dependence of azeotropic pressure on temperature as

$$\ln P^{\text{azeo}}(\text{kPa}) = 12.2537 - \frac{22066}{T^{1.3923}} + 4.2028 \times 10^{-20} T^7 \quad (25)$$

which yields for the critical point, $P_c^{\text{azeo}} = 3780$ kPa at $T_c^{\text{azeo}} = 468.2$ K. Values for the azeotropic compositions and azeotropic pressures calculated from eq 24 and 25, respectively, are included in Table V. When compared with values obtained from experimental data, the calculated values show an average deviation of 0.001 in z_1 and an average percent deviation of 0.56 for P^{azeo}.

Glossary

A, B, C, D	temperature-dependent parameters, K (eq 15)
B	second virial coefficient, cm^3/mol
f	fugacity, kPa
G	Gibbs free energy, J/mol
H	enthalpy, J/mol
k_{ij}	binary interaction coefficient in Tsonopoulos correlation
P	pressure, kPa
R	gas constant
T	absolute temperature, K
V	molar volume, cm^3/mol
x	liquid mole fraction
y	vapor mole fraction
z	azeotropic composition, mole fraction

Greek Letters

α, β, δ	parameters (eq 8)
$\alpha, \beta, \epsilon, \kappa$	temperature-dependent parameters (eq 12)
γ	activity coefficient

Superscripts

azeo	azeotropic state
c	critical state
E	excess property
l	liquid state for pure component or mixture
sat	saturated state
v	vapor state for pure component or mixture
°	standard state

Subscripts

c	critical state
i	component i
j	component j
1	n-pentane
2	acetone

Registry No. Pentane, 109-66-0; acetone, 67-64-1.

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Tetramethylammonium Perchlorate: Ion Size Parameters in Solution and in the Solid State

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The association constants at 25 °C of tetramethylammonium perchlorate in pyridine, 2-butanone, acetone, benzonitrile, and nitrobenzene have been determined. It is shown that the association constants (K_A) conform to a straight-line relation between ln K_A and $1/D$ as predicted by the Dennison–Ramsey theory of ion-pair formation. The a parameter, the distance between ions in the ion pair, of this salt determined from the slope of this straight line ($a = e^2/kT \times$ slope) is found to be 7.3 ± 0.1 Å, considerably larger than the N–Cl distance in its crystal.

Introduction

Before 1955 the most widely used relation between the dissociation constant of a salt in any solvent with sufficiently low dielectric constant, the temperature, the dielectric constant of solvents, and the interionic distance in associated ion pairs was developed by Bjerrum (*1*). However, the Bjerrum theory has certain inherent mathematical and physical defects (*2*). Denison and Ramsey (*3*) proposed a basis for counting associated ion pairs (only ions in contact are counted as ion pairs). From a thermodynamic consideration of a stepwise process for bringing about the change from an associated ion pair of a uni-univalent salt (in which the interionic distance has been called the "contact distance" and designated the a parameter) to the two free ions with interionic distance sufficiently large to permit the intervention of solvent molecules, an equation

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[†] This paper is dedicated to the memory of Professor J. B. Ramsey (1892–1965).

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$$\ln K_A = \ln K_A^0 + e^2/aDkt \qquad (1)$$

was obtained, where K_A is the association constant K_A^0 (according to the thermodynamic derivation) is the association constant of the two uncharged ions in solution, D is the dielectric constant of the solvent at temperature T, and e and k are the electronic charge and the Boltzmann constant, respectively. According to this equation, the value of the logarithm of K_A of a given salt with both ions electrically symmetrical, at a certain temperature, should vary linearly with the reciprocal of the dielectric constant of the solvent if its a parameter is independent of the dielectric constant of the solvent. The results obtained by Ramsey et al. (*4*, *5*) were shown to conform quite satisfactorily with this requirement. The values of the a parameter of numerous uni-univalent salts to which eq 1 is applicable have been derived from the slope ($=e^2/akT$) of the straight line obtained on plotting ln K_A vs. $1/D$.

