Chemical Reviews

Volume 71, Number 2 April 1971

THE MOLAL VOLUMES OF ELECTROLYTES*

FRANK J. MILLERO

University of Miami, Rosenstiel School of Marine and Atmospheric Sciences, Miami, Florida 33149

Received July 8, 1970 (Revised Manuscript Received October 9, 1970)

Contents

I. Introduction

The apparent and partial molal volumes of electrolyte solutions have proven to be a very useful tool in elucidating the structural interactions (*i.e.*, ion–ion, ion–solvent, and solvent–solvent) occurring in solution. For example, the partial molal volumes of electrolytes at infinite dilution can be used to study ion–solvent and solvent–solvent interactions, while the concentration dependence of the apparent and partial molal volumes of electrolytes can be used to study ion–ion interactions. The partial molal volumes of electrolytes can also be used to calculate the effect of pressure on ionic equilibria for processes of engineering and oceanographic importance.

In this review we will be primarily concerned with the use of the molal volumes of electrolytes in elucidating ion–ion and ion–solvent interactions in aqueous and nonaqueous solutions. Since the early development of the use of molal volume data to study structural interactions has never been reviewed, we have also included a brief account of historical development. The bulk of the review will be confined to the more recent experimental and theoretical use of molal volume or volume of mixing data of electrolyte solutions in studying structural interactions (that is, from 1957 to 1970). In this short sketch of the development of the use of molal volume data to study structural interactions, it will not be possible to review all the work indirectly related to solution volumes, such as the effect of pressure on ionic equilibria, the compressibilities of electrolyte solutions, the effects of various solutes on the temperature of maximum density of water, and similar topics. References to the volumes of nonelectrolytes in various solvents and the volumes of solutes in molten salts have also been omitted.

II. Historical Development

The volumes of electrolyte solutions have been of scientific interest for a long time. The theoretical development of solution volumes has paralleled the overall development made in other phases of solution chemistry. Although the earlier theories have been proven mistaken and future work will undoubtedly disprove some of our present ideas, it is of interest to see how our pictures of electrolyte solution volumes have developed and changed. In this section we will briefly review the earlier development of the use of the volumes of electrolyte solutions in studying structural interactions.

The historical development of the volumes of electrolyte solutions can conveniently be divided into five major divisions, with the years 1770, 1887, 1923, and 1957 as points of change. In 1770, Watson[1] made the first accurate measurements on the volume change of adding electrolytes to water; in 1887, Arrhenius[2] presented his theory on the dissociation of electrolytes into ions; in 1923, Debye and Hückel[3] presented their theory of interionic attraction; and in 1957, various workers, *e.g.*, Ackermann,[4] Buckingham,[5] Eigen,[6] Frank and Wen,[7] Kaminsky,[8] Samoilov,[9] Young, Wu, and Krawetz,[10] etc., presented a number of papers on structural

---

* Contribution No. 1301 from the University of Miami, School of Marine and Atmospheric Sciences.

(1) R. Watson, *Phil. Trans. Roy. Soc. London*, 60, 325 (1770).
(2) S. Arrhenius, *Z. Phys. Chem.*, 1, 631 (1887).
(3) P. Debye and E. Hückel, *Physik. Z.*, 24, 185 (1923).
(4) T. Ackermann, *Discuss. Faraday Soc.*, 24, 180 (1957).
(5) A. D. Buckingham, *ibid.*, 24, 151 (1957).
(6) M. Eigen, *ibid.*, 24, 25 (1957).
(7) H. S. Frank and W.-Y. Wen, *ibid.*, 24, 133 (1957).
(8) M. Kaminsky, *ibid.*, 24, 171 (1957).
(9) O. Ya. Samoilov, *ibid.*, 24, 141 (1957); see also "Structure of Aqueous Electrolyte Solutions and the Hydration of Ions" (translated by D. J. G. Ives), Consultants Bureau, New York, N. Y., 1965.
(10) T. F. Young, Y. C. Wu, and A. A. Krawetz, *Discuss. Faraday Soc.*, 24, 78 (1957).

hydration interactions in the *Discussions of the Faraday Society*.

Before 1770, a salt was thought to dissolve in water simply by filling up the void spaces without changing the volume.[11–13] The experimental evidence used to support this notion was that a glass of water did not overflow when a spoonful of salt was added.[11,13] Eller[12] made more careful experimental measurements of how much salt could be added to a given volume of water before its volume began to increase; however, he considered that his results supported the "porous" nature of water. Watson's work[1] in 1770 showed that the volume is decreased when various salts are added to a fixed volume of water. His work definitely showed that the prevailing theory of the porosity of water was incorrect; however, his work was soon forgotten and the older theory held for another 70 years (Watson tired of chemistry and entered the ministry in 1771). Little further work was done on the volumes of electrolyte solutions until 1840 when Dalton[14] made some volume measurements which he thought supported the porosity theory of water. Dalton[14] claimed that the volume of water was not changed when a salt was added except when the dissolved salt contained water (*i.e.*, the volume change was equal to the volume of water the salt contained). Holker[15] checked these results and found that the volume change on adding a salt to water could be positive or negative depending on the salt, the temperature, and the concentration. Playfair and Joule[16] repeated Holker's work and found a relationship between the volume of salt in solution and in crystal. They, however, reached different conclusions from either Dalton[14] or Holker.[15] Marignac[17] finally cleared up this confused situation by showing that Playfair and Joule's work was incorrect and that Holker's work was correct.

By 1850 the decrease in volume upon the addition of a salt to water was generally accepted and in 1854 Michel and Krafft[18] made the first quantitative measurements on the densities of solutions. Kremers[19] measured the densities of numerous salt solutions between 1855 and 1862 (much of which has never been repeated). He showed that the density was not a linear function of concentration and that the relative volumes of electrolyte solutions go through a maximum with increasing temperature. Schiff[20] studied the density of concentrated salt solutions and, by extrapolating these densities to 100%, calculated the volume of water bound in the crystal (0.8 cm^3/g). Gerlach[21] reviewed the published density data for aqueous salt solutions during this period.

The apparent (or equivalent) molal volume, ϕ_V, of an electrolyte in solution was first introduced in 1871 by Marignac[22]

$$\phi_V = (V - n_1\bar{V}_1^0)/n_2 \qquad (1)$$

where V is the volume of the solution, $n_1\bar{V}_1^0$ is the volume of water in the solution (n_1 = moles of water, $\bar{V}_1^0$ = molar volume of water), and n_2 is the number of moles (or equivalents) of electrolyte in solution. He found that the ϕ_V's increased with concentration and temperature for the salts he studied.

Favre and Valson[23] were the first to observe a regularity between the additivity of the densities or ϕ_V's of different salt solutions (first applied by Favre to heats of solution). The numbers they obtained constituted Valson's[24] density moduli (it is interesting to note that this very important discovery was made in 1872, 15 years before Arrhenius[2] presented his theory on electrolyte dissociation). Favre and Valson[23] assumed that the volume change on adding a salt to water was the resultant of two opposing effects: (i) contraction in volume due to the adsorption of water on the dissolved salt and (ii) expansion in volume due to the salt dissociating. They calculated that 7576 cal of work or a pressure change of 21 atm would be needed to decrease the volume by 1 cm^3/l. of solution. Bender[25] also discussed Valson's density moduli and showed that they are the result of a more general expression.

Ostwald[26,27] continued Favre and Valson's moduli work in another direction and found additive relations for the change in volume on the neutralization of acids and bases. Nicol[28,29] was the first to attempt to explain why the ϕ_V's of electrolytes increase with increasing concentration by using the so-called attraction theory (*i.e.*, the attraction of water for water, salt for salt, and water for salt). A salt was thought to dissolve when the attraction of water for salt exceeded that of salt for salt.

The theory of Arrhenius[2] in 1887 was of great importance in the development of the theory of solution volumes since it explained the observed additivity relationships found by Favre and Valson[23] and Ostwald.[26,27] It also gave stimulus to the field owing to the attempts of various workers to verify or disprove its consequence by experiment; for example, Schmidt[30] in 1890 showed the additivity of the ϕ_V's for various salt pairs.

In 1892, Traube[31] began a series of ϕ_V studies of solutes in solution.[31,32] He believed that the ϕ_V represented the actual volume of the salt in solution (unlike Ostwald); he explained negative ϕ_V's on the basis of the crystal water that the salt contained. He determined ϕ_V values for some 50 salts and noted the change of the ϕ_V with valence type. He devoted most of his later work to organic solvents.[32]

---

(11) J. A. Nollet, "Lecons de Physique Experimentale," Vol. 4, 1748, p 51.

(12) J. T. Eller, *Hist. Acad. Roy. Berlin*, 6, 82 (1750).

(13) J. H. Marcet, "Conversations on Chemistry," New Haven, Conn., 1809.

(14) J. Dalton, "On the Quantity of Acids, Bases and Water," pamphlet, 1840.

(15) S. Holker, *Phil. Mag.*, 27, 207 (1844).

(16) L. Playfair and J. P. Joule, *ibid.*, 27, 453 (1845).

(17) C. Marignac, *ibid.*, 28, 527 (1846).

(18) A. Michel and L. Krafft, *Ann. Chim. Phys.*, 41, 471 (1854).

(19) P. Kremers, *Ann. Phys. Chem.*, **95**, 110 (1855); 96, 39 (1855); 98, 58 (1856); 99, 58, 435 (1856); 100, 394 (1857); 105, 360 (1858); 108, 115 (1859); 111, 60 (1860); 114, 41 (1861); 120, 493 (1862).

(20) H. Schiff, *Ann. Chem. Pharm.*, 109, 325 (1859); 113, 349 (1860).

(21) G. Gerlach, *Z. Anal. Chem.*, 8, 245 (1869); 27, 271 (1888); 28, 290 (1889).

(22) C. Marignac, *Ann. Chim. (Paris)*, 22, 415 (1871).

(23) P. A. Favre and C. A. Valson, *C. R. Acad. Sci.*, **75**, 1000 (1872).

(24) C. A. Valson, *ibid.*, 73, 441, 1376 (1871).

(25) C. Bender, *Ann. Phys. Chem.*, 20, 560 (1883); 31, 873 (1887).

(26) W. Ostwald, *J. Prakt. Chem.*, 18, 328 (1878).

(27) W. Ostwald, "Lehrbuch der alleimeinen Chemie," 2nd ed, 1890; section on solutions translated into English in 1891.

(28) W. Nicol, *Proc. Roy. Soc. Edinburgh*, 11, 819 (1882).

(29) W. Nicol, *Phil. Mag.*, 15, 91 (1883); 16, 121 (1883); 18, 179 (1884); *Chem. News*, 49, 37 (1884); *Phil. Mag.*, 21, 70 (1885); 23, 385 (1887).

(30) G. Schmidt, *Monatsh. Chem.*, 11, 35 (1890).

(31) J. Traube, *Ber.*, 25, 2524 (1892); 27, 3173 (1894); *Z. Anal. Chem.*, 3, 11 (1893).

(32) J. Traube, *Ann. Phys. Chem.*, 22, 519 (1907).

Two very important theories about ϕ_V's, Drude and Nernst's[33] electrostriction theory and Tammann's[34] internal pressure (or Binnendruck) theory, developed directly from Arrhenius' work[2] and are still the basis for many theories of ion–solvent interactions today.

Tammann[34] was the first to give a reasonable theoretical explanation of solution volumes. The fundamental idea of his theory of internal pressure (π) was developed by noting that both an increase in pressure and the addition of a salt to water lowered the temperature of maximum density. Thus, a dissolved salt appears to cause the water to behave as if it were under a high external pressure. He applied this theory to solution volumes[35] by attributing the ϕ_V to (i) the change in volume of the salt due to changing the pressure from 1 atm to π, (ii) the change in volume of the solvent due to changing the pressure from 1 atm to π, (iii) the change in volume when one mixes the salt and the solvent at π to give a solution at 1 atm external pressure and π atm internal pressure. Dreyer[36] and Zwicky and Evjen[37,38] have also applied Tammann's internal pressure theory to solution volumes.

Various early workers[39–42] investigated the ϕ_V's of organic nonelectrolytes in various organic solvents and found that the ϕ_V's were nearly independent of solvent and concentration. They could find no general connection between the ϕ_V's in solution and the internal pressure.

Drude and Nernst[33] developed their electrostriction theory by assuming that ions can be treated as charged spheres in a continuous dielectric medium. They calculated the electrostrictive decrease in volume from the equation

$$\bar{V}^0(\text{elect}) = (Z^2e^2/2Dr)[\partial(\ln D)/\partial P] = -BZ^2/r \qquad (2)$$

where Z is the charge on the ion, e is the electrostatic charge, D is the dielectric constant of the solvent, r is the radius of the ion, and P is the pressure (at 25°, $B = 4.175$ in water). Various early workers[43–45] measured the ϕ_V's of various electrolytes in water and other solvents to test this theory. Carrara and Levi[43] measured ϕ_V's of various substances in water and organic solvents and found that their results agreed fairly well with Drude and Nernst's theory. Walden's work[44] further confirmed these results. He determined the ϕ_V's of Et_4NI, Pr_4NI, and KI in various organic solvents. Polowzow's measurements[45] of the ϕ_V's of various weak electrolytes in water and in benzene also supported the results of Carrara and Levi[43] and Walden.[44] Freund[40] measured the ϕ_V's of salts, acids, and bases from 0.0 to 0.4 *N* and 0 to 100°. She found that the volume change of neturalization of acids and bases was positive and decreased with temperature to 35–50° and then increased. Her paper contains a very good summary of the theories on volume changes of electrostriction in vogue around 1909.

Kohlrausch[46,47] developed a sinker method (based on a hydrostatic balance) to study the densities of electrolyte solutions. Kohlrausch and Hallwachs' work[46,47] led to the general use of the symbol ϕ_V for the apparent or equivalent molal volume. They also showed experimentally that the ϕ_V is proportional to $(S - 1)/c$ (where S is the specific gravity), which follows from the definition of the apparent molal volume

$$\phi_V = -1000(S - 1)/c + M/d^0 \qquad (3)$$

where c is the molar concentration, M is the molecular weight of the solute, d^0 is the density of the pure solvent, and S is the specific gravity ($S = d/d^0$, where d is the density of the solution). Around this time Cinelli[48] discussed the measurements of the densities of aqueous electrolyte solutions and the effect of dissolved electrolytes on the properties of water.

In 1910 Bousfield and Lowry[49] discussed the volumes of electrolyte solutions from the point of view that water is a mixture of various kinds of molecules (*i.e.*, monomers, dimers, trimers, etc.) whose equilibrium is shifted by the addition of solutes. During the period of 1910–1925, few interpretations of solution volumes were made except for the work of Heydweiller[50–53] and Baxter and coworkers.[54,55] Heydweiller[50–53] attempted to relate $1000(S - 1)/c$ to the degree of dissociation of electrolytes. While Baxter and coworkers[54,55] applied the theory of Richards[56] on the compressible ion to solution volumes, Baxter's theory[54,55] differed from that of Tammann[34] and that of Drude and Nernst[33] in that he thought both the salt and the solvent contracted. Baxter[54,55] thought that the ϕ_V was due to (i) an expansion due to the freeing of the ions from crystalline restraints, (ii) a smaller expansion due to repulsion of like charges, and (iii) a contraction due to ion–water interactions (the magnitude being dependent upon the compressibility of water and salt) mostly due to the contraction of water. He thought that changes in the polymerization of water by the ions had little effect on the ϕ_V. The decrease in the ϕ_V with decreasing concentration was attributed to ionization, and the increase in the ϕ_V with temperature was attributed to a decrease in hydration.

In 1913 Lamb and Lee[57] developed a magnetic float method of measuring the densities of solutions. Although this method can be considered a development or modification of the hydrostatic weighing method, the magnetic float method requires no suspension thread or wire. They showed that the method was capable of measuring densities to a precision of 0.1 ppm, and they were able to determine the ϕ_V's for LiCl, NaCl, KCl, NH_4Cl, $MgSO_4$, $ZnSO_4$, and Na_2CO_3 in very

---

(33) P. Drude and W. Nernst, *Z. Phys. Chem.*, **15**, 79 (1894).
(34) G. Tammann, *ibid.*, **11**, 676 (1893).
(35) G. Tammann, *ibid.*, **16**, 91, 139 (1895).
(36) F. Dreyer, *Z. Anal. Chem.*, **154**, 254 (1926).
(37) H. M. Evjen and F. Zwicky, *Phys. Rev.*, 33, 860 (1929).
(38) F. Zwicky, *Phys. Z.*, 26, 664 (1925); 27, 271 (1926); *Proc. Nat. Acad. Sci. U. S.*, 12, 86 (1926).
(39) H. Dawson, *J. Chem. Soc.*, 97, 1041, 1896 (1910).
(40) I. Freund, *Z. Phys. Chem.*, 66, 555 (1909).
(41) J. Lumsden, *J. Chem. Soc.*, 91, 24 (1907).
(42) D. Tyrer, *ibid.*, 97, 2520 (1910).
(43) G. Carrara and M. Levi, *Gazz. Chim. Ital.*, **30**, 197 (1900).
(44) P. Walden, *Z. Phys. Chem.*, **60**, 87 (1907).
(45) A. Polowzow, *ibid.*, **75**, 513 (1910).
(46) F. Kohlrausch and W. Hallwachs, *Ann. Phys. Chem.*, **50**, 118 (1893); **53**, 14 (1894).
(47) F. Kohlrausch, *ibid.*, 56, 185 (1895).
(48) F. Cinelli, *Nuovo Cimento*, **3**, 141 (1896).
(49) W. R. Bousfield and T. M. Lowry, *Trans. Faraday Soc.*, **6**, 85 (1910).
(50) A. Heydweiller, *Ber. Deut. Phys. Ges.*, 7, 37 (1909).
(51) A. Heydweiller, *Ann. Phys. (Leipzig)*, 30, 873 (1909).
(52) A. Heydweiller, *Z. Phys. Chem.*, 70, 128 (1910).
(53) A. Heydweiller, *Ann. Phys. (Leipzig)*, 31, 1063 (1910); 37, 739, 762 (1912).
(54) G. P. Baxter, *J. Amer. Chem. Soc.*, 33, 922 (1911); **40**, 192 (1918).
(55) G. P. Baxter and C. C. Wallace, *ibid.*, 38, 70 (1916).
(56) T. W. Richards, *Proc. Amer. Acad. Arts Sci.*, 37, 13 (1901).
(57) A. B. Lamb and R. E. Lee, *J. Amer. Chem. Soc.*, 35, 1666 (1913).

dilute aqueous solutions (0.0001–0.01 *c*). Geffcken, Beckmann, and Kruis[58] have also used this method.

After 1925, due to the new advances made in the knowledge of solutions (for example, Debye and Hückel's work on interionic attraction,[8] Fajans and coworkers' work[59] on the refractivity of solutions, Born's work[60] on the calculations of the sizes of atoms and ions, Webb's calculations[61] on the magnitude of the effect of a charged ion on the volume of water, and Richards and Chadwell's work[62] on water structure), it became evident that there was a need for a revision and reinterpretation of solution volumes. Thus, rapid developments were made in the measurement and interpretation of solution volumes. For example, Campbell[63] attempted to calculate the true volume of certain salts from the refractive index; Geffcken and coworkers,[58,64–71] working in Fajans' laboratory, studied the relation between the apparent molal volume and the refraction of salt solutions; Scott and coworkers[72–75] studied the relations between ϕ_V's in saturated solutions; and Redlich and coworkers[76–78] applied the Debye–Hückel theory to the concentration dependence of ϕ_V.

In 1926, Webb[61] developed a theory for the volume change produced by electrostriction in the vicinity of an ion. The electrostriction of a solvent was given by the equation

$$\bar{V}^0(\text{elect}) = \int_{r_0}^{\infty} -\frac{\Delta V_r}{V} 4\pi r^2 \, dr \qquad (4)$$

where $\Delta V_r/V$ is the fractional change of volume at a distance *r* from the center of the ion where the pressure is P_r and r_0 is the radius of the ion (*i.e.*, the region into which no solvent molecules could enter). The fractional change in volume $\Delta V_r/V$ can be obtained directly from the observed relative volume of the solvent at pressure P_r or from the compressibility equation

$$-\Delta V_r/V = \int_0^{P_r} \beta dP \qquad (5)$$

where β, the compressibility is a function of pressure. To use this equation it is necessary to know the pressure, P_r, as a function of *r*.

In 1929, Masson[79] found a valuable, although often misused, empirical generalization on the change of the ϕ_V with the square root of molar (or normal) concentration

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \qquad (6)$$

where ϕ_V^0 is the apparent molal volume at infinite dilution (equal to the partial molal volume, $\bar{V}_2^0$) and S_V^* is the experimental slope that varies with each electrolyte. Scott[74] and Geffcken[65] also examined the ϕ_V's of electrolytes using this equation and found that it adequately represents the concentration dependence of the ϕ_V's of electrolytes over a wide temperature and concentration range. Root[80] combined eq 3 and 6 and found the equation

$$d = d^0 + [(M - d^0\phi_V^0)/1000]c - (S_V^* d^0/1000)c^{3/2} \qquad (7)$$

can be used to represent the densities, *d*, of many aqueous salt solutions. Since the ϕ_V^0's and S_V^*'s have been shown to be additive for many simple salt solutions,[81] this equation can be very useful in estimating the densities of unknown solutions (*i.e.*, in concentrated solutions). Many other early workers have examined the ϕ_V's and *d*'s for electrolytes in water,[81] glycol,[82] methanol,[82–84] ethanol,[83] and acetic acid[83] by eq 6 and 7. Tabulations of ϕ_V^0's and S_V^*'s for electrolytes in water determined using these equations have been given by a number of workers.[81,85–87] Masson[79] attempted to relate the S_V^* constants to the dissociation of electrolytes, while Scott[72–75] discussed the significance of the S_V^*'s of electrolytes in concentrated solutions.

In 1931, Redlich and Rosenfeld[77,78] applied the interionic attraction theory of Debye and Hückel to the concentration dependence of ϕ_V. They attributed the increase in the ϕ_V's of electrolytes with increasing concentration to the screening of the electrostriction of the ions by the approach of counterions. They also predicted that a constant limiting slope should be obtained for a given electrolyte charge type (at constant temperature and pressure) if the Debye–Hückel theory is obeyed. By differentiating the Debye–Hückel limiting law for activity coefficients with respect to pressure, they obtained the theoretical limiting slope, S_V, using the equation

$$S_V = k w^{3/2} \qquad (8)$$

The two terms for the limiting slope are given by

$$k = N^2 e^3 (8\pi/1000 D^3 RT)^{1/2} [\partial (\ln D)/\partial P - \beta/3] \qquad (9)$$

where β is the compressibility of the solvent and the other symbols have their usual meaning,[85] and

$$w = 0.5 \sum_i \gamma_i Z_i^2 \qquad (10)$$

---

(58) W. Geffcken, Ch. Beckmann, and A. Kruis, *Z. Phys. Chem. (Leipzig), Abt. B*, 20, 398 (1933).

(59) K. Fajans, *ibid.*, 34, 125 (1934); 29, 153 (1935).

(60) M. Born, *Z. Phys.*, 1, 45 (1920).

(61) T. J. Webb, *J. Amer. Chem. Soc.*, 48, 2589 (1926).

(62) T. W. Richards and H. W. Chadwell, *ibid.*, 47, 2283 (1925).

(63) A. Campbell, *J. Chem. Soc.*, 653 (1928).

(64) W. Geffcken, *Naturwissenschaften*, 19, 321 (1930).

(65) W. Geffcken, *Z. Phys. Chem., Abt. A*, 155, 1 (1931).

(66) W. Geffcken, *ibid.*, 167, 240 (1933).

(67) W. Geffcken and A. Kruis, *Z. Phys. Chem. (Leipzig), Abt. B*, 23, 175 (1933).

(68) W. Geffcken and D. Price, *ibid.*, 26, 81 (1933); 34, 81 (1934).

(69) W. Geffcken, A. Kruis, and L. Solana, *ibid.*, 35, 317 (1937).

(70) H. Kohner, *ibid.*, 1, 427 (1928).

(71) A. Kruis, *ibid.*, 34, 1 (1936).

(72) A. F. Scott and W. R. Frazier, *J. Phys. Chem.*, 31, 459 (1927).

(73) A. F. Scott and E. J. Durham, *ibid.*, 34, 2035 (1930).

(74) A. F. Scott, *ibid.*, 35, 2315, 3379 (1931).

(75) A. F. Scott and G. L. Bridger, *ibid.*, 39, 1031 (1935).

(76) O. Redlich, *Naturwissenschaften*, 19, 251 (1930).

(77) O. Redlich and P. Rosenfeld, *Z. Elektrochem.*, 37, 705 (1931).

(78) O. Redlich and P. Rosenfeld, *Z. Phys. Chem., Abt. A*, 155, 65 (1931).

(79) D. O. Masson, *Phil. Mag.*, 8, 218 (1929).

(80) W. C. Root, *J. Amer. Chem. Soc.*, 55, 850 (1933); Ph.D. Thesis, Harvard University, Cambridge, Mass., 1932.

(81) F. J. Millero in "Structure and Transport Processes in Water and Aqueous Solutions," R. A. Horne, Ed., Wiley-Interscience, New York, N. Y., Chapter 15, 1971.

(82) R. E. Gibson and J. F. Kincaid, *J. Amer. Chem. Soc.*, 59, 579 (1937).

(83) S. D. Hamann and S. C. Lim, *Aust. J. Chem.*, 7, 329 (1954).

(84) G. Jones and H. J. Fornwalt, *J. Amer. Chem. Soc.*, 57, 2041 (1935).

(85) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, pp 358–406.

(86) B. B. Owen and S. R. Brinkley, Jr., *Chem. Rev.*, 29, 461 (1941).

(87) B. B. Owen, "Electrochemical Constants," National Bureau of Standards Circular 425, U. S. Government Printing Office, Washington, D. C., 1953.

where γ_i is the number of ions of species i and valency Z_i formed by one molecule of electrolyte. For electrolytes of a fixed valence type, w is constant and the limiting law depends only on temperature and the physical properties of the pure solvent. For dilute solutions the limiting law for the concentration dependence of the ϕ_V's or $\bar{V}_2$'s of electrolytes is given by the equations

$$\phi_V = \phi_V^0 + S_V\sqrt{c} = \phi_V^0 + kw^{3/2}\sqrt{c} \qquad (11)$$

and

$$\bar{V}_2 = \bar{V}_2^0 + {}^3/_2S_V\sqrt{c} = \bar{V}_2^0 + {}^3/_2kw^{3/2}\sqrt{c} \qquad (12)$$

Although the equations developed by Redlich and Rosenfeld are similar to the Masson equation, these theoretical equations have an entirely different meaning. The Masson equation can represent the apparent molal volume data over a considerable concentration range; however, the Redlich equation cannot be expected to be more than a limiting law for low concentrations (this fact was stressed by Redlich and Rosenfeld). The Masson equation has always been used with different S_V^*'s for different electrolytes; the theoretical equation, however, postulates a single coefficient, k, common to all electrolytes and depending only on the temperature and the properties of the pure solvent. Since the limiting law equation was derived from the theory of Debye and Hückel by means of thermodynamics alone, any failure of this equation would indicate the invalidity of the theory. Many workers have neglected this fact.

Although eq 8–12 are thermodynamically sound, their implications have been (and are still being) completely ignored by many workers, who have expressed their results using individual limiting slopes for electrolytes of the same charge type. According to Redlich and Rosenfeld, the individual differences in the slopes found in high concentrations (*i.e.*, using the Masson equation) are due to deviations from the limiting law. Consequently, extrapolations to infinite dilution using the Masson equation are unreliable.

Although Redlich and Rosenfeld[77,78] described this situation nearly 40 years ago, workers still continued to extrapolate the ϕ_V's of electrolytes to infinite dilution using the Masson equation. Part of the problem was due to an incorrect value for the limiting slope and insufficient ϕ_V data in dilute solutions. Using the ϕ_V values for the alkali halides of Baxter and Wallace,[55] Redlich and Rosenfeld determined experimental limiting slopes for 1:1 electrolytes of $S_V = 2.8$, 1.7, and 1.5, at 0, 25, and 50°, respectively.

