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COORDINATION OF FLUORIDE AND CHLORIDE ANIONS WITH ALCOHOL AND PHENOL¹

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Abstract

The extraction of tetraalkylammonium fluoride and chloride into solutions of benzylalcohol and p-nonylphenol in toluene and in osooctane has been studied. In the organic-phase concentration regions studied, these species are associated to ion pairs. The results of slope analysis and of water determination by the Karl Fischer method suggest that the extracted fluoride species tend to involve a first-shell coordination number of four. For the extracted chloride species, the number seems less well-defined, but the saturated limit may well be four also.

Introduction

In recent years, there has been renewed interest in the coordination or solvation of simple anions.⁵⁻¹⁴ Most of these solvation studies of salts have been carried out by IR or UV spectroscopic methods.^{5-11,13} A number of workers have studied the effect of alkylammonium halides on the X-H stretching frequencies of some protic solvents. Spectral shifts attributed to X-H ... anion hydrogen bonding were observed, and their magnitude generally decreased in the order $F^- > Cl^- > Br^- > I^-$,⁷ although some workers^{10,13} found an anomalous position for F^- , that is, $Cl^- > F^- > Br^- > I^-$. Using pressure-composition isotherms at low temperatures, definite integral numbers of fluoroform or chloroform have been found to coordinate to some tetraalkylammonium halides,¹² but no definite fluoride complex could be found. The effect of the anions on the PMR chemical shifts of a number of alcohols has also been investigated,¹⁵ and the chemical shifts decreased in the order $Cl^- > Br^- > I^-$, indicating a decreasing interaction with alcohol in the same order.

A recent paper¹⁴ on the extraction of tetraalkylammonium fluoride¹⁶ into toluene by alcohols and phenols indicated that definite numbers of extractant molecules were involved in the organic-phase species. These molecules were surely hydrogen-bonded to the F^- , as little interaction would be expected with large quaternary ammonium cations. Four benzyl or decyl alcohol molecules were required, and with the phenols, two species were observed: a two-phenol and a higher, probably four-phenol, F^- complex. This suggested the stepwise complexing of the F^- by phenol, as is commonly observed with metal cations and simple ligands.

It was of interest to try to obtain better data on the higher F^- -phenol complex or complexes, and to see if the F^- -alcohol data in toluene could be extended to more dilute alcohol concentrations so as to look for lower complexes. We were also curious to see whether the same alcoholation number would be obtained with a different diluent, and whether Cl^- would show the same behavior or indicate a different alcoholation and phenolation number. The Cl^- ion is larger and could accommodate a larger number of molecules around itself, but for the same reason it is less basic than F^- and so needs less solvation.

Experimental

Reagents.— Stock solutions of tetraalkylammonium fluorides were prepared by titrating the hydroxide salts with hydrofluoric acid to pH 8. The hydroxide salts were obtained by shaking suspensions of the iodides (Eastman Organic Chemicals, White Label) in water with silver oxide. Completion of the conversion was checked by addition of silver fluoride solution. Hydrochloric acid was used instead of hydrofluoric acid for preparation of the chloride salts. The fluoride concentration was standardized by a spectrophotometric determination of the accompanying tetraalkylammonium cation as described below, and the chloride solutions were standardized against silver nitrate solution using fluorescein as indicator.

Benzyl alcohol (Eastman Organic Chemicals, White Label) and p-nonylphenol (Rohm and Haas, Industrial grade) were distilled under reduced pressure, and the middle fractions dissolved in toluene (Baker Chemical Co., Analytical reagent) to give stock solutions. Similarly, benzyl alcohol solutions in isooctane (Mallinckrodt spectro grade) were also prepared.

The 118-min $^{18}\text{F}^-$ tracer was obtained from the reaction $^{16}\text{O}(^4\text{He,pn})^{18}\text{F}$ by irradiating distilled water with alpha particles at the Berkeley 88-Inch Cyclotron. The 35-min $^{38}\text{Cl}^-$ tracer was produced by neutron capture on LiCl in the Mark III Triga Berkeley Research Reactor.

The Karl Fischer reagent used for water determination was Matheson, Coleman and Bell, stabilized, premixed, single solution.

Procedure.— The aqueous solutions of fluoride, containing $^{18}\text{F}^-$ tracer, were shaken for 90 minutes with equal volumes of the organic-phase solutions of alcohol or phenol. The phases were then centrifuged and separated. Duplicate

3-ml aliquots were taken from the organic layer, and 100 or 200 μ l aliquots were removed from the aqueous phase and then diluted to 3 ml. These samples were counted in a well-type scintillation counter with a 5 cm $\times$ 5 cm Na(Tl)I crystal. The concentration of fluoride in each phase was calculated from the distribution coefficients obtained and the initial concentration of fluoride in the aqueous phase.