Since each ion in an associated ion pair in solution is bonded with only one ion of opposite charge, one would expect that the distance between the ions in an associated ion pair of a salt in solution will be appreciably less than the distance between each ion and its equidistant nearest neighbors of opposite charge in its crystal. However, this conclusion may not be valid for a salt if the solvent molecules form such a stable complex with either of its ions that these complexing solvent molecules remain an integral part of the ion in the presence of oppositely charged ion. As a rule, the smaller the positive (or negative) ion in the similar salts, the greater is the opportunity to form ion-solvent complexes.

In a previous paper, Ramsey et al. (*5*) reported that the a parameter of a uni-univalent salt, tetrapropylammonium bromide in solution was about 17% less than the N-Br distance in its crystal. We present in this study the comparison of the a parameter obtained from eq 1 of a similar salt, tetramethylammonium perchlorate in solution and in the solid state, and explore further the relationship between the a parameter in solution and the interionic distance in the crystals.

Experimental Section

Pyridine, 2-butanone, acetone, benzonitrile, and nitrobenzene from Matheson, Coleman, and Bell were purified as follows: Pyridine was dried over silica gel for 2 days and then was distilled at 115-115.5 °C/760 mm. Only the middle portion of distillation was collected. The specific conductance was about 2×10^{-8} ohm^{-1} cm^{-1}.

2-Butanone was refluxed with silica gel for more than 2 days and then was fractionally distilled twice. The boiling point was between 78 and 78.2 °C at 756.8 mm. The specific conductance was about 4×10^{-8} ohm^{-1} cm^{-1}.

Acetone was dried over calcium chloride for about 2 days and then was distilled twice, with only the middle fractions saved. The boiling point was between 55.5 and 55.6 °C at 757.9 mm. The specific conductance was less than 1.5×10^{-7} ohm^{-1} cm^{-1}.

Benzonitrile was dried over silica gel overnight and then was distilled. The distillate was washed with Na_2CO_3 to remove any benzoic acid, and the benzonitrile was extracted with ether. The extract was washed with water and dried over $CaCl_2$ for 2 days. Ether was removed, and the residue was distilled at 22 mm. The portion with a boiling point of 81 °C at 22 mm was collected. Its specific conductance was less than 2×10^{-8} ohm^{-1} cm^{-1}.

Nitrobenzene was dried over silica gel overnight then was distilled at 7 mm. The boiling point was between 78 and 78.2 °C at 7 mm. The specific conductance was less than 1.0×10^{-8} ohm^{-1} cm^{-1}. Tetramethylammonium perchlorate was prepared as follows: 24.4 g of silver perchlorate was dissolved in ca. 250 mL of H_2O. The aquesous solution was heated (to concentrate) to near precipitation; then a solution of 17.9 g of tetramethylammonium bromide in 200 mL H_2O was added dropwise with stirring. The solution was filtered while still hot and the precipitate was washed several times with hot water. The filtrate was cooled in an ice bath and then filtered again. The white crystals were washed repeatedly with cooled water until the filtrate gave a negative test for silver ion. The product was recrystallized twice from warm (80 °C) ethyl acetate. After it was cooled, a small quantity of pentane was added to the ethyl acetate solution to increase the amount of product. The white crystals were dried for 36 h under vacuum.

Conductance Measurements

Conductance measurements were made with the shielded, alternating current bridge used by previous workers (*5*). Two conductance cells of the Kraus Elenmeyer type (*6*) were used having cell constants equal to 0.1561 and 0.1491 at 25 °C, which were determined in the way previously described (*3*).

The procedures followed in the preparation of solutions, successive dilutions, and resistance measurements are described in detail in ref *4*.

Results

The values of the association constant, K_A, and the limiting equivalent conductance, Λ_0, of tetramethylammonium perchlorate in each of the five solvents were obtained by use of the equation developed by Shedlovsky (*7*).

The two basic equations involved are

$$\Lambda = \theta\Lambda_0 - \alpha(\Lambda/\Lambda_0)(c\theta)^{1/2} \qquad (2)$$

where θ is the fraction dissociated and $\alpha = 8.15 \times 10^5\ \Lambda_0/(DT)^{3/2} + 82.4/\eta(DT)^{1/2}$, η is the viscosity of the solvent, and c is the concentration of the electrolyte (equivalents per liter of solution), and

$$1/\Lambda S(z) = c\Lambda f_{\pm}^2 S(z) K_A/\Lambda_0^2 + 1/\Lambda_0 \qquad (3)$$

