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The Solvation of Ions in Liquid Sulfur Dioxide

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The variation in the density and in the sound velocity with the concentration was measured in a liquid sulfur dioxide solution of electrolytes. The amounts of solvations and the volume changes which accompany the dissolving of the electrolytes were estimated. In liquid sulfur dioxide they were found to be considerably greater than those in water. The relations between the volume changes and the solvations were also discussed.

It has been generally accepted that solvents play an important role in synthetic organic chemistry; in this connection, various attempts have been made to specify the type of effects exerted by solvents on the reaction rates. Liquid sulfur dioxide is a good ionizing aprotic solvent, and various specific phenomena have been found in this solvent.[1-4]

In order to elucidate the effect of this solvent on a chemical reaction and the relation between a chemical reaction and a solvation phenomenon, an attempt has now been made to measure the solvations of ions in liquid sulfur dioxide. In this report, the volume changes and the amounts of solvation will be measured by means of density[5] and compressibility[6] measurements in liquid sulfur dioxide, and the data for various solutes will be compared.

Experimental

Materials.—Liquid sulfur dioxide was dried with phosphorus pentoxide and distilled twice. The electrolytes used were synthesized and dried in vacuo at 60°C and recrystallized three times from solvents indicated by known methods.[7-9]

The Method of Density Measurement.[5]—The volume change, ΔV, which accompanies the dissolving of one mole of a substance may be shown as follows:

$$\begin{aligned}\Delta V &= (\text{Volume of the solution})\\ &\quad - \{(\text{Volume of the solute})\\ &\quad + (\text{Volume of the solvent})\}\\ &= \frac{1}{n}\left[\frac{W+w}{D} - \left\{\frac{w}{d_0} + \frac{W}{D_0}\right\}\right] \qquad (1)\end{aligned}$$

where W, w, D_0, d_0, D, n are the weights of a pure solvent and of a solute, the densities of a pure solvent, of a solute and of a solution, and moles of the substance respectively. In the case of solid substances, from the view point of thermodynamics, the volume of a fused substance which is supercooled must be used as the volume of the solute. As for the salt used in this experiment, since it was impossible to measure these densities in a fused state, the densities of the solid states were used in the following calculations. For those which could not be compared with previous results in the literature, the densities were measured by using a pycnometer.

The densities of the solids used in the calculation are: KI: 3.121, $(CH_3)_4NI$: 1.819, $(C_2H_5)_4NI$: 1.552, MePyrI: 1.827, $(C_2H_5)_4NBr$: 1.388, $(C_2H_5)_4NClO_4$: 1.259, $(C_2H_5)_4NCl$: 1.112, $(C_2H_5)_4NPic.$: 1.356, $(CH_3)_4NClO_4$: 1.346, MePyr ClO_4: 1.423.

MePyr=Methylpyridinium Pic.=Picrate

The Measurement of the Densities of Liquid Sulfur Dioxide Solutions of Electrolytes.—A glass float was calibrated to a standard state of pure water using a mixed solution of sulfuric acid and water. The densities of solutions of electrolytes in liquid sulfur dioxide were measured by means of the glass float in a sealed pressure vessel.

The value of the density of liquid sulfur dioxide (d=1.3700 at 25°C) obtained by the present authors differs by 0.1 percent from the value (1.3718) which was obtained by the extrapolation to 25°C of the values quoted from the International Critical Tables.[11a]

Since, however, only a correlation between the densities of solutions and the concentrations of the solutes is needed in this experiment, the values obtained by the present authors were used throughout the calculations in spite of the slight discrepancy mentioned above. The values for densities in aqueous salt solutions used

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Table I. Typical run for the calculation of the ΔV value and the v value

Sample : Pyridinium methyl perchlorate

$D_0 = 1.3700$ $\lambda_0 = 2\times 4.4808\times 10^{-1}$ mm., $M = 197.627$ (25°C)