The procedure for experiments with chloride was similar, except that the chloride was usually determined spectrophotometrically by means of its accompanying tetraalkylammonium cation.¹⁷ Samples of the solutions were diluted to concentrations between 10^{-5} and 10^{-4} M. Then, 5 ml of the diluted solution was shaken with 5 ml of 0.010 M sodium picrate, 5 ml of saturated magnesium sulfate solution, and 5 ml of chloroform (for the aqueous-phase determination), or 5 ml of distilled water (for the organic-phase determination). Absorbance of the picrate in the organic layer was measured against reagent blank at the absorption peak in each solvent, using 1-cm cells. With isooctane solutions, 5 ml dichloroethane were added to complete the extraction of tetraalkylammonium picrate. For samples less than 10^{-5} M in salt concentration, 10-cm cells were employed. The wave lengths used were 375 m μ , 362 m μ , and 372 m μ for chloroform, toluene, and isooctane-dichloroethane mixture, respectively. Interference by alcohol or by phenol was negligibly small when its concentration was less than 0.010 M.

The volume ratio of organic to aqueous phase was in most cases 1:1, although ratios of 1:2 and 1:5 were used when the distribution was high enough to cause a depletion of the salt in the aqueous phase.

Water coextracted with the salt into the organic phase was determined by the Karl Fischer method, using an electrometric end-point. Since the water uptake depended somewhat on the room temperature, the amount of water extracted by the toluene alone and by the extractant-toluene solutions were always measured also at the same time. All experiments were done at room temperature, $23 \pm 2^\circ \text{C}$.

Results

Figure 1 shows the water extracted by nonylphenol alone in toluene; the water extracted by toluene itself, calculated as the solubility of water in toluene (0.024-0.026, depending upon the temperature, $23 \pm 2^\circ \text{C}$) times the volume fraction of toluene, has been subtracted. The amount of water taken up by benzyl alcohol solutions in toluene is given in Reference 14, and these values have been rechecked in the present work. At 0.1 M alcohol, a higher value has been found than that extrapolated from the 2:1 complex indicated in Reference 14 at higher concentrations, possibly suggesting the appearance of a 1:1 benzyl alcohol-water complex.

The results of the salt extractions are shown as log-log plots of the organic-phase salt concentration vs. the organic-phase extractant concentration or vs. the aqueous salt concentration. Extractions of the fluoride are shown in Figures 2 to 5. Figures 2 and 3 are extensions of the work of the previous paper¹⁴ to lower alcohol concentration and to higher phenol concentration, respectively. In order to not have to make appreciable corrections for changes (due to extraction) in the initial aqueous fluoride salt concentration, the range of extractant concentrations is covered, not with a single, fixed aqueous fluoride molarity, but in two or three sections, each with a different initial salt concentration. They are normalized to a common curve by means of a factor determined empirically through the use of data points which overlap two sections. The original and normalized points are shown in Figures 2 and 3. In Figures 4 and 5, isooctane is used as diluent instead of toluene for extractions with benzyl alcohol.

Extractions of chloride are shown in Figures 6 to 10. Figure 6 is of extractions of tetrapentylammonium chloride with benzyl alcohol in toluene. In Figure 7 are shown plots of organic-phase tetrapentylammonium chloride concentration vs. the aqueous salt concentration for two p-nonylphenol molarities.

The third and lowest curve is a blank (no nonylphenol) in toluene alone; below 10^{-2} M aqueous chloride concentration, this blank was below the limit of spectrophotometric determination, or 10^{-7} M. Also shown are plots vs. the mean ionic activity of aqueous tetrapentylammonium chloride. The necessary aqueous activity coefficients have been estimated from smooth curves drawn through the data of Lindenbaum and Boyd¹⁸ above 0.1 M and from a computer evaluation of Poirer's expression¹⁹ below 0.01 M. Extractions of the chloride salt vs. nonylphenol in toluene are given in Figure 8, and again broken into two sections to reduce the corrections. Figures 9 and 10 show extraction of tetrahexylammonium chloride with benzyl alcohol in isooctane; one is the variation with aqueous salt concentration, and the other is as a function of alcohol molarity. The corrections to constant aqueous salt concentration and to constant organic-phase extractant concentration were made as described in the earlier paper.¹⁴

The water content of the organic-phase salt solutions in toluene are given in Tables I-V for tetraheptylammonium fluoride-nonylphenol, tetrapentylammonium chloride-nonylphenol, tetrahexylammonium chloride-nonylphenol, tetrapentylammonium chloride-benzyl alcohol, and tetraheptylammonium chloride-benzyl alcohol, respectively. The water dissolved in toluene alone has been subtracted from the data shown in the $[H_2O]_{total}$ column of the Tables. The column labeled $\bar{n}$ lists the ratio of the average number of phenol or alcohol molecules complexed per halide ion, as determined from the slope of the appropriate plot at the corresponding free extractant concentration in Figures 2, 3, and 6-8. The amount of water associated with the anion is obtained by subtracting the amount of water bound to uncomplexed phenol or alcohol from the total amount of water in

the organic-phase $[H_2O]_{total}$. After determining the amount of uncomplexed extractant by subtracting the appropriate multiple (the average coordination number, $\bar{n}$) of the anion concentration from the total extractant concentration, the water bound to the uncomplexed extractant is obtained by interpolation from additional experiments performed at the same time (and thus at the same temperature) using extractant-toluene solutions equilibrated with water alone.

