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HYDRATION OF THE HALIDE IONS IN CERTAIN ORGANIC SOLVENTS*

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ABSTRACT

The amount of water co-extracted by the halide anions into several solvents has been determined. The order was always $\text{Cl}^- > \text{Br}^- > \text{I}^-$, and at high organic-phase salt concentrations, the hydration numbers increased with increasing concentration, apparently paralleling the formation of ion pairs and higher ion aggregates. In nitrobenzene the lower, limiting values are 3.3, 1.8, and 1.0 moles of water per anion for Cl^- , Br^- , and I^- , respectively. With dichloroethane as solvent, and more particularly with chloroform, solvation of the anion by the (weakly) acid proton of the diluent replaces part of the hydration, and the hydration number observed decreases markedly. For a number of reasons, the hydration numbers observed are lower limits to the first-shell hydration or coordination number of the anion.

There has been renewed interest in the solvation of simple anions, such as the halides, with protic solvents [1-10]. The strength of alcohol-halide interactions have been shown by IR spectroscopy [1,2] to depend upon the anion in the order $F^- > Cl^- > Br^- > I^-$, as was also observed by NMR methods [3]. A similar trend was observed for water-halide interactions, again by IR techniques [4,5]. A study of UV and IR spectra suggested that the solvation number of the tetrahexylammonium iodide-alcohol complex was unity [6]. The hydration numbers of the halides as determined in aqueous solution by NMR methods [7,8] are 1.6 for F^- , 0-2 for Cl^- , and 1 for Br^- . Similar values are obtained from aqueous solution compressibilities and ionic vibration potential measurements [9], namely, $F^- = 4.0$, $Cl^- = 2.0$, $Br^- = 1.8$, $I^- = 1.5$. Mass spectrometric studies [10] have yielded values of $-\Delta H$, $-\Delta G$, and ΔS for the gas-phase stepwise hydration of the halide ions, and these results are in the expected order $F^- > Cl^- > Br^- > I^-$. The values decrease with increasing number of water molecules complexed to the anion, and show no sharp changes in magnitude, at least up to the 4 or 5 water molecules per ion studied. From pressure-composition isotherms, the existence of halide ion complexes with haloforms has been deduced [11], as had earlier been shown by both IR [2] and NMR [12] studies.

In earlier papers from this laboratory [13,14], the stepwise complexing of F^- and Cl^- by alcohols and phenols has been studied by distribution of the alkylammonium salt between an aqueous and an organic phase. Since anion solvation by water and by alcohol might not be too different in the organic phase, and since the large tetraalkylammonium cations have been shown [15] to be anhydrous, it should be possible to determine the average hydration of the halide ions in an organic solvent by measuring the alkylammonium salt

concentration and the water extracted into that phase. If the salts associated to ion pairs or to higher aggregates in the solvent, some ambiguity might be introduced in the amount of water complexed to an individual ion, so a high-dielectric-constant, dissociating medium is desirable for these studies. As a result, nitrobenzene ($\epsilon = 34.82$ at 25°C [16]) has been mainly used.

EXPERIMENTAL

Reagents

A desired tetraalkylammonium chloride or bromide was obtained from the corresponding iodide (Eastman Organic Chemicals, white label) in the manner described in earlier papers [14,15]. This involves conversion to the hydroxide by shaking with a suspension of silver oxide (Baker and Adamson, reagent grade) in water, and then titration to $\text{pH} \sim 7$ with the appropriate hydrohalic acid. The resulting solutions were standardized with known silver nitrate solutions using fluorescein as indicator. The nitrobenzene used was Eastman Organic Chemicals, white label; the dichloroethane was Matheson, Coleman, and Bell, spectrograde; and the benzene was J. T. Baker, reagent grade, as was the chloroform. The latter was stored over Linde 5A molecular sieves. The $^{82}\text{Br}^-$ tracer ($T_{1/2} = 35$ hours) was prepared by irradiating LiBr in the Vallecitos reactor and then dissolving the salt in distilled water. The Karl Fischer reagent used in the water determinations was Matheson, Coleman, and Bell stabilized, premixed single solution.

