 6

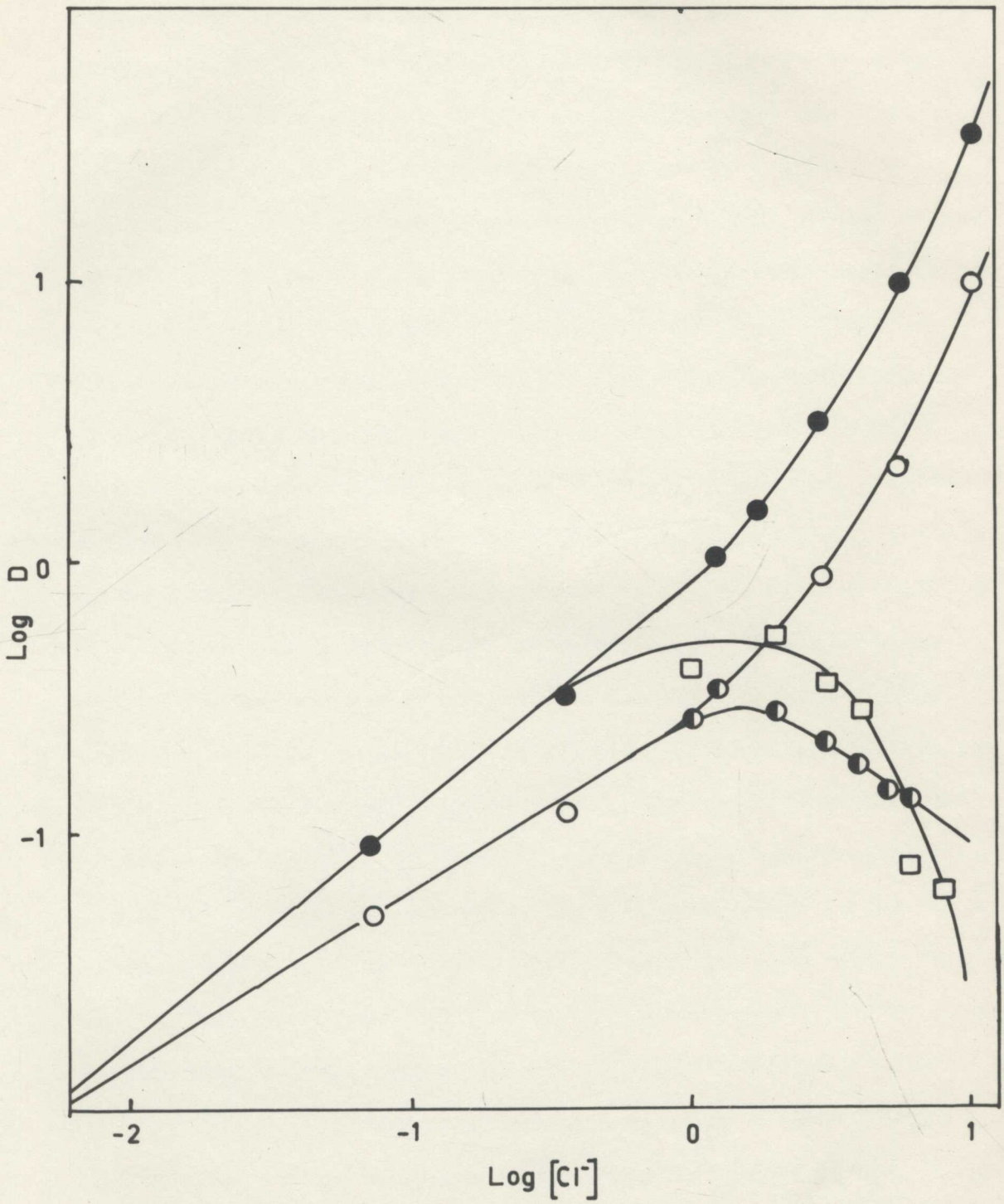
● CH_2Cl_2 with LiCl

□ CH_2Cl_2 with HCl

○ $C_2H_4Cl_2$ with LiCl

◐ $C_2H_4Cl_2$ with HCl

Data taken from Tables 4 and 5.


1
0
-1
Log D
-2
-1
0
1
Log [Cl⁻]

studies of the extraction of metal chloro complexes with quaternary ammonium ions. These studies were discussed in Section 2.2.

A number of proposals have been advanced to explain the behaviour of the metal chloro complexes. Wilson et al. (8) proposed that the hydrogen ion competes with the quaternary ammonium ion for the anionic metal complex, forming species such as H_2CoCl_4, which do not extract, and hence the distribution ratio of the metal decreases. Good and co-workers have made quite an extensive study of the extraction of metal complexes from chloride solutions by amines and quaternary salts (9) (55) (69). It was found that when $CoCl_4^{-2}$ was extracted into the organic phase (toluene) by quaternary salts, considerable amounts of hydrochloric acid were also extracted; the amount extracted increased steadily with increasing HCl concentration (55). Extraction of HCl was not observed in the absence of metal ions nor in the presence of Fe (III) or Ga (III) which form metal complexes which do not exhibit a maximum in their distribution ratios as the HCl concentration is raised (9). Evidence suggests that in the presence of $CoCl_4^{-2}$, at high acid concentrations considerable amounts of the hydrogen dichloride ion HCl_2^- are present in the organic phase (55). The existence of salts of the type R_4NHCl_2 was reported some years ago (69) (70) and their vibrational spectra have been thoroughly investigated recently (71).

Faithful et al. (57) have reported the extraction of excess nitric acid into chloroform solutions of tetraphenylarsonium nitrate. They have shown that nitric acid and the nitrate ion form the hydrogen dinitrate ion $H(NO_3)_2^-$ in chloroform.

Good has therefore proposed that competition for the quaternary

ammonium cation in the organic phase by the metal complex and the hydrogen dichloride ion, as the HCl concentration is raised, is the explanation for the decrease in the extraction (55) (9).

$$2R_4N^+Cl^-_{(org)} + CoCl_4^{=}{}_{(aq)} \rightleftharpoons (R_4N^+)_2CoCl_4^{=}{}_{(org)} + 2Cl^-_{(aq)} \quad (1)$$

$$R_4N^+Cl_{(org)} + HCl_{(aq)} \rightleftharpoons R_4N^+HCl_2^-{}_{(org)} \quad (2)$$

As the concentration of HCl is increased, reaction (2) is increasingly favoured and consequently the amount of $(R_4N^+)_2CoCl_4^{=}$ in the organic phase will be decreased. Good has however not excluded the possibility of the formation of $HCoCl_4^-$ or H_2CoCl_4 in solutions containing high hydrochloric acid concentrations as proposed by Wilson et al. (8) and concludes that both of these effects may be important.

However, none of the above proposals explains the decrease in the extraction of the triphenylmethylarsonium cation with increasing HCl concentration shown in Figures 5 and 6. The explanation that the hydrogen dichloride anion is formed in the aqueous solution above 0.4M HCl and that the species $Ph_3MeAsHCl_2$ does not extract is improbable for a number of reasons. The formation of the hydrogen dichloride anion is unlikely to occur at HCl concentrations as low as 0.5M, it has only been postulated in concentrated HCl solutions, and the formation is even more unlikely to be extensive enough to fully account for the decrease in the extraction observed at that concentration. In any case, Good et al. (55) (69) have postulated that the HCl_2^- anion is extracted into toluene, and Faithful et al. (57) have shown that the hydrogen dinitrate anion is extracted into chloroform. Therefore the large decrease in the distribution ratio which is observed is unlikely to be due to the formation of HCl_2^-

and its failure to extract into the organic solvents.

The distribution of hydrochloric acid between water and chloroform, benzene, 1,2-dichloroethane and carbon tetrachloride has been studied by Zharovskii and Litvenenko (72). The reported results have been confirmed by the author for these solvents and for dichloromethane by acid-base titration of the organic solvent after equilibration with hydrochloric acid solution; there is no significant extraction of hydrochloric acid into these solvents from HCl solutions as concentrated as 6.0M. In the presence of the triphenylmethylarsonium cation there was still no evidence for any significant extraction of hydrochloric acid (Section 7.3). Good et al. (55) also reported that no hydrochloric acid was extracted into toluene in the absence of metal ions.

The extraction of Fe (III) into diethylether from hydrochloric acid solution decreases, after reaching a maximum, as the HCl concentration is increased (2). The decrease in this system has been shown to be due to the solubility of the ether in the hydrochloric acid solution resulting in a marked decrease in the volume of the ehter phase. No difference in the volumes of the two phases in the presence of concentrated HCl was observed in the systems under discussion so the decrease cannot be attributed to the solubility of one phase in the other.

It is difficult to imagine any interactions in the organic solvent which will explain the anomalous extraction from hydrochloric acid solution, and so the explanation probably lies in the properties of the hydrochloric acid solution. It has been shown that the dielectric constant of solutions of electrolytes decreases with increasing electrolyte concentration (73) (74). The decrease has

been shown to be linear up to a concentration of about 2M; above this concentration the decrease is less than that demanded by the linear relationship (73). Sodium chloride appears to be the only salt which has been studied at concentrations above 2M; a 5M solution of NaCl has a dielectric constant of 48.4 at 25° (73). For concentrations less than 2M, Hasted Ritson and Collie (73) represent the static dielectric constant ϵ of a solution by an equation which may be written

$$\epsilon = \epsilon_w + 2\delta C$$

where ϵ_w is the static dielectric constant of water (78.5 at 25°) δ is half the molar depression of the dielectric constant and C is the concentration of the salt in moles per litre. The values of δ for some chlorides are given in Table 4.3.1.

Table 4.3.1

Half the Molar Depression of Dielectric Constant of Water by Electrolytes at 25°

Electrolyte	δ
HCl	-10
LiCl	- 7
NaCl	-5.5
KCl	- 5
RbCl	- 5
$MgCl_2$	-15
$LaCl_3$	-22

It can be seen that the dielectric constants of HCl solutions will be much lower than those of the metal chloride solutions at the same chloride concentration. Unfortunately the dielectric constant of HCl

solutions have only been measured up to concentrations of 0.5M (73), however, if the above equation is obeyed by HCl solutions then the dielectric constant of a 2M HCl solution will be below forty. In a solution with such a low dielectric constant a significant amount of the quaternary salt will be associated as ion pairs (6) and consequently the distribution behaviour of the quaternary salt will be altered. The theory developed in Section 3 assumed that a significant amount of ion pair formation did not occur in the aqueous phase, and so this theory will not apply to extraction from concentrated hydrochloric acid solutions.

The extraction of quaternary salts into organic solvents will depend on the solvation energies of the quaternary salt in the aqueous and organic solvent (2). In order that an ionic salt is able to extract into an organic solvent the loss of primary and secondary solvation energy of the ions on passing into the organic solvent must be small. The hydration energies of large quaternary cations are very small and this accounts for their ability to extract into organic solvents. The solvation energy of the quaternary salt in the organic phase is made up of a number of factors, but is primarily electrostatic in origin, arising from interactions between the ions and the solvent molecules. The formation of ion pairs in the organic solvent is indicative of the relative weakness of the interactions between the ions and the solvent molecules; the ions are able to lower their energy by interacting with each other, to form ion pairs, rather than with the solvent molecules.

When the ions of the quaternary salt are transferred from the aqueous solution to an organic solvent of low dielectric constant,

they lose most, if not all, of their hydration energy and this energy loss is then partly compensated by the energy of ion pair formation in the organic solvent. If the quaternary salt exists as ion pairs in the aqueous phase, then the quaternary salt has lost one of the factors which favours extraction into the organic solvent and the extraction may become energetically unfavourable. The formation of ion pairs in aqueous solutions of quaternary salts has been postulated by a number of workers. Diamond (75) has pointed out that because of their large size and hydrophobic nature there will be a tendency for the water structure to force quaternary cations to form ion pairs. This "water structure enforced" ion pairing ismost likely to occur with large ions with a low charge, and is only likely to occur in highly structured solvents like water. Kay and Evans (76) (77) have found evidence for a small amount of ion pair formation in solutions of tetra-n-butylammonium iodide in D_2O and H_2O from conductivity measurements. They do not believe that this ion pair formation is due to "structure enforced" ion pairing as the amount of ion pairing in the more highly structured D_2O solutions was not greater than in H_2O solutions. The ion pairing postulated in hydrochloric acid solutions is due primarily to electrostatic ion pairing which is favoured by solvents with a low dielectric constant and by small ions with a high charge.

The maximum in the distribution ratio for Ph_4AsCl from HCl solutions was reached when the HCl concentration was 2.5M (32) whereas the maximum for $Ph_3MeAsCl$ was reached when the HCl concentration was between 1.5 and 2M (Figure 5). This difference can be attributed to two effects; the concentration of Ph_4AsCl was lower than that of

$Ph_3MeAsCl$ and so ion pair formation will only occur in solutions with a lower dielectric constant, i.e. higher HCl concentrations, and the smaller unsymmetrical Ph_3MeAs^+ cation would be expected to form ion pairs in the aqueous phase more readily than Ph_4As^+ and so the maximum in the distribution ratios would be expected at lower HCl concentrations.

Smulek (36) has published some results on the distribution of tetra-n-butylammonium chloride over a range of concentration from 10^{-5}M to 10^{-3}M between a number of organic solvents and 8.0M hydrochloric acid. The only comment that Smulek made on his results was that the distribution ratio changes with the concentration of the reagent. Different behaviour was observed with different solvents; with bromoform and chlorobenzene, the distribution ratios were constant at low concentrations of Bu_4NCl, but the distribution ratios decreased at higher concentrations. The extraction of Bu_4NCl from a medium such as 8M HCl should be similar to the extraction of $Ph_3MeAsCl$ from a medium of constant excess Cl^- concentration which was discussed in Section 4.2. In solvents such as bromoform and chlorobenzene where the Bu_4NCl would be expected to exist as ion pairs, the distribution ratio should remain constant. The observed decrease in the distribution ratios at higher Bu_4NCl concentrations may also be attributed to ion pair formation in the aqueous phase, as dissociation or association in the organic solvent is expected to increase the distribution ratio. The distribution ratios reported by Smulek for the other solvents are highly irregular, possibly indicating competition between ion pair formation in the aqueous phase and dissociation or association in the organic phase.

Therefore the anomalous extraction behaviour of quaternary chlorides from hydrochloric acid solutions seems to be adequately explained by the postulate of ion pair formation of the quaternary salt in the aqueous phase. Large univalent anions such as $FeCl_4^-$ will have little tendency to form electrostatic ion pairs in aqueous solution, and as a consequence the maximum in the extraction from HCl solutions is not observed with this anion (8) (9). Large divalent anions will have a greater tendency to associate with quaternary cations and with the anion $CoCl_4^=$ a maximum is observed at about 9M HCl (9). Competition for the cation in the organic phase by the anions $CoCl_4^=$ and HCl_2^- as postulated by Good et al. (9) (55), as well as ion pair formation, is possibly important in this case.

The extraction of the cation in the presence of $CoCl_4^=$ cannot be measured by the method used in this thesis, as the anion absorbs strongly in the ultraviolet region of the spectrum.

Section 4.4 Extraction of metal complexes with quaternary salts

The extraction of metal complexes using quaternary ammonium salts has been studied using a wide variety of anionic metal complexes and a variety of cations (Section 2.2). It has been usual to study the distribution of the metal ion using radioactive isotopes. The concentration of the quaternary salts (usually in the organic phase) has generally been about 0.1M.

The results for the distribution of the triphenylmethylarsonium cation from aqueous chloride and bromide solutions into $CHCl_3$ in the presence of zinc and cadmium ions are presented in Tables 8 and 9. The concentration of the quaternary arsonium cation used was 5×10^{-3}M. It was found that the distribution ratios for the extraction of the cation were identical in the presence of the Zn^{2+} ion to those obtained when Zn^{2+} was not present. The concentration of the zinc in the aqueous phase did not affect the results (see Table 8) except that at high concentrations of Zn^{2+} and X^- (X^-=Cl^- or Br^-) a precipitate was formed which proved to be $(Ph_3MeAs)_2ZnX_4$. These results imply that at the concentration of cation used either the distribution behaviour of $(Ph_3MeAs)_2ZnX_4$ is identical to Ph_3MeAsX or that $(Ph_3MeAs)_2ZnX_4$ does not extract.

The distribution of zinc between chloroform and aqueous chloride or bromide solutions with a large number of quaternary cations was therefore investigated using radioactive Zn^{65} to follow the extraction. The concentration of the cation used was again 5×10^{-3}M and the zinc was at tracer concentrations or 2.5×10^{-3}M, the halide concentration was never less than 0.5M. No zinc could be detected in the organic phase with any of the cations studied. It is therefore, evident that no extraction of $(Ph_3MeAs)_2ZnBr_4$ or $(Ph_3MeAs)_2ZnCl_4$ into chloroform takes place when the concentration of the cation is 5×10^{-3}M.

The extraction of cadmium into chloroform was not studied using radioactive cadmium, but the extraction of the triphenylmethylarsonium cation in the presence of Cd^{2+} was identical to the results in the absence of cadmium ions up to chloride concentrations of 0.1M (Table 8). Above this concentration a precipitate of $(Ph_3MeAs)_2CdCl_4$ was observed in the distribution flask. The extraction of the cation Ph_3MeAs^+ into chloroform from bromide solutions containing cadmium ions was greater than from solutions containing no cadmium ions implying that $(Ph_3MeAs)_2CdBr_4$ was extracted. The results are shown in Fig. 7. All systems with a concentration of Br^- in the aqueous phase between 0.2M to 2.5M had a precipitate present. The amount of precipitate appeared to increase to a maximum at a bromide concentration of 0.75M and then decreased again until the solution with 3M bromide did not have this precipitate. This behaviour may be caused by the formation of higher halide complexes of cadmium i.e. $CdBr_5^{-3}$ and $CdBr_6^{-4}$ at high bromide concentrations and the increased solubility of the arsonium salts of these anions compared to $(Ph_3MeAs)_2CdBr_4$.

Figure 7

Distribution $Ph_3MeAsBr$ over a range of bromide concentration.

Plot of log D against log $[Br^-]$

$[Cation] = 5 \times 10^{-3} M$

Temperature $25^{\circ}C$

⊙ KBr alone

⊡ KBr in presence of $CdSO_4$

Figure 7

Dotted line indicates precipitate present.

Data taken from Tables 7 and 9.

Figure 7

Distribution $Ph_3MeAsBr$ over a range of bromide concentration.

Plot of log D against log $[Br^-]$

$[Cation] = 5 \times 10^{-3} M$

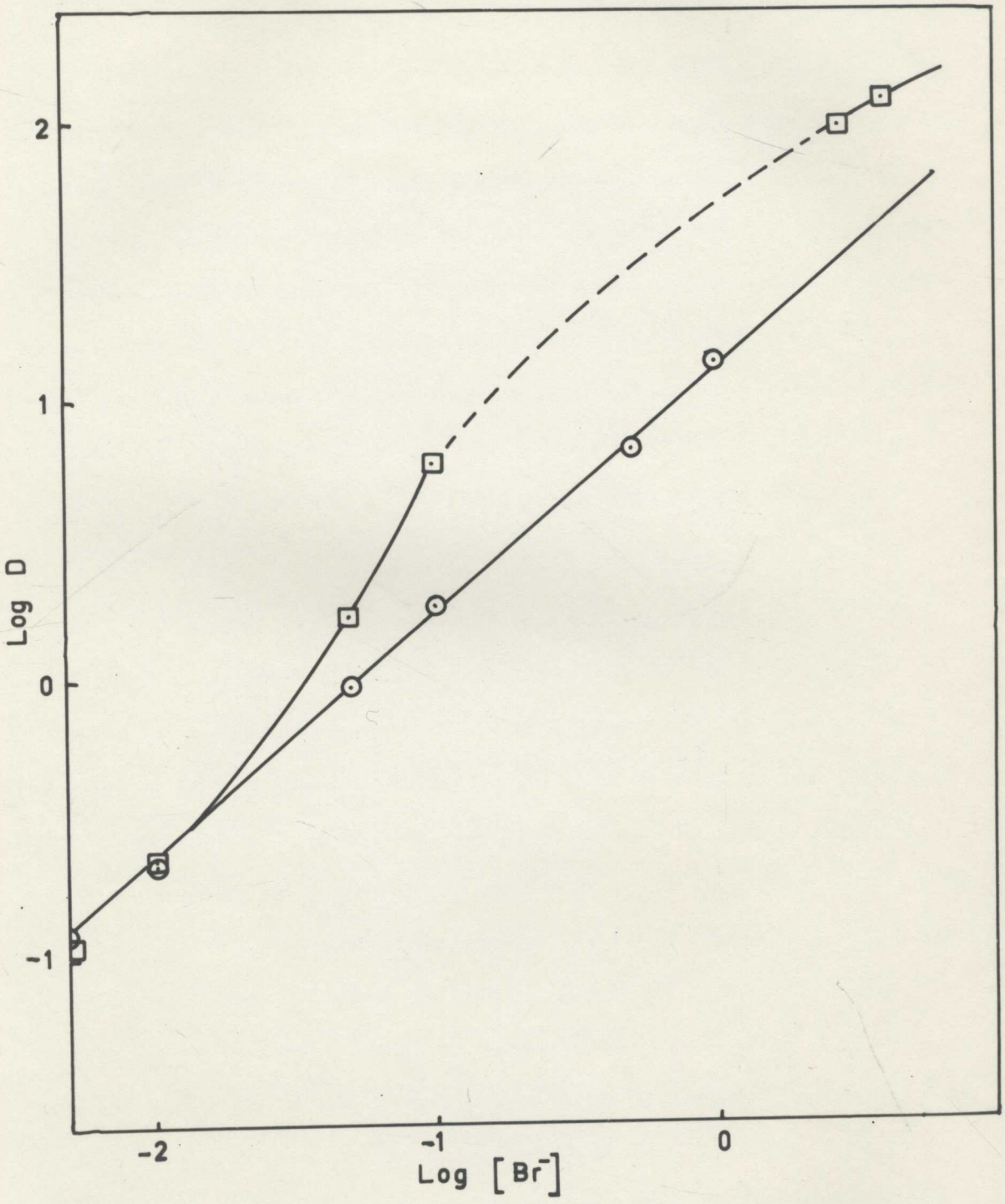
Temperature $25^{\circ}C$

⊙ KBr alone

⊡ KBr in presence of $CdSO_4$

Dotted line indicates precipitate present.

Data taken from Tables 7 and 9.


2
1
0
-1
Log D
-2
-1
0
Log [Br⁻]

Section 4.5 Distribution of Quaternary Salts over a range of concentration

In Section 3.3 a theory was presented for the extraction of quaternary salts from an aqueous solution of constant ionic strength (maintained with Na_2SO_4) into an organic solvent. It was shown that if the quaternary salt exists as ion pairs in the organic phase then the distribution ratio of the quaternary salt is proportional to the square root of the initial concentration of the quaternary salt in the aqueous phase. This relationship was calculated by using the expression:

$$D = \frac{\text{Total amount of Anion in the organic phase}}{\text{Total amount of Anion in the aqueous phase}}$$

and in this work we have measured the cation concentration. The measured distribution ratios were therefore corrected for the amount of quaternary cation which extracted from the aqueous solution in the absence of the anion. The correction was generally small as sodium sulphate was chosen to adjust the ionic strength and quaternary sulphates have been found to be very poor extractants. The distribution between four organic solvents and sodium sulphate solution of some fourteen quaternary ammonium, phosphonium and arsonium salts over a range of concentration from about 5×10^{-5}M to about 7×10^{-3}M and in one case 9×10^{-2}M has been measured and the results are given in Tables 10 to 26. The four organic solvents used were chloroform, dichloromethane, 1,2-dichloroethane and 2,2'-dichlorodiethylether, but most of the results were obtained using chloroform as the organic solvent.