Discussion

The process of handling the data by slope analysis is similar to that employed in earlier work,¹⁴ but in the present study, computer least-square-fits to a polynomial expansion in the extractant concentration were also made, as well as the graphical fits. The equation for the extraction of a tetraalkyl-ammonium salt as an ion pair into a dilute solution of a protic extractant in an inert solvent can be written

with the corresponding equilibrium constant

$$\begin{aligned} K_n^a &= \frac{(\text{R}_4\text{N}^+ \cdots \text{F}^- \cdot m\text{H}_2\text{O} \cdot n\text{ROH})_o}{(\text{R}_4\text{N}^+) (\text{F}^-) (\text{H}_2\text{O})^m (\text{ROH})_o^n} = \frac{[\text{R}_4\text{N}^+ \cdots \text{F}^- \cdot m\text{H}_2\text{O} \cdot n\text{ROH}]_o y_o}{(\text{R}_4\text{N}^+) (\text{F}^-) (\text{H}_2\text{O})^m \cdot [\text{ROH}]_o^n \cdot y_{\text{ROH}}^n} \\ &= K_n^a \frac{y_o}{y_{\text{ROH}}^n} \end{aligned} \quad (2)$$

We shall usually employ concentrations rather than activities for the tetraalkyl-ammonium salts, but this should not affect the results of the slope analyses in the dilute solutions used. In the more concentrated aqueous solutions, measured or estimated activity coefficients are used. However, it should be remembered that the equilibrium concentrations of the different species must be used. This requires that the amount of extractant complexed by water be considered if that water-extractant complex involves more than one molecule of extractant. Previous work¹⁴ has shown that in the concentration range under investigation, the benzyl alcohol-water complex in toluene does involve two molecules of alcohol per molecule of water, and follows the expression,

$$K_{H_2O} = \frac{[H_2O \cdot 2ROH]_o}{[ROH]_o^2 (H_2O)} \quad (3)$$

Figure 1 shows a log-log plot of organic-phase water vs. p-nonylphenol concentration in toluene. The slope of unity indicates that only one molecule of phenol is involved in the water complex, as previously found for 1-naphthol. The value of $K_{H_2O} = 0.11$ is slightly lower than the value of 0.15 determined for the more acidic 1-naphthol. In all of these cases we are assuming, but have not proved, that only one water molecule is in the extracted complex.

With low-dielectric-constant diluents such as toluene ($\epsilon = 2.38$ at $25^\circ C$)²⁰ and isooctane ($\epsilon = 1.94$ at $20^\circ C$),²⁰ one can expect the extracted complex to be associated to an ion pair, and this can be checked by making a log-log plot of the organic-phase salt concentration, $[X^-]_o$, vs. the aqueous, $[X^-]$, holding the extractant concentration constant. A slope of two confirms the ion-paired nature of the extracted salt (with the reasonable assumption that it is dissociated in the aqueous phase). In such a case, the complementary experiment of determining the slope of the log-log plot of $[X^-]_o$ vs. the equilibrium extractant concentration, $[ROH]_o$, holding the aqueous salt molarity constant, gives n , the coordination number of X^- towards the extractant.

In the previous paper, it was shown that the tetrahexylammonium fluoride-benzyl alcohol complex below $\sim 5 \times 10^{-3} M$ in toluene was indeed an ion pair.¹⁶ Therefore, in Figure 2 the slope of the log-log plot of $[F^-]_o$ vs. [benzyl alcohol] indicates the average coordination number of F^- for alcohol at that point. The results at low alcohol concentration yield a slope of two; the curve at higher alcohol concentrations can be resolved into an additional

component of slope four, as was previously found.¹⁴ A least-square fitting by computer to a power series expression in the alcohol concentration indicated the following equilibrium quotients for tetrahexylammonium fluoride and benzyl alcohol in toluene:

$$K_1^a = 3 \times 10^{-2} (\text{mol/l})^{-2}; K_2^a = 4 (\text{mol/l})^{-3}; K_3^a = 3 \times 10^1 (\text{mol/l})^{-4}; K_4^a = 3 \times 10^2 (\text{mol/l})^{-5}$$

This resolution of the curve is shown in Figure 2, and it can be seen that the 2:1 and 4:1 complexes predominate. A less complete study with tetraheptylammonium fluoride and benzyl alcohol yields by graphical analysis, mainly 2:1 and 4:1 species, with $K_2^a = 2 \times 10^3 (\text{mol/l})^{-3}$ and $K_4^a = 3 \times 10^5 (\text{mol/l})^{-5}$.

Use of a chemically more inert diluent, isooctane, might be expected to change the magnitude of the extraction of F^- and possibly to affect the nature of the extracted species. The log-log plot of organic-phase tetraheptylammonium fluoride vs. aqueous salt concentration for a fixed concentration of benzyl alcohol in isooctane, Figure 4, starts with a slope of 2, indicating ion-pair behavior, but levels off just below 0.01 M aqueous fluoride concentration, and then decreases. Comparable behavior was also found earlier in the hydroxide study.²¹ This is probably due to formation of a salt micelle in the aqueous-phase and to some solubilization of the benzyl alcohol into the micelle. The fact that an aqueous micelle is involved is indicated by the dependence of the concentration at which this behavior appears upon the size of the alkylammonium cation. Some dissolution of the alcohol in the micelle is necessary to explain the peak and subsequent decrease of the extraction with increasing aqueous salt concentration; formation of the micelle alone would cause the curve to approach a horizontal line, but not to decrease. Corroborating evidence

of this latter point is given by a curve (not shown) of salt extraction into toluene alone (no alcohol present) where the value of the slope begins to decrease at the same aqueous salt concentration as in Figure 4, but the curve does not peak and show a decrease even at aqueous concentrations higher than those used in Figure 4.