Redlich and Rosenfeld[77,78] suggested that the concentration dependence of the apparent molal volume be represented by the equation

$$\phi_V = \phi_V^0 + S_V\sqrt{c} + b_Vc \qquad (13)$$

where b_V is an empirical deviation constant. They noted that ϕ_V^0's and b_V's (the deviation constants of various electrolytes) appear to have a parallel behavior. This parallelism has been found both by examining the variation with temperature of these two quantities and by a comparison of the values for different alkali halides. Fajans[88] also found a similar relationship between the electrostatic part of the $\bar{V}_2^0$ and the individual deviations from the limiting law at moderate concentrations.

In 1933 Gucker[89] reviewed the development of the square root concentration dependence of the ϕ_V's of electrolytes. A year later, Gucker[90] defined the apparent molal expansibility, ϕ_E, of an electrolyte and showed that the ϕ_E's of electrolytes were a linear function of $\sqrt{c}$, similar to the Masson and Redlich and Rosenfeld equations for ϕ_V. He found that the slopes, S_E^*, were negative for all the electrolytes he examined, although the Debye–Hückel theory predicted a positive slope. This discrepancy is due to the fact that the data Gucker used was for too high a concentration for the limiting law to hold.

The discrepancies between the Masson equation and the Redlich and Rosenfeld equation in expressing the concentration dependency of the ϕ_V's of electrolytes stimulated a great deal of controversy between 1931 to 1964. Wirth and coworkers[91,92] determined the $\bar{V}_2$'s of a number of electrolytes (KCl, KBr, K_2SO_4, HCl, $NaClO_4$, $HClO_4$) in NaCl aqueous solutions at 25°. They used their $\bar{V}_2$ results to test the validity of the Redlich and Rosenfeld equation as a function of volume ionic strength. They found that the $\bar{V}_2$'s for KCl and KBr depend only on the total volume ionic strength; however, for HCl and K_2SO_4 in concentrated solutions, the $\bar{V}_2$'s are larger than the values in water at the same ionic strength. (Thus, additional terms proportional to ionic strength were necessary.)

Stewart[93] examined the ϕ_V's for 197 strong electrolytes and concluded that the limiting law was not valid. Stewart's conclusions, however, have been shown to be invalid, since he used apparent molal volume data for too high concentrations and in some cases for salts that either hydrolyze or do not completely dissociate.[94]

In 1940 Redlich[94] discussed the development of the square root concentration dependence of the ϕ_V's for electrolytes (stressing the difference between the empirical Masson equation and the equation based on the theory of Debye and Hückel). He also discussed the objections made by various workers (summarized by Stewart[93]) concerning the question as to whether the $\sqrt{c}$ law should also be applied to nonelectrolytes, the experimental proof of the limiting law with improved data, and the valence factor of the limiting law. He showed that the limiting law is approached for electrolytes in aqueous and nonaqueous solutions and that the ϕ_V's for nonelectrolytes depend linearly on the first power of the concentration in dilute solutions. He found an experimental limiting slope of 1.86 ± 0.02 for 1:1 electrolytes in water at 25°. Redlich also showed that by combining eq 3 and 13, the density, d, of an electrolyte solution can be determined from the equation

$$d = d^0 + [(M - d^0\phi_V^0)/1000]c - (S_Vd^0/1000)c^{3/2} - (b_Vd^0/1000)c^2 \qquad (14)$$

He pointed out that this equation is preferred to Root's eq 7, since it is based on the theoretical concentration dependence of the ϕ_V. This equation can be used to estimate the densities of unknown solutions by using the additivity principle (ϕ_V^0's and S_V's are always additive and b_V's appear

---

(88) K. Fajans, *J. Chem. Phys.*, 9, 283 (1941).

(89) F. T. Gucker, Jr., *Chem. Rev.*, 13, 111 (1933).

(90) F. T. Gucker, Jr., *J. Amer. Chem. Soc.*, 56, 1017 (1934).

(91) H. E. Wirth, *ibid.*, 59, 2549 (1937); 62, 1128 (1940); 70, 462 (1948).

(92) H. E. Wirth and F. N. Collier, Jr., *ibid.*, 72, 5292 (1950).

(93) G. W. Stewart, *J. Chem. Phys.*, 7, 381, 869 (1939); *Trans. Faraday Soc.*, 33, 238 (1937).

(94) O. Redlich, *J. Phys. Chem.*, 44, 619 (1940).

to be additive for simple systems). For dilute solutions (when b_V is unimportant) this equation can predict the densities of unknown solutions (provided the ϕ_V^0's are known) more precisely than the best experimental measurements.

In 1942 Redlich and Bigeleisen[95] showed that the experimentally determined heat capacities and molal volumes for the ionization of acetic acid compare favorably with the theoretical values calculated using the Born equation.[60]

They showed that new experimental ϕ_V data[96,97] confirm the Debye–Hückel limiting law for 1:1 electrolytes in dilute solutions. They also discussed the relationship between the ϕ_V^0's and b_V's (suggested earlier by Redlich and Rosenfeld)[77,78] and pointed out that the empirical relationship found by Stewart[98] can also be attributed to this parallelism. In Figure 1 we have plotted the ϕ_V^0's and b_V's for a number of electrolytes in water.[81] There appears to be a strong linear correlation between the ϕ_V^0's and b_V's for 42 of the 52 electrolytes [$b_V = 1.5 - 3.44 \times 10^{-2}\phi_V^0$]. Although this linear correlation breaks down for larger ϕ_V^0's, 46 of the 52 electrolytes can be represented by the quadratic function, $b_V = -0.412 + 2.772 \times 10^{-2}(\phi_V^0) - 2.697 \times 10^{-4}(\phi_V^0)^2$. The causes of the deviations from this correlation for the electrolytes $MgCl_2$, $LaCl_3$, $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, Et_4NCl, and n-Bu_4NCl may be due to the fact that the ϕ_V^0's do not represent the "true" volume of the electrolyte (due to electrostriction effects) or the fact that the b_V's for these electrolytes do not cover the same concentration range (ion-pairing, etc., may also cause the b_V's to be unreliable). The parallelism between the ϕ_V^0's and S_V^*'s for electrolytes found by Scott[74] can also be attributed to the parallelism between the ϕ_V^0's and b_V's since, as demonstrated in Figure 2, the b_V's of electrolytes appear to be linearly related to ($S_V^* - S_V$) by the equation $b_V = -0{,}093 + 0.522(S_V^* - S_V)$. More will be said about the deviations from the limiting law in the next section.

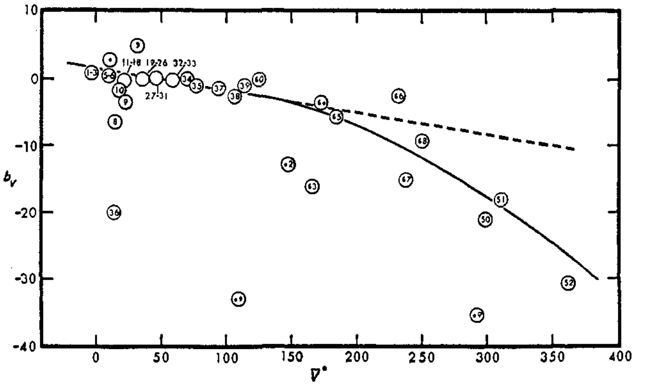

Figure 1. The apparent molal volumes of electrolytes at infinite dilution ($\phi_V^0 = \bar{V}_2^0$) in water at 25° plotted *vs.* the deviation constants b_V (taken from ref 81). The numbers in this figure refer to the following electrolytes: (1) NaF, (2) NaOH, (3) LiF, (4) Na_2SO_4, (5) KF, (6) RbF, (7) K_2SO_4, (8) $MgCl_2$, (9) $BaCl_2$, (10) $CaCl_2$, (11) HCl, (12) NaCl, (13) LiCl, (14) CsF, (15) KCl, (16) NaBr, (17) NaO_2CH, (18) LiBr, (19) RbCl, (20) KBr, (21) NaI, (22) LiI, (23) KNO_3, (24) NaO_2CCH_3, (25) CsCl, (26) RbBr, (27) $KClO_3$, (28) RbI, (29) NH_4Br, (30) CsBr, (31) KI, (32) CsI, (33) $MeNH_3Br$, (34) $NaO_2C(CH_2)_2CH_3$, (35) $EtNH_3Br$, (36) $LaCl_3$, (37) $PrNH_3Br$, (38) Me_4NCl, (39) Me_4NBr, (40) Me_4NI, (41) $K_4Fe(CN)_6$, (42) $K_3Fe(CN)_6$, (43) Et_4NCl, (44) Et_4NBr, (45) Et_4NI, (46) Pr_4NCl, (47) Pr_4NBr, (48) Pr_4NI, (49) Bu_4NCl, (50) Bu_4NBr, (51) Bu_4NI, (52) Pen_4NBr.

A number of early workers between 1933 and 1957 investigated the ϕ_V's of electrolytes in nonaqueous solvents to test the Redlich and Rosenfeld equations and to study the effect of solvent on ion–solvent interactions. Butler and Lees[98] observed that the ϕ_V's of LiCl were much smaller in ethanol than in water. Vosburgh, Connell, and Butler[99] determined the ϕ_V's of LiCl in several aliphatic alcohols (MeOH, EtOH, n-PrOH, i-BuOH, and n-BuOH) to get an idea of the variation of the ϕ_V's and S_V^*'s with the nature of the solvent. They also determined the ϕ_V's of some salts (NaI, NaCl, KI, and KCl) in methanol. The ϕ_V's of all the salts were found to obey the Masson equation over the concentration range examined. The average S_V^*'s for salts in MeOH were found to be about six times larger than the average S_V^*'s in H_2O, which is in approximate agreement with the predictions of the Redlich and Rosenfeld equations. The electrostriction of ions in alcohols was found to be greater than in water for all the systems studied. The extrapolated ϕ_V^0's in MeOH were found to be in reasonable agreement with the values calculated using Webb's theory of electrostriction.[61]

Gibson and Kincaid[82] determined the ϕ_V's and ϕ_E's for NaI, NaBr, and LiBr in glycol and LiCl in methanol. Unlike the ϕ_E's of electrolytes in water, the values in glycol and methanol were found to be negative and to increase with increasing concentration (in agreement with Debye–Hückel theory and Tammann's effective pressure theory). They interpreted these results as an indication of the importance of structural changes in water in determining the volume properties of electrolyte solutions. MacInnes and Dayhoff[100] determined the ϕ_V's of KI and I_2 in methanol using a magnetic float method. Gurney[101] in his classic book also discussed the $\bar{V}^0$'s of electrolytes in various solvents on the basis of various ion–solvent interaction models.

In 1954, Hamann and Lim[88] determined the ϕ_V's of some strong and weak electrolytes in water, methanol, ethanol, and acetic acid. From these ϕ_V's they calculated the volume change for the ionization of weak electrolytes (acids and bases) in water and methanol. Using Zwicky's arguments,[38] they postulated that the electrostriction of an ion should be inversely proportional to the compressibility of the solvent. They showed that the difference between the $\bar{V}^0$'s of ions in various solvents and water show a good linear correlation with the compressibility of the solvent.

Mention should also be made of the other early ϕ_V work of electrolytes in ethanol–water mixtures,[102] methanol,[84]

---

(95) O. Redlich and J. Bigeleisen, *Chem. Rev.*, **30**, 171 (1942).

(96) O. Redlich and L. E. Nielsen, *J. Amer. Chem. Soc.*, **64**, 761 (1942).

(97) O. Redlich and J. Bigeleisen, *ibid.*, **64**, 758 (1942).

(98) J. A. V. Butler and A. D. Lees, *Proc. Roy. Soc., Ser. A*, **131**, 382 (1931).

(99) W. C. Vosburgh, L. C. Connell, and J. A. V. Butler, *J. Chem. Soc.*, 993 (1933).

(100) D. A. MacInnes and M. O. Dayhoff, *J. Amer. Chem. Soc.*, **75**, 5219 (1953).

(101) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill, New York, N. Y., 1954.

(102) R. L. Bateman, *J. Amer. Chem. Soc.*, **71**, 2291 (1949); **74**, 5516 (1952).

liquid $MeNH_2$,[108] and ethanol.[71] Filippova[104,105] reviewed the early ϕ_V work of electrolytes in alcohols and amines. Redlich and coworkers[77,78,94] also reviewed much of the early ϕ_V work of electrolytes in nonaqueous solvents.

In 1941, Owen and Brinkley[86] developed the general methods of using $\bar{V}_2{}^0$ data to estimate the effect of pressure on ionic equilibria using the thermodynamic equation first derived by Planck[106]

$$\partial \ln K/\partial P = -\Delta\bar{V}^0/RT \qquad (15)$$

where $\Delta\bar{V}^0$, the volume change for the process, is equal to the difference between the $\bar{V}_2{}^0$'s of the products ($\Sigma\bar{V}_p{}^0$) and the $\bar{V}^0$'s of the reactants ($\Sigma\bar{V}_r{}^0$). They used this equation to calculate the effect of pressure on the ionization of water and a number of other weak electrolytes. They tabulated the $\bar{V}_2{}^0$'s and S_V*'s for a number of electrolytes in water and estimated the $\bar{V}_2{}^0$'s of electrolytes in "sea salt" (0.725 *m* NaCl) using the ionic strength principle (as well as the experimental data of Wirth and coworkers[91]).

In 1948, Jones, Taylor, and Vogel[107] measured the apparent molal expansibilities, ϕ_E's, of KCl, $BaCl_2$, and $LaCl_3$ aqueous solutions as a function of concentration and temperature. They found that the ϕ_E's *vs.* $\sqrt{c}$ were not linear for any of the salts studied (although approximately so for KCl). At 25°, the slopes, S_E*'s, of the ϕ_E's *vs.* $\sqrt{c}$ were found to be negative, although the results at low concentrations indicate that the S_E*'s may become positive (in agreement with theory). At higher temperatures, the S_E*'s were found to be positive (*i.e.*, above 55°). They found that the influence of valency on the ϕ_E's did not appear to agree with theory.

Klotz and Eckert[108] determined the ϕ_V's of H_2SO_4 in aqueous solutions. They interpreted the ϕ_V's as a function of concentration in terms of the ϕ_V's of (H^+), (HSO_4^-), and $(H^+)_2(SO_4{}^{2-})$. The $\phi_V{}^0$ of ($H^+ + HSO_4^-$) was calculated by a series of successive approximations. They calculated $\Delta\bar{V}^0 = -20.2$ cm³/mol for the volume change of ionization of the bisulfate ion at infinite dilution.

Mention should be made of some of the early methods used to evaluate ionic partial molal volumes, $\bar{V}^0$ (ion). Bernal and Fowler[109] in their classic paper on water structure demonstrated the additivity of the $\bar{V}_2{}^0$'s of electrolytes at infinite dilution. (It should be pointed out that these workers report $\bar{V}^0$'s in units of Å³/ion pair which have frequently been misquoted in units of cm³/mol.) They determined the absolute partial molal volumes of ions using a method that assumes the ratio of the partial molal volumes of the ions of a given electrolyte, MX, is equal to the ratio of the cubes of the crystal radii, $\bar{V}^0(M^+)/\bar{V}^0(X^-) = r(M^+)^3/r(X^-)^3$. Bernal and Fowler used this method on the salt CsCl and obtained $\bar{V}^0(H^+) = -3.8$ cm³/mol. Darmois[110] and Zen[111] have also used this method on the salt CsCl. Other workers have used this method on KF[112] and CsI.[113,114] Bernal and Fowler pointed out that the main contribution to the volume change associated with the solution of ions arises from the collapse of the solvent structure.

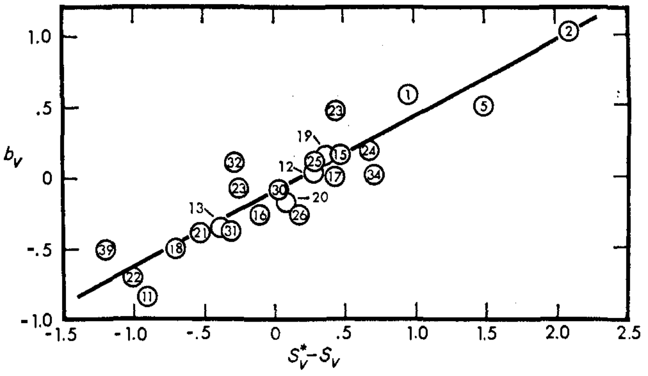

Figure 2. The deviation constants b_V's for electrolytes in water at 25° plotted *vs.* the differences between the Masson slopes and the theoretical limiting slopes, S_V* − S_V (taken from ref 81). The numbers refer to the electrolytes listed in caption for Figure 1. The solid straight line, $b_V = 0.093 + 0.522(S_V{}^* - S_V)$, was determined by a least-squares best fit.

In 1940 Wirth[115] examined the $\bar{V}^0$'s of the major ions in seawater using the Masson[79] and Root[80] equations. He was able to predict the density of seawater to ±28 ppm (from the $\bar{V}_2$'s of the major ions that make up seawater) using the ionic strength principle and the data for binary solutions. He divided the $\bar{V}$(salts) into their ionic components by assuming $\bar{V}(K^+) = \bar{V}(F^-)$, since their crystal radii are similar, which at infinite dilution gives $\bar{V}^0(H^+) = -5.1$ cm³/mol at 25°.

Fajans and Johnson[116] developed a method to separate the $\bar{V}^0$'s of electrolytes into their ionic components on the basis of the behavior of NH_4Cl solutions at 35°. From the close similarity of several properties of NH_4Cl solutions to water, they concluded that near 35° both NH_4^+ and Cl^- fit into the structure of water and $\bar{V}^0(NH_4^+) = \bar{V}^0(Cl^-) = \bar{V}^0(H_2O) = 18.0$ cm³/mol ($\bar{V}^0(H^+) = -0.2$ cm³/mol). They showed for ions either larger (*e.g.*, ClO_4^-) or smaller (*e.g.*, Na^+) than the water molecule that their partial molal expansibilities, $\bar{E}^0$'s, are strongly influenced by the breaking of the water structure. They made the first complete tabulation of the $\bar{V}^0$'s of ions in water as a function of temperature. Until recently[81] this tabulation was the most complete compilation of its kind.

In 1949, Owen and Brinkley[117] developed an extrapolation equation for ϕ_V's and $\bar{V}_2$'s of electrolytes that is based on the extended form of the Debye–Hückel equation for activity coefficients (*i.e.*, including the ion-size parameter, $\mathring{a}$)

$$\phi_V = \phi_V{}^0 + S_V\tau(\kappa a)\sqrt{c} + {}^1/_2W_V\theta(\kappa a)c + {}^1/_2K_Vc \qquad (16)$$

or

---

(103) E. A. Kelso and W. A. Felsing, *J. Amer. Chem. Soc.*, **60**, 1949 (1938).

(104) N. S. Filippova, *Usp. Khim.*, **9**, 179 (1940).

(105) N. S. Filippova, I. S. Tartakowskii, and M. E. Mansheley, *Acta Physicochim. URSS*, **14**, 257 (1941).

(106) M. Planck, *Ann. Phys. Chem.*, **32**, 462 (1887).

(107) G. Jones, F. E. Taylor, and R. C. Vogel, *J. Amer. Chem. Soc.*, **70**, 966 (1948).

(108) I. M. Klotz and C. F. Eckert, *ibid.*, **64**, 1879 (1942).

(109) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(110) E. Darmois, *J. Phys. Radium*, **2**, 2 (1941).

(111) E.-A. Zen, *Geochim. Cosmochim. Acta*, **12**, 103 (1957).

(112) Y. Kobayazi, *J. Sci. Hiroshima Univ., Ser. A*, **9**, 241 (1939).

(113) A. Eucken, *Z. Elektrochem.*, **51**, 6 (1948).

(114) O. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill, New York, N. Y., 1940.

(115) H. E. Wirth, *J. Mar. Res.*, **3**, 230 (1940).

(116) K. Fajans and O. Johnson, *J. Amer. Chem. Soc.*, **64**, 668 (1942).

(117) B. B. Owen and S. R. Brinkley, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 753 (1949).

$$\bar{V}_2 = \bar{V}_2{}^0 + \frac{{}^3/_2 S_V\sqrt{c}}{(1 + A\mathring{a}\sqrt{c})} + \frac{W_V c}{(1 + A\mathring{a}\sqrt{c})^2} + K_V c \quad (17)$$

The meanings of the various symbols are given elsewhere.[85,117] Owen and Brinkley[117] used eq 16 to extrapolate the ϕ_V's of NaCl, KCl, and HCl to infinite dilution; however, they did not use a correct value for the limiting slope, S_V. Wirth and Collier[92] also used these equations to extrapolate the ϕ_V's and $\bar{V}_2$'s of $NaClO_4$ and $HClO_4$ to infinite dilution. Owen and Brinkley[117] attributed the disagreement of the experimental $\phi_V{}^0$'s found using the Masson equation compared to their extended equation as being due to the disregard of the ion-size parameter.

This was essentially the state of affairs in molal volume work before 1957. In this year the Faraday Society held a meeting on the structural interactions in aqueous solutions and the contributions of various workers[4-10] changed the emphasis of molal volume work. The remainder of this review will be devoted to the more recent development of partial molal volume work in examining the structural interactions (*i.e.*, ion–ion, ion–solvent, and solvent–solvent) of importance in aqueous and nonaqueous solutions.

III. Ion–Ion Interactions

A. THE LIMITING LAW

The study of the concentration dependence of the apparent and partial molal volumes of electrolytes as a function of size, charge, temperature, and solvent can be very useful in examining ion–ion interactions. In this section we will review the more recent work using the apparent and partial molal volumes of electrolytes to study ion–ion interactions. The partial molal volumes, $\bar{V}_2$'s, of electrolytes are normally evaluated from density measurements. The various methods of making density measurements are reviewed elsewhere.[118-121] Only the magnetic float,[57,58,118,120-123] the hydrostatic balance,[91,96,118-120,124-126] and dilatometric[69,127] methods give data with sufficient precision to study the ϕ_V's of electrolytes in dilute solutions. The graphical methods of determining $\bar{V}_2$'s from density measurements have been described in detail elsewhere.[128] The use of the apparent molal volume, ϕ_V, to determine the partial molal volume, $\bar{V}_2$, is usually more convenient (especially for binary solutions).

As discussed in the historical development of solution volumes, between 1931 and 1957 a great controversy existed between various workers concerning the differences between the Masson eq 6 and the Redlich eq 11. In 1964, Redlich and Meyer[129] discussed the development of this controversy. They also derived theoretical values of k in water as a function of temperature based on the results of Owen and coworkers'[130] data for D (the dielectric constant) and $\partial(\ln D)/\partial P$ and the compressibility, β, data of Kell and Whalley.[131] Earlier calculations[77,78,87,89,94,95,117,132] of k in water used inaccurate β and $\partial(\ln D)/\partial P$ data.[133-135] The theoretical values for the limiting slope, k, determined by Redlich and Meyer[129] for a 1:1 electrolyte (in water) are given in Table I at 5° intervals from 0 to 70°. Values at other temperatures can be calculated from the polynomial equation (t°C).

Table I

The Debye–Hückel Theoretical Limiting Law Slope for the Apparent Molal Volume of a 1:1 Electrolyte in Water at Various Temperatures[a]

Temp, °C	*k, cm³ l.¹/² mol⁻³/²*	*Temp, °C*	*k, cm³ l.¹/² mol⁻³/²*
0	1.444	40	2.138
5	1.529	45	2.234
10	1.613	50	2.333
15	1.697	55	2.435
20	1.782	60	2.542
25	1.868	65	2.653
30	1.955	70	2.768
35	2.046		

[a] Taken from ref 129.

$$k = 1.444 + 1.6799 \times 10^{-2}t - 8.4055 \times 10^{-5}t^2 + 5.5153 \times 10^{-7}t^3 \quad (18)$$

The calculated value of $k = 1.868$ at 25° confirms the experimental value of $k = 1.86$ determined by Redlich[94] in 1940 using ϕ_V data for 1:1 electrolytes. The temperature dependence of the theoretical k's determined by Redlich and Meyer did not agree with the values determined from the earlier experimental data.[77,78] For example, at 0°, k(theoretical) = 1.444 compared to k(experimental) = 2.8, and at 50°, k(theoretical) = 2.333 compared to k(experimental) = 1.7. Thus, by 1964 most workers were convinced that the theoretical slope was approached at 25° for simple 1:1 electrolytes; however, since precise ϕ_V data were not available for polyvalent electrolytes or 1:1 electrolytes at temperatures other than 25°, the form of the valence factor and the effect of temperature on k were in doubt. Experimental and theoretical values for k in nonaqueous solvents were also in doubt owing to the lack of reliable ϕ_V data for dilute solutions and the lack of β and $\partial(\ln D)/\partial P$ data for nonaqueous solvents.

In recent years reliable apparent molal volume data in dilute aqueous solutions have confirmed both the valence factor and the temperature dependence of k. Limiting slopes

---

(118) N, Bauer and S, Z, Lewin, "Techniques of Organic Chemistry," A, Weissberger, Ed,, Interscience, New York, N. Y., 1959, p 167.

(119) H. A. Bowman and R, M, Schoonover (Appendix by M. W. Jones), *J. Res. Nat. Bur. Stand., Sect, C*, 71, 179 (1967).

(120) P. Hidnert and E, L. Peffer, "Density of Solids and Liquids," National Bureau of Standards, Circular 487, U. S. Government Printing Office, Washington, D. C., 1950.

(121) F. J. Millero, *Rev. Sci. Instrum.*, 38, 1441 (1967).

(122) F. Franks and H. T. Smith, *Trans, Faraday Soc.*, 63, 2586 (1967).

(123) D, V, Ubrich, D. W, Kupke, and J. W. Beams, *Proc. Nat, Acad. Sci, U, S.*, 52, 349 (1964).

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

(125) J. E. Desnoyers and M. Arel, *Can. J. Chem.*, 45, 359 (1967).

(126) F. Vaslow, *J. Phys. Chem.*, 70, 2286 (1966); 71, 4585 (1967).

(127) L. G. Hepler, J. M. Stokes, and R. H. Stokes, *Trans. Faraday Soc.*, 61, 20 (1965).

(128) G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, K. S. Pitzer and L, Brewer, Ed,, McGraw-Hill, New York, N. Y., 1961, p 205.

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

(130) B, B, Owen, R. C. Miller, C. E. Milner, and H. L. Cogan, *J. Phys, Chem.*, 65, 2065 (1961).

(131) G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc.* (*London*), 258, 565 (1965).

(132) O. Redlich, *J. Phys. Chem.*, 67, 496 (1963).

(133) G. Falckenberg, *Ann. Phys.*, 61, 145 (1920).

(134) S. Kyropoulous, *Z. Phys.*, 40, 507 (1926).

(135) F. E. Harris, B. W. Haycock, and B. J. Alder, *J. Phys. Chem.*, 57, 978 (1953).

of 1.868, 9.706, 14.944, 27.454, and 59.071 for 1:1, 2:1, 2:2, 3:1, and 4:1 electrolytes (respectively) have been confirmed at 25° in water. Recent work has also demonstrated that k increases in a regular manner with increasing temperature.

Hepler, Stokes, and Stokes[127] have determined the ϕ_V's of some 1:1, 3:1, and 4:1 electrolytes (NaOH, Me_4NBr, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$) in dilute (0.0002–1.0 c) aqueous solutions at 25° (using a dilatometric technique). The ϕ_V's of all the electrolytes studied by these workers were found to approach the limiting law in dilute solutions. Their results for the 3:1 and 4:1 electrolytes (respectively, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$) are shown in Figure 3. The ϕ_V's for NaOH and $K_4Fe(CN)_6$ showed positive deviations, and the ϕ_V's for Me_4NBr and $K_3Fe(CN)_6$ showed negative deviations from the limiting law in dilute solutions ($K_4Fe(CN)_6$ showed negative deviations in more concentrated solutions). The positive deviations for $K_4Fe(CN)_6$ in dilute solutions have been attributed to ion-pairing (due to the decrease in electrostriction when the ion pair is formed). They also pointed out that the ϕ_V behavior of $K_4Fe(CN)_6$ solutions at high concentrations appears to approach the behavior of a 3:1 electrolyte, indicating that a contact ion pair ($KFe(CN)_6^{3-}$) may be formed.

Braghetti and Indelli[136] have determined the ϕ_V's of some 3:1 and 4:1 electrolytes ($Na_3P_3O_9$, $K_3P_3O_9$, $Na_4P_4O_{12}$, and $K_4P_4O_{12}$) in water at 25°. Their results show that 3:1 and 4:1 electrolytes approach limiting law behavior in dilute solutions. The deviations of the 4:1 electrolytes studied by these workers are similar to the deviations found by Hepler, *et al.*,[127] for $K_4Fe(CN)_6$, and the causes may also be similar.