where $f_{\pm}$ is the mean activity coefficient of the ionic species, $S(z) = 1 + z + z^2/2 + z^3/8 + \ldots$, and $z = \alpha(c\Lambda)^{1/2}/\Lambda_0^{3/2}$. The values of K_A and Λ_0 were obtained from the intercept and slope of the straight lines of the plot of $1/\Lambda S(z)$ as ordinate and $c\Lambda f_{\pm}^2 S(z)$ as abscissa according to eq 3. To establish the most probable straight-line relation between $1/\Lambda S(z)$ and $c\Lambda f_{\pm}^2 S(z)$, the conductances were determined at five perchlorate concentrations ranging from 10^{-5} to 10^{-4} M. The values of these functions are given in Table I along with the concentration of the electrolyte, and the dielectric constants and viscosities of the five solvents (*8*, *9*-*12*). Equivalent conductances and the trial value of limiting equivalent conductance for an independent set of measurements are also given in Table I. The best values of the slope and intercept were obtained by using the method of least squares and are given in Table II. Figure 1 shows the plots of $1/\Lambda S(z)$ vs. $c\Lambda f_{\pm}^2 S(z)$ in each of the five solvents. From the values of slope and intercept, the values of K_A and Λ_0 were obtained (Table III). In Figure 2, the values of log K_A are plotted against $100/D$. According to eq 1, a linear relation between log K_A and $100/D$ should result if the a parameter of salt has the same value in each of the solution. It was evidently quite satisfactory in the arrangement of these five points, with the exception of a slight deviation for 2-butanone. The straight line shown in Figure 2 was established by the method of least squares. From the slope (=0.3326) of this line the value of the a parameter of tetramethylammonium perchlorate in each of the five solvents was determined ($a = e^2/230.3kT \times$ slope) and found to be 7.31×10^{-8} cm (7.31 Å). A standard error propagation analysis (*13*), based on reasonable estimates of the errors involved in each of the experimental operations, yield an error in a of

Table I. Physical Properties of Pure Solvents; Experimental and Derived Data at 25 °C. Salt: Tetramethylammonium Perchlorate

solvent	D	η, P	$c \times 10^4$	Λ	Λ_0(trial)	$1/\Lambda S(z) \times 10^2$	$cf_{\pm}^2\Lambda S(z) \times 10^2$
pyridine	12.01	0.008824	8.2372	51.100	90.8	1.8041	1.9166
			3.8869	60.315		1.5603	1.3120
			2.2087	67.184		1.4183	0.93804
			1.1049	73.789		1.3076	0.58174
			0.66160	77.675		1.2514	0.39350
2-butanone	18.07	0.003771	3.7597	139.65	169.3	0.67037	3.8528
			2.5558	145.72		0.64917	2.8743
			1.4736	152.61		0.62760	1.8416
			0.60715	160.24		0.60660	0.85410
			0.29826	163.89		0.59762	0.43576
acetone	20.47	0.003040	5.2588	186.83	211	0.49864	7.1450
			2.3761	197.80		0.48139	3.7816
			1.0098	205.35		0.47142	1.7973
			0.45101	209.64		0.46666	0.85902
			0.20683	211.99		0.46470	0.41081
benzonitrile	25.20	0.01246	9.1387	47.051	54	1.9770	3.1811
			5.2924	48.989		1.9261	2.0565
			2.4303	50.944		1.8857	1.0569
			1.3040	52.020		1.8662	0.60377
			0.61084	52.983		1.8492	0.29875
nitrobenzene	34.70	0.01839	7.7045	35.892	38.8	2.6475	2.3270
			5.1083	36.521		2.6258	1.6272
			2.7293	37.214		2.6050	0.91890
			1.4378	37.731		2.5913	0.52814
			0.75473	38.114		2.5809	0.27286

Table II. Data Derived from the Method of Least-Squares.[a] Salt: Tetramethylammonium Perchlorate

solvent	a	b
pyridine	0.01094 ± 0.00145	0.36 ± 0.06
2-butanone	0.0058845 ± 0.0000025	0.02123 ± 0.00005
acetone	0.0046240 ± 0.0000014	0.00505 ± 0.00002
benzonitrile	0.018390 ± 0.000033	0.0422 ± 0.0009
nitrobenzene	0.025741 ± 0.000021	0.0317 ± 0.0008

[a] a = intercept; b = slope.

