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# Excess Volume of Mixing of Quaternary Phosphonium Chlorides with Potassium Chloride in Water

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Volume changes upon mixing aqueous solutions of potassium chloride and the quaternary phosphonium chloride, $n$-$Bu_{4-n}Ph_nPCl$, ($n$=0—4), have been measured at various constant total ionic strengths ($I$=0.25, 0.5, 1.0) at 25 °C. Based on Friedman's theory for a mixed electrolyte solution, volume-interaction parameters, $v_0$, were determined at each ionic strength. The dependence of $v_0$ on $I$ shows that contributions to the excess volume due to structural effects of a pairwise interaction between the cations and triplet interactions including a single anion are most significant for the $Bu_4P^+$ ion and decrease with increasing $n$. A comparison of the $v_0$'s with the excess-volume properties of the salts in each pure solution shows that the interaction between the phosphonium cations and the potassium ion results in negative contributions to the excess volume of mixing, which also decreases as $n$ increases.

Measurements regarding the excess thermodynamic properties of aqueous mixed-electrolyte solutions have provided useful information on specific interactions between ions in solution.[1] Information on pairwise interactions between like-charged ions can be obtained by examining the mixing process of two kinds of electrolyte solutions containing a common counterion at constant ionic strength. Effects due to both the ionic atmosphere and oppositely charged ions are kept constant during the mixing process.

Wen and his associates[2,3] studied the excess volumes of mixing $\Delta_m V^E$ in the systems, tetraalkylammonium halides ($R_4NX$) and potassium halides, applying Friedman's theory[4] for mixed-electrolyte solutions. They found that the hydrophobic interactions between tetraalkylammonium ions are the major factors regarding the nonideal behavior of the mixtures in the case of R=propyl and butyl. They confirmed this conclusion by means of a more complete characterization of the hydrophobically induced cation–cation interaction.[5] They also suggested that cationic interactions between these $R_4N^+$ and $K^+$ ions gave positive contributions to $\Delta_m V^E$.

In previous papers,[6,7] we determined the volume $B$-coefficients($B_v$) for the quaternary phosphonium salts, $n$-$Bu_{4-n}Ph_nPX$, and concluded that the $B_v$'s, which are all negative, reflect mainly the effects resulting from the cation–cation interactions. The time-averaged clathratelike hydration model seemed to be plausible for the butyl groups but not for the phenyl groups. Further, the $B_v$'s were decomposed into contributions arising from the butyl–butyl, phenyl–phenyl, and butyl–phenyl interactions.

In this study, we carried out measurements to determine the excess volumes upon mixing quaternary phosphonium chloride with potassium chloride at constant ionic strength.

## Experimental

*Materials and Apparatus.* The five quaternary phosphonium salts($n$=0—4) were obtained and purified as previously reported.[8] The potassium chloride delivered from Merck(Suprapur) was used without further purification.

Volume changes upon mixing were measured using Hashitani's cells,[9] with some modification (Fig. 1). The cells(quartz) have a total capacity of *ca.* 60 cm$^3$. Each cell is divided into two rooms by a disk with a mirror surface. The room capacities were calibrated five times using conductivity water with a standard deviation of 0.004 cm$^3$. The capillary tubing attached at the top of the cap(Pyrex glass) had an inner diameter of *ca.* 0.6 mm with a minimum graduation of 0.0005 cm$^3$. This was calibrated using mercury. The inside of the capillary was coated with sillicon grease as previously reported.[10] Leakage of the solution through the disk separator was checked spectrophotometrically using a set of solutions, pure water(upper room) and a dye solution (lower room). No leakage was found.

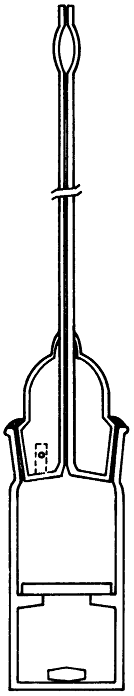

Fig. 1. The cell for measurering $\Delta_m V^E$.

