The Apparent Molar Volumes of Tetraalkylammonium Halides in Liquid Sulfur Dioxide

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The apparent molar volumes, Φv, of tetraalkylammonium halides, R_4NX (R=Me, Et, *n*-Pr, and *n*-Bu; X=Br^- and I^-), have been determined in liquid sulfur dioxide at several concentrations, and from these values the apparent molar volumes at an infinite dilution, Φv°, have been obtained for these salts at 25°C. The results indicate that, for all the salts, the Φv *vs.* $\sqrt{c}$ curves are almost straight over the concentration ranges studied. The slopes of the plots have large positive values for all the salts in this solvent. In order to study the ion-solvent interaction, the apparent molar volumes of the individual ions at an infinite dilution have been determined from those values by Conway's method. While the Φv° values of tetraalkylammonium ions are similar to those in other solvents, the Φv° values of bromide and of iodide ions in this solvent are quite small compared with those in other solvents. The results can be explained in terms of a strong anion-solvent interaction in liquid sulfur dioxide resulting from the formation of a charge-transfer complex of the halide ion with sulfur dioxide.

The study of the ion-solvent interaction is not only very interesting in itself, but also very instructive in making clear the role of a solvent in the process of Finkelstein, **Sn Ar**, and other ionic reactions in solution.[1]

On the other hand, liquid sulfur dioxide has been well known to be a peculiar solvent, for in spite of its low dielectric constant, it dissolves inorganic salts well and has a high ionizing power, and a reaction containing carbonium ion as an intermediate can proceed at an extraordinary fast rate in this solvent.[2] These facts have been explained as being due to a strong anion-solvent interaction in liquid sulfur dioxide,[2] but on the nature of the ion-solvent interaction in the solvent only a few, widely varying studies have been reported, including the studies of electrolytic conductance by Lichtin[3] and a short article on electrostriction volume measurements.[4] Therefore it is very important to investigate the ion-solvent interaction in liquid sulfur dioxide.

Though there are many ways to study ion-solvent interactions, in the present article the authors will discuss it from the view point of the apparent molar volumes of tetraalkylammonium halides, R_4NX (R=Me, Et, *n*-Pr, and *n*-Bu; X=Br^- and I^-) at an infinite dilution, $\Phi°_V$.

The measurements were also performed in acetonitrile and in methanol, and the values obtained were compared with those in the references.

Experimental

Materials. The liquid sulfur dioxide was dried over phosphorus pentoxide for at least one day, distilled twice, and degassed before use. The acetonitrile was refluxed over calcium hydride, distilled, and then repeatedly distilled from phosphorus pentoxide and from calcium hydride.[5] The methanol was treated with magnesium ribbon and distilled.[6] The tetramethylammonium bromide and iodide were obtained from Wako Pure Chemicals and were recrystallized three times each from an ethanol-water mixture and water. The other tetraalkylammonium halides were synthesized from the corresponding trialkylamine and alkyl halide in various solvents at the reflux temperature, and were recrystallized from various solvents. These solvents are summarized in Table 1.

All the salts were dried *in vacuo* at 65°C for one day before use.

Procedure. The densities of an electrolyte solution of liquid sulfur dioxide were measured in a sealed pressure vessel by means of glass float, which was calibrated to a standard state of pure water using mixed solutions of sulfuric acid and water. The values of the density of pure liquid sulfur dioxide (d_0=1.3719 at 25°C) obtained by the present study argeed well with the value (d_0=1.3718) which was obtained by the extrapolation to 25°C of the value quoted

Table 1. Solvents for the synthesis and recrystallization of tetraalkylammonium halides, R_4NX.

R_4NX	R_3N	RX	Solvent for Preparation	Recrystallization
Et_4NBr	Et_3N	EtBr	Acetone	Methanol - acetone mixture
Et_4NI	Et_3N	EtI	Acetone	Methanol - acetone mixture
n-Pr_4NBr	*n*-Pr_3N	*n*-PrBr	Acetone	Methanol - acetone mixture
n-Pr_4NI	*n*-Pr_3N	*n*-PrI	Acetone	Methanol - acetone mixture
n-Bu_4NBr	*n*-Bu_3N	*n*-BuBr	Methyl ethyl ketone	Acetone - ether mixture
n-Bu_4NI	*n*-Bu_3N	*n*-BuI	Methyl ethyl ketone	Acetone - ether mixture

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1) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

2) N. Tokura, *Bull. Chem. Res. Inst. Non-Aqueous Soln. Tohoku Univ.*, **19**, 47 (1969).