W	w	n	D	ΔV	C	$C^{1/2}$	$(\lambda/2)\times 10$	v
258.435	3.7150	0.018798	1.3792	62.54	0.09890	0.3145	—	—
281.025	7.4243	0.037567	1.3848	54.53	0.1803	0.4247	4.6038	263.8
267.570	13.0954	0.066263	1.3948	49.61	0.3293	0.5738	4.7060	243.2
257.935	16.3023	0.082490	1.4000	46.63	0.4211	0.6489	4.7775	238.3
198.596	19.7794	0.100085	1.4127	42.34	0.6475	0.8046	4.9238	208.0
242.937	41.9086	0.212059	1.4314	36.68	1.0656	1.032	5.2290	186.6
283.685	2.7797	0.014065	1.3763	62.7	0.06757	0.2599	—	—

unit. W: gram, V: ml. mol^{-1} C: mol. l^{-1}, λ: mm.

in the calculations are quoted from the International Critical Tables.[11b,c]

The Method of Compressibility Measurement.[6] —The following equation was used to calculate the amount of solvation from compressibility measurements. If a part of the solvent, v, changes to v' as a result of solvation, the volume of the solution, V, may be expressed as follows,[6] where V_0, V_1, v are the volumes of the solvent before mixing, the solute and the solvent molecules which solvate on the solute respectively:

$$V = V_0 + V_1 - v + v' \qquad (2)$$

By using β, an adiabatic compressibility which is determined experimentally by measuring the sound velocity, u, and the density, d, Eq. 4 is obtained from the relation:[6]

$$\beta = \frac{1}{u^2 d} \qquad (3)$$

$$V\beta = V_0\beta_0 + V_1\beta_1 - v\beta_0 + v'\beta_0' \qquad (4)$$

If it can be assumed that $\beta_1 = \beta_0' = 0$, Eq. 5 is obtained from Eq. 4.[6] Also, v, the amount of solvation per mole of solute, can be calculated from Eq. 6, where D_0, D, λ_0, λ, C, M, are the densities of pure solvent and of solution, the wavelengths in a pure solvent and in a solution, the concentration of the solute [mol.l^{-1}] and the molecular weight of the solute respectively.[6]

$$V\beta = V_0\beta_0 - v\beta_0 \qquad (5)$$

The number of solvation, n, was calculated from Eq. 7,[6] where v_0 is the molar volume of liquid sulfur dioxide at 25°C.

$$v = \frac{1000}{C}\left(\frac{D}{D_0} - \frac{D_0\lambda_0^2}{D\lambda^2}\right) - \frac{M}{D_0} \quad [\text{ml. mol}^{-1}] \qquad (6)$$

$$v = nv_0 \ (v_0 = 46.7 \text{ ml.mol}^{-1} \text{ at } 25°\text{C}) \qquad (7)$$

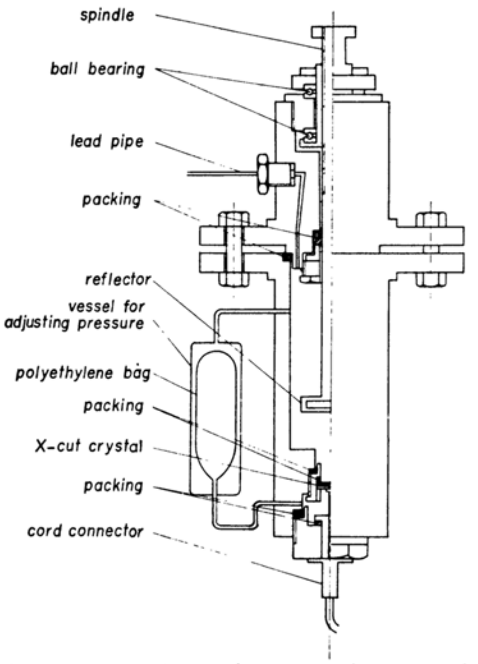

Fig. 1. Ultrasonic interferrometer for use under pressure.

