suggest that the computed ground state wave functions are similar to those obtained by the ab initio RHF method if one uses a minimal basis set. As yet unexplained anomalies exist in the calculated Hartree–Fock virtual orbitals and in the virtual orbital energies. As a result, it has not been possible to compute meaningful excitation energies by this method. Accordingly ODIN excitation energies are omitted from Tables I, III, and IV.

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Activity Coefficients of 2:1 Electrolytes in Structured Aqueous Solutions

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Abstract: A model for an ion immersed in a dielectric medium as a spherical charge surrounded by a region of dielectric gradient has been introduced previously. The treatment of this model is extended to structured solutions of all types of strong, binary electrolytes. The Madelung constant method of calculating energies is analyzed in terms of a Guntelberg charging process. The activity coefficients of the alkaline earth halides and nitrates, and of $NiCl_2$ and $CoCl_2$, are examined on the basis of a loose fluorite structure in solution. The results show excellent agreement with experimental data up to concentrations as high as 2 or 3 *M*.

A model for ions in solution pictures each ion as a spherical charge surrounded by a sea of dielectric gradient. The dielectric gradient sea surrounding one ion interacts with the electric field from another ion to produce a repulsive force, in addition to the coulombic force, between that ion pair. As a result of this additional force, 1:1 electrolytes were shown to assume a loose face-centered-cubic lattice in solution. The partial molar electrical free energy of this structured solution was found via a Madelung-type calculation. This led to an expression for activity coefficients of 1:1 electrolytes which agreed with experimental data from the lowest concentrations at which measurements had been made up to concentrations as high as 4 *M*.[2] This model also led to an interpretation of heats of dilution for 1:1 electrolytes which agreed well with experimental data.[3]

In this paper the theory will be extended to strong binary electrolytes of all valence types and a generalized expression for partial molar free energies and activity coefficients will be developed. For the binary salt $C_{\nu+}A_{\nu-}$ the type of electrolyte is designated by the ratio $z_+:z_-$. One formula unit of this salt exists in solution as ν_+ cations of charge z_+ and ν_- anions of charge z_-.

Theory

In carrying out the analysis of the specific ion–ion interactions in unsymmetrical electrolytes it became evident that the equations developed in the first paper[2] were valid for symmetrical 1:1 electrolytes in which one kind of ion (cation or anion) possessed a dielectric gradient sea while the other kind did not. The force generated by the field of one ion acting on the dielectric gradient surrounding the other was recognized, but the force generated by the field of the other acting on the gradient surrounding the one was neglected. The complete expression for the interaction force between two ions, *i* and *j*, in solution is given, to the degree of approximation in ref 2, by

$$F_{ij} = \frac{z_i z_j}{kR_{ij}^2} + \frac{3}{4}\epsilon_0 \left(\frac{z_j^2}{k_{0i}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_i V_{i\,\mathrm{sea}} + \frac{z_i^2}{k_{0j}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_j V_{j\,\mathrm{sea}}\right)\frac{1}{R_{ij}^4} \quad (1)$$

where the symbols are the same as those in ref 2. The work of bringing a pair of ions from infinite distance to R is, therefore,

$$-W^{\mathrm{el}} = \frac{z_i z_j}{kR_{ij}} + \frac{\epsilon_0}{4}\left(\frac{z_j^2}{k_{0i}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_i V_{i\,\mathrm{sea}} + \frac{z_i^2}{k_{0j}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_j V_{j\,\mathrm{sea}}\right)\frac{1}{R_{ij}^3} \quad (2)$$

We use the sign convention that positive work is work done by the system on the surroundings. Equations 1 and 2 apply to all pairwise interactions whether the charges on the two ions are like or unlike. The pairwise interactions resulting from the field-dielectric-gradient effect now show a contribution from each separate ion. Since the separate parts of the field-dielectric-gradient term cannot be evaluated and the B coefficient was determined from experimental data, the method of analyzing the data has not changed. The present development is more satisfying since the contributions of the separate, individual ions are now recognized.

The summation over all pairwise interactions will give the electrical work of a particular distribution of the ions in solution. An equivalent summation which gives the electrical work of a distribution of ions in a dielectric medium[4] is

$$-W^{\mathrm{el}} = \frac{1}{2}\sum_i\sum_j \left[\frac{z_i z_j}{k}\frac{1}{R_{ij}} + \frac{\epsilon_0}{4}\left(\frac{z_i^2}{k_{0j}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_j V_{j\,\mathrm{sea}} + \frac{z_j^2}{k_{0i}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_i V_{i\,\mathrm{sea}}\right)\frac{1}{R_{ij}^3}\right] \quad (3)$$

The form of eq 3 has been chosen so that the summations are carried out over all ions. The factor of ½ must be included to avoid counting each ion twice. When the particular distribution is that of a well-ordered structure, such as fcc or fluorite, for example, the Madelung approach can be used to find the electrical work.

The Madelung constant results from an analysis of the coulombic energy of a well-ordered three-dimensional array of ions in a solid, crystalline electrolyte. The existence of a repulsive force which was not the result of simple charge-charge interactions has been recognized,[5,6] but the Madelung constant itself refers only to the classical interactions of charges obeying Coulomb's law. The Madelung constant can be used to find the classical coulombic electrical energy, but does not directly reveal the nature of other interaction energies.