Attempts to measure the extraction into chloroform of the salt Ph_4AsNO_2 over a range of concentration gave very inconsistent readings and so the results are not given. These inconsistent readings are probably due to the oxidation of the nitrite ion in these systems.

Typical results are shown in Figs. 8 and 9 where the percentage of the quaternary salt extracted into the organic solvent is plotted against the initial concentration of the quaternary salt in the aqueous phase. Figure 8 contains the results of the distribution of five different salts between water and chloroform and Fig. 9 contains the results of the distribution of $Ph_3MeAsClO_4$ and $Ph_3MeAsNO_3$ between chloroform, dichloromethane, 1,2-dichloroethane and 2,2'-dichlorodiethylether and water. The results for $Ph_3MeAsClO_4$ and $Ph_3MeAsNO_3$ in these solvents follow the expected trend, increasing distribution ratios with increasing dielectric constant of the organic solvent. The results presented in Section 4.2 for the distribution of $Ph_3MeAsCl$ between chloroform, 1,2-dichloroethane and 2,2'-dichlorodiethylether did not show this trend. Possible reasons for this behaviour will be discussed in Section 5.3. Both Figs. 8 and 9 show the same trend; at the highest concentration measured the percentage extraction is generally at the highest value measured and as the concentration falls the proportion of the quaternary salt extracted into the organic solvent also falls, until it reaches a minimum, and then as the concentration falls still further, the percentage extraction rises rapidly. Increases of the distribution ratios with increasing concentration has been reported for the extraction of Ph_4PCl into chloroform (25) and

Figure 8

Distribution of quaternary salts over a range of concentration of the quaternary salt.

Distribution between $CHCl_3$ and water.

Plot of percentage extraction against the concentration of the quaternary salt in the aqueous phase.

Temperature 25^{o}

● Ph_3AmPI

○ $Ph_3MeAsClO_4$

◐ Ph_3MeAsI

Figure 8

◉ $Ph_3MeAsNO_3$

□ $Ph_3MeAsBr$

Data taken from Tables 11, 12, 13, 14 and 15.

Figure 8

Distribution of quaternary salts over a range of concentration of the quaternary salt.

Distribution between $CHCl_3$ and water.

Plot of percentage extraction against the concentration of the quaternary salt in the aqueous phase.

Temperature 25°

◒ Ph_3AmPI

○ $Ph_3MeAsClO_4$

◑ Ph_3MeAsI

● $Ph_3MeAsNO_3$

□ $Ph_3MeAsBr$

Data taken from Tables 11, 12, 13, 14 and 15.

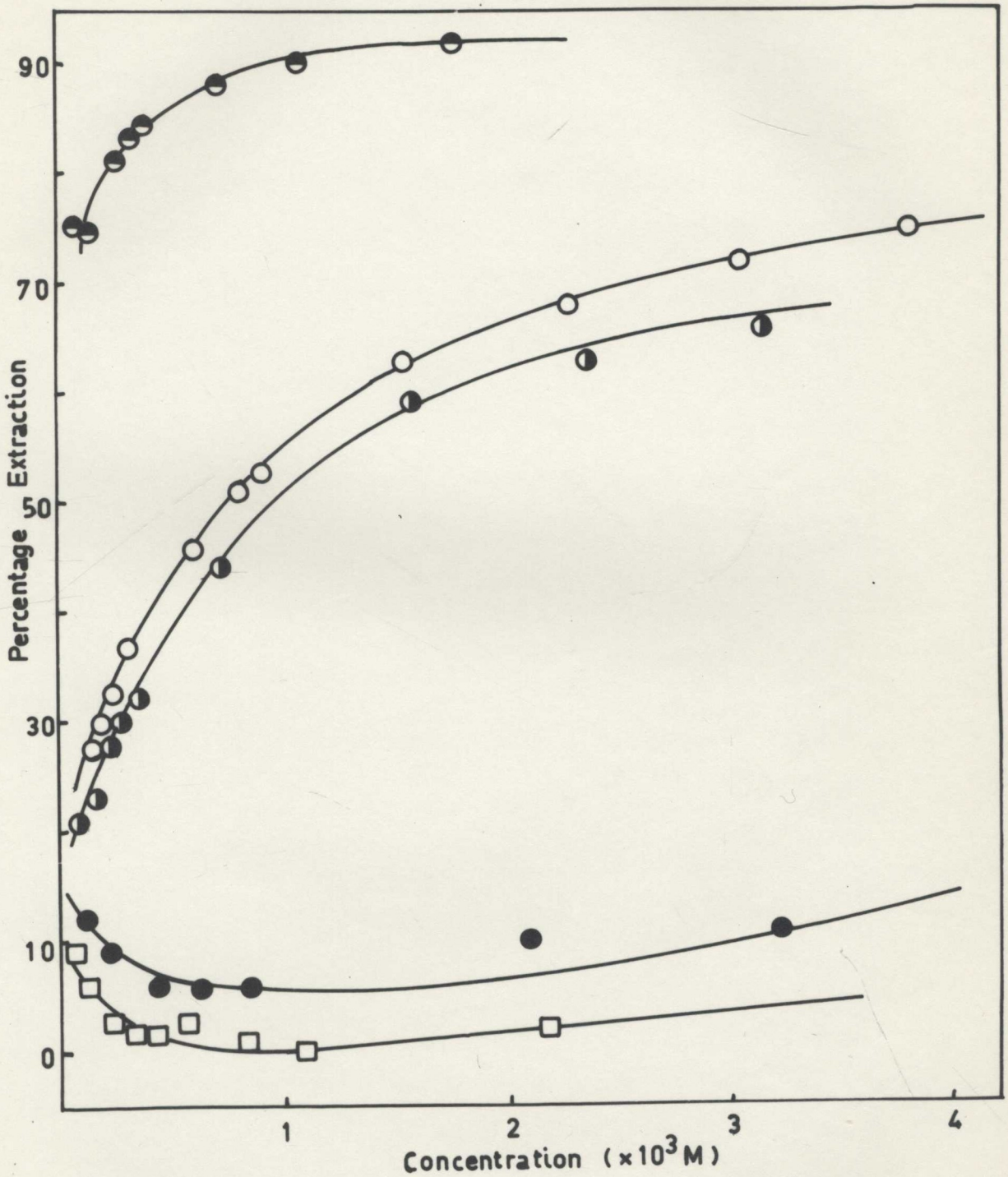

90
70
50
30
10
0
Percentage Extraction
1
2
3
4
Concentration (×10³M)

Figure 9

Distribution of quaternary salts over a range of concentration of the quaternary salt.

Distribution of $Ph_3MeAsClO_4$ and $Ph_3MeAsNO_3$ between chloroform, dichloromethane, 1,2-dichloroethane, 2,2'-dichlorodiethylether and water over a range of quaternary salt concentration.

Plot of percentage extraction against the initial concentration of the quaternary salts in the aqueous phase.

Temperature 25°

⊙	$Ph_3MeAsClO_4$	into	1,2-dichloroethane
◒	$Ph_3MeAsClO_4$	into	dichloromethane
◐	$Ph_3MeAsClO_4$	into	chloroform
⊡	$Ph_3MeAsNO_3$	into	2,2'-dichlorodiethylether
◪	$Ph_3MeAsNO_3$	into	1,2-dichloroethane
■	$Ph_3MeAsNO_3$	into	chloroform

Figure 9

Data taken from Tables 13, 14, 22, 23 and 25.

Figure 9

Distribution of quaternary salts over a range of concentration of the quaternary salt.

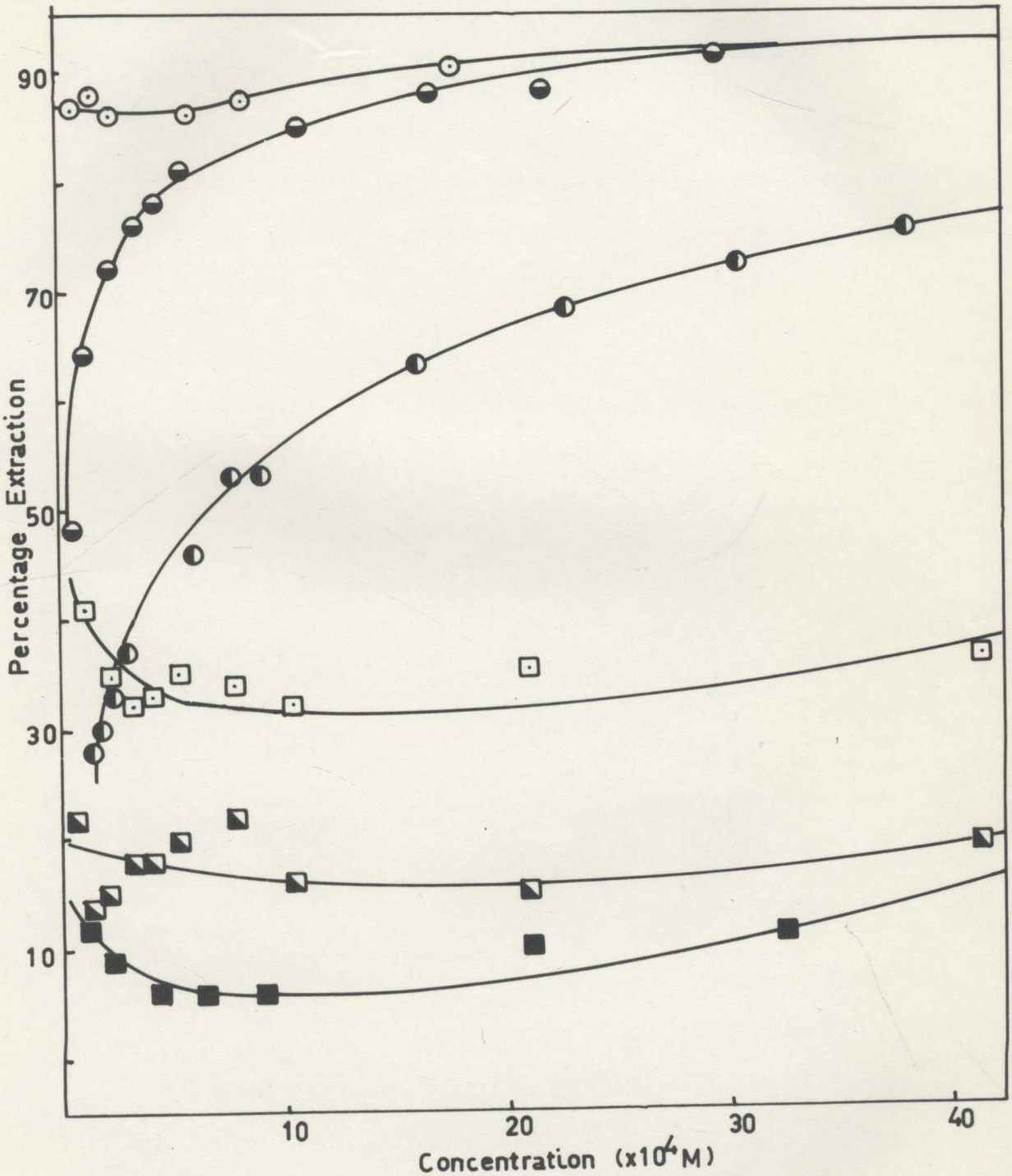
Distribution of $Ph_3MeAsClO_4$ and $Ph_3MeAsNO_3$ between chloroform, dichloromethane, 1,2-dichloroethane, 2,2'-dichlorodiethylether and water over a range of quaternary salt concentration.

Plot of percentage extraction against the initial concentration of the quaternary salts in the aqueous phase.

Temperature 25°

⊙	$Ph_3MeAsClO_4$	into	1,2-dichloroethane
◒	$Ph_3MeAsClO_4$	into	dichloromethane
◐	$Ph_3MeAsClO_4$	into	chloroform
⊡	$Ph_3MeAsNO_3$	into	2,2'-dichlorodiethylether
◪	$Ph_3MeAsNO_3$	into	1,2-dichloroethane
■	$Ph_3MeAsNO_3$	into	chloroform

Data taken from Tables 13, 14, 22, 23 and 25.


90
70
50
30
10
Percentage Extraction
10
20
30
40
Concentration (x10⁻⁴M)

of Ph_4SbF into carbon tetrachloride (110). The minimum observed in this work has not been reported previously. The minimum is shown most clearly in Fig. 10 where the results are plotted over a smaller concentration range. It is noteworthy that the minimum in the distribution ratio of a large number of salts between chloroform and water occurs at roughly the same concentration of the salt in the organic phase although the total concentration in the system varied widely. See Table 4.5.1.

Table 4.5.1

The concentration in the chloroform phase at which the minimum in the distribution ration was observed.

Salt	Concentration x 10^5M
Ph_3AmPI	1.6
Ph_3MeAsI	1.5
Ph_2Me_2AsI	1.7
$PhMe_3AsI$	2.4
$PhMe_3NI$	2.6
$Ph_3MeAsBr$	1.5
$Ph_3MeAsClO_4$	3.2
$Ph_3MePClO_4$	1.3
$Ph_3MeAsNO_3$	2.4

It should be emphasised that the results quoted in the above Table are the concentrations in the chloroform phase at the observed minima in the distribution ratio, they are not calculated

Figure 10

Distribution of quaternary salts over a range of concentration.

Distribution of various salts at low concentrations between water and various solvents.

Plot of percentage extraction against the initial concentration of the quaternary salts in the aqueous phase.

Temperature 25°

Figure 10

●	$Ph_3MeAsBr$	into	chloroform
▣	$Ph_3MeAsNO_3$	into	chloroform
◪	$Ph_3MeAsNO_3$	into	1,2-dichloroethane
○	$Ph_3MeAsClO_4$	into	chloroform
◑	Ph_3MeAsI	into	chloroform
⊖	$Ph_3MeAsClO_4$	into	chloroform
⊡	$Ph_3MeAsNO_3$	into	2,2'-dichlorodiethylether
◐	Ph_3AmPI	into	chloroform

Data taken from Tables 11, 12, 13, 14, 15, 17 and 25.

Figure 10

Distribution of quaternary salts over a range of concentration.

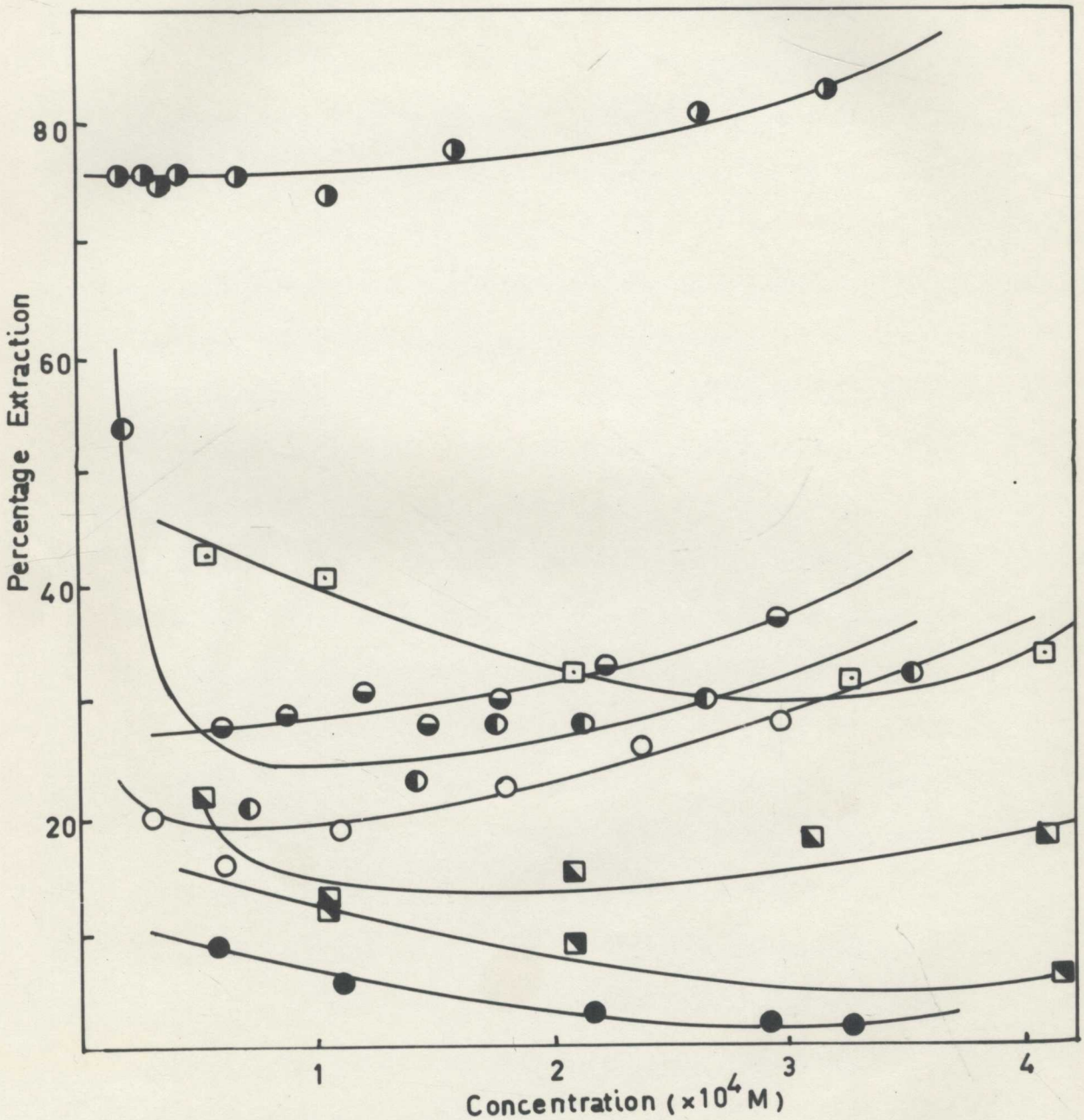
Distribution of various salts at low concentrations between water and various solvents.

Plot of percentage extraction against the initial concentration of the quaternary salts in the aqueous phase.

Temperature 25°

◑	Ph_3AmPI	into	chloroform
⊡	$Ph_3MeAsNO_3$	into	2,2'-dichlorodiethylether
⊖	$Ph_3MeAsClO_4$	into	chloroform
◐	Ph_3MeAsI	into	chloroform
○	$Ph_3MeAsPClO_4$	into	chloroform
◪	$Ph_3MeAsNO_3$	into	1,2-dichloroethane
◪	$Ph_3MeAsNO_3$	into	chloroform
●	$Ph_3MeAsBr$	into	chloroform

Data taken from Tables 11, 12, 13, 14, 15, 17 and 25.


80
60
40
20
Percentage Extraction
1
2
3
4
Concentration (×10⁴ M)

from the minima in the curves in Figure 10. If the distribution ratio of the quaternary salt is high then the concentration of the quaternary salt in the aqueous phase, after distribution will be very low. If the initial concentration is low (as it is in Fig. 10) the accuracy with which the distribution ratios may be determined is not high. There is no doubt however that the distribution ratios do increase rapidly as the concentration of the quaternary salt in chloroform falls below about 2×10^{-5}M. The other solvents dichloromethane, 1,2-dichloroethane and 2,2'-dichlorodiethylether also show a minimum in the distribution ratios of the quaternary salts with increasing concentration (see Figure 10) but because only a few salts have been studied in these solvents a table similar to Table 4.5.1 is not given.

The distribution of the salts 2-bromomethylbenzyltriphenylphosphonium bromide, 3-bromomethylbenzyltriphenylphosphonium bromide and 4-bromomethylbenzyltriphenylphosphonium bromide between the three solvents chloroform, 1,2-dichloroethane and dichloromethane are particularly interesting (Figure 11 and Tables 19, 20 and 21). If the solvation of the quaternary salts in the two phases is the major factor in determining the distribution ratios and if the solvation energies of these three salts in the organic phase are approximately the same, then the hydration energies of the cations in the aqueous phase will be the major factor governing the differences in their distribution behaviour. The hydration of these cations will be dominated by the polar bromomethyl group in the benzyl radical and a model of the 2-bromomethylbenzyltriphenyl-phosphonium cation shows that the bromomethyl group is

Figure 11

Distribution of quaternary salts over a range of concentration.

Distribution of 2-$BrCH_2BzPh_3PBr$, 3-$BrCH_2BzPh_3PBr$ and 4-$BrCH_2BzPh_3PBr$ between $CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$ and water.

Plot of percentage extraction against the initial concentration of the quaternary salt in the aqueous phase.

Temperature 25°C

◒	2-$BrCH_2BzPh_3PBr$	into	chloroform
◐	2-$BrCH_2BzPh_3PBr$	into	dichloromethane
◑	2-$BrCH_2BzPh_3PBr$	into	1,2-dichloroethane
⊙	3-$BrCH_2BzPh_3PBr$	into	chloroform
⊡	3-$BrCH_2BzPh_3PBr$	into	1,2-dichloroethane
◪	3-$BrCH_2BzPh_3PBr$	into	dichloromethane
■	4-$BrCH_2BzPh_3PBr$	into	dichloromethane
●	4-$BrCH_2BzPh_3PBr$	into	chloroform
◣	4-$BrCH_2BzPh_3PBr$	into	1,2-dichloroethane

Data from Tables 19, 20 and 21.

Figure 11

Distribution of quaternary salts over a range of concentration.

Distribution of 2-$BrCH_2BzPh_3PBr$, 3-$BrCH_2BzPh_3PBr$ and 4-$BrCH_2BzPh_3PBr$ between $CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$ and water.

Plot of percentage extraction against the initial concentration of the quaternary salt in the aqueous phase.

Temperature 25°C

◒ 2-$BrCH_2BzPh_3PBr$ into chloroform

◑ 2-$BrCH_2BzPh_3PBr$ into dichloromethane

◐ 2-$BrCH_2BzPh_3PBr$ into 1,2-dichloroethane

⊙ 3-$BrCH_2BzPh_3PBr$ into chloroform

⊡ 3-$BrCH_2BzPh_3PBr$ into 1,2-dichloroethane

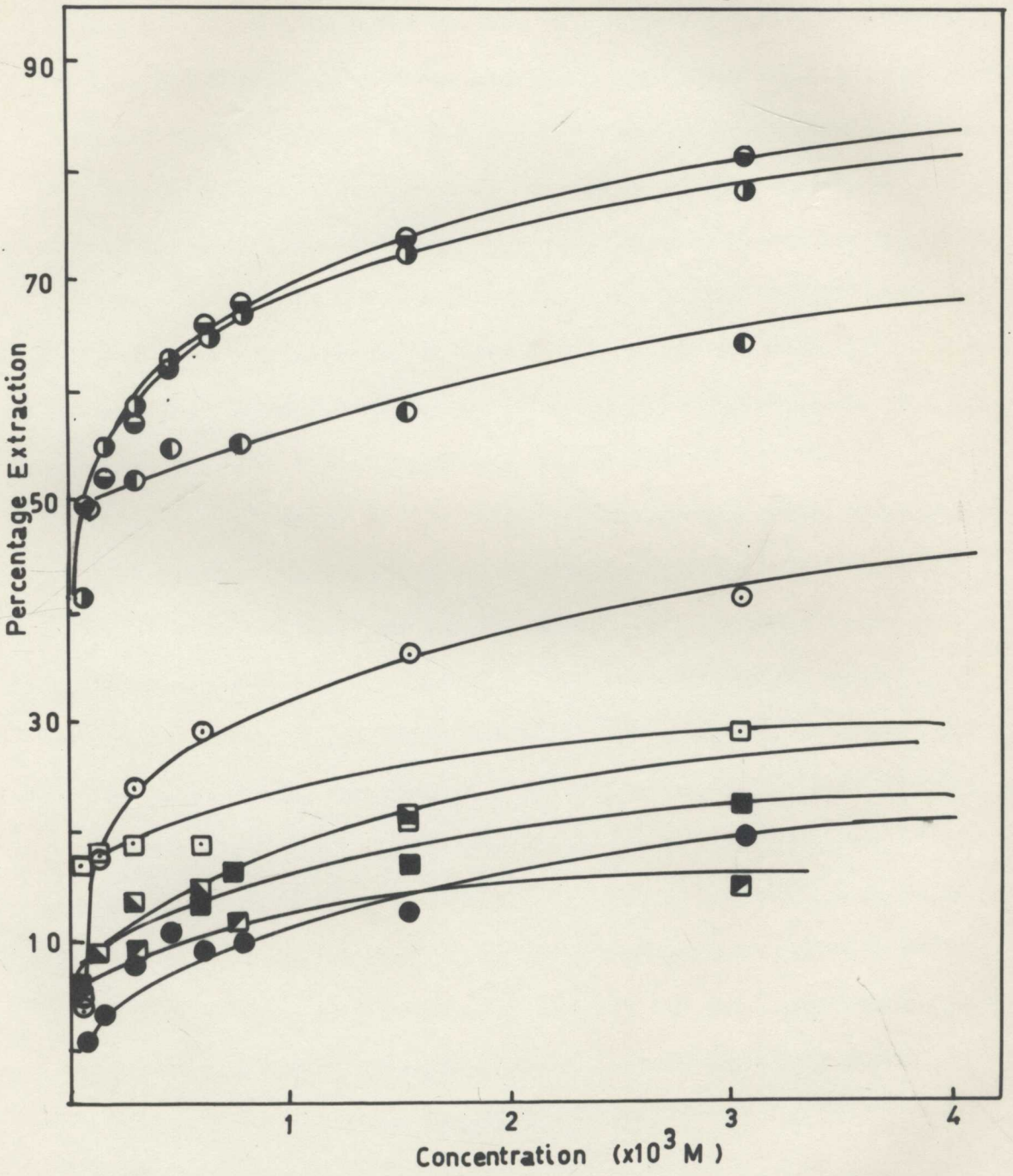
◹ 3-$BrCH_2BzPh_3PBr$ into dichloromethane

■ 4-$BrCH_2BzPh_3PBr$ into dichloromethane

● 4-$BrCH_2BzPh_3PBr$ into chloroform

◪ 4-$BrCH_2BzPh_3PBr$ into 1,2-dichloroethane

Data from Tables 19, 20 and 21.