Table III. Limiting Equivalent Conductances (Λ_0) and Association Constants (K_A) of Tetramethylammonium Perchlorate in Various Solvents at 25 °C; Dielectric Constants (D) of Pure Solvents at 25 °C

solvent	D	Λ_0	$K_A \times 10^{-2}$
pyridine	12.01	91.3 ± 0.1	30.3 ± 0.2
2-butanone	18.07	169.00 ± 0.15	6.13 ± 0.02
acetone	20.47	216.00 ± 0.06	2.36 ± 0.01
benzonitrile	25.20	54.3 ± 0.1	1.24 ± 0.04
nitrobenzene	34.07	38.8 ± 0.3	0.478 ± 0.005

approximately 1%. Thus, the value of the *a* parameter for tetramethylammonium perchlorate is 7.3 ± 0.1 Å.

Discussion

The value of the *a* parameter of tetramethylammonium perchlorate in solution found in this study is considerably larger than the distance between the centers of the oppositely charged ions in the solid state. The N–Cl distance of this salt in crystalline state determined by McCullough was 4.31 Å (*14*).

Interatomic distances derived from electron diffraction (*15*) and microwave spectroscopy (*16*) for the alkali metal halides in the vapor phase were found to be from 10 to 17% less than the corresponding minimum distances in the respective crystals. The interatomic distances from microwave spectroscopy (*17*) of thallium, indium, and gallium halides were found to be ~ 21–25% less than the corresponding crystallographic distances. If bonding in an ion pair in solution is similar to bonding in the molecule in the vapor state, it might be expected by analogy that the distance between ions in an ion pair, the *a* parameter, would be less than the distance between ions in the crystal.

In a previous work by Ramsey et al. (*5*) the value of the *a* parameter of tetrapropylammonium bromide, derived from the slope of the straight line ($a = e^2/kT \times$ slope) in six nonaqueous solvents was found to be ca. 17% less than the minimum center-to-center distance between its oppositely charged ions in the crystalline state. It appears that the result reported in this paper is contradictory.

A possible interpretation of this seeming discrepancy from our expectation, namely that the *a* parameter of a salt should be significantly less than the corresponding crystallographic distance, is conceivable. It seems reasonable, at least to some extent, to attribute the "abnormality" to the size of methyl groups in tetramethylammonium perchlorate. As we mentioned before (in the Introduction), the contact ion-pair theory may not be valid for a salt if the solvent molecules form such a stable complex with either of its ions that the complexing solvent molecules remain an integral part of the ion in the presence of oppositely charged ion. As a rule, the smaller the positive (or negative) ion in the similar salts, the greater is the opportunity to form ion–solvent complexes due to stronger interactions between solvent and electroltye. It has been found that in the study of systems containing tetraalkylammonium picrates and methyl chloride/water mixtures (*18*) the ion–solvent interaction on $(Me)_4N^+$ ion is stronger than on $(Et)_4N^+$ and $(Pr)_4N^+$ ions.

Before the interpretation of the results of this paper could be considered more than a guess, additional information, such as a systematic study of the association of $(Me)_4NClO_4$ in mixed solvents and at different temperatures (*19*), is needed. At the same time, the Denison–Ramsey theory should be reexamined.

The Denison–Ramsey theory which is based on the primitive model or the "sphere-in-a-continuum" model has conventionally been used during the past decades to describe electrolytes in which the solvent is assumed to be a continuum, characterized electrostatically by its macroscopic dielectric constant, and the ions are assumed to be charged spheres. The center-to-center distance *a* of ions of opposite charge can be calculated by using the model, from the association constant K_A. K_A can be obtained from conductance data in the range of low concentrations. The weakest point of the sphere-in-a-continuum model appears to be the assumption of continuity of solvent since $(Me)_4N^+$ and ClO_4^- should be representable as spheres. When an anion and a cation are apart by distances of the order of some tens of molecular diameters, the macroscopic dielectric constant of the solvent is a good approximation in calculating the potential energy of the two ions of an incipient pair, but as