The coulombic work determined with a Madelung constant will be the coulombic electrical free energy. However, the question of whether this free energy is the total coulombic free energy or the partial molar coulombic free energy has never been discussed since the partial molar coulombic free energy and the total coulombic free energy per mole are identical for a pure, crystalline, solid electrolyte. Previous considerations of coulombic Madelung free energies have dealt with such pure, solid, ionic crystals. In solution, however, the partial molar coulombic free energy and the total coulombic free energy per mole of electrolyte are not the same and a careful distinction must be drawn between them.

The coulombic energy found with a Madelung constant for structured 1:1 electrolytes in solution has been identified with the partial molar coulombic electrical free energy[2,7] and alternatively as the total coulombic electrical free energy per mole.[8,9] We will now show that the identification of the Madelung coulombic energy with the partial molar coulombic free energy is correct while the identification of the Madelung coulombic energy with the total coulombic free energy per mole is incorrect. We will focus our attention on the coulombic term for this discussion; the conclusions will apply to the field-dielectric-gradient term as well.

The Madelung method of calculating the coulombic part of electrical work for n moles of the structured electrolyte $C_{\nu_+}A_{\nu_-}$ can be applied with the expression[4]

$$-W^{\mathrm{el}} = \frac{1}{2}\sum_i\sum_j \frac{z_i z_j}{kR_{ij}} \quad (4)$$

where the summations are carried out over all ions in the system. Since we are not interested in the evaluation of Madelung constants but rather in the interpretation of the kind of energy found with a Madelung method, we will follow a procedure essentially the same as that used by Kendall.[10] In the double summation of eq 4 there will be $n\nu_+N$ terms in which the central ion will be the cation, and $n\nu_-N$ terms in which the central ion will be the anion, giving

$$-W^{\mathrm{el}} = \frac{n\nu_+N}{2k}\left(\sum_{j+}\frac{z_{j+}}{R_{j+}}\right)z_+ + \frac{n\nu_-N}{2k}\left(\sum_{j-}\frac{z_{j-}}{R_{j-}}\right)z_- \quad (5)$$

The sum over $j+$ represents a summation over all ions outside the central cation and R_{j+} represents the distance from the central cation to the $(j+)$th ion and the sum over $j-$ represents a summation over all ions outside the central anion and R_{j-} the distance from the central anion to the $(j-)$th ion. Each distance can be expressed in terms of the unit distance R as

$$R_{j+} = a_{j+}R \quad (6)$$

and

$$R_{j-} = a_{j-}R \quad (7)$$

In addition, since electrical neutrality requires that

$$\nu_+z_+ + \nu_-z_- = 0 \quad (8)$$

each z_j can be expressed in terms of either z_+ or z_-. We therefore write that

$$\sum_{j+}\frac{z_{j+}}{R_{j+}} = \frac{z_-}{R}\left(\sum_{j+}\frac{1}{a_{j+}'}\right) \quad (9)$$

and that

$$\sum_{j-}\frac{z_{j-}}{R_{j-}} = \frac{z_+}{R}\left(\sum_{j-}\frac{1}{a_{j-}'}\right) \quad (10)$$

where the primes on the a_j' signify that the distance factor has been adjusted by a proper ratio of ν's in those terms where necessary so that only one z variable remains in each summation. Substitution of eq 9 and 10 into eq 5 gives

$$-\frac{W^{\mathrm{el}}}{nN} = \left[\frac{\nu_+}{2}\left(\sum_{j+}\frac{1}{a_{j+}'}\right) + \frac{\nu_-}{2}\left(\sum_{j-}\frac{1}{a_{j-}'}\right)\right]\frac{z_+z_-}{kR} \quad (11)$$

so that in this formulation the Madelung constant is given by

$$A'' = \frac{\nu_+}{2}\left(\sum_{j+}\frac{1}{a_{j+}'}\right) + \frac{\nu_-}{2}\left(\sum_{j-}\frac{1}{a_{j-}'}\right) \quad (12)$$

We are now in a position to justify the identification of the partial molar electrical free energy with the work calculated by the Madelung method.

Guntelberg Charging Process

The proper identification of the coulombic part of the electrical free energy in structured solutions can be developed from a Guntelberg charging process.[11] According to the Guntelberg charging process

Table I. Coefficients in Equation 27

n	a_n	n	a_n	m	a_m
1	108	5	144	3	68
2	156	6	96	4	84
3	64	8	36	19	60
4	54	9	48	27	4
		12	8		

$$\frac{\mu_i^{\mathrm{el}}}{N} = \int_0^{z_i} \psi_i \, \mathrm{d}z_i \tag{13}$$

where μ_i^{el}/N is the chemical potential of the ith ion, N is Avogadro's number, ψ_i is the electrical potential acting on the ith ion, and z_i is the charge on the ith ion. The advantage of the Guntelberg charging process is that the integration in eq 13 is carried out at constant ionic separation, or therefore at constant R. In the Debye–Hückel approach, eq 13 is integrated at constant κ,[11,12] which is equivalent to constant R in the present approach since $1/\kappa = r$ where r is the Debye–Hückel length.[13]

