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THE EXTRACTION OF TETRAHEPTYLAMMONIUM FLUORIDE AND THE SOLVATION OF THE FLUORIDE ION[1]

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Abstract

The extraction of tetraheptylammonium fluoride into solutions of alcohols and into solutions of phenols in toluene has been studied. The dependence of the extraction on the aqueous salt concentration at a fixed concentration of extractant indicates that, in all cases, the extracted ions are associated to ion pairs in the organic phase. The extraction of the salt into varying concentrations of alcohol at a fixed aqueous salt concentration shows that four alcohol molecules are complexed with the fluoride ion. Extractions into varying concentrations of phenol also indicate a tetrasolvated fluoride ion at concentrations of phenol above ~0.004M, but below that concentration only two molecules of phenol are complexed with the anion. The behavior of water in the alcoholic and phenolic systems shows that while two molecules of water are coextracted per fluoride ion into dilute solutions of alcohol, none is coextracted into the phenolic media. An explanation is suggested for these differences in behavior.

Introduction

In recent years, there has been a great deal of interest in the first-shell coordination or solvation of simple cations,[3,4,5] especially in aqueous solution. In contrast, there has been little experimental work on the primary solvation of anions. A previous paper[6] treated the solvation of the hydroxide ion and showed that a solvent-extraction method was suitable for the experimental determination of the alcoholation of this ion in various organic diluents. The present paper provides an extension of the method to the fluoride ion, which is isoelectronic with the hydroxide ion, but is not expected to show tri-solvation as did the latter.

In such studies, the solvation number of the anion of interest is determined from partition studies by protic extractants which are dissolved in a relatively inert diluent. The variation in the salt extraction, at a constant equilibrium aqueous salt concentration, with the concentration of extractant indicates the number of extractant molecules coordinated to the salt. For the successful application of this method the extractant should be weakly acidic and capable of (hydrogen-) bonding to the anion. Dilute solutions of two alcohols, benzyl and decyl, and of two phenols, p-phenyl phenol and 1-naphthol, were used in this study. On the other hand, the diluent should undergo only a weak interaction with the electrolyte compared to that of the extractant, and toluene was chosen for this purpose. Partition of the fluoride ion into the organic phase is promoted by the use of large, hydrophobic tetraalkylammonium cations; any specific interaction between such cations and the basic centers on the extractant molecule is unlikely, so that the observed value of the solvation number should then be associated exclusively with the fluoride ion.

By choosing a cation as large as the tetraheptylammonium ion, extraction of the fluoride salt was obtained in the presence of the extractant, while without the extractant the blank value was small enough so as not to interfere except at the lowest extractant concentrations.

Experimental

Reagents. A stock solution of tetraheptylammonium fluoride, THAF, was prepared by partially converting the iodide salt (Eastman Organic Chemicals, White Label) in aqueous solution to the fluoride with silver fluoride; the conversion was then completed by passing the filtered aqueous solution, made slightly basic, through an anion exchange column (AG1-X4, Bio-Rad Laboratories) in the fluoride form. The final product was standardized by a spectrophotometric method[7] using a zirconium-alizarin reagent.

Benzyl alcohol and 1-decanol (Matheson, Coleman and Bell, White Label) were dissolved in toluene (Baker Chemical Co., analytical reagent) to give stock solutions in the region of 0.5M. Similarly, p-phenyl phenol and 1-naphthol were weighed out into toluene to give stock solutions in the region of 0.1M. Solutions of 1-naphthol were prepared freshly as required to avoid the risk of contamination by oxidation. Less concentrated solutions of the extractants were obtained by volumetric dilution.