But because of this behavior, the fixed aqueous tetraheptylammonium fluoride concentration chosen for the log-log plot of $[F^-]_o$ vs. [alcohol], Figure 5, was taken as 6.65×10^{-3} M, below the onset of micelle formation. The three experimental points yield a slope of 4, suggesting a tetrasolvate with the value $K_4^a = 2 \times 10^4 (\text{mol/l})^{-5}$. Little evidence for a disolvate appears in the limited (useful) concentration region studied, namely 0.05 to 0.2 M alcohol, although equal amounts of the 4:1 and 2:1 species occur with ~ 0.1 M benzyl alcohol in toluene, and the latter species dominates at still lower alcohol concentrations. Probably the principal reason for the existence of the 4:1 complex in isooctane to lower alcohol concentration than in toluene is the greater chemical inertness of the aliphatic diluent relative to the aromatic. The alcohol's hydroxyl group can interact with the (basic) π -electron system of the latter solvent, and so have a decreased effective concentration or activity compared to the same concentration in isooctane. But the greater inertness of isooctane also means that the fluoride complex must obtain its solvation more completely from the alcohol and less from the diluent. Both of these effects enhance the proportion of (coordinatively) saturated 4:1 complex with respect to the lower complexes in isooctane compared to toluene for a given alcohol concentration. Finally, the lower dielectric constant of isooctane contributes to the 15-fold lower K_4^a of the ion pair than in toluene.

To confirm the higher (than two) solvate of phenol with F^- suggested earlier,¹⁴ a study with nonylphenol in toluene was performed. Use of the more soluble phenol derivative, p-nonylphenol, rather than p-phenylphenol, makes possible an extension to higher phenol concentrations, as shown in Figure 3. Resolution of the resulting curve appears more complicated than with benzyl alcohol, as no complex (slope) dominates over an appreciable concentration range. Computer least-square-fits yield equilibrium quotients of

$$K_1^a = 3.4 \text{ (mol/l)}^{-2}, \quad K_2^a = 6.9 \times 10^3 \text{ (mol/l)}^{-3}, \quad K_3^a = 2.2 \times 10^6 \text{ (mol/l)}^{-4}, \\ K_4^a = 7.6 \times 10^7 \text{ (mol/l)}^{-5},$$

showing a regular change as the number of phenols complexed increases. The ratios of these quotients show a steady decrease, a factor ~ 8 ($K_2/K_1 \sim 2000$, $K_3/K_2 \sim 300$, $K_4/K_3 \sim 35$), in contrast to the irregular behavior with benzyl alcohol ($K_2/K_1 \sim 133$, $K_3/K_2 \sim 7 \frac{1}{2}$, $K_4/K_3 \sim 10$). The reason for this difference is not clear to us, but these patterns suggest that the process with phenol is the same type of reaction occurring over again in each step, e.g., the replacement of a water molecule in the first coordination shell of F^- with a phenol molecule, while that with alcohol may involve a change in mechanism during the steps. A possible explanation will be taken up later with reference to the water uptake results. It does seem, however, that four is the maximum number of alcohol or phenol molecules coordinated; allowance for a 5:1 complex did not improve the computer fits. It should also be noted that the more acidic, and so more strongly hydrogen-bonding, phenol molecules increase the extraction of the tetrahexylammonium fluoride by 3-5 orders of magnitude over that with benzyl alcohol.

The behavior of chloride ion toward protic extractants may be different from that of fluoride. It is a bigger anion and so can sterically accommodate more solvating molecules. On the other hand, because of its larger size, it needs solvation less, and so might require fewer extractant molecules. A plot of tetrapentylammonium chloride concentration in the toluene phase vs. its concentration in the aqueous phase from 3×10^{-4} to 4×10^{-2} M for 0.32 M benzyl alcohol gave a slope of two, indicating ion-pair formation under these conditions. Figure 6 shows a plot of extracted tetrapentylammonium chloride vs. benzyl alcohol concentration in toluene; the curve can be resolved into components representing 1:1, 2:1 and a higher complex. It can be seen that with the chloride anion the higher complexes occur at higher alcohol concentrations than with fluoride. This makes it harder to resolve the higher complexes in the range of alcohol concentrations available. In the present case, the computer fits for 1:1, 2:1 and 3:1 species is almost as good as for 1:1, 2:1 and 4:1 species, and both sets yield the values $K_1^a = 0.1 (\text{mol/l})^{-2}$ and $K_2^a = 3 (\text{mol/l})^{-3}$. But there simply are not enough data at high alcohol concentrations to unambiguously determine K_3^a and/or K_4^a . We can only say that there is at least one more higher complex, and we have shown it as a 4:1 complex in Figure 6, as this gives a somewhat better fit than the 3:1 complex. Also, the fact that a given complex with Cl^- occurs at a higher alcohol concentration than with F^- indicates, as do the larger values of K^a and smaller ratios of K_2^a/K_1^a for Cl^- over F^- , that the most important difference between Cl^- and F^- is the less urgent need for hydration and solvation of the former anion.