Procedure

The aqueous solution of the tetraalkylammonium halide was shaken with the organic solvent, usually for two hours. Separate experiments had shown that this was sufficient time to achieve equilibrium in the distribution. The

equilibrium concentrations of the halide salts in the two phases were then determined by one or more of three methods: spectrophotometry, titration with silver nitrate, and counting of radioactive Br^- . The spectrophotometrical procedure was the alkylammonium picrate extraction [17] used in earlier works [14,15], except for pre-shaking 10 ml aliquots of the aqueous phase with 10 ml samples of CCl_4 to avoid interference from the nitrobenzene dissolved in the aqueous phase. This CCl_4 wash did not extract any measurable quantity of the salt. Aqueous halide solutions more concentrated than 10^{-3} were determined by titration with 0.0100 M AgNO_3 using fluorescein as indicator. Such a method was also used to determine the halide in the organic phase after addition of an equal volume of isooctane and then back-extraction into water. No significant amount of halide salt is left in the organic phase in this procedure, as was shown by shaking it with a second water wash. The determinations of water in the organic phases were made by the Karl Fischer method using an electrometric end-point. All experiments were performed at room temperature, $23 \pm 2^\circ\text{C}$.

RESULTS AND DISCUSSION

In the previous paper [15], the tetraalkylammonium cations were found to be essentially anhydrous in nitrobenzene, dichloroethane, and benzene-nitrobenzene mixtures. Therefore, any water co-extracted with tetraalkylammonium salts into these diluents can be attributed to the anion, except for two possible conditions: 1) when the presence of the salt itself changes the nature of the medium enough to change the water uptake into the diluent; 2) when the salt aggregates into ion pairs, and particularly into higher ion aggregates, (even approaching inverted micelles) which may hold additional water. To minimize the first effect, we have

restricted this study mostly to solutions less than 0.1 M in organic-phase salt concentrations, or $\sim 4\%$ by volume in the worst case. To minimize the second effect, we have first studied a high-dielectric-constant medium, nitrobenzene ($\epsilon = 34.8$), where the ions might be expected to be dissociated in the range of concentrations employed. Afterwards, we have used other diluents to observe the effect of ion aggregation on water uptake.

In every case it must be determined experimentally whether the salts are dissociated or associated, and, if so, to what degree. Slope analysis has been shown to be useful for this purpose [15]. The equation for the distribution of a tetraalkylammonium halide into an organic phase can be written

depending upon whether the species in the organic phase is dissociated (1a) or is associated as ion pairs (1b). The corresponding equilibrium constants can be written

$$K^d = \frac{(R_4N^+)_o \cdot (A^- \cdot mH_2O)_o}{(R_4N^+)(A^-)(H_2O)^m} = \frac{[R_4N^+]_o [A^- \cdot mH_2O]_o y_{\pm}^2}{[R_4N^+][A^-](H_2O)^m y_{\pm}^2} \quad (2a)$$

$$K^a = \frac{(R_4N^+ \dots A^- \cdot mH_2O)_o}{(R_4N^+)(A^-)(H_2O)^m} = \frac{[R_4N^+ \dots A^- \cdot mH_2O]_o y_o}{[R_4N^+][A^-](H_2O)^m y_{\pm}^2} \quad (2b)$$

Thus, the slope of a log-log plot of the organic-phase salt activity vs. the aqueous-phase value yields the degree of association. A unit slope means complete dissociation (case a), a line of slope 2 means pure ion pairs (case b), an intermediate value means a mixture of the two, and a slope greater than two means aggregation beyond the ion pair.

Such a plot for tetrapropylammonium iodide distributing between nitrobenzene and water is shown in Fig. 1. The experimental molarities (solid circles) deviate only slightly from a straight line of unit slope. Corrections for the activity coefficient in the nitrobenzene phase were made using a Debye-Hückel expression with a distance of closest approach of 6 Å and a dielectric constant of 34.8. Corrections for the activity coefficient in the aqueous phase were made using Poirier's method [18] with a distance of closest approach that yields the values for the activity coefficient found by Lindenbaum and Boyd at 0.1 m and somewhat higher concentrations [19]. The corrected points (open circles) fall on the straight line of unit slope to about 10^{-2} M, suggesting that below that concentration tetrapropylammonium iodide is essentially dissociated in nitrobenzene.

Similar results for tetrabutylammonium bromide are also shown in Fig. 1. The experimental points lie along a line of unit slope at the lower organic-phase concentrations, and deviate slightly upwards at the higher concentrations. Again correction for the activity coefficients in both phases (calculated in the same manner) results in agreement with this line to about 10^{-2} M in the organic phase, indicating that tetrabutylammonium bromide is essentially dissociated in nitrobenzene below 10^{-2} M.

Figure 2 shows the extraction of tetrapentylammonium chloride into nitrobenzene. The raw data below 10^{-3} M in the organic phase yield a straight

line of unit slope, and correction for the activity coefficients in both phases extends the agreement to about 10^{-2} M. Again this indicates dissociation of the salt below that concentration in nitrobenzene.

