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Ion Association of Tetrabutylammonium Halides in 1,1- and 1,2-Dichloroethane and 4-Methyl-2-pentanone

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Synopsis. The ion-association equilibrium of tetrabutylammonium chloride, bromide, and iodide in the titled solvents has been investigated by solvent extraction at 298 K. In each solvent the association constants have been found to be of similar magnitude among these three salts. This is explained in terms of the larger degree of hydration in the smaller anions. The influence of coextracted water on the equilibrium is discussed.

Solvent extraction has been applied to studies on equilibrium in water-immiscible solvents.[1,2] The solvent is, however, intrinsically saturated with water and even though its amount is usually small, it may cause some effects on the equilibrium. In some solvent extraction systems a certain amount of water is extracted together with the substance in question and the coextraction of water is attributed to the hydration of the chemical species in the organic phase.[3–6] In the present study, the distribution of tetrabutylammonium halides (TBAX; X=Cl, Br, and I) is measured between an aqueous solution and three aprotic solvents; 1,1-dichloroethane (1,1-DCE, relative permittivity[7] ε_r=9.90), 1,2-dichloroethane (1,2-DCE, ε_r=10.37), and 4-methyl-2-pentanone (MIBK, ε_r=13.11); and the association constant of these salts in the organic phase is calculated. The water content of the equilibrated 1,1- and 1,2-DCE is also measured in order to compare the degree of hydration of the salts in these solvents.

Experimental

The reagents employed were of reagent grade. Both 1,1- and 1,2-DCE were washed with aqueous sodium hydrogencarbonate and then water. The former solvent was distilled and the middle distillate was used. MIBK was washed with diluted perchloric acid, an aqueous sodium hydroxide solution, and then water. Tetrabutylammonium halides were recrystallized from ethanol and ether. Their stock solutions were titrated with a standardized silver nitrate solution using uranine as the indicator.

A portion of an aqueous TBAX solution and an equal volume of an organic solvent were mechanically agitated for half an hour in a thermostated room at 298 K. The TBA^+ in the organic phase was stripped with water. When the stripping was not quantitative with water only, a certain amount of carbon tetrachloride (to DCE) or hexane (to MIBK) was added. TBA^+ both in the stripping solution and in the equilibrated aqueous phase was extracted into chloroform as its picrate, and the concentration was determined by spectrophotometry. The water content in the equilibrated 1,1- and 1,2-DCE solutions was measured with a Karl Fischer titrator. Since the extraction of TBACl was poor, the aqueous chloride-ion concentration was enhanced to 2 mol dm^{-3} by adding lithium chloride in order to attain a measurable amount of coextracted water.

Since the salt concentrations in both the aqueous and organic solutions were low, formation of ion pairs in the aqueous phase and any association of ions other than one-to-one adducts in the organic phase are assumed to be negligible. The equilibria and distribution ratio can then be written as follows using the extraction constant, K_{ex}, and the association constant, K_{as}.

$$TBA^+_{(aq)} + X^-_{(aq)} \rightleftarrows TBA^+X^-_{(org)}$$

$$K_{ex} = [TBA^+X^-]_{org}[TBA^+]_{aq}^{-1}[X^-]_{aq}^{-1}f_\pm^{-2} \quad (1)$$

$$TBA^+_{(org)} + X^-_{(org)} \rightleftarrows TBA^+X^-_{(org)}$$

$$K_{as} = [TBA^+X^-]_{org}[TBA^+]_{org}^{-1}[X^-]_{org}^{-1} \quad (2)$$

$$D = ([TBA^+X^-]_{org} + [TBA^+]_{org})/[TBA^+]_{aq} \quad (3)$$

Using the charge balance in both phases, $[TBA^+]_{aq} = [X^-]_{aq}$ and $[TBA^+]_{org} = [X^-]_{org}$, Eq. 4 can be obtained.

$$D/f_\pm = K_{ex}[TBA^+]_{aq}f_\pm + (K_{ex}/K_{as})^{1/2} \quad (4)$$

The mean activity coefficient in the aqueous solution, $f_\pm$, was calculated using Debye-Hückel's expression with the closest ion-ion distance 0.6 nm. The activity coefficient of the ionic species in the organic phase is considered to be unity because the dissociated amount of the salts in it should be very small. The distribution data were treated by a least squares program.

