[October, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (10), 2653—2657 (1976) 2653

The Heat of Solution and Solvation Number of Lithium Salts in Water–Alcohol Mixtures

Michio Mashima, Takao Takase, Shinroku Fukuda, and Norio Baba
Faculty of Engineering, Niigata University, Gakko-cho, Nagaoka-shi 940

(Received June 6, 1975)

The solvation numbers of LiCl and LiI, and of KI for comparison, in water–MeOH mixtures and water–*i*-PrOH mixtures were determined at an infinite dilution at 25 °C from the adiabatic compressibility. The heats of solution of these salts were also determined. In general, with an increase in the concentration of alcohol the solvation number increases initially to reach a maximum at 10—30 mol% alcohol, then it decreases to a minimum and increases again from about 75 mol% alcohol. The maximum solvation numbers of the salts determined are as follows: LiCl 11.2 mol/mol at 30 mol% MeOH; LiCl 11.5 mol/mol at 15 mol% *i*-PrOH; LiI 8.2 mol/mol at 12 mol% *i*-PrOH and KI 14.0 mol/mol at 10 mol% *i*-PrOH. The larger the cation, the larger the solvation number. Also, the composition of the solvant where the salt containing larger ions has a maximum solvation number has a lower concentration of alcohol. The maximum solvation number of LiI containing a larger anion is smaller than that of LiCl because an iodide ion has a much larger structure-breaking effect than a chloride ion. By the way, there seems to be difference in the structure of the mixed solvent before and after the maximum solvation number.

The heats of solution and the hydration numbers of the cobalt(III) complexes and simple salts at an infinite dilution at 25 °C have been reported.[1] In this experiment the solvation numbers of lithium chloride, lithium iodide, and potassium iodide for comparison, which are soluble in alcohol, in water–methyl alcohol (subsequently designated MeOH), and water–isopropyl alcohol (subsequently designated *i*-PrOH) mixtures, were determined at an infinite dilution at 25 °C from the adiabatic compressibility. The heats of solution of lithium chloride and lithium iodide at an infinite dilution were also determined. Moreover, the A and B coefficients of the viscosity in the Jones-Dole expression[2] of lithium chloride in water–MeOH mixtures were determined.

Experimental

Determination of Heat of Solution. The heats of solution were determined with a twin-type conduction micro calorimeter with copper-constantan thermocouples, a commercial model (CM-502) of Ōyōdenki Kenkyujo. This apparatus, wrapped in a polyethylene sheet, was put in a thermostat regulated at 25±0.01 °C. This was connected with a d. c. voltage amplifier (a commercial model PM-17A) and a recorder (a commercial model EPR-10A of Tōa Electronics, Ltd.). The heat of solution was calculated from the area drawn by the recorder. The cells for dissolving salts are made of stainless steel. The solid sample was thrown into a cell containing 40 ml of the solvent by means of the attached device. Known amounts of heat occurred in the cell with liquid paraffin when a heater was used; these amounts were then used for obtaining the comparative area, from which the heats of solution of salts were calculated. The quantity of heat which was actually measured is less than, or equals, one figure. Figure 1 shows the heats of solution of lithium chloride in the 12.9 mol% MeOH–water mixture and in the 83.5 mol% *i*-PrOH–water mixture, and that of lithium iodide in water. The heat of solution at an infinite dilution was obtained by the extrapolation of the concentration to zero because the heat of solution per mol of electrolytes decreased linearly with a decrease in the concentration in this case.

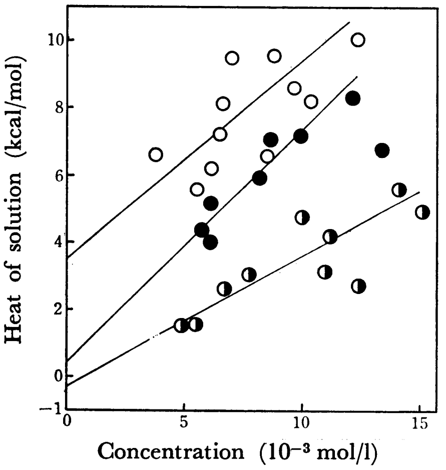

Fig. 1. Relationship between the concentration and the heat of solution (25 °C).
○: LiCl (12.9 mol% MeOH), ●: LiCl (83.5 mol% *i*-PrOH), ◑: LiI (water).

