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## The Partial Molal Volume of Ions in Various Solvents<sup>1</sup>

by Frank J. Millero

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The partial molal volumes of ions in the solvents methanol, water, and N-methylpropionamide (NMP) have been examined by using the Frank and Wen model for ion-solvent interactions. The partial molal volume of an ion is assumed to be due to three major components,  $\bar{V}^0(\text{int})$ , the intrinsic partial molal volume (equal to the crystal volume),  $\bar{V}^0(\text{disord})$ , the disordered partial molal volume (void space effects), and  $\bar{V}^0(\text{elect})$ , the electrostriction partial molal volume. The results of fitting the  $\bar{V}^0(\text{ions})$  in these solvents to various semi-empirical equations indicate that  $\bar{V}^0(\text{disord})$  is related to the structure of the solvent. This disordered effect may be visualized as the void space caused by the solvated ion rather than improper packing in the electrostricted region. The  $\bar{V}^0(\text{elect})$  of the ions in the various solvents is proportional to  $1/r$  ( $r$  = crystal radius) and in the predicted order ( $\bar{V}^0(\text{elect})$  of methanol > water > NMP).

### Introduction

Using the Frank and Wen<sup>2</sup> model for ion-solvent interactions, the partial molal volume of an ion at infinite dilution can be attributed to the following components<sup>3a</sup>

$$\bar{V}^0(\text{ion}) = \bar{V}^0(\text{int}) + \bar{V}^0(\text{elect}) + \bar{V}^0(\text{disord}) + \bar{V}^0(\text{caged}) \quad (1)$$

where  $\bar{V}^0(\text{int})$  is the intrinsic partial molal volume (the crystal volume),  $\bar{V}^0(\text{elect})$  is the electrostriction partial molal volume (the decrease in volume due to ion-solvent interactions),  $\bar{V}^0(\text{disord})$  is the disordered partial molal volume (normally attributed to void space effects), and

$\bar{V}^0(\text{caged})$  is the caged partial molal volume (due to the formation of caged or structured water around ions with hydrocarbon tails).

Since the various components of eq 1 may be small when compared to the absolute size of the ion (*i.e.*, the crystal volume), it is difficult to determine the importance of the individual components of  $\bar{V}^0(\text{ion})$  or

(1) Paper presented at Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968.

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

(3) (a) F. J. Millero, *J. Phys. Chem.*, **72**, 4589 (1968); (b) F. J. Millero and W. Drost-Hansen, *ibid.*, **72**, 1758 (1968).

separate overlapping effects. In recent papers,<sup>3-5</sup> we have tried to solve this problem by examining the effect of temperature on the  $\bar{V}^0(\text{ions})$  or the partial molal expansibilities of ions,  $\bar{E}^0(\text{ions})$ .

Other methods that can be used to elucidate the various components of  $\bar{V}^0(\text{ion})$  are to examine the effect of pressure on the  $\bar{V}^0(\text{ion})$ , the partial molal compressibility,<sup>6</sup> or to examine the  $\bar{V}^0(\text{ions})$  in various solvents. In this paper we will examine the  $\bar{V}^0(\text{ions})$  in the solvents water, methanol, N-methylpropionamide (NMP), and seawater by a simple model for ion-solvent interactions. The results will hopefully lead to a better understanding of the major components of the  $\bar{V}^0(\text{ion})$  in these solvents.