90
70
50
30
10
Percentage Extraction
1
2
3
4
Concentration (x10^3 M)

inaccessible to the surrounding water molecules and so is probably not hydrated. The values of the distribution ratios agree with this conclusion; the values in chloroform, dichloromethane and 1,2-dichloroethane at an initial aqueous concentration of 4.6×10^{-3}M are 5.1, 4.6 and 2.2 respectively while the values of the distribution ratio for triphenyl-n-amylphosphonium bromide in the same three solvents at roughly comparable concentrations are 1.7, 2.3 and 0.79 respectively. The higher distribution ratios for 2-bromomethylbenzyltriphenylphosphonium cation would be expected for a larger cation provided the larger cation does not have a larger hydration energy (see Section 5.2). Models show that the hydration of 3-bromomethylbenzyltriphenylphosphonium and 4-bromomethylbenzyltriphenylphosphonium cations should be approximately equal as the two bromomethyl groups are equally accessible to water molecules. One would therefore expect that the distribution of these two salts would be very similar. In dichloromethane the distribution ratios are indeed very similar (see Table 21). In the other two solvents, however, the distribution ratios of 3-bromomethylbenzyltriphenylphosphonium bromide are larger than those of 4-bromomethylbenzyltriphenylphosphonium bromide (Tables 19 and 20) and this differencemay be attributed to differences in the solvation energy of these cations in the organic solvent.

The theory presented in Section 3.3 predicts that if quaternary salts exist in the organic phase as ion pairs then their distribution ratios will be proportional to the square root of the initial concentration of the quaternary salt in the aqueous phase.

In Fig. 12 the logarithm of the distribution ratios of a number of salts extracting into chloroform is plotted against the logarithm of the initial concentration of the quaternary salts in the aqueous phase. The results for triphenyl-n-amylphosphonium iodide, triphenylmethylarsonium iodide and triphenylmethylarsonium nitrate at high concentrations fall on a straight line of slope 0.50 ± 0.05 in very good agreement with theory; at low concentrations the distribution ratio is higher than the value predicted by this linear relationship, indicating that dissociation of the ion pairs is occurring. The concentration in chloroform at which this dissociation first affects the distribution ratios of these three salts is in the range 5×10^{-5}M to 10^{-4}M. Dissociation of the ion pairs of triphenylmethylarsonium chloride in chloroform below 10^{-4}M was shown to affect the distribution ratios of this salt in Section 4.2.

The results of the distribution of $Ph_3MeAsClO_4$ between water and chloroform fall on a straight line of slope 0.57, also in good agreement with theory. The results for $Ph_3MeAsCl$ and $Ph_3MeAsBr$ do not fall on a straight line and this is probably due to the very low concentration of these salts in chloroform. The concentration was less than 10^{-4}M even at the highest initial aqueous concentrations shown in Figure 12 and dissociation of the ion pairs is probably still important. The results in Section 4.2 indicate that at higher concentrations of $Ph_3MeAsCl$ in chloroform, this salt does exist in chloroform as ion pairs.

The results for $Ph_3MeAsClO_4$ in four different solvents are presented in Figure 13. It can be seen that the results fall on

Figure 12

Distribution of quaternary salts over a range of concentration.

Distribution between chloroform and water

Plot of Log D against the logarithm of the initial concentration of the quaternary salt in the aqueous phase.

Temperature 25°C

Figure 12

- Ph_3AmPI
- $Ph_3MeAsClO_4$
- Ph_3MeAsI
- $Ph_3MeAsNO_3$
- $Ph_3MeAsBr$
- $Ph_3MeAsCl$

Data from Tables 10, 11, 12, 13, 14 and 15.

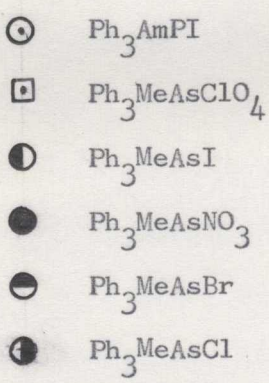
Figure 12

Distribution of quaternary salts over a range of concentration.

Distribution between chloroform and water

Plot of Log D against the logarithm of the initial concentration of the quaternary salt in the aqueous phase.

Temperature 25°C



Data from Tables 10, 11, 12, 13, 14 and 15.

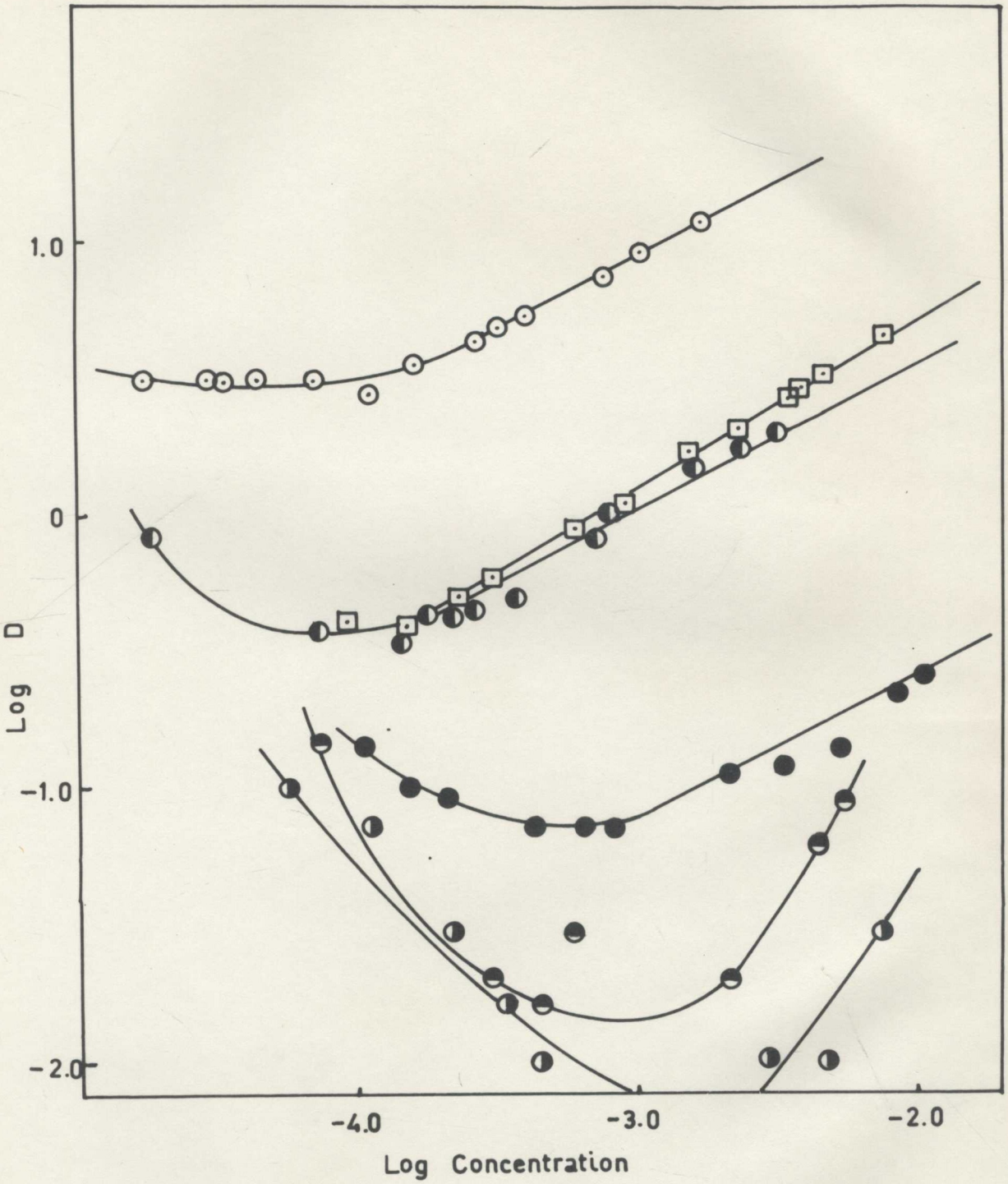

1.0
0
-1.0
-2.0
Log D
-4.0
-3.0
-2.0
Log Concentration

Figure 13

Distribution of quaternary salts over a range of concentration.

Distribution of $Ph_3MeAsClO_4$ between chloroform, dichloromethane, 1,2-dichloroethane, 2,2'-dichlorodiethylether and water.

Plot of log D against the logarithm of the initial concentration of the quaternary salt in the aqueous phase.

○ $(C_2H_4Cl)_2O$ at 25°

⊖ $C_2H_4Cl_2$ at 25°

● CH_2Cl_2 at 25°

◐ CH_2Cl_2 at 35°

◑ $CHCl_3$ at 25°

Data taken from Tables 13, 22, 23 and 24.

Figure 13

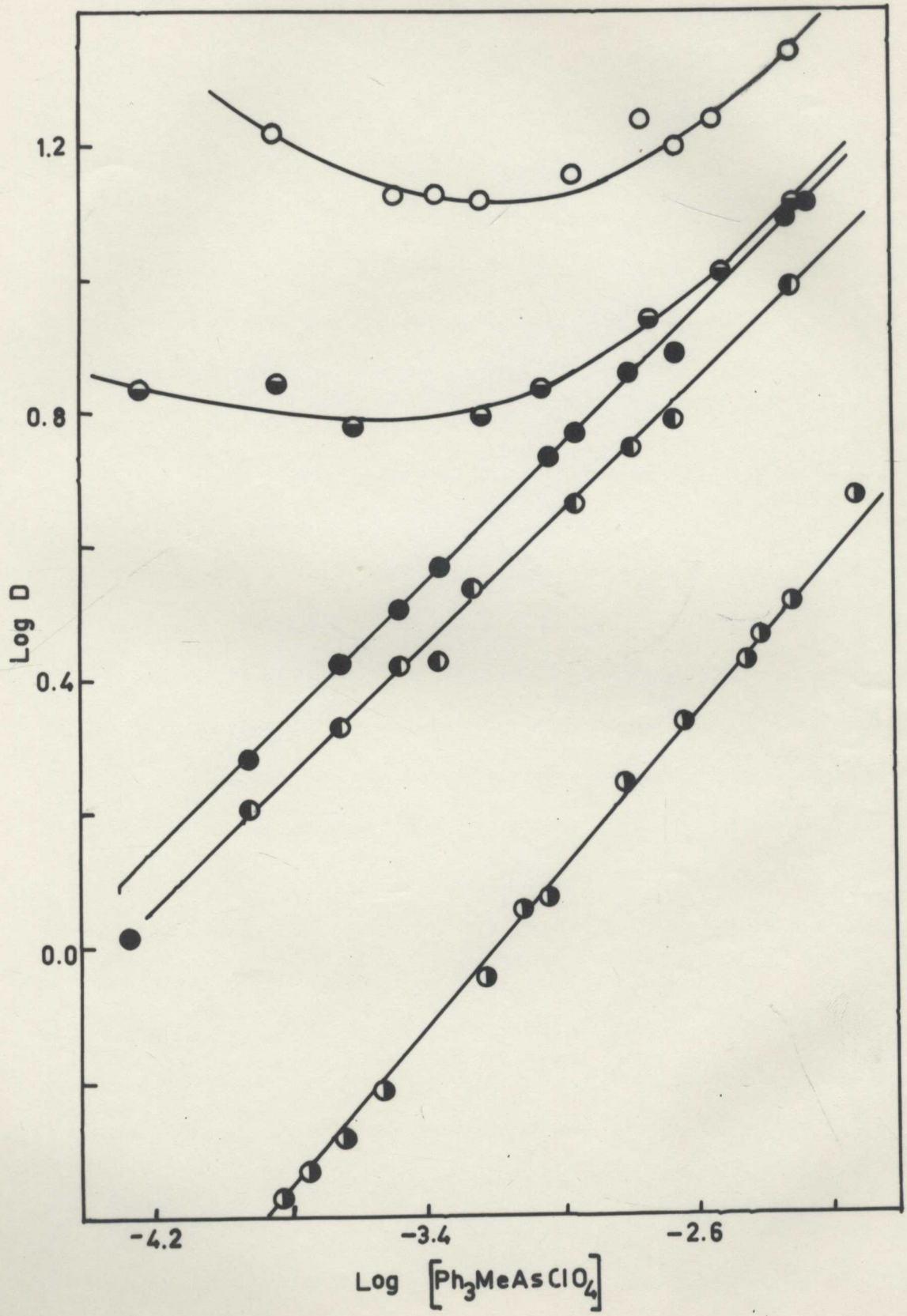
Distribution of quaternary salts over a range of concentration.

Distribution of $Ph_3MeAsClO_4$ between chloroform, dichloromethane, 1,2-dichloroethane, 2,2'-dichlorodiethylether and water.

Plot of log D against the logarithm of the initial concentration of the quaternary salt in the aqueous phase.

○	$(C_2H_4Cl)_2O$	at 25°
◒	$C_2H_4Cl_2$	at 25°
●	CH_2Cl_2	at 25°
◐	CH_2Cl_2	at 35°
◑	$CHCl_3$	at 25°

Data taken from Tables 13, 22, 23 and 24.


1.2
0.8
0.4
0.0
Log D
-4.2
-3.4
-2.6
Log [Ph3MeAsClO4]

a straight line with a slope of 0.57 for chloroform and of 0.5 for dichloromethane at both 25° and 35°. The results for 1,2-dichloroethane and 2,2'-dichlorodiethylether do not fall on a straight line, but appear to be approaching a linear relationship with a slope of 0.5 at higher concentrations. As the dielectric constant of the organic solvent is raised, dissociation of ion pairs will occur at higher concentrations of the quaternary salt in the organic phase.

In 2,2'-dichlorodiethylether dissociation of the ion pairs of $Ph_3MeAsClO_4$ affects the distribution ratio below a concentration of about 1.5×10^{-3}M whereas in 1,2-dichloroethane dissociation becomes significant below 10^{-3}M. Dissociation of the ion pairs of this salt in chloroform and dichloromethane does not become significant until the concentration is lower than 10^{-4}M. The large difference in the behaviour of dichloromethane ($\epsilon = 9.1$) and 1,2-dichloroethane ($\epsilon = 10.4$) is surprising in view of the small difference in their dielectric constants. The differences in the extraction behaviour of various solvents is discussed more fully in Section 5.3.

The results that have been presented so far in Section 4 provide good evidence that the quaternary salt exists in the organic solvent as either an ion pair or as dissociated ions. The dissociation of ion pairs in an organic solvent is favoured by low concentrations of the quaternary salt in the organic solvent and by high dielectric constant of the organic solvent. There is no evidence,

from the results presented here, for the formation of higher aggregates up to concentrations of about 7×10^{-3}M in any of the solvents studied.

Tribalat (25) in her study of the extraction of tetraphenylphosphonium chloride into chloroform over a range of concentration from 5×10^{-3}M to about 1M found that dimerisation of the ion pairs occurred in the organic phase when the concentration of this salt was about 2×10^{-3}M. No further polymerisation of the ion pairs was observed up to concentrations of about 0.4M. Evidence on the aggregation of amine salts in organic solvents suggests that for the solvents and in the concentration range considered in this work, ion pairs are the only species present in solution (56) (58) (59).

Only one salt was measured in this work at an initial aqueous concentration greater than 10^{-2}M. The distribution ratio of $Ph_3MeAsBr$ was measured at a total concentration of about 0.09M in order to check that the method of measuring the distribution ratio was valid (See Section 7.4). The concentration of $Ph_3MeAsBr$ in chloroform under these conditions was about 5×10^{-2}M. The results for the distribution of $Ph_3MeAsBr$ and $Ph_3MeAsCl$ between chloroform and water presented in Fig. 12 do not lie on a straight line of slope 0.5 and this was attributed earlier in this section to the fact that the concentration of the quaternary salt in the organic phase was low, and that dissociation of the ion pairs was still important. If, however, a straight line is drawn on a

plot of log D vs log initial aqueous concentration of the quaternary salt between the points for initial concentrations equal to 0.09M and 0.0055M a slope of 0.55 is observed indicating that over this concentration range ion pairs are probably the only important species present in the organic phase. This plot has not been reproduced in this thesis.

SECTION 5

FACTORS INFLUENCING THE EXTRACTION OF QUATERNARY SALTS FROM AQUEOUS SOLUTIONS INTO ORGANIC SOLVENTS

Section 5.1 Introduction

The distribution behaviour of some fourteen cations with eighteen different anions has been investigated at a quaternary salt concentration initially in the aqueous phase of 5×10^{-3}M. This concentration was chosen for three reasons. It was the maximum concentration at which the concentration of most of the cations could be measured spectrophotometrically without having to dilute the solution; it was also a concentration at which the percentage extraction of the quaternary salt did not change rapidly with concentration (see Figures 8 and 9). The evidence presented in Section 4 suggests that unless the distribution ratio of the quaternary salt in the organic solvent is very small, then at this concentration the quaternary salts exist in the four organic solvents studied as ion pairs and that dissociation or association of the ion pairs is not important. Association and dissociation in the organic solvent have been shown to affect the distribution ratios and in order that valid comparisons between the various salts can be made it is preferable that these effects are absent.

The aqueous phase was kept at a constant ionic strength by the addition of sodium sulphate to the aqueous solution. This salt was chosen because earlier studies had shown that the sulphate anion is not extracted by Ph_4P^+ or Ph_4As^+ (28) (29). The effect of varying ionic strength on the distribution between chloroform and water of salts of the Ph_3MeAs^+ cation was investigated and the results are presented in Table 27. It was found that if the

ionic strength was 0.02, 0.1 or 0.5 there was no significant difference in the distribution ratios of the various salts. If saturated sodium sulphate solution was used as the aqueous phase, then a large increase in the distribution ratio of the various salts is observed. It was also found that some of the cation was extracted when the only anion present was sulphate and that the amount of cation extracted was quite high from saturated sodium sulphate solution. All the other results to be discussed in this Section were obtained from an aqueous phase whose ionic strength was 0.1 and the results have been corrected for the small amount of sulphate extracted (see Section 7.3).

The organic solvents which were used cover a wide range of dielectric constant and the effect of the various solvents on the distribution ratios is discussed in Section 5.3. Attempts to study the distribution of quaternary salts by the spectrophotometric method into solvents such as nitrobenzene, toluene or benzene were unsuccessful because of the absorption of the organic solvent in the spectral region where the concentration of the cation was measured.

The results of the distribution studies are presented in Tables 28 to 31; those anions and cations which were not extracted are not given in the Tables. The following anions did not extract under the conditions used into any of the solvents with any of the cations studied; sulphate, sulphite, fluoride, iodate, dihydrogen phosphate, hydroxide, thiosulphate, acetate, oxalate and carbonate. The benzyltriethylammonium, trimethylphenylarsonium

and trimethylphenylammonium cations did not extract any of the anions studied into chloroform at the concentrations used. The largest cation studied, benzylhexadecyldimethylammonium was found to be completely extracted into chloroform from sodium sulphate solution and so no comparison between the different anions could be made. This cation was the only cation which was found to extract into carbon tetrachloride with any of the anions studied. Unfortunately due to the insolubility of the salts of this large cation in water the distribution could not be measured at a concentration of 5×10^{-3}M and so a concentration of about 2×10^{-3}M was used. The results were rather difficult to measure because of the formation of emulsions and the insolubility of some of the salts in both phases. The results indicate that qualitatively the order of extraction into CCl_4 is the same as the order observed with the other solvents (Section 5.4).

The insolubility of the salts Ph_4AsClO_4 and Ph_4PClO_4 in both water and chloroform at a concentration of 5×10^{-3}M prevented the determination of the distribution ratio of these salts. The reported solubilities of Ph_4AsClO_4 in chloroform (32) and water (65) confirm that Ph_4AsClO_4 is indeed insoluble at this concentration.

Section 5.2 The effect of cation size on the distribution ratio

The results presented in Tables 28 to 31 show that for a given anion the distribution ratio depends on the size of the cation; the larger the cation the greater the extraction. Two reasons for this increase have been discussed by Agarwal and Diamond (79), one is that large hydrophobic cations interfere with the hydrogen bonded structure of water and so tend to be ejected from the water into the less structured organic solvent. The larger the cation the greater is the interference to the water structure and so the greater the extraction. The other reason is due primarily to ion-solvent interaction; the electrostatic free energy opposing the transfer of an ion from water to an organic solvent of low dielectric constant will be less the larger the ion. This can be seen most simply from the Born charging expression for the electrostatic free energy of transfer of univalent ions of radius r_+ and r_- from water to an organic solvent.

$$F_{elect} = -\frac{e^2}{2}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)\left(\frac{1}{\epsilon_w} - \frac{1}{\epsilon_o}\right)$$

where e is the electronic charge and ϵ_w and ϵ_o are the dielectric constants of water and the organic solvent respectively. The larger the r_+ radius the smaller the positive value of F_{elect} and the greater the tendency for the ion to be extracted.

In the series Ph_3MeP^+, Ph_3EtP^+, $Ph_3n\text{-}PrP^+$ and Ph_3AmP^+ the value of the distribution ratio increases in general by a factor of about two for each additional CH_2 group in the alkyl chain. This is illustrated in Figures 14 and 15 where the logarithm of the distribution ratio is plotted as a function of the length of the alkyl group for the

Figure 14

Distribution of triphenyl-n-alkylphosphonium salts between chloroform and water.

Plot of log D as a function of the alkyl group.

Initial concentration of salts

in aqueous phase = 5×10^{-3} M

Temperature 25°C

○ Perchlorate salts

◐ Thiocyanate salts

⊖ Iodide salts

● Chlorate salts

■ Nitrate salts

▣ Bromide salts

□ Bromate salts

◪ Chloride salts

Data taken from Table 28.

