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The Osmotic and Activity Coefficients of Quaternary Phosphonium Halides in Aqueous Solutions at Freezing Point

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The osmotic and activity coefficients have been obtained cryoscopically for $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PX}(n=0\text{—}4,\ \text{X}=\text{Cl, Br})$ in aqueous solutions at freezing point. The $\gamma_\pm$ decreases with increasing n, for both the chloride and the bromide salts. With the chloride salts, $\gamma_\pm$'s for the salts of n from 0 to 2 show positive deviation from the Debye-Hückel limiting law as concentration increases, whereas $\gamma_\pm$'s for others show negative deviation. Replacement of the anion from Cl^- to Br^- results in lower $\gamma_\pm$'s for the salts of n from 0 to 2, but this elevates the other $\gamma_\pm$'s. These results were interpreted qualitatively in terms of the cosphere overlap model by Desnoyers *et al.*, by assuming a hydrophilic character of the present phenyl group. An attempt was made to evaluate the pairwise interaction coefficients(B^*) and to estimate the contributions to B^* from the interactions, butyl-Cl^- and phenyl-Cl^-.

This paper is part of a continuing study of the thermodynamic properties of aqueous solutions of the quaternary phosphonium halides, $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PX}(n=0\text{—}4)$. Since their molal volumes are nearly the same[1,2] we can expect that the size effect of the cations on the solvent water would be commom and the changes with n in their partial molal thermodynamic quantities would reflect directly the effects arising from the systematic variation in the state of cosphere water around the cation.

The activity coefficients of $(\text{C}_6\text{H}_5)_4\text{MX}$ (M=P, As, and Sb) in water at 37 °C were reported by Kalfoglou and Bowen,[3] these values are much lower than those of the usual 1 : 1 electrolytes. The authors attributed the low $\gamma_\pm$'s to the structure-breaking effects of the phenyl groups on the water structures. On the other hand the activity coefficients of tetraalkylammonium chlorides and bromides,[4,5] the higher members of which are known as typical structure-makers, are higher than that given by the Debye-Hückel limiting law. Thus, it is of interest to examine the variation of the osmotic(ϕ) and activity($\gamma_\pm$) coefficients of the present phosphonium halides with successive replacement of the butyl groups of the $n\text{-Bu}_4\text{P}^+$ ion by phenyl groups, this procedure provides an opportunity to test the group contribution to ϕ and $\gamma_\pm$. Also, the concentration dependences of ϕ's and $\gamma_\pm$'s will offer information about the pairwise interactions between each hydrocarbon cosphere and anions as well as those between the hydrocarbon cospheres.

Here, the cryoscopic method is employed to obtain the osmotic and activity coefficients.

Experimental

The phosphonium halides used for the freezing point measurements, $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PX}(n=0-4,\ \text{X}=\text{Cl, Br})$, were synthesized from the phosphines, except for the Ph_4PCl, which was a commercial product (DOTITE). The methods for synthesizing and purifying the salts were almost the same as those reported previously.[1] The sodium chloride delivered from Merck (Suprapur) was used for calibration of a thermistor, after drying. Solutions were prepared with conductivity-grade water by weight and buoyancy corrections were applied.

Cooling curves were obtained on a thermistor-differential amplifier-recorder system, which is essentially the same as that devised by Takahashi *et al.*[6] A sample solution was cooled at a rate of about 0.1 K min^{-1} or less; it was stirred constantly by a magnetic stirrer (1500 min^{-1}) in a Dewar-type cell of about 10 cm^3 inner-capacity, equipped with a rodtype thermistor. The cell was immersed in a cooling bath, the temperature of which was maintained lower by about 10K than the freezing point of the solution. Freezing was initiated by mechanical vibration of the cell assembly if super-cooling of the solution continued even at a temperature lower than the freezing point by 1 K or more. The freezing point was determined, as usual, by extrapolation of the linear part of the cooling curve to the point where the freezing would begin without the supercooling. The electric resistance of the thermistor was about 34 kΩ at 0 °C and the d.c. current which passed was regulated to be about 10 μA. Thus, the Joule's heat evolved is about 0.34 $\mu\text{J s}^{-1}$ which would hardly affect the temperature measurement under the experimental conditions. The thermistor was standardized against the freezing points of a series of aqueous solutions of sodium chloride, twelve solutions over a concentration range of 0.005 to 1.1 mol kg^{-1}, for which accurate data have been reported by Scatchard and Prentiss.[7]

