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The Viscosities and Molal Volumes of *t*-Butyl Alcohol in Metal Chelate Electrolyte Solutions

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The Viscosities and molal volumes of *t*-butyl alcohol (*t*-BuOH) in aqueous solutions of $[Fe(phen)_3]Cl_2$, $[Co(phen)_3]Cl_3$ (phen=1,10-phenanthroline), $[Co(en)_3]Cl_3$ (en=ethylenediamine), tetraphenylphosphonium chloride ($(C_6H_5)_4PCl$), tetramethylammonium chloride (Me_4NCl), tetraethylammonium chloride (Et_4NCl), and tetra-*n*-butylammonium bromide ($(n\text{-}Bu)_4NBr$) were measured at 25 °C, and solute-solvent interactions characteristic of the metal chelate cations were investigated. The apparent molal volumes of *t*-BuOH in the solutions of $[Fe(phen)_3]^{2+}$ are larger than those in the $(n\text{-}Bu)_4N^+$ and $[Co(phen)_3]^{3+}$ solutions. The hydrophobicity of $[Fe(phen)_3]^{2+}$ is not so strong because of the aromaticity of the ligand. The same can be said for $[Co(phen)_3]^{3+}$. However, on the interaction between $[Co(phen)_3]^{3+}$ and *t*-BuOH, the charge-dipole interaction and hydrophobic interaction act cooperatively to stabilize this pair through the overlap of the solvation spheres.

The solute–solvent interactions of such metal chelate ions as $[Fe(phen)_3]^{2+}$ have been studied by means of their thermodynamic,[1–4] transport,[5–6] and kinetic[7] properties. From the viscosity study, $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine) were found to be hydrophobic-structure-making ions, though their hydrophobicity is weaker than that of the tetraalkylammonium ions at the equivalent level of the partial molal volumes.[5] $[Fe(phen)_3]^{2+}$ was found to show a large salting-in effect through hydrophobic interaction on the nonelectrolytes, such as nitrobenzene, toluene, benzene, and $[Co(acac)_3]$ (Hacac=2,4-pentanedione).[2–4] It was also found that the racemization rate of the trivalent metal chelate cation, $[Co(phen)_3]^{3+}$, by the electron-transfer mechanism is strongly affected by the structural change of water on the addition of *t*-BuOH.[7] In the present study, solute-solvent and solute–solute interactions of the metal chelates were examined through the viscosities and the apparent molal volumes of *t*-BuOH in aqueous solutions of these metal chelate electrolytes.

Experimental

The metal chelate electrolytes, $[Fe(phen)_3]Cl_2\cdot 7H_2O$,[5] $[Co(phen)_3]Cl_3\cdot 6H_2O$,[8] and $[Co(en)_3]Cl_3\cdot H_2O$[9] were prepared by the literature methods and recrystallized twice from water. The tetraalkylammonium salts (Tokyo Kasei Kogyo Co., Ltd.) were purified by the methods described in the literature.[10] The tetraphenylphosphonium chloride (Merck) was used without further purification. The purities of the salts were checked by analysis. The *t*-BuOH was reagent grade (Nakarai Chemicals, Ltd.) and was used without further purification. The water was distilled from an alkaline permanganate solution. The concentrations of the electrolytes were determined by potentiometric titrations of the halide ions with $AgNO_3$ standard solutions just prior to use.

Ubbelohde viscometers with flow times for water at 25 °C of about 590 and 690 s were used. The kinetic-energy corrections for the viscometers were found to be negligible within the limits of experimental error. All the viscosity measurements were carried out in a 25.00±0.03 °C constant-temperature water bath controlled to ±0.005 °C. The flow times were measured with a stop watch and were reproducible to ±0.1 s.

The densities were measured with a digital densimeter (Anton Paar, Model DMA-02D). The thermostated bath was kept at 25.00±0.03 °C and controlled to ±0.002 °C. The densimeter was calibrated by the use of dry air and distilled water, and checked by measuring the densities of the aqueous *t*-BuOH solutions.[11] The errors in the density measurements were estimated to be within $\pm 2\times 10^{-6}$ g cm^{-3}.

Results

The relative viscosities, η_r, of the aqueous solutions of *t*-BuOH in the presence of the electrolytes could be represented by the following equation over the range of *t*-BuOH concentrations from 0.2 to 1.5 mol dm^{-3}:

$$\eta_r = \eta/\eta^\circ = 1 + BC + DC^2, \qquad (1)$$

where η_r represents the relative viscosity of the ternary solution (*t*-BuOH–electrolyte–water) with respect to the electrolyte solution used as the solvent, where η and η° are the viscosities of the ternary solution and the solvent respectively, and where C is the molar concentration of *t*-BuOH. The B coefficient is a function of the solute–solvent interaction, and the D coefficient represents the contribution of the solute–solute interaction to the relative viscosity.