Determination of Solvation Number. The solvation number at an infinite dilution, determined from the adiabatic compressibility[3,4] was obtained by measuring the velocity of sound in the solution by means of an ultrasonic interferometer which had been placed in a thermostat maintained at 25±0.01 °C. The frequency used was 1 MHz. This apparatus was a commercial model (UAC-1-2A) of Chōonpa Kōgyō. Purified water for a solvent was boiled and used immediately after cooling. The solvation number was determined from the (relative) differential specific compressibility; that is,

$$K_{x0} = \lim_{x\to 0}[(d-x)/d_1-(K/K_1)]/x$$

where d and d_1 are the densities of the solution and the solvent, and where x is the concentration of the solution. It was assumed that the composition of the sheath of solvation was the same as that of the solvent.

B-*Coefficient of Viscosity.* The kinematic viscosity of the solution was measured with a kinematic viscosimeter of the Cannon-Fenske type, while the viscosity of the solution was obtained by the multiplication of the kinematic viscosity by its density. The density was measured with a Gay-Lussac-type pycnometer with a capacity of 10 ml. The A and B coefficients of viscosity of the solution in the Jones-Dole expression[2] were calculated from the viscosity of the solution;

$$\eta = \eta_0(1+A\sqrt{c}+Bc)$$

where η_0 is the viscosity of the solvent, c is the molarity, and both A and B are the characteristic constants on the solute.

Table 1. Heats of solution in water and hydration numbers of lithium salts at an infinite dilution (25°C)

Salt	Hydration number		Heat of solution		Hydration number of Li^+ (mol/g-ion)b)	Heat of solution of Li^+ (kcal/g-ion)b)
	(mol/mol)	(10^{-4} g/ml)a)	(kcal/mol)	(10^{-3} mol/l)a)		
LiCl	4.7	3—15	+1.6	6—15	2.7	+2.8
$LiNO_3$	7.0	2—10	+0.3	5—22	2.7	+2.8
LiI	7.1	1—11	−0.3	5—15	4.4	

Hydration number (mol/g-ion)1) Cl^- 2.0, NO_3^- 4.3, I^- 2.7. Heat of solution (kcal/g-ion)1) Cl^- −1.2, NO_3^- −2.5. a) The determined range of concentration of the solution. b) Values obtained by subtracting that of an anion from that of a salt.

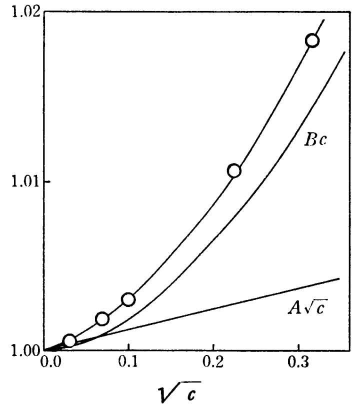

Fig. 2. Relationship between the relative viscosity and the square root of molarity of aqueous solution of lithium chloride (25 °C).

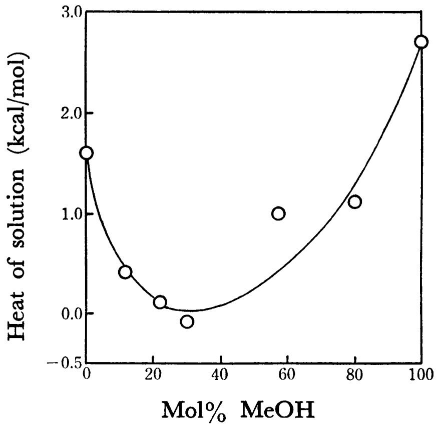

Fig. 3. Heat of solution of lithium chloride in water–MeOH mixture at infinite dilution (25 °C).

Figure 2 shows the relationship between the relative viscosity and the square root of the molarity of an aqueous solution of lithium chloride, drawn to obtain the *A* and *B* coefficients of the viscosity.

Determination of Electric Conductivity. The electric conductivity was measured with an electric conductivity outfit, a commercial model MY-7 of the Yanagimoto Mfg. Co., Ltd. The electrodes were made of platinum gild with platinum black. The equivalent electric conductivity was determined by measuring the resistance of the solution and by extrapolating the concentration to zero because the equivalent electric conductivity of strong electrolytes changed linearly against the square root of the concentration. The cell for measuring the resistance of the solution was put in a thermostat regulated at 25 °C.

Samples. The samples such as lithium salts which are of a guaranteed or extra pure grade were used without further purification. The alcohol was dried with an aluminum amalgam or dehydrated copper sulfate and distilled before use.