3) N. N. Lichtin, "Progr. Phys. Org. Chem," Vol. 1, S. G. Cohen *et al.*, eds., Interscience Publishers, New York (1963).

4) Y. Kondo, T. Goto, I. Suo, and N. Tokura, This Bulletin, **39**, 1230 (1966).

5) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

6) A. A. Mayrott, *J. Amer. Chem. Soc.*, **63**, 3079 (1941).

from the International Critical Tables,[7] within the limits of experimental error.

The densities of solutions of acetonitrile and methanol were determined by using a pycnometer with a 50-m*l* capacity. All the solutions were prepared by weight.

Results and Discussion

The experimental values of the densities of these salt solutions of liquid sulfur dioxide are given in Fig. 1.

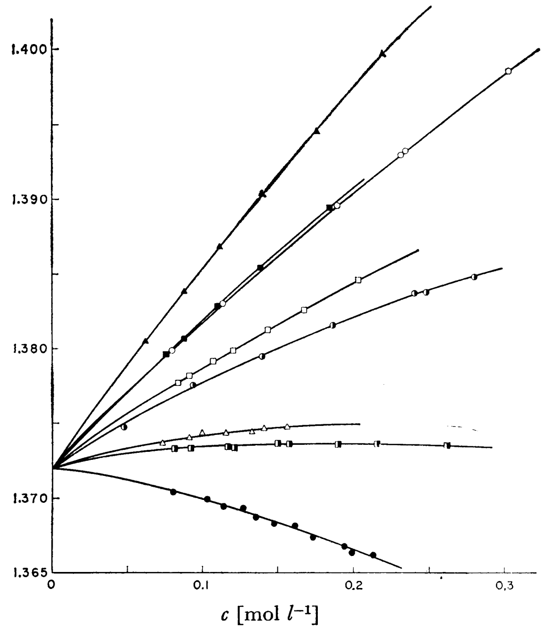

Fig. 1. Densities of liq. SO_2 solutions of tetraalkylammonium halides at 25°C.
○; Me_4NBr, ▲; Me_4NI, □; Et_4NBr, ■; Et_4NI, △; *n*-Pr_4NBr, ◐; *n*-Pr_4NI, ●; *n*-Bu_4NBr, ◨; *n*-Bu_4NI

The apparent molar volumes, Φv, were calculated from the density data by the equation:[8]

$$\Phi v = (M/d_0) - 1000(d-d_0)/cd_0 \qquad (1)$$

where d_0, M, d, and c are the density of the pure solvent, the molecular weight of the salt, the density of the solution, and the concentration of the solutes respectively.

In Figs. 2, 3, and 4, the apparent molar volumes, Φv, are plotted against the square root of the concentration of the salt, $\sqrt{c}$. In all cases, the plots of Φv *vs.* $\sqrt{c}$ gave nearly straight lines. Then, the apparent molar volumes of the salts at an infinite dilution, Φv°, and the slope, *S*v, were obtained on the basis of Eq. (2)[8] by a least-squares method:

$$\Phi v = \Phi v° + Svc^{1/2} \qquad (2)$$

These values are summarized in Tables 2 and 3.

By the Debye-Hückel limitting law, the values of *S*v can be calculated from the expression:[10]

$$Sv = Kw^{3/2} \qquad (3)$$

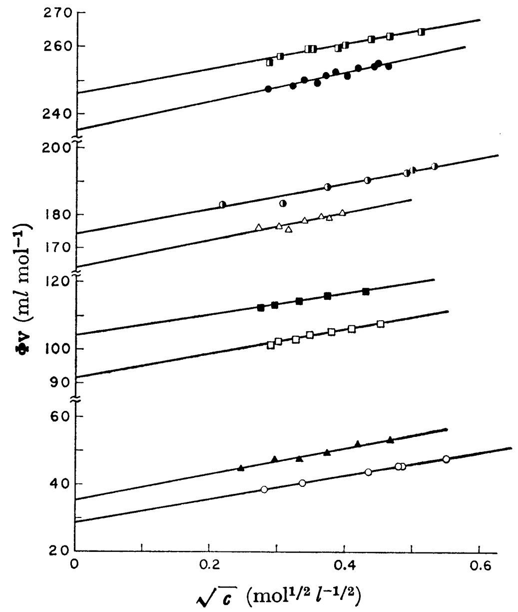

Fig. 2. Plots of Φv *vs.* $\sqrt{c}$ in liq. SO_2 at 25°C.
○; Mr_4NBr, ▲; Me_4NI, □; Et_4NBr, ■; Et_4NI, △; *n*-Pr_4NBr, ◐; *n*-Pr_4NI, ●; *n*-Bu_4NBr, ◨; *n*-Bu_4NI