The sound velocities in liquid sulfur dioxide and in an electrolyte solution were measured with an ultrasonic interferrometer at a frequency of 1 Mc./sec.

Apparatus.—The interferrometer cell shown in Fig. 1 was made of stainless steel and made it possible to measure the velocity under an equilibrium vapor pressure of liquid sulfur dioxide [ca. 3.5 atom at 25°C].

The reflector was also made of stainless steel; it moves vertically without rotation, and its position was determined by a micrometer with a traveling range of 25 mm. The pressure bottle was attached to the cell in order to keep the pressure equal on both sides of the crystal during the measurement. The sample solution was introduced through the lead pipe after the cell had been evacuated, and the measurements were conducted in a thermostat bath held at 25°C. A typical run is presented in Table I.

Results and Discussion

Figures 2 and 3 give the results of the measurements of the densities and sound velocities (wavelengths) in liquid sulfur dioxide solutions of electrolytes.

The volume change, ΔV, and the amount of solvation, calculated from Eq. 1 and Eq. 6 respectively, are plotted against the square root of the concentration of the solute in Figs. 4, 5 and 6. It has been said that ΔV and v are linear functions of $C^{1/2}$ in water;[5b,6b,7] it is apparent from Figs. 4, 5 and 6 that a similar relation holds for the results in liquid sulfur dioxide.[4]

Generally, the behavior of an electrolyte in a

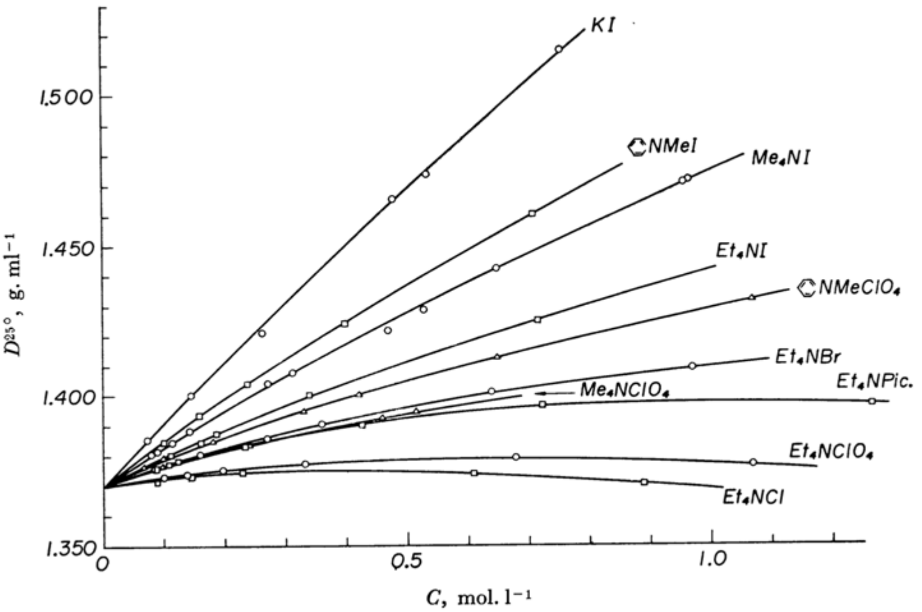

Fig. 2. Variation of the density of electrolyte solution in liq·SO_2 with the concentration of the solute.

