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Hydration of Iodide Ions in Nitrobenzene from Charge-transfer-to-solvent Spectra and ^{1}H NMR

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The charge-transfer-to-solvent (c.t.t.s.) spectrum of the iodide ion in nitrobenzene was observed in the visible region, the intensity of the spectrum being lowered by addition of a small amount of water to the solution. From the spectral changes, the first, second, and third hydration constants, $K_1=3.5$, $K_2=2.6$, and $K_3=1.4$ (mol^{-1} dm^3) were determined. On the basis of ^{1}H NMR of water in nitrobenzene solutions in conjunction with the hydration constants obtained from the spectra, it was suggested that a fraction of the water molecules bound to the iodide ion is hydrogen bonded to each other.

The solvation of anions by a small amount of protic solvents such as water and methanol in aprotic solvents plays an important role in ionic reactions such as ligand substitution[1)] and ion pair extraction,[2)] and has been studied by UV,[3)] NMR,[4—6)] IR,[7,8)] solubility,[6,9)] conductance,[10,11)] extraction,[12,13)] and isopiestic method.[14,15)] Addition of protic solvents to solutions of iodides in acetonitrile resulted in loss of a c.t.t.s. band at 40.7×10^3 cm^{-1} and growth of new bands at higher energy which were assigned to the iodide ion hydrogen bonded to a single hydroxyl proton.[3)] For ethyleneglycol chelation to the iodide ion was suggested.[3)]

Although nitrobenzene, dipolar aprotic and poorly basic, can not be used as a medium transparent in the ultraviolet region, it has widely been used as a useful solvent for ion pair extraction[16)] and conductance studies[17)] due to its solubilizing power for salts. The amount of coextracted water with anions into nitrobenzene decreases with increasing anionic radius.[12,13,15)] From isopiestic measurements, hydration constants of the perchlorate ion in nitrobenzene were estimated for five hydration models.[14)]

In connection with our study on solvent extraction of ion pair with tetraalkylammonium iodides (R_4NI)[2,16)] it was found that when tetraalkylammonium iodides are dissolved in nitrobenzene the colour results in deep yellow from yellow and the intensity decreases as a small amount of water is added to the solution. This spectrum change which is reversible with regard to water concentrations is attributed to the formation and rupture of a charge transfer complex. On the basis of the water concentration dependence of the visible spectrum and the chemical shift of water proton, we discuss the interaction among the iodide anion, nitrobenzene and water, and the structure of hydrated species.

Experimental

Tetrapropylammonium iodide (Pr_4NI) and tetraphenylphosphonium chloride (Ph_4PCl), of the reagent grade available, were further purified by several recrystallizations from ethanol–ether (peroxide free) mixtures. Nitrobenzene was purified as previously described.[16)]

Visible spectra were recorded with a Hitachi model 210-10 spectrometer, using 10 mm quartz cells at 25 °C. The absorbance for a nitrobenzene solution containing a certain concentration of $Pr_4NI$was measured as a function of water content. Nitrobenzene containing water was used as reference. ^{1}H NMR spectra were measured with a Hitachi model R-20 NMR spectrometer (60 MHz) at 25 °C, relative to tetramethylsilane in nitrobenzene as external reference. Water concentrations in nitrobenzene were determined coulometrically with a Hiranuma AQ-3 aquacounter.

Results and Discussion

(a) C.t.t.s. Spectra. Tetrapropylammonium iodide is easily dissolved in nitrobenzene and its solution gives slightly deeper yellow than that of nitrobenzene. The conductance experiment showed that no conductance change was observed in a solution at 10^{-4} mol dm^{-3} levels over the period of 1 h, suggesting that the species in nitrobenzene are stable.

The absorption spectrum of Pr_4NI (1.275×10^{-3} mol dm^{-3}) in nitrobenzene and its water concentration dependence over the range 400 to 500 nm are shown in Fig. 1 where the reference is nitrobenzene containing water of the same concentration as that in the sample cell; therefore the strong absorption due to nitrobenzene itself results in the rapid drop in absorbance below 430 nm. The addition of a small amount of water leads to a decrease in the intensity of absorption. Table 1 gives the absorbances at various concentrtions of water at 440