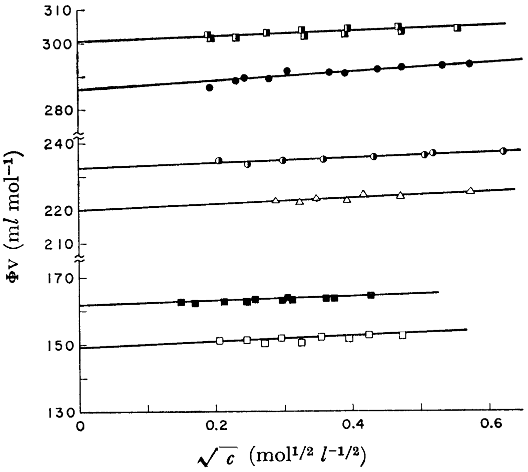

Fig. 3. Plots of Φv *vs.* $\sqrt{c}$ in methanol at 25°C.
□; Et_4NBr, ■; Et_4NI, △; *n*-Pr_4NBr, ◐; *n*-Pr_4NI, ●; *n*-Bu_4NBr, ◨; *n*-Bu_4NI

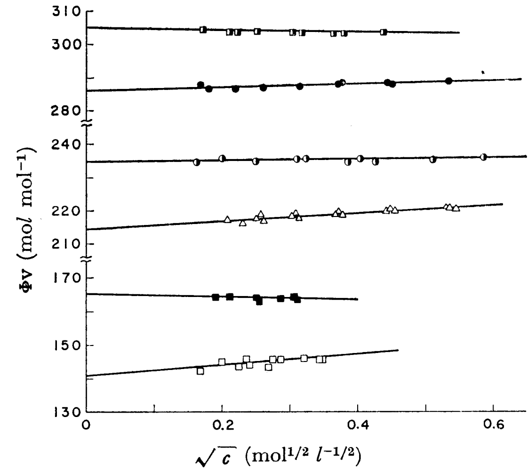

Fig. 4. Plots of Φv *vs.* $\sqrt{c}$ in acetonitrile at 25°C.
□; Et_4NBr, ■; Et_4NI, △; *n*-Pr_4NBr, ◐; *n*-Pr_4NI, ●; *n*-Bu_4NBr, ◨; *n*-Bu_4NI

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[7] N. R. C. of U. S. A., "The International Critical Tables," McGrow-Hill, New York (1933), Vol. III, p. 22.

[8] O. Redlich and D. M. Meyer, *Chem. Rev.*, **64**, 221 (1964).

[9] J. Padova and I. Abrahamer, *J. Phys. Chem.*, **71**, 2112 (1967).

[10] O. Redlich, *ibid.*, **67**, 496 (1963).

Table 2. APPARENT MOLAR VOLUMES OF TETRAALKYLAMMONIUM HALIDES AT INFINITE DILUTION IN VARIOUS SOLVENTS AT 25°C

Salt	Liq. SO_2	Acetonitrile	Methanol
Me_4NBr	28.7	—	—
Et_4NBr	91.5	140.8	149.3 149.6[9]
n-Pr_4NBr	164.0	214.7	220.0 222.1[9]
n-Bu_4NBr	235.3	286.1	286.2 285.9[9]
Me_4NI	35.5	—	—
Et_4NI	104.2	165.1	161.9
n-Pr_4NI	173.4	234.9	232.6
n-Bu_4NI	246.3	305.0	300.5

unit: $ml\ mol^{-1}$

Table 3. THE VALUES OF Sv IN VARIOUS SOLVENTS

Salt	Liq. SO_2	Acetonitrile	Methanol
Me_4NBr	34.9	—	—
Et_4NBr	36.0	15.1	6.7 7.7[9]
n-Pr_4NBr	41.6	11.4	8.5 6.1[9]
n-Bu_4NBr	43.0	4.6	12.5 11.2[9]
Me_4NI	38.6	—	—
Et_4NI	31.2	−4.3	5.5
n-Pr_4NI	39.4	0.9	6.8
n-Bu_4NI	36.3	−4.8	6.9

unit: $ml\ mol^{-3/2}\ l^{1/2}$

where:

$$w = (1/2)\sum_i \nu_i Z_i^2$$

$$K = 2N^2e^3(2\pi/1000RT)^{1/2}D^{-3/2}\ (\mathrm{d}\ln D/\mathrm{d}p-\beta/3)$$

where N, D, β are Avogadro's number, the dielectric constant, and the compressibility of the solvent respectively, and where the other terms have their usual meanings.