With the more inert and lower-dielectric constant diluent isooctane, extraction is poorer so that a larger cation had to be used. Figure 9 shows

the extraction of tetrahexylammonium chloride vs. the aqueous salt concentration for 0.20 and 0.080 M benzyl alcohol. Both curves rise initially with a slope of two, indicating extraction of ion pairs, and then abruptly level off and actually decrease slightly. Again we think this behavior is due to the formation of salt micelles in the aqueous phase at the higher salt concentrations, and the solubilization therein of some of the benzyl alcohol from the organic phase. The effect becomes larger, the higher the concentration of aqueous salt and of organic-phase alcohol, and is somewhat less severe with the tetrahexylammonium cation than with the tetraheptylammonium ion used with fluoride.

Taking this behavior into account, the two plots in Figure 10 of extracted Cl^- vs. benzyl alcohol for 2.30×10^{-2} and 5.75×10^{-3} M aqueous salt concentration show the existence of only a 4:1 complex from 0.20 to 0.05 M benzyl alcohol. The value of K_4^a obtained for tetrahexylammonium chloride in this case is $2.4 \times 10^3 (\text{mol/l})^{-5}$, and again, as with F^- , the range of 4:1 species overlaps the region of alcohol concentration which with toluene as diluent yields lower solvates. Thus, under the more forcing condition of having as diluent the relatively inert isooctane, which cannot solvate either the alcohol or the extracted anion as well as can toluene, the extraction of the anion is hindered and it must achieve solvation in the organic phase more completely with the alcohol. The result is more complete formation of the (saturated) 4:1 alcohol complex than with toluene as diluents. If we could follow the extraction down to lower alcohol concentrations, it seems reasonable to expect, however, that we would observe a (not necessarily regular) stepwise de-alcoholation of the extracted complex.

Figure 7 shows a log-log plot of organic-phase tetrapentylammonium chloride concentration vs. the aqueous-phase salt concentration for two p-nonylphenol solutions in toluene, as well as for blank solutions containing no phenol. After correcting for the aqueous-phase activity coefficients, it can be seen that over most of the range studied, straight lines of slope two are obtained, showing the existence of ion pairs in the organic phase. However, the tops of both curves do deviate upwards from the lines drawn with slopes of two; this may indicate an error in the increasingly large corrections applied, or that the species are really starting to aggregate beyond the ion pair. Thus, data for the log-log plots of tetrapentylammonium chloride extracted vs. the p-nonylphenol concentration at constant aqueous salt molarity should be taken below an organic-phase chloride concentration of a few times 10^{-3} M. In order to achieve this and to hold down the size of the corrections for changes in the aqueous-phase salt concentration by extraction, the measurements shown in Figure 8 were taken in two sections, normalized together by overlapping points at 1.20×10^{-2} and 2.00×10^{-2} M phenol. The curve is complex; resolution by a computer least-square-fit leads to 1:1, 2:1, 3:1 and 4:1 nonylphenol-chloride complexes in the range of phenol concentrations studied. The values of the equilibrium quotients so obtained are: $K_1^a = 2.2 \text{ (mol/l)}^{-2}$, $K_2^a = 8.7 \times 10^2 \text{ (mol/l)}^{-3}$, $K_3^a = 2.7 \times 10^4 \text{ (mol/l)}^{-4}$, and $K_4^a = 7 \times 10^4 \text{ (mol/l)}^{-5}$, respectively, for this extraction of tetrapentylammonium chloride by p-nonylphenol in toluene. Again, as with F^- , the stepwise formation of the phenol complexes seems to be quite regular with the ratios of consecutive quotients, $K_2^a/K_1^a \sim 400$, $K_3^a/K_2^a \sim 30$, $K_4^a/K_3^a \sim 2.6$, decreasing each time by a roughly-constant factor (~ 12). Again, we think this suggests that the same process is taking place at each step

(although the factor of ~ 12 is larger than the statistical factor for simple replacement of ~ 2). Rather similar results have been obtained for the extraction of tetrabutylammonium chloride by 1-naphthol in toluene, except that extraction is a little higher (values of K^a somewhat larger) because of the greater acidity of 1-naphthol over nonylphenol.

Just as with benzyl alcohol as extractant, the concentration of phenol necessary to yield a particular average coordination number is higher with Cl^- than with F^- , again reflecting the former anion's less urgent need for solvation. Similarly, the higher values of K^a for Cl^- show that the weaker hydration of the Cl^- in the aqueous phase makes its extraction easier.