The coulombic ψ_i in eq 13 can be found easily for structured ions in solution as

$$\psi_i = \sum_j \frac{z_j}{kR_{ij}} \tag{14}$$

which, using eq 9, gives

$$\psi_+ = \frac{z_-}{kR}\left(\sum_{j+} \frac{1}{a_{j+}'}\right) \tag{15}$$

Equation 15 can be substituted into eq 13 to give

$$\frac{\mu_+^{\mathrm{el}}}{N} = \int_0^{z_+} \frac{z_-}{kR}\left(\sum_{j+} \frac{1}{a_{j+}'}\right) \mathrm{d}z_+ \tag{16}$$

which, on the substitution of eq 8, gives

$$\frac{\mu_+^{\mathrm{el}}}{N} = \frac{1}{kR}\left(\sum_{j+} \frac{1}{a_{j+}'}\right)\left(-\frac{\nu_+}{\nu_-}\right)\int_0^{z_+} z_+ \mathrm{d}z_+ = \frac{1}{kR}\left(\sum_{j+} \frac{1}{a_{j+}'}\right)\left(-\frac{\nu_+}{\nu_-}\right)\frac{z_+^2}{2} = \frac{1}{kR}\left(\sum_{j+} \frac{1}{a_{j+}'}\right)\frac{z_+z_-}{2} \tag{17}$$

The development following eq 15–17 for anions gives

$$\frac{\mu_-^{\mathrm{el}}}{N} = \frac{1}{kR}\left(\sum_{j-} \frac{1}{a_{j-}'}\right)\frac{z_+z_-}{2} \tag{18}$$

The chemical potential for a mole of electrolyte is

$$\mu^{\mathrm{el}} = \nu_+\mu_+^{\mathrm{el}} + \nu_-\mu_-^{\mathrm{el}} \tag{19}$$

which on the substitution of eq 17 and 18 gives

$$\frac{\mu^{\mathrm{el}}}{N} = \left[\frac{\nu_+}{2}\left(\sum_{j+} \frac{1}{a_{j+}'}\right) + \frac{\nu_-}{2}\left(\sum_{j-} \frac{1}{a_{j-}'}\right)\right]\frac{z_+z_-}{kR} \tag{20}$$

In view of eq 12, eq 20 now tells us that

$$\frac{\mu^{\mathrm{el}}}{N} = \frac{A''z_+z_-}{kR} \tag{21}$$

or that the classical Madelung calculation of the coulombic electrical work is to be identified with the partial molar electrical free energy and not with the total free energy as claimed by Glueckauf[8] and Frank and Thompson.[9] Equation 21 corresponds to the identification used in ref 2; the justification for this identification using the Guntelberg charging process is better than the justification given in ref 2.

In view of eq 21 and 2, for structured ions in solution, the generalized equation for the partial molar electrical free energy for any strong binary ionic salt in solution (deviations from ideal behavior are assumed to be electrical in nature) is

$$\frac{\mu^{\mathrm{el}}}{N} = \frac{\bar{G}_2^{\mathrm{el}}}{N} = \frac{A''z_+z_-}{k}\frac{1}{R} + \frac{\epsilon_0}{4} \times \left[B_1''\left(\frac{2z_+^2}{k_{0-}^2}\right)\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_- V_{-\,\mathrm{sea}} + B_2''\left(\frac{2z_-^2}{k_{0+}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_+ V_{+\,\mathrm{sea}}\right) + B_3''\left(\frac{z_+^2}{k_{0-}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_- V_{-\,\mathrm{sea}} + \frac{z_-^2}{k_{0+}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_+ V_{+\,\mathrm{sea}}\right)\right]\frac{1}{R^3} \tag{22}$$

where A'' is the Madelung constant and B_1'', B_2'', and B_3'' are Madelung-like constants for the particular structure displayed by the electrolyte in solution. The Madelung-like constants, B_i'' in eq 22, have been considered previously for solid, crystalline electrolytes.[14]

The Madelung constants, A'' in eq 22, can be found in various ways and can be expressed with various values depending on which "unit distance" is selected.[5,6] We have used R as the shortest distance between a cation and anion in the particular structure being considered.

Activity Coefficients

The particular structure in solution is not known a priori but can be found from experimental data. With the symmetrical 1:1 electrolytes the X-ray data and the activity coefficient data agreed with a fcc structure.[2] For the 1:2 and 2:1 electrolytes, as will be shown below, X-ray and activity coefficient data agree with the fluorite structure in solution. The Madelung constant, A'', has been calculated for many structural types and can be used in eq 22. Care must be exercised when using these values, however, since a certain flexibility is allowed in choosing the "unit distance" and in the handling of the z's in the summation. The Madelung-like constants, B_1'', B_2'', and B_3'', could be determined for these various structural types but checking them against experimental data will be impossible until more is known about the dielectric gradient characteristics of individual ions.

From eq 22 the generalized expression for the mean mole fraction (rational) ionic activity coefficient becomes

$$\log f_\pm = \frac{A''z_+z_-N}{(\ln 10)\nu \boldsymbol{R}Tk}\left(\frac{1}{R}\right) + \frac{\epsilon_0 N}{(\ln 10)4\nu \boldsymbol{R}T} \times \left[B_1''\left(\frac{2z_+^2}{k_{0-}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_- V_{-\,\mathrm{sea}}\right) + B_2''\left(\frac{2z_-^2}{k_{0+}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_+ V_{+\,\mathrm{sea}}\right) + B_3''\left(\frac{z_+^2}{k_{0-}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_- V_{-\,\mathrm{sea}} + \frac{z_-^2}{k_{0+}^2}\left|\frac{\mathrm{d}k}{\mathrm{d}R}\right|_+ V_{+\,\mathrm{sea}}\right)\right]\frac{1}{R^3} \tag{23}$$

where $\nu = \nu_+ + \nu_-$ for the salt $\mathrm{C}_{\nu_+}\mathrm{A}_{\nu_-}$, $\boldsymbol{R}$ is the gas constant, and T is the absolute temperature. For all structures R^{-1} is given by

$$R^{-1} = a_{A''}\left(\frac{N}{1000}\right)^{1/3} c^{1/3} \tag{24}$$

where c is concentration in moles per liter, N is Avogadro's number, and $a_{A''}$ is a value found from the particular structure under consideration, so the generalized expression for activity coefficients is

$$\log f_\pm = -Ac^{1/3} + Bc \tag{25}$$

for all strong binary electrolytes in solution. A can be calculated from fundamental values if the structure is known while B cannot, at least at the present time. Alternatively,

