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Solute-Solvent Interactions in Ion Pair Extraction of Tetraalkylammonium Iodides. II. The Effect of Hydration of Iodide in Organic Solvents on the Extraction Constant

Kazuaki Ito, Etsuro Iwamoto, and Yuroku Yamamoto*

Department of Chemistry, Faculty of Science, Hiroshima University, Naka-ku, Hiroshima 730

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Solubilities of tetraalkylammonium iodides Et_4NI, Pr_4NI, and Bu_4NI in nitrobenzene, in water, and in their mutually saturated solvents, and of Pr_4NI in 1,1-dichloroethane and in its water saturated solvent were measured at 25 °C. Conductances of Et_4NI, Pr_4NI, and Bu_4NI in nitrobenzene and Bu_4NI in 1,1-dichloroethane, 1,2-dichloroethane, and dichloromethane have also been measured at 25 °C. A small amount of water in organic solvents increases the solubilities of the salts roughly twice those in pure solvents and decreases the association constants around 15% while a small amount of organic solvent in water gives a slight effect. Effects of mutual saturation of water and organic solvent on extraction equilibria of R_4NI were discussed in terms of the selective hydration of the iodide.

In the preceding paper,[1] we have investigated the extraction equilibria of tetraalkylammonium iodides (R_4NI) between water and eight organic solvents, and proposed a new treatment of "ionic" and "neutral" extraction constants. The results indicated that the influences of the solvents on the extractability of R_4NI can be interpreted in terms of the following properties; the dielectric constant for the ionic part, the solubility parameter for the neutral, and the hydrogen bonding for both.

The ion pair extraction is primarily concerned with the distribution of salts between water and an immiscible organic phase, but both water and organic solvent molecules are slightly soluble in each other. In addition, water is coextracted into the organic phase[2–6] with ion pairs, and organic solvent molecules are salted-in in the aqueous phase.[7,8] However, little is known concerning to what degree the mutual saturation of solvents contributes to the ion pair extraction equilibria.

The purpose of this paper is to investigate interactions between ion pairs and a minute quantity of water in an organic solvent or of organic solvent in aqueous phase by solubility and conductivity measurements and to clarify their effects on the process of ion pair extraction in connection with solvent effects on extractability of R_4NI.

Experimental

The purification of the solvents, {nitrobenzene (NB), 1,1-dichloroethane (1,1-DCE), 1,2-dichloroethane (1,2-DCE), and dichloromethane (DCM)} and of tetraalkylammonium iodides, R_4NI (R=Et, *n*-Pr, and *n*-Bu) and the distribution ratio measurements were the same as those reported previously.[1] The distribution ratio was calculated using the expression, D=[specific activity (cpm ml^{-1}) of radionuclide ^{131}I in organic phase]/[specific activity (cpm ml^{-1}) in aqueous phase].

The conductivity bridge and cell used have been described previously.[1] Anhydrous organic solutions were prepared in a dry box filled with dry nitrogen gas under slight pressure.

Solubility measurements were carried out as follows; (1) saturated solutions of the salts in pure water and organic solvents (*ca.* 40 ml) were prepared by vigorously agitating the solvents with an excess of the salts for at least 2 d in a thermostated water bath (25±0.05 °C). (2) Saturated solutions of the salts in organic solvents equilibrated with water (and vice versa) were prepared with an excess of both the salts and water (and of both the salts and organic solvents). An aliquot (*ca.* 1 ml) of the saturated aqueous solution was passed through a sintered-glass filter and weighed. Solubilities were determined by potentiometric titration of the iodide ion with silver nitrate. Salts in organic solvents were back-extracted into water for the titration; the salt-saturated organic solutions (*ca.* 1 ml) were shaken with water (*ca.* 50 ml) and the organic phase was separated from the aqueous phase by filtration (Toyo filter paper No. 5B). This procedure was repeated several times to back-extract the salt completely. The aqueous filtrates were combined, followed by titration. Measurements were usually continued for 1 week although the solubility equilibria were obtained in at least 2 d. Preliminary measurements confirmed that the back-extraction was completely carried out even in the nitrobenzene solution of Bu_4NI for which the solubility in water is very small compared with those of Pr_4NI and Et_4NI.