Results and Discussion

Table 1 shows the heats of solution in water and the hydration numbers of three kinds of lithium salts at an infinite dilution at 25 °C. The heat of solution in water and the solvation number of a lithium ion were obtained by subtracting those of a negative ion from those of lithium salts, because the additive property held on both the heats of solution in water and the hydration numbers of a nitrate ion and a chloride ion of the simple salts.1) The hydration number of a lithium ion obtained from that of chloride was, consequently, consistent with that obtained from nitrate, *i.e.*, 2.7 mol/g-ion. Similarly, the heat of solution of a lithium ion was +2.8 kcal/g-ion. However the hydration number of a lithium ion, obtained from the others, did not agree with that obtained from the others, *i.e.*, 4.4 mol/g-ion.

The heats of solution of lithium chloride in water–MeOH mixtures at an infinite dilution at 25 °C are shown in Fig. 3. The heat of solution decreases initially with an increase in the concentration of MeOH to a minimum value at about 30 mol% MeOH, but thereafter it increases. A similar tendency in this system had been reported by Slansky.5) The heat of mixing per mol of water and MeOH has a maximum value at about 30 mol% MeOH.6) The viscosity,7) the velocity of sound,8) and the refractive index9) of the mixture have also maxima at almost the same

Table 2. Heats of solution and solvation numbers of lithium chloride and lithium iodide in water, MeOH, and *i*-PrOH respectively (25 °C)

Salt	Solvent	Heat of solution (kcal/mol)	Solvation number (mol/mol)	Heat of solution / Solvation number (kcal/mol)
LiCl	Water	+1.6	4.7	+0.34
	MeOH	+2.7	7.7	+0.35
	i-PrOH	+4.4	10.3	+0.43
LiI	Water	−0.3	7.1	−0.04
	i-PrOH	+3.4	2.5	+1.36

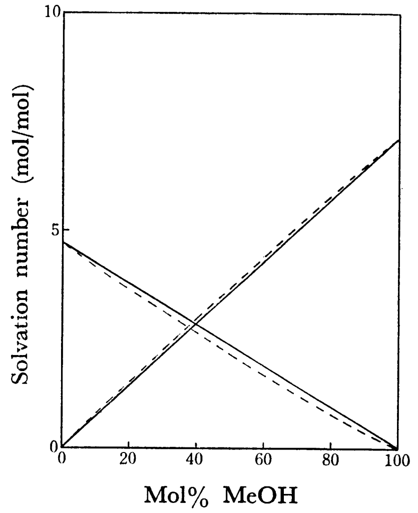

Fig. 4. Relationship between the composition of the sheath of solvation and that of the solvent.
----: Calculated value.

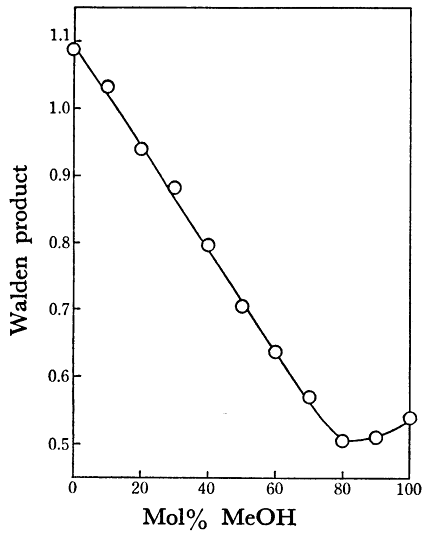

Fig. 5. Walden product of lithium chloride in water–MeOH mixtures at infinite dilution (25 °C).

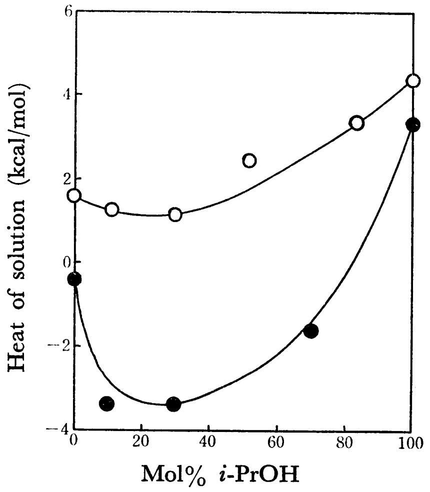

Fig. 6. Heats of solution of lithium chloride and lithium iodide in water–*i*-PrOH mixture at infinite dilution (25 °C).
○: LiCl, ●: LiI.