Since the concentration ranges used in this investigation are comparatively high, the values of Sv in Table 3 can not reasonably be expected to provide a basis for testing the applicability of the Debye-Hückel limitting law to the solvent system. Also, it is not possible to calculate the theoretical values of Sv from Eq. (3), since the required values of the pressure dependence of the dielectric constant and of the compressibility of the solvent are not available for liquid sulfur dioxide. Though it may be seen that, for all salts studied, the Sv values in this solvent are positive and are quite large compared with those in other solvents, the theoretical implication of the observed difference could not be explored, partly for the reason mentioned above.

In order to make clear the nature of the ion-solvent interaction, it is necessary to assign the absolute ionic partial molal volumes. Conway and his collaborators developed a method by which the Φv values of tetraalkylammonium halides can be divided into the Φv° values of the cation and of the anion in water.[11,12]

Among several methods developed for assigning the absolute ionic partial molar volumes,[13] the most convenient way for the present study seemed to be to follow the one developed by Conway and his collaborators,[11,12] since only a limitted number of the

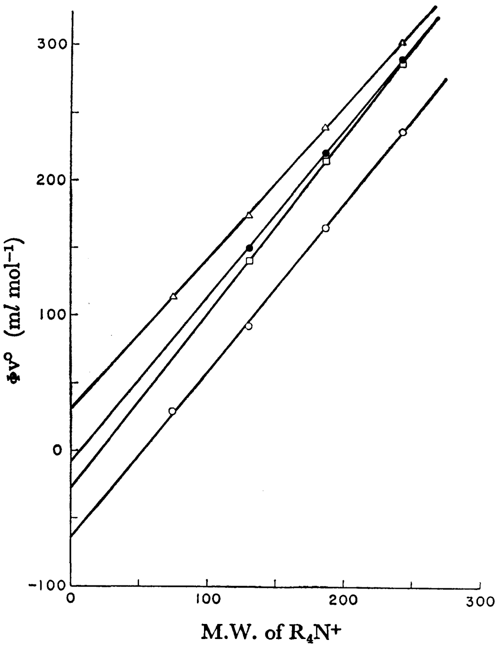

Fig. 5. Plots of Φv° of tetraalkylammonium bromides *vs.* molecular weights of cations.
△; H_2O, ●; MeOH, □; Acetonitrile, ○; liq. SO_2

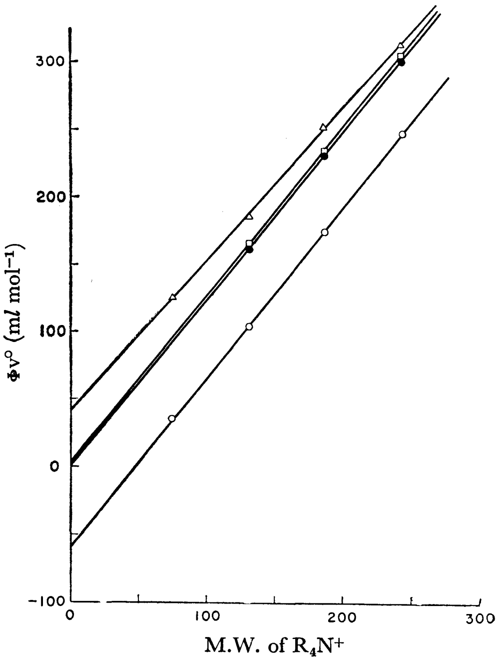

Fig. 6. Plots of Φv° of tetraalkylammonium iodides *vs.* molecular weights of cations.
△; H_2O, ●; MeOH, □; Acetonitrile, ○; liq. SO_2

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11) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Z. Phy. Chem.*, **230**, 157 (1965).

12) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, **62**, 2738 (1966).

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Table 4. Apparent molar volumes of ions at infinite dilution in various solvents at 25°C (m*l* mol^{-1})

Ions	Liq. SO_2	CH_3CN	MeOH	DMF[a,b] 13)	NMA[a,b] 14)	FA[a] 15)	H_2O 12)
Br^-	−65.5	−27.4	−8.7	—	—	—	30.8
I^-	−58.2	2.8	1.5	5.5	14.2	24.8	42.3
Me_4N^+	93.9	—	—	—	—	—	83.5
Et_4N^+	159.7	165.3	159.2	160.6	161.2	160.7	143.4
n-Pr_4N^+	230.6	237.1	229.9	233.3	233.3	230.7	208.7
n-Bu_4N^+	302.6	307.8	296.9	302.1	308.7	297.6	270.2
b(slope) (m*l* g^{-1})	1.24	1.27	1.23	1.25	1.26	1.23	1.11

a) $\Phi v^\circ_{R_4N^+}$ have been calculated by $\Phi v^\circ_{R_4N^+} = \Phi v^\circ_{R_4NI} - \Phi v^\circ_{I^-}$.
b) The values at 35°C.

required data are available for the present solvent system.

