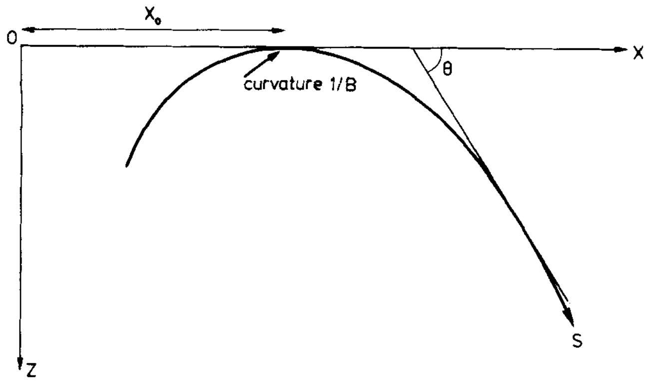

Fig. A1.

In dimensionless form, this becomes

$$\frac{d\theta}{dS} = \frac{1}{B} + Z - \frac{\sin\theta}{X} \qquad (A2)$$

in which $S = sc^{1/2}$, $X = xc^{1/2}$, $B = bc^{1/2}$, and $Z = zc^{1/2}$, where $c = (\rho_h - \rho_l)g/\sigma$. The distance of the apex from the axis of symmetry is $X_0 = x_0c^{1/2}$.

Furthermore, the variables X, Z, S, and θ are related geometrically by

$$\frac{dX}{dS} = \cos\theta; \quad \frac{dZ}{dS} = \sin\theta \qquad (A3)$$

and the variation with S of the volume of revolution $V = vc^{3/2}$ and surface area of revolution $A = ac$ are given by

$$\frac{dV}{dS} = \pi X^2 \sin\theta \qquad (A4)$$

$$\frac{dA}{dS} = 2\pi X \qquad (A5)$$

At the apex, the boundary conditions are

$$X = X_0; \quad \frac{d\theta}{dS} = \frac{1}{B} \qquad (A6)$$

and

$$\theta = S = Z = V = A = 0 \qquad (A7)$$

Written in the above form, the equations apply to both the outer and inner interfaces of the meniscus.

For the outer interface, $X > X_0$ and θ, S, Z, V and A are positive. For the inner interface, θ and S are negative, $X < X_0$ and Z, V and A are positive.

These equations have been integrated using a Runge-Kutta technique with a stringent error control (Hartland and Hartley, 1976) for twenty values of X_0 between 0.1 and 10 and forty values of B between 0.01 and 100. Tables have been produced accurately to six figures of the values of X, Z, S, A, and V at 5 deg intervals in θ between 0 and 270 deg. More values at different initial values of X_0 and B and at any value of θ can be produced at will from the computer program.

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A New Thermodynamic Representation of Binary Electrolyte Solutions Nonideality in the Whole Range of Concentrations

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A system of equations based on the ionic atmosphere theory of Debye and Huckel, Born model contribution, and local compositions of the nonrandom two-liquid (NRTL) model is developed to represent isothermal activity coefficients, in the whole range of concentrations, for solutions in an undissociated solvent of a partially or completely dissociated electrolyte.

The physical constants and the four adjustable parameters necessary to represent the osmotic coefficient, for fifteen strong aqueous electrolytic solutions, are given at 298.15°K and atmospheric pressure. Vapor-liquid equilibrium, for the hydrochloric acid-water system at 298.15°K, is represented for acid compositions ranging from infinite dilution to 18 M using a known dissociation constant and six parameters.

SCOPE

Properties of very concentrated electrolyte solutions which are the bases of fluid phase equilibria calculation are needed in chemical engineering applications, especially in the design of separation processes. The purpose of this work is to represent vapor-liquid equilibria of binary systems, especially water-inorganic acid or salt mixtures, in a very large range of concentrations using analytical equations for the activity coefficients in the

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liquid phase. Even for binary systems, most analytical equations found in the literature are limited to high electrolyte dilutions because knowledge about interactions is limited to these concentrations. The electrostatic forces between ions are known to be the strongest contribution to nonideality for high dilutions. In addition to these long range interactions between ions, the representation of ionic solution properties for higher electrolyte concentrations requires taking into account short range interactions between all species. This is especially important in the case of partial dissociation when ions, undissociated electrolyte, and solvent molecules are present together in the solution.

Classical thermodynamics provide a rigorous method to derive consistent activity coefficients according to the Gibbs-Duhem equation by appropriate differentiation of the excess Gibbs energy function of the system. The main problem is to construct that function, taking into consideration molecular interactions between the real species involved in the system.

The proposed analytical excess Gibbs energy expression allows a continuous connection between the well-known Debye and Hückel equations for the total dissociation and NRTL equations in absence of any dissociation. Fluid phase equilibria of binary electrolytic systems can be calculated in the whole range of concentrations whatever the ionic strength.

CONCLUSIONS AND SIGNIFICANCE

An analytical expression for the total excess Gibbs energy of a binary electrolytic system is proposed. It can be used with all kinds of electrolytes in an undissociated solvent in the whole concentration range. It takes into account a partial dissociation of the electrolyte, but simpler expressions are obtained assuming total dissociation. Consistent isothermal activity coefficients derived from the excess Gibbs energy function are given in both cases.

A test of the new equations is provided by their application to fifteen binary aqueous mixtures where total dissociation of the electrolyte is assumed. Even in the largest concentration ranges, the model has four adjustable parameters only. Two are involved in the dielectric constant expression of the Born model contribution, and the remaining two are NRTL parameters related to ion-solvent interaction. A refinement of the representation, in the range of dilutions where the mean ionic activity coefficient presents a minimum, is to take the closest distance of approach of two ions as an additional adjustable parameter.

The vapor-liquid equilibrium calculation of the system water-hydrochloric acid at 298.15°K was selected as an application of the model in its most extended form. With the assumption of partial dissociation, the dissociation equilibrium constant and two additional adjustable NRTL parameters, related to interactions between neutral molecules, are required.

The theoretical basis of the electrostatic contributions to excess Gibbs energy provides physical information through the numerical values of the adjustable parameters. For instance, the large contribution of the Born model term, for high concentrations of lithium chloride in water, is consistent with the variation of the dielectric constant in electrolytic systems. The weight of each contribution to the mean ionic activity coefficient was studied for the system water-sodium chloride at 298.15°K and atmospheric pressure. Finally, the proposed model makes possible the calculation of vapor-liquid equilibria, with the same equations, from infinite dilution in solvent to the electrolyte saturation composition.

The generalized use of an expression of the excess Gibbs energy to derive activity coefficients and calculate phase equilibria is limited to nonelectrolyte solutions. The effect of ionic dissociation on activity coefficients was explained by the theory of Debye and Hückel of ion-ion interactions at very high dilutions of the electrolyte; recently, Pitzer (1973) extended the application of Coulombic theories to an electrolyte molality of 6 M by use of adjustable parameters, and Stokes and Robinson (1973) developed a complex hydration model which gives a good representation of the osmotic coefficient of strong electrolytes up to 20 to 30 M.

The model proposed in this paper includes contributions of ion-ion, ion-molecule, and molecule-molecule interactions to the excess Gibbs energy of mixtures, where an electrolyte is partially or totally dissociated in a solvent. The representation is valid in the whole range of concentrations for all kinds of electrolytes with a limited number of adjustable parameters, taking into account, if necessary, the dissociation constant. The present paper presents the theory for binary mixtures, which could be extended to multicomponent systems.

DISSOCIATION OF THE ELECTROLYTE IN THE SOLVENT

The binary electrolytic system consists of N°_S moles of solvent and N°_{AB} moles of electrolyte. In absence of any information on the equilibrium constants of ion pairs formation, it is assumed that real species are free cations A^{z+}, free anions B^{z-}, undissociated electrolyte $A_{\nu_+}B_{\nu_-}$ (noted in this work AB), and solvent molecules S. If ion pairs really exist in the solution, they are assumed to interact with other species like undissociated AB molecules. In the case of total dissociation, the solution contains three components only.

The true mole fractions ξ_j of real species j and the true activity coefficients γ_j are related by the dissociation equilibrium equation

$$K(T) = \frac{(\xi_A\gamma_A)^{\nu_+}(\xi_B\gamma_B)^{\nu_-}}{\xi_{AB}\gamma_{AB}} \tag{1}$$

in which $K(T)$ depends on the choice of the reference states chosen for the ions and undissociated AB molecules.