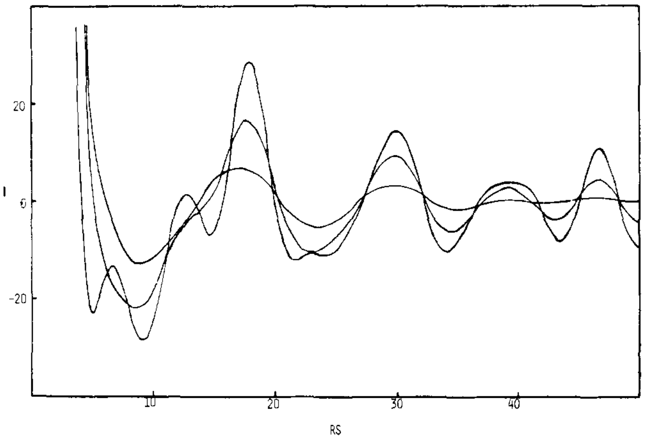

Figure 1. Intensity of scattered X-rays vs. rs as given by eq 27 for a single cell of fluorite structure with cation and anion having equal scattering powers. The curve nearest the ordinate has $a^2r^2 = 0$, the next curve has $a^2r^2 = 1$, and the curve furthest from the ordinate has $a^2r^2 = 4$.

A can be evaluated for various structures and that structure which agrees with, for example, activity coefficient data, assigned to the electrolyte in solution.

2:1 Electrolytes

In order to apply eq 25, the structure assumed by ions in solution must be known. The analysis of X-ray diffraction patterns from the 1:2 electrolyte chloroplatinic acid indicated that a loose fluorite lattice was assumed in solution.[2] Since the behavior of 1:2 electrolytes should not differ from the behavior of 2:1 electrolytes, the 2:1 electrolytes should assume the same fluorite structure.

Albright's X-ray diffraction data[15] on concentrated solutions of $CaCl_2$ lend further support to the existence of a loose fluorite lattice in solution. His electron radial distribution functions do not show this structure directly, but the method[2] applied to chloroplatinic acid and LiBr and LiCl solutions does reveal the structure. The Wierl equation with exponential is

$$I \propto \sum_i \sum_j z_i z_j e^{-a^2 r_{ij}^2} \left(\frac{\sin (s r_{ij})}{s r_{ij}} \right) \tag{26}$$

For a single fluorite cell in which cation and anion have equal scattering powers, eq 26 becomes

$$I \propto \sum_n^{1-6,\underline{8},9,12} \frac{a_n e^{-(n/4)a^2r^2} \sin ((\sqrt{n}/2)rs)}{(\sqrt{n}/2)rs} + \sum_m^{3,4,\underline{19},27} \frac{a_m e^{-(m/16)a^2r^2} \sin ((\sqrt{m}/4)rs)}{(\sqrt{m}/4)rs} \tag{27}$$

where the coefficients a_n and a_m are given in Table I. A plot of eq 27 with proportionality constant of one is shown in Figure 1, for $a^2r^2 = 0$, 1, and 4, where r is the unit cell length. Figure 1 indicates that maxima are present at $rs(\max 1) = 17.88$, 17.72, and 17.2 for $a^2r^2 = 0$, 1, and 4, respectively, and $rs(\max 2) = 30.04$, 29.76, and 29.6 for $a^2r^2 = 0$, 1, and 4, respectively.

Professor Albright has kindly made available his original data[16] on his most concentrated solution of $CaCl_2$, a salt which should have approximately equal scattering powers of cation and anion, a condition specified for eq 27. Using the mole ratios of salt to water, and density from the International Critical Tables, this salt has a concentration of 4.84 M and therefore a fluorite unit cell length of $r = 11.4$ Å. A plot of Albright's I vs. s is shown in Figure 2 and definite changes in slope occur at the two points expected for structured ions, namely, $s(1) = 1.49$–1.57 and $s(2) = 2.60$–2.64. Professor Albright also pointed out that the geometry of his system was chosen to maximize the counting efficiency at large values of s which has the undesirable effect of reducing peak resolution at low s, so that the change in slope rather than a more definite maximum is not surprising.