In the present experiment, the apparent molar volumes of ions in liquid sulfur dioxide, acetonitrile, and methanol were determined on the basis of their method.

According to his procedure, the Φv° values of tetraalkylammonium halides were plotted against the molecular weight of the cation: these plots are shown in Figs. 5 and 6. For the series of tetraalkylammonium bromides and of iodides, straight lines were obtained, as is shown in part in Figs. 5 and 6 for all the solvent systems.

In Fig. 5, the extrapolation of the straight line to a zero-cation molecular weight should directly lead to the apparent molar volumes of the bromide ion at an infinite dilution in the respective solvent,12) while in Fig. 6, such an extrapolation should correspondingly lead to the Φv° of the iodide ion.12) Averaging the two series of measurements, the Φv° values of tetraalkylammonium ions, $\Phi v^\circ_{R_4N^+}$, can be calculated by means of Eq. (4):

$$\Phi v^\circ_{R_4N^+} = (1/2)\{(\Phi v^\circ_{R_4NBr} - \Phi v^\circ_{Br^-}) + (\Phi v^\circ_{R_4NI} - \Phi v^\circ_{I^-})\} \quad (4)$$

where $\Phi v^\circ_{R_4NX}$ and $\Phi v^\circ_{X^-}$ are the apparent molar volumes of tetraalkylammonium halide and of halide anion at an infinite dilution.

These apparent molal volumes of ions at an infinite dilution, Φv°_i, and the slopes of the plots of Figs. 5 and 6, b, which were obtained by the least-squares methods on the basis of the equation, are shown in Table 4:

$$\Phi v^\circ_{R_4NX} = \Phi v^\circ_{X^-} + b \text{ (M. W. of cation)} \quad (5)$$

Two or three interesting feature are to be seen in Table 4.

One of these is that the slope of the plot, b, takes a nearly constant value throughout the various solvents with the exception of water. This leads to an insensitive change in the ionic molal volume of the cation, $\Phi v^\circ_{R_4N^+}$, over these solvents. This result is not unexpected provided that the cation-solvent interaction is of an uniform nature throughout these solvents. The smaller values of the slope, b, and of the ionic molal volumes of cations in water may be ascribed to the hydrophobic interaction between the tetraalkylammonium ion and water molecules.

In contrast to the constancy of these slopes, the values of the intercept, which according to Conway's proposal, correspond to the inonic molar volumes of the anions, scatter with a change in the solvent over much wider ranges than would be expected from the experimental uncertainties.

On the basis of the characteristic values of the intercept, the solvents or the nature of the solvent-anion interaction are likely to be classifiable into three or four groups, *i.e.*, large negative (liq. SO_2), small positive (acetonitrile, methanol, *N,N*-dimethyl formamide), moderate positive (*N*-methyl acetoamide, formamide), and large positive (water).

For the case of amides, the observed transition of the $\Phi v^\circ_{I^-}$ from *N,N*-dimethyl formamide to formamide, that is to say, the tendency of the $\Phi v^\circ_{I^-}$ values to approach that of water, with an increase in the number of amino hydrogens, is consistent with the variation in the absolute ionic entropies accompanying the same solvent change.16) Therefore, some of the solvent characteristics would seem to be specifically reflected in both thermodynamic variables. This might be the "structuredness" of the solvents.16)

At any rate, water and liquid sulfur dioxide constitute two extreme causes. These results suggest that anion-solvent interaction is markedly strong in this solvent in comparison with that in other solvents. It is well known that sulfur dioxide forms charge-transfer complexes with halide anions in water,17) methanol,17) and acetonitrile.18)

As a result of the formation of a charge-transfer complex of halide anions with sulfur dioxide, the absorption maxima were observed at 341 nm in water at 20°C17) and at 355 nm in methanol at 22.6°C.17) The absorption maximum was also observed at 383 nm in liquid sulfur dioxide at 20°C.19)

Considering these facts, the strong anion-solvent interaction in liquid sulfur dioxide can be explained by the formation of a charge-transfer complex of halide anions with sulfur dioxide.

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15) R. Gopal and M. A. Siddigni, *Z. Physik. Chem.* (Frankfurt), **67**, 122 (1969).

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17) J. Jander and G. Turk, *Angew. Chem.*, **75**, 792 (1963).

18) E. R. Lippincott and F. W. Welch, *Spectrochim. Acta*, **17**, 123 (1961).

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