Using the mean ionic activity coefficient in a mole fraction scale and the dissociation coefficient $\alpha(N^\circ{}_{AB}, N^\circ{}_S, T)$, a dissociation constant can be defined, for infinite dilution reference states (*), in a molality scale

$$K^*{}_m(T) = \frac{(\gamma^*{}_\pm)^\nu \alpha^\nu \nu_+{}^{\nu_+} \nu_-{}^{\nu_-} x_{AB}{}^{(\nu-1)}}{\gamma^*{}_{AB}(1-\alpha)[\alpha x_{AB}(\nu-1)+1]^{(\nu-1)}} \left(\frac{1\,000}{M_S}\right)^{(\nu-1)} \tag{2}$$

VAPOR-LIQUID EQUILIBRIUM OF A BINARY ELECTROLYTIC SYSTEM

The osmotic coefficient ϕ_{AB} for the mixture electrolyte AB solvent S, which can be related to $\gamma^*{}_\pm$ by integration of the Gibbs-Duhem equation, is defined by

$$\phi_{AB} = -\frac{1\,000 \ln(\gamma_S \xi_S)}{\nu M_S m^\circ{}_{AB}} \tag{3}$$

If the electrolyte is nonvolatile, the activity of water $(\gamma_w \xi_w)$ for moderate pressures is the ratio of the total pressure to the saturation pressure of pure liquid water at the same temperature.

When the electrolyte is volatile, the equilibrium calculation is much more complicated; at room temperature, the vapor phase dissociation of the electrolyte is usually neglected. The equality of fugacities of undissociated component j in the two phases can be written as

$$P y_j \Phi_j{}^V(T,P,y) = \xi_j \gamma_j(T,\xi) f_j{}^{rL}(T,P^r) \exp \int_{P^r}^{P} \frac{\bar{v}_j{}^L}{RT}\, dP \tag{4}$$

The vapor reference state of each component is the pure ideal gas at equilibrium temperature. When the parameters are known for both components, the correlation of Nothnagel et al. (1973) is the most suitable to calculate $\Phi_j{}^V$.

It can be shown (from Prigogine and Defay, 1954) that the apparent chemical potential of electrolyte AB in the solution is equal to the true chemical potential of undissociated AB molecules; consequently

$$\overset{ar}{\mu}_{AB}(T) + RT \ln \overset{a}{\gamma}_{AB} x_{AB} = \overset{r}{\mu}_{AB}(T) + RT \ln \gamma_{AB} \xi_{AB} \tag{5}$$

If the reference state of the electrolyte AB is the pure liquid AB at T and P^r, neglecting pressure effects, the limit of $\overset{a}{\gamma}_{AB}$ is unity when x_{AB} goes to one, and therefore

$$(\overset{ar}{\mu}_{AB} - \overset{r}{\mu}_{AB})/RT = \ln a'_{AB} \tag{6}$$

The calculation of $\overset{a}{\gamma}_{AB}$ from γ_{AB} requires the knowledge of the activity a'_{AB} of undissociated AB molecules in the pure liquid electrolyte AB at temperature T. If the dissociation of the pure liquid electrolyte is known to be negligible at this temperature, and if a pure liquid reference state is chosen for undissociated AB molecules at T, a'_{AB} is equal to unity, and Equation (5) gives

$$\overset{a}{\gamma}_{AB} = \frac{\gamma_{AB} \xi_{AB}}{x_{AB}} \tag{7}$$

The same equation is obtained for the solvent. Equations (1) or (2) and (5) or (7) and mass balance relate the activity coefficient of undissociated AB molecules γ_{AB} to the apparent activity coefficient of the electrolyte AB, $\overset{a}{\gamma}_{AB}$, and the mean ionic activity coefficient $\gamma^*{}_\pm$ usually reported in experimental work.

Consistent activity coefficients are obtained from the excess Gibbs energy of the real mixture by means of

$$RT \ln \gamma_j = \left(\frac{\partial G^E}{\partial N_j}\right)_{T,P,N_{i \neq j}} \tag{8}$$

in which G^E is the difference between the Gibbs energy of the system in the real state and the Gibbs energy of the ideal mixture of the pure components. Therefore, it is possible to calculate vapor-liquid equilibria in binary electrolyte solutions from G^E by using Equations (4), (7), (8), (2), and mass balances.

DECOMPOSITION OF THE EXCESS GIBBS ENERGY

In a thorough bibliographic review (Cruz, 1977), it appears that nonideality in electrolyte solutions is always attributed to unlike interactions between the species. Long range Coulombic interactions between ions are preponderant at high electrolyte dilutions, whereas short range interactions between ions and neutral molecules, or between neutral molecules, are expected to be the major contribution to nonideality in concentrated electrolyte mixtures.

The excess Gibbs energy is therefore assumed to be the sum of two terms, one related to long range forces between ions G^I and the other to short range forces between all the species G^{II}:

$$G^E(N_{AB}, N_{A^+}, N_{B^-}, N_S, T, P) = G^I + G^{II} \tag{9}$$

In order to get a description of equilibrium properties of the solution, several models were tested (Cruz and Renon, 1974, 1976). The algebraic equations for G^I and G^{II} were selected also in view of their possible extension to multicomponent mixtures.

Debye-Hückel Contribution

Following Fowler and Guggenheim (1949), the first contribution is taken as the total electrical work necessary to charge all the ions in the total volume V. If the solvent has a macroscopic dielectric constant D_S, this expression is the complete Debye-Hückel term

$$G^E{}_{\text{DEBYE-HÜCKEL}} = -\frac{\epsilon^2 N (N_A z^2{}_+ + N_B z^2{}_-)}{D_S} \left\{ \frac{K^\circ}{(\mathring{a}K^\circ)^3} \left[\frac{1}{2} (\mathring{a}K^\circ)^2 - \mathring{a}K^\circ + \ln(1 + \mathring{a}K^\circ) \right] \right\} \tag{10}$$

where

$$K^\circ = \left(\frac{8\epsilon^2 N \pi I}{1\,000\, D_S k T}\right)^{1/2}$$

$$\text{and} \quad I = \frac{1}{2}\left(\frac{1\,000 (N_A z^2{}_+ + N_B z_-{}^2)}{V}\right)$$

Born model contribution

In addition to other theoretical limitations of this expression, the effect produced by the decrease of the average dielectric constant of the solution, when increasing electrolyte concentration, is neglected. Conway and Barradas (1966) pointed out that Equation (10) applies only to interactions between distant solvated ions in a continuous medium of average dielectric constant D_S. The net electrical work necessary to transfer all the ions from a solvent of dielectric constant D_S to a medium of dielectric constant D can be expressed by means of the Born or the Debye and McAulay theories cited by Harned and Owen (1958). Therefore, as suggested by Scatchard (1936), the classical Born contribution can be incorporated into G^I:

$$G^I = G^E{}_{\text{DEBYE-HÜCKEL}} + G^E{}_{\text{BORN}}$$

with

$$G^E{}_{\text{BORN}} = \frac{\epsilon^2 N}{2}\left(\frac{1}{D} - \frac{1}{D_S}\right)\left(\frac{N_A z^2{}_+}{r_A'} + \frac{N_B z^2{}_-}{r_B'}\right) \tag{11}$$

r_A' and r_B' are the effective radii of the true positive and negative charged spheres transferred between the two solutions. According to the concept of cospheres (Franks, (1973), these are the radii of the cavities, surrounding the ions, in which the solvent undergoes a complete dielectric saturation. The method of estimating these constants, from the saturated cavity theory of Onsager presented by Pottel (1973), is given in Appendix B.