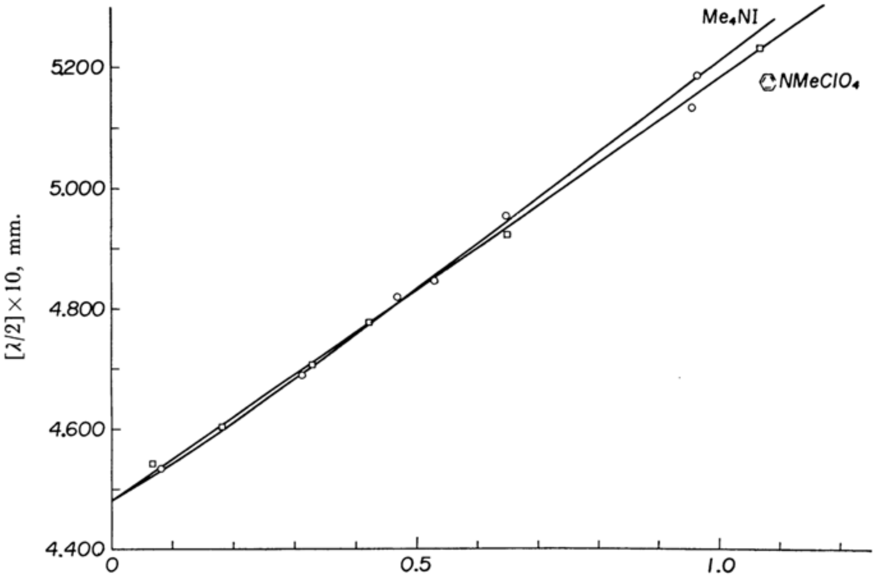

Fig. 3. Variation of wavelength with the concentration of the solute.

non-aqueous solvent is quite different from that in water. It has often been discussed also on the behavior in liquid sulfur dioxide. It was impossible to conduct measurements over the entire range where data are required for a detailed discussion and formulation of an electrolyte, since in this experiment the measurements were limited to the region where ΔV is a linear function of $C^{1/2}$, we did not consider the detailed nature of the electrolyte. The results obtained by extrapolating to a zero concentration of the solute are summarized in Table II.

From the view point of thermodynamics, the standard state of the electrolyte must be a state of fused salt in a supercooled state, and the volume changes which were calculated using the data for the solid state must include those which accompany the fusion of the solid substance.

The differences in the $[-\Delta Ve]$ value between iodides and perchlorates are presented in Table

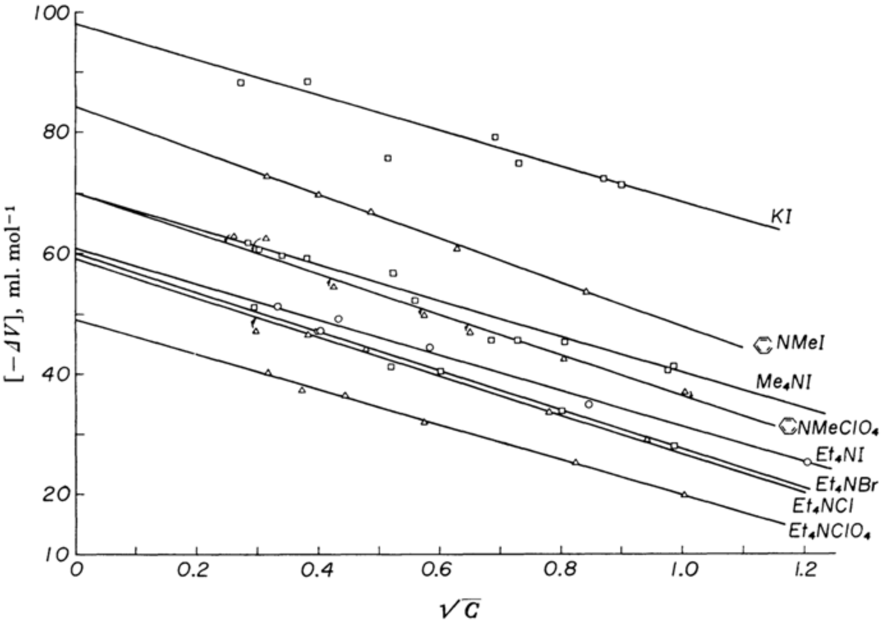

Fig. 4. Plots of the $[-\Delta V]$ value vs. $C^{1/2}$ of the solute.