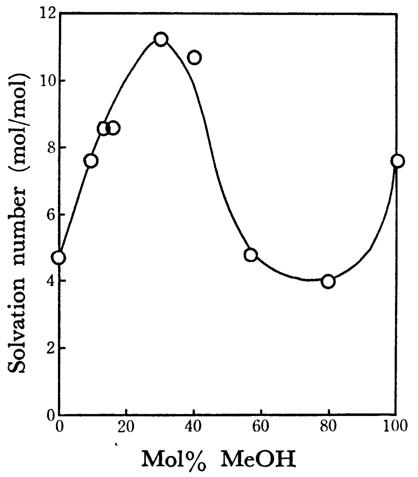

Fig. 7. Solvation number of lithium chloride in water–MeOH mixture at infinite dilution (25 °C).

compositions. The heats of solution and solvation numbers of lithium chloride and lithium iodide in water, MeOH, and *i*-PrOH at an infinite dilution at 25 °C are indicated in Table 2. The composition of the sheath of solvation was calculated from the heat of solution per mol of hydrated water or solvated MeOH (Table 2) so that the calculated value of the heat of solution was consistent with the actually determined value (shown in Fig. 3), assuming that the solvation number increases linearly against the concentration of MeOH. Consequently, the composition of the sheath of solvation was little different from that of the solvent, shown by the dotted lines in Fig. 4. Figure 5 shows the Walden products[10] of lithium chloride in water–MeOH mixtures at an infinite dilution at 25 °C. It may be seen in Fig. 5 that the Walden product decreases almost linearly, without having a constant value, in the water-rich region. From these results it seems reasonable to assume that lithium chloride does not solvate selectively water or MeOH in water–MeOH mixtures.[11]

Figure 6 shows the heats of solution of lithium chloride and lithium iodide in water–*i*-PrOH mixtures at an infinite dilution at 25 °C. The heat of solution has a minimum value at 15—20 mol% *i*-PrOH. The heat of mixing[6] and the velocity of sound[8] of the mixture have maxima at almost the same concentration of *i*-PrOH, much like water–MeOH mixtures.

Figure 7 shows the solvation number of lithium chloride in water–MeOH mixtures at an infinite dilution at 25 °C, determined from the adiabatic compressibility. The composition of the sheath of solvation was assumed to be identical with that of the solvent in this case, according to the estimation described above. The solvation number of lithium chloride in water–MeOH mixtures increases with an increase in the MeOH content up to a maximum at about 30 mol% MeOH, thereafter it decreases to a minimum at about 75 mol% MeOH, and then increases again. Thus, the solvation number is probably strongly influenced by the structure of the solvent, that it has a maximum seems to be attributable to a difference in

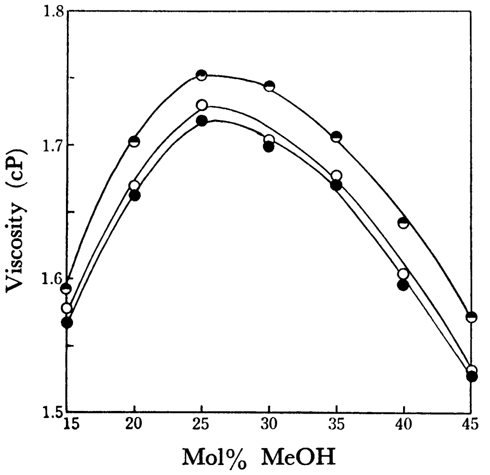

Fig. 8. Viscosity of water–MeOH mixtures containing lithium chloride at 25 °C.
◓: LiCl 0.1 mol/l, ○: LiCl 0.01 mol/l, ●: LiCl 0.001 mol/l.

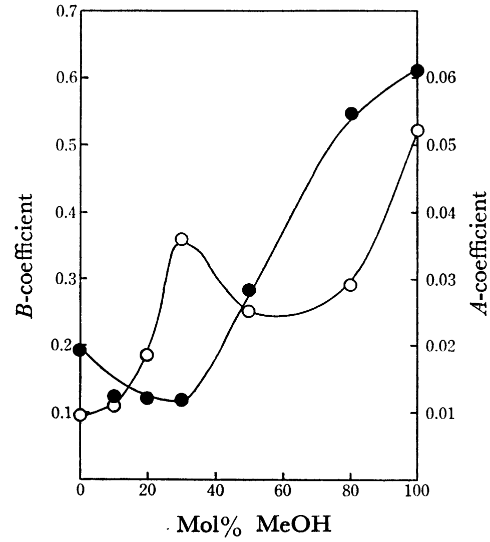

Fig. 9. *A* and *B*-coefficient of viscosity of lithium chloride in water–MeOH mixture (25 °C).
○: *A*-coefficient of viscosity,
●: *B*-coefficient of viscosity.