The value of the average dielectric constant D of the medium surrounding a saturated cavity is expected to be close to the value of the average macroscopic dielectric constant of the solution. As D is generally unknown, an empirical expression related to Kirkwood's equation cited by Decroocq (1968) is proposed for the variation of D with electrolyte concentration. It is a generalization of the Hasted et al. (1968) equation for high electrolyte concentrations:

$$D = D_S + \omega_{AB}(D_{AB} - D_S) + \frac{\Delta_D\left[\dfrac{2\,000\,\overline{\delta}}{v^\circ{}_{AB}} - (D_{AB} - D_S)\right]\omega_{AB}(1 - \omega_{AB})}{\omega_{AB}\left[\dfrac{2\,000\,\overline{\delta}}{v^\circ{}_{AB}} - (D_{AB} - D_S)\right] + \Delta_D} \tag{12}$$

The two adjustable parameters for this equation are D_{AB}, which has the significance of the dielectric constant of pure electrolyte when it exists in a liquid state at equilibrium temperature, and Δ_D, which is a dielectric nonideality parameter.

When the apparent volume fraction of electrolyte ω_{AB} comes close to zero, the Hasted equation, limited to 2 M concentrations, is recovered:

$$D = D_S + 2\overline{\delta} c^\circ{}_{AB} \tag{13}$$

The last term of Equation (12) is the contribution of the excess dielectric constant calculated by comparison with the ideal Kirkwood theory:

$$D = D_{AB}\omega_{AB} + D_S\omega_S \tag{14}$$

This equation is recovered from expression (12) when Δ_D is zero or from Equation (13) when Hasted's depression is equal to

$$\overline{\delta} = (D_{AB} - D_S)v^\circ{}_{AB}/2\,000 \tag{15}$$

Pottel's data (1973) at 1 M concentrations give a coherent set of upper limiting values of $\overline{\delta}$ for alkali-halide electrolytes in water. These values are preferred to Hasted's measurements because one finds linear correlations between individual ionic values δ_j (see Appendix B) and Pauling's (1940) ion radii or partial molar volumes of ions at infinite dilution.

In this work, Equation (11) is considered as a semiempirical equation with two adjustable parameters: D_{AB} and Δ_D. Yet, the excess contribution can be neglected for high electrolyte dilutions, and Equation (11) is predictive if Hasted's depression is known. The dielectric nonideality parameter Δ_D is required only at high electrolyte concentrations in the range where the decrease of dielectric constant D becomes smaller.

The expressions for the ionic interactions assume an unsymmetrical convention for the definition of activity coefficients.

For undissociated species, like AB and S, the ideal reference state is the pure liquid at a reference pressure and equilibrium temperature. For the ionic species, it is infinite dilution (noted by an asterisk) in the pure solvent at the same pressure and temperature.

Therefore, the activity coefficients obtained by partial derivation of G^I have the following limiting values:

$$\gamma_A{}^* \to 1 \quad \text{when} \quad \xi_A \to 0 \quad \text{and} \quad \gamma_{AB} \to 1 \quad \text{when} \quad \xi_{AB} \to 1$$

$$\gamma_B{}^* \to 1 \quad \text{when} \quad \xi_B \to 0 \quad \text{and} \quad \gamma_S \to 1 \quad \text{when} \quad \xi_S \to 1$$

$$\xi_A \to 0 \quad \text{means:} \quad \xi_S \to 1, \quad \xi_{AB} = 0 \quad \text{and} \quad \xi_B = 0$$

NRTL Contribution

After tests of various equations (Cruz and Renon, 1974, 1976), three reasons led to the selection of NRTL model proposed by Renon and Prausnitz (1968).

1. It is able to represent equilibrium properties of strongly nonideal systems of nonelectrolytes.
2. The concept of local composition allows a reduction of the number of adjustable parameters.
3. The generalization of NRTL equations to multicomponent systems requires binary parameters only.

The true local mole fraction ξ_{ki} of molecule k around a central molecule i is defined by

$$\xi_{ki} = \frac{\xi_k G_{ki}}{\sum_j \xi_j G_{ji}} \quad \text{with} \quad \begin{cases} G_{ki} = \exp(-\alpha_{ki}\tau_{ki}) \\ \tau_{ki} = C_{ki}/RT \\ \alpha_{ki} = \alpha_{ik} \quad \text{and} \quad C_{ii} = 0 \end{cases} \tag{16}$$

C_{ki} is an energy of transfer parameter, whereas α_{ki} is a molecular sorting parameter related to the nonrandomness of the distribution of components k and i around a central molecule i. Its numerical value usually lies between 0.1 and unity. In the present work, an average value of α_{ki} equal to 0.2 has been found adequate for a good representation of isothermal data.

An additional quantity Z_{ki} is defined to simplify the writing of the NRTL equation for the molar excess Gibbs energy of a multicomponent mixture:

$$g^E{}_{\text{NRTL}} = \sum_i \xi_i \sum_k \xi_{ki} C_{ki} = \sum_i \xi_i \frac{\sum_k \xi_k Z_{ki}}{\sum_j \xi_j G_{ji}} \tag{17}$$

with

$$Z_{ki} = G_{ki}C_{ki} = \exp\left(-\alpha_{ki}\frac{C_{ki}}{RT}\right)C_{ki} \tag{18}$$

In the electrolytic model, recalling that ion pairs are counted as if they are undissociated AB molecules, the free ions A^{z+} and B^{z-} are assumed to be mainly surrounded by solvent molecules, and consequently the true local mole fractions of solvent S around free ions are close to one. This structure of solution implies that undissociated AB molecules are surrounded by AB and solvent molecules S only.

These asumptions could be unrealistic if total dissociation was assumed at high electrolyte concentrations because the number of solvent molecules may not be sufficient to completely surround free ions. For this reason, a partial dissociation must be taken into account in order to increase the ratio solvent/free ions for high electrolyte concentrations. This remark also applies to the ionic contribution G^I which is not appropriate, for instance, to calculate molten salts equilibrium properties. Yet, empirical applications of the equation proposed in this work show that the model is adaptable enough to represent experimental equilibrium data keeping a total dissociation assumption even at high electrolyte concentrations.

Formally, these assumptions on the structure of solution are equivalent to the following simplification of (17). When the probability for component k to be in the immediate neighborhood of i is zero, G_{ki} is zero, the NRTL parameter C_{ki} goes to infinity, and Z_{ki} goes also to zero. A physical explanation for this behavior is proposed in Appendix A.

Equation (17) takes the simple form

$$g^E{}_{\mathrm{NRTL}} = \xi_A C_{S,A} + \xi_B C_{S,B} + \xi_{AB}\left(\frac{\xi_S Z_{S,AB}}{\xi_{AB} + \xi_S G_{S,AB}}\right) + \xi_S\left(\frac{\xi_A Z_{A,S} + \xi_B Z_{B,S} + \xi_{AB} Z_{AB,S}}{\xi_A G_{A,S} + \xi_B G_{B,S} + \xi_{AB} G_{AB,S} + \xi_S}\right) \quad (19)$$

The nonionic contribution G^{II} should use the same unsymmetrical convention as the ionic contribution G^I. The normalization of activity coefficients is achieved using the following expression:

$$G^{II} = G^E{}_{\mathrm{NRTL}} - RT[N_A \lim_{\xi_A\to 0}(\ln \gamma_A{}^{\mathrm{NRTL}}) + N_B \lim_{\xi_B\to 0}(\ln \gamma_B{}^{\mathrm{NRTL}})] \quad (20)$$

If we take into account macroscopic electrical neutrality and the definition of Z_{ki}, Equations (19) and (20) give

$$G^{II} = N_{AB}\left[\frac{N_S Z_{S,AB}}{(N_S G_{S,AB} + N_{AB})}\right] + N_S\left[\frac{N_A Z_{\pm S} + N_{AB} Z_{AB,S}}{(N_A G_{\pm S} + N_{AB} G_{AB,S} + N_S)}\right] - N_A Z_{\pm S} \quad (21)$$

where $Z_{\pm S}$ and $G_{\pm S}$ are given by

$$Z_{\pm S} = Z_{A,S} + \frac{\nu_-}{\nu_+} Z_{B,S}$$

$$G_{\pm S} = G_{A,S} + \frac{\nu_-}{\nu_+} G_{B,S}$$

When a complete dissociation is assumed, this semiempirical equation becomes very simple:

$$G^{II} = Z_{\pm S} N_A\left[\frac{N_S}{(N_A G_{\pm S} + N_S)} - 1\right] \quad (22)$$

On the contrary, if no dissociation is supposed, the NRTL equation for nonelectrolytes is recovered:

$$G^{II} = N_{AB}\left[\frac{N_S Z_{S,AB}}{(N_S G_{S,AB} + N_{AB})}\right] + N_S\left[\frac{N_{AB} Z_{AB,S}}{(N_{AB} G_{AB,S} + N_S)}\right] \quad (23)$$

For the general case of partial dissociation, Equation (21) requires four adjustable parameters: $Z_{\pm S}$, $G_{\pm S}$, $C_{AB,S}$, $C_{S,AB}$. The number of parameters is reduced to two ($Z_{\pm S}$ and $G_{\pm S}$) in Equation (22) when a total dissociation is assumed. In the case of no dissociation and isothermal data, with a given $\alpha_{AB,S}$ value, two NRTL parameters $C_{AB,S}$ and $C_{S,AB}$ are needed in Equation (23) in order to calculate $Z_{AB,S}$, $Z_{S,AB}$, $G_{S,AB}$ and $G_{AB,S}$.