*Measurements of* $\Delta_m V^E$. Throughout the following procedures, the cells were kept in a water bath (25±0.003 °C). The two solutions, which had been degassed and equilibrated to the bath temperature, were introduced stepwise into each separated room. The cap was fixed with Decotinsky cement after adjusting the meniscus height in the capillary. The cell was thoroughly immersed in the bath and the equilibrium meniscus-height(initial volume) was read with a precision of $1\times10^{-4}$ cm$^3$. Then, the disk separator was shifted by turning the cell upside down, the contents were thoroughly mixed by a magnetic stirrer, and the final meniscus-height(final volume) was measured.

Generally, for every mixing system, the measurements were carried out for more than ten of volume ratios and at ionic strengths of 0.25, 0.5, and 1.0 (mol kg$^{-1}$). The volume changes of mixing ranged from 0.002 to 0.03 cm$^3$.

## Results and Discussion

The Friedman's theory for mixed electrolytes[4] leads to an expression for the excess volume of mixing two electrolyte solutions of identical ionic strength $I$ as;

$$\Delta_m V^E/W = I^2 y(1-y)[v_o + (2y-1)v_1], \qquad (1)$$

where $W$ is the weight(kg) of the solvent water and $y$ the mole ratio of one electrolyte to the total electrolytes and $v_o, v_1, ..$, are the volume-interaction parameters. The quantity of lhs. of Eq. 1 is the excess volume of mixing per kg of solvent and is related to the experimental data through the equation

$$\Delta_m V^E/W = mV_\phi(\text{mixture}) - ymV_\phi(\text{AX}) - (1-y)mV_\phi(\text{BX}) \qquad (2)$$

where $V_\phi$(MX) is apparent molar volume of MX in its pure solution, $m$ the molality(equal to $I$ in the present systems) and X, a common anion. The interaction parameters may be expressed as[11]

$$v_o = v_{\text{pairs}} + Iv_{\text{triplets}},\ v_1 = Iv^1{}_{\text{triplets}} \qquad (3)$$

$$v_{\text{pairs}} = 2v^*_{\text{AB}} - v^*_{\text{AA}} - v^*_{\text{BB}}\cdots, \qquad (4)$$

where $v_{\text{pairs}}$ is the contribution to the excess volume of mixing from pairwise interactions between cations and $v_{\text{triplets}}$ is the contribution from the triplet interactions of the cation–cation–anion type and; $v^1{}_{\text{triplets}}$ is the contribution from the other types of triplet interactions. The $v^*_{ij}$'s are functions of ionic strength. In this paper, subscripts A and B stand for the phosphonium cation and the potassium ion, respectively. As employed by Wen and Nara,[3] the difference of excess volumes of two separate solutions, $v^*$, at an identical ionic strength $I$ can be expressed by,

$$v^* = [V^E(\text{BX}) - V^E(\text{AX})]/I^2 = v^*_{\text{BB}} + 2v^*_{\text{BX}} - v^*_{\text{AA}} - 2v^*_{\text{AX}}\cdots \qquad (5)$$

The excess volume can be written in the form,

$$V^E(\text{MX}) = m(V_\phi - \overline{V}^\circ) = m(A_v m^{1/2} + B_v m + C_v m^2 + \cdots) \qquad (6)$$

where $\overline{V}^\circ$ is the standard partial molar volume of MX, and $A_v$ is the Debye-Hückel limiting slope and; $B_v$, $C_v$,.. are empirical parameters. Combining Eq. 6 with Eq. 5, we obtain the relation,

$$v^* = B_v(\text{BX}) - B_v(\text{AX}) + I[C_v(\text{BX}) - C_v(\text{AX})]\cdots \qquad (7)$$

In Fig. 2, the volume changes of mixing per kg of solvent water are plotted against the mole ratio of the phosphonium salt, $y$, at three ionic strengths and 25 °C. The height of a curve at $y$=0.5 gives $v_o$ and the skewness is governed by $v_1$ (Eq. 1). As the ionic strength decreases, the skewness becomes less, and almost disappears at the lowest ionic strength, 0.25 mol kg$^{-1}$, for all systems examined. The values for the volume-interaction parameter $v_o$ (Eq. 1) were determined from $\Delta_m V^E$ by a least-squares method based on Eq. 1 and are tabulated in Table 1, along with the $B_v$'s.[6,7] Figure 3 is a plot of the $v_o$ against the ionic strength, where the systems $Me_4NBr$/KBr and $Bu_4NCl$/KCl[2] are also shown, for comparison.