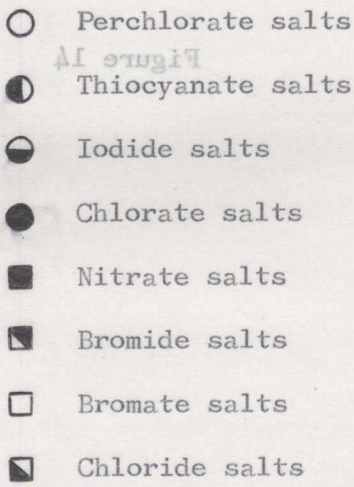
Figure 14

Distribution of triphenyl-n-alkylphosphonium salts between chloroform and water.

Plot of log D as a function of the alkyl group.

Initial concentration of salts in aqueous phase = 5×10^{-3} M

Temperature 25°C



Data taken from Table 28.

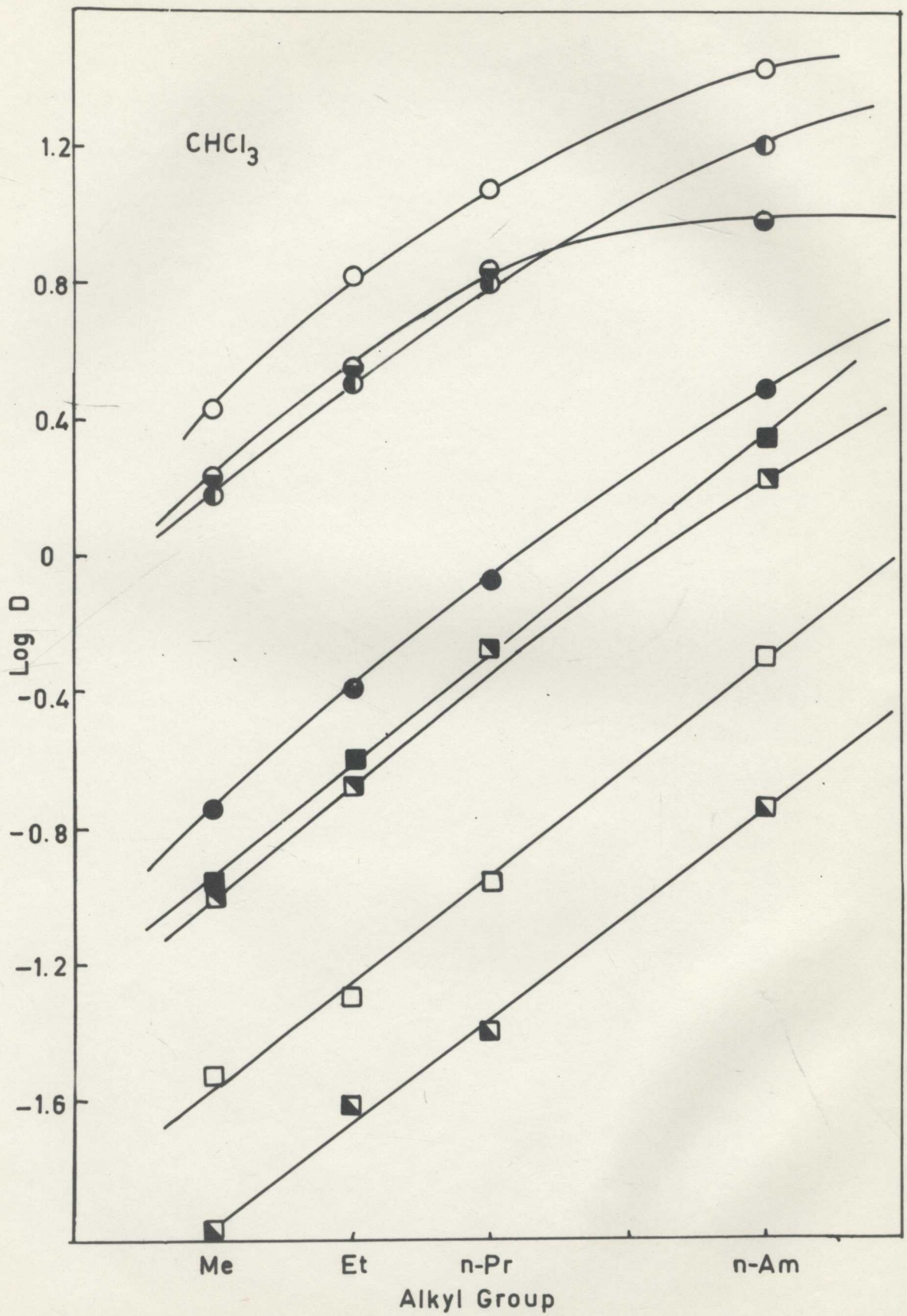

CHCl3
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
Log D
Me
Et
n-Pr
n-Am
Alkyl Group

Figure 15

Figure 15

Distribution of triphenyl-n-alkylphosphonium salts between 1,2-dichloroethane and water.

Plot of log D as a function of the alkyl group.

Initial concentration of salts in aqueous phase = 5×10^{-3}M

Temperature 25°C

○ Perchlorate salts

◐ Thiocyanate salts

◒ Iodide salts

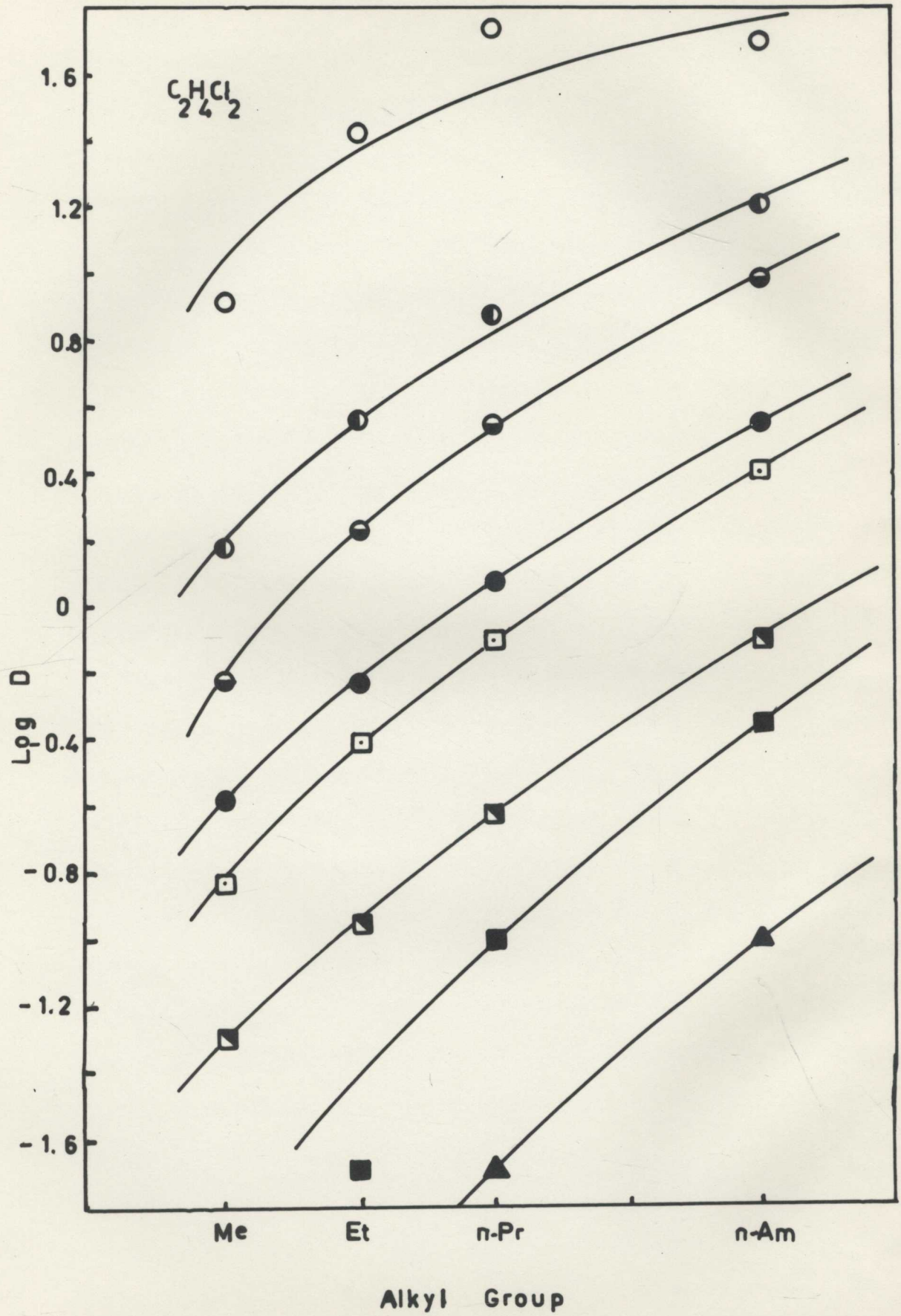
● Chlorate Salts

⊡ Nitrate salts

◪ Bromide salts

■ Bromate salts

▲ Chloride salts


$C_2H_2Cl_4$
1.6
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
Log D
Me
Et
n-Pr
n-Am
Alkyl Group

distributions between chloroform and 1,2-dichloroethane and aqueous solution. Similar figures are obtained with the other solvents. These results are in fair agreement with those of Collander (80), Agarwal and Diamond (79) and Senise (10). Collander (80) found a factor of between 2 and 4 per additional CH_2 group for the extraction of a wide variety of organic species from water into diethylether. Agarwal and Diamond (79) found a factor of about 100 as the difference in the distribution ratios of tetrahexylammonium and tetrapentylammonium hydroxides distributing between water and a solution of alcohols in benzene i.e. a factor of about 3 per CH_2 group. The results for the extraction of tetrabutylammonium and tetrapropylammonium hydroxides into dilute solutions of alcohols in nitrobenzene indicated a factor of about 2 per CH_2 group. Senise (10) has studied the distribution of triphenyl-n-alkylphosphonium tetrathiocyanato metal complexes between water and benzene, toluene, ethylbenzene, cyclohexane or cyclohexene when the n-alkyl group was varied from methyl to n-octadecyl. Senise does not report the increase per CH_2 group, but found that with seven carbon atoms in the alkyl chain a high value of the distribution ratio was reached which then remained constant or decreased slightly with further increases in the alkyl chain length. This effect may also be seen in Figs 14 and 15 where for the perchlorate, thiocyanate and iodide ions which have high distribution ratios, the rate of increase per CH_2 group decreases as the alkyl chain length increases.

Distribution ratios for salts of the Ph_4P^+ and Ph_4As^+ cations between water and chloroform have been reported previously by Bock et al. (28) (29). These workers studied the distribution of the anion at a 2:1

ratio of cation to anion concentration. The results presented in Table 28 are for a 1:1 ratio of cation to anion concentration, and the values of the distribution ratio are lower than those reported by Bock, as is to be expected under these conditions. The distribution ratios for salts of the cations Ph_4As^+ and Ph_4P^+ reported in Table 28 are identical within experimental error, indicating very little difference due to the difference in size between these two cations (see page 76). The results reported by Bock et al. (28) (29) and Morris and Orenberg (81) also indicate that there is very little difference between these two cations. Tribalat (26) has reported the distribution ratios of Ph_4AsCl and Ph_4PCl between $CHCl_3$ and water to be 200 and 25 respectively, and these figures have been quoted as indicating the effect of ion size on the distribution ratio (1). These figures were obtained from measurements of the solubility of these salts in water and chloroform and would only be identical to the distribution ratios if the system were ideal.

Whilst no significant differences in the distribution ratios were observed for Ph_4As^+ and Ph_4P^+ salts, slight but significant differences were observed for the salts of the Ph_3MeAs^+ and Ph_3MeP^+ cations (Tables 28 to 31). In all four solvents studied, the phosphonium salts had the smaller distribution ratios. Similar differences, which may be due to the effect of cation size, are observed between the salts of $Ph_3n\text{-}PrP^+$ and Ph_3AllP^+ where, because of the smaller size of the allyl group $CH_2 = CH - CH_2$ - compared to the propyl group $CH_3 - CH_2 - CH_2$ -, the distribution ratios of the salts of the Ph_3AllP^+ cation are always smaller than those of the

salts of the $Ph_3n\text{-}PrP^+$ cation. The effect seems however to be much larger than would be expected for the small difference in size of these two cations and the increased hydration of the Ph_3AllP^+ cation compared to the $Ph_3n\text{-}PrP^+$ cation due to the presence of the double bond is probably the most important effect. This dependence of the distribution ratio on the hydration energy of the cation has been discussed previously in Section 4. The actual increase in the hydration energy of the cation necessary to explain the magnitude of the observed effect is quite small. This is discussed more fully in Section 6.2.

In order to gain a more quantitative insight into the effect of cation size on the distribution ratio the approximate radii of some of the cations have been calculated. Large quaternary cations have been assumed by some workers to be spherical but as Grunwald et al. (82) have pointed out, they are far from symmetrical and these workers have taken the radius of the tetraphenylphosphonium cation to be the harmonic mean of the shortest and longest distances from the centre to the outer surface of the ion. The value which they calculated was 4.2Å. In the treatment given below, a different procedure has been adopted, the calculated radii are the maximum radii, i.e. for the Ph_4P^+ cation the radius is taken to be the distance from the centre of the ion to the extremity of the phenyl groups. A tetrahedral distribution of the groups around the central atom and a hard sphere model for the ion were assumed. The radii were calculated assuming bond lengths which were quoted by Sutton (83)

Table 5.2.1

Bond lengths used to calculate the radii of the cations

Bond	Bond Length
P-C	1.87Å
As-C	1.98Å
C-C (in benzene)	1.40Å
C-H (in benzene)	1.08Å
C-H (in methane)	1.09Å
van der Waals radius of H	1.20Å
van der Waals radius of CH_3	2.00Å

The radii of the unsymmetrical compounds, e.g. Ph_3AmP^+ have been calculated using a weighed average of the symmetrical compounds. The contribution to the radius of the n-alkyl groups has been calculated by taking the radii of the tetra-n-alkylammonium ions as calculated by Robinson and Stokes (84) and correcting for the differences in the alkyl chain length due to the replacement of N by P or As.

The calculated radii are given in Table 5.2.2.

Table 5.2.2

Calculated Radii of Quaternary Cations

Cation	Radius
Ph_4As^+	7.0Å
Ph_4P^+	6.9Å
Ph_3AmP^+	6.6Å
$Ph_3n\text{-}PrP^+$	6.4Å
$Ph_3iso\text{-}PrP^+$	6.35Å
Ph_3EtP^+	6.3Å
Ph_3AllP^+	6.2Å
Ph_3MeAs^+	6.25Å
Ph_3MeP^+	6.15Å
$Ph_2Me_2As^+$	5.5Å
$PhMe_3As^+$	4.75Å

The influence of cation size for a number of different salts in four different solvents may be seen in Fig. 16 where the logarithm of the distribution ratios is plotted against the reciprocal of the cation radius calculated above. For all the cations except Ph_4As^+ and Ph_4P^+, i.e. the most symmetrical cations, there is an approximately linear relationship between the logarithm of the distributionratio and the reciprocal of the radius. Similar relationships are observed with all the other anions in all the solvents. This relationship between the reciprocal of the radius of the ion and the logarithm of the distribution ratio of the salt was first observed by Guymer (85) in her study of the extraction of permanganate by quaternary arsonium cations.

The distribution behaviour of the triphenyl-n-propylphosphonium and triphenyl-iso-propylphosphonium cations call for some detailed comment. Senise (10) (86) (87) has reported remarkable differences in the extraction of a number of metal complexes using these cations (See Section 2.1). The results (presented in Tables 28 to 31) for the extraction of the salts of these cations are therefore of special interest. The results obtained indicate that thereis a difference in the extraction behaviour of the two cations, but the effect is much smaller than that reported by Senise for the metal complex salts. The larger cation $Ph_3n\text{-}PrP^+$ is expected to extract anions better than $Ph_3iso\text{-}PrP^+$ and this is indeed observed for extraction into dichloromethane, 1,2-dichloroethane and 2,2'-dichloro-diethylether. However, the distribution ratios for triphenyl-iso-propylphosphonium salts between chloroform and water are greater than

Figure 16

Distribution of quaternary salts as a function of the size of the cation.

Plot of log D against the reciprocal of the cation radius.

Temperature 25°

⊙ Perchlorate salts into 2,2'-dichlorodiethylether

⊡ Iodide salts into 1,2-dichloroethane

◐ Nitrate salts into chloroform

◪ Bromate salts into dichloromethane

Data taken from Tables 28, 29, 30, 31 and 5.2.2.

Figure 16

Distribution of quaternary salts as a function of the size of the cation.

Plot of log D against the reciprocal of the cation radius.

Temperature 25°

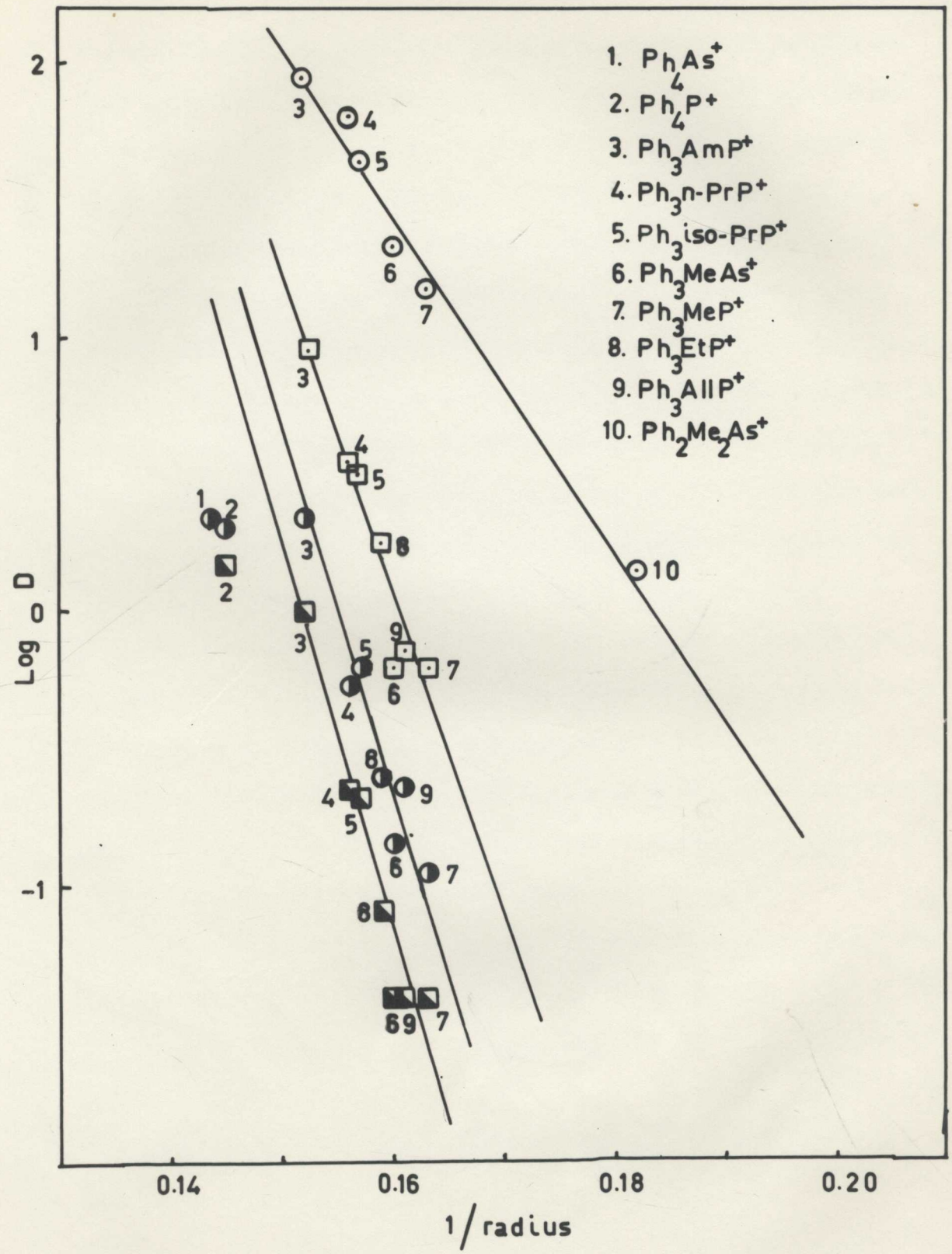
⊙ Perchlorate salts into 2,2'-dichlorodiethylether

⊡ Iodide salts into 1,2-dichloroethane

◑ Nitrate salts into chloroform

◪ Bromate salts into dichloromethane

Data taken from Tables 28, 29, 30, 31 and 5.2.2.


1. Ph_4As^+
2. Ph_4P^+
3. Ph_3AmP^+
4. $Ph_3n\text{-}PrP^+$
5. $Ph_3iso\text{-}PrP^+$
6. Ph_3MeAs^+
7. Ph_3MeP^+
8. Ph_3EtP^+
9. Ph_3AllP^+
10. $Ph_2Me_2As^+$
Log D
1/radius
2
1
0
-1
0.14
0.16
0.18
0.20

the distribution ratios of the triphenyl-n-propylphosphonium salts (see Table 28). This increase in the extraction of the $Ph_3iso\text{-}PrP^+$ salts must be due to the increased solvation of ion pairs of the $Ph_3iso\text{-}PrP^+$ cation in chloroform.

The effect of substitution on the benzyl group has been discussed in Section 4.5 in relation to the distribution of 2-bromomethyl-, 3-bromomethyl-, and 4-bromomethyl-benzyltriphenylphosphonium bromides over a range of concentration. Unfortunately it was not possible to study the distribution of salts of these cations other than the bromides, as attempts to convert the bromide to the sulphate resulted in the decomposition of the cation. The decomposition product was not isolated in a pure state but an impure sample showed a strong absorption in its infrared spectrum which was in thefrequency range expected for a P = O bond. The decomposition of quaternary phosphonium salts in alkaline solution to give phosphine oxides is a reaction which has been investigated recently (88). Such decomposition was not observed in this work with the other phosphonium cations but it has been found that benzyl groups are eliminated from quaternary phosphonium compounds more readily than any other groups (88 and references therein).

Section 5.3 The effect of different solvents on the distribution ratio

It has been reported that the extraction of quaternary salts into different solvents decreased with decreasing dielectric constant of the organic solvent (31), (36). The five solvents carbon tetrachloride, chloroform, dichloromethane, 1,2-dichloroethane and 2,2'-dichlorodiethyl-ether used in this work cover a wide range of dielectric constant and therefore of expected extraction behaviour. The solvent with the lowest dielectric constant, carbon tetrachloride ($\epsilon = 2.2$), did not extract any salt of the cations in Table 28. The only cation studied which was extracted into carbon tetrachloride was the benzyl-hexadecyldimethylammonium cation. The behaviour of this cation was discussed in Section 5.1.

The distribution ratios of the salts of the Ph_3AmP^+ cation between the other organic solvents and aqueous solution are presented below in Table 5.3.1. The figures have been taken from Tables 28 to 31 for ease of comparison.