Additional information of the nature of the various complexes of F^- and Cl^- is furnished by the determination of the amounts of water coextracted with them. Phenol is more acidic than water,²² so that it should hydrogen-bond more strongly to anions than does water. Thus with (small) strongly-solvated anions where these molecules can be bound into a first-shell coordination sphere, it might be expected that phenol can displace water molecules from the first shell. From Table I, it can be seen that with F^- the 4:1 phenol complex has very little water associated with it (of the order of 1/2 mole), and that the 2:1 complex has ~ 2 water molecules with it. It is not clear to us what the 1/2 mole of water signifies, but we believe that the sum of the water and phenol numbers indicate that the higher phenol-fluoride complexes are essentially demonstrating a coordination number of four for F^- . These data are in agreement with, though they do not prove, the suggestion based on the equilibrium quotient ratios that with phenol each step involves the replacement of a water in the first coordination shell, with retention of a fixed coordination number. In this case the number is four.

The water uptake situation seems less clear with the chloride anion. Tables II and III indicate that, as the average number of complexed phenols increases from 1.6 to 2.8, the average number of water molecules involved decreases only from 1.1 to 0.6. Thus, the sum of the number of phenol and water molecules is not a constant, and is closer to 3 than to 4 in this concentration range. Certainly, because of the lower electric field around the larger Cl^- ion, one might expect its first-shell water molecules to be bound less tightly than with F^- . The higher limiting equivalent conductance in water of Cl^- than F^- (Reference 22), although Cl^- has the larger crystallographic radius, indicates, indeed, that fewer water molecules are carried along by Cl^- . In addition, other work in this laboratory²³ shows that the extraction of Cl^- without any extractant present leads to ~ 3 moles of water per Cl^- (F^- extracts with more). Yet with enough phenol present, four molecules of phenol can be bound to a Cl^- ; and although it is only our assumption that they are all hydrogen-bonded to the anion to form its first coordination shell, this does seem plausible. The main point is that in the organic phase, when the chloride anion goes from solvation by water to solvation by phenol, it appears to increase its average number of solvation molecules from ~ 3 to 4. A possible explanation is that when a hydrated Cl^- distributes into the organic phase, it cannot carry a full first-shell of water with it because of the lack of secondary solvation available to these water molecules in that phase. That is, there are no molecules present capable of hydrogen bonding to these (exposed) first-shell waters. So perhaps two water molecules are bound more tightly to each Cl^- to provide it with solvation, with a distribution of species with 0, 1, or 2 additional, but less-tightly bound water molecules present to average to ~3 moles/ Cl^- . But when the water molecules are replaced by phenol, the backside of the latter do not need hydrogen bonding and can receive adequate solvation from the surrounding

toluene molecules, and so the Cl^- ion can expand its coordination number, within possible steric limits, to the observed value of 4.

The water uptake of the benzyl alcohol complexes follows a still different pattern, but may indicate the same general behavior. The 4:1 F^- complex with alcohol has been previously shown¹⁴ to involve ~ 2 water molecules, and Tables IV and V suggest that the average 2:1 and 3:1 alcohol-chloride species both have ~ 2 water molecules also. Since benzyl alcohol is much less acidic than phenol and probably comparable to (even less acidic than) water, it may not be able to displace all the water from the first coordination shell around the anions as can phenols. Thus the 4:1 alcohol complex with both anions may retain two water molecules in the first coordination shell, with two alcohols also in that shell and two more bound, not directly to the anion, but to the water molecules, thus providing the latter with solvation to their rear side and acting as a buffer between them and the organic diluent. At lower alcohol concentrations, alcohol is lost from the complex in a stepwise fashion, but the first two alcohols lost are most likely to be the ones bound to the water molecules. After that, it might be expected to become more difficult to replace with water the two last alcohol molecules bound directly to the anion. Such a sequence would explain why the 3:1 species shows up poorly with alcohol and F^- , but is a major component with phenol, since with the latter extractant, each step is the same, namely replacement of a water with a phenol molecule (or vice-versa). This alcohol complexing sequence is also in agreement with the observed feature that, when using the more inert diluent isooctane, the 4:1 complex occurs more readily for both F^- and Cl^- than with toluene; since the lower complexes would have water molecules on the anion exposed to the

poorly solvating isooctane diluent, these complexes would be somewhat more disfavored with respect to the saturated alcohol complex than in toluene.

The results of this work indicate that the complexation of F^- and Cl^- by water-immiscible phenols and alcohols is a stepwise process similar to the complexation of cations by ligands. With phenols the process seems a quite regular replacement of water by the more acidic and more strongly hydrogen-bonding organic molecules, as indicated by the regular decrease in the ratios of K_i/K_{i+1} and by the decrease in coextracted water as the number of coordinated phenols increases. With benzyl alcohol, the process may be different; especially with F^- there is a favoring of the 4:1 and 2:1 species. In addition, both anions seem to retain ~ 2 water molecules with the 4:1 (F^-) and 3:1 (Cl^-) complexes. It is suggested that perhaps the less acidic alcohol molecules cannot displace these two waters from the first shell of the anions, but merely hydrogen bond to them. For F^- , the 4:1 species with either alcohol or phenol could be made dominant, and there was no indication, in the concentration range studied, of a higher complex. With Cl^- , the 4:1 species could be observed, but it was not possible to go to high enough extractant concentrations to say anything about higher complexes.