Procedure. The solutions of THAF, containing a measured quantity of $^{18}F^-$ tracer ($t_{1/2}$ = 110m.), were shaken for 20 minutes with the solutions of alcohol in toluene. This equilibration time was chosen after experiments with shaking times varying from 10 to 60 minutes all showed identical partition of the

fluoride tracer. The volume ratio of organic phase to aqueous phase was in all cases 5:3. The samples were then centrifuged and 2 ml aliquots were taken from the organic phase for γ-counting in a well-type scintillation counter with a 2" × 2" Na(Tl)I crystal. The time at the beginning of each count was recorded. A standard ^{18}F sample containing the same volume of tracer as had been initially introduced into the extractant samples was similarly counted throughout the run, and a decay curve was constructed for the standard sample. The organic-phase concentration of fluoride in a sample could then be determined as the product of the initial aqueous concentration of THAF and the ratio of organic-phase counting rate to the standard sample's counting rate at the same instant of time. The equilibrium aqueous-phase THAF concentration is then obtained by difference from the initial aqueous-phase and the equilibrium organic-phase concentrations, taking due regard of the volume ratios of the two phases.

The procedure for experiments with the phenolic extractants was similar. The volume ratio, organic to aqueous, was in most cases 10:1. However, ratios of unity, 1:2 and 1:10 were used when the distribution was high enough to cause a depletion of electrolyte in the aqueous phase which would be serious at a 10:1 ratio.

The partition of 1-naphthol between toluene and water (serious only for one sample, with a 1:10 volume ratio) was determined by preparing a standard solution of 1-naphthol in water (9.0×10^{-4} M) and measuring the absorbance of this solution and of its dilutions over a 20-fold range at 2900Å. Standard solutions of 1-naphthol in toluene were then equilibrated with water and with aqueous solutions containing varying amounts of THAF, and the

absorbance of samples drawn from the aqueous phase at equilibrium were measured and compared to those on the standardization curve.

Investigations of the monomer-dimer equilibrium at 25° for the alcohols and the phenols in dry toluene were made on a vapor-pressure osmometer(Model 301-A Mechrolab Inc., Mountain View, California). Known solutions of biphenyl were used to calibrate the instrument.

Water determinations in the organic phase were made by the Karl Fischer method using an electrometric end-point. All experiments were done at 22 ± 2°.

Results

Investigations were first made of the extraction of water into toluene solutions of 1-naphthol over the concentration range 0.01 to 0.5M, and into solutions of benzyl alcohol and 1-decanol over the range of alcohol concentrations 0.1 - 0.8M. Solutions of these extractants were equilibrated with water, and the concentration of water in the organic phase was determined by the Karl Fischer method. Extraction into toluene alone gave a value for the solubility of water in toluene of 0.023M (lit. values[8] 0.02 - 0.022M), which, when multiplied by the appropriate volume fraction of toluene in a given solution of extractant, has been subtracted from the measured total concentration of water in the organic phase. A log-log plot of these adjusted organic-phase water concentrations vs. concentration of alcohol is shown in Fig. 1 and that for solutions of 1-naphthol in toluene is presented in Fig. 2.

By the same method, determinations were also made of water coextracted with THAF into the organic phase. After equilibrating 0.386M benzyl alcohol

solutions with concentrations of THAF ranging from 9.8×10^{-3} M to 2.06×10^{-2} M, determination was made of the total concentration of water in the organic phases. Since the activity of water in a 0.02M solution of THAF will be very close to unity, the difference between the measured concentration of water and that which would extract into the benzyl alcohol in the absence of salt gives $[H_2O]'$, the concentration of coextracted water. The mean of the ratios $[H_2O]'/[THAF]_o$ which are shown in Table I is 2.3 ± 0.1.

TABLE I

Water Coextracted with THAF into 0.386M Benzyl Alcohol in Toluene

Equil. Concn.. THAF(org.)	Total Concn. H_2O(org.)	Concn. H_2O(alc.)	$[H_2O]'$	$\frac{[H_2O]'}{[THAF]_o}$
2.06×10^{-2}	6.06×10^{-2}	1.2×10^{-2}	4.9×10^{-2}	2.4
1.32×10^{-2}	4.15×10^{-2}	1.4×10^{-2}	2.8×10^{-2}	2.1
9.8×10^{-3}	3.98×10^{-2}	1.6×10^{-2}	2.4×10^{-2}	2.4

Similar experiments performed with solutions of 1-naphthol showed that no measurable quantity of water was coextracted with THAF when the latter was extracted by solutions of 1-naphthol in toluene.