Table 5.3.1.
Distribution ratios of salts of Ph_3AmP^+

Anion	Solvent			
	$CHCl_3$ $\epsilon = 4.8$	CH_2Cl_2 $\epsilon = 9.1$	$C_2H_4Cl_2$ $\epsilon = 10.4$	$(C_2H_4Cl)_2O$ $\epsilon = 21.2$
ClO_4^-	27	70	50	90
NCS^-	16	40	16	4.7
I^-	9.5	8.5	9.5	6.8
ClO_3^-	3.0	5.6	3.5	4.0
NO_3^-	2.2	4.6	2.5	3.1
Br^-	1.7	2.3	0.79	0.85
BrO_3^-	0.51	1.0	0.44	0.64
Cl^-	0.18	0.22	0.08	0.17

The inspection of the figures in the above Table discloses very little correlation between the distribution ratio and the dielectric constant of the organic solvent. The results for the halide and thiocyanate salts in particular are anomalous, the distribution ratios for chloroform, the solvent with the lowest dielectric constant being larger than the distribution ratios for 2,2'-dichlorodiethylether, the solvent with the highest dielectric constant. The use of bulk dielectric constants as a measure of the interactions between the solvent and ionic solutes may be criticized in that the properties of the bulk liquid are unlikely to be the properties of the molecules of the liquid under the influence of the strong electric field around an ion. Recently, however, it has been pointed out that the microscopic dielectric constant around large ions with a low surface charge density is probably close to the bulk dielectric constant of the solvent (82) (89).

Intermolecular forces between the solute and solvent would include coulombic, directional, inductive, dispersion, charge-transfer as well as hydrogen bonding forces and so it is unlikely that any single property of the bulk solvent will explain its solvating properties. However, a number of experimental measures of microscopic solvent polarity are available; these have been derived by working backwards from the effect of the solvent on a solvent-dependent standard process (90).

The parameter which seems to be the most applicable in the present study has been derived from the position of the charge transfer absorption band of 1-alkylpyridinium salts in various solvents. This parameter, the Z-value of the solvent, is the molar transition

energy calculated from the position of the charge transfer absorption maximum of these salts in the solvent (91). However, a more comprehensive solvent polarity scale, the E_T-values, has been developed from the molar transition energies of the solvatochromic band of pyridinium N-phenolbetaines in the various solvents. As the agreement between the Z-values and E_T-values is good, the comparison between the solvents will be discussed in terms of E_T-values. The E_T-values quoted by Reichardt (90) vary from 63.1 kcal/mole for water down to 30.9 kcal/mole for n-hexane. The values for 1,2-dichloroethane, dichloromethane, chloroform and carbon tetrachloride are 41.9, 41.1, 39.1 and 32.5 kcals/mole respectively. Unfortunately the E_T-values of 2,2'-dichlorodiethylether does not seem to have been measured. If these E_T-values are accepted as a measure of the solvating power of the quaternary salt ion pairs by these solvents, then the relatively small differences in the extracting power of the three solvents 1,2-dichloroethane, dichloromethane and chloroform are partly explained. Although the dielectric constant of chloroform is about one half that of 1,2-dichloroethane or dichloromethane, the E_T-values of the three solvents are almost identical. The exact order of extraction of the quaternary salts is not explained by E_T-values, indeed this order changes with different anions.

The distribution ratios of the quaternary salts in dichloromethane, at an initial concentration of 5×10^{-3}M are consistently higher than those in 1,2-dichloroethane even though the E_T-value of dichloromethane is slightly lower. The order of extraction at other concentrations may be different, particularly if dissociation of ion pairs is occurring in one solvent but not in the other (see figure 13). At an

initial concentration in the aqueous phase of 5×10^{-3}M, most of the salts studied exist as ion pairs in the organic solvent (Section 4) and comparisons between the various solvents should be valid at this concentration.

Smulek (36) has pointed out that ion pairs of quaternary salts in organic solvents have large dipole moments and that electrostatic dipole-dipole interactions are likely to be very important in the solvation of ion pairs. The greater extracting power of dichloromethane compared to 1,2-dichloroethane may therefore be attributed to the larger dipole moment of dichloromethane ($\mu = 1.54$) compared to 1,2-dichloroethane ($\mu = 1.19$). Dipole moments of the organic solvent fail to explain the high values of D observed for the halide and thiocyanate ion pairs in chloroform ($\mu = 1.21$) or the low values particularly for NCS^- observed with 2,2'-dichlorodiethyl-ether ($\mu = 2.4$).

The dipole moments of the ion pairs of a given salt may, however, vary with the organic solvent. It has been shown both by infrared (92) (93) and microwave studies (94) that chloroform molecules are capable of forming hydrogen bonds with proton acceptors, and that in fact they do so with the halide ions of quaternary ammonium halide ion pairs. Higuchi et al. (95) have studied the extraction of some pharmaceutical amines into chloroform and have calculated what they believe to be the number of chloroform molecules associated with each ion pair. The numbers range from 5 for Br^-, Cl^- and NO_3^- to 4 for I^- down to 2 for the picrate ion. A solid 1:1 adduct of triphenylmethylarsonium bromide with iodoform, which presumably involves a hydrogen bond between the iodoform molecule and bromide

ions, has been reported (96). Such hydrogen bonds would increase the solvation in the organic solvent and so would tend to increase the distribution ratio. This increase in solvation may be attributed to the fact that the hydrogen bond increases the charge separation, and so increases the dipole moment of the ion pair. The low values of D obtained in 2,2'-dichlorodiethylether particularly for the NCS^- ion, may be due to the absence of specific interactions between this solvent and the thiocyanate ion pairs. The effect of the solvent on the distribution ratio of quaternary salts is complicated and there does not seem to be any one property of the solvent which will explain the observed order of extraction of the anions. The dielectric constant of the solvent appears to be the most useful single property for predicting the likely distribution behaviour of large cations and large anions. In this case the microscopic dielectric constant of the solvent around the ion pairs is probably close to that of the bulk liquid, but it must be recognized that specific interactions between the solvent and the ion pairs, particularly with those ion pairs containing small anions, may have a profound influence on the distribution ratios.

Section 5.4 The effect of the nature of the anion on the distribution ratio

The order of extraction of the anions into the organic solvents was the same for all cations viz. $ClO_4^- > NCS^- > I^- > ClO_3^- > NO_3^- > Br^- > BrO_3^- > Cl^-$ with the exception that for some cations the orders for NO_3^- and Br^- and NCS^- and I^- were reversed (see Tables 28 to 31). The distribution ratios for the MnO_4^- anion with the cations Ph_4As^+, Ph_3MeAs^+, $Ph_2Me_2As^+$ and $PhMe_3As^+$ (85) indicated that this anion was extracted better than the perchlorate ion. No divalent anions were found to extract, and a number of monavalent anions e.g. F^- and acetate, also failed to extract. Krasnov et al. (18) from a study of the extraction of chloride, bromide, iodide, nitrate, perchlorate, thiocyanate and sulphate ions with three triphenylmethane dyes claimed that as a first approximation the values of the distribution ratio of the halide ions were determined by the radius of the anion. However, the effect of the nature of the anion could also be seen; for example the thiocyanate ion, whose reported radius (1.95Å) is equal to that of the bromide ion (1.96Å), extracted into organic solvents much better than did the bromide ion. This increase was attributed to the presence of a pair of electrons on the nitrogen which was capable of forming hydrogen bonds to solvent molecules. In the previous Section however, it was postulated that bromide ions may also be hydrogen bonded to solvent molecules. The assignment of meaningful radii to unsymmetrical ions like NCS^- or NO_3^- and the comparison of these radii to the radii of spherically symmetrical halide ions is a procedure which is open to some doubt.

The distribution ratios for the spherically symmetrical halide ions reported in Tables 28 to 31 all increase in the order $F^- < Cl^- < Br^- < I^-$, the order of increasing crystal radius. However, for the halate ions the order of increasing distribution ratio $IO_3^- < BrO_3^- < ClO_3^-$ is the opposite order to the order of increasing crystal radius. The values of the radii of the anions discussed here and other properties of the anions to be discussed below are collected together in Table 32. The values of the radii of the anions have been taken from those quoted by Nightingale (97). The Born charging expression (Section 5.2) assumes that the radii of the ions do not change with the nature of the solvent. This approximation is a good one for the large quaternary cations which are not hydrated in aqueous solution, but will not be as good for anions. In aqueous solution most anions are hydrated and the effective radii of the ions are increased, while in organic solvents the anions are probably not as strongly solvated and the effective radii of the ions are probably closer to the crystal radii. The hydration radii of a number of anions were reported by Nightingale (97) and they are also given in Table 32. If the distribution ratios are compared with the reported values of the hydrated radii no correlation is observed. Thus the values of both the crystal and hydrated radii do not explain the observed order of extraction of the anions.

It is a thermodynamic fact that the distribution coefficient is determined by the differences of the chemical potentials of the solute in the two phases. Diamond et al. (2) (19) (20) (21) (22)

in particular, have emphasised the importance of the change in the solvation energy of the solute on passing from the aqueous to the organic phase as the major factor governing the size of the distribution ratio. This approach has been used in Section 4 to explain the distribution behaviour of quaternary salts. In the aqueous phase the total hydration energy of quaternary salts which contain large hydrophobic cations will be dominated by the hydration energy of the anion unless the anion is also large and hydrophobic. The change in the solvation energy of the anion on passing from the aqueous solution into the organic solvent will therefore be the major factor controlling the extraction of the quaternary salt. Differences in the free energy of the extraction process are determined by differences in the enthalpy and not by differences in the entropy of the extraction process (18). The enthalpies of solvation of the anions in the organic solvents are not known, but it has been suggested that the enthalpies of solvation of anions in aprotic solvents are in the reverse order to the enthalpies of solvation in protic solvents (101). Anions which have the largest solvation energies in protic solvents like water have the smallest solvation energies in aprotic solvents like chloroform. Therefore the enthalpy of hydration of the anion should be the major factor in determining the distribution ratio of the quaternary salt.

In Figures 17 and 18 the percentage extraction of quaternary salts of Ph_3AmP^+ and Ph_3MeP^+ into the organic solvents chloroform, dichloromethane, 1,2-dichloroethane and 2,2'-dichlorodiethylether is plotted against the enthalpies of hydration of the anions.

Figure 17

Figure 17

Distribution of quaternary salts as a function of the enthalpy of hydration of the anion.

Percentage extraction of Ph_3AmP^+ salts plotted against the enthalpy of hydration of the anion.

Temperature 25°

⬡ Ph_3AmP^+ salts into 2,2'-dichlorodiethylether

● Ph_3AmP^+ salts into dichloromethane

■ Ph_3AmP^+ salts into 1,2-dichloroethane

◐ Ph_3AmP^+ salts into chloroform

Data taken from Tables 28, 29, 30, 31 and 32.

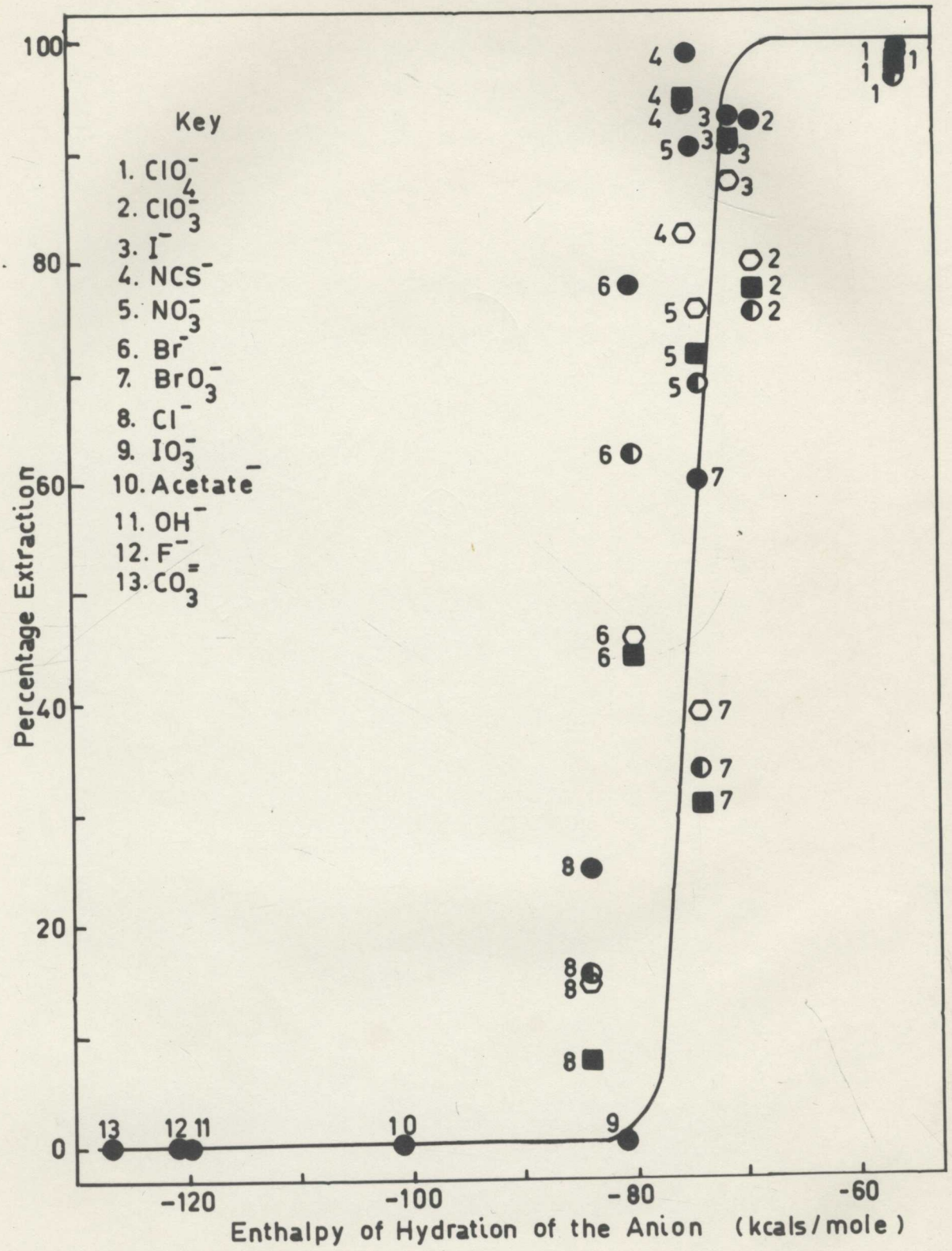

Key
1. ClO_4^-
2. ClO_3^-
3. I^-
4. NCS^-
5. NO_3^-
6. Br^-
7. BrO_3^-
8. Cl^-
9. IO_3^-
10. Acetate$^-$
11. OH^-
12. F^-
13. $CO_3^=$
Percentage Extraction
100
80
60
40
20
0
-120
-100
-80
-60
Enthalpy of Hydration of the Anion (kcals/mole)

Figure 18

Distribution of quaternary salts as a function of the enthalpy of hydration of the anion.

Percentage extraction of Ph_3MeP^+ salts plotted against the enthalpy of hydration of the anion.

Temperature 25°

- ⬡ Ph_3MeP^+ salts into 2,2'-dichlorodiethylether
- ● Ph_3MeP^+ salts into dichloromethane
- ■ Ph_3MeP^+ salts into 1,2-dichloroethane
- ◐ Ph_3MeP^+ salts into chloroform

Data taken from Tables 28, 29, 30, 31 and 32.

Figure 18

Distribution of quaternary salts as a function of the enthalpy of hydration of the anion.

Percentage extraction of Ph_3MeP^+ salts plotted against the enthalpy of hydration of the anion.

Temperature 25°

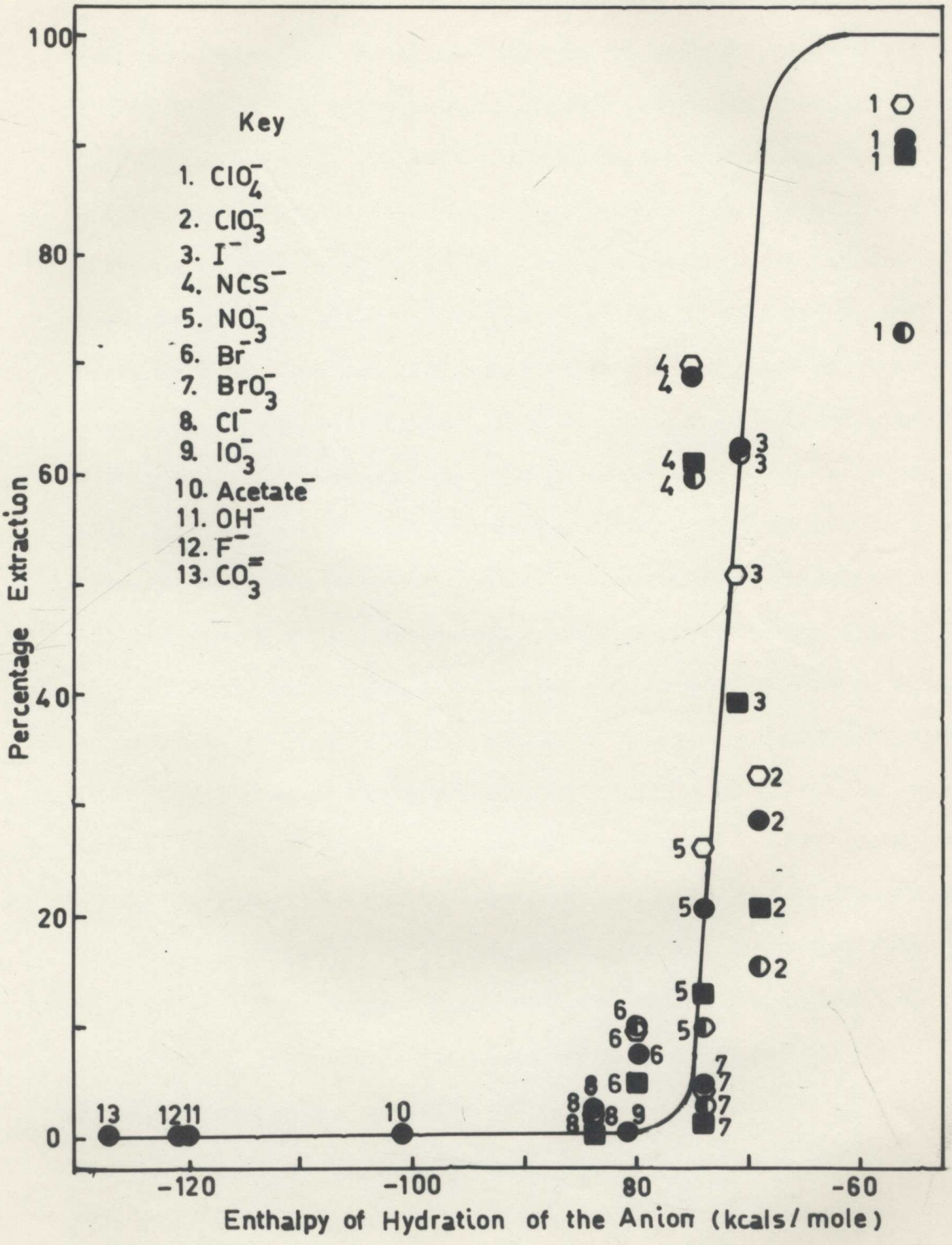
⬡ Ph_3MeP^+ salts into 2,2'-dichlorodiethylether

● Ph_3MeP^+ salts into dichloromethane

■ Ph_3MeP^+ salts into 1,2-dichloroethane

◐ Ph_3MeP^+ salts into chloroform

Data taken from Tables 28, 29, 30, 31 and 32.


Key
1. ClO_4^-
2. ClO_3^-
3. I^-
4. NCS^-
5. NO_3^-
6. Br^-
7. BrO_3^-
8. Cl^-
9. IO_3^-
10. Acetate$^-$
11. OH^-
12. F^-
13. $CO_3^=$
Percentage Extraction
100
80
60
40
20
0
-120
-100
80
-60
Enthalpy of Hydration of the Anion (kcals/mole)

The shape of the curve drawn in Figures 17 and 18 has been calculated from the equation of Ionin and Kurina (23) by assuming that the change in entropy of the extraction process and the enthalpies of solvation in the organic phase are the same for all the salts and that the activites of the salts in both phases are equal, that is, by assuming the distribution ratio is determined solely by changes in the enthalpies of hydration of the anion. The curve was then moved along the x axis until it gave the line of best fit through the experimental points. The equation derived by Ionin and Kurina (23) is discussed more fully in Section 6.2. The values for the enthalpies of hydration of the anion used in Figures 17 and 18 and recorded in Table 32 have been taken from a number of sources. The values for fluoride, chloride, bromide, iodide, hydroxide and perchlorate have been taken from those quoted by Halliwell and Nyburg (98). The values for the iodate and bromate ions are those quoted by Yatsimirskii (99) while all of the other values are taken from those given by Vasil'ev et al. (100).

It can be seen that there is a strong correlation between the percentage extraction and the enthalpies of hydration of the anion. The correlation is not exact and indeed it would not be expected to be exact. The accuracy with which the enthalpies of hydration of the anions are known is not high; it is probably not better than $\pm$ 5 kcals/mole. We have also assumed that the solvation energies of the anions in the organic solvent are identical and this may be quite a poor approximation. Increased solvation energies of halide and thiocyanate ions have been postulated in Section 5.3 to explain some of the results reported in Tables 28 to 31.

Figures 17 and 18 indicate that only those anions whose enthalpies of hydration are more positive than about -75 ± 10 kcals/mole will be extracted into organic solvents by quaternary cations. Differences in the extracting power of the different cations are significant, but the difference in the curves drawn for Ph_3AmP^+ and Ph_3MeP^+ in Figures 17 and 18 is less than 5 kcals/mole. This indicates that the most important single factor determining whether a given anion will be extracted into an organic solvent by a quaternary cation is the enthalpy of hydration of the anion. The size of the distribution ratio, of the anions that do extract, is determined by the radius of the cation used to extract the anion and by the solvating properties of the organic solvent. Chu, Whitney and Diamond (102) have proposed a similar explanation to the one outlined above to explain anion exchange resin selectivities. The extent of hydration of the anions and differences in the local water structure both inside and outside the resin, play an important part in determining resin selectivity. The hydration of the ions in the resin phase will certainly be reduced below that in the dilute external solution, and so the ions must be partially dehydrated on passing from the aqueous solution into the resin. No attempt was made however, to compare the results obtained for the resin selectivities with the known values of the enthalpies of hydration. The order of extraction of the acids $HClO_4$, HBr and HCl by tri-n-octylamine has been compared with the enthalpies of hydration of the anions (103). This appears to be the only instance in the literature of the extraction of anions being correlated with the known values of the enthalpies of hydration.

Marcus in the conclusion to his review on the solvent extraction of inorganic species states that "more information on the hydration of ions, and in particular of anions, including anionic complexes, both with respect to hydration numbers and the enthalpy and entropy of hydration is needed" (5). The enthalpies of hydration of most of the anions studied in the present work are known, but no information seems to be available on the enthalpies of hydration of metal complex anions. The extraction behaviour of a number of metal complexes may, however, be rationalised on the basis of their expected enthalpies of hydration. For example it has been reported that the anion $Fe(NCS)_6^{-3}$ is almost quantitatively extracted into o-dichlorobenzene by the triphenylmethylarsonium cation (104); the anions $Fe(CN)_6^{-4}$ or $Fe(CN)_6^{-3}$ however are not extracted under the same conditions (105). The $Fe(NCS)_6^{-3}$ anion, is considerably larger than the $Fe(CN)_6^{-3}$ anion, and because of its smaller charge density its enthalpy of hydration should be much less negative and its extraction is therefore possible.

Section 5.5 The extraction of quaternary salts as a function of temperature

The effect of temperature on the extraction of quaternary salts has been mentioned in Section 4 and by studying this effect it is possible to calculate the entropy and the enthalpy of the extraction process. It is known that differences in the free energy of the extraction process of various salts are determined by the differences in ΔH and not by differences in ΔS (18). Therefore, in the discussion presented in this Section entropy values have been ignored. The distribution ratios of salts of the Ph_3AmP^+ cation between water and the three solvents chloroform, dichloromethane and 1,2 -dichloroethane measured at three different temperatures 15°, 25° and 35°C are given in Tables 28, 29 and 30. The distribution ratios of salts of the Ph_4As^+ cation between water and chloroform also measured at 15°, 25° and 35°C are given in Table 28. In general it was found that the distribution ratios decreased with increasing temperature, i.e. the extraction is an exothermic process. This decrease in the value of the distribution ratio with increasing temperature was observed under a variety of conditions and over a wide range of cation and anion concentration (see Tables 7 and 22 and Figures 4 and 13).