Taking pure water as the reference solvent, the relative viscosity can be represented as follows:

$$\eta/\eta_w = \eta^\circ/\eta_w + B'C + D'C^2, \qquad (2)$$

where η_w is the viscosity of pure water, and where B' and D' are $B\eta^\circ/\eta_w$ and $D\eta^\circ/\eta_w$ respectively. These equations differ in their reference states. In the present study, Eq. 2 was used, because B' reflects the differences more clearly than B. The B' and D' coefficients obtained by the least-squares method are given in Table 1. The B coefficient of *t*-BuOH in pure water at 25 °C is in good agreement with the literature value.[12]

The apparent molal volumes, ϕ_v, of *t*-BuOH in the electrolyte solutions were calculated from the density data.[11] The partial molal volumes at infinite dilution in aqueous electrolyte solutions, V^∞, were obtained by

Table 1. B' and D' coefficients of Eq. 2 for t-BuOH in various electrolyte solutions

Electrolyte	C mol dm^{-3}	B' mol^{-1}dm^3	D' mol^{-2}dm^6
(Pure water)		0.372 (0.373)[a]	0.108
[Fe(phen)$_3$]Cl$_2$	0.06683	0.404	0.111
	0.09669	0.421	0.113
[Co(phen)$_3$]Cl$_3$	0.07251	0.427	0.113
	0.09386	0.443	0.117
[Co(en)$_3$]Cl$_3$	0.08320	0.385	0.115
	0.1267	0.394	0.121
Ph$_4$PCl	0.07839	0.391	0.107
	0.1136	0.404	0.109
Bu$_4$NBr	0.05095	0.395	0.105
	0.1019	0.417	0.111
Et$_4$NCl	0.09815	0.383	0.109
	0.1684	0.392	0.114
Me$_4$NCl	0.1648	0.373	0.114
	0.2031	0.378	0.110
NaCl	0.1034	0.379	0.103
NaBr	0.09996	0.378	0.102

a) Ref. 12.

Table 2. Partial molal volumes of t-BuOH in various electrolyte solutions

Electrolyte	C mol dm^{-3}	V^∞ cm^{3}mol^{-1}
(Pure water)		87.83 (87.90)[a]
[Fe(phen)$_3$]Cl$_2$	0.04985	87.59
	0.09828	87.38
[Co(phen)$_3$]Cl$_3$	0.09386	87.18
	0.2246	86.20
[Co(en)$_3$]Cl$_3$	0.04818	87.71
	0.09636	87.72
Ph$_4$PCl	0.04595	87.58
	0.1004	87.39
Bu$_4$NBr	0.05095	87.45
	0.1008	87.01
Et$_4$NCl	0.04910	87.57
	0.09815	87.37
Me$_4$NCl	0.08120	87.59
	0.1172	87.60
NaCl	0.1034	87.85
NaBr	0.09996	87.88

a) Ref. 11.

fitting the apparent molal volumes to this equation:

$$\phi_v = V^\infty + A_v C + B_v C^2, \qquad (3)$$

where C is the molar concentration of t-BuOH and where A_v and B_v are the fitting parameters. The V^∞ and fitting parameters, A_v and B_v, were obtained by the least-squares method and are given in Table 2.

Discussion

In the presence of the electrolyte, the viscosity B' coefficient of t-BuOH increases with an increase in the concentration of the electrolyte, as is shown in Fig. 1. The increase in the B', coefficient can be attributed to the t-BuOH–electrolyte interaction and the obstruction effect.[13] Of course, it is difficult to evaluate these two effects separately, but it can be assumed that it is proportional to the volume fraction and, therefore, to the partial molal volume of the electrolyte, by analogy with the obstruction effect in conductance and diffusion.[13] Therefore, the B' coefficients in various electrolyte solutions at 0.1 mol dm^{-3} are plotted against the partial molal volumes of the electrolytes in Fig. 2, which shows that the B' coefficients increase with an increase in the partial molal volumes of electrolytes in pure water. The plot for $(C_6H_5)_4PCl$ falls on the line connecting plots for pure water, NaCl, Me$_4$NCl, and [Co(en)$_3$]Cl$_3$. The plot for [Fe(phen)$_3$]Cl$_2$ does not deviate markedly from the line.