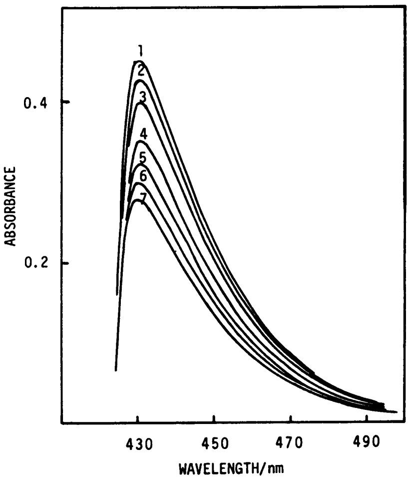


Fig. 1. Spectra of Pr_4NI (1.275×10^{-3} mol dm^{-3}) in nitrobenzene solutions using 10 mm cells as a function of water concentration in mol dm^{-3}; 1, 0.005; 2, 0.0213; 3, 0.0376; 4, 0.0702; 5, 0.103; 6, 0.135; 7, 0.168.

TABLE 1. ABSORBANCES OF $Pr_4NI(1.275\times10^{-3}$ mol $dm^{-3})$ IN NITROBENZENE AT 440 nm AS A FUNCTION OF WATER CONCENTRATION AT 25 °C

$[H_2O]$/mol dm^{-3}	Absorbance	$\frac{\varepsilon_{obsd}}{10\ mm^{-1}\ mol^{-1}\ dm^3}$
0.0050	0.346	271
0.0132	0.333	261
0.0213	0.325	255
0.0376	0.309	242
0.0702	0.280	220
0.103	0.255	200
0.135	0.232	182
0.152	0.221	173
0.160	0.219	172
0.168	0.215	169

TABLE 2. HYDRATION CONSTANTS OF IODIDE IONS IN NITROBENZENE AT 25 °C

n	1	2	3
ε_0	281	277	274
ε_1	0.0	0.4	0
ε_2		0.0	0
ε_3			0
K_1	5.0	3.9	3.5
K_2		2.1	2.6
K_3			1.4
σ[a]	3.6	1.7	1.1

a) $\sigma=\{\sum(\varepsilon_{calcd}-\varepsilon_{obsd})^2/(N-1)\}^{1/2}$, where ε_{calcd}, ε_{obsd} are apparent molar extinction coefficient calculated and observed, respectively, and N is the number of data.

nm where Lambert's law was confirmed to hold for the intensity over the range of light pass 1 to 10 mm. This water concentration dependence of the absorbance is reversible: The drying of wet nitrobenzene solutions by calcium chloride increases the absorbance again. The results mentioned above indicate that the shoulder of spectra observed above 430 nm are due to the formation of a charge transfer complex between the iodide ion and nitrobenzene or c.t.t.s. spectra. Such c.t.t.s. spectrum in the visible region is not observed for chloride, bromide, and perchlorate, which being expected on the basis of the ionization potentials of the halide ions.[18,19] The decrease in the intensity with increasing water concentration can be assigned to the hydration of the iodide ion, the iodide–nitrobenzene interaction being weakened. A similar effect of addition of a protic solvent on c.t.t.s. spectra in a aprotic solvent was also observed; addition of methanol and water results in loss of the c.t.t.s. band with a maximum at $40.7\times10^3\ cm^{-1}$ for iodide in acetonitrile and in growth of a new band at $41.8\times10^3\ cm^{-1}$ due to the iodide ion hydrogen bonded to the protic solvents.[3]

Since the ionic association constant, 33,[16] for Pr_4NI in nitrobenzene at 25 °C gives a degree of dissociation of 0.97 at 1.275×10^{-3} mol dm^{-3}, the effect of ion pairing is negligible for the following calculation. The hydration of the iodide ion is represented as

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

with the corresponding formation constants,

$$K_n = [I^-\cdot nH_2O]/[I^-\cdot(n-1)H_2O][H_2O]. \quad (1)$$

The apparent molar extinction coefficient (ε_{app}) is written as

$$\varepsilon_{app} = [I^-](\varepsilon_0 + \varepsilon_1K_1[H_2O]+\varepsilon_2K_1K_2[H_2O]^2 + \varepsilon_3K_1K_2K_3[H_2O]^3 + \cdots)/[I^-]_{total}, \quad (2)$$