Under the conditions used to measure the change of the distribution ratio with temperature reported in Tables 28 to 30, it has been shown (Section 4.5), that ion pairs are the only important species in the organic phase. Using the same symbols that were used in Section 3, the extraction process may be represented simply by

$$R_4P^+ + X^- \rightleftharpoons (R_4P^+, X^-)_o$$

The equilibrium constant K and the distribution ratio D for this equation are given by

$$K = \frac{[R_4PX]_o}{[R_4P][X]}$$

$$\text{and } D = \frac{[R_4PX]_o}{[R_4P]}$$

$$\text{therefore } K = \frac{D}{[X]}$$

$$\text{Now } \Delta G = \Delta H - T\Delta S$$

$$= -2.303\ RT \log K$$

where ΔG, ΔH, and ΔS are the free energy, enthalpy and entropy changes of the extraction process respectively, T is the absolute temperature and R is the gas constant.

$$\text{Therefore } \Delta H - T\Delta S = -2.303\ RT \log D + 2.303\ RT \log [X]$$

$$\log D = \frac{-\Delta H}{2.303R}\left(\frac{1}{T}\right) + \frac{\Delta S}{2.303R} + \log [X] \quad \text{— (1)}$$

Assuming that ΔS has a value comparable to that found for the extraction of triphenylmethane dye salts into chloroform, i.e. $\Delta S \approx -20$ e.u, then the changes in $\log [X]$ over the temperature range studied may be neglected and equation (1) has the form

$$\log D = A\left(\frac{1}{T}\right) + B \quad \text{———————} \quad (2)$$

where A and B are constants

$$A = -\frac{\Delta H}{2.303R} \text{ and } B = \frac{\Delta S}{2.303R} + \log [X]$$

Equation 2 therefore predicts a linear relationship between log D and the reciprocal of the absolute temperature.

Figures 19 and 20 show the relationship between log D and 1/T for Ph_3AmP^+ salts extracting into dichloromethane and chloroform. The expected linear relationship is observed indicating that the above

Figure 19

Variation of the distribution ratio as a function of temperature.

Plot of log D against the reciprocal of the absolute temperature for Ph_3Amp^+ salts extracted from water into dichloromethane

Figure 19

- ⊙ ClO_4^-
- ◉ NCS
- ● I
- ◐ ClO_3^-
- ◒ NO_3^-
- ○ Br^-
- ⊖ BrO_3^-
- ⊘ Cl^-

Data taken from Table 29.

Figure 19

Variation of the distribution ratio as a function of temperature.

Plot of log D against the reciprocal of the absolute temperature for Ph_3AmP^+ salts extracted from water into dichloromethane

- ⊙ ClO_4^-
- ◐ NCS
- ● I
- ◑ ClO_3^-
- ◒ NO_3^-
- ○ Br^-
- ◒ BrO_3^-
- ⊘ Cl^-

Data taken from Table 29.

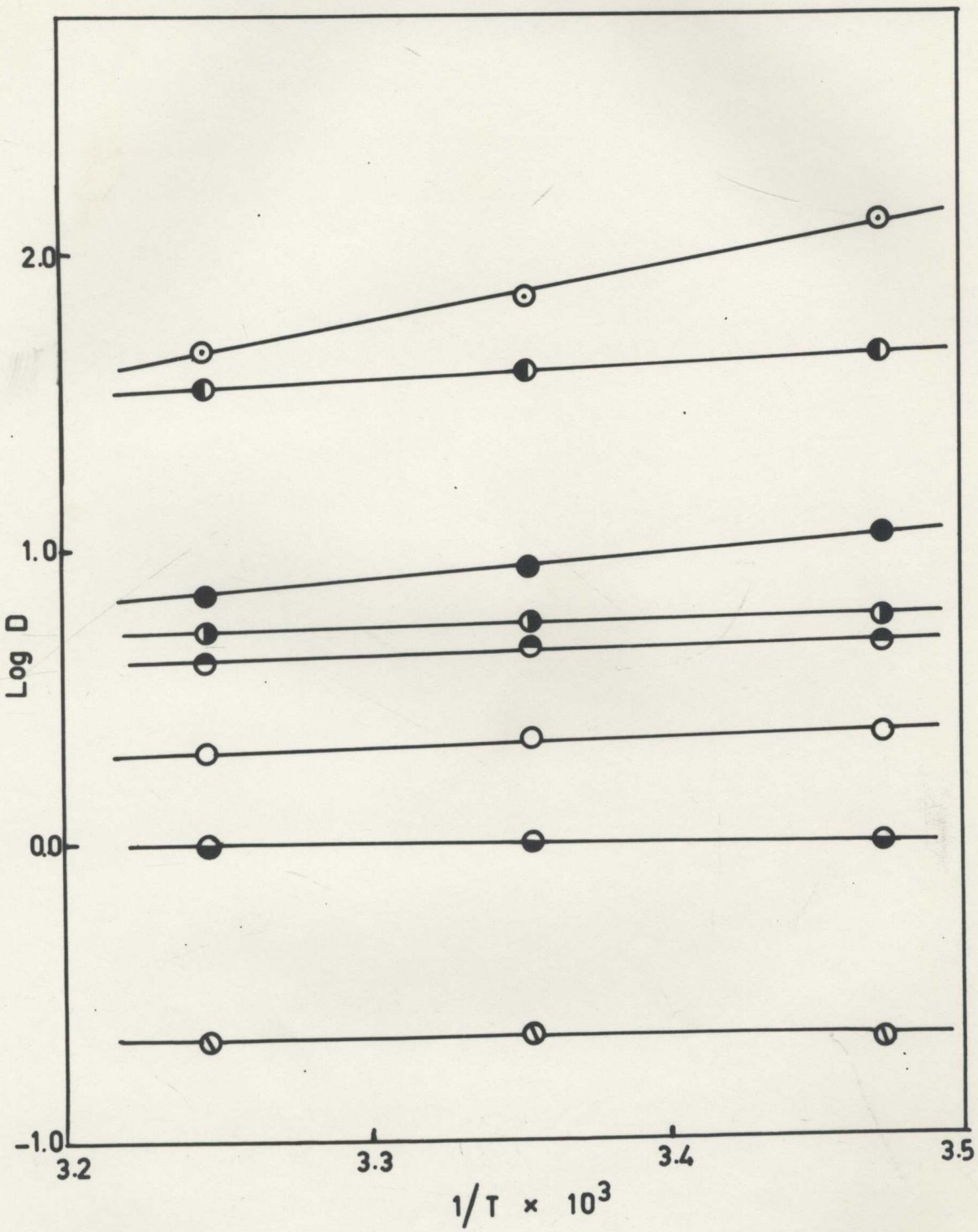

2.0
1.0
0.0
-1.0
Log D
3.2
3.3
3.4
3.5
1/T × 10³

Figure 20

Variation of the distribution ratio as a function of temperature.

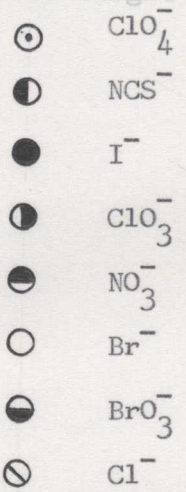
Plot of log D against the reciprocal of the absolute temperature for Ph_3AmP^+ salts extracted from water into $CHCl_3$.

Data taken from Table 28.

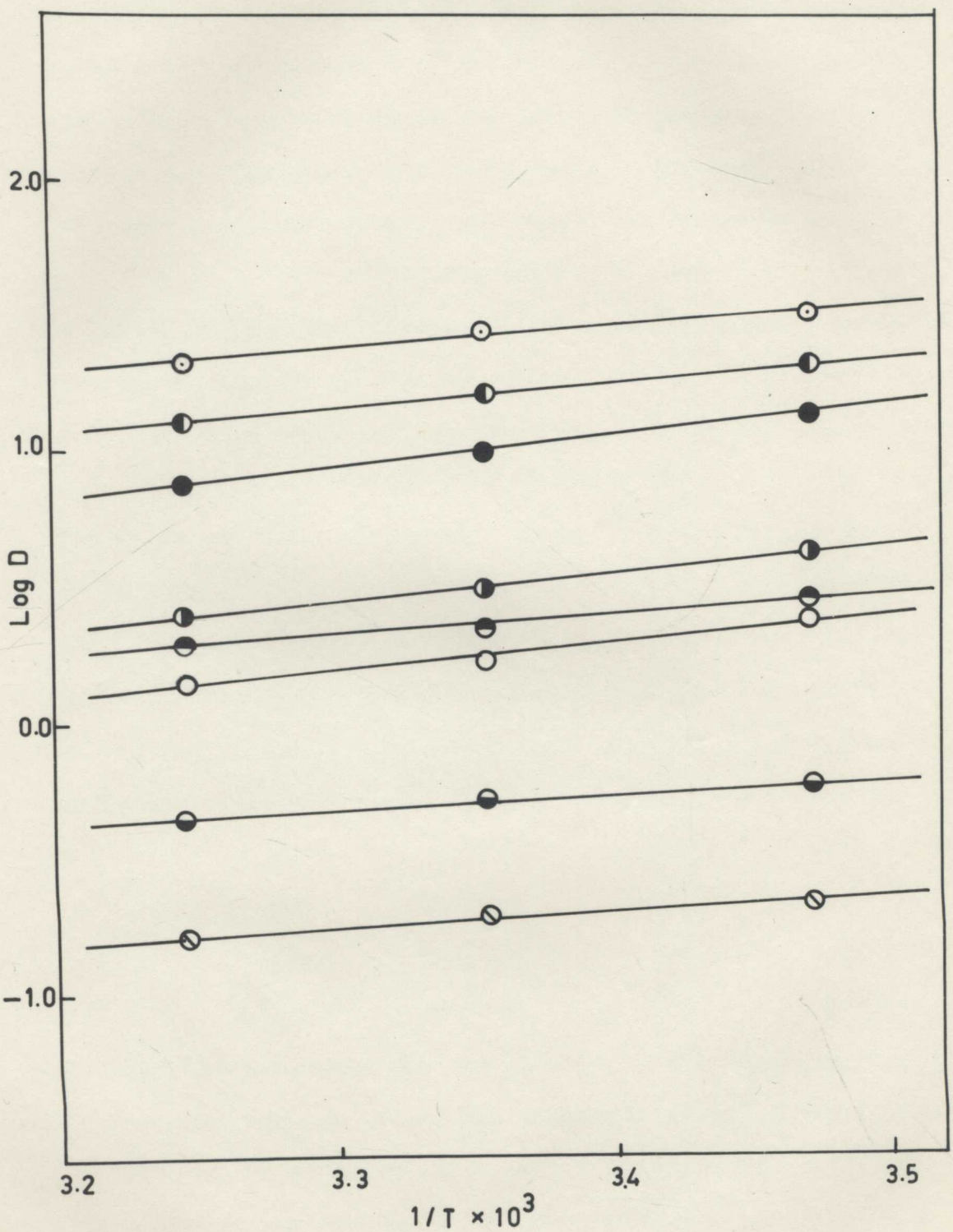
Figure 20

Variation of the distribution ratio as a function of temperature.

Plot of log D against the reciprocal of the absolute temperature for Ph_3AmP^+ salts extracted from water into $CHCl_3$.



Data taken from Table 28.


2.0
1.0
0.0
−1.0
Log D
3.2
3.3
3.4
3.5
1/T × 10³

equation is a good approximation. Similar figures are obtained for Ph_3AmP^+ salts and Ph_4As^+ salts extracting into 1,2-dichloroethane and chloroform respectively.

The values of the enthalpy of the extraction process have been calculated from the values of D in Tables 28 to 30 using equation (2) by the method of least squares. The results are presented in Table 5.5.1.

Table 5.5.1

Values of the enthalpies of extraction of some quaternary salts into various solvents at 25°.

Standard state is ionic strength 0.1 in aqueous phase.

Values of $-\Delta H$ in kcals/mole

	Ph_4As^+	Ph_3AmP^+		
Anion	$CHCl_3$	$CHCl_3$	CH_2Cl_2	$C_2H_4Cl_2$
ClO_4^-	insoluble	3.5 ± 0.5	9.1 ± 1.0	10.1 ± 1.0
NCS^-	7.0 ± 1.0	4.0 ± 0.5	2.3 ± 0.5	4.4 ± 0.5
I^-	8.2 ± 1.0	4.7 ± 0.5	3.8 ± 0.5	4.7 ± 0.5
ClO_3^-	4.8 ± 0.5	4.8 ± 0.5	0.5 ± 0.5	2.9 ± 0.5
NO_3^-	4.5 ± 0.5	3.5 ± 0.5	0.5 ± 0.5	1.9 ± 0.5
Br^-	5.9 ± 0.7	4.4 ± 0.5	0.9 ± 0.5	5.2 ± 0.5
BrO_3^-	3.3 ± 0.5	1.5 ± 0.5	0	1.5 ± 0.5
Cl^-	6.2 ± 1.0	5.2 ± 0.7	0	3.6 ± 0.5

It should be remembered that the enthalpy of the extraction process includes the enthalpy of ion pair formation as well as differences in the enthalpy of hydration and solvation in the two phases.

The values of the enthalpy of the extraction process reported in Table 5.5.1 are more positive than those reported for the enthalpy of extraction of triphenylmethane dye salts (18). This can be

explained by the fact that the dehydration of the larger triphenylmethane cations requires less energy, and that the solvation of the ion pair in the organic solvent probably increases the larger the ion pair (101). The differences in the values for Ph_4As^+ and Ph_3AmP^+ salts extracting into chloroform are probably due to the same effect; the larger Ph_4As^+ cation has a more negative enthalpy of extraction. A similar relationship may be observed for the extraction of anions. In general the enthalpy of extraction becomes more positive as the size of the anion decreases. The halide ions seem to be anomalous in chloroform and 1,2 -dichloroethane; that is the enthalpy values seem to be too negative. This is probably due to the fact that the halide ions in the ion pairs are hydrogen bonded to the solvent molecules, increasing the solvation energy of the ion pairs in these solvents. The values calculated for the chloride and bromate ions in particular should be treated with some caution because the salts of these anions may not exist as ion pairs in the organic phase (Section 4.5) and the results would not be comparable to the values for the other salts.

SECTION 6

GENERAL DISCUSSION

Section 6.1 The nature of the species in the organic solvent

All the evidence from the distribution behaviour of the quaternary salts presented in Section 4 suggests that the quaternary salts exist as ion pairs or as dissociated ions in the organic solvent. The dissociation of the ion pairs in the organic solvent is favoured by solvents of high dielectric constant and by low concentrations of the quaternary salts in the organic phase.

The extraction of water into the organic solvents by the quaternary salts was not investigated in the present work. The concentration of water in a saturated solution of chloroform is about ten times the concentration of the quaternary salt used in this investigation (56). The determination of the amount of additional water present in chloroform due to the extraction of the quaternary salts would therefore be very difficult. There is good evidence however, that water is extracted into the organic solvent with some quaternary salts and that this water is associated with the ion pairs in the organic phase. Mueller and Diamond (56) found that water was extracted in the organic phase during the distribution of trilaurylammonium salts between water and a number of organic solvents. The amount of water extracted into the organic phase decreased in the order cyclohexane > benzene > toluene > carbon tetrachloride > chloroform and for a given solvent it decreased in the order $Cl^- > Br^- > I^- > NCS^-$.

Evidence that quaternary arsonium salts also extract water into chloroform has been discovered by Hosking (107) who found that triphenylmethylarsonium iodide prepared by extracting the salt from

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water into chloroform and then precipitating the iodide with anhydrous ether is in fact a hydrated salt. Faithful and Tuck (108) have reported similar observations for tetraphenylarsonium salts extracted into dichloromethane. The concentration of the quaternary salt in these systems was such that the extraction of water into the organic solvent together with the quaternary salt must be occurring. A number of quaternary salts prepared during the course of this work by evaporation of an aqueous solution to dryness, dissolution of the solid in chloroform and subsequent precipitation of the salt by the addition of ethyl acetate have also proved to be hydrated salts (121).

The presence of the water in the organic solvent did not significantly affect the aggregation of the trilaurylammonium salts (56). It is interesting that the presence of a small amount of ethyl alcohol in the chloroform used in the present study was found to have no effect on the distribution ratios of the quaternary salts (see Section 7.3).

Two types of ion pairs in organic solvents, 'contact' and 'solvent-shared' ion pairs have been distinguished from a study of the absorption spectra of the ion pairs in organic solvents. In 'solvent-shared' ion pairs the cation is apparently separated from the anion by at least one solvent molecule. The absorption spectra of 'contact' ion pairs are interpreted as being a charge transfer from the anion to the cation rather than charge transfer to the solvent. The ions are therefore thought to be in 'contact'. Quaternary salts in dichloromethane are thought to exist as 'solvent-shared' ion pairs (109). There is no evidence from

solutions which contain water associated with the quaternary salt for any interaction between the oxygen of the water and the cation, but the evidence does suggest hydrogen bonding of water to the anion (129). The water is probably not separating the cation from the anion but is probably bonded to the anion (56).

Section 6.2 Solvation of the ion pairs in both phases

The results presented in Sections 4 and 5 emphasize that the major factor which governs the difference in the extraction of the various quaternary salts is the change in solvation energy of the quaternary salts on passing from the aqueous into the organic phase. Ionin and Kurina (23) have derived an equation from theoretical considerations which shows the dependence of the distribution ratio of an electrolyte on the difference in solvation energies in the two solvents and on the activities of the electrolyte in the two phases. Their equation is:

$$\log D = \frac{A_S - A_H}{2.3nRT} + \log \frac{\gamma_w}{\gamma_o}$$

where D is the distribution ratio, A_S and A_H are the total solvation and hydration energies of the electrolyte respectively, n is the number of ions formed in dissociating the electrolyte and γ_w and γ_o are the activity coefficients of the ions in the aqueous and the organic phases. R and T have their usual significance.

If we assume that $\log \frac{\gamma_w}{\gamma_o} = 0$, an assumption which is probably true at the concentrations used in this thesis, then it is possible to calculate the distribution ratio for a 1:1 electrolyte by assuming hypothetical differences in the solvation and hydration energies as is done in Table 6.3.1.

Table 6.3.1

Values of D calculated assuming differences in the solvation energies

$A_S - A_H$ Kcals/mole	log D	D
8	2.93	1000
5	1.83	67.6
3	1.099	12.6

$A_S - A_H$ Kcals/mole	log D	D
1	0.366	2.3
0	0	1.0
-1	-0.366	0.43
-3	-1.099	0.08
-8	-2.93	0.001

By assuming that the difference in solvation energies of quaternary salts is due solely to differences in the enthalpy of hydration of the anions the above values of D have been used to calculate the curve drawn through the experimental points in Figures 17 and 18. This equation indicates that if the solvation energy of the electrolyte in the organic solvent is equal to its hydration energy then the electrolyte will distribute itself equally between the two solvents and that only small differences between the solvation and hydration energies give rise to large differences in the distribution ratio.

The manner in which the distribution ratio varies with the differences in the size and nature of the cation has been discussed in Section 5.2. The differences between a number of cations e.g. $Ph_3n\text{-}PrP^+$ and Ph_3AllP^+ and between the 2-bromo-, 3-bromo- and 4-bromomethylbenzyltriphenylphosphonium bromides were discussed in terms of the expected differences in the hydration energies of these cations. The difference in the hydration energies of the $Ph_3n\text{-}PrP^+$ and Ph_3AllP^+ cations, due to the presence of the double bond in the latter, would not be expected to be large and the figures in Table 6.3.1 indicate that a difference of only 1.0 to 1.5 kcal/

mole is sufficient to explain the differences observed in the value of D. This difference is obtained with all four organic solvents and with all the anions studied, indicating that it is an effect which is associated with the hydration of the cation in the aqueous phase.

The differences in the extraction behaviour of the different bromomethylbenzyltriphenylphosphonium cations was explained by the differences in the hydration of the bromomethyl group substituted at different positions around the benzyl ring, due to steric hindrance (Section 4.5). The hydration energy of the bromomethyl group would not be expected to be very large and in fact differences of between 2 and 3 kcals/mole are all that is necessary to explain the observed results.

Section 6.3 The extraction of tetraphenylstibonium salts

The extraction behaviour of tetraphenylstibonium salts is quite different from that of tetraphenylarsonium or tetraphenylphosphonium salts. The behaviour of this cation has been described in Section 2.1. Bock and Grallath (35) in their study of the extraction of Ph_4Sb^+ salts into chloroform found that Ph_4SbOH and Ph_4SbF were extracted into chloroform. They found the order of decreasing distribution ratios into chloroform at pH values between 2 and 3 was $NCS^- > HCrO_4^- > NO_3^- > Br^- > Cl^- > F^- > ClO_3^-$ This order is very similar to the order observed for the extraction into chloroform of salts of the Ph_4As^+ and Ph_4P^+ cations measured by Bock et al. (28) (29) and to the order found in this work, except that the value for the chlorate anion appears to be rather low and Ph_4Sb^+ is able to extract F^- and OH^- which are not extracted by Ph_4As^+ or Ph_4P^+. Orenberg and Morris (110) have also studied the extraction of tetraphenylstibonium salts into chloroform. The results obtained by these authors agree well with those of Bock and Grallath (35). The main factor governing the extraction of tetraphenylstibonium salts into chloroform or carbon tetrachloride still seems to be the change in solvation of the salt on passing from the aqueous to the organic phase, but the Ph_4Sb^+ cation is able to extract anions with much higher hydration enthalpies.

Differences in the aggregation of the salts of Ph_4Sb^+ compared to Ph_4As^+ seem to be an unlikely explanation for this increased extraction, as the aggregation of tetraphenylstibonium fluoride in both carbon tetrachloride and chloroform does not proceed

beyond dimer formation (34) (111). While dimer formation was not observed in the present work, it has been observed with Ph_4PCl (25). Therefore either a lower hydration energy of the tetraphenylstibonium ion in the aqueous solution and/or a greater solvation energy of the ion pair in the organic solvent is necessary to explain the observed behaviour.

The hydration of a large quaternary cation is probably a function of its radius and the larger size of Ph_4Sb^+ compared to Ph_4As^+ will mean that the hydration energy of the Ph_4Sb^+ will be less than that of Ph_4As^+. The difference in size between Ph_4Sb^+ and Ph_4As^+ is larger than the difference between Ph_4As^+ and Ph_4P^+ but very little difference is observed in the extraction behaviour of these two cations (Table 28). Therefore the large difference in the extraction behaviour between Ph_4Sb^+ and Ph_4As^+ is unlikely to be wholly attributable to the difference in the hydration energies of these cations. Therefore, some sort of interaction in the organic solvent, which increases the solvation energy in the organic phase, is probably occurring. Such an interaction cannot be due to the slightly acidic hydrogen of the chloroform interacting with the fluoride ion as was postulated in in Section 5.3 for the other halides to explain their increased extraction, as carbon tetrachloride does not have an acidic proton. A possible reason for this anomalous behaviour of Ph_4Sb^+ may be found in an explanation offered to explain the polarographic behaviour of the Ph_4Sb^+ cation (112). The polarographic reduction of Ph_4As^+ and Ph_4P^+ appears to proceed via a single two electron step in aqueous solution while Ph_4Sb^+ is reduced in two separate

one electron steps. There is evidence that the Ph_4Sb^+ is absorbed on the electrode surface prior to the first reduction step. Morris et al. (112) postulate that the Ph_4Sb^+ ion, being more covalent and having a larger central atom than Ph_4As^+, may be able to distort readily from the tetrahedral configuration to adopt a distorted trigonal bi-pyramid with mercury at one of the apices. A distorted trigonal bi-pyramid is believed to be the structure of triphenylstibine dichloride (113) but a square pyramidal structure may also be possible as this has been shown to be the structure of pentaphenylstibine (114).