Franks and Smith[122] determined the ϕ_V's of a number of 1:1 electrolytes (NaCl, KCl, Me_4NBr, Et_4NBr, Pr_4NBr, and Bu_4NBr) and a 2;2 electrolyte ($MgSO_4$) in dilute aqueous solutions (0.002 to 0.1 m) at 5 and 25° using a magnetic float method. The ϕ_V's for all the electrolytes studied by these workers approach the limiting law. The deviations from the limiting law for the electrolytes NaCl, KCl, and $MgSO_4$ were found to be positive, and the deviation for the tetraalkylammonium bromides (R_4MBr's) were found to be negative. The deviations for all the electrolytes studied were more pronounced at 5° than at 25°. Franks and Smith also discussed the apparent molal expansibilities, ϕ_E's, of these electrolytes and showed that the S_E*'s for NaCl and KCl become positive in dilute solutions as required by theory. Franks and Smith's apparent molal volume work was the first to demonstrate experimentally that the theoretical limiting law is approached at temperatures other than 25°.

Dunn[137–140] determined the ϕ_V's (using the method of Hepler *et al.*[127]) of some 1:1 electrolytes (HCl, KNO_3, NaCl, KCl, KBr, KI, and Bu_4NBr), 2:1 electrolytes (Na_2SO_4, K_2SO_4, $MgCl_2$, $CaCl_2$, and $BaCl_2$), and a 3:1 electrolyte ($LaCl_3$) in dilute solution (0.001 to 1.0 m) at 25°. He also determined the ϕ_V's of some 1:1 and 2:1 electrolytes (NaCl, KCl, KBr, KI, $BaCl_2$, and $CaCl_2$) from 0 to 65° at 5° intervals. His ϕ_V results clearly demonstrate that the Debye–Hückel limiting slope is approached for 1:1 and 2;1 electrolytes over the temperature range of 0 to 65°. Positive deviations of the ϕ_V's were found for the electrolytes KNO_3, K_2SO_4, Na_2SO_4, KCl, NaCl, and KBr, and negative deviations were found for the electrolytes HCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, $LaCl_3$, KI, and Bu_4NBr at 25°. Dunn found that the deviations (*i.e.*, the b_V's) for 1:1 and 2:1 electrolytes from the limiting law become less positive (*i.e.*, $\partial b_V/\partial t$ is negative) at higher temperatures. At 0° positive deviations occur for most common 1:1 and 2:1 electrolytes, while at 50° negative deviations occur. His ϕ_V's results at 25° for $MgCl_2$, $CaCl_2$, $BaCl_2$, and $LaCl_3$ are shown in Figure 3.

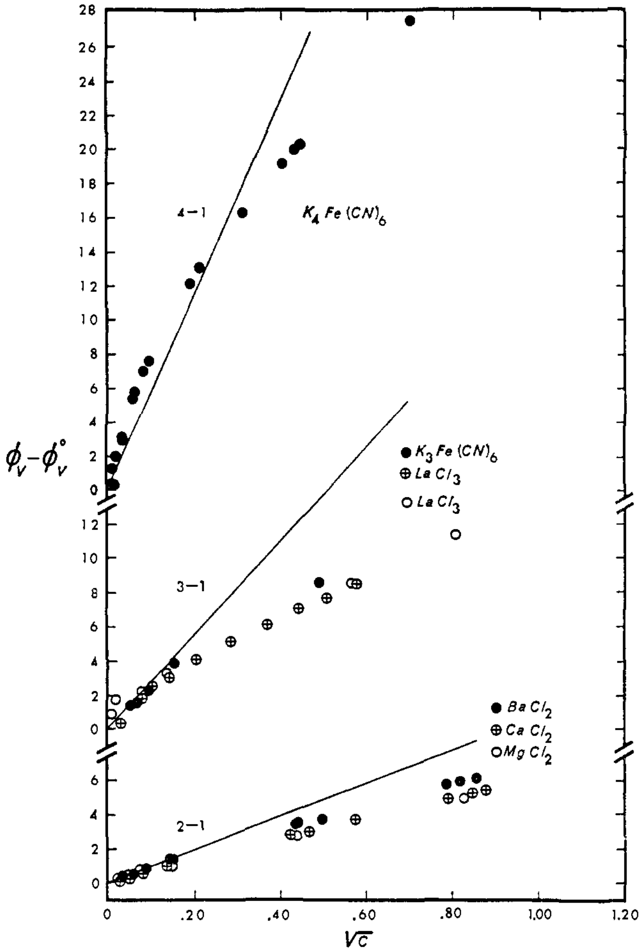

Figure 3. The relative apparent molal volumes ($\phi_V - \phi_V^0$) *vs.* $\sqrt{c}$ for some 2:1 (ref 137), 3;1 (ref 127, 137, 141), and 4:1 (ref 127) electrolytes in water at 25°. The straight lines are the Debye–Hückel limiting law slopes.

Spedding, Pikal, and Ayers[141] have determined the ϕ_V's at 25° for a number of 3:1 electrolytes (rare earth chlorides and nitrates) in dilute aqueous solutions (0.002–0.2 m) using a magnetic float method. The ϕ_V's of all the electrolytes studied by these workers approach the limiting law; however, the ϕ_V's show large negative deviations (except for $Nd(NO_3)_3$, which has positive deviations), even at low concentrations. Except for $Nd(NO_3)_3$, these deviations are consistent with the interionic attraction theory, provided the equations of Owen and Brinkley[117] are used to represent the ϕ_V's as a function of $\sqrt{c}$ (*i.e.*, using an ion-size parameter, $\mathring{a}$). The

---

(136) C. Braghetti and A. Indelli, *Ann. Chim. (Rome)*, 59, 418 (1969).

(137) L. A. Dunn, *Trans. Faraday Soc.*, 62, 2348 (1966).

(138) L. A. Dunn, Ph.D. Dissertation, University of New England, Armidale, Australia, 1967.

(139) L. A. Dunn, *Trans. Faraday Soc.*, **64**, 1898 (1968).

(140) L. A. Dunn, *ibid.*, 64, 2951 (1968).

(141) F. H. Spedding, M. J. Pikal, and B. O. Ayers, *J. Phys. Chem.*, 70, 2440 (1966).

Redlich eq 11 could not be used to extrapolate the results to infinite dilution since the b_V's are a function of concentration. Their ϕ_V's results for $LaCl_3$ at 25° are shown in Figure 3.

The recent ϕ_V work of Millero[121,142–145] also shows that the limiting law is approached in dilute aqueous solutions for the electrolytes NaF, $NaBPh_4$, Ph_4AsCl, and NaCl from 0 to 50°. The ϕ_V's for the electrolytes $NaBPh_4$ and Ph_4AsCl[144,145] at 0, 25, and 50° in dilute aqueous solutions (0.001–0.1 m) are shown in Figure 4. It is interesting to note that both salts have negative deviations from the limiting law (except for Ph_4AsCl at 0°); however, the effect of temperature on the deviations are different ($\partial b_V/\partial t$ is positive for $NaBPh_4$ and negative for Ph_4AsCl).

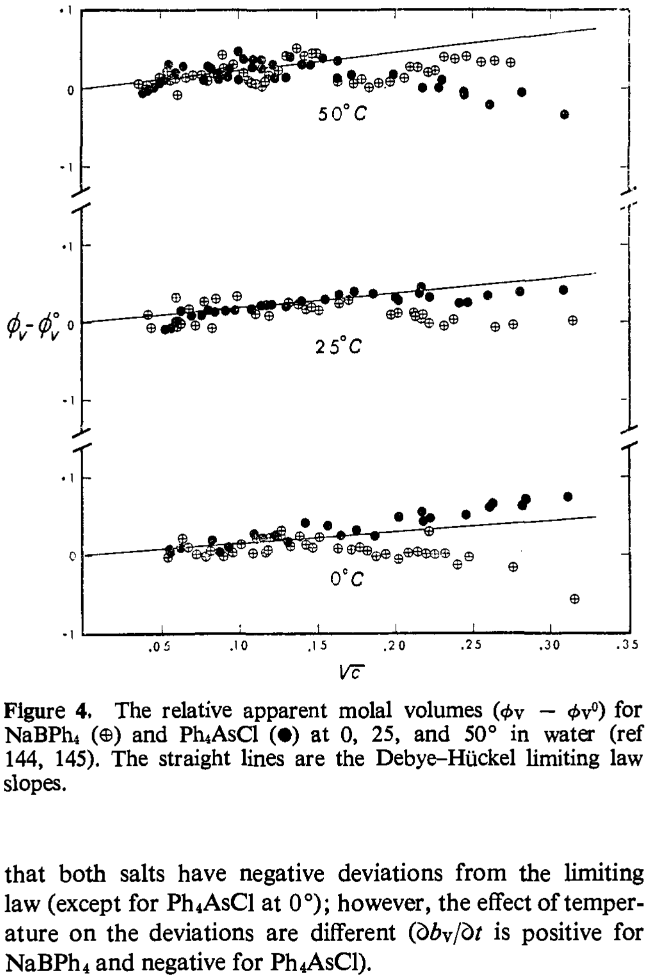

Figure 4. The relative apparent molal volumes ($\phi_V - \phi_V^0$) for $NaBPh_4$ (⊕) and Ph_4AsCl (●) at 0, 25, and 50° in water (ref 144, 145). The straight lines are the Debye–Hückel limiting law slopes.

Vaslow[126,146] has determined the ϕ_V's for the electrolytes LiCl, NaCl, KCl, RbCl, CsCl, LiB, LiI, NaBr, and NaI at 25°, LiCl, NaCl, and LiI at 5°, and LiCl at 35° in aqueous solutions. In very dilute solutions all of the electrolytes studied by Vaslow approach limiting law behavior. The ϕ_V's as a function of $\sqrt{c}$ in moderately concentrated solutions appear to go through abrupt changes in slope.

The very careful work of Conway, *et al.*,[124,146–150] on the R_4N^+ halides, the work Desnoyers, *et al.*,[125,151] on the R_4NH_3Br's and the alkali metal halides, King's work[152] on some weak acid salts, the work of Wirth, *et al.*,[153,154] on the R_4NBr's and $NaHSO_4$, and the study of Franks, *et al.*,[155,156] on some sodium alkyl sulfates also confirm the limiting law behavior of electrolytes in dilute aqueous solutions.

Theoretical and experimental S_V values in nonaqueous solvents are not generally known with the accuracy of aqueous solutions since few reliable ϕ_V data are available for dilute solutions, and reliable values for β and $\partial(\ln D)/\partial P$ are not known. Redlich and coworkers[77,78,94,129] have discussed the earlier values of S_V for methanol and ethanol electrolyte solutions. Padova and Abrahamer[157] have recently shown that the limiting law slope, $S_V = 15.77$, is approached for electrolytes (R_4N^+ halides) in methanol at 25°. Dunn[138] has recently calculated the limiting law slope in formamide ($S_V = 1.104$) at 25° from experimentally determined $\partial(\ln D)/\partial P$ data. He has also shown[138] that the ϕ_V's of KCl in formamide approach this limiting law slope.

Recent ϕ_V work[158–164] has shown that S_V^* is negative in the solvents *N*-methylacetamide,[161,164] formamide,[158–160,163] and *N*-methylpropionamide.[163] The negative S_V^*'s in formamide can be attributed to negative deviations from the limiting law (since Dunn has calculated the theoretical value to be 1.104). However, since no data are available for the β's and $\partial(\ln D)/\partial P$ in *N*-methylacetamide and *N*-methylpropionamide, it is not possible to equate these values to the limiting slope or say that the deviations are positive or negative. The fact that $\partial\phi_V/\partial\sqrt{c}$ can be negative or positive in solvents other than water does point out that the types of ion–ion interactions responsible for the deviations (positive or negative) are not unique to aqueous solutions.

B. DEVIATIONS FROM THE LIMITING LAW

The causes of the deviations of the ϕ_V's of electrolytes from the limiting law have been discussed by a number of workers in recent years. By examining the concentration dependence of the ϕ_V's of electrolytes using the Redlich eq 11, the magnitude and sign of the deviation constants (b_V's) as a function of size, charge, temperature, and solvent system can be used as a direct measure of the ion–ion interactions that cause the deviations. Table II lists the b_V's for a number of electrolytes in water at 25°.[81]

Desnoyers, Arel, Perron, and Jolicoeur[151] have determined the ϕ_V's of a number of alkali halides in water at 25° in the concentration range 0.03–0.5 M. From these results they determined the deviation constants, b_V. The b_V parameters were found to increase with the size of the cation for all the halides studied with the exception of the fluorides where

---

(142) F. J. Millero, *J. Phys. Chem.*, 71, 4567 (1967).

(143) F. J. Millero, *ibid.*, 74, 356 (1970).

(144) F. J. Millero, *J. Chem. Eng. Data*, 15, 562 (1970).

(145) F. J. Millero, *ibid.*, in press.

(146) F. Vaslow, *J. Phys. Chem.*, 73, 3745 (1969).

(147) B. E. Conway and R. E. Verrall, *ibid.*, 70, 1473 (1966).

(148) B. E. Conway and R. E. Verrall, *ibid.*, 70, 3952 (1966).

(149) R. E. Conway and L. H. Laliberte, *ibid.*, 72, 4317 (1968).

(150) R. E. Verrall and B. E. Conway, *ibid.*, 70, 3961 (1966).

(151) J. E. Desnoyers, M. Arel, G. Perron, and C. Jolicoeur, *ibid.*, 73, 3346 (1969).

(152) E. J. King, *ibid.*, 73, 1220 (1969).

(153) R. E. Lindstrom and H. E. Wirth, *ibid.*, 73, 218 (1969).

(154) H. E. Wirth, *ibid.*, 71, 2922 (1967).

(155) F. Franks and H. T. Smith, *ibid.*, 68, 3581 (1964).

(156) F. Franks, M. J. Quickenden, R. R. Ravenhill, and H. T. Smith, *ibid.*, 72, 2668 (1968).

(157) J. Padova and I. Abrahamer, *ibid.*, 71, 2112 (1967).

(158) R. Gopal and R. K. Strivastava, *ibid.*, 66, 2704 (1962).

(159) R. Gopal and R. K. Strivastava, *J. Indian Chem. Soc.*, 40, 99 (1963).

(160) R. Gopal and M. A. Siddiqi, *Z. Phys. Chem.*, 67, 122 (1969).

(161) R. Gopal and M. A. Siddiqi, *J. Phys. Chem.*, 73, 3390 (1969).

(162) F. J. Millero, *ibid.*, 72, 3209 (1968).

(163) R. Gopal and K. Singh, *Z. Phys. Chem.*, 69, 81 (1970).

(164) R. Gopal, M. A. Siddiqi, and K. Singh, personal communication, 1970.

Table II

Deviation Constants b_V for Some Electrolytes in Water at 25° [a]

Salt	b_V, *cm³ l. mol⁻²*	*Salt*	b_V, *cm³ l. mol⁻²*
HCl	−1.03	RbCl	0.17
LiF	1.1	RbBr	−0.26
LiCl	−0.36	RbI	−0.05
LiBr	−0.55	RbF	0.55
LiI	−0.76	CsCl	0.12
NaCl	0.02	CsBr	0.09
NaBr	−0.22	CsI	0.11
NaI	−0.39	CsF	0.25
NaF	0.54	NH_4Br	0.55
NaOH	0.95	Me_4NCl	−2.5
NaO_2CH	0.01	Me_4NBr	−0.79
NaO_2CCH_3	0.20	Me_4NI	0.0
$NaO_2C(CH_2)_2CH_3$	0.03	$MeNH_3Br$	−0.63
Na_2SO_4	2.96	Et_4NCl	−16.0
KF	0.52	Et_4NBr	−10.0
KCl	0.11	Et_4NI	−5.6
KBr	−0.06	$EtNH_3Br$	−0.92
KI	−0.30	*n*-Pr_4NCl	−23.8
KNO_3	0.72	*n*-Pr_4NBr	−15.0
$KClO_3$	0.42	*n*-Pr_4NI	−9.2
K_2SO_4	5.17	*n*-$PrNH_3Br$	−1.3
$K_3Fe(CN)_6$	−12.8	*n*-Bu_4NCl	−35.5
$K_4Fe(CN)_6$	−33.1	*n*-Bu_4NBr	−21.2
n-Bu_4NI	−18.0	$La(NO_3)_3$	−12.9
n-$BuNH_3Br$	−1.7	$PrCl_3$	−23.3
n-Pen_4NBr	−30.5	$NdCl_3$	−20.5
n-$PenNH_3Br$	−1.9	$Nd(NO_3)_3$	−32.4
n-$HexNH_3Br$	−2.1	$SmCl_3$	−28.4
n-$HepNH_3Br$	−2.9	$CdCl_3$	−27.3
n-$OctNH_3Br$	−3.1	$TbCl_3$	−30.0
$NaBPh_4$	−6.94	$DyCl_3$	−29.4
Ph_4AsCl	−1.75	$HoCl_3$	−24.5
$MgCl_2$	−6.3	$ErCl_3$	−25.2
$CaCl_2$	−1.25	$Er(NO_3)_3$	−31.5
$BaCl_2$	−3.21	$YbCl_3$	−20.0
$LaCl_3$	−20.8	$Yb(NO_3)_3$	−23.5

[a] Data taken from the compilation made by Millero.[81]

the opposite order is observed. They interpreted the b_V parameters and the corresponding deviations from the limiting law by using a structural interaction model. The model is based on Frank and Robinson's suggestion[165] that ion–ion interactions can be affected by the influence of ions on the structure of water. The model also considers the ideas developed by Gurney[101] with his co-sphere theory and by Frank[166,167] through his concepts of structural salting-out and salting-in. The general rule developed by these workers is as follows: "two solutes will attract each other if their structural influences, or their tendencies to orient water molecules, are compatible with each other; conversely, an incompatibility in these structural influences or tendencies will result in repulsive forces." They also used this model to account qualitatively for most excess thermodynamic functions of the R_4NX's.

Millero[148] has recently measured the ϕ_V's of NaCl in dilute solutions from 0 to 55°. From these results he determined the deviation constants b_V. The deviation constant b_V and $\bar{E}^0$ as a function of temperature were found to parallel each other (as noted by earlier workers[77,78]) in that both $\partial b_V/\partial t$ and $\partial \bar{E}^0/\partial t$ were negative. These results indicate that ion–ion interactions are related to the effect of temperature on the structure of the hydrated ions or the structure of water between the interacting ions. Cation–anion ion-pairing was examined as a possible cause for the observed deviations, and a general method of calculating association constants from $\bar{V}_2$ data was presented. Stoichiometric association constants, $K_A{}^* = 0.35$, 0.18, and 0.11, respectively, at 0, 25, and 55° were found to represent the $\bar{V}_2$ data for NaCl solutions over the concentration range from 0.25 to 1.0 *c*. Because of the large number of assumptions made in these calculations, the results should be considered with some reservations. The calculations do show that ion-pairing can be used to explain the positive deviations from the limiting law (*i.e.*, within experimental error), and the general techniques developed in this paper may prove useful in examining ion-pair formation in other salt systems (*i.e.*, where this type of ion–ion interaction is the dominant effect as adjudged from other measurements).

Lindstrom and Wirth[158] applied similar techniques to the ϕ_V's of H_2SO_4 and $NaHSO_4$ in aqueous solutions (at 25°). They estimated the dissociation quotient for the bisulfate in the volume ionic range from 0 to 4. They found $\Delta\bar{V}^0 = 21.6$ for the infinite dilution volume change for the process $H^+ + SO_4{}^{2-} \rightarrow HSO_4{}^-$. Spiro, *et al.*,[168] and Millero[169] have also examined the concentration dependence of $\bar{V}_2$ by using an ion-pairing interaction model. Many other workers[83,85,96,108,152] have used these techniques in reverse to calculate the ϕ_V's of un-ionized weak electrolytes (acids or bases). Lee[170] has recently calculated the ϕ_V of the ion pair $MgSO_4{}^0$ as a function of concentration by these methods.

Conway and Laliberte[149] have recently determined the b_V's for some electrolytes (NaF, NaCl, NaBr, Et_4NBr, and Bu_4NBr) in D_2O at 25°. For the salts NaF, NaCl, and NaBr, b_V is larger in D_2O than in H_2O, while for Et_4NBr and Bu_4NBr, b_V is larger in H_2O than in D_2O (that is, less negative). These results indicate the importance of considering the structure of the solvent when discussing b_V's or deviations from the limiting law. It should be pointed out, however, that these authors took the theoretical S_V to be the same in these two solvents, and part of these differences may be due to differences in $\partial(\ln D)/\partial P$ and β for D_2O and H_2O (*e.g.*, the β of D_2O is greater than H_2O from 0 to 65°[171] while $\partial(\ln D)/\partial P$ for D_2O and H_2O are nearly the same[172]).

Vaslow[126,146] has carefully examined the concentration dependence of some alkali halides at 5, 25, and 35°. He found (as have earlier workers[68,69,79,173]) that the ϕ_V's of these electrolytes *vs.* $\sqrt{c}$ in moderately concentrated solutions appear to go through abrupt changes in slope near 1 *N*. He attributes two possible sources for these transitions; a change in solution structure or a change in the form of the ion radial distribution

---

(165) H. S. Frank and A. L. Robinson, *J. Chem. Phys.*, 8, 933 (1940).

(166) H. S. Frank, *J. Phys. Chem.*, 67, 1554 (1963).

(167) H. S. Frank, *Z. Phys. Chem. (Leipzig)*, 228, 364 (1965).

(168) T. G. Spiro, A. Revesz, and J. Lee, *J. Amer. Chem. Soc.*, 90, 4000 (1968).

(169) F. J. Millero, *Limnol. Oceanogr.*, 14, 376 (1969).

(170) S. Lee, Ph.D. Dissertation, Yale University, University Microfilms, Ann Arbor, Mich., Ord. No. 66-4906; *Diss. Abstr. B*, 27, 131 (1966).

(171) F. J. Millero and F. K. Lepple, *J. Chem. Phys.*, 54, 946 (1971).

(172) R. L. Kay, personal communication, 1970.

(173) A. Bodanszky and W. Kauzmann, *J. Phys. Chem.*, 66, 177 (1962).

function as found by Kirkwood,[174] Although his measurements confirm that two segments exist in the ϕ_V *vs.* $\sqrt{c}$ for some salts, none of his findings can prove conclusively that these segments are due to a physical transition. Lee and Hyne[175] have recently found similar transitions in the R_4N^+ halides in ethanol–water mixtures.

In recent years many workers have studied the ϕ_V's of electrolytes that contain a hydrocarbon portion because of the peculiar effects such electrolytes appear to have on the structural properties of water. The concentration dependence of the ϕ_V's of electrolytes that contain a hydrocarbon portion (*e.g.*, the tetraalkylammonium halides, R_4NX's) appear to be abnormal when compared to the more common electrolytes (*e.g.*, the alkali halides). The ϕ_V's for the R_4NX's have been shown to have large negative deviations from the limiting law and to go through various maxima and minima as the concentration is increased. The effects of temperature on the deviation constants b_V for the large R_4NX salts have also been shown to be different from common electrolytes; *e.g.*, $\partial b_V/\partial t$ is positive for Bu_4NBr[122] and negative for NaCl.[122,140,148] The large negative deviations for the ϕ_V's of the R_4NX's from the limiting law have been attributed to ion-pairing,[127,154,176] "hydrophobic bonding,"[155] "iceberg" effects,[7,177–180] micelle formation,[154] "salting-in" effects,[124,125,147,148,151,181,182] and induced cation–cation interactions.[122,179,180,183–185]

Wen and Saito[179] determined the ϕ_V's of four symmetrical tetraalkylammonium bromides, R_4NBr's (R = Me, Et, *n*-Pr, and *n*-Bu), at 25° and one R_4NBr at 15, 25, and 35° (R = *n*-Bu). They found that the S_V^*'s were negative for all the salts studied except for Me_4NBr. At high concentrations ϕ_V's *vs.* $\sqrt{c}$ for *n*-Bu_4NBr and *n*-Pr_4NBr were found to go through a minimum, and then the ϕ_V's increased. They discussed these results in terms of solute–water interactions (with specific emphasis on the effect of the R_4N^+ ion on the structure of water), and for *n*-Bu_4NBr the results were discussed in terms of a "clathrate-like" structure. Wen and Saito[180] have determined the ϕ_V's of two symmetrical tetraethanolammonium halides. Their results are in agreement with the notion that the substitution of the terminal CH_3 groups with OH diminishes the peculiarities of the R_4N^+ ions in water (*i.e.*, with the terminal OH groups the cations have a smaller effect on the structure of water).

Conway, Verrall, and Desnoyers[124] have determined the ϕ_V's of a series of R_4NCl's, R_4NBr's, and R_4NI's at 25° over the concentration range of 0.01 to ~0.1 *m*. They fitted their ϕ_V results to the Redlich equation, and all the salts give large negative values for the deviation constants b_V's. The b_V's of the R_4NX's were found to increase with increasing size of the X^- ion and to decrease with increasing size of the R_4N^+ ion. They showed that the expansion of Owen and Brinkley[117] equation yields

$$\bar{V}_2 - \bar{V}_2^0 = {}^3/_2 S_V\sqrt{c} + [K_V + W_V - S_V A\mathring{a}]c + [S_V(A\mathring{a})^2 - 2AW_V]c^{3/2} + \ldots \quad (19)$$

Thus, the deviation constant b_V of the Redlich equation can be given by

$$b_V = [K_V + W_V - S_V A\mathring{a}]/2 \quad (20)$$

Since $\mathring{a}$ is related to the size of the ion or $\bar{V}^0$, this equation explains why b_V decreases with increasing size (shown in Figure 1). Exploratory calculations by these workers indicate that the negative b_V values for the R_4N^+ halides cannot be satisfactorily accounted for by any choice for the distance of closest approach (related to the $A\mathring{a}$ term) or the effect of pressure on the distance of closest approach $\partial(\ln \mathring{a})/\partial P$ (related to the W_V term). For example, they found for $\mathring{a}$ equal to the crystal radii, $\partial(\ln \mathring{a})/\partial P$ varies from $+40 \times 10^{-12}$ dyn^{-1} cm^2 for Me_4N^+ to -450×10^{-12} dyn^{-1} cm^2 for Am_4N^+. This term is unknown for any of the R_4N^+ ions; however, one would expect $\partial(\ln \mathring{a})/\partial P$ to become more negative the larger the ion (it would hardly vary as much as indicated). They point out that the main contributions for the deviations from the limiting law in moderately concentrated solutions are associated with long-range coulombic interactions, primary hydration of ions, mutual salting-out, and ion-pairing. They suggested that the cause of the large negative b_V's for these R_4N^+ halides could be attributed to a mutual salting-out effect (*i.e.*, the cause of the b_V's increasing with increasing size of the halide ion) and a mutual salting-in effect (*i.e.*, the cause of the b_V's decreasing with increasing size of the R_4N^+ ion).

Desnoyers and Arel[125] have determined the ϕ_V's of a large number of RNH_3Br salts (R varies from H to *n*-octyl) at 25° using a sinker method. They found that negative deviations occur for all the salts they studied. The negative b_V's were found to be approximately a linear function of the number of carbon atoms (nc) in the R chain ($b_V = -0.36 - 0.33$nc). They interpreted the deviations for these salts as being due to mutual salting-in effects. For the larger salts (R = *n*-C_7H_{15} and *n*-C_8H_{17}), $\phi_V - S_V\sqrt{c}$ initially decreases, goes through a minimum, and then increases very rapidly as $\sqrt{c}$ increases. They attribute this behavior to micelle formation and discuss the causes of the positive volume change for micelle formation. They conclude that the ϕ_V's of all "hydrophobic" solutes (nonelectrolytes, large symmetrical ions, or colloidal surfactants) behave in a similar manner after the long-range coulombic interactions are considered. They interpret the ϕ_V concentration dependence of these solutes in terms of the true volume of the solute and a competition between the increase in "ice-likeness" of the solvent and loss of free volume near the solute during "hydrophobic" hydration.

Franks and Smith[155] have determined the $\bar{V}_2$'s of sodium dodecyl sulfate and the sodium salt of 2′-hydroxy-5′-sulfophenylazo-2-naphthol in the submicellar concentration range. They found that the $\bar{V}_2$'s of both salts showed negative deviations from the limiting law even at low concentrations. The results were interpreted by postulating the formation of dimers as a result of hydrophobic bonding and as a resultant shift in the hydration equilibrium. Desnoyers and Arel,[125] however, have questioned these conclusions (as have Franks and Smith in their later paper[122]).