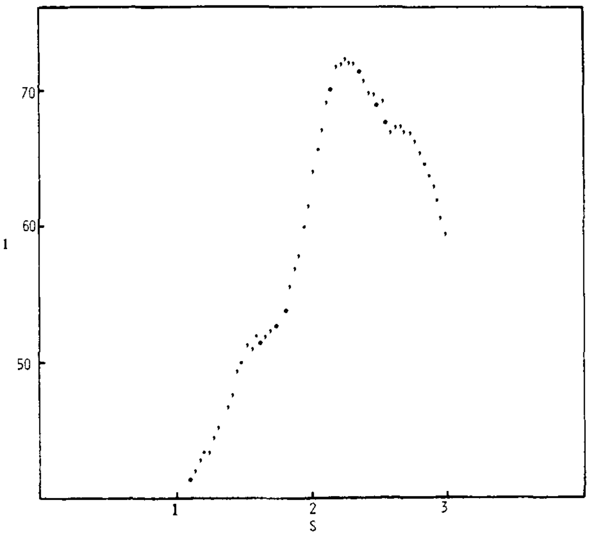

Figure 2. X-Ray intensity vs. s (= $[4\pi/\lambda] \sin \theta$) for 4.84 M $CaCl_2$ solution in water as obtained by Albright.[15,16]

The loose fluorite structure for 2:1 electrolytes can be tested further with eq 25. For the fluorite structure the Madelung constant, A'' in eq 22, has the value 2.51939[17] if the distance R is the shortest distance between cation and anion. In this case, $R^{-1} = (2/\sqrt{3})(2Nc/1000)^{1/3}$ and therefore $a_{A''}$ in eq 24 has the value $(2/\sqrt{3})(2)^{1/3}$. Using $k = 78.36$ at 25°,[18] eq 25 for 2:1 electrolytes in water becomes

$$\log f_{\pm} = -0.64100\, c^{1/3} + Bc \tag{28}$$

To make use of tabulated activity coefficient data the expressions for mean molal and mean mole fraction ionic activity coefficients[19] can be combined to give

$$\log \gamma_{\pm} + 0.64100 c^{1/3} + \log (1 + [\nu m M_1/1000]) = Bc \tag{29}$$

For 2:1 electrolytes, $\nu = \nu_+ + \nu_- = 3$. The form of eq 29 is preferred to that used in ref 2, eq 14.

The left-hand side of eq 29 can be plotted against c, and should give a straight line with slope B. Such plots for the alkaline earth halides and nitrates and $NiCl_2$ and $CoCl_2$ at 25° are shown in Figures 3–7 and straight lines are observed up to concentrations as high as 1 M (2 N) in all cases and in some cases as high as 3 M (6 N). The data were taken from the tables in Robinson and Stokes.[20] The slopes and intercepts, determined by linear regression analysis, for the linear portions of these curves are shown in Table II. The relationship between molality and molarity was determined from density data in the International Critical Tables.

Discussion

The straight lines obtained over a broad concentration range for the 2:1 electrolytes in Figures 3–7 indicate that the behavior of these salts can be interpreted on the basis of a model of a loose fluorite structure in solution. This is further confirmation of the importance of the field-dielectric-gradient forces operating between ions in aqueous solution.

The sign of the higher valence species should have no effect on the final structure and we would expect both 1:2 and

Table II. Slopes and Intercepts for the Linear Portions of the Curves Shown in Figures 3-7

Salt	Slope	Intercept
$MgCl_2$	0.45390	-0.0253
$MgBr_2$	0.55911	-0.0256
MgI_2	0.65388	-0.0176
$Mg(NO_3)_2$	0.42750	-0.0247
$CaCl_2$	0.39824	-0.0277
$CaBr_2$	0.47877	-0.0267
CaI_2	0.56914	-0.0185
$Ca(NO_3)_2$	0.22156	-0.0309
$SrCl_2$	0.36357	-0.0261
$SrBr_2$	0.42921	-0.0245
SrI_2	0.53322	-0.0174
$BaCl_2$	0.28957	-0.0217
$BaBr_2$	0.36933	-0.0229
BaI_2	0.51441	-0.0221
$CoCl_2$	0.41521	-0.0226
$NiCl_2$	0.42381	-0.0263

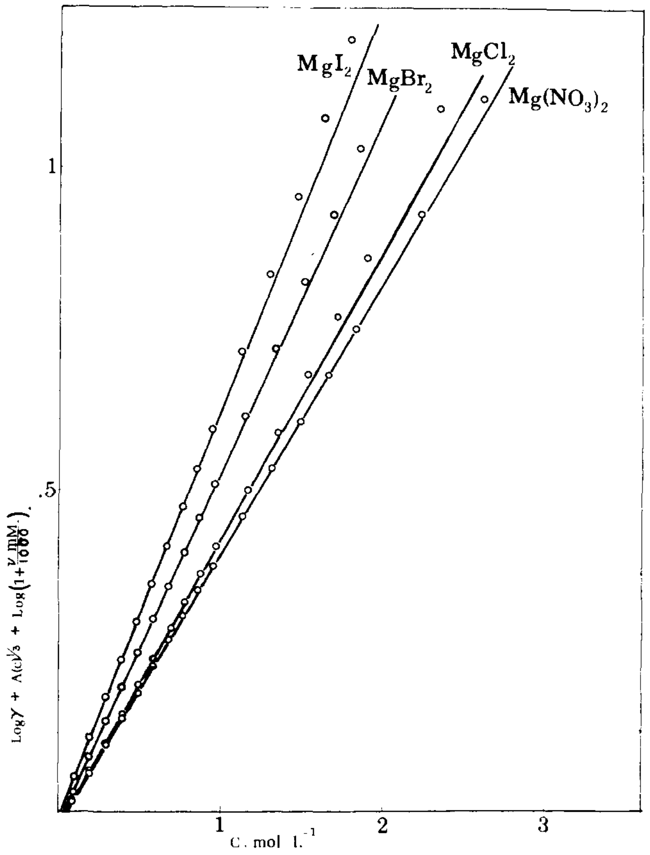

Figure 3. The left-hand side of eq 29 plotted against the molar concentration for magnesium halides and nitrate at 25°C in water.