### Partial Molar Volume of Ions in Various Solvents at Infinite Dilution

The additivity of the partial molal volumes of salts,  $\bar{V}^0(\text{salts})$ , at infinite dilution in the solvents water,<sup>7</sup> seawater,<sup>8</sup> NMP,<sup>9</sup> and methanol,<sup>10</sup> has been shown; however, the division of  $\bar{V}^0(\text{salts})$  into their ionic components,  $\bar{V}^0(\text{ions})$ , cannot normally be made by direct experimental methods. Zana and Yeager<sup>11</sup> reported the first estimates of the  $\bar{V}^0(\text{ions})$  in water based on a direct experimental method using an ultrasonic technique. However, until Zana and Yeager's experimental method<sup>11</sup> is used in other solvents, we are forced to use nonthermodynamic methods of dividing  $\bar{V}^0(\text{salts})$ . Mukerjee<sup>12</sup> has summarized the various estimates of  $\bar{V}^0(\text{H}^+)$  in water and finds  $\bar{V}^0(\text{H}^+) \approx -4.5$  ml/mol at 25°. This value of  $\bar{V}^0(\text{H}^+)$  agrees very well with Mukerjee's earlier estimate<sup>13</sup> made by assuming the  $\bar{V}^0$  of the monovalent monoatomic cations and anions were a smooth function of the crystal radii cubed. Since Mukerjee's method of dividing  $\bar{V}^0(\text{ions})$  gives reasonable values in water and also is simple to use, we have used his method to examine the  $\bar{V}^0(\text{ions})$  in various solvents.<sup>9,10,14</sup> His method has the added advantage of giving one relationship for the  $\bar{V}^0$  of cations and anions, thus providing a uniform comparison between various solvents. Table I gives the  $\bar{V}^0(\text{ions})$  in the solvents water, seawater, NMP, and methanol at 25° determined by Mukerjee's method using  $\bar{V}^0(\text{salts})$  taken from the literature.<sup>9,10,13-15</sup>

Recently, Ellis<sup>16</sup> has used Criss and Cobble's correspondence method<sup>17</sup> to estimate the  $\bar{V}^0(\text{ions})$  at various temperatures based on  $\bar{V}^0(\text{ions})$  at 25°. Criss and coworkers<sup>18</sup> have also used the correspondence method to determine the partial molal entropy of ions in various solvents from their values in water. Since  $\bar{V}^0(\text{ions})$  in water at 25° determined by various methods are in agreement,<sup>12</sup> the correspondence method may be a useful method of dividing the  $\bar{V}^0(\text{ions})$  in various solvents. Using the correspondence method, one obtains the equation

$$\bar{V}^0(\text{ion})^S = a\bar{V}^0(\text{ion})^W + b \quad (2)$$

**Table I:** The Partial Molal Volume of Ions in Various Solvents at 25° (ml/mol)

Ion	Crystal <sup>a</sup>	NMP <sup>b</sup>	Sea-water <sup>c</sup>	Water <sup>d</sup>	Methanol <sup>e</sup>
H <sup>+</sup>	...	3.4	-3.7	-4.5	-14.6
Li <sup>+</sup>	1.2	...	...	-5.2	-14.0
Na <sup>+</sup>	2.2	6.0	-4.4	-5.7	-12.6
K <sup>+</sup>	5.9	11.1	5.9	4.5	-2.6
Rb <sup>+</sup>	8.2	...	...	9.5	...
Cs <sup>+</sup>	12.2	...	...	16.9	...
F <sup>-</sup>	6.3	...	...	3.4	...
Cl <sup>-</sup>	14.9	24.7	23.3	22.3	9.3
Br <sup>-</sup>	18.7	29.8	30.3	29.2	16.6
I <sup>-</sup>	25.4	...	41.4	40.8	24.3
NO <sub>3</sub> <sup>-</sup>	21.1	33.6	34.8	33.5	...

<sup>a</sup> Calculated from the equation  $\bar{V}^0(\text{ion})$  in the crystal equals  $2.52r^3$ , using Pauling crystal radii quoted in ref 3a except for Li<sup>+</sup>, where the Goldschmidt radius, 0.78 Å, was used. <sup>b</sup> From ref 9. <sup>c</sup> From ref 14. <sup>d</sup> From ref 13, except for  $\bar{V}^0(\text{F}^-)$  calculated from  $\bar{V}^0(\text{NaF})$  given in ref 15. <sup>e</sup> From ref 10.

where  $a$  and  $b$  are constants obtained by a least-square best fit of  $\bar{V}^0(\text{ions})$  in the solvent, S and water, W. Figure 1 shows a plot of  $\bar{V}^0(\text{ions})$  in the solvents S plotted vs. the  $\bar{V}^0(\text{ions})$  in water, determined by Mukerjee's method (Table I). The correspondence equation is obeyed (within experimental error) showing that the two methods of dividing  $\bar{V}^0(\text{salts})$  are essentially the same. We obtain constants  $a = 0.814$ , 0.764, 0.976 and  $b = -9.0$ , 8.0, 1.5 ml mol<sup>-1</sup>, respectively, for the solvents methanol, NMP, and seawater.