Since TBA^+ can be regarded as anhydrous in 1,1-DCE as well as in 1,2-DCE,[3,5] the coextracted water interacts with the anions and the apparent mean hydration number of the anion in the solvents, n_h, is calculated by Eq. 5;

$$n_h = (w_t - w_0)/[TBAX]_{org,total} \quad (5)$$

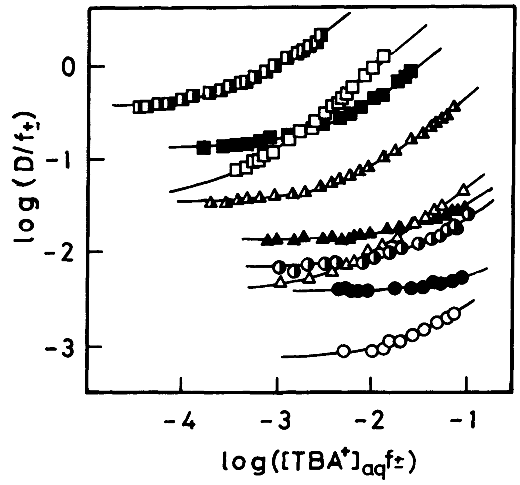

Fig. 1. Distribution ratio of TBAX against the equilibrated salts concentration in the aqueous phase compensated with the activity of the ions in the aqueous phase. X: Cl^- (circles), Br^- (triangles), and I^- (squares). Solvent: 1,1-DCE (open), 1,2-DCE (half filled), and MIBK (filled). Solid lines give the calculated values by using the constants in Table 1.

Table 1. Extraction and Association Constants of Tetrabutylammonium Halides and Apparent Hydration Number of the Halide Ion in the Organic Solvents

X^-	K_{ex}			K_{as}			n_h	
	1,1-DCE	1,2-DCE	MIBK	1,1-DCE	1,2-DCE	MIBK	1,1-DCE	1,2-DCE
Cl^-	3.2×10^{-2}	0.29	3.8×10^{-2}	5.7×10^{4}	6.0×10^{3}	2.3×10^{3}	2.1	2.7
Br^-	0.80	7.0	0.38	4.8×10^{4}	5.7×10^{3}	1.9×10^{3}	1.38	2.0
I^-	1.1×10^{2}	7.0×10^{2}	3.9	7.6×10^{4}	5.3×10^{3}	2.3×10^{3}	0.61	0.88

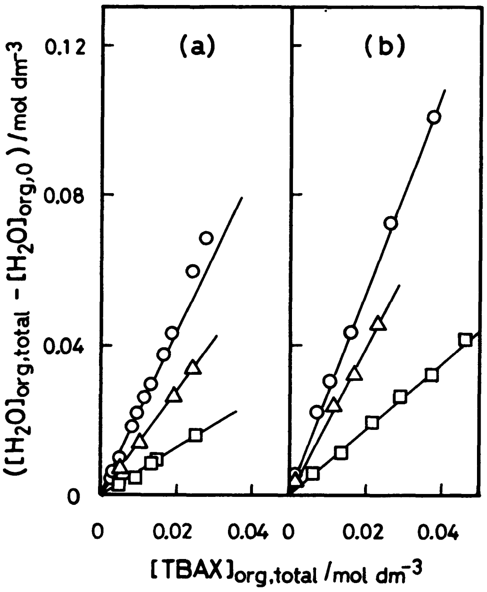

Fig. 2. Coextracted water with TBAX into 1,1-DCE (a) and 1,2-DCE (b). X: Cl^- (○), Br^- (△), and I^- (□). The solid lines are with the slope of n_h in Table 1.

where w_t and w_0 represents the water concentrations in the organic phase equilibrated with an aqueous solution containing and without containing TBAX, respectively.

Results and Discussion

The distribution data are given in Fig. 1 and the calculated constants are shown in Table 1. The ion-association equilibrium of tetraalkylammonium salts has often been studied by several methods. The association constant for the present salts and solvents is available in the literature only for the iodide in DCE. By electrolytic conductivity the values for dry and water-saturated 1,1-DCE have been compared as; 7.30×10^4 (dry) and 6.54×10^4 (wet), and for 1,2-DCE, 6.70×10^3 (dry) and 5.83×10^3 (wet).[8] Another value for dry 1,2-DCE is reported to be 8.0×10^3[9] From the solvent extraction data in Ref. 10, it can be calculated to be 5.37×10^4 for 1,1-DCE and 5.89×10^3 for 1,2-DCE, respectively.