In general, two effects may be accompanied by the mixing process. One is the dilution effect for ions, which will result in a decrease in cosphere overlapping between the phosphonium cations as well as other ions. This effect for the salt AX at low concentrations is approximately expressed by the volume $B$-coefficient with a negative sign, $-B_v$(AX). Another is the effect due to the occurrence of a new type of cationic interaction pair, that is, the phosphonium cation and the K$^+$ ion, which is expressed by $v^*_{\text{AB}}$ (Eq. 4).

As seen from Eqs. 3 and 4, the $v_o$ value at $I$=0 reflects cationic pairwise interactions only. However, to experimentally determine $v_o(I=0)$ is very difficult because

Table 1. Volume interaction parameter $v_o$(Eq. 3) and $v^*$(Eq. 5)[a)]

| | $Bu_4PCl$ | | $Bu_3PhPCl$ | | $Bu_2Ph_2PCl$ | | $BuPh_3PCl$ | | $Ph_4PCl$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| $I$ | $v_o$ | $v^*$ | $v_o$ | $v^*$ | $v_o$ | $v^*$ | $v_o$ | $v^*$ | $v_o$ | $v^*$ |
| 0.25 | 6.7 | 13.3 | 4.4 | 8.5 | 3.4 | 6.6 | 3.1 | 5.3 | 2.8 | 5.3 |
| 0.5 | 5.0 | 10.7 | 2.7 | 7.0 | 2.1 | 5.6 | 2.0 | 4.8 | 1.8 | 4.8 |
| 1.0 | 2.3 | 7.2 | 1.2 | 4.9 | 1.1 | 4.2 | 1.0 | 3.9 | 1.0 | 4.0 |
| $B_v$[b)] | −16.71 | | −10.52 | | −7.87 | | −5.81 | | −5.77 | |

a) Units; $v_o$ and $v^*$/cm$^3$ kg mol$^{-2}$, $B_v$/cm$^3$ dm$^3$ mol$^{-2}$. b) Ref. 6 and 7.

$\Delta_m V^E$ is proportional to the square of the ionic strength (Eq. 1). The curves in Fig. 3 suggest large positive values for $v_0(I=0)$, showing that the pairwise interactions are large for all the systems ($n$=0—4). If the assumption is made that the activity coefficients of the ions are constant independent of ionic strength, then we can expect a linear relation between $v_0$ and $I$, as discussed by Wen[11] (*cf.* Eq. 3). Since the dependence of the activity coefficient of ions on ionic strength decreases with increasing $I$, we can conclude that the successive substitution of phenyl groups of the $Ph_4P^+$