The most successful semiempirical correlation<sup>13,19</sup> of  $\bar{V}^0(\text{ions})$  in water have been made using an equation of the form

$$\bar{V}^0(\text{ion}) = Ar^3 - BZ^2/r \quad (3)$$

where the first term is equal to  $\bar{V}^0(\text{int}) + \bar{V}^0(\text{disord})$  and the second term is equal to  $\bar{V}^0(\text{elect})$ ,  $A$  and  $B$

- (4) F. J. Millero, W. Drost-Hansen, and L. Korson, *J. Phys. Chem.*, **72**, 2251 (1968).
- (5) F. J. Millero and W. Drost-Hansen, *J. Chem. Eng. Data*, **13**, 330 (1968).
- (6) F. J. Millero and F. Lepple, paper in preparation.
- (7) A. M. Couture and K. J. Laidler, *Can. J. Chem.*, **34**, 1209 (1956).
- (8) I. W. Duedall and P. K. Weyl, *Limnol. Oceanogr.*, **12**, 52 (1967).
- (9) F. J. Millero, *J. Phys. Chem.*, **72**, 3209 (1968).
- (10) F. J. Millero, unpublished results.
- (11) R. Zana and E. Yeager, *J. Phys. Chem.*, **70**, 954 (1966); **71**, 521 (1967).
- (12) P. Mukerjee, *ibid.*, **70**, 2708 (1966).
- (13) P. Mukerjee, *ibid.*, **65**, 744 (1961).
- (14) F. J. Millero, *Limnol. Oceanogr.*, **14**, 376 (1969).
- (15) F. J. Millero, *J. Phys. Chem.*, **71**, 4567 (1967).
- (16) A. J. Ellis, *J. Chem. Soc.*, **A**, 1138 (1968).
- (17) C. M. Criss and J. W. Cobble, *J. Amer. Chem. Soc.*, **86**, 5385 (1964).
- (18) C. M. Criss, R. P. Held, and E. Luksha, *J. Phys. Chem.*, **72**, 2970 (1968).
- (19) L. G. Hepler, *ibid.*, **61**, 1426 (1957).

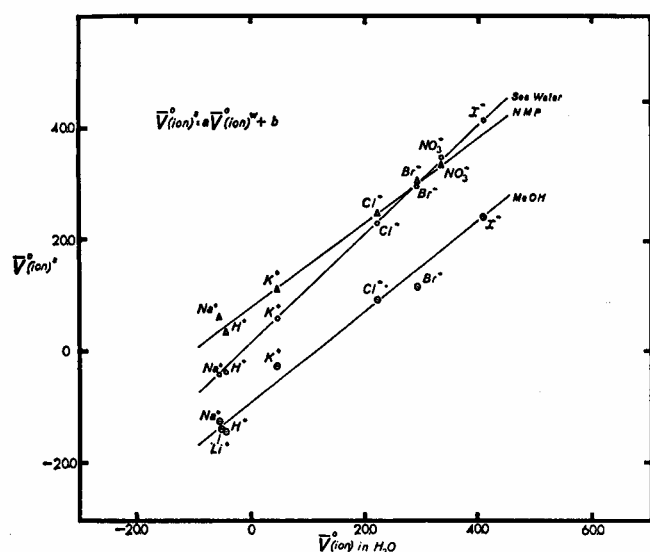


Figure 1. The partial molal volume of an ion in solvent,  $S$ ,  $\bar{V}^0(\text{ion})^S$ , plotted vs. the partial molal volume of an ion in water,  $\bar{V}^0(\text{ion})^W$ .

are constants,  $Z$  is the charge on the ion, and  $r$  is the crystal radius of the ion. Recently, various workers<sup>20,21,22</sup> have attempted to separate the intrinsic size of an ion and void space effects (*i.e.*,  $\bar{V}^0(\text{int})$  and  $\bar{V}^0(\text{disord})$ ) by using the semiempirical equations

$$\bar{V}^0(\text{ion}) = 2.52r^3 + A'r^2 - B'Z^2/r \quad (4)$$

$$\bar{V}^0(\text{ion}) = 2.52(r + a)^3 - B''Z^2/r \quad (5)$$

by assuming the void space is proportional to the surface of the ion (eq 4)<sup>20</sup> or the void space could be represented by a spherical shell around the ion (eq 5).<sup>21</sup>