All these salts can be expected to associate more readily in lower-dielectric-constant media than nitrobenzene, so similar extraction studies were performed using dichloroethane ($\epsilon = 10.36$ at 25°C [16]) as solvent. The results for the tetrapentylammonium chloride are given in Fig. 2. The raw data (solid circles) yield a unit slope below an organic-phase concentration of 3×10^{-5} M, and above such a concentration they deviate upwards. Correction for the aqueous-phase activity coefficients makes little change, but the organic-phase coefficients, calculated by means of a Debye-Hückel expression with a distance of closest approach of 6 Å, can become very small. Such large corrections bring into question the validity of using this treatment for the organic-phase activity coefficients. But even so it appears that above about 10^{-2} M the salt is mostly associated to ion pairs, thus fulfilling the expectation of greater ion association in dichloroethane than in nitrobenzene.

In benzene-nitrobenzene mixtures, the salts are also expected to be more associated than in nitrobenzene. As can be seen in Fig. 3 for tetrapentylammonium chloride and two bromide salts, the slopes of the curves obtained are 2 or larger in almost all the concentration regions studied. With decreasing nitrobenzene content, the ease of extraction decreases (the effect of the lower effective dielectric constant), and the slope of the curve increases (increasing aggregation). Both results are as expected, and are probably less marked than in a pure diluent of the same dielectric constant, because in the mixed solvent, solvent sorting probably occurs, with the polar nitrobenzene molecules preferentially appearing in the vicinity of the ions.

With the nature (molecularity) of the ionic species in the organic phase determined, the measurements of the water co-extracted into nitrobenzene with the I^- , Br^- , and Cl^- anions, Table I, can be examined. Since the water dissolved in the nitrobenzene alone (calculated as the product of the nitrobenzene volume fraction times the water solubility in nitrobenzene) has been subtracted, the remaining water can be associated with the anion. However, one must keep in mind the two provisions already mentioned at the beginning of this section about possible deviations in the water uptake due to changes in the nature of the solvent and to ion association. The ratios of organic-phase water to salt molarity are shown in the last column. At the lower concentrations measured, the ratio for Cl^- appears to be constant at 3.3, and then at concentrations above a few times 10^{-2} M in the organic phase the ratio increases with increasing salt concentration. Since the chloride salt in nitrobenzene also starts to show significant association above that concentration, as illustrated in Fig. 2, it seems probable that these two features are related. That is, some excess water may be bound in the salt aggregate. This effect is very marked with the F^- ion, and will be discussed in a later paper dealing with that ion. But the most significant ionic hydration data, therefore, should be taken from the lower salt concentrations where the species is dissociated. This yields a water/ Cl^- ratio of 3.3. The non-integral value obtained means that a mixture of species with different hydration numbers is present. The extraction study of Cl^- with alcohol [14] suggested a maximum coordination, or first-shell solvation number, at least under the conditions employed, of four molecules. Since the hydrogen-bonding interaction of water to Cl^- in the present complexes should not be very different from that of the alcohols (the acidity of water and the alcohols is not greatly different, although water is the more acidic), similar solvation numbers might be expected. Thus, the ratio of water to salt obtained,

3.3, can be interpreted as an appropriate average number, at this temperature and water activity, of a 4:1 and probably all lower species.

The ratio of water to salt molarity of tetrabutylammonium bromide in nitrobenzene is also shown in Table I. Again a constant value, 1.8, is found in the lower concentration region where the bromide is dissociated according to Fig. 1. The ratio becomes slightly larger at higher organic-phase concentrations, and again this trend may perhaps be correlated with the start of ion association as indicated in Fig. 1. For the dissociated Br^- , the value 1.8 is smaller than that for the Cl^- anion, as is certainly expected, and should be considered an average of a distribution of values. The actual species may consist largely of a 2:1 complex, or may be nearly equal amounts of 4:1, 3:1, 2:1, 1:1, and bare ions, or any other distribution leading to an average value of 1.8.

Similarly, water uptake by tetrapropylammonium iodide was measured and is given in Table I. One mole of water extracted per I^- , and no dependence of this value on the organic-phase salt concentration is noticeable up to 0.1 M. This hydration number is still smaller than that for Br^- , as expected. The value of 1.0 could mean that all I^- anions carry exactly one water molecule with them, but more likely represents a distribution of 0:1, 1:1, and 2:1 $\text{H}_2\text{O}:\text{I}^-$ species and may possibly include even higher complexes.