2:1 electrolytes to assume a fluorite structure. The 1:2 salts should behave like 2:1 salts. We have analyzed activity coefficient data for one group of 1:2 salts, the alkali sulfates, and they do not behave as predicted. Previous work on the 2:1 and 1:2 electrolytes[21] has indicated that the alkaline earth halides and $CoCl_2$ and $NiCl_2$ are very strong electrolytes in aqueous solution while the alkali sulfates are not. Since a fundamental requirement of the theory is complete dissociation, failure of the alkali sulfates is not surprising.

Equation 29 indicates that the plots in Figures 3-7 should intercept the origin, but the intercepts miss (0,0). The original extrapolations, based on a square-root law, should be corrected to bring the intercept through the origin and this will give a new set of standard chemical potentials and a new set of activity coefficients for each of the alkaline

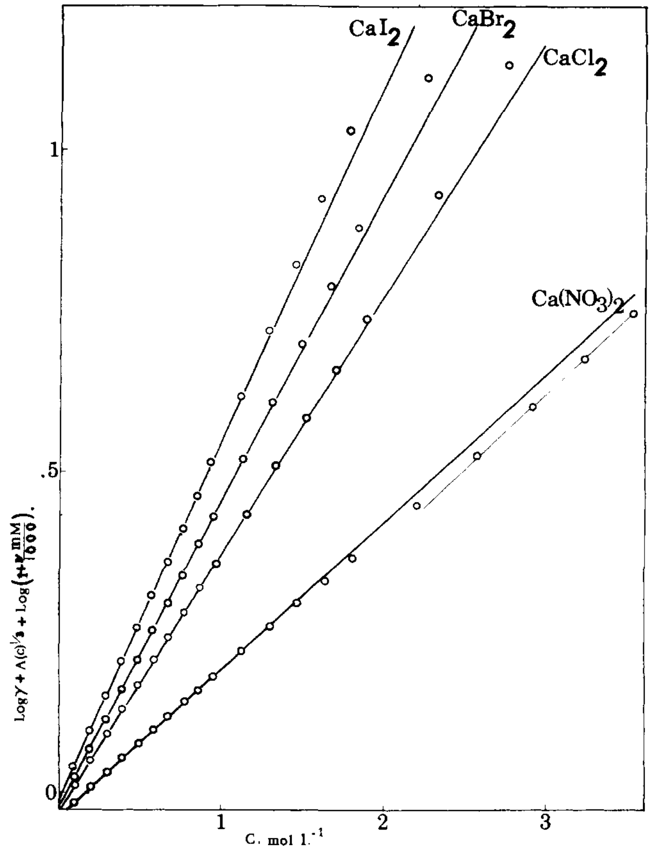

Figure 4. The left-hand side of eq 29 plotted against the molar concentration for calcium halides and nitrate at 25° in water.

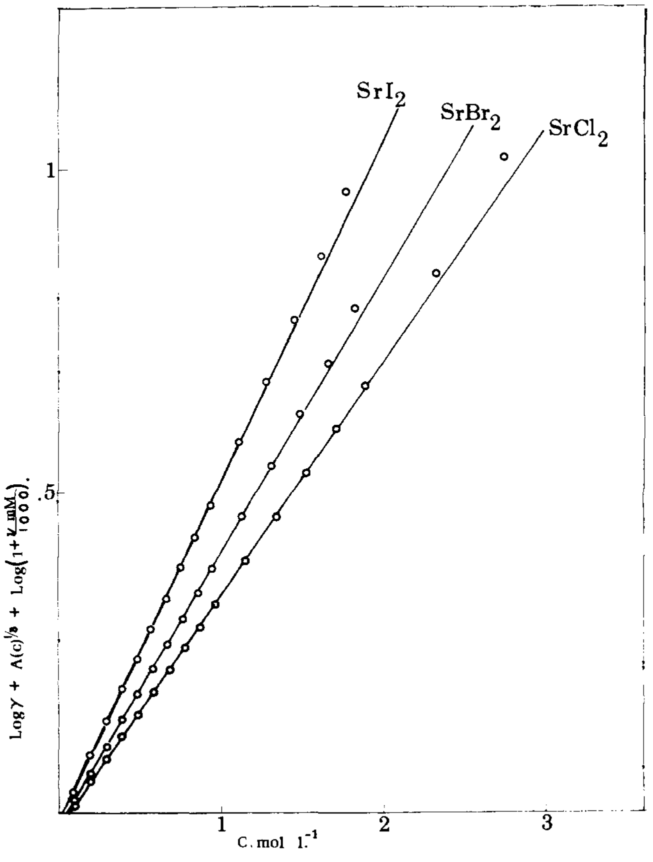

Figure 5. The left-hand side of eq 29 plotted against the molar concentration for strontium halides at 25°C in water.