If a distortion of the tetrahedral structure of Ph_4Sb^+ is possible at a dropping mercury electrode then the formation of ion pairs of tetraphenylstibonium salts may also result in the distortion of the cation to allow closer approach of the anion to the centre of the cation. The solvation of such an ion pair would be expected to be very different from the solvation of ion pairs of tetraphenylarsonium salts and the distribution behaviour would be correspondingly different. Small anions such as fluoride or hydroxide would be able to approach the cation more closely than large anions for the same amount of distortion, and this possibly explains why the effect is so great for these anions.

SECTION 7

EXPERIMENTAL

Section 7.1 The ultraviolet spectra of quaternary salts

The concentration of the cations in aqueous solution was determined by measuring the optical density of the solution at one wavelength in the range 258-265mμ. All of the cations studied absorb in this region of the spectrum due to the presence of either phenyl or benzyl groups in the cation. The measurements of the optical density at a fixed wavelength were made using a Hilger Uvispek single beam spectrophotometer using either matched 1cm or 1mm silica cells. The wavelength was chosen to give a suitable optical density reading with the most concentrated solution used. Beer's Law was obeyed at all the wavelengths studied.

The concentration of the quaternary salt was determined from a calibration curve which was remeasured each day readings were taken. The spectra in the range 245-280mμ of aqueous solutions of all of the cations studied were measured using a Unicam S.P. 700 automatic recording spectrophotometer using 1cm silica cells and some typical spectra are presented in Figure 21. The wavelengths (in mμ) of the maximum in the absorption spectrum for all the cations studied are presented in Table 7.1.1. The spectra of the three salts 2-$BrCH_2BzPh_3PBr$, 3-$BrCH_2BzPh_3PBr$ and 4-$BrCH_2BzPh_3PBr$ were identical and only the maxima for 2-$BrCH_2BzPh_3PBr$ are given in Table 7.1.1. The absorption spectra of the quaternary cations in the 260 mμ regions of the spectrum are very similar to that of benzene in the same region. The positions of the maxima presented in Table 7.1.1 indicate that there is a slight bathochromic shift in the spectra of the quaternary arsonium cations as the number of phenyl groups in

Figure 21

Absorption spectra of three quaternary cations in aqueous solution.

Ph_3AmP^+

Ph_3MeP^+

Ph_3MeAs^+

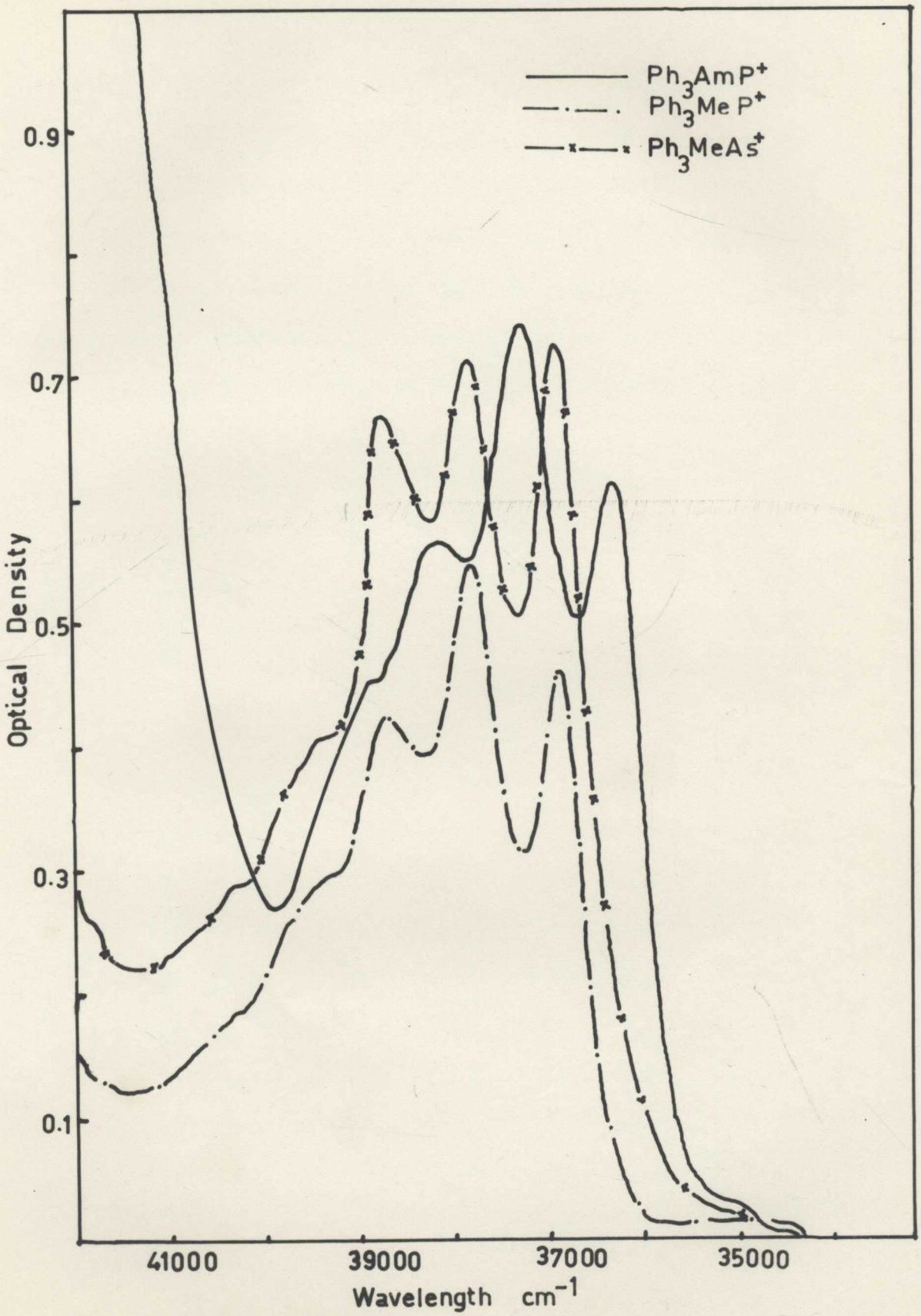
Figure 21

Absorption spectra of three quaternary cations in aqueous solution.

——— Ph_3AmP^+

—·—· Ph_3MeP^+

—×—× Ph_3MeAs^+


Ph3AmP+
Ph3MeP+
Ph3MeAs+
0.9
0.7
0.5
0.3
0.1
Optical Density
41000
39000
37000
35000
Wavelength cm-1

the cation increases. A similar shift may be observed in the reported results for the corresponding quaternary phosphonium cations (115). The ultraviolet spectra of a number of these cations in ethyl alcohol solutions have been reported previously; Ph_4As^+ (65) (115) (116); Ph_3MeAs^+ (117) (118); $PhMe_3As^+$ (119); Ph_4P^+ (115); Ph_3EtP^+ (115); Ph_3MeP^+ (115); $PhMe_3N^+$ (115) (119). The results presented in Table 7.1.1. for the absorption maximum in aqueous solution agree very well with the reported values.

TABLE 7.1.1

Position of maxima in the ultraviolet spectra of quaternary salts

Cations	Wavelength of Peaks (mμ)		
Ph_4As^+	259	265.5	272
Ph_3MeAs^+	258.5	264	270.5
$Ph_2Me_2As^+$	257.5	264	270.5
$PhMe_3As^+$	256	262	269
Ph_4P^+	263	268.5	276
Ph_3AmP^+	262.5	268.5	276
$Ph_3n\text{-}PrP^+$	262.5	268.5	276
$Ph_3iso\text{-}PrP^+$	263	269	276
Ph_3AllP^+	262	267.5	274
Ph_3EtP^+	262	267.5	275
Ph_3MeP^+	261	268.5	274.5
$2\text{-}BrCH_2BzPh_3P^+$	261.5	267	272.5
$BzEt_3N^+$	257	263	269.5
$PhMe_3N^+$	257.5	263	269.5
$BzCeMe_2N^+$	254	258	264

Section 7.2 Apparatus

The distribution of the quaternary salts between the two solvents was carried out in two types of distribution flasks. The first type consisted of a 50ml round-bottomed flask with a B10 ground glass top which was fitted with a plastic stopper. The distribution was carried out using 20 mls of both the aqueous and organic phases. The second type of distribution flask was obtained from Arthur H. Thomas Co., Philadelphia, and consisted of a flat bottomed glass vial fitted with a polyethylene stopper and a plastic screw top. The distribution was carried out in these flasks using 10 mls of both the aqueous and organic phases.

The flasks were mounted in a water bath maintained at a constant temperature, generally 25.0 $\pm$ 0.5°C, and they were then rotated end over end at about 50 revolutions per minute by an electric motor for at least two hours and generally overnight. The mixing of the two phases was more efficient using the flat bottomed glass vials but no difference in the results was obtained using either type of flask. No trouble was experienced with emulsion formation except with the benzylhexadecyldimethylammonium cation where the emulsion which formed quickly separated provided that no precipitate was present in the distribution flask.

The measurement of the distribution of the tetrachlorozincate ion with the various cations was performed by measuring the distribution of the radioactive Zn^{65} isotope between the two phases. The two phases were separated and the amount of zinc extracted was measured by determining the activity in both phases using an Ecko Automatic

Scaler Type 530F. No activity above the background count could be observed in the organic phase with any of the systems studied, confirming that no zinc was extracted.

Section 7.3 Extraction Procedure

The stock solutions for the studies of the distribution of the quaternary salts over a range of concentration were prepared by direct weighing. The solutions were made up with sodium sulphate solution so that the ionic strength was maintained at 0.1. Solutions more dilute than this solution were then prepared by dilution of known amounts of the stock solution with sodium sulphate solution. In those few cases where the solubility of the quaternary salt in water was not sufficiently high to prepare a concentrated stock solution, the quaternary salt was dissolved in the organic solvent, and the other solutions were prepared by dilution of this stock solution with the organic solvent. Then either 10 or 20 mls of these quaternary salt solutions, depending on the distribution flask used, were pipetted into the distribution flask, an equal quantity of either organic solvent or sodium sulphate solution was added and the flask was placed in the water bath and rotated as described in Section 7.2.

For all other measurements a stock solution of the quaternary sulphate (concentration 1.25×10^{-2}M) was first prepared by dissolving the quaternary iodide, bromide or chloride in hot water, adding an excess of finely divided silver oxide and boiling the mixture for about ten minutes. This treatment resulted in the decomposition of all the phosphonium cations containing a benzyl group but little or no decomposition was observed with the other cations studied. After cooling the solution to room temperature, the silver halide and excess silver oxide were removed by filtration and sufficient sulphuric acid was added to convert the

hydroxide to the sulphate and sodium sulphate was added to adjust the ionic strength to 0.1.

The concentration of the quaternary cation in this stock solution was determined spectrophotmetrically and the solution was then used as a source of cation, to which the appropriate anion at the required concentration could be added. The concentration and ionic strength were finally adjusted with sodium sulphate solution. This prepared solution (10 or 20 mls) was then added to the distribution flask and the organic solvent was added.

When the quaternary salt was insoluble in aqueous solution at the required concentrations (perchlorates and thiocyanates were often insoluble, particularly with the larger cations) the solutions to be distributed were prepared in the distribution flask. The concentration of these insoluble salts in the aqueous phase, after distribution, was less than the concentration of a saturated aqueous solution, so the quaternary salt was still distributing between the two phases.

The variation of the distribution ratio with the pH of the aqueous phase was not measured for any of the salts studied but previous work has shown that the distribution ratios of quaternary salts are independent of pH (28) (29). The pH of a few of the aqueous phases were measured, however, and were found to be in the range pH 3 to pH 5.

All the distributions were done at least in duplicate.

Errors

The method used to determine the concentration of the quaternary salt in the aqueous phase is capable of determining the concentration to an accuracy of $\pm$ 1%. This means that the percentage of the salt extracted into the organic phase could be determined to within $\pm$ 2%. The precision of the determination of the distribution ratios depends on the numerical value of the distribution ratio. For values of D between 0.01 and 0.1 the error in D is estimated to be $\pm$ 10% and for values between 0.1 and 10 the error is estimated to be $\pm$ 5%. The precision falls off sharply, as D increases above 10, because of the low concentrations in the aqueous phase and for $D > 50$ the value may be in error by more than 20%. The average value of at least duplicate determinations of D is reported.

Purification of Organic Solvents

The solvents dichloromethane and 1,2-dichloroethane were B.D.H. Laboratory Reagent quality and were fractionated before use, fractions boiling between 39-41°C and 82.5-83.5° respectively were used. 2,2'-dichlorodiethylether was obtained from Townsend and Mercer Pty. Ltd. and was of unknown quality. It was not possible to fractionate this solvent as extensive decomposition occurred at its boiling point so it was distilled twice under reduced pressure (water pump), the fraction boiling between 125-130° being used.

The chloroform used was obtained from a variety of sources and all samples contained ethyl alcohol as a stabilizing agent.

The ethyl alcohol could be removed from the chloroform by shaking the chloroform with concentrated sulphuric acid (twice), acidic permanganate solution (twice), and then distilled water. Experiments showed that removal of the alcohol had no significant effect on the distribution ratios of the quaternary salts. Therefore the chloroform used in most of the experiments reported here was not purified in any way.

The rate of attainment of equilibrium of the distributing species was measured in the case of Ph_3MePI distributing between water and chloroform. The optical densities of a number of identical solutions were measured after a period of rotation in the water bath. The results are presented in Table 7.3.1.

Table 7.3.1.

Distribution of Ph_3MePI between chloroform and aqueous solutions.

Equilibrating Time	Optical Density
2 hours	0.565
7 hours	0.567
72 hours	0.571
168 hours	0.568

The results show that the system has come to equilibrium within two hours. Previous determinations on the rate of equilibrium of quaternary ammonium compounds indicated that they equilibrated within fifteen minutes (8). As a precaution however, all the systems studied were equilibrated for a time in excess of two hours, generally overnight. The fact that equilibrium had been attained was also indicated by the observation that the results

obtained with the quaternary salt initially in the organic phase were identical with the results obtained with the salts initially in the aqueous phase.

The possible extraction of HCl into the organic solvents chloroform, dichloromethane, 1,2-dichloroethane was a matter of some importance in connection with the extraction of Ph_3MeAs^+ from HCl solutions (Section 4.3). The concentration of HCl in the organic phase was determined by taking 5 mls of the organic phase, after the extraction of Ph_3MeAs^+ from aqueous solutions of various HCl concentrations (up to 5M), adding this to 10 mls of standard sodium borate solution (0.1M) and shaking and back titrating the sodium borate solution with hydrochloric acid. No extraction of HCl into the organic phase was detected by this method, a result in agreement with the results obtained by Zharovskii and Litvenenko (72).

Section 7.4 Independent determinations of the distribution ratio

The measurement of the distribution ratios of the quaternary salts by determining theconcentration of the cation in the aqueous phase after distribution may give a false value of the distribution ratio if there are other extractable anions present in solution. The aqueous solution in the large majority of the systems studied contained a large excess of sulphate ions in addition to the anion of interest. It was found that with anions which were not expected to extract, the final concentration of the cation in the aqueous solution was slightly less than the initial concentration, and was equal to the final cation concentration when sulphate was the only anion in solution.

This effect increased as the cation size increased. The observed distribution ratios were corrected for this decrease, assuming that the decrease was due to the extraction of the quaternary sulphate and that its distribution ratio was independent of the cation concentration in the aqueous phase. The situation is somewhat analogous to the distribution of $Ph_3MeAsCl$ over a range of cation concentration between 0.5M KCl solutions and organic solvents described in Section 4.2.

The validity of the assumption that the distribution ratio is independent of the cation concentration for extractions into chloroform is shown by the results in Table 2, where the distribution ratios of $(Ph_4As)_2SO_4$ over a wide range of cation concentration are seen to be independent of the cation concentration. With the other solvents no measurements have been made, but the results in Section 4.2 indicate the distribution ratios

in 1,2-dichloroethane and 2,2'-dichlorodiethylether are not independent of the cation concentration at low cation concentrations. However, for an initial concentration of quaternary salt of 5×10^{-3}M, low concentrations of the cation in the aqueous phase indicate high distribution ratios which will be little affected by the correction due to the sulphate extraction, even if this increases above the value measured at a concentration of 5×10^{-3}M.

The extraction of the quaternary sulphate into the organic solvent is probably the most important reason for the small decrease in the optical density observed in solutions containing only anions which were not expected to extract. The decrease in the optical density is dependent on the aqueous sulphate concentration and the distribution ratio of triphenylmethylarsonium sulphate from saturated sodium sulphate solution is quite high (Table 27). The absorption of the quaternary salts on to the glass of the distribution flask and the concentration of the quaternary salts at the interface of the two solvents may also be factors which influence this decreased optical density. The presence of small amounts of halide ion in the stock solution due to the incomplete precipitation and solubility of the silver halides may also contribute to the decreased optical density.

It was felt advisable to measure the distribution of some of the quaternary salts by measuring the anion concentration in either the aqueous or the organic phase, and preferably both, in order to check the corrected distribution ratios obtained spectrophotometrically. This was done by determining the thiocyanate

and bromide concentrations in both phases after the distribution of the triphenylmethylarsonium salts. The thiocyanate concentration in both the aqueous and chloroform phases after distribution of $Ph_3MeAsNCS$ (concentration 5×10^{-3}M) was measured by the method developed by Ellis and Gibson for the determination of cobalt (120). The chloroform phase was evaporated to dryness, the residue dissolved in water and then the thiocyanate, in both the original aqueous phase and the solution of the residue, was separately extracted into o-dichlorobenzene as $(Ph_4As)_2Co(NCS)_4$ and the concentration of $Co(NCS)_4^=$ in the o-dichlorobenzene was measured colorimetrically. The distribution ratio determined in this way was 1.7, which compares satisfactorily with the corrected result measured by the determination of the cation in the aqueous phase spectrophotometrically (D = 1.6). The distribution ratio of $Ph_3MeAsBr$ at an initial concentration of 0.0895M in the aqueous phase between chloroform and water was determined by measurement of the bromide concentration in both phases by Volhard's method and by measuring the optical density of the aqueous phase after dilution. The distribution ratio determined by measuring the concentration of bromide ions in both phases was 1.55 while the ratio determined by measuring the concentration of the cation in the aqueous phase was 1.51. These results are in excellent agreement, and indicate that the method used to determine the distribution ratios was valid.

Section 7.5 Preparation of quaternary salts

A number of quaternary salts studied in the course of this work are available commercially and the following salts were purchased from Fluka, A.G.:

tetraphenylarsonium chloride, tetraphenylphosphonium chloride, 2-bromo-, 3-bromo-, 4-bromomethylbenzyltriphenylphosphonium bromides, allyltriphenylphosphonium bromide, benzyltriethylammonium chloride and benzylhexadecyldimethylammonium chloride.

The preparation of the remaining phosphonium salts will be described briefly in this section. The preparation of most of the arsonium salts used in the course of this work have been described elsewhere (121) (117). The method of preparation of the phosphonium compounds followed closely those of the arsonium compounds and are therefore only summarized below.

Preparation of quaternary phosphonium iodides

These compounds were prepared by refluxing ethanol solutions of triphenylphosphine (B.D.H. Lab. Reagent) and the alkyl iodide. They were precipitated by the addition of ether and were recrystallised from water. The properties and analysis of these compounds are summarized below:

Compound	m.p.	Literature m.p.	Analysis Found	Calculated
Ph_3MePI	182-83°	184-184.5 (122)	C 56.4% H 4.5%	56.4% 4.5%
$Ph_3EtPI.H_2O$	140-142°	-	C 55.9% H 5.3%	55.1% 5.1%
$Ph_3n\text{-}PrPI$	196-98°	-	C 58.3% H 5.2%	58.1% 5.1%

Compound	m.p.	Literature m.p.	Analysis Found	Calculated
Ph_3iso-PrPI	192-95°	199° (123)	C 58.5% H 5.5%	58.1% 5.1%
Ph_3AmPI	160-62°	-	C 59.6% H 5.8%	60.0% 5.7%

The presence of a molecule of water of crystallisation in $Ph_3EtPI.H_2O$ was confirmed by its infrared spectrum. The melting point of the anhydrous material is 167-167.5 (122).

Preparation of triphenylmethylphosphonium perchlorate

Prepared from the iodide by dissolving the iodide in water and adding sodium perchlorate solution. The perchlorate precipitated immediately, and was recrystallised from ethanol m.p. 159-60°.

Analysis	Found C;	60.6%	Calculated C;	60.6%
	H;	4.9%	H;	4.8%

Preparation of triphenylmethylphosphonium nitrate

Prepared from the iodide by preparation of the hydroxide by precipitation of silver iodide by silver oxide and neutralisation of the hydroxide with nitric acid. The solution was evaporated to dryness and the nitrate was recrystallised from chloroform/ethyl acetate. m.p. 128-29°.

Analysis	Found C;	67.3%	Calculated C;	67.3%
	H;	5.3%	H;	5.4%
	N;	4.1%	N;	4.1%

Preparation of triphenylmethylarsonium perchlorate

Triphenylmethylarsonium perchlorate was prepared by the method used to prepare triphenylmethylphosphonium perchlorate. m.p. 149-50°

Analysis	Found C;	54.1%	Calculated C;	54.2%
	H;	4.5%	H;	4.3%

Infrared spectra of the quaternary salts

The infrared spectra of all the salts which were prepared during the course of this work were recorded on a Perkin Elmer Spectrophotomer 221 in nujol mulls or KBr discs in the range 3000-600 cm^{-1}. The infrared spectra of most of the arsonium and phosphonium salts prepared have been reported and discussed in the literature (121) (122) (125) (126) (127) (128) and the results obtained are in good agreement with the reported results and so they will not be discussed further.

APPENDIX

All the concentrations of the quaternary salts in Tables 1 to 32 are the initial concentration in the aqueous phase.

TABLE 1

Distribution of $Ph_3MeAsCl$ between various organic solvents and water over a range of $Ph_3MeAsCl$ concentrations with chloride concentration 0.5M. Temperature 25°.

$[Ph_3MeAsCl]$	Distribution Ratio		
$x10^4M$	$CHCl_3$	$C_2H_4Cl_2$	$(C_2H_4Cl)_2O$
74.0	0.48	0.46	0.43
66.6	0.49	0.43	0.44
44.4	0.45	0.41	0.46
29.6	0.45	0.43	0.55
22.2	0.44	0.44	0.58
14.8	0.45	0.45	0.62
7.4	0.48	0.54	1.49
5.9	0.52	0.64	1.75
4.4	0.49	0.68	2.10
3.0	0.53	0.73	2.70
1.48	0.57	0.89	4.50
0.74	0.76	1.30	-

TABLE 2

Distribution ratios for $(Ph_4As)_2SO_4$ between chloroform and water over range of concentration.

$$[Na_2SO_4] = 0.03\ M$$

Concn. $[Ph_4As^+]$ x 10^4M	D
114.5	0.08
57.3	0.10
22.9	0.07
17.2	0.08
11.5	0.07
5.73	0.10
2.29	0.08
1.15	0.08
0.57	0.11
0.23	0.09

TABLE 3

Distribution ratio of $Ph_3MeAsCl$ between $CHCl_3$ and water over Range of Chloride Concentration in Aqueous Solution.