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Footnotes and References

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- (16) In Reference 14, the fluoride salt used was stated to be tetraheptylammonium fluoride; from the present work and additional experiments that have been performed, it is clear that the salt was mislabelled and that it was tetrahexylammonium fluoride. This does not change the argument presented in that paper on the solvation of the fluoride ion.

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Table I

Water Coextracted With Tetraheptylammonium Fluoride Into:

0.206 M p-nonylphenol in toluene

$[\text{THpAF}]_o$	$\bar{n}$	$[\text{phenol}]_{\text{free}}$	$[\text{H}_2\text{O}]_{\text{total}}^a$	$[\text{H}_2\text{O}]$	$\frac{[\text{H}_2\text{O}]}{[\text{TH}_p \text{ AF}]_o}$
0.0140	3.7	0.154	0.0245	0.0091	0.6
0.0266	3.6 ₅	0.109	0.0260	0.0151	0.6
0.0527	3.4	0.027	0.0264	0.0247	0.5
0.0883	2.3	0.003	0.0979	0.0976	1.1

0.0971 M p-nonylphenol in toluene

0.00912	3.5	0.065	0.0124	0.0059	0.6
0.0184	3.4	0.034	0.0148	0.0114	0.6
0.0329	2.8	0.005	0.0283	0.0278	0.9
0.0430	2.2	0.001	0.0818	0.0817	1.9

^aWater dissolved in toluene alone subtracted.

Table II

Water Coextracted With Tetrapentylammonium Chloride Into:

0.115 M p-nonylphenol in toluene.

$[\text{TPAC}]_o$	$\bar{n}$	$[\text{phenol}]_{\text{free}}$	$[\text{H}_2\text{O}]_{\text{total}}^a$	$[\text{H}_2\text{O}]$	$\frac{[\text{H}_2\text{O}]}{[\text{TPAC}]_o}$
0.0114	2.8	0.0828	0.0153	0.0071	0.6
0.0180	2.7	0.0658	0.0158	0.0093	0.5
0.0277	2.6	0.0429	0.0173	0.0131	0.5

^aWater dissolved in toluene subtracted.

Table III

Water Coextracted With Tetrahexylammonium Chloride Into 0.0200 M p-nonylphenol in Toluene

$[\text{THxAC}]_{\text{total}}$	$[\text{THxAC}]_{\text{o}}^{\text{a}}$	$\bar{n}$	$[\text{H}_2\text{O}]_{\text{total}}^{\text{b}}$	$[\text{H}_2\text{O}]_{\text{blank THxAC}}^{\text{c}}$	$[\text{H}_2\text{O}]$	$\frac{[\text{H}_2\text{O}]}{[\text{THxAC}]_{\text{o}}}$
1.09×10^{-2}	1.04×10^{-2}	1.6	0.0136	0.0016	0.0117	1.1
8.48×10^{-3}	8.13×10^{-3}	1.7 ₅	0.0102	0.0011	0.0085	1.0
5.75×10^{-3}	5.47×10^{-3}	1.9 ₅	0.0072	0.0009	0.0054	0.9

^aTetrahexylammonium chloride extracting into toluene alone (no phenol) subtracted from first column.

^bWater dissolved in toluene alone subtracted.

^cRatio of water with uncomplexed tetrahexylammonium chloride to uncomplexed tetrahexylammonium chloride concentration is 3.2.

Table IV

Water Coextracted With Tetrapentylammonium Chloride
Into 0.500 M Benzyl Alcohol in Toluene.

$[\text{TPAC}]_o$	$\bar{n}$	$[\text{H}_2\text{O}]_{\text{total}}^a$	$[\text{H}_2\text{O}]_{\text{alcohol}}$	$[\text{H}_2\text{O}]$	$\frac{[\text{H}_2\text{O}]}{[\text{TPAC}]_o}$
8.78×10^{-3}	3.1	0.0513	0.0363	0.0150	1.7
2.00×10^{-2}	3.1	0.0716	0.0320	0.0396	2.0

^a water dissolved in toluene alone subtracted.

Table V

Water Coextracted With Tetraheptylammonium Chloride
Into 0.100 M Benzyl Alcohol in Toluene

$[\text{THpAC}]_o^a$	$\bar{n}$	$[\text{H}_2\text{O}]_{\text{total}}^b$	$[\text{H}_2\text{O}]_{\text{alcohol}}$	$[\text{H}_2\text{O}]_{\text{blank THpAC}}^c$	$[\text{H}_2\text{O}]$	$\frac{[\text{H}_2\text{O}]}{[\text{THpAC}]_o}$
4.57×10^{-3}	1.8	0.0140	0.0037	0.0010	0.0093	2.0
6.63×10^{-3}	1.8	0.0186	0.0034	0.0013	0.0139	2.1
9.43×10^{-3}	1.8	0.0239	0.0030	0.0016	0.0193	2.0

^aTetraheptylammonium chloride extracting into toluene alone (no alcohol) subtracted.

^bWater dissolved in toluene alone subtracted.

^cRatio of water with uncomplexed chloride to uncomplexed chloride concentration is 3.2.

Figure Captions

Fig. 1. Variation of water content of organic phase (toluene diluent) with p-nonylphenol concentration: initial concentration of p-nonylphenol, ; equilibrium concentration of p-nonylphenol, $\circ$.