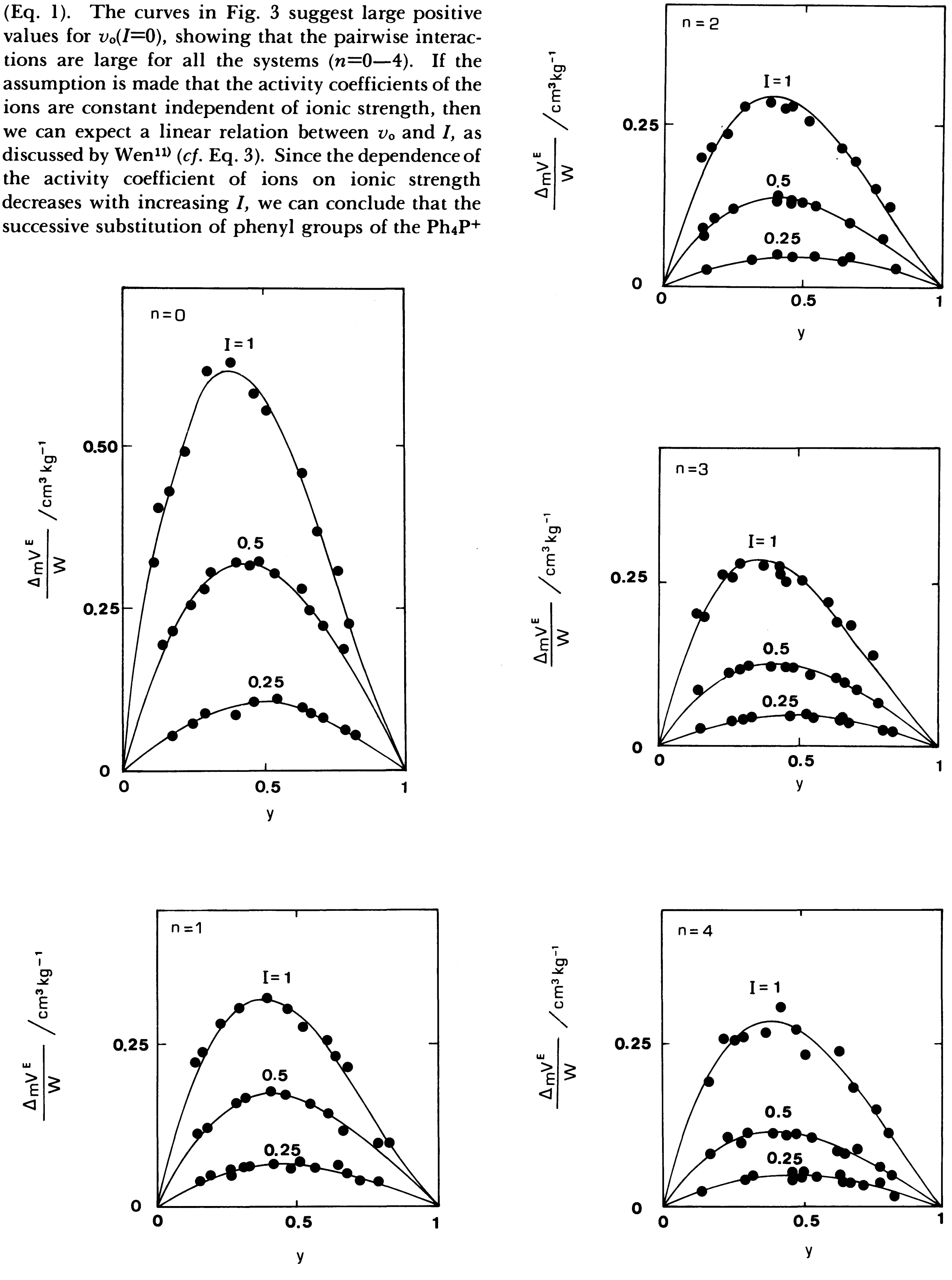

Fig. 2. The volume changes on mixing per kg of solvent water as functions of the mole ratio ($y$) of phosphonium chloride in the system, $n$-$Bu_{4-n}Ph_nPCl/KCl$ ($n$=0—4), at 25 °C.

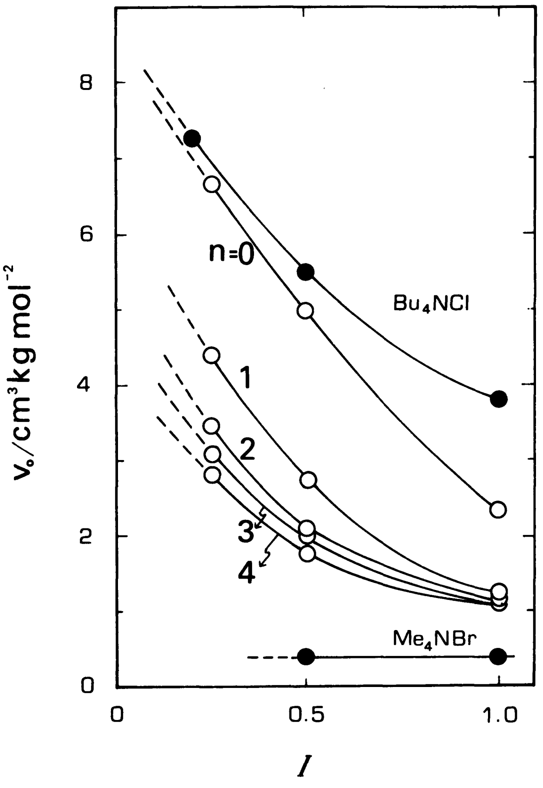

Fig. 3. The volume interaction paramenters $v_o$(-○-) in the systems, $\mathrm{Bu}_{4-n}\mathrm{Ph}_n\mathrm{PCl/KCl}$ ($n$=0—4), as functions of ionic strength $I$, at 25 °C. The data for the systems $\mathrm{Bu_4NCl/KCl}$ and $\mathrm{Me_4NBr/KBr}$, (-●-), were taken from Ref.2.