The equation for the total excess Gibbs energy of the four components system is

$$G^E = -\frac{\epsilon^2 N(N_A z_+{}^2 + N_B z_-{}^2)}{D_S}\left\{\frac{K^\circ}{(\mathring{a}K^\circ)^3}\left[\frac{1}{2}(\mathring{a}K^\circ)^2 - \mathring{a}K^\circ + \ln(1 + \mathring{a}K^\circ)\right]\right\} + \frac{\epsilon^2 N}{2}\left\{\left(D_S + \omega_{AB}(D_{AB} - D_S) + \frac{\Delta_D\left[\frac{2\,000\bar{\delta}}{v^\circ{}_{AB}} - (D_{AB} - D_S)\right]\omega_{AB}(1 - \omega_{AB})}{\omega_{AB}\left[\frac{2\,000\bar{\delta}}{v^\circ{}_{AB}} - (D_{AB} - D_S)\right] + \Delta_D}\right)^{-1} - \frac{1}{D_S}\right\}\left(\frac{N_A z_+{}^2}{r_A{}'} + \frac{N_B z_-{}^2}{r_B{}'}\right) + N_{AB}\frac{N_S Z_{S,AB}}{(N_S G_{S,AB} + N_{AB})} + N_S\left[\frac{N_A Z_{\pm S} + N_{AB} Z_{AB,S}}{(N_A G_{\pm S} + N_{AB} G_{AB,S} + N_S)}\right] - N_A Z_{\pm S} \quad (24)$$

An average value of 4.10^{-8} cm for the distance of closest approach $\mathring{a}$ is generally assumed for electrolytes in water at 298.15°K.

If partial dissociation is assumed, six adjustable parameters are theoretically necessary: D_{AB} and Δ_D for the Born contribution and $Z_{\pm S}$, $G_{\pm S}$, $C_{AB,S}$, and $C_{S,AB}$ for the NRTL term if $\alpha_{S,AB}$ is fixed at the value 0.2. For the total dissociation, the four adjustable parameters are D_{AB}, Δ_D, $Z_{\pm S}$, and $G_{\pm S}$. The true numbers of moles for components j, N_j are easily obtained from apparent numbers of moles of electrolyte $N^\circ{}_{AB}$ and solvent $N^\circ{}_S$ when the dissociation is complete, but for a partial dissociation, a dissociation coefficient α must be calculated in Equation (2) from a value of $K_m{}^*(T)$ usually available in tables of constants.

The values of N, R, ϵ, and k are given in the Notation section according to NBS listings (1963). Numerical data and correlations required for the calculation of physical quantities used in Equation (24) are given in Appendix B.

DATA TREATMENT

The calculation of the best parameters in the representation of experimental data was performed either by a gradient method of minimization (Demidovitch and Maron, 1973) or the classical Newton-Gauss algorithm, in a form used by Renon et al. (1971).

The minimization is carried out on sums of squares of deviations between calculated and experimental quantities:

$$S_\gamma = \sum_{i=1}^{n} (\ln \gamma^{*\mathrm{cal}}_{\pm m,i} - \ln \gamma^{*\mathrm{exp}}_{\pm m,i})^2 \quad (25)$$

$$S_\phi = \sum_{i=1}^{n} (\phi^{\mathrm{cal}}_{AB,i} - \phi^{\mathrm{exp}}_{AB,i})^2 \quad (26)$$

The corresponding square roots of the estimation variances are

$$\sigma_\gamma = [S_\gamma/(n - p)]^{1/2} \quad (27)$$

$$\sigma_\phi = [S_\phi/(n - p)]^{1/2} \quad (28)$$

COMPLETELY DISSOCIATED ELECTROLYTES

The expression of the mean ionic activity coefficient is derived from Equations (8) and (24):

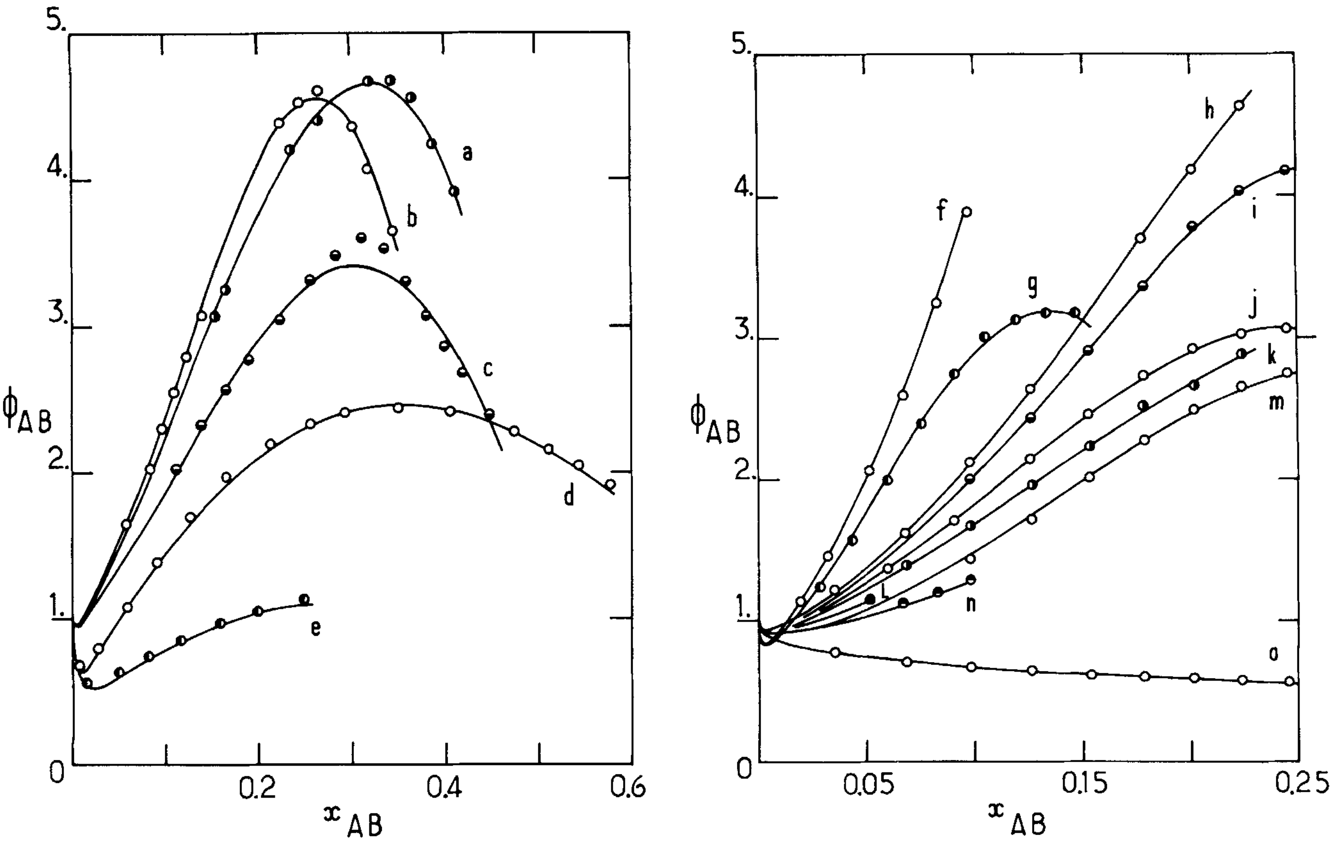

Fig. 1a and 1b. Representation of osmotic coefficient in aqueous mixtures: a) HBr, b) HI, c) HCl, d) H_2SO_4 e) H_3PO_4, f) $CaBr_2$, g) $CaCl_2$, h) $HClO_4$, i) LiBr, j) LiCl, k) KOH, l) HNO_3, m) NaOH, n) NaCl, o) NH_4NO_3.