---

(174) J. G. Kirkwood, *Chem. Rev.*, 19, 275 (1936).

(175) I. Lee and J. C. Hyne, *Can. J. Chem.*, 46, 2333 (1968).

(176) B. J. Levien, *Aust. J. Chem.*, 18, 1161 (1965).

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

(178) S. Schiavo, B. Scrosati, and A. Tommasini, *Ric. Sci.*, 37, 211 (1967).

(179) W.-Y. Wen and S. Saito, *J. Phys. Chem.*, 68, 2639 (1964).

(180) W.-Y. Wen and S. Saito, *ibid.*, 69, 3569 (1965).

(181) B. E. Conway, J. E. Desnoyers, and A. C. Smith, *Phil. Trans. Roy. Soc.* (*London*), 256, 389 (1964).

(182) J. E. Desnoyers and C. Jolicoeur, "Modern Aspects of Electrochemistry," J. O. M. Bockris and B. E. Conway, Ed., Plenum Publishing Co., New York, N. Y., 1969, p 1.

(183) W.-Y. Wen and K. Nara, *J. Phys. Chem.*, 71, 3907 (1967).

(184) W.-Y. Wen, K. Nara, and R. H. Wood, *ibid.*, 72, 3048 (1968).

(185) W.-Y. Wen and K. Nara, *ibid.*, 72, 1137 (1968).

Franks and Smith[122] determined the ϕ_V's of some R_4NBr's in dilute solutions. They showed that the ϕ_V's approach limiting law behavior in very dilute solutions. The ϕ_V's for the R_4NBr's showed large negative deviations that appeared to be more pronounced at low temperatures (*i.e.*, more negative). They interpreted the concentration dependence of the ϕ_V's for the R_4NBr's in terms of cation–cation interactions, induced by cooperative ion–water interactions. The ϕ_E's for the R_4NBr's were shown to yield large positive deviations from the limiting law behavior (while the ϕ_V's for NaCl and KCl show negative deviations from the limiting law).

Franks, Quickenden, Ravenhill, and Smith[156] showed that the ϕ_V's of sodium decyl, sodium dodecyl, and sodium tetradecyl sulfates at 5 and 25° in the submicellar range show large negative deviations from the limiting law. For the salt sodium dodecyl sufate the ϕ_V's above micellization (which is accompanied by a large positive volume change) fall with increasing concentration. The negative deviations of the ϕ_V's in the submicellar range have been attributed to cooperative "hydrophobic" hydration effects, while the negative deviation above the micellization may be due to changes in hydration which arise from change in the degree of counterion binding or changes in the distribution of micellar sizes.

Wirth[154] has examined the ϕ_V's of the R_4NBr's using an ion association model. He found that the observed ϕ_V's for Me_4NBr from 0 to 5 *m* could be explained using an ion-pairing association constant, $K_A = 1.24$. In addition to ion-pairing he found that the formation of dimers (quadruple ions) and micelles could be used to explain the concentration dependence of the ϕ_V's of Et_4NBr and Pr_4NBr (for Et_4NBr, $K_A = 2.40$ and $K_D = 0.99$ from 0.1 to 1.5 *m*, and for Pr_4NBr, $K_A = 3.1$ and $K_D = 2.0$ from 0.1 to 1.0 *m*). Above 4.0 *m* Et_4NBr and 1.4 *m* Pr_4NBr solutions, he believes micelle formation is important. Although Wirth has demonstrated that ion association can be used to explain the negative deviations from the limiting law, the type of ion pair formed is not the classical type since the volume change for most electrostatic ion pairs is positive (one would thus expect positive deviations from the limiting law). The formation of an ion pair with a volume less than the free ions is possible, however, for the large R_4N^+ ions since the smaller anion could penetrate the aliphatic portion of the cation when the ion pair is formed, causing the volume to decrease.

Broadwater and Evans[186] have determined the ϕ_V's for $[Bu_3N(CH_2)_8NBu_3]Br_2$ in water at 10 and 25° since it may serve as a model for the Bu_4N^+–Bu_4N^+ cation–cation pair. They found that the volume behavior of this electrolyte was similar to that observed for Bu_4NBr (*i.e.*, the ϕ_V *vs.* $\sqrt{c}$ was found to go through a minimum). They concluded that the observed effects indicate that this large divalent salt affects water structure in the same manner as Bu_4NBr.

Gopal and Siddiqi[187,188] determined ϕ_V's of some R_4NI's (R = Me, Et, Pr, and Bu) in water from 25 to 80°. The slopes (S_V^*'s) of the ϕ_V *vs.* $\sqrt{c}$ for all the R_4NI's (except Me_4NBr) were negative at all temperatures. The slopes (S_V^*'s) become more negative at higher temperatures for the Et_4N^+, Pr_4N^+, and Bu_4N^+ iodides; however, for Me_4NI, S_V^* increases with increasing temperature. Since the theoretical slope, S_V, is positive over the entire temperature range, these results indicate that $\partial b_V/\partial t$ is negative for the larger R_4NI's. These results are not in agreement with the ϕ_V work of Wen and Saito[179] for Bu_4NBr (who found $S_V^* = -9.0$, -8.4, and -6.3, at 15, 25, and 30°, respectively) and the results of Franks and Smith[122] who found that $\partial b_V/\partial t$ was positive for the larger R_4NBr's. This discrepancy may be due to the fact that Gopal and Siddiqi used the I^- salt, while Wen and Saito and Franks and Smith used the Br^- salt, or due to the different temperature ranges covered. Gopal and Siddiqi[187,188] made the mistake (frequently made) of discussing the concentration dependence of the ϕ_V's of electrolytes in terms of ion–solvent interactions instead of ion–ion interactions.

Schiavo, *et al.*,[178] have also determined the $\bar{V}$'s of R_4N^+ halides as a function of temperature (15–65°). They used their results to calculate the $\bar{V}$ of H_2O ($\bar{V}_1$) in these solutions and examined the $\bar{V}_1$'s as a function of temperature and concentration. They found that the $\bar{V}_1$'s increased with increasing concentration). The relative partial molal volume of water ($\bar{V}_1 - \bar{V}_1^0$) for the Et_4Br, Pr_4Br, and Bu_4Br solutions decreased with increasing temperature, while for Me_4Br ($\bar{V}_1 - \bar{V}_1^0$) was found to be nearly independent of temperature. They used the Frank and Wen[7] model for the structure of water and ion–water interactions to interpret their results.

Millero[144,145] has recently determined the ϕ_V's of the symmetrical salts $NaPh_4B$ and Ph_4AsCl at 0, 25, and 50° in dilute aqueous solutions (0.001–0.1 *m*) using a magnetic float method. The relative apparent molal volumes, $\phi_V - \phi_V^0$, for these salts given are shown in Figure 4. Both salts show negative deviations from the limiting law except for Ph_4AsCl at 0°. The $\partial b_V/\partial t$ for $NaPh_4B$ is positive, while $\partial_V/\partial t$ is negative for Ph_4AsCl. These results demonstrate the problems involved in attributing the causes of the deviations from the limiting law to a specific type of interaction. For example, one might attribute the negative deviations for these salts as being due to cation–cation (Ph_4As^+–Ph_4As^+) or anion–anion (Ph_4B^-–Ph_4B^-) interactions in a manner similar to the large R_4N^+ halides; the temperature dependence of b_V's, however, indicates that the ion–ion interactions in the Ph_4AsCl system are more like NaCl than Bu_4NCl. These results point out the necessity of considering all the possible ion–ion interactions (cation–cation, anion–anion, cation–anion, and higher order triplet interactions) when discussing the deviations from the limiting law.

Recently, studies have been made on the ϕ_V's of the R_4N^+ halides in formamide,[160,163] *N*-methylacetamide,[161] dimethylformamide,[114] and methanol.[157] Gopal, *et al.*,[160,161,163] determined the ϕ_V's of some R_4NI's in formamide and *N*-methylacetamide at 25–80°. The slopes of ϕ_V's *vs.* $\sqrt{c}$ for the small R_4N^+ halides were positive, while the larger R_4N^+ halides had negative slopes. The increase in the ϕ_V's as a function of concentration for the small R_4N^+ halides (and other electrolytes) were attributed to electrostatic ion–solvent interactions, while the decrease in the ϕ_V's for the larger R_4NI's were attributed to cation–cation and cation–anion penetrations. They also point out that the "locking up" of solvent molecules inside the void space formed by the large R_4N^+ ions could also attribute to the decrease in the ϕ_V's of the large R_4N^+ halides. Since Dunn's work[188] yields a positive limiting slope in formamide (1.104), the negative S_V^*'s found for the R_4NI's in this solvent indicate that the deviations (*i.e.*, b_V) are also negative. Since they did not publish the S_V^*'s values in formamide, it is not possible to determine if the smaller R_4NI's with positive S_V^*'s also have negative deviations (*i.e.*, if S_V^* is less than S_V). Since the theo-

---

(186) T. L. Broadwater and D. F. Evans, *J. Phys. Chem.*, 73, 164 (1969).

(187) R. Gopal and A. K. Rastogi, *J. Indian Chem. Soc.*, 43, 269 (1966).

(188) R. Gopal and M. A. Siddiqi, *J. Phys. Chem.*, 72, 1814 (1968).

retical slope is unknown in *N*-methylacetamide and dimethylformamide, it is not possible to determine if the deviations are positive or negative for the R_4N^+ halides in this solvent. For example, if the S_V is more negative than the S_V^*'s for the large R_4NI's in *N*-methylacetamide or dimethylformamide, the deviations can be positive even though S_V^* is negative.

Padova and Abrahamer[157] determined the ϕ_V's of NH_4Br, some R_4NBr's (R = Et, *n*-Pr, *n*-Bu), Me_4NCl, and Et_4NCl at 25° in MeOH. All the salts were found to follow the Root and Masson equations over the concentration range studied (0.05–1.0 *c*). The ϕ_V's were found to increase with increasing concentration unlike the results in water, formamide, and *N*-methylacetamide. The S_V^* values were found to be lower than the theoretical slope of 15.77, which means that the b_V's are negative or all the salts have negative deviations from the limiting law. Thus, although S_V^* is not negative for the R_4NX's in methanol as in water, the b_V's are negative in both solvents. These results point out the importance of considering only the deviations (*i.e.*, b_V) from the limiting law and not the magnitude or sign of S_V^* when discussing the relative ion–ion interactions in various solvents.

Until experimental $\partial(\ln D)/\partial P$ and β become available for solvents other than water, the relative ion–ion interactions in various solvents will remain unclear. Further ϕ_V work in very dilute solutions using the magnetic float or dilatometric techniques for some simple 1:1 electrolytes in nonaqueous solvents may be a faster and easier way of determining the limiting slopes. Limiting slopes are also necessary to examine the relative causes of the deviations from the limiting law since only b_V and $(S_V^* - S_V)$ (which appear to be related, see Figure 2) are directly related to the deviations.

In recent years some workers[127,136,140,141,169] have found that the ϕ_V's as a function of concentration for some 2:1, 3:1, and 4:1 electrolytes cannot be adequately represented by the Redlich eq 11 (*i.e.*, b_V appears to be a function of concentration). Some workers[141,148,189] have thus expressed the ϕ_V's or $\bar{V}_2$'s as a function of concentration using the Owen and Brinkley eq 16, which includes the ion-size parameter, $\mathring{a}$. Spedding, *et al.*,[141] determined the ion-size parameter from conductance data, while Millero[148] and Indelli and DeSantis[189] allow the ion-size parameter to be an adjustable parameter.

C. MULTICOMPONENT ELECTROLYTE SOLUTIONS

Because of the importance of multicomponent electrolyte solutions in systems such as seawater and body fluids, many recent volume studies[168–170,183–185,190–210] have been made on solutions made up of several electrolytes. The measurement of the excess volume of mixing electrolyte solutions is an excellent way of studying ion–ion interactions. If the measurements are made on electrolytes with a common ion, the pair-wise cation–cation and anion–anion interactions of like charged ions can be conveniently studied. The Brønsted theory of specific interactions,[211] extended by Guggenheim[212] and Scatchard and Prentiss,[213] has also been tested by measuring the volume of mixing electrolyte solutions. The volume properties of mixed electrolyte solutions are normally represented by the mean apparent molal volume, Φ, which is given by the equation

$$\Phi = (V - n_1 V_1^0)/(m_2 + m_3) \tag{21}$$

The mixture rule of Young and Smith[214] describing the mean apparent molal volume

$$\Phi = (m_2\phi_2 + m_3\phi_3)/(m_2 + m_3) \tag{22}$$

(where m_i is the molality of electrolyte *i* and ϕ_i is the apparent molal volume of electrolyte *i* at ionic strength equal to $m_2 + m_3$ in the binary mixture) has been shown to accurately represent the molal volume data of mixed salt solutions of Wirth and coworkers.[91,92,207,208] Wirth[91] and Young and Smith[214] found that a correction term, *D*, had to be added to eq 22 for some systems. The suggested form of *D* is

$$D = y_2 y_3 k I \tag{23}$$

where *k* is a constant, $y_2 = m_2/(m_2 + m_3)$, and *I* is the ionic strength. *D* can also be calculated from the observed volume change, ΔV, of mixing two electrolyte solutions at constant ionic strength ($D = \Delta V/(m_2 + m_3)$).

Wirth and coworkers[92,207,208] have found that at high ionic strengths *D* had to be represented by the relation

$$D = k y_2 y_3 + k' y_2^2 y_3 \tag{24}$$

when *D* was not symmetrical around a mole fraction of y_2 = 0.5. They also showed that Young, Wu, and Krawetz's cross square rule[10] holds for *D* at y_2 = 0.5 for a number of electrolyte mixtures. Wirth and LoSurdo[208] have examined the effect of temperature (5–45°) on the volume of mixing various electrolyte solutions at various ionic strengths. *D* at y_2 = 0.5 was found to decrease with increasing temperature for all the systems they studied except for Na_2SO_4–LiCl–H_2O mixtures, because of the formation of the ion pair $LiSO_4^-$.[208] For the volume of mixing 1:1 and 2:1 electrolytes, the results are normally expressed in terms of equivalents. For the mean equivalent volume, one has

---

(189) A. Indelli and R. DeSantis, *J. Chem. Phys.*, **51**, 2782 (1969).

(190) W. Davis, Jr., J. E. Mrochek, and C. J. Hardy, *J. Inorg. Nucl. Chem.*, **28**, 2001 (1966).

(191) I. W. Duedall and P. K. Weyl, *Rev. Sci. Instrum.*, **38**, 528 (1965).

(192) I. W. Duedall and P. K. Weyl, *Limnol. Oceanogr.*, **12**, 52 (1967).

(193) I. W. Duedall, *Environ. Sci. Technol.*, **2**, 706 (1968).

(194) Yu. A. Epikhin, M. S. Stakhanova, and M. Kh. Karapetyants, *Zh. Fiz. Khim.*, **38**, 692 (1964).

(195) Yu. A. Epikhin, M. S. Stakhanova, and M. Kh. Karapetyants, *ibid.*, **40**, 377 (1966).

(196) B. M. Fabuss, A. Korosi, and A. K. M. Shamsul, *J. Chem. Eng. Data*, **11**, 325 (1966).

(197) Ya. Ya. Fialkov, *Ukr. Khim. Zh.*, **29**, 576 (1963).

(198) Ya. Ya. Failkov, *Zh. Obshch. Khim.*, **33**, 3461 (1963).

(199) Ya. Ya. Fialkov and V. S. Zhikharev, *ibid.*, **33**, 3789 (1963).

(200) Ya. Ya. Fialkov and G. N. Fenerli, *Ukr. Khim. Zh.*, **31**, 141, 258 (1965).

(201) T. H. Lilley, *Trans. Faraday Soc.*, **64**, 2947 (1968).

(202) F. J. Millero in "A Treatise on Skin," Vol. I, H. R. Elden, Ed., Wiley-Interscience, New York, N. Y., 1971, Chapter 11.

(203) R. M. Rush and G. Scatchard, *J. Phys. Chem.*, **65**, 2240 (1961).

(204) F. Saegusa, *Sci. Rep. Tohoku Univ., Ser. 1*, **34**, 192 (1950).

(205) M. S. Stakhanova and V. A. Vasilev, *Zh. Fiz. Khim.*, **37**, 1568 (1963); *Chem. Abstr.*, **59**, 10811 (1963).

(206) A. Tsujioka, *Nippon Kagaku Zasshi*, **80**, 467 (1959).

(207) H. E. Wirth, R. E. Lindstrom, and J. N. Johnson, *J. Phys. Chem.*, **67**, 2339 (1963).

(208) H. E. Wirth and A. LoSurdo, *J. Chem. Eng. Data*, **13**, 226 (1968).

(209) L. A. Woolf, *J. Phys. Chem.*, **67**, 273 (1963).

(210) Y. C. Wu, *ibid.*, **74**, 3781 (1970).

(211) J. N. Brønsted, *J. Amer. Chem. Soc.*, **44**, 877 (1922); **45**, 2898 (1923).

(212) E. A. Guggenheim, *Phil. Mag.*, **19**, 448 (1935).

(213) G. Scatchard and S. S. Prentiss, *J. Amer. Chem. Soc.*, **54**, 2696 (1932).

(214) T. F. Young and M. B. Smith, *J. Phys. Chem.*, **58**, 716 (1954).

$$\Phi' = (V - n_1\bar{V}_1^0)/(e_2 + e_3) \qquad (25)$$

where e_2 and e_3 are the equivalents of salts 2 and 3. Young's rule then becomes

$$\Phi' = (e_2\phi_2' + e_3\phi_3')/(e_2 + e_3) = E_2\phi_2' + E_3\phi_3' \qquad (26)$$

where ϕ_2' and ϕ_3' are the apparent equivalent volumes of the electrolytes 2 and 3 at the ionic strength corresponding to $e_2 + e_3$ and E_2 and E_3 are the equivalent fractions, $E_2 = e_2/(e_2 + e_3)$.

Friedman[215,216] predicted (by using Mayer's[217] ionic solution theory) that like charged ions should have specific interactions and that these interactions should be more important than triplet interactions for many systems. By differentiating the excess free energy of mixing, ΔG_m^{ex}, with respect to pressure, the volume of mixing can be obtained.

$$\Delta V_m(y,I) = I^2y(1 - y)[v_0 + v_1(1 - 2y) + v_2(1 - 2y)^2 + \ldots] \qquad (27)$$

where I is the molal ionic strength, y is the solute mole fraction, and $v_0 = RT(\partial g_0/\partial P)$, $v_1 = RT(\partial g_1/\partial P)$, etc., are interaction parameters.[216] v_0 is a measure of the magnitude of the interaction, and v_1, etc., are measures of the triplet and higher order terms. When the higher order terms are small, ΔV_m plotted *vs.* y is nearly a perfect parabola with a maximum at $y = 0.5$ (using the notation of Wirth and Young and Smith, $\Delta V_m = D$ and $k = v_0$). Wen and coworkers[183–185] have measured the ΔV_m for a number of electrolytes, including the tetraalkylammonium salts in water and deuterium oxide. They analyzed their results in terms of Friedman's ionic solution theory.[215,216] Their results indicate that cation–cation interactions are responsible for the anomalous volume properties of the tetraalkylammonium halides.

The volumes (and heats) of mixing for various aqueous electrolyte solutions have recently been reviewed.[202,218] A study has been made on the mean apparent molal volumes of several electrolytes in *N*-methylpropionamide,[162] and it was found that the deviations from Young's rule were very large compared to aqueous solutions (*i.e.*, ΔV_m was very large). Many other studies[219–224] have been made on the volumes of mixing aqueous solutions (or the volumes of multicomponent salt solutions); however, the results are not very reliable.

IV. Ion–Solvent Interactions

A. AVAILABLE INFINITE DILUTION PARTIAL MOLAL VOLUME DATA

The partial molal volumes, $\bar{V}_2^0 = \phi_V^0$, of electrolytes at infinite dilution (where ion–ion interactions vanish) are particularly appropriate to study ion–solvent interactions, since volume properties are easy to visualize geometrically and relatively easy to determine experimentally. The study of the partial molal volumes of electrolytes at infinite dilution as a function of size, charge, temperature, and solvent system can be very useful in obtaining a better understanding of ion–solvent and solvent–solvent interactions.

To obtain reliable $\bar{V}^0$ data (needed to study ion–solvent interactions), it is necessary to measure the density difference between the solution, d, and the pure solvent, d_0, for dilute solutions with great precision and also to extrapolate the ϕ_V's to infinite dilution with the aid of the Debye–Hückel limiting law (*i.e.*, when possible).

A critical analysis of the presently available ϕ_V data in water[81] leads to the conclusion that only a few of the published results are suitable for the accurate evaluation of ϕ_V^0's. Most of the literature values quoted in standard texts[85] were derived by using the Masson equation on ϕ_V data obtained from density measurements at relatively high ($c > 0.1$) concentrations where the limiting law is invalid. As is readily apparent from Figure 3, if one extrapolates the high concentration ϕ_V's to infinite dilution (*i.e.*, using the linear portion above $\sqrt{c} = 0.5$), errors of 1.5, 3.0, and 8.0 cm³/mol are obtained for 2:1, 3:1, and 4:1 electrolytes, respectively. Braghetti and Indelli's[136] ϕ_V work on 3:1 and 4:1 electrolytes indicates that an improper extrapolation to infinite dilution from the linear portion of ϕ_V *vs.* $\sqrt{c}$ in high concentrations can cause errors of as much as 10 cm³/mol (*i.e.*, for a 4:1 electrolyte).

Since the deviations for most 1:1 electrolytes from the limiting law are small at 25°, previous workers have been fortunate to obtain reasonable infinite dilution $\bar{V}_2^0$ values using the Masson equation. For example, one obtains $\bar{V}^0 = 16.62$ cm³/mol for NaCl[122,126,140,143] at 25° using the Redlich equation and 16.67 cm³/mol using the Masson equation.[91] At 0°, however, the differences are considerably greater (*e.g.*, $\bar{V}^0 = 12.90$ cm³/mol using the Redlich equation[140,143] and $\bar{V}^0 = 12.36$ cm³/mol using the Masson equation[74] for NaCl). For some 1:1 electrolytes whose ϕ_V's show large deviation from the limiting law, an improper extrapolation can cause the $\bar{V}^0$'s to be in error by as much as 3.0 cm³/mol ($\phi_V^0 = 300.37$ cm³/mol using the Redlich equation and $\phi_V^0 = 302.9$ cm³/mol using the Masson equation for Bu_4NBr at 25°).[81] It is unfortunate that many workers continue to publish $\bar{V}^0$'s that have been determined by an improper extrapolation to infinite dilution without giving the original ϕ_V data from which more reliable values can be determined. The $\bar{V}^0$'s of electrolytes in nonaqueous solvents are less reliable than in aqueous solutions owing to the lack of precise ϕ_V data for dilute solutions (as well as a lack of $\partial(\ln D)/\partial P$ and β data to calculate the theoretical limiting slope, S_V).

In recent years, there has been a number of very careful ϕ_V studies[81] in dilute aqueous solutions that have yielded very reliable infinite dilution values. Recent work has also yielded $\bar{V}^0$ data for a number of electrolytes over a wide temperature range.[81] The very careful ϕ_V work in recent years by Braghetti and Indelli,[136] Conway, *et al.*,[124,147–150] Desnoyers, *et al.*,[125,151] Dunn,[137–140] Franks, *et al.*,[122,155,156] Hepler, *et al.*,[127] King,[152] Levien,[176] Wirth, *et al.*,[153,154,207,208] Millero, *et al.*,[121,142–145,225–229] Spedding, *et al.*,[141] and Vaslow[126,146]

---

(215) H. L. Friedman, *J. Chem. Phys.*, 32, 1351 (1960).

(216) H. L. Friedman, "Ionic Solution Theory," Interscience, New York, N. Y., 1962.

(217) J. D. Mayer, *J. Chem. Phys.*, 18, 1426 (1950).

(218) H. S. Harned and R. A. Robinson, "Multicomponent Electrolyte Solutions," Pegamon Press, Oxford, England, 1968.

(219) R. W. Bremner, T. G. Thompson, and C. L. Utterback, *J. Amer. Chem. Soc.*, 60, 2616 (1938).

(220) C. Drucker, *Ark. Kemi, Mineral Geol.*, **14A**, 1 (1941).

(221) J. Ingham, *J. Chem. Soc.*, 542, 1917, 2059, 2381 (1928).

(222) A. Kozdon, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 16, 209 (1968).

(223) J. Regnauld, *L'Institut*, 111 (1865).

(224) Q. Zaslavskii, E. Standel, and V. Tavarov, *Z. Anal. Chem.*, 180, 241 (1929); 186, 171 (1930).

(225) F. J. Millero and W. Drost-Hansen, *J. Phys. Chem.*, 72, 1758 (1968).

(226) F. J. Millero, W. Drost-Hansen, and L. Korson, *ibid.*, 72, 2251 (1968).

(227) F. J. Millero, *ibid.*, 72, 4589 (1968).