The thermistor resistance was fitted to this equation as a function of T:

$$\log R = \log R^\circ + b(1/T-1/T^\circ) + c(1/T-1/T^\circ)^2,$$

where T° is 273.15 K and R° is the resistance at T°; the parameters b and c were determined by the least-squares method to fit the observed resistances to the freezing points of the aqueous sodium chloride solutions, with a standard deviation, 3×10^{-5}, in $\log R$. The temperature coefficient of the thermistor was about $-1.3\ \text{k}\Omega\ \text{K}^{-1}$, which enabled us to attain a resolution of 1×10^{-4} K by amplifying. The reproducibility of the freezing point measurements for conductivity-grade water and dilute solutions was within 3×10^{-4} K provided that the stirring was steady and that the reference (R_{ref}) and standard (R_{st}) resistors, decade-types of six figures, were set in a thermostat bath (35±.2 °C), as was the case of the present measurement. Each cooling curve was always preceded and followed by the measurements for the couple, R_{st}-R_{ref}, to compare with the couple, $R_{\text{thermistor}}$-R_{ref}. This procedure enables us to eliminate any drift in the recorder or in the amplifier. No aging effect of the thermistor was found, within experimental reproducibility, as confirmed by occasional measurements for the freezing point of pure water.

Results and Discussion

The Lewis-Randall function, j, was obtained from the freezing point depression, θ, by the equation:[8]

TABLE 1. VALUES OF j-FUNCTIONS FOR n-Bu$_{4-n}$Ph$_n$PX IN AQUEOUS SOLUTIONS

Molality	j	Molality	j	Molality	j	Molality	j
n-Bu$_4$PCl		n-Bu$_4$PBr		0.03263	0.0588	0.4791	0.2332
0.00251	0.0164	0.00501	0.0270	0.04074	0.0704	0.5175	0.2440
0.00657	0.0250	0.01497	0.0527	0.05587	0.0809		
0.01496	0.0339	0.02455	0.0560	0.05862	0.0831	n-Bu$_2$Ph$_2$PBr	
0.04011	0.0458	0.03483	0.0672	0.1035	0.1110	0.00516	0.0248
0.06716	0.0502	0.05603	0.0816	0.1557	0.1336	0.00771	0.0359
0.1018	0.0519	0.06497	0.0842	0.1606	0.1359	0.01008	0.0370
0.1462	0.0517	0.07407	0.0996	0.1970	0.1481	0.02419	0.0556
0.1991	0.0499	0.08493	0.0979	0.2688	0.1723	0.04597	0.0903
n-Bu$_3$PhPCl		n-Bu$_3$PhPBr		0.3620	0.2024	0.07544	0.1120
0.00559	0.0254	0.00633	0.0366	n-BuPh$_3$PCl		n-BuPh$_3$PBr	
0.01325	0.0356	0.01450	0.0511	0.01020	0.0432	0.00514	0.0279
0.02344	0.0488	0.03215	0.0696	0.02037	0.0614	0.00731	0.0313
0.05512	0.0677	0.03401	0.0732	0.04001	0.0865	0.01499	0.0482
0.09793	0.0820	0.07890	0.1134	0.06872	0.1162	0.01921	0.0528
0.1478	0.0904	0.1439	0.1597	0.1158	0.1580	0.02514	0.0649
0.2173	0.1017	0.2338	0.2048	0.1661	0.2020	0.03088	0.0739
0.2954	0.1076	0.3391	0.2459	0.2400	0.2614		
0.4006	0.1121	0.4490	0.2822	Ph$_4$PCl		Ph$_4$PBr	
0.4856	0.1161	0.5533	0.3110	0.00322	0.0272	0.00566	0.0281
0.6466	0.1127	0.6513	0.3368	0.00645	0.0364	0.00778	0.0367
0.8068	0.1104	0.7594	0.3646	0.01429	0.0590	0.00964	0.0375
1.045	0.0993	0.8606	0.3860	0.02512	0.0780	0.01154	0.0427
1.251	0.0889			0.03514	0.0956	0.01528	0.0536
n-Bu$_2$Ph$_2$PCl				0.05401	0.1258		
0.01363	0.0405	0.4135	0.2198	0.06962	0.1525		