The constants for these equations have been evaluated for the  $\bar{V}^0(\text{ions})$  in methanol,  $\text{H}_2\text{O}$ , seawater, and NMP at  $25^\circ$  graphically and by a least-square best fit method (with the aid of an IBM computer). The constants are tabulated in Table II (along with the standard deviations) and plotted vs.  $D$  and  $1/D$  where  $D$  is the dielectric constant of the solvent (Figures 2 and 3).

The comparison of the constants  $A$ ,  $A'$ , and  $a$  (or the  $\bar{V}^0(\text{int})$  and  $\bar{V}^0(\text{disord})$  for ions) is shown in Table II and in Figure 2 plotted vs.  $D$ , the dielectric constant of the solvents ( $D(\text{MeOH}) = 31.5$ ,<sup>23</sup>  $D(\text{H}_2\text{O}) = 78.5$ ,<sup>23</sup>  $D(\text{NMP}) = 176$ ). The constants for seawater are not given in Table II (or shown in Figure 2 and 3) because they may be meaningless due to ion-pair formation.<sup>14</sup> The constants  $A$  in methanol, water, and NMP are larger than the theoretical value calculated by assuming that the ion is a perfect hard sphere ( $4/3 \pi N \times 10^{-24} = 2.52$ ). Thus,  $\bar{V}^0(\text{int})$  appears to increase by 32% in methanol, 77% in water, and 59% in NMP. The magnitude and order of the constants  $A$ ,  $A'$ , and  $a$  show no simple correlation to common physical properties such as dielectric constant (Figure 2). The constants are also not in the order expected ( $\text{NMP} < \text{H}_2\text{O} <$

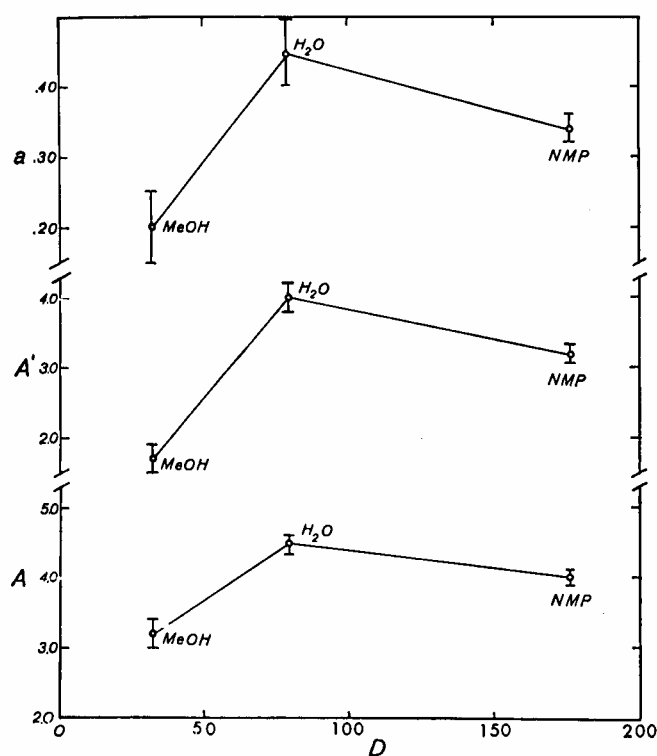


Figure 2. Semiempirical constants,  $A$ ,  $A'$ , and  $a$  for the  $\bar{V}^0(\text{int}) + \bar{V}^0(\text{disord})$  term of eq 3, 4, and 5 (respectively) plotted vs.  $D$ , the dielectric constant of the solvents.

$\text{MeOH}$ ) for the expansion of an ion due to differences in internal electrostatic pressure (*i.e.*, the compressibility of the solvents).