Table III

Conventional Partial Molal Volumes of Ions in Water at 0, 25, and 50° [a]

Ion	$\bar{V}^0$*(conv)* *cm*^{3} *mol*$^{-1}$	*Ion*	$\bar{V}^0$*(conv),* *cm*^{3} *mol*$^{-1}$	*Ion*	$\bar{V}^0$*(conv),* *cm*^{3} *mol*$^{-1}$	*Ion*	$\bar{V}^0$*(conv)* *cm*^{3} *mol*$^{-1}$
			0°				
$\mathrm{H^+}$	0.0	$\mathrm{Me_4N^+}$	88.59	$\mathrm{Ba^{2+}}$	−15.79	$\mathrm{SCN^-}$	31.3
$\mathrm{Li^+}$	−0.45	$\mathrm{Et_4N^+}$	147.47	$\mathrm{La^{3+}}$	−40.71	$\mathrm{PhSO_3^-}$	93.8
$\mathrm{Na^+}$	−3.51	$n\text{-}\mathrm{Pr_4N^+}$	212.53	$\mathrm{F^-}$	−2.21	$\mathrm{MnO_4}$	38.5
$\mathrm{K^+}$	7.17	$n\text{-}\mathrm{Bu_4N^+}$	271.10	$\mathrm{Cl^-}$	16.45	$\mathrm{ClO_4^-}$	40.7
$\mathrm{Rb^+}$	12.31	$\mathrm{Ph_4As^+}$	291.12	$\mathrm{Br^-}$	23.06	$\mathrm{CO_3^{2-}}$	−9.8
$\mathrm{Cs^+}$	19.68	$\mathrm{Mg^{2+}}$	−21.81	$\mathrm{I^-}$	33.57	$\mathrm{SO_4^{2-}}$	11.1
$\mathrm{Ag^+}$	−2.14	$\mathrm{Ca^{2+}}$	−19.84	$\mathrm{OH^-}$	−6.8	$\mathrm{CrO_4^{2-}}$	13.6
$\mathrm{NH_4^+}$	17.47	$\mathrm{Sr^{2+}}$	−20.77	$\mathrm{NO_3^-}$	26.6	$\mathrm{Ph_4B^-}$	270.67
			25°				
$\mathrm{H^+}$	0.00	$\mathrm{Be^{2+}}$	−12.0	$\mathrm{Pr^{3+}}$	−42.53	$\mathrm{ClO_3^-}$	36.66
$\mathrm{Li^+}$	−0.88	$\mathrm{Mg^{2+}}$	−21.17	$\mathrm{La^{3+}}$	−39.10	$\mathrm{BrO_3^-}$	35.3
$\mathrm{Na^+}$	−1.21	$\mathrm{Ni^{2+}}$	−24.0	$\mathrm{Th^{4+}}$	−53.5	$\mathrm{IO_3^-}$	25.3
$\mathrm{K^+}$	9.02	$\mathrm{Co^{2+}}$	−24.0	$\mathrm{F^-}$	−1.16	$\mathrm{ClO_4^-}$	44.12
$\mathrm{Rb^+}$	14.07	$\mathrm{Zn^{2+}}$	−21.6	$\mathrm{Cl^-}$	17.83	$\mathrm{HSO_4^-}$	35.67
$\mathrm{Cs^+}$	21.34	$\mathrm{Fe^{2+}}$	−24.7	$\mathrm{Br^-}$	24.71	$\mathrm{HSeO_4^-}$	31.1
$\mathrm{Ag^+}$	−0.7	$\mathrm{Mn^{2+}}$	−17.7	$\mathrm{I^-}$	36.22	$\mathrm{H_2PO_4^-}$	29.1
$\mathrm{Tl^+}$	10.6	$\mathrm{Cu^{2+}}$	−27.76	$\mathrm{OH^-}$	−4.04	$\mathrm{H_2AsO_4^-}$	35.2
$\mathrm{NH_4^+}$	17.86	$\mathrm{Cd^{2+}}$	−20.0	$\mathrm{Ph_4B^-}$	277.62	$p\text{-}\mathrm{CH_3PhSO_3^-}$	119.6
$\mathrm{Me_4N^+}$	89.57	$\mathrm{Ca^{2+}}$	−17.85	$\mathrm{ReO_4^-}$	48.18	$\mathrm{PhO^-}$	68.7
$\mathrm{Et_4N^+}$	149.12	$\mathrm{Hg^{2+}}$	−19.3	$\mathrm{OCN^-}$	26.12	$\mathrm{S^{2-}}$	−8.2
$n\text{-}\mathrm{Pr_4N^+}$	214.44	$\mathrm{Sr^{2+}}$	−18.16	$\mathrm{SeCN^-}$	49.68	$\mathrm{SO_4^{2-}}$	13.98
$n\text{-}\mathrm{Bu_4N^+}$	275.66	$\mathrm{Pb^{2+}}$	−15.5	$\mathrm{BF_4^-}$	44.18	$\mathrm{SeO_4^{2-}}$	21.0
$\mathrm{Ph_4As^+}$	300.65	$\mathrm{Ba^{2+}}$	−12.47	$\mathrm{SO_3F^-}$	47.93	$\mathrm{CO_3^{2-}}$	−4.3
$n\text{-}\mathrm{Am_4N^+}$	339.2	$\mathrm{Al^{3+}}$	−42.2	$\mathrm{SO_3NH_2^-}$	41.49	$\mathrm{CrO_4^{2-}}$	19.7
$\mathrm{MeNH_3^+}$	36.11	$\mathrm{Fe^{3+}}$	−43.7	$\mathrm{NO_3^-}$	29.00	$\mathrm{WO_4^{2-}}$	25.7
$\mathrm{EtNH_3^+}$	52.94	$\mathrm{Cr^{3+}}$	−39.5	$\mathrm{NO_2^-}$	26.2	$\mathrm{MoO_4^{2-}}$	28.9
$n\text{-}\mathrm{PrNH_3^+}$	69.44	$\mathrm{Yb^{3+}}$	−44.22	$\mathrm{SCN^-}$	35.7	$\mathrm{PtCl_6^{2-}}$	150.0
$n\text{-}\mathrm{BuNH_3^+}$	85.50	$\mathrm{Er^{3+}}$	−42.86	$\mathrm{CHO_2^-}$	26.27	$\mathrm{HPO_4^{2-}}$	7.7
$n\text{-}\mathrm{PenNH_3^+}$	101.44	$\mathrm{Ho^{3+}}$	−41.76	$\mathrm{CH_3CO_2^-}$	40.46	$\mathrm{S_2O_3^{2-}}$	34.0
$n\text{-}\mathrm{HexNH_3^+}$	117.33	$\mathrm{Dy^{3+}}$	−40.83	$\mathrm{CH_3CH_2CO_2^-}$	54.0	$\mathrm{C_2O_4^{2-}}$	16.0
$n\text{-}\mathrm{HepNH_3^+}$	133.23	$\mathrm{Tb^{3+}}$	−40.24	$\mathrm{CH(CH_2)_2CO_2^-}$	70.40	$\mathrm{Cr_2O_7^{2-}}$	73.0
$n\text{-}\mathrm{OctNH_3}$	149.15	$\mathrm{Gd^{3+}}$	−40.41	$\mathrm{PhSO_3^-}$	108.9	$\mathrm{SO_3^{2-}}$	8.9
$\mathrm{(HOEt)_4N^+}$	152.0	$\mathrm{Sm^{3+}}$	−42.33	$\mathrm{HCO_3^-}$	23.4	$\mathrm{AsO_4^{3-}}$	−15.6
$\mathrm{[Bu_3N(CH_2)_8NBu_3]^{2+}}$	528.5	$\mathrm{Nd^{3+}}$	−43.31	$\mathrm{MnO_4^-}$	42.5	$\mathrm{Fe(CN)_6^{3-}}$	120.8
						$\mathrm{Fe(CN)_6^{2-}}$	74.0
			50°				
$\mathrm{H^+}$	0.00	$\mathrm{NH_4^+}$	19.20	$\mathrm{Mg^{2+}}$	−20.90	$\mathrm{Br^-}$	25.49
$\mathrm{Li^+}$	−1.24	$\mathrm{Me_4N^+}$	91.2	$\mathrm{Ca^{2+}}$	−18.22	$\mathrm{I^-}$	37.52
$\mathrm{Na^+}$	−0.30	$\mathrm{Et_4N^+}$	151.6	$\mathrm{Sr^{2+}}$	−17.69	$\mathrm{OH^-}$	−4.35
$\mathrm{K^+}$	9.57	$n\text{-}\mathrm{Pr_4N^+}$	218.9	$\mathrm{Ba^{2+}}$	−11.73	$\mathrm{NO_3^-}$	30.3
$\mathrm{Rb^+}$	14.71	$n\text{-}\mathrm{Bu_4N^+}$	285.0	$\mathrm{F^-}$	−1.4	$\mathrm{ClO_4^-}$	45.1
$\mathrm{Cs^+}$	22.22	$\mathrm{Ph_4As^+}$	309.82	$\mathrm{Cl^-}$	18.00	$\mathrm{SO_4^{2-}}$	16.0$_3$
						$\mathrm{Ph_4B^-}$	283.93

[a] Taken from the compilation of $\bar{V}^0$ data given in ref 81.

have yielded reliable $\bar{V}^0$ data for a number of electrolytes in aqueous solutions. Ellis and coworkers[230–234] density studies have yielded $\bar{V}^0$'s for a number of 1:1 and 2:1 electrolytes in water over a wide temperature range (25–200°). A number of less accurate studies of the $\bar{V}^0$'s of electrolytes in water have been made in recent years.[186–188, 235–249] The recent compilation[81] contains a complete and up-to-date list of the $\bar{V}^0$'s of electrolytes in aqueous solution from 0 to 200°. Tables III and IV give the partial molal volumes of electrolytes in water from

---

(228) F. J. Millero and W. Drost-Hansen, *J. Chem. Eng. Data*, **13**, 300 (1968).

(229) F. J. Millero, *J. Phys. Chem.*, **73**, 2417 (1969).

(230) A. J. Ellis, *Chem. Commun.*, 21, 802 (1966).

(231) A. J. Ellis, *J. Chem. Soc. A*, 1579 (1966).

(232) A. J. Ellis, *ibid.*, *A*, 660 (1967).

(233) A. J. Ellis, *ibid.*, *A*, 1138 (1968).

(234) A. J. Ellis and I. M. McFadden, *Chem. Commun.*, **47**, 516 (1968).

(235) E. F. Balashova, *Uch. Zap. Mord. Gos. Univ.*, **60**, 16 (1967).

(236) T. Batuccas, *Rev. Real. Acad. Cienc. Exactas, Fis. Natur. Madrid*, 60, 407 (1966).

(237) I. A. Dibrov, V. P. Mashovets, and R. P. Matveeva, *J. Appl. Chem. USSR*, 37, 38 (1964).

(238) A. Iguchi, *Kagaku Sochi*, **11**, 58 (1969).

(239) T. Isono, *Rika Gaku Kenkyusho Hokoku*, 42, 238 (1966).

(240) A. Katoyama, T. Matsuura, N. Kuroki, and K. Konishi, *Sen-i Gakkaishi*, 21, 598 (1965).

(241) I. N. Maksimova, *Zh. Fiz. Khim.*, 39, 551 (1965).

(242) B. F. Markov, V. D. Prisyazhnyi, and S. V. Volvok, *Fiz. Khim. Elektrochim. Rasplav. Solei*, 70 (1965).

(243) V. P. Mashovets, I. A. Dibrov, B. S. Kragali, and R. P. Matveeva, *Zh. Prikl. Khim. (Leningrad)*, 38, 2344 (1965).

(244) M. A. Raqib, *Sci. Res.*, **5**, 237 (1968).

(245) A. V. Satyavati, *Indian J. Pure Appl. Phys.*, 6, 248 (1968).

(246) W. R. Gilkerson and J. L. Stewart, *J. Phys. Chem.*, **65**, 1465 (1961).

Table IV

The Conventional Partial Molal Volumes of Ions in Water from 75 to 200° ($cm^3\ mol^{-1}$)[a]

Ion	*75°*	*100°*	*125°*	*150°*	*175°*	*200°*
H^+	0.0	0.0	0.0	0.0	0.0	0.0
Li^+	−1.8	−2.7	−3.6	−4.7	−7.0	−8.1
Na^+	0.8	0.8	0.9	1.2	0.5	−0.1
K^+	10.3	9.5	9.4	9.3	7.8	7.3
Cs^+	23.2	23.0	23.2	23.5	22.3	23.1
NH_4^+	19.5	19.5	19.3	19.1	18.8	20.0
Me_4N^+	95.8	. . .	. . .	. . .	. . .	. . .
Et_4N^+	159.3	. . .	. . .	. . .	. . .	. . .
n-Pr_4N^+	227.5	. . .	. . .	. . .	. . .	. . .
n-Bu_4N^+	304.1	. . .	. . .	. . .	. . .	. . .
Mg^{2+}	−21.7	−23.4	−26.0	−29.0	−34.0	−37.0
Ca^{2+}	−19.1	−20.0	−23.7	−25.7	−27.0	−30.7
Sr^{2+}	−16.8	−17.4	−19.8	−22.4	−25.5	−29.0
Ba^{2+}	−7.7	−8.1	−10.5	−11.9	−15.0	−17.0
F^-	−3.1	−3.7	−6.4	−10.3	−14.4	−21.3
Cl^-	17.4	16.0	14.1	11.2	7.0	0.5
Br^-	25.1	24.9	23.9	21.5	19.2	13.0
I^-	37.2	38.7	37.5	35.8	34.6	30.2
OH^-	−5.2	. . .	. . .	. . .	. . .	. . .
NO_3^-	30.7	31.9	31.6	30.0	28.2	22.3
ClO_4^-	46.9	47.9	48.6	48.2	46.5	43.0
SO_4^{2-}	13.8	11.5	6.2	−0.7	−10.3	−22.9

[a] Taken from the compilation of $\bar{V}^0$ data given in ref 81.

0 to 200° at 25° intervals (given in ionic form). Recent work has also been done on the $\bar{V}^0$'s of polyelectrolytes,[250-252] clays,[253] and surface-active electrolytes[155,156,254-260] in aqueous solutions. The earlier work on the $\bar{V}^0$'s of electrolytes in nonaqueous solvents has been reviewed elsewhere.[77,94,104,105,129] The $\bar{V}^0$'s of electrolytes in acetic acid,[83] methanol,[82-84,98-100,157,229,261-265] ethanol,[71,99,264,266] propanol,[99,264] butanol,[99] formamide,[158-160,163] dimethylformamide,[164] N-methylacetamide,[161,164] acetonitrile,[267] N-methylpropionamide,[162,229] formic acid,[268] carboxylic acids,[269] CCl_4,[270] glycol,[82] nitrobenzene,[246] chlorobenzene,[246] *o*-dichlorobenzene,[246] liquid ammonia,[271,272] ethylenediamine,[273] deuterium oxide,[149,248,274] sulfuric acid,[275,276] selenic acid,[277,278] molten phosphoric acid,[279] methylamine,[103] acetone–water,[280] dioxane–water mixtures,[281-284] methanol-water mixtures,[285] ethanol-water mixtures,[102,175,280] NaCl solutions,[86,99,170,205,220,258,286] seawater,[169,191-193] 6 *M* urea,[287] and pentaerythritalwater mixtures[209] have been determined by various workers. Mention should also be made of the $\bar{V}^0$ work on amino acids[288-295] and proteins.[123,296-299] The $\bar{V}^0$'s of electrolytes in some of these solvents are given in Tables V–XIX.

B. IONIC PARTIAL MOLAL VOLUMES

The additivity of the partial molal volume of electrolytes at infinite dilution in water has been adequately demonstrated by a number of workers.[23,24,26,74,81,109,151,300] This additivity principle often extends to moderate concentrations when ion-pairing is not extensive.[81,192] Part of the difficulty of using the $\bar{V}^0$'s of electrolytes to study ion–solvent interactions arises from the problem of assigning absolute ionic partial molal volumes. Since the proton is frequently the ion that is adjusted or estimated by various methods, it is convenient to tabulate the $\bar{V}^0$(ion)'s on the conventional basis[86] by assigning $\bar{V}^0(H^+)$ a value of zero. The true absolute partial molal volume of an ion, $\bar{V}^0$(ion), of charge Z is given by

---

(247) T. Isono and R. Tamamushi, *Electrochim. Acta*, 12, 1479 (1967).
(248) R. E. Robertson, S. E. Sugamori, R. Tse, and C. Y. Wu, *Can. J. Chem.*, 44, 487 (1966).
(249) K. H. Dücker, *Ber. Bunsenges. Phys. Chem.*, 74, 416 (1970).
(250) H. Inagaki and A. Teramoto, *Makromol. Chem.*, 47, 185 (1961).
(251) N. Ise and T. Okubo, *J. Amer. Chem. Soc.*, 90, 4527 (1968).
(252) U. P. Strauss and Y. P. Leung, *ibid.*, 87, 1476 (1965).
(253) A. K. Helmy, F. F. Assaad, M. N. Hassan, and H. Sadek, *J. Phys. Chem.*, 72, 2358 (1968).
(254) L. Benjamin, *ibid.*, 70, 3790 (1966).
(255) J. M. Corkill, J. F. Goodman, and T. Walker, *Trans. Faraday Soc.*, 63, 768 (1967).
(256) L. M. Kushner, B. C. Duncan, and J. E. Hoffman, *J. Res. Nat. Bur. Stand.*, 49, 85 (1952).
(257) H. Lal, *J. Colloid Sci.*, 8, 414 (1953).
(258) D. G. Rands and J. R. Lyerla, Jr., *Trans. Ill. State Acad. Sci.*, 58, 200 (1965).
(259) K. Shinoda, and T. Soda, *J. Phys. Chem.*, 67, 2072 (1963).
(260) D. Sitgter, *J. Colloid Interface Sci.*, 23, 379 (1967).
(261) F. K. Ewart and H. R. Raikes, *J. Chem. Soc.*, 1907 (1926).
(262) C. H. Rochester and B. Rossall, *Trans. Faraday Soc.*, 65, 992 (1969).
(263) G. Schwitzg and J. Barthel, *Z. Phys. Chem.*, 68, 79 (1969).
(264) J. Sobkowski and S. Minc, *Rocz. Chem.*, 35, 1127 (1961).
(265) J. B. Stark and E. C. Gilbert, *J. Amer. Chem. Soc.*, 59, 1818 (1937).
(266) E. F. Ivanova and N. A. Ismailov, *Zh. Fiz. Khim.*, 34, 1021 (1960).
(267) R. P. T. Tomkins, E. Andalaft, and G. J. Janz, *Trans. Faraday Soc.*, 65, 1906 (1969).
(268) V. N. Fesenko, E. F. Ivanova, and G. P. Kotlyarova, *Zh. Fiz. Khim.*, 42, 2667 (1968).
(269) L. A. Kotorlenko, *Ukr. Khim. Zh.*, 33, 664 (1967).
(270) S. H. Roth, University Microfilms, Ann Arbor, Mich., Ord. No. 63-5325, 110 pp; *Diss. Abstr.*, 24, 4013 (1964).
(271) S. R. Gunn and L. G. Green, *J. Chem. Phys.*, 36, 363 (1962).
(272) S. R. Gunn and L. G. Green, *J. Amer. Chem. Soc.*, 85, 358 (1963).
(273) F. C. Schmidt, W. E. Hoffman, and W. B. Schapp, *Proc. Indiana Acad. Sci.*, 72, 127 (1962).
(274) V. S. Kogan and T. G. Omarov, *Fiz. Tverd. Tela*, 7, 933 (1965).
(275) R. H. Flowers, R. T. Gillespie, and E. A. Robinson, *J. Chem. Soc.*, 845 (1960).
(276) R. T. Gillespie, *Chem. Phys. Ionic Solutions, Selec. Invited Pap., Discuss., 1964*, 1 (1966).
(277) N. M. Selivanova and M. Kh. Karapetyants, *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.*, 6, 534 (1963).
(278) S. Wasif, *J. Chem. Soc.*, 1324 (1964).
(279) R. A. Munson and M. E. Lazarus, *J. Phys. Chem.*, 71, 3242 (1967).
(280) J. Padova, *J. Chem. Phys.*, 39, 2599 (1963).
(281) S. Devi and P. B. Das, *J. Indian Chem. Soc.*, 42, 501 (1965).
(282) H. Mohapatra and P. B. Das, *ibid.*, 44, 573 (1967).
(283) B. G. Oliver and A. N. Campbell, *Can. J. Chem.*, 47, 4207 (1969).
(284) N. C. Das, H. Mohapatra, and P. B. Das, *J. Indian Chem. Soc.*, 43, 373 (1966).
(285) N. M. Baron, *Tr. Leningrad. Tekhnol. Inst. im Lensoveta*, 37, 10, 19 (1957); *Chem. Abstr.*, 53, 2751*a* (1959); 52, 11531*i* (1958).
(286) F. Saegusa, *Sci. Rep. Tohoku Univ., Ser. 1*, 34, 192 (1950).
(287) W. A. Hargraves and G. C. Kresheck, *J. Phys. Chem.*, 73, 2349 (1969).
(288) E. J. Cohn, T. L. McMeekin, J. T. Edsall, and M. H. Blanchard, *J. Amer. Chem. Soc.*, 56, 784 (1934).
(289) M. E. Dayhoff, G. E. Perlmann, and D. A. MacInnes, *ibid.*, 74, 2515 (1952).
(290) H. D. Ellerton, G. Reinfelds, D. E. Mulcahy, and P. J. Dunlop, *J. Phys. Chem.*, 68, 398 (1964).
(291) F. T. Gucker, Jr., W. L. Ford, and C. E. Moser, *ibid.*, 43, 153 (1939).
(292) F. T. Gucker, Jr., and W. L. Ford, *ibid.*, 45, 309 (1941).
(293) F. T. Gucker, Jr., and T. W. Allen, *J. Amer. Chem. Soc.*, 64, 191 (1942).
(294) J. Jung, *Z. Phys. Chem. Abt. B*, 3, 204 (1929).
(295) H. J. V. Tyrrell and M. Kennerley, *J. Chem. Soc. A*, 2724 (1968).
(296) H. B. Bull and K. Breese, *J. Phys. Chem.*, 72, 1817 (1968).
(297) M. J. Hunter, *ibid.*, 71, 3717 (1967).
(298) W. Kauzmann, A. Bodanszky, and J. Rasper, *J. Amer. Chem. Soc.*, 84, 1777 (1962).
(299) J. Rasper and W. Kauzmann, *ibid.*, 84, 1771 (1962).
(300) A. M. Couture and K. J. Laidler, *Can. J. Chem.*, 34, 1209 (1956).

Table V

Partial Molal Volumes of Electrolytes in Methanol at 25°

Electrolyte	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$	*Electrolyte*	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$
HCl	−1.5[a]	Me_4NCl	83.0[j]
	−2.7[b]		
		Et_4NCl	140.7[j]
LiCl	−3.8[c]		
		Et_4NBr	148.0[j]
LiBr	3.5[d]		
		n-Pr_4NBr	220.0[j]
NaCl	−3.3[c]		
	2.0[b]	*n*-Bu_4NBr	286.2[j]
NaBr	5.1[e]	PipBr	91.2[e]
NaI	11.8[c]	NaOPh	50.5[b]
	12.8[d]		
KCl	7.3[f]	Na 4-bromophenol	69.0[b]
		Na 4-formylphenol	69.0[b]
KBr	15.2[g]		
	15.7[h]	Na 4-*tert*-butylphenol	118.9[b]
KI	21.9[c]	Na 3,5-di-*tert*-butylphenol	187.0[b]
	21.5[i]		
	20.8[h]		
KSCN	28.2[h]	Na 2,6-di-*tert*-butyl-4-nitrophenol	204.2[b]
$Ca(NO_3)_2$	21.0[h]	Na 2,6-di-*tert*-butyl-4-bromophenol	183.1[b]
$NaOCH_3$	2.1[b]		
NH_4Br	20.8[j]	Na 2,6-di-*tert*-butyl-4-formylphenol	197.8[b]
NH_4NO_3	32.6[h]	PyBr	71.3[e]
	31.0[e]		

[a] Taken from ref 264. [b] Taken from ref 262. [c] Taken from ref 98 and 99. [d] Taken from ref 82. [e] Taken from ref 83. [f] Recalculated using the density data given in ref 84 and 99. [g] Taken from ref 84. [h] Taken from ref 265. [i] Taken from ref 100. [j] Taken from ref 157.

$$\bar{V}^0(\text{ion}) = \bar{V}^0(\text{conv}) + Z\bar{V}^0(\text{H}^+) \tag{28}$$

where $\bar{V}^0$(conv) is the conventional partial molal volume. The estimation of the $\bar{V}^0(\text{H}^+)$ has been made by a number of methods. Panckhurst[301] and Millero[81] have recently reviewed and discussed these methods. Some of the new methods that have been used at 25° in aqueous solutions in recent years are outlined below.

Couture and Laidler[300,302] found that if they adjusted the $\bar{V}^0(\text{H}^+) = -6.0$ cm^3/mol, both cations and anions could be represented by the same semiempirical equation (eq 35). Stokes and Robinson[303] have assumed that the large monovalent anions Br^- and I^- are not hydrated and that they contribute to the volume of the system an amount due to "random close packing" (*i.e.*, $\bar{V}^0(\text{I}^-) = 4.35r^3$, where r is the Pauling crystal radius).[304] This method yields $\bar{V}^0(\text{H}^+) = -7.6$ cm^3/mol. Mukerjee[305] estimated $\bar{V}^0$(ion) by selecting the value of $\bar{V}^0(\text{H}^+)$ ($= -4.5 \pm 0.2$ cm^3/mol) that would make the $\bar{V}^0$'s of monovalent monoatomic cations and anions fall on a smooth curve as a function of the crystal radii cubed (Pauling). Padova[306,307] has assumed that the I^- ion is not hydrated and $\bar{V}^0(\text{I}^-) = \bar{V}^0(\text{int}) = 37.1$ cm^3/mol, where $\bar{V}^0$(int) is the intrinsic partial molal volume. Padova[306,307] calculated $\bar{V}^0$(int) for various ions from compressibility data on salt solutions by assuming $\bar{V}^0$(int) for H^+ to be zero. Noyes[308] assumed that when an ion is sufficiently large, $\bar{V}^0$(elect) can be calculated from the Drude–Nernst equation. He used the following semiempirical equations to estimate $\bar{V}^0(\text{H}^+)$

$$\bar{V}^0(\text{int}) - \bar{V}^0(\text{conv}) = \bar{V}^0(\text{H}^+) + 4.175/r + C_2/r^2 \text{ for cations} \tag{29}$$

$$\bar{V}^0(\text{conv}) - \bar{V}^0(\text{int}) = \bar{V}^0(\text{H}^+) - 4.175/r + A_2/r^2 \text{ for anions} \tag{30}$$

where C_2 and A_2 are empirical constants. By assuming various forms for $\bar{V}^0$(int), *e.g.*, $\bar{V}^0(\text{int}) = 2.52r^3 + Jr^2$ or $\bar{V}^0(\text{int}) = 2.52(r + a)^3$, $\bar{V}^0(\text{H}^+)$, C_2, A_2, and J or a were evaluated using a least-squares "best" fit. This method yields $\bar{V}^0(\text{H}^+) = -2.8$ cm^3/mol, with $J = 3.63$, $C_2 = -4.56$, and $A_2 = -27.11$ using Pauling radii.[81] Panckhurst has also used this method.[301] Glueckauf[309] has assumed that $\bar{V}^0(\text{int}) = 2.52(r + 0.55)^3$ and that $\bar{V}^0(\text{elect}) = B''/\bar{r}$ (where $\bar{r} = r(\text{ion}) + r(\text{H}_2\text{O})$). By plotting the $\bar{V}^0$'s for the alkali metal chlorides minus $\bar{V}^0$(int) of the cation (Na^+ to Cs^+ *vs.* $1/\bar{r}$ and extrapolating to $1/\bar{r} = 0$, he obtained $\bar{V}^0(\text{Cl}^-) = 22.3$ cm^3/mol or $\bar{V}^0(\text{H}^+) = -4.5$ cm^3/mol. Conway, Verrall, and Desnoyers[124,310] assumed that the plot of the $\bar{V}^0$'s of R_4NX *vs.* the molecular weight of the cation, R_4N^+, is a straight line. They obtained the $\bar{V}^0$ of X^- by extrapolating to zero molecular weight and found $\bar{V}^0(\text{H}^+) = -6.0$ cm^3/mol. Millero and Drost-Hansen[225] have used this method for the R_4NBr's at 5 and 25° determined by Franks and Smith.[122] From these results they obtained $\bar{E}^0(\text{H}^+) = -0.010$ cm^3/(mol deg) at 15°. Panckhurst[301] has criticized the use of the molecular weight of the cation as the independent variable and cited other possible choices such as carbon number.[311] King[312] has recently modified this method of determining ionic $\bar{V}^0$'s using a technique that avoids the criticism raised by Panckhurst.[301] His method is based on the concept of van der Waals volumes, V_w, and packing densities, f, of ions, which are related to the $\bar{V}^0$(ion)'s by the equation

$$f = V_w/\bar{V}^0(\text{ion}) \tag{31}$$

For salts with cation V_w's greater than 50 cm^3/mol, he finds that the linear equation

$$\bar{V}^0(\text{R}_3\text{NHX}) - \bar{V}^0(\text{HX}) = (1/f^+)V_w(\text{R}_3\text{NH}^+) - \bar{V}^0(\text{H}^+) \tag{32}$$

can adequately represent the $\bar{V}^0$ data for some 22 salts containing 13 different cations (where $\bar{V}^0$(HX)'s are the partial molal volumes of the hydrohalic acids, $\bar{V}^0(\text{R}_3\text{NHX})$'s are the partial molal volumes of the alkylammonium halides, and f^+ is the packing density of the large cations). Using a C–N bond length of 1.465 Å, he obtains $\bar{V}^0(\text{H}^+) = -4.9 \pm 0.7$ cm^3/mol ($f^+ = 0.655 \pm 0.003$); while using a C–N bond length of 1.520

---

(301) M. H. Panckhurst, *Rev. Pure Appl. Chem.*, 19, 45 (1969).

(302) A. M. Couture and K. J. Laidler, *Can. J. Chem.*, 35, 207 (1957).

(303) R. H. Stokes and R. A. Robinson, *Trans. Faraday Soc.*, 53, 301 (1957).

(304) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(305) P. Mukerjee, *J. Phys. Chem.*, 65, 740, 744 (1961).

(306) J. Padova, *J. Chem. Phys.*, 39, 1552 (1963).

(307) J. Padova, *ibid.*, 40, 691 (1964).

(308) R. M. Noyes, *J. Amer. Chem. Soc.*, 86, 971 (1964).

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

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

(311) The criticisms of Panckhurst[301] regarding the extrapolation method of Desnoyers, Verrall, and Conway[124,310] have recently been refuted by Desnoyers and coworkers, personal communication, 1970.

(312) E. J. King, *J. Phys. Chem.*, 74, 4590 (1970).