Water solubilities in organic solvents were determined coulometrically with a Hiranuma AQ-3 aquacounter. Nitrobenzene solubilities in water were determined by spectrophotometry at 252 nm after extraction into cyclohexane.[8a] Densities were obtained by an Anton Paar Model DMA O2D digital density meter at 25±0.01 °C.

Results

The solubilities of Et_4NI, Pr_4NI, and Bu_4NI at 25 °C are given in Table 1. A small amount of water in nitrobenzene increases the solubilities of R_4NI largely, while a small amount of nitrobenzene in water affects hardly. The increase in solubility of R_4NI in nitrobenzene corresponds to the salting-in of water by R_4NI. It was found that Pr_4NI (0.476 mol dm^{-3}) in nitrobenzene increases the solubility of water from 0.168 to 0.620 mol dm^{-3} and Pr_4NI (0.561 mol dm^{-3}) in water increases the solubility of nitrobenzene from 0.0156 to 0.0231 mol dm^{-3}. For the water–1,1-DCE system, a small amount of water increases also the solubility of Pr_4NI. Our value for Pr_4NI in dry 1,1-dichloroethane (1.96×10^{-2} mol dm^{-3}) agrees with the value (2.04×10^{-2} mol dm^{-3}) obtained by Abraham *et al.*[9] The solid phase in equilibrium with the saturated solution was checked by chemical analysis and differential thermal analysis, and no solvate was found.

TABLE 1. SOLUBILITIES IN mol dm^{-3} OF R_4NI AT 25 °C

Salt	H_2O ($S_w°$)	H_2O equilibrated with NB (S_w)	$S_w/S_w°$	NB ($S_o°$)	NB equilibrated with H_2O (S_o)	$S_o/S_o°$
Et_4NI	1.416 [a]			1.82×10^{-2}	3.33×10^{-2}	1.83
n-Pr_4NI	5.40×10^{-1}	5.61×10^{-1}	1.04	1.74×10^{-1}	4.76×10^{-1}	2.74
n-Bu_4NI	6.77×10^{-2}	6.84×10^{-2}	1.01	6.60×10^{-1}	1.27	1.92
Salt	H_2O ($S_w°$)	H_2O equilibrated with 1,1-DCE (S_w)	$S_w/S_w°$	1,1-DCE ($S_o°$)	1,1-DCE equilibrated with H_2O ($S_o°$)	$S_o/S_o°$
n-Pr_4NI	5.40×10^{-1}	5.68×10^{-1}	1.05	1.96×10^{-2}	4.94×10^{-2}	2.52

a) From Ref. 16, molal scale was converted to molar scale.

TABLE 2. ASSOCIATION CONSTANT, $K_a°$ AND K_a AT 25 °C

Solvent	Salt	Anhydrous solvent ($K_a°$)	Water-saturated solvent (K_a)	$K_a°/K_a$
NB	Et_4NI	38 ± 1	35 [a]	1.09
NB	n-Pr_4NI	35 ± 1	33 [a]	1.06
NB	n-Bu_4NI	38 ± 1	33 [a]	1.15
1,2-DCE	n-Bu_4NI	$(6.70\pm0.07)\times10^3$	5.83×10^3 [a]	1.15
1,1-DCE	n-Bu_4NI	$(7.30\pm0.10)\times10^4$	6.54×10^4 [a]	1.12
DCM	n-Bu_4NI	$(3.77\pm0.04)\times10^4$	3.26×10^4 [a]	1.16

a) From Ref. 1.

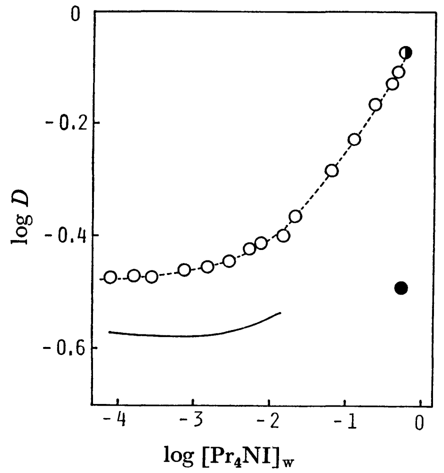

Fig. 1. Concentration dependence of distribution ratio for Pr_4NI in the water–nitrobenzene system at 25 °C. Solid line is the curve calculated from the extraction constants in Table 4. ◑: Solubility ratio for the mutually saturated solvent system, ●: solubility ratio for the pure solvent system.