$$\ln \gamma^*_{\pm} = -\frac{\epsilon^2|z_+z_-|}{D_S kT}\left\{\frac{K^\circ}{2(1+\mathring{a}K^\circ)} + \frac{K^\circ}{(\mathring{a}K^\circ)^3}\left[-\frac{\mathring{a}K^\circ}{2} + \ln(1+\mathring{a}K^\circ) - \frac{\mathring{a}K^\circ}{2(1+\mathring{a}K^\circ)}\right]\frac{\overline{v}_{AB}c^\circ{}_{AB}}{1\,000}\right\}$$
$$+ \frac{\epsilon^2}{2\nu kT}\left(\frac{\nu_+z_+{}^2}{r_A{}'} + \frac{\nu_-z_-{}^2}{r_B{}'}\right)\left[\left(\frac{1}{D} - \frac{1}{D_S}\right) - \frac{1}{D^2}\left(1 - \frac{c^\circ{}_{AB}\overline{v}_{AB}}{1\,000}\right)\omega_{AB}\left(\frac{\partial D}{\partial \omega_{AB}}\right)_T\right]$$
$$+ \frac{Z_{\pm S}\nu_+}{\nu RT}\left[\frac{\xi_S{}^2}{(\xi_A G_{\pm S} + \xi_S)^2} - 1\right] \quad (29)$$

$\overline{v}_{AB}$ is calculated by partial derivation of V in the expression of density (see Appendix B). Most of literature data are provided in a molality scale.

The mean molal ionic activity coefficient $\gamma^*{}_{\pm m}$ is obtained by

$$\ln \gamma^*{}_{\pm m} = \ln \gamma^*{}_{\pm} - \ln(1 + 0.001\, M_S m^\circ{}_{AB}\nu) \quad (30)$$

The true activity coefficient of solvent is derived in a similar manner:

$$\ln \gamma_S = -\frac{\epsilon^2|z_+z_-|\nu}{D_S kT}\left\{\frac{K^\circ}{(\mathring{a}K^\circ)^3}\left[-\frac{\mathring{a}K^\circ}{2} + \ln(1+\mathring{a}K^\circ) - \frac{\mathring{a}K^\circ}{2(1+\mathring{a}K^\circ)}\right]\frac{\overline{v}_S c^\circ{}_{AB}}{1\,000}\right\}$$
$$+ \frac{\epsilon^2}{2kTD^2}\left(\frac{\nu_+z^2{}_+}{r_A{}'} + \frac{\nu_-z^2{}_-}{r_B{}'}\right)c^\circ{}_{AB}\omega_{AB}\frac{\overline{v}_S}{1\,000}\left(\frac{\partial D}{\partial \omega_{AB}}\right)_T$$
$$+ \frac{Z_{\pm S}G_{\pm S}\xi_A{}^2}{RT(\xi_A G_{\pm S} + \xi_S)^2} \quad (31)$$

An additional advantage of using an excess Gibbs energy is the direct derivation of consistent γ_S and $\gamma^*{}_{\pm m}$ without integration of the Gibbs-Duhem equation, which is automatically verified. Table 1 shows the results of the representation of osmotic coefficient data of the literature for fifteen systems at 298.15°K and atmospheric pressure (Robinson and Stokes, 1970; Haase et al., 1963; Platford, 1975).

Figures 1*a* and 1*b* represent experimental points and calculated ϕ_{AB} curves vs. apparent mole fraction of electrolyte x_{AB} for some typical systems of the Table 1.

The case of polyacids raises the problem of partial dissociation. If a 2:1 dissociation is assumed for sulfuric acid (ions H^+ and $SO_4{}^=$ only), the results are given in Table 1. An attempt to correlate the same experimental data taking into account the 1:1 dissociation only (H^+ and $HSO_4{}^-$) gives an equivalent value of σ for the whole concentration range. Yet, a higher deviation is obtained for the high dilution experimental points.

Likewise, H_3PO_4 is known to have three dissociation steps. But, for a concentration of 10^{-5} M, $H_2PO_4{}^-$ represents 95% of the anion species (Platford, 1975). So, a 1:1 dissociation was chosen in the range of concentrations of the data.

A model taking into account several dissociation steps certainly should provide a better adjustment, especially in the range where various ionic species exist together. The low numerical value of Δ_D for these two systems, and particularly for H_2O-H_3PO_4, would indicate an ideal

TABLE 1. REPRESENTATION OF OSMOTIC COEFFICIENT OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES

	$Z_{\pm S}$ kJ(g-mole)	$G_{\pm S}$	$10^{-2}\,\Delta_D$	D_{AB}	Range of molalities (g-mole)/ (kg of solvent)	σ_ϕ	Number of experimental points	Source of data
HCl	62.519	0.70608	−0.70666	8.5257	0.11-47.1	0.05	43	Haase (1963)
HBr	1 018.2	0.03336	−0.82884	4.0126	0.10-38.1	0.03	36	Haase (1963)
HI	3 597.7	0.010936	−0.94670	5.5920	0.10-29.3	0.03	33	Haase (1963)
$HClO_4$	10.574	4.5434	−0.72025	4.8884	1-16	0.002	16	Robinson (1970)
HNO_3	22.959	2.5648	−0.61289	1.0046	0.1-3	0.002	17	Robinson (1970)
KCl	1 198.9	0.041557	−0.78833	3.2189	1-16	0.015	16	Robinson (1970)
NaOH	3 485.1	0.020279	−0.80723	2.5423	0.1-20	0.02	37	Robinson (1970)
NaCl	43.913	0.96393	−0.73997	1.0400	0.006-6	0.002	26	Robinson (1970)
LiCl	31.253	0.99509	−0.96871	19.616	0.1-20	0.01	37	Robinson (1970)
LiBr	784.42	0.035158	−1.0669	15.434	0.1-20	0.02	29	Robinson (1970)
$CaCl_2$	288.28	0.85796	−0.83998	8.9671	0.0001-10	0.02	40	Robinson (1970)
$CaBr_2$	1 171.7	0.17870	−0.88347	1.0002	0.1-6	0.015	23	Robinson (1970)
NH_4NO_3	46.168	1.3812	−1.0057	12.707	1-20	0.002	20	Robinson (1970)
H_2SO_4	12.588	15.106	−0.43026	16.317	0.1-76	0.03	64	Robinson (1970)
H_3PO_4	9.4148	38.346	−0.14636	24.583	0.4-18.5	0.03	26	Platford (1975)

dielectric constant behavior [Equation (14)], but it is reasonable to think that adjustable parameters have not much significance in that case. This explains the discrepancies of Δ_D with the average constant value for other systems (Table 1).

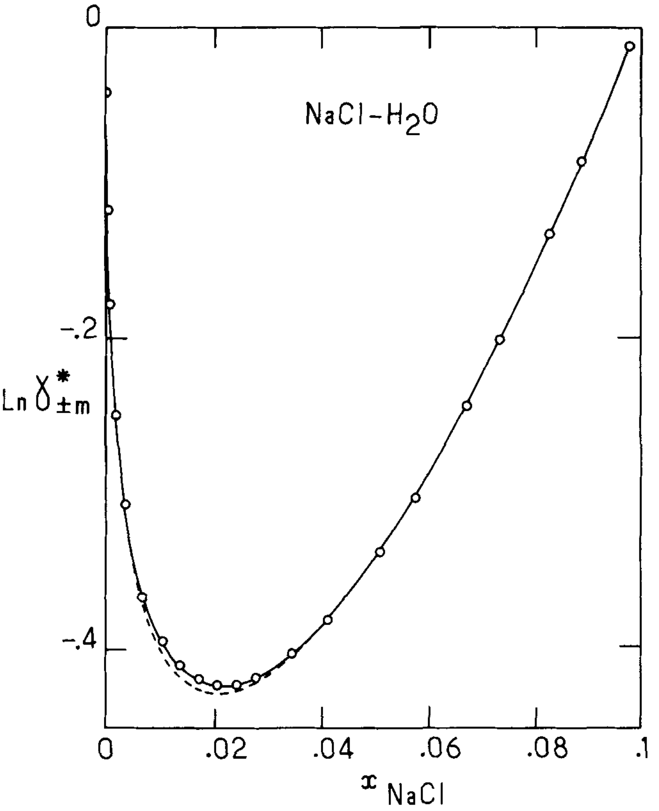

Fig. 2. Improvement of the representation of mean ionic activity coefficients, in the H_2O-NaCl system, when $\mathring{a}$ is adjusted (———), dotted curve is obtained for $\mathring{a} = 4\ 10^{-8}$ cm.