Table VI

Partial Molal Volumes of Electrolytes in Formamide at Various Temperatures

	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$						
Electrolyte	*25°*	*30°*	*35°*	*40°*	*50°*	*60°*	*70°*
LiCl	19.6^a	...	21.6^b	22.0^b	21.0^b	20.1^b	19.0^b
NaCl	21.1^c	...	...	...	...	...	...
NaBr	28.0^c	...	...	...	...	...	...
NaI	39.8_5^c	...	...	...	...	...	...
$NaNO_3$	33.5_5^c	...	...	...	...	...	...
KCl	32.0^c	...	...	...	...	...	...
KBr	38.9^c	...	...	...	...	...	...
KI	50.7_5^c	...	51.0^b	51.2^b	51.4^b	50.1^b	48.8^b
KNO_3	44.1^c	...	...	...	...	...	...
RbCl	35.9^a	...	...	...	...	...	...
RbBr	42.6^a	...	...	...	...	...	...
RbI	54.6_5^a	...	...	...	...	...	...
$RbNO_3$	48.2_5^a	...	...	...	...	...	...
CsCl	42.3^a	...	...	...	...	...	...
CsBr	49.3^a	...	...	...	...	...	...
CsI	61.0_5^a	...	...	...	...	...	...
$CsNO_3$	54.6_5^a	...	...	...	...	...	...
Et_4NI	185.5^b	186.0^b	186.6^b	187.1^b	187.6^b	188.1^b	188.5^b
n-Pr_4NI	255.5^b	257.0^b	258.4^b	259.4^b	261.0^b	262.2^b	263.2^b
n-Bu_4NI	322.4^b	324.2^b	325.8^b	325.2^b	329.2^b	331.0^b	333.1^b
n-Pen_4NI	394.0^b	396.5^b	398.5^b	400.5^b	402.2^b	403.6^b	404.6^b
n-Hex_4NI	...	...	463.6^b	465.4^b	468.6^b	472.1^b	475.0^b
NH_4Cl	37.2^c	...	...	...	...	...	...
NH_4Br	44.0_5^c	...	...	...	...	...	...
NH_4I	49.2^c	...	...	...	...	...	...

^{a} Taken from ref 159. ^{b} Taken from ref 160. ^{c} Taken from ref 158.

Table VII

Partial Molal Volumes of Electrolytes in *N*-Methylacetamide at Various Temperatures

	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$						
Electrolyte	*35°*	*40°*	*45°*	*50°*	*60°*	*70°*	*80°*
LiCl^a	20.5	20.2	20.0	19.7	19.2	18.4	17.8
NaCl^b	26.0	...	...	...	...	...	...
NaBr^b	32.6	...	...	...	...	...	...
$NaNO_3$^{b}	35.0	...	...	...	...	...	...
NaI^b	42.0	...	...	...	...	...	...
KBr^b	40.2	...	...	...	...	...	...
KI^{a,b}	45.9,^{a} 45.0^b	46.2^a	46.5^a	46.7^a	46.4^a	45.4^a	44.8^a
KNO_3^{b}	42.8	...	...	...	...	...	...
NH_4Cl^{b}	35.5	...	...	...	...	...	...
NH_4Br^{b}	44.7	...	...	...	...	...	...
NH_4I^{b}	51.7	...	...	...	...	...	...
NH_4NO_3^{b}	47.3	...	...	...	...	...	...
$Sr(NO_3)_2$^{b}	54.6	...	...	...	...	...	...
$Ba(NO_3)_2$^{b}	57.8	...	...	...	...	...	...
Et_4NI^{a}	175.4	177.1	178.2	179.9	181.9	182.8	183.7
n-Pr_4NI^{a}	247.5	249.2	251.0	252.5	254.8	256.0	256.9
n-Bu_4NI^{a}	322.9	324.6	325.8	327.0	329.0	330.6	331.8
n-Pen_4NI^{a}	391.1	393.4	395.6	397.8	402.1	406.2	409.9
n-Hex_4NI^{a}	461.2	463.1	464.7	466.4	468.7	471.1	473.4
n-Hep_4NI^{a}	527.3	530.0	532.4	535.4	539.4	543.5	547.6

^{a} Taken from ref 161. ^{b} Taken from ref 164.

Å, he obtains $\bar{V}^0(H^+) = -4.2 \pm 0.8$ cm^3/mol. Millero[313] has recently examined the use of the $\bar{V}^0$ of the salt Ph_4AsBPh_4 as a means of determining ionic partial molal volumes. He found $\bar{V}^0(H^+) = -4.1$ cm^3/mol using Bernal and Fowler's methods[109] using radii determined from conductance data (*i.e.*, Stokes radii); $\bar{V}^0(H^+) = -4.4$ to -6.6 cm^3/mol using King's methods[312] $[\bar{V}^0(Ph_4As^+)/\bar{V}^0(BPh_4^-) = V_w(Ph_4As^+)/V_w(BPh_4^-)]$; and $\bar{V}^0(H^+) = -4.9$ cm^3/mol using tetrahedral

---

(313) F. J. Millero, *J. Phys. Chem.*, **75**, 280 (1971).

Table VIII

Partial Molal Volumes of Electrolytes in Deuterium Oxide at Various Temperatures

Electrolyte	$\bar{V}^0$, *cm³ mol⁻¹* 25°	20°	15°	10°	5°
NaF	−3.79,[a] −3.12[b]	−3.71[b]	−4.62[b]	−5.11[b]	−6.19[b]
NaCl	15.76[a]	...	...	...	...
NaBr	23.30[a]	...	...	...	...
NaI	33.84[b]	33.42[b]	31.59[b]	30.61[b]	29.02[b]
$NaPhSO_3$	101.77[b]	...	99.37[b]	98.13[b]	97.37[b]
Et_4NBr	174.53[a]	...	...	...	...
n-Bu_4NBr	301.90[a]	...	...	...	...

[a] Taken from ref 149. [b] Taken from ref 248. As pointed out in by Desnoyers (ref 346) these results are not very reliable because of errors in the calculations. The results for $NaPhSO_3$ at 5 and 10° were actually made at 8 and 11°, respectively.

Table IX

Partial Molal Volumes of Electrolytes in 35.1‰ Salinity Seawater and 0.725 *m*, NaCl Solutions at 25° [a]

	$\bar{V}^0$, *cm³ mol⁻¹*			
	Experimental		*Estimated*	
Electrolyte	*Seawater (35.1‰)*	*0.725 m NaCl*	*Owen and Brinkley*[e]	*Millero*[f]
HCl	...	19.6[c]	...	20.1
NaCl	18.9[b]	19.0[c,d]	...	18.8
KCl	29.2[b]	29.3[c]	...	28.9
NaBr	...	25.8[d]	...	25.7
KBr	...	36.2[c]	...	35.8
KI	...	...	47.3	47.4
KOH	...	...	8.4	7.2
$NaNO_3$	30.5[b]	...	...	30.0
KNO_3	40.7[b]	...	41.1	40.1
$KHCO_3$	37.4[b]	...	36.0	34.0
Na_2SO_4	21.0[b]	20.6[d]	21.0	15.4
K_2SO_4	41.6[b]	41.4[c]	...	35.6
$MgCl_2$	19.6[b]	19.3[d]	18.4	19.6
$CaCl_2$	22.0[b]	23.0[d]	22.6	22.0
$BaCl_2$	...	...	27.1	27.0
$MgSO_4$	2.9[b]	1.9[d]	...	−2.6
$Ca(NO_3)_2$	45.1[b]	...	...	44.4
Na_2CO_3	...	...	1.5	−2.4

[a] 35.1‰ salinity seawater (salinity = total solids in parts per thousand) is assumed to be equivalent to 0.725 *m* NaCl. [b] Taken from ref 192. [c] Taken from the calculations made by Owen and Brinkley (ref 86) from the $\bar{V}$ measurements of Wirth (ref 91). [d] Taken from ref 170. [e] Estimated by Owen and Brinkley (ref 86). [f] Estimates for the "free" ions made by Millero (ref 169).

Table X

Partial Molal Volumes of Electrolytes in *N*-Methylpropionamide at Various Temperatures[a]

Electrolyte	$\bar{V}^0$, *cm³ mol⁻¹* 15°	20°	25°	30°	35°	40°
HOBz	...	...	100.2	...	...	...
NaCl	...	...	30.7	...	...	...
NaBr	...	...	35.8	...	...	...
$NaNO_3$	40.6	40.3	39.6	40.1	39.9	39.7
NaOBz	...	...	103.6	...	...	...
KCl	...	...	35.5	...	...	...
KBr	...	...	40.9	...	...	...

[a] Taken from ref 162.

Table XI

Partial Molal Volumes of Electrolytes in Monomethylamine at Various Temperatures[a]

Electrolyte	$\bar{V}^0$, *cm³ mol⁻¹* 0°	10°	17.5°	18.0°	25°
LiCl	−12.36	−15.59	−17.51	...	−19.21
$NaNO_3$	17.45	14.80	...	13.42	12.32

[a] Taken from ref 103.

Table XII

Partial Molal Volumes of Electrolytes in Dioxane–Water Mixtures[a]

Electrolyte	$\bar{V}^0$, *cm³ mol⁻¹*	*Composition*[c]	*Electrolyte*	$\bar{V}^0$, *cm³ mol⁻¹*	*Composition*[c]
NaCl[a]	17.0	10.0	K_2SO_4[b]	125.0	10.0
	12.5	20.0		125.0	20.0
	12.5	30.0			
			$SrCl_2$[b]	19.5	10.0
KCl[a]	25.5	10.0		15.0	20.0
	24.0	20.0		12.5	30.0
	21.2$_5$	30.0			
Na_2SO_4[b]	74.5	10.0			
	76.0	20.0			
	79.5	30.0			

[a] Taken from ref 284 (composition in wt % and temperature at 40°). [b] Taken from ref 281 and 282 (composition in wt % and temperature at 35°). [c] In per cent dioxane.

Table XIII

Partial Molal Volumes of Electrolytes in Acetone–Water Mixtures at 25°

Electrolyte	$\bar{V}^0$, *cm³ mol⁻¹*	*Composition*[b]	*Electrolyte*	$\bar{V}^0$, *cm³ mol⁻¹*	*Composition*[b]
NaAc	43.1	8.5	$MnCl_2$	26.7	8.5
	30.2	21.2		17.0	21.2
KAc	44.7	8.5	$Mg(Ac)_2$	63.0	8.5
	41.9	21.2		52.2	21.2
Na_2SO_4	25.5	8.5	$Ba(Ac)_2$	76.2	8.5
	15.4	21.2		61.4	21.2
$MgSO_4$	8.3	8.5			
	−16.5	21.2			

[a] Taken from ref 280 (composition in wt %). [b] In per cent acetone.

covalent radii for >B< and >As< and the equation $\bar{V}^0(PhAs^+) - \bar{V}^0(BPh_4^-) = 2.52r(>As<)^3 - 2.52r(>B<)$.[31]

Zana and Yeager[314,315] have determined the $\bar{V}^0$'s of a large number of ions, including $\bar{V}^0(H^+)$, from ionic vibration potential measurements. For the proton they obtained $\bar{V}^0 = -5.4$ cm³/mol. As pointed out by Mukerjee, Zana and Yeager's results appear to be the only experimentally determined values which do not depend entirely on $\bar{V}^0$ data. In 1966, Mukerjee[316] summarized the various estimates made for $\bar{V}^0(H^+)$ in water at 25°. He showed that the average value of $\bar{V}^0(H^+) = -4.5 \pm 1.2$ cm³/mol agreed very well with the earlier value[305] he estimated and with the experimental value

---

(314) R. Zana and E. Yeager, *J. Phys. Chem.*, 70, 954 (1966).
(315) R. Zana and E. Yeager, *ibid.*, 71, 521, 4241 (1967).
(316) P. Mukerjee, *ibid.*, 70, 2708 (1966).

Table XIV

Partial Molal Volumes of Electrolytes in Ethanol–Water Mixtures

Electrolyte	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$	*Composition*^{d}	*Electrolyte*	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$	*Composition*^{d}
NaAc^a	32.7	8.5	$BaCl_2$^{b}	22.5	20.0
	34.9	18.5		29.1	40.0
				31.3	50.0
KAc^a	47.5	8.5		25.8	60.0
	46.9	18.5			
			Me_4NCl^{c}	98.1	10.0
Na_2SO_4^{a}	21.1	8.5		85.7	20.0
	28.0	18.5		80.7	30.0
				88.7	40.0
$MgSO_4$^{a}	−0.4	8.5			
	1.4	18.5	Et_4NCl^{c}	156.0	10.0
				153.7	20.0
$MnCl_2$^{a}	21.4	8.5		152.0	30.0
	25.7	18.5		152.8	40.0
Mg(Ac)$_2$^{a}	51.5	8.5	n-Pr_4NCl^{c}	219.0	10.0
	61.4	18.5		218.3	20.0
				219.5	30.0
Ba(Ac)$_2$^{a}	72.9	8.5		214.7	40.0
	76.4	18.5			
			n-Bu_4NCl^{c}	286.8	10.0
$SrCl_2$^{b}	32.77	20.0		286.4	20.0
	33.8	40.0		288.5	30.0
	34.8	60.0		277.7	40.0
	31.8	80.0			

[a] Taken from ref 281 (composition in weight and temperature at 25°). [b] Taken from ref 102 (composition in weight and temperature at 25°). [c] Taken from ref 175 (composition in mole % and temperature at 50.2°). [d] In per cent ethanol.

Table XV

Partial Molal Volumes of Electrolytes in Molten Phosphoric Acid at 80° [a]

Electrolyte	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$	*Electrolyte*	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$
LiH_2PO_4	48.6	$LiClO_4$	51.8
NaH_2PO_4	50.8	$HClO_4$	54.4
KH_2PO_4	57.8	$Mg(H_2PO_4)_2$	87.1
$KHSO_4$	59.1	H_2O	17.4

[a] Taken from ref 279.

Table XVI

Partial Molal Volumes of Electrolytes in Sulfuric Acid at 25° [a]

Electrolyte	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$	*Electrolyte*	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$
$LiHSO_4$	47	$TlHSO_4$	62
$NaHSO_4$	46	NH_4HSO_4	59
$KHSO_4$	53	$H_3O^+HSO_4^-$	61
$RbHSO_4$	59	$Ca(HSO_4)_2$	84
$CsHSO_4$	68	$Sr(HSO_4)_2$	87
$AgHSO_4$	53	$Ba(HSO_4)_2$	96

[a] Taken from ref 275.

Table XVII

Partial Molal Volumes of Electrolytes in Selenic Acid at 35° [a]

Electrolyte	$\bar{V}^0$, *cm*^{3} *mol*$^{-1}$
$NaHSeO_4$	57.62
$KHSeO_4$	61.87
NH_4HSeO_4	68.15

[a] Taken from ref 278.

Table XVIII

Partial Molal Volumes of Electrolytes in Various Solvents at 25°

Electrolyte	$\bar{V}^0$ ^{a}	*Electrolyte*	$\bar{V}^0$ ^{a}
Formic Acid[268]		6 *M* Urea[287]	
NaCl	15.5	HCl	34.6
NaI	31.5	NaCl	24.9
KCl	18.5	NaO_2CH	32.4
KBr	23.4	NaO_2CCH_3	46.9
KI	34.5	$NaO_2CCH_2CH_3$	62.2
RbCl	28.3	$NaO_2C(CH_2)_2CH_3$	80.9
RbI	44.5		
CsCl	33.4	Acetic Acid[83]	
CsI	49.5	PipBr	103.1
		Ethanol[83,98,264]	
Ethylenediamine[273]		HCl	3.0
$AgNO_3$	20.0		
LiCl	13.5	LiCl	−4.4
$NaNO_3$	35.5	PipBr	100.4
HgI_2	112.0	Propanol[99,264]	
n-Bu_4NI	325.0	HCl	9.6
Glycol[82]		LiCl	0.1
LiBr	21.7	1-Butanol[99]	
NaBr	27.3	LiCl	2.5
NaI	38.4		
KI	47.2	2-Methyl-1-propanol[99]	
Nitrobenzene[246]		LiCl	1.1
Bu_4NPi	407.0	Acetonitrile[267]	
o-Dichlorobenzene[246]		NaI	−6.4
Bu_4NI	302.0	Chlorobenzene[246]	
		Bu_4NPi	402.0

[a] In cm^3 mol^{-1}.

determined by Zana and Yeager,[314,315] As pointed out elsewhere,[81] to compare the values for $\bar{V}^0(H^+)$ obtained by these various methods (as well as those by earlier workers), it is necessary to use the same $\bar{V}^0$ data, as well as the most reliable $\bar{V}^0$ data. Earlier workers frequently used inaccurate $\bar{V}^0$ data and often various workers have compared their results to others without normalizing the data. For example, Panckhurst,[301] using unreliable $\bar{V}^0$ data, calculated $\bar{V}^0(H^+) = -1.14$ cm^3/mol using Noyes' methods,[308] while the more reliable $\bar{V}^0$ data yield $\bar{V}^0(H^+) = -2.77$ cm^3/mol.[81]

With the exception of the methods of Fajans and Johnson,[116] Padova,[306,307] Conway, *et al.*,[124,310] Zana and Yeager,[315,316] and King,[312] the majority of the methods used to estimate $\bar{V}^0(H^+)$ require values for the crystal radii. Pauling[304] or Goldschmidt[317] radii give similar values for $\bar{V}^0(H^+)$; however, the Gourary and Adrian radii[318] yield values for $\bar{V}^0(H^+)$ that are more positive by about 5.0 cm^3/mol.[81]

Panckhurst[301] has criticized most of the methods used by various workers to estimate $\bar{V}^0(H^+)$; he feels that the only

---

(317) V. M. Goldschmidt, *Skr. Norske Videnskaps-Akad. Oslo. I, Mat.-Naturv. Klasse*, 1 (1926).

(318) B. S. Gourary and F. J. Adrian, *Solid State Phys.*, 10, 127 (1960).

Table XIX

Partial Molal Volumes of Electrolytes in Dimethylformamide at Various Temperatures[a]

Electrolyte	$\bar{V}^0$, *cm³ mol⁻¹* 35°	40°	50°	60°	70°
NaBr	12.05	11.75	11.40	11.20	10.95
NaI	21.00	20.70	20.40	20.05	19.80
$NaNO_3$	24.05	23.75	23.30	22.85	22.30
KI	35.60	35.45	35.25	35.05	34.80
NH_4Br	32.20	32.00	31.70	31.45	31.10
NH_4I	38.00	37.75	37.50	37.20	36.90
NH_4NO_3	41.20	40.68	40.05	39.40	38.80
Et_4NI	166.10	167.00	168.60	170.10	171.90
n-Pr_4NI	238.80	240.00	241.60	243.50	245.00
n-Bu_4NI	307.60	308.90	311.00	313.60	315.60
n-Pen_4NI	377.90	379.05	381.60	384.60	387.00
n-Hex_4NI	449.10	450.70	453.00	455.55	457.90
n-Hep_4NI	515.10	516.60	520.10	523.90	527.50

[a] Data taken from the unpublished work of Gopal and coworkers, personal communication, 1970.

valid methods are those used by Noyes[308] and Fajans and Johnson.[116] He selects a value of $\bar{V}^0(H^+) = 1.5 \pm 2.0$ cm³/mol as the "best" value which is the average value obtained using Pauling[304] and Gourary and Adrian[318] crystal radii by Noyes' methods.[308] Using more reliable $\bar{V}^0$ data, Millero[81] obtained $\bar{V}^0(H^+) = -0.05$ cm³/mol as the "best" value using the same methods. Thus, although some of the criticism made by Panckhurst are valid, most of the methods yield results for $\bar{V}^0(H^+)$ between 0 and -5.0 cm³/mol (*i.e.*, $\bar{V}^0(H^+)$ is negative).

As pointed out elsewhere,[81] the errors in the estimate of the $\bar{V}^0$(ions) made by Zana and Yeager[314,315] due to the criticism raised by Panckhurst appear to be well within their quoted experimental error of ±2.0 cm³/mol. Because of the internal consistency of the $\bar{V}^0$(ions) determined by Zana and Yeager, we feel that the $\bar{V}^0(H^+)$ should be close to -5.0 cm³/mol at 25°.

The problem of what radii to use is not clear at present, and we prefer to use either Pauling[304] or Goldschmidt[317] radii because their tabulations are more extensive. The fact that the choice of $\bar{V}^0(H^+) \approx -5.0$ cm³/mol and the use of Pauling radii yield similar values for the $\bar{V}^0$'s of cations and anions of the same size may be accidental; however, it does make the comparison of $\bar{V}^0$(ions) as a function of temperature and solvent system a lot simpler. One would expect the orientation of water at cations and anions to be different[5] and the electrostriction for anions to be larger than for cations of the same size due to hydrogen-bonding effects.[310,319]

The values for $\bar{V}^0(H^+)$ in water at 25° estimated by various methods are tabulated in Table XX. The average value for $\bar{V}^0(H^+)$ is -4.2 ± 1.5 cm³/mol or -4.7 ± 1.1 cm³/mol if the two low values are omitted. The $\bar{V}^0(H^+)$ has recently been estimated by using these methods in water from 0 to 200°.[81] All of the methods with the exception of Glueckauf's[309] and Padova's[306,307] give reasonable values for $\bar{V}^0(H^+)$ as a function of temperature. Although the $\bar{V}^0(H^+)$ results determined by various methods were found[81] to differ at a given temperature, the partial molal expansibilities of the proton, $\bar{E}^0(H^+)$'s, determined by all of the methods appear to be a linear function of temperature (°C).

$$\bar{E}^0(H^+) = -0.008 - 3.40 \times 10^{-4}t \qquad (33)$$

Table XX

Comparison of the Estimates for the Ionic Partial Molal Volume of the Proton in Water at 25° [a]

$\bar{V}^0(H^+)$, *cm³ mol⁻¹*	*Author*
−3.8	Bernal and Fowler,[109] Darmois,[110] Zen[111]
−5.3	Kobayazi[112]
−2.7	Rice,[114] Eucken[113]
−5.1	Wirth[115]
−0.2	Fajans and Johnson[116]
−6.0	Couture and Laidler[300,302]
−7.6	Stokes and Robinson[303]
−4.5	Mukerjee[305]
−0.9	Padova[306,307]
−2.8	Noyes,[308] Panckhurst[301]
−2.6	Glueckauf[309]
−6.0	Conway, Verrall, and Desnoyers[134,310] Millero and Drost-Hansen[225]
−5.4	Zana and Yeager[314,315]
−4.5	King[312]
−5.0	Millero[313]

[a] Recalculated using the same V^0 data.[81]

By integrating this equation and using a selected value for $\bar{V}^0(H^+)$ at 25°, it is possible to estimate the $\bar{V}^0(H^+)$ from 0 to 200°. Using Zana and Yeager's value for $\bar{V}^0(H^+) = -5.4$ cm³/mol at 25°, we obtain the equation

$$\bar{V}^0(H^+) = -5.1 - 0.008t - 1.7 \times 10^{-4}t^2 \qquad (34)$$

The $\bar{V}^0(H^+)$'s calculated by this method at various temperatures agree with the values calculated by Ellis[233] using the Criss and Cobble correspondence method[320]

$$\bar{V}^0(\text{ion})^t = a\bar{V}^0(\text{ion})^{25} + b \qquad (35)$$

where *a* and *b* are temperature-dependent constants given elsewhere.[233]

Values for $\bar{V}^0$(ion) have also been estimated for nonaqueous solvents at 25°.[157,162,169,175,229,279] Millero has used Mukerjee's methods[305] to estimate $\bar{V}^0(H^+)$ in methanol,[229] *N*-methylpropionamide,[162,229] and seawater.[169,229] He found $\bar{V}^0(H^+) = -14.6$ cm³/mol in methanol,[229] 3.4 cm³/mol in *N*-methylpropionamide,[162,229] and -3.7 cm³/mol in seawater.[169,229] Although Mukerjee's methods[305] may not yield true absolute $\bar{V}^0$(ion) values, his method is easy to use in nonaqueous solvents and has the added advantage of giving one relationship for the $\bar{V}^0$'s of cations and anions (thus providing a uniform comparison between various solvents). The values estimated for $\bar{V}^0(H^+)$ in the solvents methanol, *N*-methylpropionamide, and seawater made by Millero[169,229] were found to agree very well with values determined by using the correspondence method[320] given by the equation

$$\bar{V}^0(\text{ion})^S = a'\bar{V}^0(\text{ion})^W + b' \qquad (36)$$

where $\bar{V}^0(\text{ion})^S$ is the partial molal volume of the ion in solvent S and $\bar{V}^0(\text{ion})^W$ is the partial molal volume of the ion in water (a' and b' are empirical constants).

Padova and Abrahamer[157] have estimated the $\bar{V}^0$ of Br^- equal to 6 cm³/mol in methanol by assuming that Br^- is hydrated by only one methanol molecule and using the equation

$$\bar{V}^0(Br^-) = \bar{V}^0(Br)_S - h^0\bar{V}_1{}^0 \qquad (37)$$

---

(319) B. E. Conway, *Ann. Rev. Phys. Chem.*, **17**, 500 (1966).

(320) C. M. Criss and J. W. Cobble, *J. Amer. Chem. Soc.*, **86**, 5385 (1964).

where $\bar{V}^0(\mathrm{Br}^-)_\mathrm{S}$ is the solvated volume of Br^- (equal to 47.0 cm³/mol); h^0 is the solvation number (equal to 1.0), and $\bar{V}_1^0$ is the molar volume of methanol (equal to 41.0 cm³/mol). Their result for $\bar{V}^0(\mathrm{H}^+) = -4.0$ cm³/mol is more positive by 10.6 cm³/mol than the estimates made by Millero.[229] Padova's methods of determining $\bar{V}^0$(ion)'s in water have also been shown to give values for $\bar{V}^0(\mathrm{H}^+)$ that are more positive (by 5.0 cm³/mol) than Mukerjee's methods. At present, it is not possible to say which value is correct. We feel that the value derived by Mukerjee's methods should give at least a reasonable estimate for $\bar{V}^0(\mathrm{H}^+)$; thus, we prefer the value $\bar{V}^0(\mathrm{H}^+) \approx -14.6$ cm³/mol in methanol. Part of the reason for selecting the lower value for $\bar{V}^0(\mathrm{H}^+)$ in methanol is based on the feeling that all ions should have lower $\bar{V}^0$(ion)'s in methanol, not just the anions (due to electrostriction).

Munson and Lazarus[279] have estimated $\bar{V}^0$(ion) in molten $\mathrm{H_3PO_4}$ by assuming $\bar{V}^0(\mathrm{H_2PO_4^-}) = \bar{V}^0(\mathrm{H_2PO_4^+})$.

Lee and Hyne[175] have estimated the $\bar{V}^0(\mathrm{Cl}^-)$ in ethanol–water mixtures from their $\bar{V}^0$ data on the $\mathrm{R_4NCl}$'s (R = Me, Et, Pr, and Bu) using the methods of Conway, Verrall, and Desnoyers.[124,310] Below $X_\mathrm{EtOH} = 0.3$, $\bar{V}^0(\mathrm{Cl}^-)$ was found to decrease from ~22.0 to −10 cm³/mol, while above $X_\mathrm{EtOH} = 0.3$, $\bar{V}^0(\mathrm{Cl}^-)$ was found to increase. The $\bar{V}^0(\mathrm{R_4N^+})$'s were found to go through a minimum at $X_\mathrm{EtOH} = 0.1$, which the authors interpret as being due to the "maximum structuredness of water." At $X_\mathrm{EtOH} = 0.3$, the $\bar{V}^0(\mathrm{R_4N^+})$'s maximize, which the authors interpret as being caused by the free volume of the solvent structure being at a minimum while the effect of charge on the ions is at a maximum. Because of the complexities of the ion–solvent and solvent–solvent interactions in these mixtures, these results must be considered with reservations. For example, the $\bar{V}^0(\mathrm{Cl}^-)$'s determined by using the method of Conway, *et al.*, in methanol may be in error.

The need for obtaining absolute ionic $\bar{V}^0$'s to study ion–solvent or solvent–solvent interactions is quite clear from Lee and Hyne's work.[175] It is even more apparent when examining the discussions by Padova and Abrahamer[157] on the solvation of the $\mathrm{R_4N^+}$ ions in water and methanol. For example, their estimated ionic $\bar{V}^0$'s for the $\mathrm{R_4N^+}$ ions indicate that $\bar{V}^0$(elect) for these ions is small in both water and methanol, while the estimated ionic $\bar{V}^0$'s based on Millero's estimates[229] indicate that $\bar{V}^0$(elect) for the $\mathrm{R_4N^+}$ ions is small in water and rather large in methanol. Until Zana and Yeager's experimental ultrasonic method is used in methanol (and in other solvents), we are unable to decide which method yields reliable ionic partial molal volumes.