Total $\left[Ph_3MeAs^+\right] = 5 \times 10^{-3}M$

Temperature 25°

$\left[Cl^-\right]$	Source of Chloride Ions			
	LiCl	KCl	CsCl	HCl
0.005M	0.01	0.01	-	0.01
0.01M	0.02	0.01	-	0.02
0.025M	0.04	-	-	0.05
0.05M	0.06	0.06	-	0.06
0.1M	-	0.11	-	-
0.25M	-	0.26	-	-
0.5M	0.53	0.53	0.49	0.45
0.75M	-	0.79	-	-
1.0M	1.2	1.1	1.0	0.65
2.0M	-	-	2.6	0.71
3.0M	5.6	-	5.2	0.60
4.0M	-	-	-	0.48
5.0M	12	-	12.5	0.31
8.0M	30	-	-	0.06

TABLE 4

Distribution ratio of $Ph_3MeAsCl$ between CH_2Cl_2 and water over a range of Chloride ion Concentration in the Aqueous Solution.

Total $[Ph_3MeAs^+]$ = 5×10^{-3}M

Temperature 25°

$[Cl^-]$	LiCl	HCl
.005M	0.01	-
.07M	0.09	-
0.35M	0.20	-
1.0M	-	0.39
1.24M	1.0	-
1.74M	1.5	-
2.0M	-	0.55
2.88M	3.2	-
3.0M	-	0.35
4.0M	-	0.28
5.5M	10	-
6.0M	-	0.07
8.0M	-	0.06
10.0M	35	-

TABLE 5

Distribution ratio of $Ph_3MeAsCl$ between $C_2H_4Cl_2$ and water over a range of Chloride ion concentration in the Aqueous phase.

Total $[Ph_3MeAs^+] = 5 \times 10^{-3}M$

Temperature 25°

$[Cl^-]$	Source of Chloride Ion	
	LiCl	HCl
0.005M	0.01	-
0.07M	0.05	-
0.35M	0.12	-
1.0M	-	0.26
1.24M	0.33	-
2.0M	-	0.28
2.88M	0.86	-
3.0M	-	0.22
4.0M	-	0.18
5.0M	-	0.14
5.5M	2.2	-
6.0M	-	0.13
10.0M	10	-

TABLE 6

Distribution Ratios of Ph_3AmPCl and Ph_4AsCl between $CHCl_3$ and water over a range of Chloride concentration in the Aqueous Phase.

Total [Cation] = 5×10^{-3}M

Temperature 25°

[KCl]	Ph_3AmPCl	Ph_4AsCl
0.005M	0.18	0.16
0.01M	0.64	0.37
0.05M	3.2	1.20
0.1M	6.2	2.20
0.5M	30	-
1.0M	65	32

TABLE 7

Distribution Ratios of $Ph_3MeAsBr$, Ph_3AmPBr and Ph_4AsBr between chloroform and water over a range of Bromide concentration in the Aqueous Phase.

Total [Cation] = 5×10^{-3}M

[KBr]	$Ph_3MeAsBr$	Ph_3AmPBr		Ph_4AsBr
	25°	25°	35°	25°
0.005M	0.12	1.7	1.4	1.6
0.01M	0.24	7.4	5.0	5.6
0.05M	0.97	50	30	35
0.1M	1.85	100	55	70
0.5M	6.8	250	150	-
1.0M	14	450	300	400

TABLE 8

Distribution Ratio of $Ph_3MeAsCl$ between $CHCl_3$ and water over Range of Chloride Concentration in the presence of Zinc and Cadmium Sulphates.

$[Ph_3MeAs^+] = 5 \times 10^{-3}M$

Temperature 25°

	Concn. $ZnSO_4$			Concn $CdSO_4$
[KCl]	.0025M	.005M	0.1M	.0025M
0.005M	0.01	0.01	0.01	0.01
0.01M	0.04	0.02	0.01	0.01
0.025M	-	0.05	-	-
0.05M	0.07	0.07	0.05	0.07
0.01M	0.11	0.13	0.10	0.10
0.5M	0.53	0.55	0.50	(a)
1.0M	1.10 (b)	1.20	[illegible]	(a)
3.0M	5.5 (b)	(a)	(a)	
5.0M	15 (b)			
10.0M	70 (b)			

(a) A precipitate of $(Ph_3MeAs)_2ZnCl_4$ or $(Ph_3MeAs)_2CdCl_4$ was observed in distribution flask.

(b) Concentration of chloride adjusted with LiCl.

TABLE 9

Distribution Ratios of $Ph_3MeAs\ Br$ between $CHCl_3$ and water over a range of Bromide Concentrations in the presence of Zinc and Cadmium Sulphates.

$$\left[Ph_3MeAs^+\right] = 5 \times 10^{-3}M$$

Temperature 25°

	Concn $ZnSO_4$	Concn. $CdSO_4$
$[KBr]$	.0025M	.0025M
0.005M	0.12	0.11
0.01M	0.23	0.22
0.05M	1.06	1.70
0.1M	1.91	6.05
0.5M	7.2	(a)
1.0M	15	(a)
3.0M	64	95
4.0M		120

For the results in the absence of metal ions see Table 7.

(a) All solutions with $\left[Br^-\right]$ varying from 0.2M to 2.5M had a precipitate present. The amount of precipitate appeared to increase to a maximum at about 0.75M and then decreased again until the 3M solution again had no ppt.

TABLE 10

Distribution $Ph_3MeAsCl$ between $CHCl_3$ and Na_2SO_4 Solution over range of Concentration at 25°.

$[Ph_3MeAsCl] \times 10^4 M$	D	Percentage Extraction
73.2	0.03	3
58.7	0.01	1
29.3	0.01	1
14.6	< 0.01	-
11.0	< 0.01	-
7.33	< 0.01	-
5.87	0.03	3
4.40	0.01	1
2.93	0.02	2
1.47	0.10	9
0.73	0.15	13

TABLE 11

Distribution $Ph_3MeAsBr$ between $CHCl_3$ and Na_2SO_4 Solution over Range of Concentration at 25°.

$[Ph_3MeAsBr]$ x 10^4M	D	Percentage Extraction
895 (a)	1.5	60
54.6	0.09	8
43.7	0.06	6
21.8	0.02	2
109	< 0.01	-
8.19	0.01	1
5.46	0.05	3
4.37	0.02	2
3.28	0.02	2
2.18	0.03	3
1.09	0.07	6
0.55	0.10	9

(a) See Section 7 for details of how this concentration was measured.

TABLE 12

Distribution Ph_3MeAsI between $CHCl_3$ and Na_2SO_4 Solution over a Range of Concentration at 25°.

$[Ph_3MeAsI] \times 10^4 M$	D	Percentage Extraction
31.4	1.98	66
23.6	1.74	63
15.7	1.46	59
7.07	0.81	44
3.54	0.49	32
2.65	0.45	30
2.12	0.42	28
1.77	0.43	28
1.42	0.34	23
0.71	0.29	21
0.18	1.21	54

TABLE 13

Distribution $Ph_3MeAsClO_4$ between $CHCl_3$ and Na_2SO_4 Solution over Range of Concentration at 25°.

$[Ph_3MeAsClO_4] \times 10^4 M$	D	Percentage Extraction
76.1	4.7	82
45.7	3.3	77
38.1	3.0	75
30.5	2.6	72
22.8	2.1	68
15.2	1.7	63
8.89	1.1	53
7.61	1.1	53
5.93	0.87	46
2.96	0.58	37
2.22	0.49	33
1.78	0.43	30
1.48	0.39	28
1.19	0.46	31
0.89	0.40	29
0.59	0.38	28

TABLE 14

Distribution $Ph_3MeAsNO_3$ between $CHCl_3$ and Na_2SO_4 Solution over Range of Concentration at 25°.

$[Ph_3MeAsNO_3] \times 10^4 M$	D	Percentage Extraction
104.2	0.26	20
83.4	0.22	18
52.1	0.14	12
32.2	0.12	11
20.9	0.11	10
8.34	0.07	6
6.25	0.07	6
4.17	0.07	6
2.09	0.09	9
1.04	0.14	12

TABLE 15

Distribution Ph_3AmPI between $CHCl_3$ and Na_2SO_4 Solution over Range of Concentration at 25°.

$[Ph_3AmPI] \times 10^4 M$	D	Percentage Extraction
16.0	11.9	92
10.6	9.23	90
7.64	7.38	88
6.80	7.09	88
6.46	5.99	86
3.99	5.39	84
3.19	4.87	83
2.66	4.33	81
1.60	3.53	78
1.06	2.84	74
0.68	3.15	76
0.43	3.20	76
0.34	3.05	75
0.28	3.18	76
0.17	3.15	76

TABLE 16

Distribution of Ph_2Me_2AsI between $CHCl_3$ and Na_2SO_4 over a range of concentrations at 25°.

$[Ph_2Me_2AsI] \times 10^4$ M	D	Percentage Extraction
20.2	0.09	8
19.9	0.09	8
13.3	0.06	6
10.1	0.01	1
6.6	0.06	6
5.0	0.04	4
4.0	0.05	5
3.3	0.04	4
2.7	0.08	8
2.0	0.16	14
1.3	0.16	14
1.0	0.17	16
0.67	0.30	23
0.33	1.06	52

TABLE 17

Distribution $Ph_3MePClO_4$ between $CHCl_3$ and Na_2SO_4 over a range of Concentration at 25°.

$[Ph_3MePClO_4] \times 10^4 M$	D	Percentage Extraction
17.86	1.3	57
11.91	1.0	50
5.95	0.62	38
4.47	0.51	34
2.98	0.40	28
2.38	0.35	26
1.79	0.29	22
1.19	0.24	19
0.60	0.19	16
0.30	0.25	20

TABLE 18

Distribution of $PhMe_3AsI$ between $CHCl_3$ and Na_2SO_4 solution over a range of concentration at 25°.

$[PhMe_3AsI] \times 10^4 M$	D	Percentage Extraction
37.4	0.02	2
24.9	0.02	2
14.6	0.01	1
9.34	0.01	1
7.48	0.04	4
4.98	0.06	6
3.89	0.06	6
2.49	0.10	9
0.97	0.17	14

TABLE 18a

Distribution of Ph_3MeNI between $CHCl_3$ and Na_2SO_4 solution over a range of concentration at 25°.

$[PhMe_3NI] \times 10^4 M$	D	Percentage Extraction
48.9	0.01	1
33.9	0.01	1
22.6	0.01	1
14.5	0.03	3
8.48	0.03	3
6.78	0.07	7
4.35	0.14	12
3.39	0.24	19

TABLE 19

Distribution of 2-$BrCH_2BzPh_3PBr$, 3-$BrCH_2BzPh_3PBr$ and 4-$BrCH_2BzPh_3PBr$ between $CHCl_3$ and Na_2SO_4 solution over a range of concentration at 25°.

$[BrCH_2BzPh_3PBr]$	D			Percentage Extraction		
x 10^4M	2-Br	3-Br	4-Br	2-Br	3-Br	4-Br
46.0	5.1	0.81	0.27	84	45	21
30.6	4.3	0.69	0.24	81	41	19
15.3	2.7	0.56	0.14	73	36	12
7.76	2.1	-	0.11	68	-	10
6.13	1.9	0.41	0.10	66	29	9
4.60	1.6	-	0.12	62	-	11
3.06	1.3	0.31	0.09	57	24	8
1.53	1.1	0.21	0.03	52	17	3
0.78	1.0	0.04	0.01	50	4	1

TABLE 20

Distribution 2-$BrCH_2BzPh_3PBr$, 3-$BrCH_2BzPh_3PBr$ and 4-$BrCH_2BzPh_3PBr$ between $C_2H_4Cl_2$ and Na_2SO_4 solution over a range of concentration at 25°.

$[BrCH_2BzPh_3PBr]$ x 10^4M	D			Percentage Extraction		
	2-Br	3-Br	4-Br	2-Br	3-Br	4-Br
46.0	2.2	-	0.20	69	-	17
30.6	1.8	0.40	0.17	64	29	15
15.3	1.4	0.26	0.15	58	21	13
7.76	1.2	-	0.14	55	-	12
6.13	-	0.23	0.16	-	19	14
4.60	1.2	-	0.18	55	-	15
3.06	1.1	0.23	0.10	52	19	9
1.53	1.1	0.22	0.10	52	18	9
0.78	1.4	0.20	0.05	58	17	5

TABLE 21

Distribution 2-$BrCH_2BzPh_3PBr$, 3-$BrCH_2BzPh_3PBr$ and 4-$BrCH_2BzPh_3PBr$ between CH_2Cl_2 and Na_2SO_4 solution over a range of Concentration at 25°.

$[BrCH_2BzPh_3PBr]$ x 10^4M	D			Percentage Extraction		
	2-Br	3-Br	4-Br	2-Br	3-Br	4-Br
46.0	4.6	0.46	0.36	82	32	27
30.6	3.7	-	0.28	78	-	22
15.3	2.7	0.28	0.21	73	22	17
7.76	2.0	-	0.20	67	-	17
6.13	1.9	0.18	0.16	66	15	14
4.60	1.7	0.21	-	63	17	-
3.06	1.4	0.16	0.11	58	14	10
1.53	1.2	0.10	0.13	55	9	12
0.78	0.70	-	0.06	41	-	6

TABLE 22

Distribution $Ph_3MeAsClO_4$ between CH_2Cl_2 and Na_2SO_4 over a range of concentration at 25° and 35°.

$[Ph_3MeAsClO_4]$ x 10^4M	D 25°	D 35°	Percentage Extraction 25°	Percentage Extraction 35°
55.4	13	-	93	-
48.9	12	9.5	92	90
21.8	7.6	6.0	88	86
16.3	7.1	5.5	88	85
10.8	5.7	4.5	85	82
5.10	4.3	3.3	81	78
4.35	3.6	2.6	78	72
3.27	3.1	2.5	76	72
2.18	2.5	2.0	72	67
1.09	1.8	1.5	64	60
0.54	0.93	1.7	48	63

TABLE 23

Distribution $Ph_3MeAsClO_4$ between $C_2H_4Cl_2$ and Na_2SO_4 Solution over Range of Concentration at 25°.

$[Ph_3MeAsClO_4]$ x 10^4M	D	Percentage Extraction
29.5	10	91
17.7	8.5	90
8.85	6.7	87
5.90	6.1	86
2.45	5.9	86
1.48	6.9	88
0.59	6.8	87
0.30	6.2	86

TABLE 24

Distribution $Ph_3MeAsClO_4$ between $(C_2H_4Cl)_2O$ and Na_2SO_4 solution over a range of concentration at 25°.

$[Ph_3MeAsClO_4]$ x 10^4M	D	Percentage Extraction
48.9	22	96
29.4	17	95
21.8	16	94
17.7	17	95
10.8	14	93
5.50	14	93
4.35	13	93
3.27	13	93
2.18	21	95
1.09	26	96
0.54	26	96
0.30	28	97

TABLE 25

Distribution $Ph_3MeAsNO_3$ between $C_2H_4Cl_2$ and $(C_2H_4Cl)_2O$ and Na_2SO_4 solution over a range of concentration at 25°.

$[Ph_3MeAsNO_3]$ x 10^4M	D		Percentage Extraction	
	$C_2H_4Cl_2$	$(C_2H_4Cl)_2O$	$C_2H_4Cl_2$,	$(C_2H_4Cl)_2O$
51.6	0.24	0.56	22	36
41.3	0.23	0.56	19	36
20.7	0.18	0.53	15	35
10.3	0.19	0.48	16	32
7.74	0.28	0.52	22	34
5.16	0.25	0.55	20	35
4.13	0.23	0.50	18	33
3.10	0.22	0.47	18	32
2.07	0.18	0.54	15	35
1.03	0.15	0.70	13	41
0.52	0.29	0.75	22	43

TABLE 26

Distribution Ph_4AsCl between $C_2H_4Cl_2$ and Na_2SO_4 solution over a range of Concentration at 25°.

$[Ph_4AsCl]$ x 10^4M	D	Percentage Extraction
103.7	0.27	21
51.9	0.10	9
41.5	0.12	11
31.1	0.10	9
20.7	0.09	8
15.6	0.06	6
10.4	0.06	6
7.76	0.10	9
5.19	0.08	8
3.11	0.06	6
2.07	0.08	8
1.04	0.19	16

TABLE 27

Uncorrected Distribution Ratios for Ph_3MeAs^+ salts between $CHCl_3$ and Water over range of ionic strengths (Ionic Strength Adjusted with Na_2SO_4)

Ionic Strength	ClO_4^-	NCS^-	I^-	ClO_3^-	NO_3^-
0.02	3.2	1.6	1.8	0.24	0.17
0.1	3.2	1.6	1.8	0.22	0.17
0.5	3.2	1.6	1.8	0.24	0.17
Saturated Na_2SO_4	21	15	13	3.0	2.1

	Br^-	BrO_3^-	Cl^-	$SO_4^=$
0.02	0.15	0.07	0.04	0.02
0.1	0.13	0.06	0.04	0.03
0.5	0.14	0.06	0.04	0.03
Saturated Na_2SO_4	2.3	2.1	0.73	0.58

TABLE 28

Distribution Ratios for various Salts between $CHCl_3$ and Na_2SO_4 Solution at 5×10^{-3}M concentration.

Cation	Temp	ClO_4^-	NCS^-	I^-	ClO_3^-
Ph_3AmP^+	15°	31	20	13	4.2
	25°	27	16	9.5	3.0
	35°	21	13	7.4	2.4
Ph_4As^+	15°	-[a]	37	16	3.5
	25°	-[a]	25	8.5	2.7
	35°	-[a]	17	6.2	2.0
Ph_4P^+	25°	-[a]	26	9.0	2.9
Ph_3nPrP^+	"	12.0	6.3	6.9	0.84
$Ph_3isoPrP^+$	"	13.7	6.5	7.3	1.0
Ph_3EtP^+	"	6.5	3.1	3.6	0.40
Ph_3AllP^+	"	4.1	2.6	2.0	0.38
Ph_3MeAs^+	"	3.2	1.6	1.8	0.19
Ph_3MeP^+	"	2.7	1.5	1.7	0.18
$Ph_2Me_2As^+$	"	0.15	0.05	0.09	0

a Distribution ratios could not be measured because the perchlorate salts were insoluble in both phases at the concentration used.

TABLE 28 (continued)

Cation	Temp.	NO_3^-	Br^-	BrO_3^-	Cl^-
Ph_3AmP^+	15°	2.8	2.3	0.51	0.23
	25°	2.2	1.7	0.51	0.18
	35°	1.9	1.4	0.43	0.16
Ph_4As^+	15°	2.5	2.2	0.45	0.18
	25°	2.2	1.6	0.38	0.16
	35°	1.5	1.1	0.31	0.09
Ph_4P^+	25°	2.0	1.7	0.40	0.14
Ph_3nPrP^+	"	0.53	0.52	0.11	0.04
$Ph_3isoPrP^+$	"	0.62	0.72	0.12	0.06
Ph_3EtP^+	"	0.25	0.17	0.05	0.02
Ph_3AllP^+	"	0.23	0.19	0.04	0.02
Ph_3MeAs^+	"	0.14	0.12	0.03	0.01
Ph_3MeP^+	"	0.11	0.10	0.03	0.01
$Ph_2Me_2As^+$	"	0	0	0	0

TABLE 29

Distribution Ratios for various Salts between CH_2Cl_2 and Na_2SO_4 solution at 5×10^{-3}M concentration.

		Anions			
Cation	Temp	ClO_4^-	NCS^-	I^-	ClO_3^-
Ph_3AmP^+	15°	125	45	11	5.8
	25°	70	40	8.5	5.6
	35°	45	35	7.0	5.3
Ph_4P^+	25°	110	75	15	14
Ph_3nPrP^+	"	60	10	4.3	2.1
$Ph_3isoPrP^+$	"	65	8.7	3.9	1.8
Ph_3EtP^+	"	40	5.3	4.9	0.90
Ph_3AllP^+	"	11.5	4.3	2.0	0.75
Ph_3MeAs^+	"	11.0	2.4	1.9	0.53
Ph_3MeP^+	"	9.5	2.2	1.7	0.40

		NO_3^-	Br^-	BrO_3^-	Cl^-
Ph_3AmP^+	15°	4.7	2.3	1.0	0.22
	25°	4.6	2.3	1.0	0.22
	35°	4.1	2.1	1.0	0.22
Ph_4P^+	25°	10	3.5	1.5	0.33
Ph_3nPrP^+	"	1.4	0.68	0.22	0.03
$Ph_3isoPrP^+$	"	1.3	0.57	0.21	0.02
Ph_3EtP^+	"	0.62	0.25	0.08	0.01
Ph_3AllP^+	"	0.46	0.24	0.04	0.01
Ph_3MeAs^+	"	0.43	0.24	0.04	0.02
Ph_3MeP^+	"	0.26	0.08	0.04	0.02

TABLE 30

Distribution Ratios for various Salts between $C_2H_4Cl_2$ and Na_2SO_4 Solution at 5 x 10^{-3}M Concentration.

				Anion	
Cation	Temp.	ClO_4^-	NCS^-	I^-	ClO_3^-
Ph_3AmP^+	15°	80	22	12	4.2
	25°	50	16	9.5	3.5
	35°	25	13	6.3	3.1
Ph_3nPrP^+	25°	55	7.5	3.2	1.2
$Ph_3isoPrP^+$	"	50	7.1	2.9	1.0
Ph_3EtP^+	"	27	3.7	1.7	0.58
Ph_3AllP^+	"	6.5	2.2	0.71	0.45
Ph_3MeAs^+	"	10.6	1.7	0.60	0.30
Ph_3MeP^+	"	8.2	1.5	0.60	0.26
		NO_3^-	Br^-	BrO_3^-	Cl^-
Ph_3AmP^+	15°	2.8	1.05	0.48	0.09
	25°	2.5	0.79	0.44	0.08
	35°	2.3	0.44	0.40	0.06
Ph_3nPrP^+	25°	0.77	0.23	0.10	0.02
$Ph_3isoPrP^+$	"	0.64	0.20	0.10	0.02
Ph_3EtP^+	"	0.39	0.11	0.02	0.01
Ph_3AllP^+	"	0.23	0.08	0.04	0.01
Ph_3MeAs^+	"	0.18	0.05	0.02	0.01
Ph_3MeP^+	"	0.15	0.05	0.01	0

TABLE 31

Distribution ratios for various salts between $(C_2H_4Cl)_2O$ and Na_2SO_4 solution at 5×10^{-3}M concentration.

Cation	Temp.	ClO_4^-	NCS^-	I^-	ClO_3^-
Ph_3AmP^+	25°	90	4.7	6.8	4.0
Ph_3nPrP^+	25°	65	2.9	3.1	1.6
$Ph_3isoPrP^+$	25°	45	2.7	3.0	1.4
Ph_3MeAs^+	25°	21	2.4	1.1	0.53
Ph_3MeP^+	25°	15	2.3	1.0	0.49

		NO_3^-	Br^-	BrO_3^-	Cl^-
Ph_3AmP^+	25°	3.1	0.85	0.64	0.17
Ph_3nPrP^+	25°	1.2	0.35	0.20	0.04
$Ph_3isoPrP^+$	25°	1.0	0.27	0.19	0.04
Ph_3MeAs^+	25°	0.37	0.13	0.03	0.02
Ph_3MeP^+	25°	0.35	0.10	0.04	0.02

TABLE 32

Properties of Anions

Anions	Crystal Radius Å	Hydrated Radius Å	Enthalpy of Hydration kcal/mole
ClO_4^-	2.92	3.38	-56
NCS^-	1.95	-	-75
I^-	2.16	3.31	-71
ClO_3^-	2.88	3.41	-69
NO_3^-	2.64	3.35	-74
Br^-	1.95	3.30	-80
BrO_3^-	3.08	3.51	-74
Cl^-	1.81	3.34	-87
F^-	1.36	3.52	-121
OH^-	1.76	3.00	-120
NO_2^-	1.55	-	-98
HCO_3^-	-	-	-91
$CO_3^=$	2.66	3.94	-127
MnO_4^-	3.09	3.45	-59
$SO_4^=$	2.90	3.79	-265
$Acetate^-$	1.59	-	-101
IO_3^-	3.30	3.74	-81

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