Here, the B' coefficients can not be divided into the

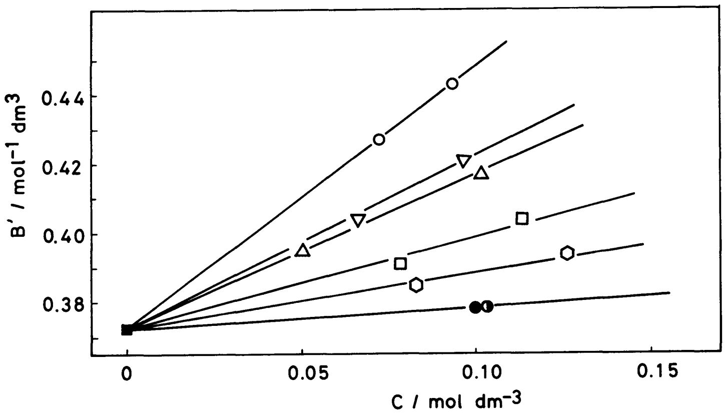

Fig. 1. Dependence of B′ coefficient of t-BuOH on electrolyte concentration.
■: In pure water, ◑: in NaCl solution, ●: in NaBr solution, ⬡: in [Co(en)$_3$]Cl$_3$ solution, □: in $(C_6H_5)_4PCl$ solution, △: in Bu$_4$NBr solution, ▽: in [Fe(phen)$_3$]Cl$_2$ solution, □: in [Co(phen)$_3$]Cl$_3$ solution.

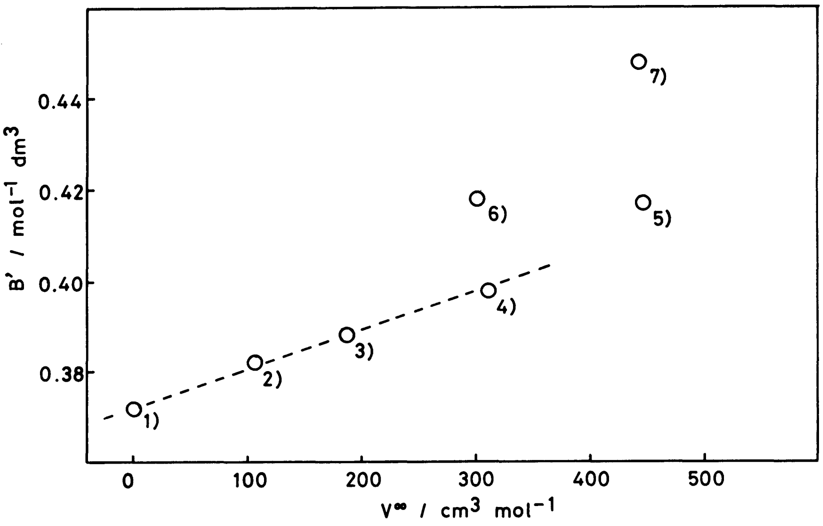

Fig. 2. Relation between B' coefficient of *t*-BuOH in electrolyte solution (0.1 mol dm^{-3}) and partial molal volume of electrolyte in water.
1): In pure water, 2): Me_4NCl,[a] 3) $[Co(en)_3]Cl_3$,[b] 4): $(C_6H_5)_4PCl$,[c] 5): $[Fe(phen)_3]Cl_2$,[d] 6): Bu_4NBr,[a] 6): $[Co(phen)_3]Cl_3$.[b]
Partial molal volumes of electrolytes in water were taken from references: a) Ref. 18), b) Ref. 19), c) Ref. 20), d) Ref. 1).

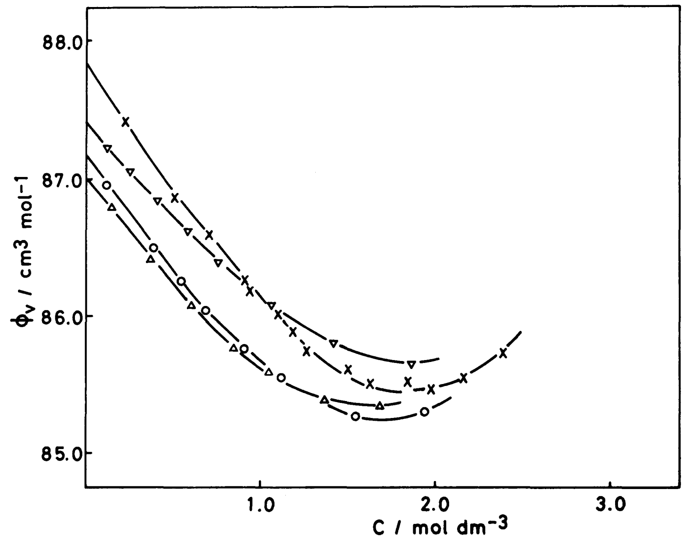

Fig. 3. Apparent molal volumes of *t*-BuOH in water and electrolyte solutions.
×: In pure water, ▽: in $[Fe(phen)_3]Cl_2$ solution (0.09828 mol dm^{-3}), ○: in $[Co(phen)_3]Cl_3$ solution (0.09386 mol dm^{-3}), △: in Bu_4NBr solution (0.1008 mol dm^{-3}).