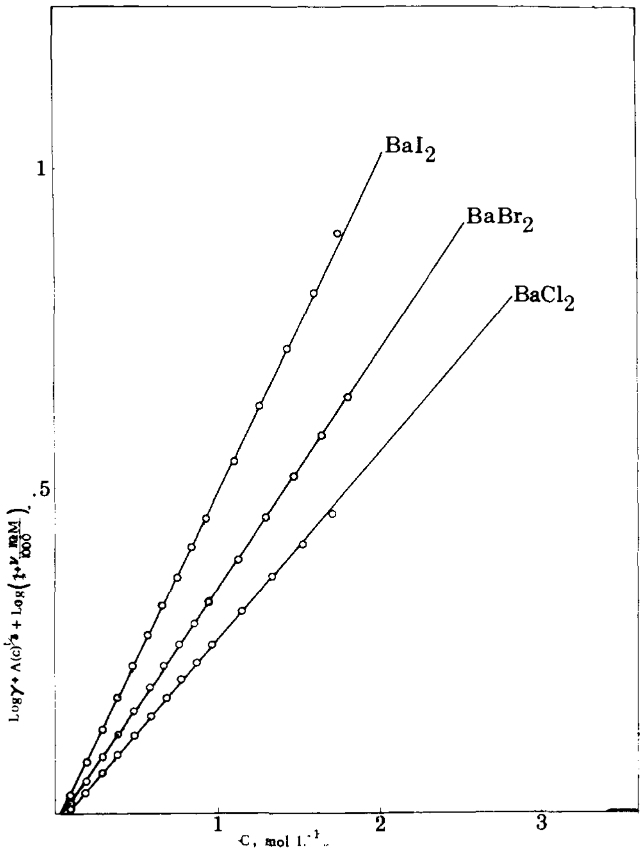

Figure 6. The left-hand side of eq 29 plotted against the molar concentration for barium halides at 25°C in water.

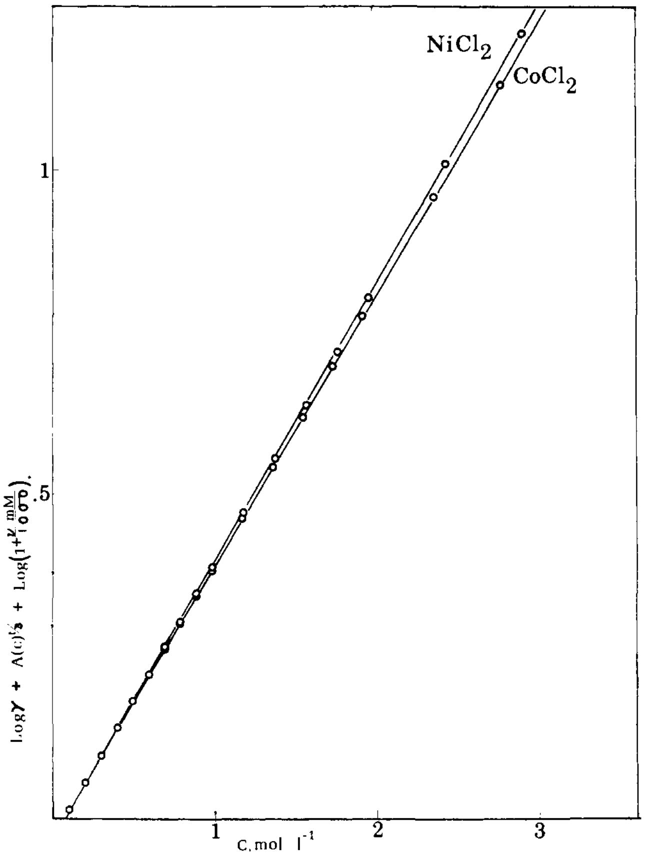

Figure 7. The left-hand side of eq 29 plotted against the molar concentration for $NiCl_2$ and $CoCl_2$ at 25°C in water.

earth halides and nitrates and $CoCl_2$ and $NiCl_2$. No attempt to correct the tables has been made in this paper.

As can be seen from eq 22 and 23, the B coefficient in eq 25 is related to the interactions between ions and the water adjacent to the ions. Of the many experimental and theoretical methods used to investigate the interaction between ions and solvent one of the most informative has been the study of the thermodynamics of hydration of ions.[22-26] Noyes[22] used the electrical free energy of hydration and the crystallographic radii of ions to find the effective dielectric constant (ϵ_{eff}) necessary to satisfy the Born equation. He concluded that the solvent immediately adjacent to an ion behaved as if it displayed a low dielectric constant and the bulk dielectric constant of water was reached, at least in one estimation, at distances greater than 2.86 Å from the center of a cation. Noyes did not specify the way in which the dielectric constant changed as a function of distance from the ion, but Glueckauf[27] assumed a continuous variation of dielectric constant with distance to calculate thermodynamic values which agreed with the values found by Noyes. The conclusions reached by Noyes and the model adopted by Gluekauf have many similarities to the model used for the field-dielectric-gradient effect, in particular, a low dielectric constant near the ion increasing to the bulk dielectric constant within a few ångströms from the ion.

A correlation exists between Noyes' ϵ_{eff} and B of eq 25. Noyes carefully noted that ϵ_{eff} is not the local dielectric constant. His approach to the relationship between ϵ_{eff} and ϵ_{loc} led to his estimation of the distance from a cation where ϵ_{loc} became the dielectric constant of the bulk solvent. Noyes pointed out that ϵ_{eff} is a single parameter used to collect all contributions to the electrical free energy of hydration resulting from the application of the Born equation, except for the ionic radius and ionic charge which were kept as explicit parameters. Equations 22 and 23 indicate that B is related to $|dk/dR|\,V_{\text{sea}}/k_0^2$ where k_0 is the low dielectric constant of the solvent at the surface of the ion. Because B contains $1/k_0^2$ and ϵ_{eff} has been chosen to behave like a dielectric constant, a correlation between $1/\epsilon_{\text{eff}}^2$ and B was investigated. Since single ion activity coefficients cannot be obtained, finding a B_+ and a B_- for cations and anions respectively does not seem possible. However, one can use the B's for a set of salts with a common anion to indicate the variations with cations, and a set of salts with a common cation to indicate the variations with anions. Figure 8 shows a plot of $1/\epsilon_{\text{eff}}^2$ against B for several salts composed of different cations with a common chloride anion, and for several salts composed of different anions with a common cation. The correlation indicates that a single model applies both to the thermodynamics of ion–ion interactions and to ion–solvent interactions. One particularly gratifying aspect of this