TABLE 2. COEFFICIENTS OF j-FUNCTION (Eq. 2)

Salt	a_0	a_1	a_2	σ[a)]	B^*[b)]
n-Bu$_4$PCl	2.154	−0.1918	0.05975	0.0004	0.872
n-Bu$_3$PhPCl	1.350	−0.02855	−0.02804	0.0015	0.467
n-Bu$_2$Ph$_2$PCl	1.226	0.1958		0.0022	0.231
n-BuPh$_3$PCl	−0.592			0.0020	−0.194
Ph$_4$PCl	−1.336			0.0031	−0.437
n-Bu$_4$PBr	0.326			0.0042	0.107
n-Bu$_3$PhPBr	−0.124			0.0066	−0.041
n-Bu$_2$Ph$_2$PBr	−0.288			0.0036	−0.094
n-BuPh$_3$PBr	−0.444			0.0019	−0.145
Ph$_4$PBr	−0.724			0.0021	−0.237

a) The standard deviation between the observed and reproduced j-values. b) The coefficient given by Eq. 7 multiplied by 0.4343.

$$j = 1 - \theta/(\lambda\nu m), \tag{1}$$

where λ is the molal lowering of the freezing point of water, 1.860 K mol^{-1} kg, and ν the number of moles of ions formed from 1 mol of electrolyte (*i.e.*, 2 for the present case). The error in j comes mostly from the error in θ and becomes increasingly large as concentration decreases; it amounts to 0.016 due to an error in θ, 3×10^{-4} K, for solution of 5×10^{-3} mol kg^{-1} which was the lowest concentration in the present measurements. The values of j listed in Table 1 are the average values from several measurements for each solution of low concentrations (below 0.1 mol kg^{-1}) and from triple measurements for solutions of higher concentrations.

An empirical form for the j-function was assumed:

$$j = \frac{Am^{1/2}}{1+a_0m^{1/2}} + a_1m + a_2m^2, \tag{2}$$

where A is the Debye-Hückel limiting slope, 0.377 mol$^{-1/2}$ kg$^{1/2}$, and other parameters, a_i, were adjusted to fit the observed j values by the least-squares method. The parameters determined for the n-Bu$_{4-n}$Ph$_n$PX salts are summarized in Table 2, where the standard deviations between the observed and reproduced j values are also listed.

The activity coefficients were calculated by the equation:

$$\ln \gamma_\pm = -j - \int_0^m j\,\mathrm{d}\ln m + \xi\int_0^\theta \frac{\theta}{\nu m}\mathrm{d}\theta, \tag{3}$$

where the last term including ξ(0.00054)[8)] contributes hardly at all to $\ln \gamma_\pm$, *i.e.*, only a few units in the fourth decimal of $\ln \gamma_\pm$, and was neglected here. Placing Eq. 2 into Eq. 3 and integrating, we obtain the relation:

Table 3. Osmotic coefficients and activity coefficients of n-Bu$_{4-n}$Ph$_n$PX in aqueous solutions at freezing point

Molality	ϕ	$\log\gamma_\pm$	Molality	ϕ	$\log\gamma_\pm$
n-Bu$_4$PCl			n-Bu$_4$PBr		
0.01	0.971	−0.041	0.01	0.963	−0.048
0.02	0.963	−0.055	0.02	0.949	−0.067
0.05	0.952	−0.076	0.04	0.929	−0.094
0.1	0.948	−0.093	0.06	0·914	−0.114
0.2	0.950	−0.108	0.08	0.902	−0.131
n-Bu$_3$PhPCl			n-Bu$_3$PhPBr		
0.02	0.956	−0.061	0·01	0.962	−0.049
0.05	0.937	−0.091	0.02	0.946	−0.070
0.1	0.920	−0.120	0.05	0.913	−0.112
0.2	0.902	−0.154	0.1	0.876	−0.159
0.5	0.885	−0.205	0.2	0.821	−0.228
1	0.896	−0.234	0.5	0.708	−0.369
1.2	0.908	−0.236	0.8	0.621	−0.475
n-Bu$_2$Ph$_2$PCl			n-Bu$_2$Ph$_2$PBr		
0.01	0.964	−0.047	0.01	0.961	−0.050
0.02	0.951	−0.066	0·02	0.944	−0.071
0.05	0.924	−0.102	0.04	0.920	−0.102
0.1	0.894	−0.142	0.06	0.901	−0.126
0.2	0.852	−0.198	0.08	0.884	−0.147
0.5	0.759	−0.314			
n-BuPh$_3$PCl			n-BuPh$_3$PBr		
0.01	0.960	−0.051	0.005	0.972	−0.035
0.02	0.942	−0.074	0.01	0.960	−0.051
0.05	0.903	−0.121	0.02	0.943	−0.072
0.1	0.853	−0.178	0.03	0.929	−0.090
0.2	0.771	−0.270			
Ph$_4$PCl			Ph$_4$PBr		
0.01	0.956	−0.054	0.005	0.972	−0.036
0.02	0.934	−0.080	0.01	0.959	−0.052
0.04	0.897	−0.121	0.02	0.941	−0.075
0.06	0.863	−0.157			