The representation of data at high dilutions is improved by taking the distance of closest approach $\mathring{a}$ as an additional parameter. Comparison of the curves in Figure 2 shows the improvement for the representation of ln $\gamma^*_{\pm NaCl}$ (data at 298.15°K and atmospheric pressure of Robinson and Stokes, 1970). Table 2 gives the values of parameters and the variances of deviations in four different adjustments using or not $\mathring{a}$ as a parameter and treating the data of activity coefficients or osmotic coefficients.

The model is adaptable enough to adjust experimental data, even in cases where the assumption on the number of dissociation steps is not exactly satisfied. In this case, the minimization program finds a set of parameters, but no physical interpretation should be given to their numerical values. On the contrary, if physical data are known and if the model is applied in the range of its physical significance, the value of some of the adjusted parameters expresses a relation with other physical properties. Figure 3 shows a comparison of the dielectric constant curve calculated from Equation (12), using parameters of Table 1, with the experimental D in the case of the water-lithium chloride system. Experimental points below 2 M concentrations are taken from Hasted's data (1973). For higher concentrations, graphical data of Gottlob given by Franks (1973) are shown.

It is also clear that in this example the two initial values of parameters involved in the Born contribution could have been advantageously selected from the dielectric constant data on mixtures, but the final adjustment is sensitive to the precise values of these parameters.

Figure 4 gives the various contributions of short and long range interactions to the expression of ln $\gamma^*_{\pm NaCl,m}$ at 298.15°K at low mole fractions. Parameters of the model are given in Table 2 (line 2). For high dilutions,

TABLE 2. REPRESENTATION OF AQUEOUS SOLUTIONS OF SODIUM CHLORIDE (ROBINSON AND STOKES, 1970)

	Parameters					Number of experimental points	Range of molalities (g-mole)/ (kg of solvent)	Represented property	Standard-deviations	
	$Z_{\pm S}$ kJ/(g-mole)	$G_{\pm S}$	$10^{-2}\,\Delta_D$	D_{AB}	$10^8\,a°$ cm				σ_ϕ	σ_γ
(1)	44.102	0.94215	−0.73562	1.4258	4.0000	39	0.0055—6	γ		0.004
(2)	45.742	0.96307	−0.75809	1.3250	4.3119	39	0.0055—6	γ		0.001
(3)	43.913	0.96393	−0.73997	1.0400	4.0000	26	0.0064—6	ϕ	0.002	
(4)	45.980	0.96342	−0.77018	2.4398	4.3108	26	0.0064—6	ϕ	0.001	

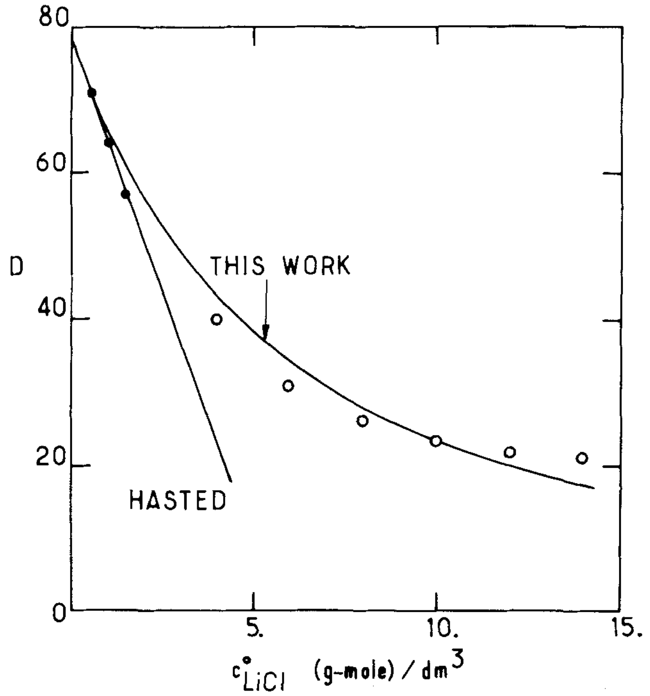

Fig. 3. Comparison between experimental and calculated average dielectric constant of the H_2O-LiCl solution. ○ ● experimental data (respectively from Gottlob and Hasted).

the largest term corresponds to the Debye-Hückel contribution; it is a negative contribution. The Born model contribution (salting out effect) is positive and becomes the largest numerical term when electrolyte concentration increases. The NRTL term is a negative contribution. Here, the last two effects are represented by roughly linear ln $\gamma^*_\pm$ contributions vs. apparent mole fractions of electrolyte. The corrective term to convert the activity coefficient to a molal scale $X \rightarrow M$ cannot be neglected for high electrolyte concentrations.

The equation presented in this paper can be approximated in the range 0 to 2 M by an usual expression for $\gamma^*_\pm$

$$\ln \gamma^*_\pm = -\frac{\epsilon^2|z_+z_-|}{D_S kT}\,\frac{K^\circ}{2(1+\mathring{a}K^\circ)} + \beta x_{AB} \quad (32)$$

which gives a good representation in this limited range of concentrations. $\mathring{a}$ and β are taken as adjustable parameters. In general, β is a positive factor because the salting out effect is larger than the short range effect in this range of concentrations.

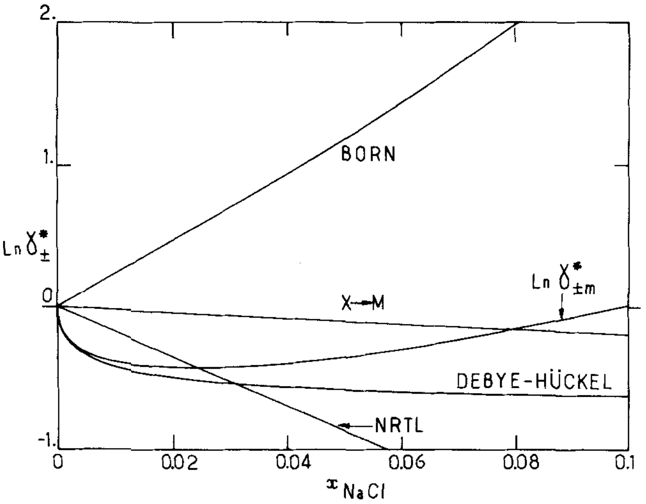

Fig. 4. Contributions to the mean ionic activity coefficient in the H_2O-NaCl mixture.

PARTIALLY DISSOCIATED ELECTROLYTES

The activity coefficients can still be derived from G^E by the same procedure. In addition, an expression is obtained for the activity coefficient of undissociated electrolyte γ_{AB}.