For extractions of THAF into dilute solutions of alcohol in toluene, aqueous concentrations of THAF from 0.0005 to 0.05M were equilibrated with solutions of alcohol over the concentration range 0.07 to 0.5M. A log-log plot of organic-phase concentration vs. aqueous concentration of THAF for

extractions into 0.193M benzyl alcohol and into 0.433M 1-decanol in toluene is shown in Fig. 3. The extraction of THAF into toluene alone is not significant over this range of concentrations and so no blank correction is necessary. The solid lines represent experimental data and the dotted lines show the same data corrected to a constant equilibrium concentration of alcohol, an adjustment which will be discussed later.

Figures 4 and 5 show the dependence of the extraction on alcohol concentration for the systems involving benzyl alcohol and 1-decanol, respectively, where the continuous lines denote experimental data and the dotted lines show the data after correction to a constant aqueous concentration of THAF and to equilibrium values of alcohol concentration.

Extractions into dilute solutions of 1-naphthol and p-phenyl phenol are shown as a function of aqueous THAF concentration in Figs. 6 and 7, respectively, where the continuous and dashed lines have the same significance as in Fig. 3. The dependence of the extraction on phenol is shown in Figs. 8, 9, 10, and 11, and is corrected to the appropriate constant aqueous salt concentration (see Discussion section). As can be seen in Figs. 9, 10, and 11, at very low concentrations of phenol the organic concentration of THAF attains a constant value and is effectively a measure of the extraction into toluene alone. These values, taken as 1.2×10^{-8}M, 1.0×10^{-6}M, and 1.5×10^{-6}M in Figs. 9, 10, and 11, respectively, have been subtracted from all other points; the corrected curve is shown with solid squares.

In the few cases where a 1:10 volume ratio of organic phase to aqueous phase was used, allowance for the small losses in extractant concentration to the aqueous phase have been made by determining a partition constant for

1-naphthol between toluene and water, and also between toluene and 2.74×10^{-4} M THAF in water. In both cases a value for D, the ratio of organic concentration to aqueous concentration of 1-naphthol, of 46.5 ± 1 was found.

Data from vapor-pressure osmometry experiments yield a mean molecular weight of the extractant. The values so determined for the extractants in dry toluene over the concentration ranges used in this work agreed, within experimental error, with those expected for the monomer, and one would not expect a greater tendency for association in wet toluene. As an example, Table II gives the results found for 1-naphthol in toluene.

TABLE II

Mean Molecular Weight of 1-Naphthol in Toluene

Concn. (molar)	Mol. wt. (obs.)
0.26	149
0.17	144
0.085	147
0.043	148

Molecular weight of monomer = 144.16

Discussion

Alcohol-H_2O and Phenol-H_2O. It has been assumed that the equilibrium between water and extractant is independent of any other extraction equilibrium that may occur in the system. For the equilibrium

$$nROH(org) + H_2O = H_2O.nROH(org) \tag{1}$$

where ROH represents an alcoholic or a phenolic extractant, the equilibrium constant is given by

$$\mathcal{K}_{H_2O} = \frac{(H_2O.nROH)_o}{(H_2O)(ROH)_o^n} = \frac{[H_2O.nROH]_o y_{H_2O.nROH}}{(H_2O)[ROH]_o^n y_{ROH}^n} \tag{2}$$

In the above expression parentheses denote activities; brackets, molarities; and y, molar activity coefficients. It has been assumed, since the concentration of extracted water is much smaller than that of the extractant, that the complex is a monohydrate. Furthermore, in the relatively dilute solutions studied, it might be hoped that the activity coefficient ratio will be constant. Then eq. 2 can be rewritten

$$K_{H_2O} = \frac{[H_2O.nROH]_o}{[ROH]_o^n(H_2O)} \tag{3}$$

If the water activity remains close to unity, eq. 3 suggests that a log-log plot of $[H_2O.nROH]_o$ vs. $[ROH]_o$ will yield the value of n.