Distribution ratios of Pr_4NI for the nitrobenzene–water extraction system were determined as a function of the salt concentration (Fig. 1). The distribution ratio increases with increasing the salt concentration and the solubility ratio ($D=0.848$) of Pr_4NI for mutually equilibrated solvents falls on the extended line. This also provides another evidence that no solvate is found.

The ionic association constant, K_a and the limiting conductance, Λ_0 of R_4NI were determined by the method of Shedlovsky.[10] The calculation was carried out using the conductances of the salts covering from 2×10^{-3} to 2×10^{-5} mol dm^{-3}. Shown in Table 2 are the ionic association constants of R_4NI in water-free and water-saturated organic solvents at 25 °C. The results indicated that the association constants in water-free solvents are larger by 10—15% than those in water-saturated solvents.

Discussion

Organic Phase. The quantity of water coextracted increases linearly with increasing salt concentration,[2–4] although the degree of dissociation of ion-pair changes markedly.[1] Pr_4NI,[3b] Bu_4NI,[4] $[Fe(phen)_3]I_2$,[2a] and $[Fe(bpy)_3]I_2$,[2a] coextract 0.98, 0.91, 1.1, and 1.1 mol of water per iodide ion into nitrobenzene, respectively, while Bu_4NBPh_4 does not coextract any water molecules. Similarly, in this study the values of 1.0, 0.95, and 1.1 mol of water per iodide ion were obtained in the saturated solutions of Et_4NI, Pr_4NI, and Bu_4NI, respectively. The value of 1.0 does not mean that the iodide anion in nitrobenzene carry exactly one water molecule, but more likely represents a distribution of the species involving hydrated and nonhydrated iodide anions and ion pairs.

The hydration of iodide anions (the ionic part) and ion pairs (the neutral part) is represented by the following equilibria,

$$I^-\cdot(m-1)H_2O + H_2O \rightleftharpoons I^-\cdot mH_2O$$

$$R_4NI\cdot(n-1)H_2O + H_2O \rightleftharpoons R_4NI\cdot nH_2O$$

with the corresponding formation constants,

$$K_m^- = [I^-\cdot mH_2O]/[I^-\cdot(m-1)H_2O]\,[H_2O], \tag{1}$$

$$K_n^p = [R_4NI\cdot nH_2O]/[R_4NI\cdot(n-1)H_2O]\,[H_2O]. \tag{2}$$

The hydration constants ($K_1^-=3.45$ mol dm^{-3}, $K_2^-=2.60$, and $K_3^-=1.37$) were determined from the dependence of the c.t.t.s. spectra between I^- and nitrobenzene in the visible region on water contents in nitrobenzene solution of Pr_4NI.[11]

A small amount of protic solvent such as methanol significantly decreases the degree of ionic association for halide salts in low dielectric solvents.[12] The solubilities of water in the organic solvents used here are so small (below 0.02 mol fraction) that the water effects on dielectric constants are considered to be negligeble.[13] The change in the association constant by adding a small amount of water in organic solvents, thus, can be attributed to the hydration of the iodide anion.

The ionic association constant in organic solvents containing water is written by using Eqs. 1 and 2,

$$K_a = ([R_4NI]/[R_4N^+][I^-]f_\pm{}^2)(1+\sum^{n} K^p_1 K^p_2 \cdots K^p_n [H_2O]^n)/$$
$$(1+\sum^{m} K^-_1 K^-_2 \cdots K^-_m [H_2O]^m). \qquad (3)$$

The first parenthesis on the right hand side in Eq. 3 is K°_a, the ionic association constant in pure organic solvent. The ratio of K°_a to K_a yields the relation,

$$(K^\circ_a/K_a) = (1+\sum^{m} K^-_1 K^-_2 \cdots K^-_m [H_2O]^m)/$$
$$(1+\sum^{n} K^p_1 K^p_2 \cdots K^p_n [H_2O]^n). \qquad (4)$$