$$-\ln\gamma_\pm = \frac{Am^{1/2}}{1+a_0m^{1/2}} + \frac{2A}{a_0}\ln(1+a_0m^{1/2}) + 2a_1m + \frac{3}{2}a_2m^2. \tag{4}$$

In Table 3, the osmotic coefficients ϕ and the activity coefficients $\log\gamma_\pm$ are listed. The present results are, as a whole, accompanied by errors of a few units in the third decimal place of j and are considered to be preliminary ones, especially with the bromide salts, mainly because the measurements for them were confined to low concentration ranges owing to their limited solubilities.

The mean chemical potential for an electrolyte may be described by:[9]

$$\mu_\pm = \mu_\pm^\circ + RT\ln c + Sc^{1/2} + RT[B_2(\kappa)c + B_3(\kappa)c^2 + \cdots], \tag{5}$$

where the coefficient S is given by the Debye-Hückel limiting law. According to Friedman and Krishnan,[9] $B_2(\kappa)$ reflects mainly the effects arising from the pairwise interactions between ions due to the short-range focres, though it depends also on the ionic strength through the Debye κ, and is decomposed into three contributions from the pairwise ionic interactions, $++$, $+-$, and $--$. For a 1 : 1 electrolyte it can be expressed as

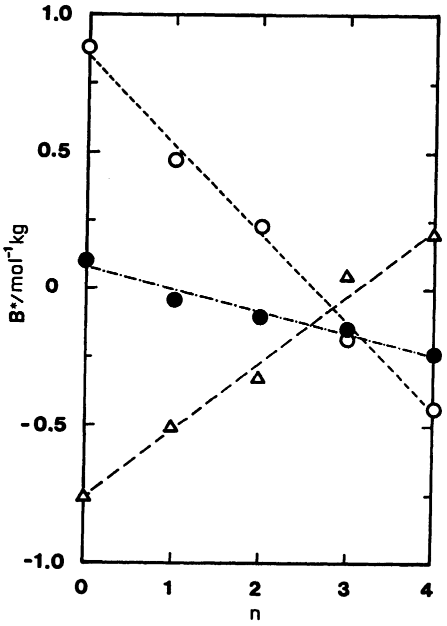

Fig. 1. The B^* coefficient and the difference between the bromide salts and the chloride salts, ΔB^*, as functions of the number of phenyl groups on the cation, n.
---○---, B^*(chloride); —·—●—·—, B^*(bromide); —△—, ΔB^*.

$$B_2(\kappa) = \frac{1}{4}[B_{++}(\kappa) + 2B_{+-}(\kappa) + B_{--}(\kappa)]. \tag{6}$$

Expanding Eq. 4 into polynomial of $m^{1/2}$, we obtain the equation,

$$\ln\gamma_\pm = -Am^{1/2} + Bm + Cm^{3/2} + \cdots,$$

where the first term of the right hand side is the Debye-Hückel limiting term and the coefficient B is given by,

$$B = 2(Aa_0 - a_1). \tag{7}$$

In the last column of Table 2, the values for B^* which is the B coefficient for $\log\gamma_\pm$, *i.e.*, 0.4343 B, are listed. The B^* coefficients may be assumed, as a first approximation, to be proportional to $B_2(\kappa)$, since in dilute solutions the excess part of $\ln\gamma^\pm$ from the Debye-Hückel limiting law would mainly originate from pairwise interactions between ions due to short-range forces and the difference between the two concentration scales is negligible.