C. INTERPRETATION OF IONIC PARTIAL MOLAL VOLUMES

Interpretations of partial molal volumes of ions at infinite dilution have been made by a number of workers over the past 13 years. Couture and Laidler[300,302] were the first to examine, in detail,[321] the $\bar{V}^0$(ion) values as a function of size and charge using a semiempirical approach. They found that the $\bar{V}^0$'s of cations and anions at 25° in water could be represented by the semiempirical equation (with $\bar{V}^0(\mathrm{H}^+) = -6.0$ cm³/mol)

$$\bar{V}^0(\text{ion}) = 16.0 + 4.9r^3 - 26|Z| \qquad (38)$$

where r is the Goldschmidt crystal radius of the ion[317] and $|Z|$ is the absolute charge on the ion. They also found that the $\bar{V}^0$'s of oxyanions[302] could be represented by the equation

$$\bar{V}^0(\text{anion}) = 58.5 + 0.89r_\mathrm{A}^3 - 26|Z| \qquad (39)$$

where $r_\mathrm{A} = 0.25nr$ (n is the number of charge bearing liquids and r is the sum of the Pauling[304] interionic distance r_{12} plus the van der Waals radius of the oxygen atom, 1.4Å). Both of these equations have been criticized owing to the terms 16.0 and 58.5 having no connection with r or Z.[306]

Most recent interpretations of the $\bar{V}^0$(ion) values as a function of size and charge have been developed by assuming that $\bar{V}^0$(ion) is made up of two major components

$$\bar{V}^0(\text{ion}) = \bar{V}^0(\text{int}) + \bar{V}^0(\text{elect}) \qquad (40)$$

where $\bar{V}^0$(int) is the intrinsic partial molal volume of the ion and $\bar{V}^0$(elect) is the electrostriction partial molal volume of the ion. Hepler[322] was the first to use this equation as the basis of examining the $\bar{V}^0$(ion) values. Hepler considered ions to be contained in spherical cavities in water and he took the volume of the cavity, $\bar{V}^0$(int), to be proportional to the cube of the crystal radius of the ion. The volume change due to the compression of the cavity, $\bar{V}^0$(elect), was taken to be

$$\bar{V}^0(\text{elect}) = \int_r^\infty \int_0^P \beta \mathrm{d}P 4\pi r^2 \mathrm{d}r \qquad (41)$$

Following the work[38,61] of others, Hepler took the pressure due to the charge on the ion to be proportional to Z^2/r^4. Upon integration of this equation he showed $\bar{V}^0$(elect), due to compression of the solvent by the internal pressure caused by the ion, is proportional to Z^2/r (which is similar to the decrease in volume due to compression of the dielectric medium). Hepler thus examined the variation of the $\bar{V}^0$(ion) values with charge and size using the semiempirical equation

$$\bar{V}^0(\text{ion}) = Ar^3 - BZ^2/r \qquad (42)$$

He found the constants $A = 5.3$ and $B = 4.7$ for cations and $A = 4.6$ and $B = 19.0$ for anions. The major criticism of Hepler's treatment is that he used $\bar{V}^0$(ion) based on $\bar{V}^0(\mathrm{H}^+) = -0.2$ cm³/mol[116] rather than $\bar{V}^0(\mathrm{H}^+) \approx -5.0$ cm³/mol.

Mukerjee[305,316] used a similar semiempirical equation to examine the $\bar{V}^0$(ion) values in water as a function of charge and size. He, however, assumed that the radius of an ion in solution, r_s, is given by the relation $r_\mathrm{s} = r(1 + K)$, where r is the Pauling crystal radius and K is a constant ($K = 0.213$). Mukerjee's equation is thus

$$\bar{V}^0(\text{ion}) = 2.51r^3(1 + K)^3 - B^*Z^2/r(1 + K) \qquad (43)$$

For monovalent ions, Mukerjee found $A = 2.52(1 + K)^3 = 4.49$ and $B = B^*/(1 + K) = 8.0$ (with a mean deviation of ±0.2 cm³/mol). He found that the equation broke down for divalent and trivalent cations whose $\bar{V}^0$'s were found to follow the equations

$$\bar{V}^0(\text{ion}) = 4.49r^3 - 32.5 \text{ for divalent cations} \qquad (44)$$

$$\bar{V}^0(\text{ion}) = 4.49r^3 - 58.5 \text{ for trivalent cations} \qquad (45)$$

For polyatomic ions, Mukerjee found that these equations were valid if $\bar{V}^0$(int) was taken to be $0.88 \times 2.51r^3$ where r is the M–O distance plus 1.40 Å (the van der Waals radius of oxygen).

Other workers have examined $\bar{V}^0$(ion) in seawater,[169] methanol,[229] liquid $\mathrm{NH_3}$,[261] and *N*-methylpropionamide (NMP)[162,229] using eq 42. Values of $A = 3.3$ and $B = 16.0$ in

---

(321) F. H. Lee, *J. Chin. Chem. Soc.* (*Taipei*), 9, 46 (1942).

(322) L. G. Hepler, *J. Phys. Chem.*, 61, 1426 (1957).

methanol,[229] $A = 4.35$ and $B = 3.0$ in NMP,[162,229] $A = 4.35$ and $B = 43$ in liquid NH_3,[277] and $A = 4.58$ and $B = 7.5$ in seawater[169] have been determined at 25°. Gunn and Green[271] used Hepler's equation and Couture and Laidler's equation to calculate $\bar{V}^{\theta} = 94$ cm^3/mol for the solvated electron in liquid NH_3. The effects of temperature on the constants A and B have also been determined in water from 0 to 200°.[91,227,323]

The semiempirical constants for A in various solvents are all larger than the theoretical value of $A = 2.52$ calculated from the crystal volume, $\bar{V}^0$(cryst), by assuming that ions are perfect hard spheres

$$\bar{V}^0(\text{cryst}) = 4\pi N/3 \times 10^{-24} \times r^3 = 2.52r^3 \qquad (46)$$

The results of estimates of $\bar{V}^0$(int) from compressibility measurements[74,306,379] also indicate that $\bar{V}^0$(int) is larger in solution than in crystal. The cause of this increase in volume has been attributed to an increase in the radii of ions in solution compared to the radii in the crystal,[303,305,324,325] an additional free volume associated with ions in solution,[81,177,227,300,302] or void space packing effects.[181,182,309,310,319,326–328]

Hamann[324] and more recently Whalley[325] have calculated the electrostriction $\bar{V}^0$(elect) for a compressible ion (similar to Baxter's earlier treatment). Whalley considers that the change in the size of the ion cavity can be larger than the contribution due to changes in the solvent (*i.e.*, if electrical saturation does not occur). He treats water as a structureless dielectric continuum. Conway, *et al.*,[310,319,327] have questioned Whalley's conclusions. They point out that water is hardly a structureless continuum and that the dielectric constant in the saturated regions near ions calculated by Whalley may be underestimated. There is also quite a large amount of evidence to show that the radii of ions in solution and in the crystal are nearly the same.[316,326,327,329,330]

Benson and Copeland[326] showed that the success of Mukerjee's methods to correlate $\bar{V}^0$(ion) values can be understood in terms of the isomorphic replacement of water molecules (*i.e.*, in a cubic lattice made up of ions whose sizes are similar to the H_2O molecule). The large values for $\bar{V}^0$(int) are shown to be accounted for by the void volume of an ion and not the result of the expansion of the ion when going from the crystal to solution. By using a simple free volume model, they show that the radius of an ion in solution or in crystal should be the same to within ±0.02 Å. They also point out that dipole–dipole repulsions between solution shell molecules may prevent the large ions from having large hydration numbers.

Since the internal pressure in solution is comparable to that in the crystal[326] and pairs of ions enter solution with energies[329] approximately equal to lattice energies in the solid salt, most workers feel that the radius of an ion in solution is approximately equal to the radius of the ion in the crystal. Thus, the cause of $\bar{V}^0$(int) being larger than $\bar{V}^0$(cryst) is normally[81] attributed to void space packing effects or some other positive disorder effect, $\bar{V}^0$(disord). Stokes and Robinson[303] have experimentally shown (by measuring the void space for the packing of spheres) that $\bar{V}^0(\text{int}) = 4.35r^3$ by assuming that an ion contributes to the volume of the system an amount due to "random close packing" of spheres which also supports this contention.

In recent studies[81,124,142–145,162,202,225,226,301,308–310,328] attempts have been made to separate $\bar{V}^0$(int) into the two components $\bar{V}^0$(cryst) + $\bar{V}^0$(disord) by the equations

$$\bar{V}^0(\text{int}) = 2.52r^3 + (A - 2.52)r^3 \qquad (47)$$

$$\bar{V}^0(\text{int}) = 2.52r^3 + A'r^2 \qquad (48)$$

$$\bar{V}^0(\text{int}) = 2.52(r + a)^3 = 2.52r^3 + [2.52(r + a)^3 - 2.52r^3] \qquad (49)$$

In eq 47, $\bar{V}^0$(disord) is assumed to be proportional to r^3;[81,229,305,322] semiempirical values of $A = 4.48$[81] yield $\bar{V}^0$(disord) $= 1.96r^3$ in water at 25°. In eq 48, $\bar{V}^0$(disord) is proportional to r^2 or the surface of the ion;[124,310] semiempirical values of $A' = 4.09$,[308] 4.03,[301] and 4.0[229] in water at 25°, $A' = 1.7$ in methanol[229] at 25°, and $A' = 3.2$ in *N*-methylpropionamide at 25°[229] have been determined by various workers. The semiempirical values for A' in water can be compared to the theoretical value of $A' = 3.15$ calculated by Conway, *et al.*[124,310] They calculated the void space or disordered volume by making the following assumptions: (i) the crystal radius = the radius of the ion in solution; (ii) when $r(\text{ion}) > r(H_2O)$, eq 46 holds; (iii) when r(ion) equals $r(H_2O)$, $\bar{V}^0(\text{int}) = (2r)^3N$ holds and the ion and water molecules are locally cubically or hexagonally packed; and (iv) there is a smooth transition between these limiting conditions.

In eq 49, one assumes[81,308,309,328] that the effective radii of all ions in solution are larger than the corresponding crystal radii by a constant amount. Semiempirical values of $a = 0.45$[81,229,303] and $a = 0.44$[301] in water at 25°, $a = 0.20$[229] in methanol at 25°, and $a = 0.34$[229] in *N*-methylpropionamide at 25° have been determined by various workers. Glueckauf[309] has calculated $\bar{V}^0$(int) of ions in water by assuming that (i) an ion with a radius equal to a water molecule (1.38 Å) has a $\bar{V}^0$(int) equal to that of a water molecule (*i.e.*, an isomorphic replacement of a water molecule with an ion) and (ii) the "dead space" associated with a spherical ion is proportional to its surface. He postulated that the dead space corresponds to a hollow sphere of a constant thickness and $\bar{V}^0$(int) is given by eq 49, where $a = [\bar{V}^0(H_2O)/2.52]^{1/3} - 1.38$ Å $= 0.55$ Å. Glueckauf found that ions fall into two distinct groups according to the magnitude of the parameter $\sqrt{Z}/\bar{r}$ at the dipole center of the first hydrated layer of water molecules (where Z is the charge on the ion and $\bar{r} = r(\text{cryst}) + r(H_2O) \pm \delta$; δ is the distance of the dipole center and the center of the water molecule). For ions where $\sqrt{Z}/\bar{r} < 0.5$, $\bar{V}^0$(elect) is given by (for the monovalent cations and anions)

$$\bar{V}^0(\text{elect}) = -33Z^2/\bar{r} \qquad (50)$$

when δ is taken to be zero. Ions with $\sqrt{Z}/\bar{r} > 0.5$ (Li^+ and polyvalent cations) show much lower values for $\bar{V}^0$(elect) than expected from eq 50. This was explained by postulating an expansion near an ion when the electrostatic field exceeds a certain value. He feels that these findings support the suggestion of Frank and Evans[177] that "ice-like" formation occurs around the structure promoting ions with $\sqrt{Z}/\bar{r} > 0.5$. In a later paper[328] Glueckauf extended this treatment to 200° using

---

(323) G. Curthoys and T. G. Mathieson, *Trans. Faraday Soc.*, 66, 43 (1970).

(324) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths, London, 1957.

(325) E. Whalley, *J. Chem. Phys.*, 38, 1400 (1963).

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

(327) J. E. Desnoyers, R. E. Verrall, and B. E. Conway, *J. Chem. Phys.*, 43, 423 (1965).

(328) E. Glueckauf, *Trans. Faraday Soc.*, 64, 2423 (1968).

(329) R. H. Stokes, *J. Amer. Chem. Soc.*, 86, 979, 982 (1964).

(330) J. Burak and A. Treinin, *Trans. Faraday Soc.*, 59, 1490 (1963).

the $\bar{V}^0$ data of Ellis and coworkers.[230–234] He assumed that the local compressibility of the water molecules surrounding the ions is decreased with increasing polarization. He thus feels that the inner hydrated water molecules of polyvalent ions contribute very little to the electrostriction effect. Glueckauf[328] points out that since polarization is caused by electrostatic fields (given by $E = Ze/Dr^2$), the correct parameter to use with variable temperature is $\sqrt{Z}/D\bar{r}^2$ and not $\sqrt{Z}/\bar{r}$. He found that large anions have an abnormal increase in $\bar{V}^0$(int) at high temperatures. Ellis[230–234] has related the high temperature $\bar{V}^0$ behavior of electrolytes to the density of pure water and correlated his results using methods similar to those developed by Glueckauf.[309,328] He found that the Na^+ and Mg^{2+} ions and the oxyanions have a different $\bar{V}^0$ temperature behavior than the other ions he studied.

Values for the semiempirical constants A,[81,323] A',[81] and a[81,231–233] have recently been determined for aqueous solutions from 0 to 200°. The results[81] of $\bar{V}^0$(disord) in water as a function of temperature are given in Figure 5; also incuded are theoretical results obtained by Ellis[231–233] using Glueckauf's method.[309]

Millero[229] has examined the semiempirical constants A, A', and a in water, methanol, and *N*-methylpropionamide. The resulting constants were found to show no simple correlation to common physical properties such as dielectric constant of the solvents. The constants were also found not to be in the order expected (NMP < H_2O < MeOH) for the expansion of an ion due to differences in internal pressures or compressibilities of the solvents. These results indicate that void space effects are important in solvents other than water. He interpreted the increase in $\bar{V}^0$(int) to a disordered effect caused by the solvated ion (*i.e.*, including the electrostricted region) not being able to "fit" into the structure of the solvent (rather than improper packing in the electrostricted region). He noted that $\bar{V}^0$(disord) appears to be largest for the most highly ordered solvent. Before one can select the exact form of the positive disorder or void space effect, more must be known about the structure of solvents and the geometry of the coordination shell.

The theoretical prediction of electrostriction caused by various ions is difficult because of the uncertainty of the form of the interaction of an ion and the water molecule. The Drude–Nernst equation predicts values of $B = 4.175$ in water and 22.0 in methanol at 25°[229] compared to semiempirical values of $B = 8.0$,[229,306] 10.0,[229,306] and 11.0[229] in water and $B = 10.0$[229] in methanol. The semiempirical value of $B = 2$–3 in *N*-methylpropionamide[229] (and most nonaqueous solvents) cannot be compared to a theoretical value from the Drude–Nernst equation since $\partial(\ln D)/\partial P$ is unknown. Benson and Copeland[326] have used a modified version of the Drude–Nernst equation and found $B = 6.0$ in water. Millero[81] has recently calculated $\bar{V}^0$(elect) using the Drude–Nernst equation in water from 0 to 200°. The results for $\bar{V}^0$(elect) are shown in Figure 6 along with the semiempirical values.[81] The semiempirical values for B or $\bar{V}^0$(elect) are larger (*i.e.*, $\bar{V}^0$(elect) is more negative) than the theoretical values obtained from the Drude–Nernst equation over the entire temperature range. The semiempirical values for $\bar{V}^0$(elect) also appear to go through a maximum as the temperature is increased, while $\bar{V}^0$(elect) calculated from the Drude–Nernst equation decreases smoothly with increasing temperature. The causes of these differences have been attributed to dielectric saturation effects.[138,181,306,367,310,319,327]

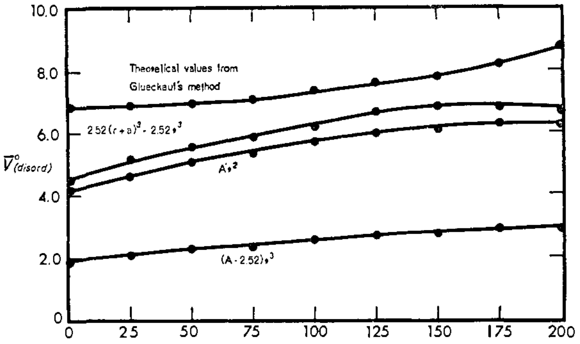

Figure 5. The disorder or void space partial molal volume, $\bar{V}^0$(disord), of a monovalent ion with $r = 1.0$ Å from 0 to 200° (ref 81).

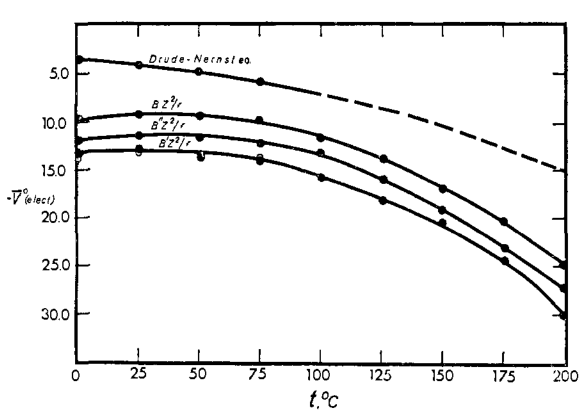

Figure 6. The electrostriction partial molal volume, $\bar{V}^0$(elect), of a monovalent ion with $r = 1.0$ Å from 0 to 200°. Based on the semiempirical equations $-\bar{V}^0(\text{ion}) = Ar^3 - B/r$, $\bar{V}^0(\text{ion}) = 2.52r^3 + A'r^2 - B'/r$, and $V^0(\text{ion}) = 2.52(r + a)^3 - B''/r$ (ref 81).

The more recent[138,181,306,307,327] attempts of calculating V^0(elect) by considering dielectric saturation effects have started by using the equation developed by Frank,[331]

$$1/V(\partial V/\partial E)_T = -E/4\pi(\partial D/\partial P)_{E,T} \qquad (51)$$

Padova[306,307] has given a detailed and thorough calculation of electrostriction considering dielectric saturation effects. By integrating this equation, he obtains

$$\bar{V}^0(\text{elect}) = {}^1\!/_2 N \int_{r_e}^{\infty} \int_0^E (\partial D/\partial P)_{E,T}\, d(E^2)\, r^2\, dr \qquad (52)$$

For a monovalent ion with $r = 1.0$ Å, Padova's equation yields $\bar{V}^0$(elect) = −13.0 cm³/mol at 25° in water.[81] This model overestimates the electrostriction for small univalent and divalent ions and does not consider the intrinsic size of ions or void space effects. Improvements of Padova's approach may be made by not integrating the electrostatic volume to the surface of the ion where the continuum model is not applicable.[319,327]

Desnoyers, Verrall, and Conway[327] have also calculated $\bar{V}^0$(elect) by considering dielectric saturation effects, as well as such factors as the pressure dependence of the compressibility, the dielectric constant, and the refractive index of the solvent. They substituted the compression equation ($dv/v = \beta dP$) into eq 45 and obtained the equation

---

(331) H. S. Frank, *J. Chem. Phys.*, 23, 2023 (1955).

$$dP = (E/4)\pi\beta(\partial D/\partial P)_{E,T}\,dE \qquad (53)$$

By using the compressibility equation, the volume change, $\Delta v/v$, associated with the pressure change, dP (given by eq 53), has been calculated by Desnoyers, *et al.*,[327] as a function of field strength, E. By calculating the specific volume change as a function of ionic field rather than the total $\bar{V}^0$(elect) of the individual ion, they avoided the problem of integrating to the surface of the ion. For a monovalent ion with $r = 1.0$ Å, $\bar{V}^0(\text{elect}) \approx -13.4$ cm^3/mol.[81] Both Padova's[306,306] and Desnoyers, *et al.*,[327] methods of calculating $\bar{V}^0$(elect) yield values in fair agreement with the semiempirical values.

Dunn[138] has extended the calculation of Desnoyers, *et al.*,[327] to temperatures from 0 to 70°. Although Dunn[138] made no attempt to calculate a numerical value for $\bar{V}^0$(elect), his results do show that the $\bar{V}^0$(elect), calculated by including dielectric saturation effects, goes through a maximum as the temperature increases and that the maximum is a function of field strength (the higher the field strength the lower the maximum). Thus, the inclusion of dielectric saturation effects also appears to account for the maximum observed in $\bar{V}^0$(elect) as a function of temperature from the semiempirical equations.[81] Similar calculations in other solvents cannot be made because of the lack of reliable compressibility and dielectric constant data as a function of pressure.

The Drude–Nernst equation predicts that $\bar{V}^0$(elect) should be proportional to Z^2/r, while the results for divalent,[81,305] trivalent,[81,305] and quadrivalent[127,136] ions apparently do not follow this relationship. The $\bar{V}^0$(elect) for a 1-Å divalent ion is nearly four times greater than for a monovalent ion,[81] in agreement with the Z^2 relationship; however, $\bar{V}^0$(elect) for a 1-Å trivalent ion is about seven times greater than a monovalent ion of similar size and not in agreement with the Z^2 relationship. Couture and Laidler[300] noted that for ions with nearly the same radius, $\bar{V}^0$(ion) is lowered by approximately 20 cm^3/mol for each unit increase of charge. They also found that $\bar{V}^0(\text{elect}) \approx -26|Z|$.

Hepler, *et al.*,[127] found a difference of 46.6 ml/mol for the difference in the $\bar{V}^0$'s of the $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ ions. This difference is nearly twice as large as that predicted by Couture and Laidler;[300] however, in agreement with the Z^2/r relation,[126] Braghetti and Indelli's[136] $\bar{V}^0$'s results for $Na_3P_3O_9$, $K_3P_3O_9$, $Na_4P_4O_{12}$, and $K_4P_4O_{12}$ yield a difference in the $\bar{V}^0$'s of $P_3O_9^{3-}$ and $P_4O_{12}^{4-}$ corresponding to each PO_3^- group that is smaller than predicted by the increase in charge.

Other workers have suggested Z^2/r^2,[138,301,308] $Z^{3/2}/r$,[232,233] or $\sqrt{Z}/r$[309,328] relationships for the $\bar{V}^0$(elect) of ions. Since the Z^2/r relationship appears to hold for the partial molal expansibility[227] of divalent ions, it appears that a positive contribution must be added to eq 40. Possible causes for this positive effect (which also appears to be important for Li^+ and F^- ions) have been attributed to $\bar{V}^0$(disord)[81] or $\bar{V}^0$(struct)[227,309,323,328] where $\bar{V}^0$(struct) is the long-range "structure forming" effect of the ions on water. Since the Li^+ appears to have a positive contribution (*i.e.*, over and above eq 40) in other solvents,[229] we prefer to attribute the positive contribution to $\bar{V}^0$(disord) or to electrostriction saturation effects (*i.e.*, the inability of the outer hydrated water molecules to "see" the true charge on the ion). The difference of $\bar{V}^0$(elect) for cations and anions of the same size has been discussed in detail elsewhere.[81] Most of the results[81] indicate that $\bar{V}^0$(elect) is larger for anions than for cations of the same size. The effect of temperature on $\bar{V}^0$(elect) of cations and anions also appears to be different.

Spedding, Pikal, and Ayers[141] found that the $\bar{V}^0$'s for some aqueous rare earth cations (La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Yb^{3+}) do not vary smoothly with ionic radius of the cation. The $\bar{V}^0$'s decrease with decreasing ionic radius from La^{3+} to Nd^{3+} and from Tb^{3+} to Yb^{3+}, but from Nd^{3+} to Tb^{3+} the values increase with decreasing ionic radius. They postulate that a change in the coordination number of the hydrated ion at a critical radius accounts for this behavior. Padova[332] has examined the relationship between the $\bar{V}^0$'s and viscosity "B" coefficients for this same series of rare earths. He calculated hydration numbers from 8.5 for La^{3+} to 11 for Dy^{3+}, which agree with the number of 9 determined by Spedding, *et al.*, for La^{3+} to Na^{3+}, but do not agree with the number of 8 found for Gd^{3+} to Er^{3+}. Padova also shows that the $\bar{V}^0$(ion)'s do not decrease smoothly with the intrinsic radius (or crystal radius) for these rare earth cations.

The various components for $\bar{V}^0$(ion) in water[81] for a monovalent ion with $r = 1.0$ Å are given in Figure 7 as a function of temperature (0–200°). At low temperatures $\bar{V}^0$(disord) is the predominant factor, and at high temperatures $\bar{V}^0$(elect) is the predominant factor. The maximum observed in $\bar{V}^0$(ion) as a function of temperature is due to the competition between $\bar{V}^0$(elect) and $\bar{V}^0$(disord). For highly charged small ions, $\bar{V}^0$(elect) is the dominant factor over the entire temperature range and the maximum occurs at lower temperatures.

Gopal and Siddiqi[160,161,164] have shown that the $\bar{V}^0$'s of common electrolytes (LiCl, KI, and the small R_4NI's) in formamide, dimethylformamide, and *N*-methylacetamide go through a maximum around 40–50°, while no maximum is observed for the $\bar{V}^0$'s for the larger R_4NI's. The causes of the maximum in the $\bar{V}^0$'s of electrolytes in formamide, dimethylformamide, and *N*-methylacetamide are probably similar to the causes in water (*i.e.*, a competition between $\bar{V}^0$(elect) and $\bar{V}^0$(int)). The partial molal expansibility, $\bar{E}^0 = \partial\bar{V}^0/\partial T$, for the large R_4NI's (R = Hex and Hep) in formamide and *N*-methylacetamide remain almost temperature independent. Since the $\bar{V}^0$'s determined by Gopal and Siddiqi[160,161,164] have not been obtained by using the limiting law to aid in the extrapolations to infinite dilution, their $\bar{V}^0$'s are probably not too reliable (especially since the ϕ_V's show large deviations from limiting law behavior—showing both positive and negative S_V's*).

Panckhurst[301] has recently criticized the division of $\bar{V}^0$(ions) into the components $\bar{V}^0$(int) and $\bar{V}^0$(elect). He points out that the division is only valid for very large ions (greater than 10 Å) and that little is to be gained from an analysis of $\bar{V}^0$(int) and $\bar{V}^0$(elect) for small ions. He then proceeds to discuss $\bar{V}^0$(ions) in terms of the molecular structure of water. Panckhurst[301] uses Gurney's[101] model for ion–water interactions as a starting point to interpret the $\bar{V}^0$(ions). Gurney attributed two contributions to the $\bar{V}^0$(ions), one arising from the replacement of a a water molecule by the ion and one from the differences between the average coordination number of an ion (n_i) and of a water molecule (n_w). Panckhurst attributes the $\bar{V}^0$(ion) to three terms: (i) $\bar{V}_B$, the changes in volume due to the replacement of an ion; (ii) the changes in volume due to changes in coordination number $[(n_i - n_w)\bar{V}_B + 15.14r_w(r_i^2 + 2r_ir_w - 3r_w^2)$, where r_w and r_i are the radii of water and the ion, respectively]; and (iii) the changes in volume associated with "structure forming" and "structure breaking" ions, $n(\bar{V}_A - \bar{V}_B)$, where $\bar{V}_A$ is the average molar volume of the water mole-

---

(332) J. Padova, *J. Phys. Chem.*, 71, 2347 (1967).

cules affected by "structure breaking" and "making." The complete expression for $\bar{V}^0$(ion) is

$$\bar{V}^0(\text{ion}) = \bar{V}_B - (n_i - n_w)\bar{V}_B + 15.14r_w(r_i^2 + 2r_ir_w^2 - 3r_w^2) + n(\bar{V}_A - \bar{V}_B) \quad (54)$$

$\bar{V}_A$ is greater or less than $\bar{V}_B$, the bulk molar volume, according to whether the ion promotes or breaks structure. Because of the problems involved in calculating average coordination numbers for ions,[328] Panckhurst's methods appear to be too cumbersome to use.