In the mixed-solvent system studied, benzene-nitrobenzene, one can expect that the more polar solvent molecules (nitrobenzene) will preferentially locate around the ions while the less polar molecules (benzene) are relatively farther away. Thus, the molecular atmosphere around the ions in the mixture would not be as different from that in pure nitrobenzene as might perhaps

be expected, although the effective dielectric constant in the medium would be lower than in nitrobenzene and so would be the water solubility. Some data on water uptake with tetrapentylammonium chloride and bromide into benzene-nitrobenzene mixtures are given in Tables II and III, respectively. The H_2O :halide ion ratios are essentially the same as those obtained in pure nitrobenzene, although the slopes in Figs. 1-3 indicate that the degrees of aggregation are considerably larger.

In Table II are also given the results for the water co-extracted with tetrapentylammonium chloride into dichloroethane, and it can be seen that the values are smaller than those in nitrobenzene, although they do increase with increasing salt concentration. This increase may be due to the increasing ion aggregation with concentration already mentioned. But why should the value of the ratio be reduced in dichloroethane with respect to nitrobenzene? A possibility may be the ability of dichloroethane to interact directly with the Cl^- through its hydrogen, that is, show weakly acid behavior. This interaction, though weak, could compete with the much stronger water- Cl^- interaction because of the overwhelmingly greater number of dichloroethane molecules in the organic phase. The result of such a hydrogen-bonding contact of dichloroethane molecules with the Cl^- , transient as it may be, would be a slight replacement, and hence decrease, in the number of water molecules carried by the anion, as observed in Table II, and should also tend to suppress ion aggregation slightly.

If such an interaction does occur with dichloroethane, it should be possible to magnify the effect by using a more acidic organic diluent such as chloroform. The proton of this molecule is known to (hydrogen-) bond to

halide anions, and complexes have been described [2,11,12]. Indeed, the data in Table II show that the water co-extracted by Cl^- into this solvent, 1.0 H_2O per Cl^- , is greatly reduced below the 3.3 molecules co-extracted into nitrobenzene. This result suggests the importance of solvation of the anion by the organic diluent in displacing waters of hydration; an estimate of first-shell hydration number would have to come from data taken with a much more inert diluent than CHCl_3 . In fact, there is evidence from observation of the NMR spectrum that even nitrobenzene interacts with the halide salts; there is a downfield shift of the para- and meta-protons which is proportional to the concentration of halide salt [20].

CONCLUSIONS

The hydration numbers of the halide anions in nitrobenzene at 23°C and at essentially unit water activity are in the expected order $\text{Cl}^- > \text{Br}^- > \text{I}^-$, and the actual numbers, 3.3(Cl^-), 1.8(Br^-), and 1.0(I^-) are remarkably similar to the values found by Bockris and Saluja [9] in aqueous solution by compressibility and ionic vibration methods. The values found in the present study should be a lower limit to the first-shell coordination number of the anions for a number of reasons. One is that the hydration number determined is an average value for a distribution of species. Another is that the organic diluent is not inert and so plays a role in solvating the salt (otherwise there could be no extraction). Although with nitrobenzene this is probably not first-shell solvation, with chloroform, definite complexes with the halides are made. The present work shows that the amount of water co-extracted per mole of Cl^- falls from 3.3 moles in nitrobenzene and in

benzene-nitrobenzene mixtures to 1.0 mole in chloroform. The solvent dichloroethane is an intermediate case, lowering the amount of water co-extracted with Cl^- by about 30% from the nitrobenzene value.

Thus, a first-shell hydration or coordination number of at least 4 is probable for Cl^- , in agreement with the solvation number found in isooctane [14]. But only weaker lower limits of 2 and 1 can be set for Br^- and I^- . It has been found in the gas-phase hydration of the halide anions [10] that $-\Delta G$ for the stepwise addition of water molecules decreases gradually and monotonically with increasing number of water molecules coordinated, at least up to the 5, 4, and 3 water molecules per ion observed for F^- , Cl^- and Br^- , and I^- , respectively. There was no indication of any sudden change or step at a favored complex. Hydration of the ions in an organic solvent is a different situation due to the presence of the surrounding organic molecules and dissolved water, but preliminary experiments, not described in this paper, show that as the water activity is decreased from unity to ~ 0.1 by vapor-phase equilibration of the tetralkylammonium salts in the organic solvent, the hydration numbers for F^- , Cl^- , and Br^- fall monotonically (almost linearly for Br^-) with the water activity. No plateaus indicating a strong preference for a particular lower hydration number were observed, in agreement with the gas-phase results.