The B^*'s for the salts and the differences in B^* between the bromide and chloride salts, ΔB^*, are shown as functions of n in Fig. 1. Some features are to be noted: 1 the B^*, and hence $\log\gamma_\pm$, decreases successively with increasing n for both the chloride and bromide salts, 2) the n dependence of B^* is marked with the chloride salts, while it is not marked with the bromide salts, and 3) the ΔB^* is negative for Bu$_4$PX, while it is positive for Ph$_4$PX; those for the intermediate salts appear to distribute between these two ΔB^*'s. Qualitatively, these features are explicable by the structural hydration interaction model proposed by Desnoyers *et al.*,[10] if the phenyl groups in the present cations are assumed to be hydrophilic rather than hydrophobic, as suggested by Kalfoglou and Bowen[3] and from the volumetric studies.[2,11] In their model, the interactions between ions are classified into four types based on a qualitative consideration about the states of water in the cosphere overlap region: hydrophobic-hydrophobic-(I), hydrophobic-hydrophilic(II), hydrophilic-hydrophilic (ions with opposite charge (III), and hydrophilic-hydrophilic (ions with the same charge) (IV). The contributions to the excess partial molal Gibbs free energy $\bar{G}^{ex}$, and hence also to B_2, are negative for the interactions I and III and positive for those II and IV. This leads to the sign assignment for B_{ij}: for Bu_4PX, $B_{++}<0$ and $B_{+-}>0$, and for Ph_4PX, $B_{++}>0$ and $B_{+-}<0$. Since for each of the two salts the sign of B^* is the same as that of B_{+-}, it comes to be that the cation-anion interactions are dominant for both the cations among the ion-ion interactions $++$, $+-$, and $--$. The chloride ion may be more hydrophilic than the bromide ion in the sense that the former ion is more effective in electrostrictive hydration and B_{+-} for Bu_4PCl would be more positive than that for Bu_4PBr, while the reverse would be true for the Ph_4P^+ ion, *i.e.*, B_{+-} for Ph_4PCl would be more negative than that for Ph_4PBr. The hydrophilic character assumed for the present phenyl groups would be caused by a rather large polarizability due to the π electrons and delocalized charges on them induced by the large electronegativity of $P(V)^+$, as revealed by an NMR study.[12]

With the intermediate cations ($n=1$—3), the opposite effects due to the interactions, butyl-X^- and phenyl-X^-, appear to successively cancel each other, suggesting that the cosphere around each group is affected only weakly by the nearest groups on the same cation. A similar result has been obtained from the volume studies.[2,11]

As examined in the volume studies, the B^* would also be expressed as a quadratic equation of n, if the contribution from the cation-cation interactions are of considerable importance. Although the present results are not accurate enough to discuss the B^*_{++} values the B^* for the chloride salts seems to be a linear function of n. If this is the case, this means that the B^* coefficients are nearly equal to $(1/2)B^*{}_{+-}$'s (Eq. 6) and hence we can split the contributions, butyl-Cl^- and phenyl-Cl^-. Roughly, they may be given from the B^*'s for Bu_4PCl and Ph_4PCl by dividing $2B^*$ by four, and neglecting B^*_{++} and B^*_{--}, that is, about 0.4 and -0.1 mol^{-1} kg, respectively.

In conclusion, two points are to be noted: First, the present and previous[2,11] results seem to support a simple assumption that the state of cosphere water around any group on the present cations is independent of the nearest groups on the same cation and each of group cospheres(i) interacts with another cosphere(j) around a simple anion or group on another cation with a relative probability proportional to the concentration product, $c_i c_j$, in dilute solutions. A similar assumption has been used by Wood *et al.*[13,14] for predicting pairwise interaction enthalpies and free energies of nonelectrolytes in dilute aqueous solutions. Applying the Wood method, Visser *et al.*[15] have estimated the enthalpy parameter for the pairwise interaction between the methylene group on tetraalkylammonium ions and the bromide ion. Second, the cosphere overlap model by Desnoyers *et al.*, which is somewhat different from that used by Friedman and his coworkers[16,17] and Streng and Wen,[18] seems to be reasonable and useful to interpret qualitatively ion-ion interactions in aqueous solutions, though the model would be limited to qualitative use until our knowledge on the structures around various ions as well as those of pure water would become more profound.

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