A log-log plot of organic-phase water concentration vs. initial concentration of ROH, Fig. 1, shows at low concentrations of alcohol a line whose gradient attains a value between 1 and 2, but is close to 2. This suggests that two alcohols are complexed to one water. A correction of the data to the equilibrium, rather than initial, concentration of alcohol by means of the relation $[ROH]_o = [ROH]_{initial} - n[H_2O]_o$ was applied. This brings even the points at higher alcohol concentrations onto a line of slope 2.0, with a value of $K'_{H_2O} = 0.15$ for both the benzyl alcohol and the 1-decanol systems.

The data obtained for the system water- 1-naphthol were similarly treated. A log-log plot of organic-phase water concentration against initial concentration of 1-naphthol, Fig. 2, shows a slope of unity suggesting only one naphthol per extracted water. The correction to equilibrium concentrations then generates a line of slope n = 1.0 with $K'_{H_2O} = 0.15$. The more strongly acidic phenols surely coordinate to water through their hydroxylic proton, $ROH....OH_2$, and one molecule is sufficient to solvate the water molecule. This is in contrast to the alcohol systems where a disolvate was observed, and where we are not sure of the direction of the hydrogen bonds involved.

<u>ROH-H_2O-THAF.</u> The equation for the extraction of a tetraalkylammonium fluoride into a dilute solution of a protic extractant in an "inert" solvent can be written

$$nROH(org) + mH_2O + R_4N^+ + F^- \rightarrow R_4N^+...F^-.mH_2O.nROH(org) \qquad (4a)$$

or

$$nROH(org) + mH_2O + R_4N^+ + F^- \rightarrow R_4N^+(org) + F^-.mH_2O.nROH(org) \qquad (4b)$$

depending on whether the species in the organic phase is associated as ion pairs (4a), or dissociated (4b).

The corresponding equilibrium constants are

$$\mathcal{K}^{a}_{R_4NF} = \frac{(R_4N^+...F^-.mH_2O.nROH)_o}{(R_4N^+)(F^-)(H_2O)^m(ROH)^n_o} = \frac{[R_4N^+...F^-.mH_2O.nROH]_o y_o}{(R_4N^+)(F^-)(H_2O)^m[ROH]^n_o y^n_{ROH}} \tag{5a}$$

$$\mathcal{K}^{d}_{R_4NF} = \frac{(R_4N^+)_o(F^-.mH_2O.nROH)_o}{(R_4N^+)(F^-)(H_2O)^m(ROH)^n_o} = \frac{[R_4N^+]_o[F^-.mH_2O.nROH]_o y^2_{\pm}}{(R_4N^+)(F^-)(H_2O)^m[ROH]^n_o y^n_{ROH}} \tag{5b}$$

Activity coefficients of THAF in water have not been determined and so the product, $(R_4N^+)(F^-)$, in eq. 5 must be replaced by a product of concentrations. This is not expected to introduce significant errors for the dilute solutions used in this work, since, at higher salt concentrations, values of the molal aqueous activity coefficient, $\gamma_{\pm}$, for tetrapropyl and tetrabutyl ammonium fluoride[9] are known and they are still not far from unity (TPAF $\gamma_{\pm}$ = 0.859, m =0.1; TBAF $\gamma_{\pm}$ = 0.904, m = 0.1), and somewhat larger values might be expected to obtain for THAF in water. Also, the activity of water remains very nearly unity. Furthermore, for the dilute solutions considered here, the ratio of organic-phase activity coefficients in eq. 5 is again assumed to be constant. If the numerator of eq. 5 is replaced by $[F^-]^z_o$ to represent the organic phase concentration of salt, with z = 1 for case (a) and z = 2 for case (b), then both reduce to the simpler form

$$K'_{R_4NF} = \frac{[F^-]^z_o}{[R_4N^+][F^-][ROH]^n_o} \tag{6}$$

Whether association or dissociation obtains in the organic phase can be determined by studying the extraction as a function of the aqueous THAF concentration at a constant equilibrium concentration of extractant. A log-log plot of $[F^-]_o$ vs. $[R_4N^+][F^-]$ is shown in Fig. 3 for extractions into 0.433M 1-decanol and into 0.193M benzyl alcohol. At low aqueous concentrations of THAF the slope has a value of unity corresponding to the value z = 1 and indicating that the extracted salt is ion paired. At the higher concentrations of THAF an increasingly large fraction of alcohol is complexed with the extracted species, and a correction to the condition of constant (initial) equilibrium alcohol concentration is necessary. The corrected value of organic concentration of THAF is obtained from the expression (justified below)