Table II. Data obtained in this experiment (25°C)

Electrolyte	$[-\Delta Ve]$ ml. mol^{-1}	v ml. mol^{-1}	Number of solvation
KI	98		
MePyrI	84		
Me_4NI	70	375	8
Et_4NI	61		
Et_4NBr	60		
Et_4NCl	59		
$Et_4NPic.$	65		
Et_4NClO_4	49		
$MePyrClO_4$	70	320	6.8
Me_4NClO_4	60		
KI in H_2O	8		
Et_4NCl in H_2O	−13		

Table III. The stoichiometric additivity of the $[-\Delta Ve]$ values

Counter cation	$[-\Delta Ve]_{\mathrm{Iodide}}-[-\Delta Ve]_{\mathrm{Perchlorate}}$
$MePyr^+$	14 ml. mol^{-1}
Me_4N^+	10 ml. mol^{-1}
Et_4N^+	12 ml. mol^{-1}
Av.	12 ml. mol^{-1}

III. From the table, it is apparent that these differences are constant within the range of ±2 ml. mol^{-1}, which would be within the limit of experimental errors for the measurement in liquid sulfur dioxide. Since the ΔVe value is stoichiometrically additive, as is shown above, it would be possible to use the ΔVe value as a measure of the solvation of the constituent ion. The ΔVe values for the salts which have the same counter ion are compared in Table IV. From Table IV, it may be seen that the important factors influencing the ΔVe values, that is, effecting the solvation of the ion, are the bulkiness and the shape of the ion, which controls the approach of a solvent molecule to the ion.

Table IV. A comparison of the $[-\Delta Ve]$ value for the ion

For iodide

$$\begin{array}{ccccccc} K^+ & > & \overset{+}{\mathrm{MePyr}} & > & \mathrm{Me_4\overset{+}{N}} & > & \mathrm{Et_4\overset{+}{N}} \\ 98 & & 84 & & 70 & & 61 \end{array}$$

For tetraethyl ammonium

$$\begin{array}{ccccccccc} \mathrm{Picrate}^- & & I^- & & Br^- & & Cl^- & & ClO_4^- \\ 65 & > & 61 & \geqq & 60 & \geqq & 59 & > & 49 \end{array}$$

As may be seen from Table II, the ΔVe value for potassium iodide in liquid sulfur dioxide is −98, much smaller than that in water, −8. The same relation holds for the value of Et_4NCl (−59 in liquid sulfur dioxide, +15 in water). This suggests that there exists a considerable interaction between the solute and solvent molecules for such a large solute as Et_4NI in liquid sulfur dioxide.

The small $[\Delta Ve]$ value in a sulfur dioxide solution may be explained by the following two points:

1) Sulfur dioxide is slightly associated in the liquid state, as is shown in its low boiling temperature and small vaporizing heat, and it may be easily compressed in the vicinity of the ionic charge.

2) The sulfur dioxide molecule is larger than the water molecule, and the interaction of sulfur dioxide with a large ion such as the tetraethyl ammonium ion may be predominant. The solvation

TABLE V. THE ΔVe VALUE AND THE DISSOCIATION CONST. OF THE SALTS

Salt	Picrate	Iodide	Bromide	Chloride	Perchlorate
$K_d \times 10^4$ for Me_4N^+ ion[4)	19.5	13.9	11.8	10.3	8.4
$[-\Delta Ve]$ for Et_4N^+ ion	65	61	60	59	49

Salt	$MePyr^+$	$Me_4\overset{+}{N}$
$K_d \times 10^4$ for Picrate[4)	29	19.5
$[-\Delta Ve]$ for Perchlorate	70	60