If the affinity of water for the iodide anion is greater than that for the iodide ion pair, the extent of ion pair association decreases in the presence of water. A small amount of water in nitrobenzene decreases the association constants of R_4NI by about 10% and the cation dependence is small (Table 2). This reveals that the hydration constants of the ion pairs are almost constant and are slightly less than that of the iodide anion. It has been reported that cation effects[14] were not observed in the formation phenol–halide anion complexes for a variety of quaternary ammonium salts in solvents of low dielectric constant such as dichloromethane in which salts are extensively ionic-associative. Ion pair formation between tetraalkylammonium cations and halide anions is almost electrostatic and has very modest geometrical requirements compared to mono-, di, and trialkylammonium salts which bear the sites for complex formation due to hydrogen bond.[14,15] So the hydration of the iodide ion pair is not so much different from that of the iodide anion. All the association constants of Bu_4NI in anhydrous NB, 1,2-DCE, 1,1-DCE, and DCM are about 15% greater than those in water-saturated solvents. The result that the value of K°_a/K_a is almost constant among the organic solvents would be partly because there is no specific interactions between the iodide and the solvents.

Aqueous Phase. The solubility of salts in water equilibrated with organic solvents is governed by the overall effect of mutual interactions among the three components (ion, water, and organic solvent) and can be examined from the view point of salting effects. Tetraalkylammonium salts increase the solubility of nitrobenzene in water although alkali metal halides such as NaBr do not.[8a] The salting-in by R_4N^+ is controlled mainly by the water structural effects through hydrophobic interactions which are decreased in the order, $Am_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$.[8a] Pr_4NI and Bu_4NI in the salt-saturated solutions increase solubilities of nitrobenzene with 48% and 9.6% in comparison with those in pure water, respectively (Table 3). The salting-in coefficient of Bu_4NI is reasonably larger (negative value) than that of Bu_4NBr (−0.513).[8a] Salting-in effects on benzene by aliphatic ions such as Bu_4N^+ were found to be weaker than those of aromatic ions such as Ph_4P^+ and BPh_4^- since van der Waals forces are less effective for aliphatic ions than for aromatic ions.[8b] Thus, the weaker interaction between R_4N^+ and nitrobenzene does not so much contribute to the solubility of R_4NI in aqueous phase.

TABLE 3. THE SALTING-IN OF NITROBENZENE BY R_4NI IN THE SALT-SATURATED AQUEOUS SOLUTION AT 25 °C

	Solubility		k_s[a]
	Nitrobenzene S/mol dm^{-3}	Salt C_s/mol dm^{-3}	
(Pure water)	0.0156[b]	—	—
n-Pr_4NI	0.0231	0.561	−0.304
n-Bu_4NI	0.0171	0.0684	−0.583

a) Salting effect coefficient $k_s = 1/C_s \times \log (S^\circ/S)$, where S° and S are the solubility of nitrobenzene in water and in a salt solution, respectively. b) From Ref. 8a.

Extraction Constant. In the extraction of tetraalkylammonium iodides the equilibrium is represented as

$$R_4N^+_w + I^-_w + R_4NI_w \rightleftharpoons R_4N^+_o + I^-_o + R_4NI_o,$$

where the subscripts w and o designate the aqueous and organic phases, respectively. The fraction of triple ions is so small that the triple ion term can be disregarded.[1] The extraction constant for the ionic species is

$$K_i = [R_4N^+]_o[I^-]_o f^2_{\pm o}/[R_4N^+]_w[I^-]_w f^2_{\pm w} \qquad (5)$$

for the associated species

$$K_n = [R_4NI]_o/[R_4NI]_w, \qquad (6)$$

$$K_n' = [R_4NI]_o/[R_4N^+]_w[I^-]_w f^2_{\pm w}. \qquad (7)$$

When the association constant of all the salts in water is taken as unity, we get the relation $K_n = K_n'$ since $[R_4NI]_w = [R_4N^+]_w[I^-]_w \, f^2_{\pm w}$ where $f_\pm$ is the mean ionic activity coefficient. The activity coefficient of ion pair is taken as unity. As mentioned above, since water and organic solvents are salted in by R_4NI for the solvent extraction system, the transfer free energy of R_4NI is different from that of the ion pair from one pure solvent to another pure solvent. The tetraalkylammonium cations are essentially non-hydrated in organic solvents and the solubilities of R_4NI in water equilibrated with organic solvents are almost the same as those in water, so Eqs. 5 and 6 can be rewritten upon introduction of Eqs. 1 and 2.