Since the various components of the $\bar{V}^0$(ions) may be small when compared to $\bar{V}^0$(cryst), it is difficult to examine the individual components of $\bar{V}^0$(ion) or to separate them. By examining the effect of temperature on the $\bar{V}^0$(ions), or the partial molal expansibility of the ion, $\bar{E}^0$(ion), it is possible to solve this problem since $\bar{E}^0$(cryst) can be taken to be approximately zero for most common ions (except for the R_4N^+ ions). Millero and coworkers[162,225–228] have recently examined the $\bar{E}^0$'s of a large number of ions in water at 25°. The $\bar{E}^0$'s of the simple monovalent cations and anions[227,228] were found to vary in size or radius in an inverse order (as noted by Fajans and Johnson).[116] Thus, although various workers have been successful in treating ion–solvent interactions of these simple monovalent ions by a common relationship, the $\bar{E}^0$'s indicate that ion–water interactions are different for cations and anions of similar size (and not a smooth function of the crystal radius). The $\bar{E}^0$'s of divalent ions[227] were found to vary with crystal radius, unlike the values for $\bar{V}^0$(elect) for these ions.[305] The $\bar{E}^0$'s of the divalent cations as a function of size are in the opposite order to the $\bar{E}^0$'s of the monovalent cations. These results indicate that the hydration of divalent and monovalent cations is different and also point out that the $\bar{E}^0$'s of ions are a much more sensitive probe of ion–solvent interactions than the $\bar{V}^0$'s. Millero[227] examined the $\bar{E}^0$'s of ions (qualitatively) by using the Frank and Wen model for ion hydration.[7] The $\bar{E}^0$'s of the R_4NCl's[225] have also been examined. The $\bar{E}^0$'s of the R_4NCl's were not a linear function of molecular weight as found for the $\bar{V}^0$'s.[124,310] The $\bar{E}^0$'s of the Pr_4Cl and Bu_4Cl appeared to be high compared to Me_4NCl and Et_4NCl. These results were interpreted as being due to the expansibility changes in the structure of water caused by the large R_4N^+ cations, $\bar{E}^0$(struct). $\bar{E}^0$(struct) decreased with increasing temperature and increased with increasing size of the R_4N^+. The similarity of the $\partial\bar{E}^0/\partial t$ of the R_4N^+ cations and the aliphatic alcohols was discussed, and it was postulated that the abnormal volume properties of the R_4N^+ halides may be normal for solutes able to cause "hydrophobic" bonding.

The $\bar{V}^0$'s and $\bar{E}^0$'s of the large R_4N^+ ions appear to have a structural contribution different from the simple monovalent ions. The most striking difference is that the $\partial^2\bar{V}^0/\partial T^2 = \partial\bar{E}^0/\partial T$ is positive for the R_4N^+ ions and negative for the more common ions.[81,188,225] Hepler[333] has recently developed a method of examining the sign of $\partial^2\bar{V}^0/\partial T^2$ for various solutes in terms of long-range "structure breaking" and "structure making" effects of solutes on the structure of water using the thermodynamic relation

$$(\partial\bar{C}_p{}^\circ/\partial P)_T = -T(\partial^2\bar{V}^0/\partial T^2)_P = -T(\partial\bar{E}^0/\partial T)_P \quad (55)$$

where $\bar{C}_p{}^\circ$ is the partial molal heat capacity of the solute at infinite dilution. The negative $\bar{C}_p{}^\circ$ values for various electrolytes has been attributed to the ability of the electrolytes to break down the structure of water.[128] Hepler[333] reasons that since pressure should also break down the structure of water, $\partial\bar{C}_p{}^\circ/\partial P$ should be positive or $\partial^2\bar{V}^0/\partial T^2$ should be negative for a "structure breaking" solute. By similar reasoning, Hepler[333] predicts that a positive value for $\partial^2\bar{V}^0/\partial T^2$ should be associated with "structure making" solutes.[334] Other workers[4,8,195,335,336] have noted the parallelism between the effect of temperature on the $\bar{V}^0$ and $\bar{C}_p{}^\circ$ of ions in aqueous solutions.

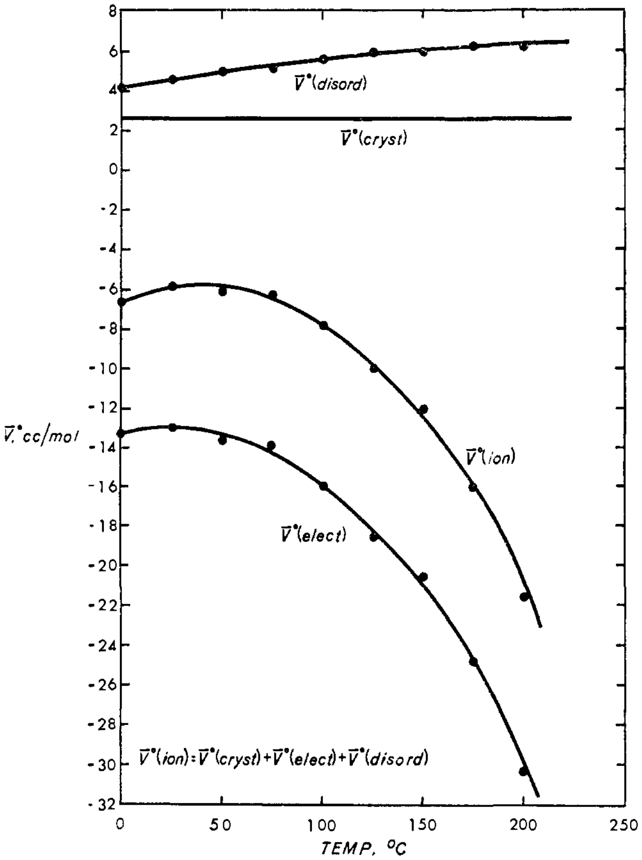

Figure 7. The components of the partial molal volume of a monovalent ion with $r = 1.0$ Å in water from 0 to 200° (ref 81).

The short-range solvating properties of ions[9] has been discussed[81] by considering the sign of the relation $\bar{V}^0$(ion) − $\bar{V}^0$(cryst) for ions. When this quantity is negative, the ion is classified as an electrostatic "positive solvating" ion, and, when the quantity is positive, the ion can be classified as a "negative solvating" ion. It has also been shown[81] that there is a direct parallelism between the sign of the viscosity "B" coefficients of ions (which also can be used to classify the short range solvating properties of ions[7–9]) and the sign of the quantity $\bar{V}^0$(ion) − $\bar{V}^0$(cryst).

Bramhall[337] developed a similar relationship between the $\bar{V}^0$(ions) and the viscosity "B" coefficients. He defined a term $\alpha = [\bar{V}^0(\text{ion}) - \bar{V}^0(\text{cryst})]/1000$ and showed that this parameter is linearly related to $[B - \bar{V}^0(\text{cryst})/400]$ independent of

---

(333) L. G. Hepler, *Can. J. Chem.*, 47, 4613 (1969).

(334) Similar arguments have been used for aqueous nonelectrolyte solutions by J. L. Neal and D. A. I. Goring, *J. Phys. Chem.*, 74, 658 (1970).

(335) M. Eigen and E. Wicke, *Z. Elektrochem.*, 55, 354 (1951); *J. Phys. Chem.*, 58, 702 (1954).

(336) M. S. Stakhanova, M. Kh. Karape'tyants, V. A. Vasilev, and Yu. A. Epikhim, *Zh. Fiz. Khim.*, 38, 2420 (1964).

(337) A. D. Bramhall, *Nature*, 197, 967 (1963).

the sign and charge on the ions. A number of other workers[247,251,268,280,301,306,307,332,338–342] have also shown that the viscosity and partial molal volumes of electrolyte solutions appear to be related. For example, Padova[280,306,332,339,340] has shown that for spherical ions, the "*B*" coefficient is equal to 2.5 times the hydrated volume, $\bar{V}_h{}^0$, which is related to the $\bar{V}^0$(ions) by the equation

$$\bar{V}_h{}^0 = \bar{V}^0(\text{ion}) + n\bar{V}^0(\text{H}_2\text{O}) \qquad (56)$$

where n is the hydration number and $\bar{V}^0(\text{H}_2\text{O})$ is the partial molal volume of water. Other workers[301,303,343–345] have attempted to calculate hydration numbers from $\bar{V}^0$ data. For example, Goto[343] has calculated the electrostriction for a number of 1:1 electrolytes and related them to hydration numbers. He also discussed the formation of a "clathrate" around small ions. Padova[306,307] has estimated the average theoretical electrostriction per mole of water to be −2.1 cm^3/mol. Thus, the theoretical solvation numbers, n, can be calculated from the equation

$$n = \frac{[\bar{V}^0(\text{ion}) - \bar{V}^0(\text{int})]}{-2.1} = \frac{\bar{V}^0(\text{elect})}{-2.1} \qquad (57)$$

Because of the problems involved in estimating $\bar{V}^0$(int), it is difficult to determine reliable solvation numbers by this method (his results, however, are in general agreement with the estimates made by other workers).[301,302] Stokes and Robinson[303] have used a similar technique to estimate hydration numbers

$$n = -[\bar{V}^0(\text{ion}) - 4.35r^3]/18 \qquad (58)$$

where r may be estimated from the ion size parameters.

The $\bar{V}^0$'s of electrolytes in D_2O have recently been determined by various workers.[149,248] They found that the volumes of transfer from H_2O to D_2O of the salts NaF, NaCl, NaBr, NaI, and $NaPhSO_3$ were negative and the volumes of transfer of the salts Et_4NBr and n-Br_4NBr were positive.[346] Since one might expect $\bar{V}^0$(int) and $\bar{V}^0$(elect) to be nearly the same in D_2O and H_2O, this change in volume appears to be related to the long-range "structure breaking" and "structure making" effects of these ions on the structure of the solvent.[7,149,177,248]

Although the structural concepts[7,9,177] of solutes on water structure have been questioned[347] in recent years, the fact that these concepts have been very useful in explaining a vast quantity of diverse experimental data makes them very useful (that is, if one is careful to define the type of structure that is being considered, *e.g.*, either long-range structural effects or short-range structural effects). Since the $\bar{V}^0$'s of ions or electrolytes appear to behave in both aqueous and nonaqueous solvent systems in a similar manner,[160,161,164,188] we prefer[81,142–144,202,225–229] to explain the effect of temperature on $\bar{V}^0$(ion) in terms of solvation effects (*i.e.*, $\bar{V}^0$(int) and $\bar{V}^0$(elect)) rather than long-range solvent structural effects (*i.e.*, "ice-like" interactions).[7,177] Further work on the $\bar{V}^0$'s of electrolytes and nonelectrolytes in nonaqueous solvents as a function of size, charge, and temperature may prove useful in examining the structural effects of importance in various solvents.

V. Applications

A. VOLUME CHANGES FOR THE IONIZATION OF PROTONIC ACIDS AND BASES

In this section, we will review some of the recent applications of molal volume studies in elucidating structural interactions of systems not covered in the sections on ion–ion and ion–solvent interactions.

Many studies have been made on the volume changes associated with the ionization of protonic acids and bases. The older data for the volume changes associated with the ionization of acids and bases are reviewed elsewhere.[14,27,85,95,129,223,224,319,324,348] In recent years a number of volume studies have been made on the ionization of water,[127,173,349,350] formic acid,[152] acetic acid,[152,235,351] n-butyric acid,[152] glycinium ion,[152] and the alkylamine hydrogen halide salts[150] in aqueous solutions and phenols in methanol.[262] The volume change, $\Delta\bar{V}^0{}_A$, associated with the ionization of an acid (HA) at infinite dilution is given by the equation

$$\Delta\bar{V}^0{}_A = \bar{V}^0(\text{H}^+) + \bar{V}^0(\text{A}^-) - \bar{V}^0(\text{HA}) \qquad (59)$$

This volume change has been examined by a number of workers[152,319,324,348] to test various ion–water interaction theories. The $\Delta\bar{V}^0{}_A$'s for the ionization of acids are normally negative because of the electrostriction of the water produced by the ions H^+ and A^-. Using the simple Drude–Nernst[33] or Born[60] theory, $\Delta\bar{V}^0{}_A$ is given by

$$\Delta\bar{V}^0{}_A = Ne^2/2D[\partial(\ln D)/\partial P](1/r_{\text{H}^+} + 1/r_{\text{A}^-}) \qquad (60)$$

The simple Drude–Nernst or Born theory also predicts that for ionization reactions, the $\Delta\bar{V}^0{}_A$'s should be proportional to the entropy changes, $\Delta\bar{S}^0{}_A$'s. Although eq 60 cannot[152] be used to predict the relative volume changes for a closely related set of acids, Hepler[348] has shown that for a number of weak acids the $\Delta\bar{V}^0{}_A$'s and $\Delta\bar{S}^0{}_A$'s are related in a linear manner. Kauzmann and coworkers[298] and Verrall and Conway[150] have also examined the relationship between the $\Delta\bar{V}^0{}_A$'s and $\Delta\bar{S}^0{}_A$'s for the ionization of some weak acids.

Most of the earlier published values for the $\Delta\bar{V}^0{}_A$'s of acids determined from $\bar{V}^0$ data are not very reliable (mainly owing to errors in extrapolation to infinite dilution and the scarcity of reliable $\bar{V}^0$ data in dilute solutions). For example, reported values for the $\Delta\bar{V}^0{}_A$ of acetic acid in water at 25° range from −9.2 to −12.5 cm^3/mol.[152] Until recently[349] the volume change for the ionization of water at infinite dilution at 25° was in error. Owen and Brinkley[86] calculated $\Delta\bar{V}^0{}_A = -23.5$ cm^3/mol for the ionization of water at infinite dilution using unreliable data for the $\bar{V}^0$'s of HCl and NaOH. Bodanszky and Kauzmann[173] later calculated $\Delta\bar{V}^0 = -21.28$ cm^3/mol for the

---

(338) E. Darmois, *J. Chim. Phys.*, 43, 15 (1946).

(339) J. Padova, *Bull. Res. Council Israel, Sect. A*, 10, 63 (1961).

(340) J. Padova, *J. Chem. Phys.*, 38, 2635 (1963).

(341) G. Sutra, *C. R. Acad. Sci.*, 222, 875 (1946); *J. Chem. Phys.*, 43, 289 (1946).

(342) W. Walker, *Phil. Mag.*, 27, 288 (1914).

(343) S. Goto, *Bull. Chem. Soc. Jap.*, 37, 1685 (1964).

(344) K. Tamura and T. Sasaki, *ibid.*, 36, 975 (1963).

(345) T. Yasunoga and T. Sasaki, *J. Chem. Soc. Jap., Pure Chem. Sect.* (*Nippon Kagaku Zassi*), 72, 89 (1951).

(346) J. E. Desnoyers has pointed out that the $\bar{V}^0$'s of electrolytes in D_2O given in ref 243 are in error: personal communication, 1970.

(347) A. Holtzer and M. F. Emerson, *J. Phys. Chem.*, 73, 26 (1969).

(348) L. G. Hepler, *ibid.*, 69, 965 (1965).

(349) L. A. Dunn, R. H. Stokes, and L. G. Hepler, *ibid.*, 69, 2808 (1965).

(350) D. A. Lown, H. R. Thirsk, and L. Wynne-Jones, *Trans. Faraday Soc.*, 64, 2073 (1968).

(351) D. A. Lown, H. R. Thirsk, and L. Wynne-Jones, *ibid.*, 66, 51 (1970).

ionization of water, but they used unreliable $\bar{V}^0$ data for NaOH. The very careful $\bar{V}^0$ work for HCl[95,137] and NaOH[127] yields $\Delta\bar{V}^0_A = -22.11$ cm^3/mol[349] for the volume change associated with the ionization of water at infinite dilution at 25°. Since no reliable $\bar{V}^0$ data are available for HCl and NaOH in dilute solutions at other temperatures, it is not possible to calculate reliable $\Delta\bar{V}^0_A$'s for the ionization of water. The volume changes for other proton transfer processes can also be very large; for example, King[152] has recently calculated $\Delta\bar{V}^0_A = -8.43$, -11.50, -14.22, and -6.80 cm^3/mol, respectively, for formic acid, acetic acid, *n*-butyric acid, and the glycinium cation. His results for acetic acid are in excellent agreement with the earlier values reported by Redlich and Nielson[96] and Wirth;[352] however, for formic, butyric, and the glycine cation, the earlier results[83] show differences of as much as 0.8 cm^3/mol from the values determined by King.[152]

King[152] has shown that the variations of the $\Delta\bar{V}^0_A$'s for the ionization for large acids with size can be accounted for by differences in void volumes of the acid and its conjugate base. This variation of the $\Delta\bar{V}^0_A$'s with size is contrary to that predicted by the simple Drude–Nernst or Born theory. Owing to the linear relation of $\Delta\bar{V}^0_A$'s to $\Delta\bar{S}^0_A$'s for the ionization of weak acids,[348] one might postulate that these void space effects may also be responsible for the failure of the Born equation in predicting the size variations of the other thermodynamic properties of ionization (*i.e.*, ΔH_A and ΔG_A). For the smaller acids, King[152] found that both void space effects, $\bar{V}^0$(disord), and the electrostriction effects, $\bar{V}^0$(elect), must be considered (and possibly other structural effects, $\bar{V}^0$(struct)). Since the effect of temperature[40] on the $\Delta\bar{V}^0_A$'s of ionization and $\bar{V}^0$(ion)'s appear to be parallel (both go through a maximum), one might postulate that the effect of temperature on all the thermodynamic properties of ionization of weak electrolytes are caused by the same effect that causes the maximum in the $\bar{V}^0$'s of ions discussed earlier (*i.e.*, a competition between $\bar{V}^0$(elect) and $\bar{V}^0$(disord)).

Rochester and Rossall[262] have determined the volume changes associated with the ionization of a number of substituted phenols in methanol. The $\Delta\bar{V}^0_A$'s were found to be larger in magnitude in methanol than in water (as found earlier by Hamann and Lim[83]) owing to the larger electrostriction of ions in methanol. For example, they found that the $\bar{V}^0$'s of phenol in water and methanol were nearly equal; however, for sodium phenoxide, the $\bar{V}^0$ is smaller in methanol than in water. They found a linear correlation between the pK_A and the $\Delta\bar{V}^0$'s for all the phenols they studied. They also found a linear relationship between the viscosity "*B*" coefficients for the phenols and their sodium salts.

B. VOLUME CHANGES FOR NONPROTONIC ASSOCIATION AND DISSOCIATION

Although many studies have been made on the volume changes associated with the ionization of protonic acids and bases, until recently, the volume changes associated with simple nonprotonic ion association or dissociation processes have received little attention. Strauss and Leung[252] have measured the volume changes of mixing anionic polyelectrolytes with alkali metal and alkaline earth metal cations. They found that the volume changes were very large and comparable with protonic reactions. They interpreted the results as evidence for site binding of cations to the polyanions as opposed to ionic atmospheric binding. These studies may prove to be very useful in the interpretation of the interactions of other solutes (*e.g.*, proteins or clays) with ionic species.

Spiro, Revesz, and Lee[168] have examined the volume changes for reactions of complex cations with various anions to study the formation of inner- and outer-sphere complexes. They found that the volume changes of both inner- and outer-sphere complexes were similar and also of the same order of magnitude as protonic reactions. Their comparison of the volume changes for related systems under closely similar conditions have proved very useful, although the establishment of a general criterion for distinguishing between the two structural types was not possible. Their methods (as well as other workers[143,153,154,169]) of calculating association constants from volume data may offer a novel approach in studying other ion-complex formation processes. Spiro, *et al.*,[168] also showed that the entropy changes, $\Delta\bar{S}^0$'s, for ion-complex processes appear to be related to the volume changes, $\Delta\bar{V}^0$'s, as Hepler[348] found for acid and base processes.

Mention should also be made of the measurements of the volume changes associated with the interactions of solutes with proteins[296,298,299,353] and with the formation of micelles.[155,156,254–256,259,260]

Marshall[354] has recently shown that the volume changes for ion-pair formation processes at high temperatures are given by the equation (see, however, discussions of Matheson[355])

$$\Delta\bar{V}^0(\text{ion pair}) = -k\beta RT \tag{61}$$

where k is equal to the average change in the number of hydrated water molecules upon dissociation of a solvated ion pair (or weak electrolyte), and β is the compressibility of the solvent. This relationship is similar to Hamann and Lim's[83] findings that the difference between the $\bar{V}^0$'s of electrolytes in various solvents compared to water are proportional to the compressibilities of the solvent. One can arrive at a similar conclusion by assuming that $\bar{V}^0$(elect) is proportional to the compressibility and that $\bar{V}^0$(int) for the ion pair is equal to $\bar{V}^0$(int) for the free ions.[143] For example, for the dissociation of the ion pair, MX^0, into the free ions, $M^+ + X^-$, one obtains

$$\Delta\bar{V}^0(\text{ion pair}) = \bar{V}^0(M^+) + \bar{V}^0(X^-) - \bar{V}^0(MX^0) \tag{62}$$

Substituting $\bar{V}^0(\text{ion}) = \bar{V}^0(\text{int}) + \bar{V}^0(\text{elect})$ for the various components and assuming that $\bar{V}^0(\text{int})^{M^+} + \bar{V}^0(\text{int})^{X^-} = \bar{V}^0(\text{int})^{MX^0}$, we obtain

$$\Delta\bar{V}(\text{ion pair}) = \bar{V}^0(\text{elect})^{M^+} + V^0(\text{elect})^{X^-} - \bar{V}^0(\text{elect})^{MX^0} \tag{63}$$

If $\bar{V}^0$(elect) is assumed to be proportional to the compressibility times the number of water molecules hydrated to the ion, n(i), we obtain

$$\Delta\bar{V}^0(\text{ion pair}) \propto \beta[n(M^+) + n(X^-) - n(MX^0)] \propto \beta k \tag{64}$$

Because of the importance of understanding the nature of aqueous urea solutions on the denaturing of proteins, Hargraves and Kresheck[287] have recently determined the $\bar{V}^0$'s of various solutes (alcohols, amino acids, carboxylic acids, and salts) in 6 *M* urea. They found that the $\bar{V}^0$'s for all the solutes

---

(352) H. E. Wirth, *J. Amer. Chem. Soc.*, 70, 462 (1948).

(353) L. M. Krausz, *ibid.*, 92, 3168 (1970).

(354) W. L. Marshall, *J. Phys. Chem.*, 74, 346 (1970).

(355) R. A. Matheson, *ibid.*, 73, 3635 (1969); W. R. Gilkerson, *ibid.*, 74, 746 (1970).

were larger in 6 *M* urea than in pure water. The electrostriction of an ion in 6 *M* urea thus appears to be less than in pure water. Other workers[356] have found that the denaturation of ribonuclease decreased the volume by 240 cm^3/mol. This negative volume change is similar to the volume change accompanying helix–coil transformation.[357] Other workers, however, have reported positive,[358–360] negligible,[361–363] and negative[364] volume changes for the denaturation of proteins in urea solutions.

As mentioned earlier, one of the most important practical applications of molal volume data in fields like oceanography is in determining the effect of pressure on ionic equilibria[86] using eq 15. Duedall and Weyl[191–193] have measured the $\bar{V}^0$'s (at infinite dilution in the ionic medium) for a number of salts ($NaCl$, KCl, Na_2SO_4, $MgSO_4$, $KHCO_3$, $Ca(NO_3)_2$, $NaNO_3$, and KNO_3) in synthetic seawater as a function of salinity (total solids) and temperature (0–30°). The $\bar{V}^0$'s of salts in 0.725 *m* NaCl (which is nearly the same ionic strength as seawater) have also been determined by various workers. Owen and Brinkley[208] calculated the $\bar{V}^0$'s of the electrolytes HCl, NaCl, KCl, KBr, and K_2SO_4 in 0.725 *m* NaCl from Wirth's $\bar{V}$ data.[91] Lee[170] has calculated the $\bar{V}^0$'s of NaBr, $MgCl_2$, Na_2SO_4, and $MgSO_4$ in 0.725 *m* NaCl from his volume measurements. Other workers have determined the $\bar{V}^0$'s of acetic acid,[362] Na_2CO_3,[286] K_2CO_3,[286] and CsCl[205] in NaCl solutions. It is interesting to note that the $\bar{V}^0$'s of most of the salts determined in synthetic seawater and 0.725 *m* NaCl are nearly equal. Thus, the ionic strength principle appears to be valid except when ion-pairing effects are predominant.

Millero[169] has divided the $\bar{V}^0$'s of electrolytes in seawater and 0.725 *m* NaCl into their ionic components and analyzed these ionic $\bar{V}^0$'s in seawater using a simple model for ion–water interactions. The volumes of transfer of ions from pure water to seawater, $\Delta\bar{V}^0$(trans), were found to obey the linear equation

$$\Delta\bar{V}^0(\text{trans}) = 0.37(Z^2/r) + 0.83 \qquad (65)$$

where *r* is the crystal radii and *Z* is the charge on the ion. He used this equation to estimate the $\bar{V}^0$'s of a large number of free ions in seawater as a function of temperature and salinity (total solids). From the ions OH^-, HCO^-, CO_3^{2-}, and SO_2^{2-} large positive deviations from eq 65 were found. These positive deviations were interpreted by postulating the formation of ion pairs.

Lown, Thirsk, and Wynne-Jones[350] have developed a simple equation (*i.e.*, compared to that proposed by Owen and Brinkley[208]) for the calculation of the pressure dependence of the dissociation constant using partial molal volume and partial molal compressibility data at 1 atm (applicable to 2000 atm). They also showed that the changes in the volumes, $\Delta\bar{V}^0$'s, and the changes in the partial molal compressibilities, $\Delta\bar{K}^0$'s, for a wide range of acid and base equilibria are approximately linear. This observation may be very useful in predicting the effect of pressure on other ionization equilibria for which $\Delta\bar{K}^0$ is not known. In a more recent paper,[351] they showed that this linear relationship holds for the ionization of acetic acid over a wide temperature range (25–225°) at a constant pressure. In this later paper they also discussed the relationship of the volume changes of ionization to other thermodynamic quantities (*e.g.*, $\Delta\bar{S}^0$).

Helmy, *et al.*,[253] have determined the ϕ_V's and $\bar{V}_2$'s of aqueous NaCl and Na-kaolin solutions at 30°. They found that the $\bar{V}^0$ of NaCl is greater in 5% Na-kaolin than in water. The $\bar{V}$'s of Na-kaolin were found to increase with particle concentration both in water and 0.5 *M* NaCl and to be larger in NaCl then in water. The Na-kaolin was found to decrease the volume of water by 13.5 cm^3/mol at infinite dilution, which is the same order of magnitude as that caused by monovalent ions. They also found satisfactory agreement between the experimental and calculated values for the departure of Na-kaolin in NaCl solutions from idea behavior.

Other workers have used partial molal volume data for such diverse things as examining the volume changes in concrete[365] and determining intrinsic diffusion coefficients of electrolytes.[209,366]

Future work will undoubtedly lead to many other novel ways of using molal volume and volume of mixing data of electrolyte solutions in studying the interactions of other systems. Partial molal volume data of electrolytes in nonaqueous solvents are needed, as well as studies on the effect of pressure on the partial molal volumes of electrolytes (*i.e.*, the partial molal compressibilities). It is hoped that this review will stimulate the use of volume studies in interpreting the structural interactions in other systems.

Acknowledgments. The author wishes to thank Mr. Edward Hoff for aiding in the literature search and Colonel Jonathan Knox for drawing the figures. The author also wishes to thank Dr. Loren G. Hepler and Dr. Harry P. Hopkins, Jr., for reading the manuscript and offering many helpful comments. The support of the Office of Naval Research (Contract NONR 4008[02]) and the National Science Foundation (GA-17386) for this study is greatly appreciated.

---

(356) D. N. Holcomb and K. E. Van Holde, *J. Phys. Chem.*, 66, 1999 (1962).

(357) H. Noguchi and J. T. Yang, *Biopolymers*, 1, 259 (1963).

(358) P. A. Charlwood, *J. Amer. Chem. Soc.*, 79, 766 (1957).

(359) S. Katz and T. G. Ferris, *Biochemistry*, 5, 3246 (1966).

(360) R. B. Simpson and W. Kauzmann, *J. Amer. Chem. Soc.*, 75, 5139 (1953).

(361) W. L. Gagen and J. Holme, *J. Phys. Chem.*, 68, 723 (1964).

(362) H. Neurath and A. M. Saum, *J. Biol. Chem.*, 128, 347 (1939).

(363) F. J. Reithel and J. D. Sakura, *J. Phys. Chem.*, 67, 2497 (1963).

(364) L. K. Christensen, *C. R. Acad. Sci.*, 28, 37 (1952).

(365) T. C. Powers, *Mater. Constr.*, 1, 487 (1968).

(366) G. W. Powell, *Trans. Amer. Ind. Mech. Eng.*, 233, 1906 (1965).