$$[F^-]'_o = [F^-]_o[ROH]'^4_o/[ROH]^4_o \qquad (7)$$

where the primed quantities refer to the desired condition of fixed (initial) equilibrium alcohol concentration, e.g., $[ROH]'_o = [ROH]_{initial}$, and unprimed quantities refer to the measured equilibrium values, with

$$[ROH]_o = [ROH]_{initial} - 2[2ROH.H_2O] - 4[F^-]_o \qquad (8)$$

It can be seen that the corrected concentration $[F^-]'_o$ raises the points to the dashed line of slope 1.0 and indicates that the extracted species is an ion pair over the entire range of concentrations studied.

At a constant equilibrium aqueous concentration of THAF, a log-log plot of $[F^-]_o$ vs. equilibrium concentration of alcohol should generate a line of slope n, where n is the number of extractant molecules in the complex. Such plots have been constructed for extractions by benzyl alcohol in Fig. 4. When plotted against initial concentration of alcohol the line has a slight curvature and a gradient that lies between 3 and 4. This suggests that four molecules of alcohol are involved in the extracted complex. Corrections to the actual equilibrium alcohol concentration by means of eq. 8 with the suggested value of n=4 gives the points in Fig. 4 plotted as open circles. These do, indeed, fall on a line of slope n = 4.0, validating the use of $4[F^-]_o$ in eq. 8 and giving the quartic dependence on alcohol concentration used in eq. 7.

If the molarity of THAF in the aqueous phase is not held constant, but instead, is varied simultaneously with the concentration of alcohol, then a value for the solvation number may be determined from a log-log plot of $[F^-]_o/[R_4N^+][F^-]$ vs. $[ROH]_o$. This procedure was followed for extractions into solutions of 1-decanol, and, as shown in Fig. 5, also gives a value n = 4.0, again after correction to equilibrium alcohol concentration.

Further interest in this system attached to the problem of determining m, the number of water molecules coextracted per molecule of THAF. As described in the Results section, this investigation revealed the presence of somewhat more than two molecules of water extracted per ion pair of THAF. The presence of coextracted water seems to reflect the difference in acidity between water and an alcohol. Water is a stronger acid than the alcohols used here and, furthermore, water molecules may well be able to approach the site of anionic

charge more closely than can those alcohols, and to this extent will be more able to satisfy the solvation requirements of the fluoride ion in the organic medium. But on the other hand, a water molecule, in particular one bound to a fluoride ion, obtains better solvation itself from other water molecules in the aqueous phase than from the dilute organic-phase alcohol solution, and such a lack of secondary solvation should hinder its coextraction. Thus, in the competition between water and alcohol to complex with the extracted species, a balance is achieved wherein the resultant is an ion pair solvated by both, e.g., $[R_4N^+...F^-(H_2O)_m(ROH)_4]_o$, where m, in the region of concentration of $[F^-]_o \sim 0.01\underline{M}$, has a value around 2.

There is probably a stronger hydrogen-bonded interaction between the fluoride ion and benzyl alcohol than between that ion and 1-decanol. The aryl group tends to withdraw electronic charge away from the terminal hydroxyl group and so the formal positive charge on its proton is greater than that on the same site in 1-decanol. The consequence of this stronger solvation by benzyl alcohol is reflected in the higher values of the distribution coefficient than those for 1-decanol under otherwise identical conditions. A similar difference between the use of benzyl alcohol and 1-decanol has been observed in an earlier study of hydroxide extractions.[6]

The phenolic extractants used in this work have acidity constants which are at least seven or eight orders of magnitude greater than those for the alcohols. It can be argued that the use of phenols should thus yield much better extraction of anions into the organic phase than the alcohols because of their enhanced coordination to the anion. Additionally, their greater acidity, and hence greater solvating ability, may well be sufficient to cause

a reduction in the solvation number of the fluoride ion in the toluene phase. As with the alcohol-toluene systems already described, the dilute phenolic systems studied might be expected to yield an ion-paired extracted species in the toluene diluent of low dielectric constant. Indeed, the data plotted in Figs. 6 and 7 for the extraction of THAF by a constant concentration, 7.4×10^{-3} M p-phenyl phenol and 6.4×10^{-3} M 1-naphthol, give log-log slopes of 1, indicating that in both cases the organic species is an ion pair.