contributions of the cation and the anion, but it may be safely assumed that the cationic contributions are the main factor in the large difference of the B' coefficients between the solutions of $(n\text{-}Bu)_4NBr$ and $(C_6H_5)_4PCl$, or $[Fe(phen)_3]Cl_2$ and $[Co(phen)_3]Cl_3$.

The larger B', coefficient of *t*-BuOH in the $(n\text{-}Bu)_4N^+$ solution was attributed to the strongly hydrophobic interaction.[11,14–16] The smaller B' value for $(C_6H_5)_4P^+$ means that the hydrophobicity becomes weak upon the introduction of the aromatic character.[5,17] The same can be said for the hydrophobicity of $[Fe(phen)_3]^{2+}$.

The large B' coefficient in the solution of $[Co(phen)_3]^{3+}$ compared with that in the $[Fe(phen)_3]^{2+}$ solution needs to be explained other than in terms of the hydrophobicity, because the hydrophobicity of $[Co(phen)_3]^{3+}$ should be weaker than $[Fe(phen)_3]^{2+}$ because of its trivalent charge. On the other hand, it seems that the ion-dipole interaction by the trivalent charge of the ion can not cause the large B' coefficient by itself, because the B' coefficient is not so large in the solution of the trivalent ion with much smaller volumes of $[Co(en)_3]^{3+}$.

As is shown in Fig. 3, the ϕ_v of *t*-BuOH decreases with an increase in the concentration of *t*-BuOH and reaches a minimum at about 1.9 mol dm^{-3} in pure water. This minimum corresponds to the composition of the maximum structure of the solution.[11] For the case of ϕ_v in the $(n\text{-Bu})_4N^+$ solution the minimum in ϕ_v shifts to a lower concentration as a result of the cooperative effect of *t*-BuOH and $(n\text{-Bu})_4N^+$. In the solution of $[Fe(phen)_3]^{2+}$, the minimum shifts only a little, which indicates that such a cooperative action does not occur for the pairs of $[Fe(phen)_3]^{2+}$ and *t*-BuOH.

When the V^∞ values of *t*-BuOH in electrolyte solutions of about 0.1 mol dm^{-3} in Table 2 are compared, the V^∞ values are nearly equal in alkali halide solutions, slightly smaller in Me_4N^+, and smallest in $(n\text{-Bu})_4N^+$, compared with the V^∞ value in pure water. Such a trend can be expected from the effects of these ions on the water structure, but the fairly small V^∞ value in $[Co(phen)_3]^{3+}$ can not be explained from the structural property. The most probable explanation for the V^∞ and B' values of *t*-BuOH in $[Co(phen)_3]^{3+}$ is that $[Co(phen)_3]^{3+}$ attracts *t*-BuOH in the vicinity of the hydrophobic ligands by means of such long-range forces as the charge-dipole interaction.[3] After that, the van der Waals interaction between *t*-BuOH and $[Co(phen)_3]^{3+}$ becomes effective and the overlap of the hydration sphere occurs.[3] This also causes the large B' coefficient of *t*-BuOH in the solution of $[Co(phen)_3]^{3+}$.

From the above observations, it may be concluded that the hydrophobic interaction between the $[Fe(phen)_3]^{2+}$ ion and the aliphatic solute of *t*-BuOH is weak because of the aromatic character of the ligands. However, for the pair of the $[Co(phen)_3]^{3+}$ ion and *t*-BuOH, the cooperative action of ion-dipole and hydrophobic interaction is very effective in stabilizing the water structure.

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$$\phi_v = V^\infty + 27.45C^{1/2} + b_vC,$$

while the parameters, V^∞ and b_v, for $[Co(en)_3]Cl_3$ (187.4 cm^3 mol^{-1} and -15.8 cm^3 dm^3 mol^{-2} and for $[Co(phen)_3]Cl_3$ (441.8 cm^3 mol^{-1} and -50.1 cm^3 dm^3 mol^{-2}) were determined by the least-squares method.

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