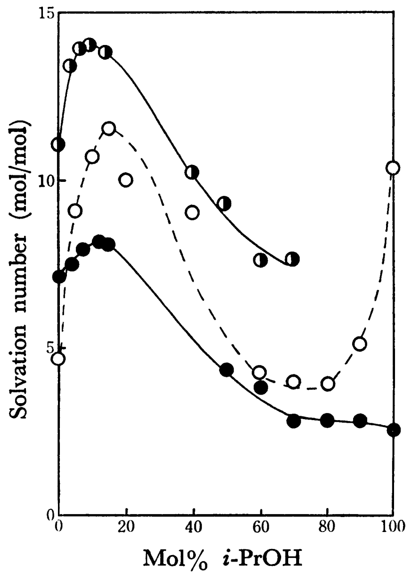

Fig. 10. Solvation numbers of lithium chloride, lithium iodide and potassium iodide in water–*i*-PrOH mixture at infinite dilution (25 °C).
○: LiCl, ●: LiI, ◑: KI.

the structure of the solvent before and after the maximum solvation number, much like water–ethanol systems.[12–15] Many physicochemical properties of water–MeOH mixtures have maxima in a water-rich region. For example, the viscosity of the solution has a maximum at about 25 mol% MeOH, as is shown in Fig. 8. The maximum solvation number of lithium chloride in water–MeOH mixtures is 11.2 mol/mol at about 30 mol% MeOH.

In view of the values of the hydration number previously determined by the present authors,[1] the larger a cation is, the larger the hydration number. Also, the larger the electric charge of the cation, the smaller the hydration number. This result is the reverse of the concept universally believed. The ionic hydration numbers obtained by the authors were $Li^+=2.7$, $K^+=8.4$. The hydration number of the lithium ion was smaller than the literature data, *e.g.*, $Li^+=4.0$,[16] while that of the potassium ion was larger than $K^+=3.5$.[16] Hence, the solvation number determined from the velocity of sound in the solution appears to contain the region in which the molecules around the ion are fixed (A-region) and a part of the outer region (B-region) of the Frank and Wen model for the sheath of solvation.[17,18]

The *A* and *B* coefficients of the viscosity of lithium chloride in water–MeOH mixtures were determined in an effect to investigate the interaction between the solute ion and the solvent in the mixtures at an infinite dilution at 25 °C. These values are plotted against the MeOH content in Fig. 9. The *A* coefficient has a maximum and the *B* coefficient has a minimum at about 30 mol% MeOH, where the solvation number is at its maximum. Consequently, it is considered that the coulombic force between the solute ions is at the maximum, and that the interaction between the solute ion and the solvent is at the minimum, at this composition.[19,20] In a water-rich region, the sheath of solvation determined by this method can be considered to increase with an increment in the MeOH content, because the distance between the solute ion and the solvent increases, as may be seen from the *B* coefficient of viscosity. As a result, the solvation number increases with an increase in the MeOH content when the degree of the increment in the thickness of the sheath of solvation is not very large. Accordingly, when the solvation number determined by this method is at the maximum, the interaction between the ion and the solvent is at the minimum because the distance between them is greatest at that composition, and the heat of solution of the salt is at the minimum, too. The Walden products of lithium chloride in water–MeOH mixtures, as may be seen in Fig. 5, show that the apparent average size of the cation and the anion solvated increases with an increase in the MeOH content in the water-rich region, it has no constant value in that region. However, the solvation number of *t*-butyl chloride in water–ethanol mixtures has a minimum, determined by Arnett and his co-workers.[12,13] This may be related to the fact that the Walden product of lithium chloride in water–ethanol mixtures has nearly a constant value from 0 to 25 wt% ethanol,[21] despite the effect of the size of the solute.

The solvation numbers of lithium chloride, lithium iodide, and potassium iodide in water–*i*-PrOH mixtures at an infinite dilution at 25 °C are shown in Fig. 10. The experiment on potassium iodide could not be carried out, though, in a solvent more than about 70 mol% *i*-PrOH because the salt was little soluble in the solvent. The maximum solvation numbers of the salts determined are as follows: lithium chloride, 11.5 mol/mol at 15 mol% *i*-PrOH; lithium iodide, 8.2 mol/mol at 12 mol% *i*-PrOH; and potassium iodide, 14.0 mol/mol at 10 mol% *i*-PrOH.