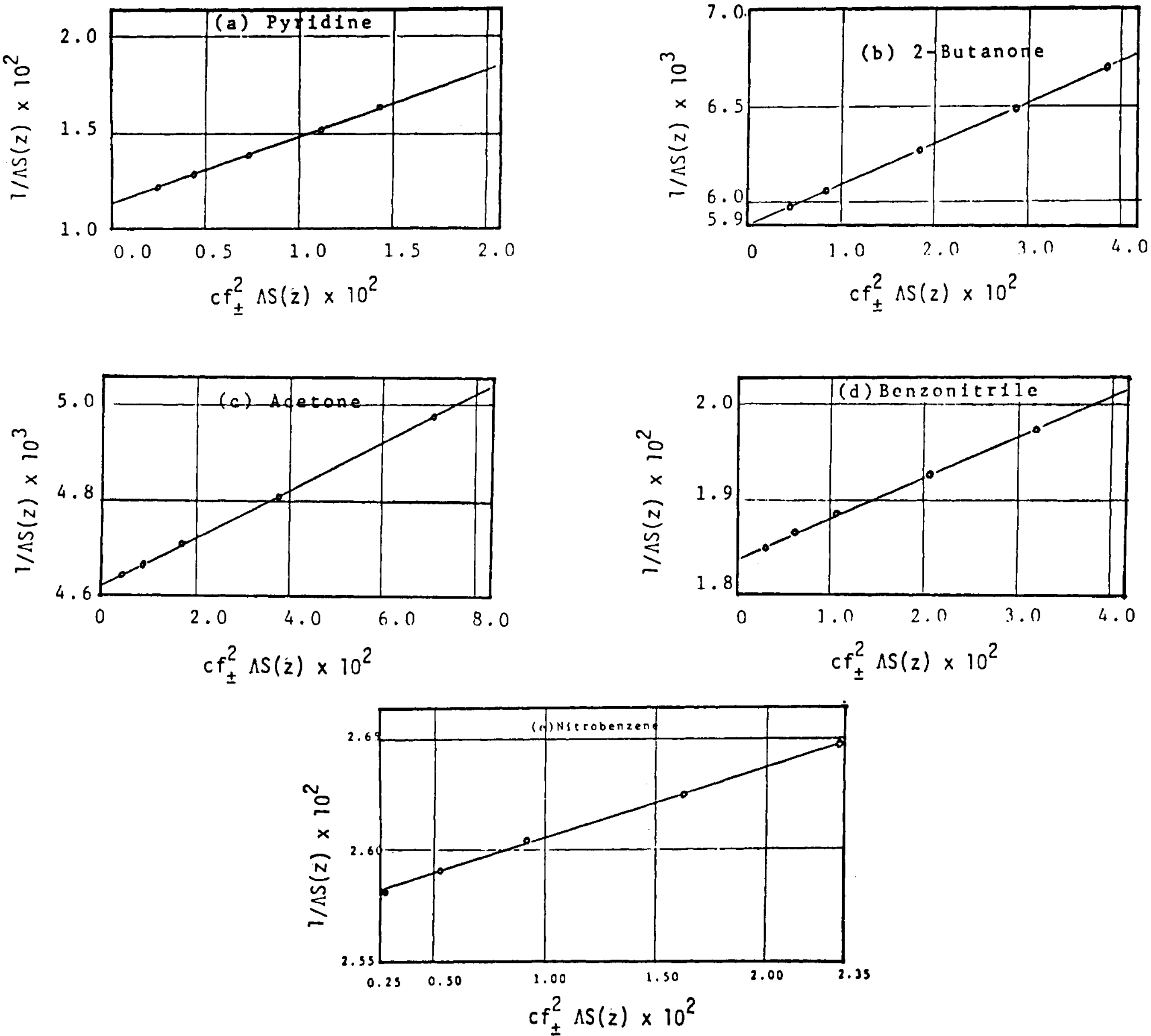

Figure 1. Shedlovsky plot: tetramethylammonium perchlorate in various solvents at 25 °C. Points correspond to those given in Table I: (a) pyridine, (b) 2-butanone, (c) acetone, (d) benzonitrile, (e) nitrobenzene.