The cause of the increase of  $\bar{V}^0(\text{int})$  in water has been attributed to void space packing effects.<sup>20-22</sup> These results indicate that void space packing effects are also important in the solvents, methanol and NMP. It is easy to visualize void space effects in water since the radii of simple ions and water molecules are nearly the same size. However, void space effects in methanol and NMP are difficult to visualize (*i.e.*, in the sense discussed by Glueckauf<sup>21</sup> and Conway, *et al.*<sup>20</sup>) since the solvent molecules are larger than normal ions. It thus appears that the increase in  $\bar{V}^0(\text{int})$  may be related to the disordered region surrounding the solvated ion,  $\bar{V}^0(\text{disord})$ . This disordered effect may be visualized as the void space caused by the solvated ion (*i.e.*, including the electrostricted region) rather than improper packing in the electrostricted region.

If one considers the structure of the solvents,  $\bar{V}^0(\text{disord})$  appears to be largest in the most highly ordered solvent ( $\text{H}_2\text{O}$ ). Criss and coworkers<sup>18</sup> have

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

(21) E. Glueckauf, *Trans. Faraday Soc.*, **61**, 914 (1965).

(22) S. W. Benson and C. S. Copeland, *J. Phys. Chem.*, **67**, 1194 (1963).

(23) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," ACS Monograph No. 137, Reinhold Publishing Corp., New York, N. Y., 1958.

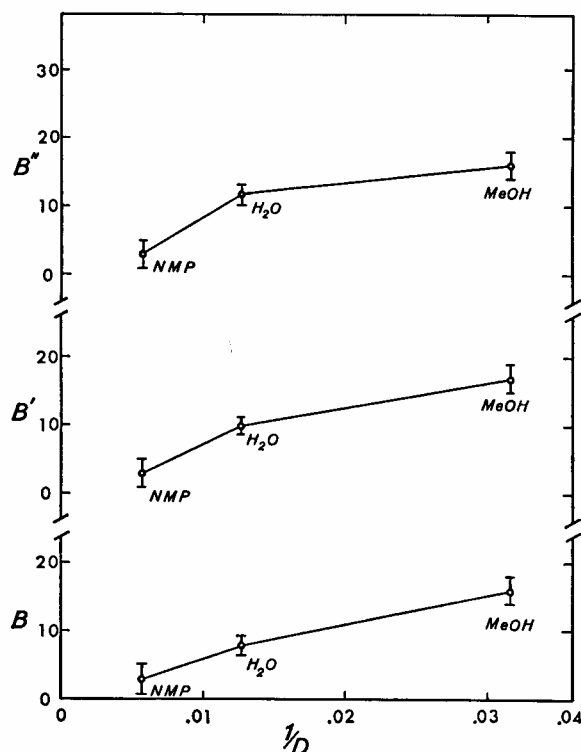


Figure 3. Semiempirical constants,  $B$ ,  $B'$ , and  $B''$  for the  $\bar{V}^0(\text{elect})$  term of eq 3, 4, and 5 (respectively) plotted vs.  $1/D$ , the reciprocal of the dielectric constant of the solvents.

observed a similar behavior for the partial molal entropy of ions in various solvents. More must be known about the structure of the solvents and the geometry of the coordination shell before one can select the exact form of this positive disorder effect ( $\bar{V}^0(\text{disord})$ ).

The  $\bar{V}^0(\text{elect})$  terms of the semiempirical equations are given in Table II and plotted vs.  $1/D$  in Figure 3. The constants,  $B$ ,  $B'$ , and  $B''$  are in their expected order (i.e.,  $B(\text{MeOH}) > B(\text{H}_2\text{O}) > B(\text{NMP})$ ) based on the assumption that  $\bar{V}^0(\text{elect})$  is proportional to  $1/D$  or  $\beta$ , the compressibility of the solvents. From the simple continuum model one can calculate the electrostriction of an ion using the Drude-Nernst<sup>24</sup> equation

$$\bar{V}^0(\text{elect}) = \frac{-NZ^2e^2}{2Dr} \left[ \frac{d \ln D}{dP} \right] = \frac{-BZ^2}{r} \quad (6)$$