where $[I^-]_{total}$ is the total concentration of iodide ions and ε_0, ε_1, ε_2, and ε_3 the apparent absorptivity of nonhydrated, 1 : 1, 1 : 2, 1 : 3 hydrated iodide ions, respectively. Assuming $n=1$, 2, and 3, the hydration constants were calculated by use of the dependence of the absorbance at 440 nm on the water concentration (Table 1) and the monomer-dimer equilibrium constant $K_s(=[(H_2O)_2/[H_2O]^2)$, 1.054 $mol^{-1}\ dm^3$, for water in nitrobenzene at 25 °C:[20] First, the concentrations of monomer water and nonhydrated iodide ions were obtained from the K_s value and an initial value of K_n, and then an iterative calculation was carried out to minimize the standard deviation, $[\sum(\varepsilon_{calcd}-\varepsilon_{obsd})^2/(N-1)]^{1/2}$, with a given value of ε_0 where ε_{calcd} and ε_{obsd} are apparent molar extinction coefficient calculated and observed, respectively, and N is the number of data. The best fitting values for each case are given in Table 2. For both $n=1$ and 2, ε_1 and ε_2 are nearly zero, showing that the hydration of iodide ions almost disrupts the charge-transfer transition. For $n=3$ the hydration constants were calculated, by assuming that ε_1, ε_2, and ε_3 are zero. The K_1 value, 3.5, for iodide ions is comparable to 2.4 for perchlorate ions in nitrobenzene obtained by the isopiestic method.[14]

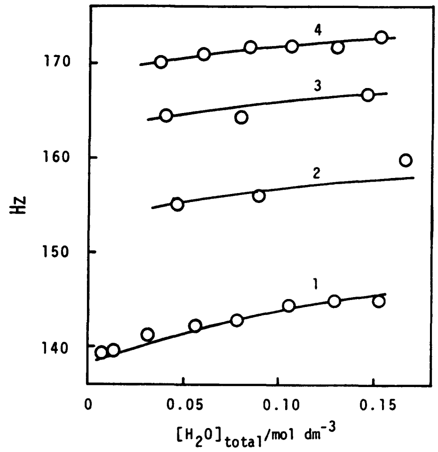


Fig. 2. Chemical shifts of water protons in the presence of Pr_4NI in nitrobenzene. Solid lines show the calculated values. Concentration of Pr_4NI in mol dm^{-3}; 1, 0.0; 2, 0.05; 3, 0.100; 4, 0.143.

(b) ${}^1H$ NMR Spectra of Water. A single resonance line for water protons in nitrobenzene was obtained irrespective of the presence of Pr_4NI and Ph_4PCl. Figures 2 and 3 show the chemical shifts of water protons as a function of water and salt concentrations. Hydrogen bonding usually leads to a down-field shift.[4,6] In Fig. 2 the increased down field shift with water concentration irrespective of the presence of salts is ascribed to the increased dimerization of water and hydration of ions, respectively.

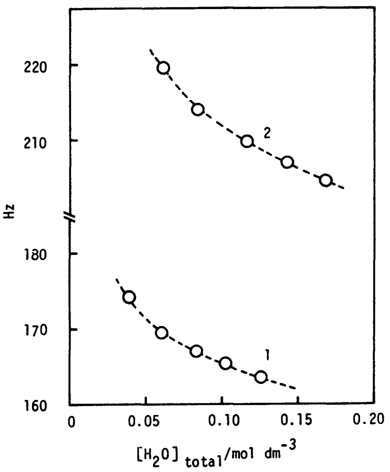


Fig. 3. Chemical shifts of water protons in the presence of Ph_4PCl in nitrobenzene. Concentration of Ph_4PCl in mol dm^{-3}; 1, 0.0109; 2, 0.0471.

In a way similar to the case for c.t.t.s. spectra, the observed chemical shift (δ_{obsd}) of water protons is represented as, in the absence of salts,