Fig. 2. Dependence of tetrahexylammonium fluoride extraction on benzyl alcohol concentration in toluene at an initial aqueous fluoride concentration of 1.36×10^{-2} M (organic-phase blank of 1.00×10^{-7} M subtracted) and of 3.88×10^{-3} M, $\bullet$; latter data corrected by factor of 11.8 to former data, $\blacktriangle$. Monosolvate, by computer fit, — — — ; total organic-phase fluoride minus monosolvate, Δ ; disolvate, — — — ; total fluoride minus mono- and disolvate, $\square$; trisolvate, — — — ; total fluoride minus mono-, di-, and trisolvate, $\blacksquare$; tetrasolvate, — — —.

Fig. 3. Dependence of tetrahexylammonium fluoride extraction on p-nonylphenol concentration in toluene at initial aqueous fluoride concentrations of 2.60×10^{-2} , 2.95×10^{-3} , and 2.60×10^{-4} M, $\bullet$; corrected to constant (initial) equilibrium aqueous fluoride concentration, $\circ$. Data from 2.60×10^{-2} M and 2.60×10^{-4} M curves normalized to fit 2.95×10^{-3} M points, Δ and ∇ , respectively. Monosolvate, by computer fit, — — — ; total organic-phase fluoride minus monosolvate, $\blacktriangle$; disolvate, — — — ; total fluoride minus mono- and disolvate, $\square$; trisolvate, — — — ; total fluoride minus mono-, di-, and trisolvate, $\blacksquare$; tetrasolvate, — — —.

Fig. 4. Dependence of tetraheptylammonium fluoride extraction on aqueous fluoride concentration at a fixed benzylalcohol concentration of 0.10 M in isooctane.

Fig. 5. Dependence of tetraheptylammonium fluoride extraction on benzyl alcohol concentration in isooctane at an initial aqueous fluoride concentration of 6.65×10^{-3} M with blank (2.76×10^{-6} M) subtracted, ●; data corrected to a constant (initial) equilibrium aqueous fluoride concentration, ○.

Fig. 6. Dependence of tetrapentylammonium chloride extraction on benzyl alcohol concentration in toluene at an initial aqueous fluoride concentration of 2.19×10^{-2} M with blank (1.53×10^{-6} M) subtracted, ●; correction for alcohol used up by water, □. Monosolvate, by computer fit, ———; total organic-phase chloride concentration minus monosolvate, Δ; disolvate, ———; total chloride minus mono- and disolvate, ■; tetrasolvate, ———. Resolution into mono-, di-, and trisolvates gives almost as good a fit.

Fig. 7. Dependence of tetrapentylammonium chloride extraction on aqueous chloride concentration at final p-nonylphenol concentrations in toluene: initial concentration of p-nonylphenol = 1.18×10^{-1} M, ●; data corrected to a constant (initial) equilibrium concentration of p-nonylphenol, ○; corrected to mean ionic activity of aqueous chloride, ▼; initial concentration of p-nonylphenol = 1.05×10^{-2} M, ■; data corrected to a constant (initial) equilibrium concentration of p-nonylphenol, □; corrected to mean ionic activity of aqueous chloride, ◇. Extraction by toluene alone (no phenol), ▲; corrected to mean ionic activity of aqueous chloride, Δ.

Fig. 8. Dependence of tetrapentylammonium chloride extraction on p-nonylphenol concentration in toluene at fixed chloride concentrations: initial aqueous chloride concentration of 1.92×10^{-2} M (organic-phase blank of 1.68×10^{-6} M subtracted) and of 2.21×10^{-3} M, ●; corrected to constant (initial)

equilibrium aqueous chloride concentration, ■. Data from 2.21×10^{-3} M aqueous chloride normalized up (by factor of 43.6) to curve for 1.92×10^{-2} M aqueous chloride, ▲. Monosolvate by computer fit, ———; total organic-phase chloride concentration minus monosolvate, ○; disolvate, ———; total chloride minus mono- and disolvate, △; trisolvate, ———; total chloride minus mono-, di-, and trisolvate, □; tetrasolvate, ———.

Fig. 9. Dependence of tetrahexylammonium chloride extraction on aqueous chloride concentration at fixed concentrations of benzyl alcohol in isooctane: benzyl alcohol concentration of 2.0×10^{-1} M, □; benzyl alcohol concentration of 8.0×10^{-2} M, ○.

Fig. 10. Dependence of tetrahexylammonium chloride extraction on benzyl alcohol concentration in isooctane at fixed chloride concentrations: aqueous chloride concentration of 2.30×10^{-2} M, ○; aqueous concentration of 5.75×10^{-3} M, □; data corrected to equilibrium alcohol concentration, ■.

XBL705-2972

Fig. 1

XBL7110-4611

Fig. 2

XBL7110-4614

Fig. 3

XBL 705-2977

Fig. 4

XBL705-2973

Fig. 5

XBL7110-4610

Fig. 6

XBL7110-4612

Fig. 7

XBL7110-4613

Fig. 8

XBL701-2191

Fig. 9

XBL701-2190

Fig. 10

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