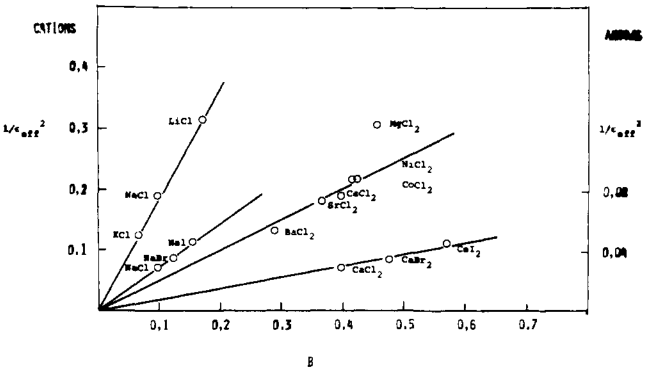

Figure 8. The correlation of $1/\epsilon_{\text{eff}}^2$ (Noyes[22]) with B of eq 25. The alkali chloride and alkaline earth chloride lines refer to the left ordinate; the sodium halide and calcium halide lines refer to the right ordinate.

correlation is the recognition of a difference between cations and anions. Thus, both B and $1/\epsilon_{eff}^2$ increase with an increase of anionic crystallographic radius, and both B and $1/\epsilon_{eff}^2$ increase with a decrease of cationic crystallographic radius.

A further possible relationship between B and ion-solvent interactions can be seen by noting that $(-\delta B/\delta T)$ (ref 3) is either positive or slightly negative for those univalent salts which contain ions that are considered "structure makers" (H^+, Li^+, F^-) and much more negative for univalent salts which contain ions that are considered to be "structure breakers".[24] A reexamination of heats of dilution for 2:1 electrolytes using the field-dielectric-gradient model should shed further light on this observation.

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Gas Phase Proton Affinities of Several Fluoroethylenes

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Abstract: Determinations of the proton affinities of C_2H_3F, CH_2CF_2, *cis*- and *trans*-CHFCHF, and C_2HF_3 using ion cyclotron resonance techniques are reported. The proton affinities are found to be 168 ± 1, 177 ± 3, 164 ± 2, 165 ± 2, and 167 ± 1 kcal/mol, respectively. The heats of formation of the protonated species derived from the proton affinities are compared with heats of formation of fluoroethyl cations derived in other ways. It is concluded that the most probable structures for the protonated species are CH_3CHF^+, $CH_3CF_2^+$, CH_2FCHF^+, and $CH_2FCF_2^+$. Limits on the previously unknown heats of formation of the 1,2-difluoroethylenes are determined from the proton affinities.

The enthalpy change for reaction 1 is a direct measure of the relative stabilities of alkyl cations R_1^+ and R_2^+. Recent

$$R_1^+ + R_2X \rightarrow R_2^+ + R_1X \qquad (1)$$

measurements of the gas phase equilibrium constants for reactions of this type have provided relative heats of formation of alkyl cations.[1-3] Another direct measure of relative alkyl cation stability is the enthalpy change for reaction 2

$$AH^+ + B \rightarrow BH^+ + A \qquad (2)$$

where A and B are olefins. The protonated olefins are, of course, alkyl cations. The complexity of the gas phase ion chemistry of mixtures of olefins in most cases prevents the direct measurement of equilibrium constants for reaction 2.[4-10] The proton affinities[11] of olefins can be determined using ion cyclotron double resonance,[12,13] however, and provide equivalent information since the enthalpy change for reaction 2 is the difference between the proton affinities of A and B.

The object of the present study is to determine the proton affinities of several fluoroethylenes. Some information about the stabilities of the corresponding fluoroethyl cations is available from study of fluoride transfer reactions analogous to reaction 1.[2,3] Heats of formation derived from mass spectrometric appearance potentials have been reported for several of the fluoroethyl cations.[14-16] Discrepancies between the various mass spectral measurements are to some extent resolved by the fluoride transfer reaction study, but the fluoroethylene proton affinities provide an indispensable addition to the available data on fluoroethyl cations.

There is some ambiguity in the structure of some of the fluoroethyl cations. The structure of $C_2H_4F^+$ has been the subject of a recent study.[17] The difluoro- and trifluoroethyl cations each have several possible isomers. The proton affinities of the fluoroethylenes indicate which fluoroethyl cations have stable isomers.

An interesting application of the proton affinity data arises in the case of the 1,2-difluoroethylenes. The heats of formation of the neutrals are not well known, but limits on the heat of formation of the 1,2-difluoroethyl cation have been established.[2,3] Limits on the neutral heats of formation of the 1,2-difluoroethylenes can therefore be deduced from the proton affinities.

The theory of ion cyclotron double resonance and its application to the determination of proton affinities has been discussed.[12,13] It has been generally established that if the single resonance signal intensity of ion A decreases when ion B is irradiated at its cyclotron frequency, then B reacts to form A at a rate that decreases with increasing ion kinetic energy. At the neutral pressures ($\sim 10^{-5}$ Torr) and drift