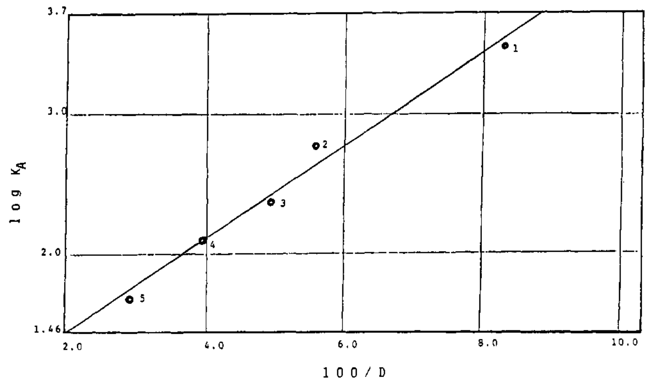

Figure 2. Dependence of the association constant of tetramethylammonium perchlorate on the macroscopic dielectric constant of the solvent. Points correspond to those given to the solvent in Table III: (1) pyridine, (2) 2-butanone, (3) acetone, (4) benzonitrile, (5) nitrobenzene.

the mutual distance approaches several molecular diameters, it has been found that the approximation fails because solvent molecules will be polarized by induction and/or orientation by the intense ionic fields, not to mention the possible interaction between ions (*20–24*). It is this range of small distances which contribute most to the integral which relates a, D, and K_A. According to the above argument, in eq 1, K_A is not simply a function dependent only on contact distance and dielectric constant; rather, it depends as well on the short-range ion–solvent interactions which are system-specific (*25–27*).

Over the years, many models for ion-pair formation, which take into account specific solvent–ion interactions, have been developed (*27–33*). It would be interesting to reevaluate the association of $(Me)_4NClO_4$ in the five solvents which are reported in this study with these models and to compare the results with those from the Denison–Ramsey theory. However, due to the limited data available, other approaches will not be discussed here.

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Registry No. $(Me)_4NClO_4$, 2537-36-2.

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Densities of Aqueous Electrolyte Solutions. A Model for a Data Bank

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A model is proposed for establishing a data bank of densities of aqueous electrolyte solutions. The model, based on the concept of the apparent molar volume, involves separation of the molar volume of the salt and of a parameter accounting for deviation of a system from additivity into cationic and anionic contributions. The model has been tested on a model set of aqueous solutions of alkali metal and ammonium halides (with the exception of fluorides) and nitrates at 25 °C over maximum concentration ranges. All the unknown parameters are obtained simultaneously by a regression method applied to all the experimental data involved. In this way, literature data for a set of 24 systems have been described by means of just 10 parameter pairs, which provide density values correct to three decimal places.

Introduction

A rigorous way of expressing the density, d, of a binary system is in terms of the molar volume V

$$V = (M_1x_1 + M_2x_2)/d \qquad (1)$$

where M_1 and M_2 are the molecular weights of the two components and x_1 and x_2 are their mole fractions. With the concentration dependence of density transformed into the concentration dependence of the molar volumes of the components, we can take up the question of additivity of the molar volumes

$$V = V_1x_1 + V_2x_2 = V_sx + V_w(1 - x) \qquad (2)$$

where V_1 and V_2 are the molar volumes of pure components at the same temperature. For most binary systems, including the systems water-salt which are the subject of the present paper, deviations from additivity occur:

$$\Delta V^E = V - V_1x_1 - V_2x_2 \qquad (3)$$

There are several approaches to accounting for these deviations. The classical thermodynamic approach operates with partial molar volumes of components, which are each a function of composition. Of more practical importance, however, is the semiempirical concept of the apparent molar volume (*1-3*). It was not the aim of present paper to provide an accurate description of densities of dilute solutions. Such data have been included in the set treated, but they overlap with somewhat less accurate results for the region of higher concentrations. For statistical reasons, therefore, the effects consistent with the Debye-Hückel theory are not demonstrable.

Model for the Dependence of Molar Volume on Composition

In this paper we adhere to the concept of the apparent molar volume of water, which is more logical than the concept of the apparent molal volume of the salt (*2*) and is capable of describing the deviations from additivity over the whole concentration range. In deriving a relation for the molar volume of a system, we start from the quasi-lattice model of solution, with water distributed between the cationic and anionic sublattices in the ratio of the stoichiometric coefficents of salt M_pX_q, i.e., $p:q$. Now, the probability of finding a water molecule in the immediate neighborhood of an ion is proportional to