ion by butyl groups results in elevating the triplet and higher order interactions. This is illustrated in Fig. 3 and seems to be consistent with the clathrate-like hydration model for a butyl group assumed in previous studies.[6,7] The remarkable decrease in $V_o(\mathrm{Bu_4PX})$ with concentration was attributed to pairwise interaction between the cations in low concentrations and higher order interactions including the anions at high concentrations in which water-separated pairing of the cations was regarded as essential to reduce the solution volume.

It was shown in previous papers that the $B_v$'s are negative for all the phosphonium halides ($n$=0—4) and mainly reflect contributions from the cation-cation interactions, that is, $v_{\mathrm{AX}}^*$ in Eq. 5 would be relatively much smaller in magnitude than $v_{\mathrm{AA}}^*$. The small $B_v$ value for KCl, 0.08 $\mathrm{cm^3\,mol^{-2}\,dm^3}$[12], suggests that $v_{\mathrm{BB}}^*+2v_{\mathrm{BX}}^*$ (Eq. 5) would be negligible in comparison with the large magnitudes of $v_{\mathrm{AA}}^*$ for the phosphonium cations. A comparison of $v_o$'s with $v^*$'s (Table 1) reveals that all the $v_o$ values are considerably smaller than the $v^*$ values, about halves of $v^*$'s, even at the ionic strength of 0.25 where the $v^*$ values for all the systems are close to the magnitudes of $B_v(\mathrm{AX})$'s (*cf.* Eq. 7). Thus, it follows that the interactions between unlike cations ($v_{\mathrm{AB}}^*$) are mostly responsible for the differences between the magnitudes of $v_{\mathrm{pairs}}$ and $v^*$. This difference is largest for a system with $n$=0 and decreases with $n$, indicating that the butyl cosphere-$\mathrm{K^+}$ interaction results in decrease in solution volume.

This conclusion is contradictory to a suggestion made by Wen,[11] who attributed the difference found for the $n$-$\mathrm{Bu_4NCl}$-KCl system to the $\mathrm{Bu_4N^+}$-$\mathrm{Cl^-}$ interaction.

The second hydration layer, the B-zone in the Frank and Wen's hydration model, of the $\mathrm{Bu_4P^+}$ ion would be more structured and, hence, more bulky than bulk water, as illustrated by a Monte Carlo simulation for a methane molecule in water.[13] Thus, the negative change in volume accompanied by the butyl-$\mathrm{K^+}$ interaction is explicable if the assumption is made that the $\mathrm{K^+}$ ion breaks the second layer structure of the butyl cosphere but not the first layer; if the $\mathrm{K^+}$ ion breaks also the first layer a volume increase should be accompanied owing to disappearence of the caging effect,[11] which is assumed for clathrate-like hydration.

It is of interest to note that the interaction between the $\mathrm{Ph_4P^+}$ and $\mathrm{K^+}$ ions also contributes negatively to the solution volume, *i.e.*, $v_{\mathrm{AB}}^*<0$, even though the $\mathrm{Ph_4P^+}$ ion behaves not always as a structure maker for solvent water[10] and its hydration dissimilar to clathrate-like one is assigned. In this regard, the Geiger's hydration model is of interest. Geiger[14] has simulated the effect of charges on the hydration of a nonpolar spherical solute with the size of a Xenon atom by the molecular dynamic technique. He obtained the result that the originally rigid hydrophobic hydration shell (zero charge) is "softened" from its inner sphere and its outer sphere remains more or less unchanged when electric charges below unit are given. If the delocalized charges on the phenyl groups[15,16] play a role in a way similar to this model, the water molecules in the B-zone of the groups would be more structured than bulk water and, hence, the interaction between the B-zone and the $\mathrm{K^+}$ ion could result in a negative contribution to the solution volume due to a relaxing of the structured water in the B-zone to the bulk water.

For intermediate systems with $n$=1—3, the behavior found in $v_{\mathrm{AB}}^*$ can be understood qualitatively as the sum of the effects found in the systems with $n$=0 and 4.

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