$$K''_i = K_i \times (1+\sum^{m} K^-_1 K^-_2 \cdots K^-_m [H_2O]^m_o) \qquad (8)$$

$$K''_n = K_n \times (1+\sum^{n} K^p_1 K^p_2 \cdots K^p_n [H_2O]^n_o) \qquad (9)$$

The extraction constants K''_i and K''_n for Pr_4NI in the water–nitrobenzene system were obtained at each concentration from the association constants (Table 2)

TABLE 4. EXTRACTION CONSTANTS OF n-Pr_4NI FOR NITROBENZENE–WATER SYSTEM AT 25 °C

From solubility ratio in pure solvents		From distribution ratio at C_t[a] $= 1.0\times10^{-3}$ mol dm^{-3}	
K_t	8.00×10^{-2}	K_t''	1.51×10^{-1} [b]
K_n	2.81	K_n''	5.02 [b]

a) C_t: The initial salt concentration in aqueous phase.
b) From Ref. 1.

and distribution ratios (Fig. 1). Activity coefficients of Pr_4NI in aqueous phase, which were reported by Lindenbaum and Boyd,[16] were converted to molarity scale from molality scale. Activity coefficients of ions in nitrobenzene were calculated by using the extended Debye-Hückel equation with a value for $\mathring{a}$ of 6 Å. The satisfactory constancy of extraction constants was also observed up to *ca.* 0.02 mol dm^{-3} in nitrobenzene phase as for Bu_4NI in the NB, 1,1-DCE, 1,2-DCE, and DCM systems,[1] showing that the parenthesis terms in Eqs. 8 and 9 are constant. The deviation from the constancy of extraction constants at higher concentration may be attributed to higher aggregates for the solvent extaction system and to the change in water activity in addition to the inadequate application of the Debye-Hückel equation to such concentrated nitrobenzene solutions. The extraction constants K_t and K_n for Pr_4NI in the pure solvent system, which were calculated in a similar way, are also given in Table 4. For this pure solvent system these extraction constants may be almost constant over a wider concentration range because no hydrates and triple ions are formed in nitrobenzene.[1] So imaginary distribution ratios of Pr_4NI in pure solvent system were calculated at any concentration to reproduce the extraction constants obtained and are shown in Fig. 1. This result shows that at an initial salt concentration of 1.0×10^{-3} mol dm^{-3} the hydration of the iodide in nitrobenzene increases the distribution ratio by 31% (from 0.263 for pure case to 0.345 for the mutual saturation case).

For nitrobenzene system the parenthesis terms in Eqs. 8 and 9 are 1.6 and 1.5, respectively, which were calculated using K_a°/K_a $(=1.1)$ from Eq. 4, the hydration constants of the iodide ion, water solubility, and the self-association constant of water (1.054 mol^{-1} dm^3) in nitrobenzene.[17] These values and the extraction constants for the pure solvent system give $K_t''=1.3\times10^{-1}$ in Eq. 8 and $K_n''=4.2$ in Eq. 9 which are in good agreement with those obtained from the distribution ratio at the initial concentration 1.0×10^{-3} mol dm^{-3} (Table 4). The hydration for Pr_4NI in the nitrobenzene system thus decreases ΔG_t and ΔG_n by *ca.* 1.5 kJ mol^{-1} which is less than the methylene group contribution 2.6 kJ mol^{-1}.[1] Furthermore, as is seen from the hydration effects on the association constants (Table 2), the decrease in ΔG_t and ΔG_n by the hydration does not seem to depend so much on the organic solvents used.

Our conclusion is that the mutual saturation in both phases affects the extraction equilibria of tetraalkylammonium iodides. Especially the role of a small amount of water which is salted-in in organic solvents is marked but does not depend on the solvents.

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