Comparing the solvation number of lithium iodide with that of potassium iodide, both values have roughly the same tendency with regard to the MeOH content, and potassium iodide, which has a larger cation, has a larger solvation number than lithium iodide at all the compositions. Therefore, a potassium ion seems to have an apparent larger sheath of solvation than a lithium ion. On the other hand, the apparent sheath of solvation of a lithium ion appears to be smaller and to be composed of the A region for the most part, because the ion is solvated strongly, much as in pure MeOH.[22,23]

Next, the effect of the solvent on the solvation number will be discussed. As may be seen in Figs. 7 and 10, the maximum solvation number of lithium chloride in a water–*i*-PrOH mixture is larger than that in water–MeOH mixtures, and the composition of the solvent where lithium chloride has the maximum value in water–*i*-PrOH mixtures exists in a lower concentration of alcohol than that in water–MeOH mixtures. This is probably because the apparent sheath of solvation of the salt increases in size for *i*-PrOH molecules which are larger than MeOH molecules.

Comparing the solvation number of lithium chloride with that of lithium iodide, lithium iodide, which has a larger anion, has a larger hydration number than lithium chloride, much as in the case of cations. However, lithium iodide has a smaller solvation number than lithium chloride from about 3 mol% *i*-PrOH, and the maximum solvation number of lithium iodide is smaller than that of lithium chloride. The reason for this is that: the B region of the sheath of solvation of an iodide ion is extremely large because it has a much larger structure-breaking effect than a chloride ion.[24] As a result, the A region and a part of the B region of the ion are determined as the sheath of solvation, resulting in its having a smaller solvation number than a chloride ion.

In the range of high *i*-PrOH concentrations, the solvation number of lithium iodide does not increase, unlike as in the case of lithium chloride. This tendency is presumably due to the same effect of an iodide ion.

References

1) M. Mashima, K. Sakai, W. Takamura, and T. Takase, *Nippon Kagaku Kaishi*, **1974**, 1024; M. Mashima, H. Usami, S. Suzuki, and T. Takase *ibid.*, **1975**, 963.

2) G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).

3) H. Shiio, *J. Am. Chem. Soc.*, **80**, 70 (1958).

4) F. Kawaizumi, H. Nomura, and Y. Miyahara, *Nippon Kagaku Zasshi*, **87**, 939 (1966).

5) C. Slansky, *J. Am. Chem. Soc.*, **62**, 2430 (1940).

6) T. Katayama, *Kagaku Kogaku*, **26**, 361 (1962).

7) G. Tamman and M. E. Pillsbury, *Z. Anorg. Chem.*, **172**, 243 (1928).

8) B. Jacobson, *Arkiv for Kemi*, **2**, 177 (1950).

9) K. Y. Chu and A. R. Thompson, *J. Chem. Eng. Data*, **7**, 358 (1962).

10) P. Walden, H. Ulich, and G. Busch, *Z. Phys. Chem.*, **123**, 429 (1926).

11) R. W. Gurney, "Ionic Processes in Solution," Dover Publications Inc., New York (1953), p. 69.

12) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

13) E. M. Arnett, and D. R. Mckelvey, *J. Am. Chem. Soc.*, **88**, 2548 (1966).

14) F. Hibbert, F. A. Long, and F. A. Water, *J. Am. Chem. Soc.*, **91**, 2381 (1969).

15) I. Lee and J. B. Hyne, *Can. J. Chem.*, **46**, 2339 (1968).

16) J. O'M. Bockris and P. P. S. Saluja, *J. Phys. Chem.*, **76**, 2140 (1972).

17) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

18) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

19) R. H Stokes and R. H. Mills, "Viscosity of Electrolytes and Related Properties," Pergamon Press Inc., New York (1965).

20) M. Kaminsky, *Discuss. Faraday Soc.*, **24**, 171 (1957).

21) G. Wada, *Nippon Kagaku Zasshi*, **77**, 391 (1956).

22) A. R. Gordon, J. A. Davies, and R. L. Kay, *J. Chem. Phys.*, **19**, 749 (1951).

23) A. R. Gordon, R. E. Jervis, D. R. Muir, and J. P. Butler, *J. Am. Chem. Soc.*, **75**, 2855 (1953).

24) O. D. Bonner and C. F. Jumper, *Infrared Phys.*, **13**, 233 (1973).