This equation serves only as an approximation and is valid only for large, isolated ions. Using the most recent value for  $d \ln D/dP$  and  $D$  for water<sup>25</sup> and methanol,<sup>26</sup> values of  $B = 4.2$  in  $\text{H}_2\text{O}$  and 24 in  $\text{MeOH}$  are obtained. A similar calculation for NMP is not possible since  $d \ln D/dP$  is not known. The agreement between the calculated values of  $B$  in methanol and water with the correlation values is fair, considering the approximate nature of the Drude-Nernst equation.  $\bar{V}^0(\text{elect})$  can be calculated by more elaborate methods by considering dielectric saturation effects;<sup>27</sup> however, the calculations are normally complex and cannot be

**Table II:** Comparison of the Constants for the Semiempirical Equations of the Partial Molal Volumes of Monovalent Ions at Infinite Dilution in Methanol, Water, and N-Methylpropionamide at 25°

Eq 3, $\bar{V}^0(\text{ion}) = Ar^3 - Bz^2/r^a$			
Solvent	$A$ , ml mol <sup>-1</sup> Å <sup>-3</sup>	$B$ , ml mol <sup>-1</sup> Å	Std dev
Methanol	$3.3 \pm 0.2$	$16 \pm 2$	$\pm 1.6$ ml/mol
Water	$4.5 \pm 0.1$	$8 \pm 1$	$\pm 0.5$
NMP	$4.0 \pm 0.1$	$3 \pm 2$	$\pm 0.4$

Eq 4, $\bar{V}^0(\text{ion}) = 2.52r^3 + A'r^2 - B'Z^2/r^a$			
Solvent	$A'$ , ml mol <sup>-1</sup> Å <sup>-2</sup>	$B'$ , ml mol <sup>-1</sup> Å	Std dev
Methanol	$1.7 \pm 0.2$	$16 \pm 2$	$\pm 1.5$
Water	$4.0 \pm 0.2$	$10 \pm 1$	$\pm 0.8$
NMP	$3.2 \pm 0.1$	$2 \pm 2$	$\pm 0.4$

Eq 5, $\bar{V}^0(\text{ion}) = 2.52(r + a)^3 - B''Z^2/r^b$			
Solvent	$a$ , Å	$B''$ , ml mol <sup>-1</sup> Å	Std dev
Methanol	$0.20 \pm 0.05$	$16 \pm 2$	$\pm 1.3$
Water	$0.45 \pm 0.05$	$11 \pm 1$	$\pm 0.9$
NMP	$0.34 \pm 0.02$	$2 \pm 2$	$\pm 0.4$

<sup>a</sup> Constants determined by graphic methods. <sup>b</sup> Constants determined by least-square "best" fit method.

made for the solvents, methanol and NMP, due to the lack of data. If one assumes that  $\bar{V}^0(\text{elect})$  is proportional to the compressibility of the solvents,<sup>28,29</sup> one would expect  $\bar{V}^0(\text{elect})$  in methanol to be about 2.7 times as great as in water, which is in fair agreement with the  $B$  constants. (The compressibility of NMP has not been measured to the best of our knowledge.) Since the  $\bar{V}^0$ 's of polyvalent salts are not available in the solvents methanol and NMP, little can be said about the effect of charge on the electrostriction or the  $B$  constants.

As more data become available for the solvent systems mentioned in this paper (and other solvent systems) for other monovalent and polyvalent ions as a function of temperature, the correlation equations can be improved and more can be learned about ion-solvent interactions in various solvents.

**Acknowledgment.** The author wishes to acknowledge the support of the Office of Naval Research, Grant No. NONR 4008 (02), for this study.

- (24) P. Drude and W. Nernst, *Z. Phys. Chem.*, **15**, 79 (1894).
- (25) B. B. Owen, R. C. Miller, R. C. Milner, and H. L. Cogan, *J. Phys. Chem.*, **65**, 2065 (1961).
- (26) J. Padova and I. Abrahamer, *ibid.*, **71**, 2112 (1967).
- (27) J. E. Desnoyers, R. E. Verrall, and B. E. Conway, *J. Chem. Phys.*, **43**, 243 (1965).
- (28) R. E. Gibson, *J. Amer. Chem. Soc.*, **59**, 1521 (1937).
- (29) G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc. (London)*, **258**, 1094 (1965).