The mean ionic activity coefficient, in the molality scale, is given by

$$\ln \gamma^*_{\pm m} = -\frac{\epsilon^2|z_+z_-|}{D_S kT}\left\{\frac{K^\circ}{2(1+\mathring{a}K^\circ)} + \frac{K^\circ}{(\mathring{a}K^\circ)^3}\left[-\frac{\mathring{a}K^\circ}{2} + \ln(1+\mathring{a}K^\circ) - \frac{\mathring{a}K^\circ}{2(1+\mathring{a}K^\circ)}\right]\frac{\bar{v}_{AB}c^\circ{}_{AB}\alpha}{1\,000}\right\}$$
$$+ \frac{\epsilon^2}{2\nu kT}\left(\frac{\nu_+z^2{}_+}{r_A'} + \frac{\nu_-z^2{}_-}{r_B'}\right)\left[\left(\frac{1}{D} - \frac{1}{D_S}\right) - \frac{\alpha}{D^2}\left(1 - \frac{c^\circ{}_{AB}\bar{v}_{AB}}{1\,000}\right)\omega_{AB}\left(\frac{\partial D}{\partial \omega_{AB}}\right)_T\right]$$
$$+ \frac{\nu_+\xi_S[\xi_{AB}G_{AB,S}(Z_{\pm S}/RT - \tau_{AB,S}G_{\pm S}) + \xi_S Z_{\pm S}/RT)]}{\nu(\xi_A G_{\pm S} + \xi_{AB}G_{AB,S} + \xi_S)^2}$$
$$- \frac{\nu_+Z_{\pm S}}{\nu RT} - \ln\{1 + 0.001\,M_S m^\circ{}_{AB}[\alpha(\nu - 1) + 1]\} \quad (33)$$

The equation for the true activity coefficient of undissociated AB molecules is

$$\ln \gamma_{AB} = -\frac{\epsilon^2|z_+z_-|\nu}{D_S kT}\left\{\frac{K^\circ}{(\mathring{a}K^\circ)^3}\left[-\frac{\mathring{a}K^\circ}{2} + \ln(1+\mathring{a}K^\circ) - \frac{\mathring{a}K^\circ}{2(1+\mathring{a}K^\circ)}\right]\frac{\bar{v}_{AB}c^\circ{}_{AB}\alpha}{1\,000}\right\}$$
$$- \frac{\epsilon^2}{2kTD^2}\left(\frac{\nu_+z_+{}^2}{r_A'} + \frac{\nu_-z_-{}^2}{r_B'}\right)\left(1 - \frac{c^\circ{}_{AB}\bar{v}_{AB}}{1\,000}\right)\alpha\omega_{AB}\left(\frac{\partial D}{\partial \omega_{AB}}\right)_T + \frac{\xi_S{}^2\tau_{S,AB}G^2{}_{S,AB}}{(\xi_S G_{S,AB} + \xi_{AB})^2}$$
$$+ \frac{\xi_S\xi_A G_{AB,S}(\tau_{AB,S}G_{\pm S} - Z_{\pm S}/RT) + \xi_S{}^2\tau_{AB,S}G_{AB,S}}{(\xi_A G_{\pm S} + \xi_{AB}G_{AB,S} + \xi_S)^2} \quad (34)$$

For thermodynamical consistence, these activity coefficients must satisfy the dissociation equilibrium equation. Generally, the equilibrium constants, given in the literature, correspond to $K_m{}^*(T)$. The reference state chosen for the undissociated AB molecules is often infinite dilution in the pure solvent at reference pressure and equilibrium temperature. It follows that

$\gamma_{AB}{}^* \rightarrow 1$ when $\xi_{AB} \rightarrow 0$ ($\xi_S \rightarrow 1$, ξ_A and ξ_B equal zero).

$\gamma_{AB}{}^*$ is readily obtained from Equation (34):

$$\ln \gamma_{AB}{}^* = \ln \gamma_{AB} - \lim_{\xi_{AB}\rightarrow 0} (\ln \gamma_{AB})$$
$$= \ln \gamma_{AB} - \tau_{S,AB} - \tau_{AB,S}G_{AB,S} \quad (35)$$

In the same way, the following relation is obtained for the solvent:

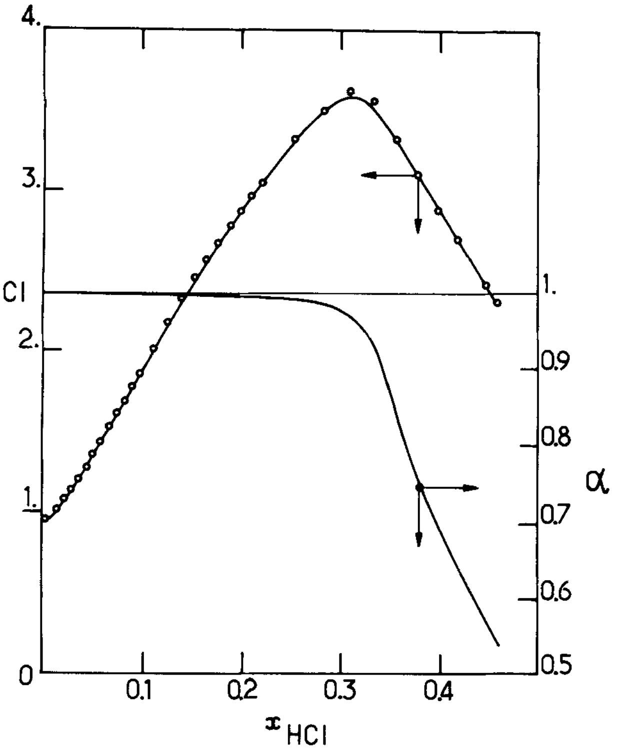

Fig. 5. Improvement of representation of the osmotic coefficient in H_2O-HCl system assuming partial dissociation. ○ data of Haase et al.

$$\ln \gamma_S = -\frac{\epsilon^2|z_+z_-|\nu}{D_SkT}\left\{\frac{K^\circ}{(\mathring{a}K^\circ)^3}\left[-\frac{\mathring{a}K^\circ}{2}+\ln(1+\mathring{a}K^\circ)\right.\right.$$

$$\left.\left.-\frac{\mathring{a}K^\circ}{2(1+\mathring{a}K^\circ)}\right]\frac{\bar{v}_Sc^\circ{}_{AB}\alpha}{1\,000}\right\}+\frac{\epsilon^2}{2kTD^2}\left(\frac{\nu_+z_+{}^2}{r_A{}'}+\frac{\nu_-z_-{}^2}{r_B{}'}\right)$$

$$\frac{c^\circ{}_{AB}\alpha\bar{v}_S\omega_{AB}}{1\,000}\left(\frac{\partial D}{\partial\omega_{AB}}\right)_T+\frac{\xi_{AB}{}^2G_{S,AB}\tau_{S,AB}}{(\xi_SG_{S,AB}+\xi_{AB})^2}$$

$$+\frac{\xi_AZ_{\pm S}/RT+\xi_{AB}G_{AB,S}\tau_{AB,S}}{(\xi_AG_{\pm S}+\xi_{AB}G_{AB,S}+\xi_S)}$$

$$-\xi_S\frac{\xi_AZ_{\pm S}/RT+\xi_{AB}G_{AB,S}\tau_{AB,S}}{(\xi_AG_{\pm S}+\xi_{AB}G_{AB,S}+\xi_S)^2} \qquad (36)$$

The apparent $\gamma^{*\exp}_{\pm m}$ usually reported in the literature is not true mean molal ionic activity coefficient in the case of partial dissociation (Haase, 1965). Therefore, $\ln \gamma^{*\text{cal}}_{\pm m}$ has to be corrected to correspond to the reported one by a term $\ln \alpha$ added to $\ln \gamma^*{}_{\pm m}$ given by Equation (33).

If $K^*{}_m(T)$ is known, an iterative method gives the dissociation coefficient α by solving Equation (2) during the optimization process.

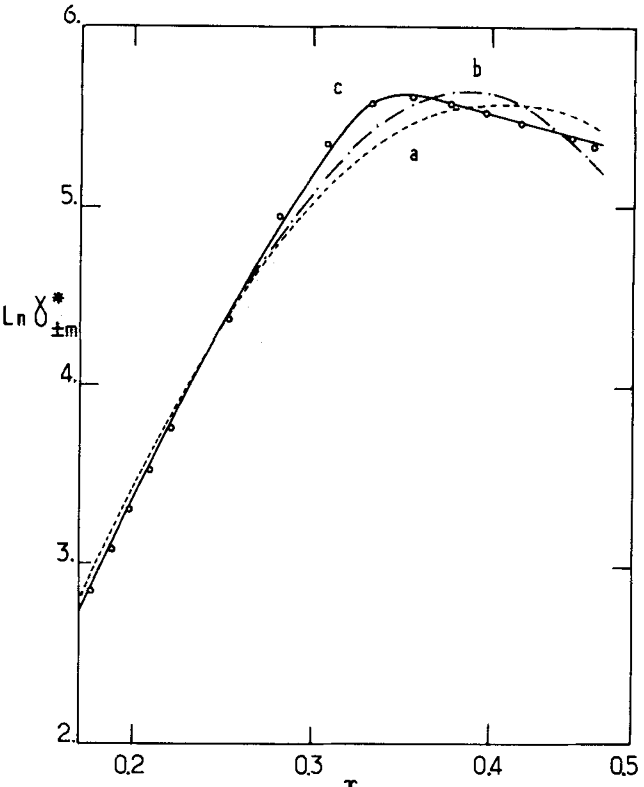

Fig. 6. Comparison of (a) Haase equation—(b) total dissociation and (c) partial dissociation equations for H_2O-HCl data.