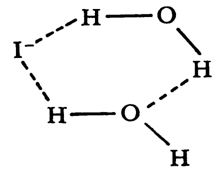
$$\delta_{obsd} = (\delta_0[H_2O]+2\delta_s K_s[H_2O]^2)/[H_2O]_{total}, \quad (3)$$

in the presence of salts,

$$\begin{aligned}\delta_{obsd} = {} & (\delta_0[H_2O] + 2\delta_s K_s[H_2O]^2 + \delta_1 K_1[I^-][H_2O] \\ & + 2\delta_2 K_1 K_2[I^-][H_2O]^2 \\ & + 3\delta_3 K_1 K_2 K_3[I^-][H_2O]^3)/[H_2O]_{total}, \quad (4)\end{aligned}$$

where δ_0, δ_s, δ_1, δ_2, and δ_3 are chemical shifts for non-bonded monomeric and dimeric water, 1 : 1, 1 : 2, and 1 : 3 hydrates, respectively. Although in the salt concentration range used in the NMR study the degree of ionic association for Pr_4NI is marked (0.14 for 0.01 mol dm^{-3} and 0.44 for 0.15 mol dm^{-3}), the hydration of iodide ions is not affected significantly by the association.[2,12–15] Thus, the association effect was disregarded. The chemical shifts, δ_0(138) and δ_s(175) from Eq. 3 and δ_1(232), δ_2(245), and δ_3(265) from Eq. 4 were estimated from K_s and K_1, K_2, and K_3 obtained from the c.t.t.s. spectra. It is noteworthy that the chemical shift increases stepwise with increasing degree of hydration of iodide, $\delta_1 < \delta_2 < \delta_3$, contrary to the behaviour for lithium ions in propylene carbonate.[4] Furthermore, the chemical shift for iodide increases with increasing the water concentration, while that for chloride decreases (Fig. 3). The increased down-field shift for iodide would be explained in terms of chelation of water molecules bound to iodide ions; models I for n=2 and II for n=3.

I



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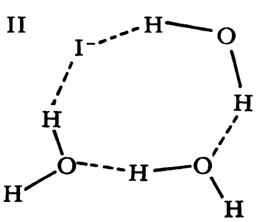

The chemical shift for chloride ions is much larger than that for iodide ions, showing the stronger hydration of chloride ions. It is likely that the orientation of water molecules towards chloride ions through hydrogen bonding is too strong to make a chelate ring such as the one observed for iodide ions.

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References

1) T. Fujiwara, K. Matsuda, and Y. Yamamoto, *Inorg. Nucl. Chem. Lett.*, **16**, 301 (1980).

2) K. Ito, E. Iwamoto, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **55**, 2143 (1982).

3) M. C. R. Symons and S. E. Jackson, *J. Chem. Soc., Faraday Trans. 1*, **75**, 1919 (1979).

4) D. R. Cogly, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, **75**, 1477 (1971).

5) M. C. R. Symons and V. K. Thomas, *J. Chem. Soc., Faraday Trans., 1*, **77**, 1891 (1981).

6) R. L. Benoit and S. Y. Lam, *J. Am. Chem. Soc.*, **96**, 7385 (1974).

7) I. D. Kuntz, Jr., and C. J. Cheng, *J. Am. Chem. Soc.*, **97**, 4852 (1975).

8) M. C. R. Symons, T. A. Shippy, and P. P. Pastogi, *J. Chem. Soc., Faraday Trans., 1*, **76**, 2251 (1980).

9) M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Am. Chem. Soc.*, **89**, 1582 (1967).

10) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **91**, 4681 (1969).

11) D. J. Pirson and P. L. Huyskens, *J. Solution Chem.*, **3**, 503 (1974).

12) Y. Yamamoto, T. Tarumoto, and T. Tarui, *Bull. Chem. Soc. Jpn.*, **46**, 1466 (1973).

13) T. Kenjo and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **36**, 183 (1974).

14) T. Tarui, *J. Inorg. Nucl. Chem.*, **37**, 1213 (1975).

15) C. M. Arnett, B. Chawla, and N. J. Hornung, *J. Solution Chem.*, **6**, 781 (1977).

16) a) E. Iwamoto, K. Ito, and Y. Yamamoto, *J. Phys. Chem.*, **85**, 894 (1981); b) E. Iwamoto, H. Ohmori and Y. Yamamoto, *ibid.*, **87**, 1776 (1983).

17) E. Hirsch and R. M. Fuoss, *J. Am. Chem. Soc.*, **82**, 1018 (1960).

18) M. J. Blandamer and M. F. Fox, *Chem. Rev.*, **69**, 59 (1969).

19) P. C. Dwivedi and C. N. R. Rao, *Spectrochimica Acta, Part A*, **26**, 1535 (1970).

20) S. D. Christian, A. A. Taha, and B. W. Gash, *Quart. Rev. Chem. Soc.*, **24**, 20 (1970).