The amount of the water uptake of the salts is shown in Fig. 2. After agitation with pure water, 1,1-DCE and 1,2-DCE contained 0.066 mol dm^{-3} and 0.126 mol dm^{-3} of water, respectively. These values were used as w_0 in the calculation of the hydration number for the iodide and the bromide. When equilibrated with 2 mol dm^{-3} of aqueous lithium chloride solution, 1,1-DCE contained 0.060 mol dm^{-3} of water and 1,2-DCE did 0.120 mol dm^{-3}. These were used in the calculation of n_h for the chloride. The extraction of lithium chloride was negligible. The difference of the water concentration between these two experiments is caused by the decrease of water activity in the lithium chloride solution.[11] However, since the initial concentration of TBAX was at most 0.1 mol dm^{-3}, the water activity change should be slight in each aqueous TBAX solution so that each w_0 is valid for the different concentrations of TBAX. In Fig. 2 the plots for the chloride in 1,1-DCE show upper deviation with increasing salt concentration. In this case the extrapolated value onto the lower concentration was taken as its n_h. The obtained values of n_h are given in Table 1.

A wet solvent can be regarded as a mixed solvent with water. Since water has large relative permittivity (78.3), the wet solvents discussed here have larger permittivity than the dry ones. Assuming the linear contribution of water to the permittivity of the solution and using w_0 and the relative permittivity values of pure solvent and water, the permittivity of the water-saturated 1,1-DCE is calculated to be 10.2 instead of 9.9 for the pure solvent. Similar calculations give 10.8 for the water-saturated 1,2-DCE instead of 10.4.[12] The experimentally observed enhancement for 1,2-DCE is, however, reported to be only 0.105 (10.387 instead of 10.282) when it contains 0.118 mol dm^{-3} of water which is close to saturation.[13] On the basis of Fuoss's expression,[14] the decrease in the association constant caused by the change of the permittivity of the water-saturated solvents is estimated to be around 10% both for 1,1-DCE (for the increase from 9.9 to 10.2) and for 1,2-DCE (from 10.3 to 10.4).[15] Ito et al.[8] have compared the association constants of TBAI between several dry and wet solvents and concluded that the saturated amount of water reduces the association constants around 15% irrespective of the solvents examined. Therefore, even when the permittivity change by the coexisting water seems to be small, it should be considered in a precise discussion.

The values of n_h in Table 1 are in the order chloride>bromide>iodide in both solvents. This order is that of the hydration tendency of the anions. It means that the organic solvent molecules solvate weakly and the hydrated water molecules are only partially replaced. For three anions the n_h values are always smaller in 1,1-DCE than in 1,2-DCE. This has been explained by Diamond[5] in terms of the acidity of the solvent, namely, the capability of hydrogen-bond formation with the anions which is stronger in 1,1-DCE. Water dissolves into MIBK up to 0.8 mol dm^{-3}, which interferes with the determination of a reliable hydration number of the anions in this solvent. Since MIBK is a basic solvent, water will react as an acid with the MIBK molecules. This may also change the properties of the solvent.

As seen in Table 1, the association constants of TBAX in MIBK are almost equal for the three salts. This is totally different from the order observed in dry basic aprotic solvents;[16] for example in acetone, the association constant of TBA^+ salts is 435 for the chloride, 264 for the bromide, and 143 for the iodide. It is also known that the order of K_{as} for halide salts in solvating type solvents such as alcohols is chloride<bromide<iodide.[16] Not only for MIBK, none of the K_{as} in Table 1 follow the two typical orders. Considering the n_h values together, this may be explained by the opposite tendency being overlapped; the hydrated water gives a solvating effect and the bulk solvent remains almost inert. In other words, the effective radius of the anions in each solvent should be similar in the three halide ions by hydration. If the ion-ion distance of the ion pairs is similar, whatever ions are solvated or hydrated, the association constants should be of similar magnitude.

The influence of the coextracted water will be larger for the extraction of the more hydrating species and, in the opposite extreme, comparison of the behavior of anhydrating substances in wet and dry solvents will give information about the net change of the physical properties of the solvent induced by the coexisting water.

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15) The association constant is expressed in Ref. 14 as;

$$K_{as} = (4\pi N\mathring{a}^3/3000)\cdot\exp(e^2/\mathring{a}\varepsilon_r kT)$$

where $\mathring{a}$ is the distance of the ions in a pair in the unit of cm. At 298 K we obtain the following equation.

$$\log K_{as} = 21.40 + 3\log\mathring{a} + 2.43\times10^{-6}/\mathring{a}\varepsilon_r$$

If the value of $\mathring{a}$ is supposed to be constant, e.g. 5×10^{-8} cm, the final term of the above equation is about $50/\varepsilon_r$. Assuming the $\mathring{a}$ value to be constant, we can estimate the $\log K_{as}$ values for different ε_r with this equation.

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