Figure 8 shows the dependence of the extraction, at a fixed aqueous concentration of THAF, 2.74×10^{-4} M, on the concentration of 1-naphthol. After the data have been corrected to a constant aqueous equilibrium concentration, there appears to be a discontinuity in gradient at a naphthol concentration of about 4×10^{-3} M. A line of slope two drawn through the lower points (where the various corrections are negligible) and extended as a dotted line to higher concentrations yields organic-phase salt concentrations which may tentatively be identified as those of a disolvated species. Subtraction from the total experimental concentration of $[F^-]_o$ allows division of the measured concentration into a disolvate and a higher component. Final corrections to equilibrium naphthol concentration are then made commensurate with the amount of di- and assumed tetrasolvate in the organic phase. This yields a slope of 3.8+ for the upper line, suggesting, indeed, the presence of a tetrasolvate. The extraction from an aqueous concentration of 2.74×10^{-3} M THAF as a function of p-phenyl phenol concentration, Fig. 9, shows more unambiguously a discontinuity at the same order of phenol concentration, with a disolvated ion-pair below 4×10^{-3} M p-phenyl phenol and a higher solvated species above this concentration, and the various corrections also

generate a line of slope 3.8. At a still higher initial concentration of THAF, 2.74×10^{-2}M, extractions into both p-phenyl phenol and 1-naphthol solutions show, over most of the accessible range of extractant concentrations, the presence of the disolvated species (Figs. 10 and 11). But under these conditions, already at 0.001M extractant, approximately 20% of the phenol is complexed as a disolvate. Beyond this concentration and through the critical region of 4×10^{-3}M, the concentration of THAF in the organic phase is so high as to make the tetrasolvated complex a physical impossibility. It should be noted that the question whether a small fraction of trisolvated species is formed in the transition region between the disolvated and tetrasolvated fluoride ion is left unanswered in the present work.

There is already considerable experimental evidence that phenols do undergo stronger interactions with halide ions than do alcohols. Studies of the acidity constant of HCl[10] in dioxane solution in the presence of small amounts of phenols show increases in K_a which are much greater than those induced by the addition of alcohols. Also Swain[11] has studied the reaction between triphenylmethyl chloride and methanol in benzene and an excess of pyridine, in which the first step involves the ionization of the halide. Stronger solvation of the chloride ion seems to take place when small amounts of phenol (pK_a=9.998) are introduced into the reactants and the rate of formation of the methyl ether is increased by a factor of seven, while the addition of p-nitrophenol (pK_a=7.14) increases the rate twentyfold.

The consequence of stronger acid-base interactions between the fluoride ion and phenolic extractants rather than alcohols is that, over a considerable concentration range, only two molecules of the phenol are required to solvate the ion pair, while four molecules of alcohol are required. An extension of

this idea suggests that still stronger anion-extractant interactions, as might be obtained with a still more acidic extractant such as a long-chain carboxylic acid, may yield a still smaller coordination number.

A second consequence of the stronger anion interactions with phenol has to do with the coextracted water. As has been already mentioned, water is a stronger acid than alcohol and may solvate anions more effectively, and does, in fact, appear coordinated with the fluoride ion in the alcohol extraction systems. However, in the phenolic systems, the phenol provides a more acidic site for the solvation of anions and so might be expected to displace the water. A study of the water behavior in the organic phase shows, indeed, that no detectable amount of water is coextracted with the fluoride ion.

From this study, and the previous one on the hydroxide ion, it appears clear that the coordination number of small anions toward acidic molecules can be determined by the solvent extraction method used, and that this coordination number decreases with increasing acidic strength of the solvating molecules.

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Footnotes and References

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