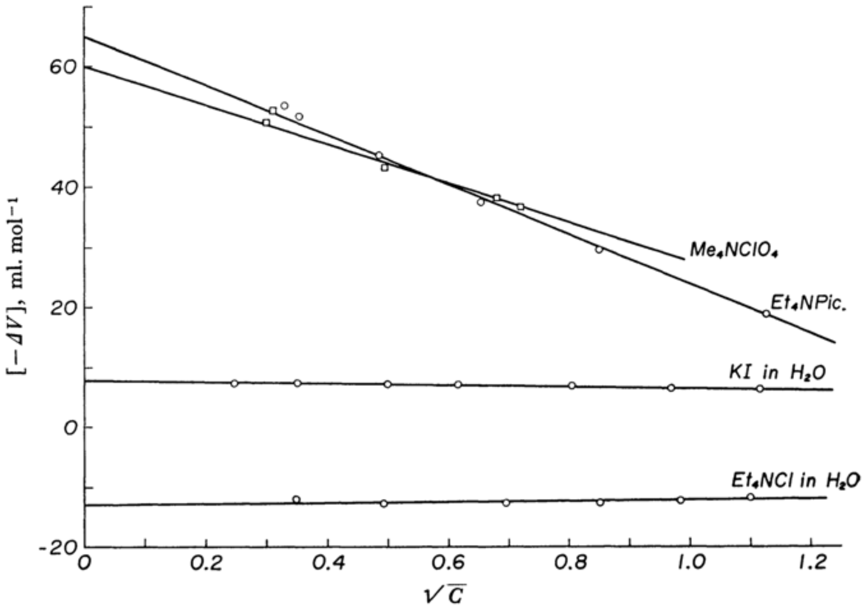

Fig. 5. Plots of the $[-\Delta V]$ value vs. $C^{1/2}$ of the solute.

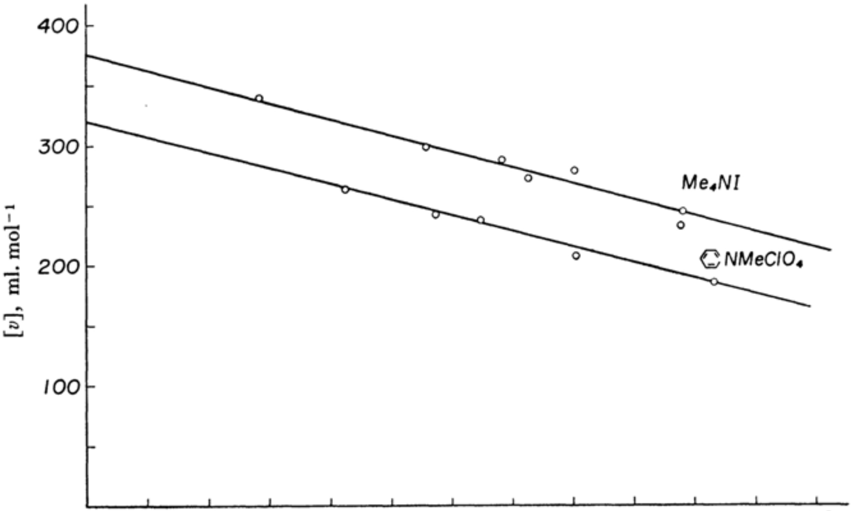

Fig. 6. Plots of the v value vs. $C^{1/2}$ of the solute.

number in a sulfur dioxide solution as calculated from Eq. 6 is eight for Me_4NI and about seven for $MePyr\cdot ClO_4$. Judging from these values it is again likely that such large solutes are considerably solvated in liquid sulfur dioxide.

It is generally accepted that the volume change is a measure of solvent-solute interactions, but this does not necessarily indicate the thermodynamic stability of the solute in the solution. However, as is shown in Table V, in liquid sulfur dioxide the order of the increase in the $[-\Delta Ve]$ value is in accord with that in the K_d value.[4)]

It would be reasonable to assume that the $[-\Delta Ve]$ values thus obtained express the thermodynamic behavior of the ion in liquid sulfur dioxide.