Finally, with Cl^- and Br^- the process of ion aggregation in the more concentrated organic-phase salt solutions seems to result in somewhat larger hydration numbers. This could be due to the fact that the ion aggregate (resembling a small inverted micelle) provides an electrostatically "better" environment for water than does a single halide ion. But since the effect is extremely marked with F^- and does not seem to appear with I^- even though salts of the

latter are also aggregated, we believe this effect has its origin in the ability of fluoride ions, and to a lesser extent chloride and bromide ions, to fit into, and even to promote, a hydrogen-bonded network with water. This subject will be taken up in a later paper on the hydration of the fluoride salts.

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FOOTNOTES AND REFERENCES

- * Work performed under the auspices of the U. S. Atomic Energy Commission.
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Table I. Water co-extracted with tetraalkylammonium salts in nitrobenzene.

Salt	Equil. Molarity of Salt(org)	Equil. Molarity of Water(org) ^a	Ratio of Water to Salt Molarity
	$\times 10^2$	$\times 10^2$	
Tetrapentylammonium chloride	15.8	62.6	3.96
	6.63	24.7	3.72
	2.94	9.8	3.3
	1.04	3.4	3.3
	0.53	1.8	3.3
Tetrabutylammonium bromide	31.9	70.3	2.20
	10.4	20.9	2.01
	4.40	8.1	1.8
	2.02	3.6	1.8
	0.74	1.3	1.8
Tetrapropylammonium iodide	14.2	13.3	0.94
	5.19	5.4	1.04
	2.54	2.6	1.0
	1.20	1.1	0.9
	0.23	0.2 ₃	1.

^aThe water extracted by the diluent alone (diluent volume fraction $\times$ water solubility in diluent) has been subtracted.

Table II. Water co-extracted with tetrapentylammonium chloride into various solvents.

Solvent	Equil. Molarity of $\text{Cl}^-(\text{org})$	Equil. Molarity of Water(org) ^a	Ratio of Water to Salt Molarity
	$\times 10^2$	$\times 10^2$	
Dichloroethane	—	11.5	
	19.0	59.3	3.12
	8.61	24.7	2.87
	3.63	9.7	2.7
	1.46	3.8	2.6
	0.43	0.9 ₅	2.2
	0.17	0.4 ₁	2.4
Chloroform	—	6.4	
	21.1	21.3	1.01
	10.6	10.7	1.01
	5.30	5.5 ₃	1.0
	2.11	2.3 ₆	1.1
	1.06	1.1	1.0
	—	8.8	
50% Nitrobenzene + 50% benzene	5.71	20.0	3.50
	1.21	4.0	3.3
40% Nitrobenzene + 60% benzene	—	7.1	
	7.88	27.2	3.45
	2.78	9.3	3.3

^aThe water dissolved by the volume fraction of solvent alone has been subtracted.

Table III. Water co-extracted with tetrapentylammonium bromide into 80% benzene + 20% nitrobenzene.

Equil. Molarity of Br ⁻ (org) × 10 ²	Equil. Molarity of Water(org) ^a × 10 ²	Ratio of Water to Salt Molarity
—	5.1	
11.2	20.9	1.87
3.01	5.1	1.7
0.97	1.5	1.5

^aThe water dissolved by the volume fraction of solvent alone has been subtracted.

FIGURE CAPTIONS

Fig. 1. Distribution of tetrapropylammonium iodide (circles, right-hand ordinate scale) and tetrabutylammonium bromide (triangles, left-hand scale) between nitrobenzene and water. Filled symbols are the raw data; open symbols are data corrected for activity coefficients in the organic and aqueous phases. Dashed lines drawn with unit slope.

Fig. 2. Distribution of tetrapentylammonium chloride into nitrobenzene (triangles) and into dichloroethene (circles). Filled symbols are raw data; open symbols are data corrected for activity coefficients in the organic and aqueous phases. Dashed lines are drawn with unit slope.

Fig. 3. Distribution of tetrapentylammonium chloride between 50 volume % benzene-50 volume % nitrobenzene and water, $\diamond$, and between 60 volume % benzene-40 volume % nitrobenzene and water, Δ . Distribution of tetrapentylammonium bromide (circles) and tetrabutylammonium bromide (squares) between 80 volume % benzene-20 volume % nitrobenzene and water. Solid curves are drawn through the raw data; symbols to the left of the curves are the bromide data corrected for aqueous-phase activity coefficients.

Fig. 1

XBL733-2364

Fig. 2

XBL733-2363

Fig. 3

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