These equations were applied to the hydrochloric acid-water literature data at 298.15°K and atmospheric pressure from Haase et al. (1963). An approximate value of $K^*{}_m(T)$ is provided by Charlot (1974) in $pK^*{}_m$ form. At 198.15°K, $pK^*{}_{HCl}$ equals −3.8.

The calculated dissociation coefficient and adjusted osmotic coefficient curves are shown in Figure 5. This last curve is to be compared to the calculated curve obtained with a four adjustable parameters equation (Figure 1) using the same experimental data to appreciate the improvement for mole fractions of hydrochloric acid around 0.3.

Figure 6 shows values of $\ln \gamma^*{}_{\pm m}$ at high electrolyte concentrations using either the Haase polynomial equation (1965), the total dissociation Equation (29) using parameters obtained by direct adjustment of experimental values of $\ln \gamma^*{}_{\pm m}$, or the partial dissociation Equations (33) to (35) and (2) with parameters adjusted to represent experimental osmotic coefficients using Equations (33) to (36) and (2).

The parameters and results of adjustments in the last two cases are given in Table 3.

Haase's model is good because the adjustment is consistent with the Debye-Hückel limiting law for high dilutions and quite satisfactory when the electrolyte molality is increasing. The partial dissociation Equations (33)

TABLE 3. COMPARISON BETWEEN REPRESENTATIONS OF H_2O-HCl EQUILIBRIUM DATA
a) HAASE—b) THIS WORK WITH TOTAL DISSOCIATION—c) THIS WORK WITH PARTIAL DISSOCIATION

	Parameters						Standard deviations			
	$Z_{\pm S}$ kJ/(g-mole)	$G_{\pm S}$	$10^{-2}\,\Delta_D$	D_{AB}	$C_{AB,S}$ kJ/(g-mole)	$C_{S,AB}$ kJ/(g-mole)	σ_γ	σ_ϕ	Represented property	Number of experimental points
a)							0.089		γ	43
b)	67.221	0.64332	−0.70537	8.4556			0.051		γ	43
c)	25.755	1.56575	−0.67317	9.7173	−12.327	16.639	0.026	0.19	ϕ	43

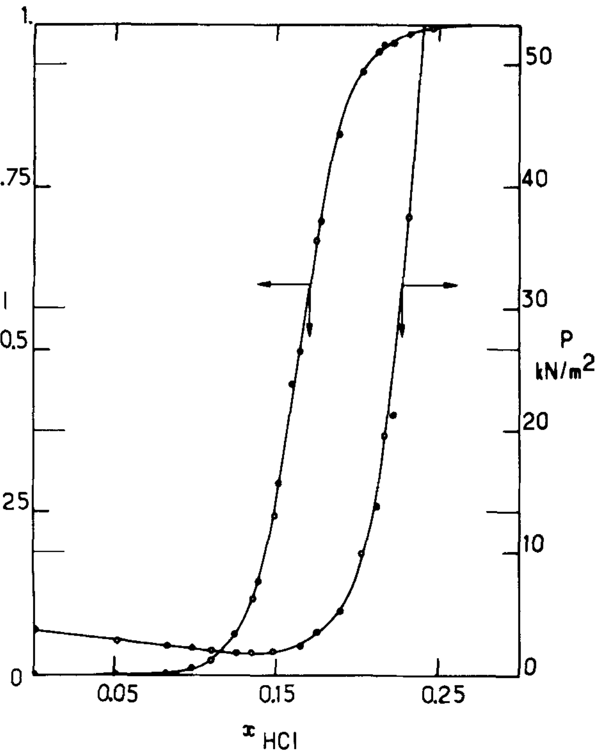

Fig. 7. Vapor-liquid equilibrium of the system H_2O-HCl assuming partial dissociation. ● data from Haase et al., ○ data from Vega and Vera.

to (36) and (2) are especially useful at high concentrations in very large molality ranges from 0 to 47 M. Yet, Haase's equations must rather be compared with the total dissociation Equations (29) to (31) because they do not require to use an equilibrium constant.

For the system water-hydrochloric acid at 298.15°K and atmospheric pressure, with a partial dissociation assumption, it can also be shown that the selected K^*_m value is not a sensitive parameter for the adjustment of $\ln \gamma^*_{\pm m}$ or ϕ_{HCl}. For instance, an σ_γ value equivalent to those reported in Table 3, line c, was obtained with $pK^*_{HCl} = -1.45$.

VAPOR-LIQUID EQUILIBRIUM CALCULATION

The system chosen to illustrate the calculation of vapor-liquid equilibrium is water-hydrochloric acid at 298.15°K. Complete experimental data (T, P, x, y) are obtained by Haase et al. (1963) from vapor pressure measurements of Fritz and Fuget (1956) and by Vega and Vera (1976) from vapor pressure data given by Perry (1963).

Because of its low dielectric constant and electrical conductivity, the dissociation can be neglected in pure liquid hydrochloric acid at 298.15°K. Therefore, Equation (7) is used in this application. At given x and T, P and y are calculated by solving the system of Equations (4) written in the following simplified form:

$$P y_j \Phi_j^V(T, P, y) = x_j \gamma_j^a(T, x) P_j^s(T) \Phi_j^{Vs}(T, P_j^s) \exp \int_{P_j^s}^{P} \frac{v_j^{\circ L}}{RT} dP \quad (j = AB,S) \qquad (37)$$

Table 4. Vapor-Liquid Equilibrium of HCl-H_2O System Assuming Partial Dissociation (Haase, Naas and Thumm H_2O-HCl Data at 298.15 K)

x_{HCl}^{Exp}	y_{HCl}^{Exp}	y_{HCl}^{Cal}	(kN/m²) P^{Exp}	P^{Cal}
0.083	0.003	0.004	2.99_3	2.34_4
0.098	0.009	0.010	2.18_7	2.14_3
0.112	0.024	0.026	1.94_0	1.96_4
0.126	0.062	0.065	1.84_0	1.82_4
0.139	0.143	0.144	1.78_7	1.77_1
0.153	0.294	0.301	1.88_0	1.88_8
0.165	0.496	0.490	2.30_0	2.27_6
0.178	0.696	0.692	3.22_6	3.25_4
0.190	0.829	0.829	5.06_6	5.09_2
0.201	0.904	0.906	8.29_3	8.11_0
0.213	0.958	0.952	13.7_3	13.7_6
0.223	0.972	0.973	21.3_3	21.3_7

Table 5. Vapor-Liquid Equilibrium of HCl-H_2O System Assuming Partial Dissociation (Vega and Vera H_2O-HCl Data at 298.15 K)

(g-mole)/ (kg of solvent) $m^\circ{}_{HCl}^{Exp}$	y_{HCl}^{Exp}	y_{HCl}^{Cal}	(kN/m²) P^{Exp}	P^{Cal}
3.045	0.0003	0.0003	2.66_6	2.72_0
4.462	0.0018	0.0014	2.40_0	2.44_0
6.017	0.0095	0.0083	2.08_0	2.10_6
6.854	0.022	0.020	1.92_0	1.93_3
7.735	0.051	0.048	1.77_3	1.80_0
8.656	0.116	0.111	1.72_0	1.70_7
9.635	0.243	0.241	1.76_0	1.74_7
10.67	0.446	0.450	2.10_6	2.09_3
11.75	0.668	0.676	3.01_3	3.02_6
12.90	0.836	0.842	5.18_6	5.21_3
14.13	0.928	0.931	9.85_2	9.93_2
15.42	0.970	0.970	19.5_2	19.3_3
16.81	0.987	0.987	37.4_1	37.3_3
18.28	0.994	0.994	69.0_5	69.3_8

When a pure liquid reference state is chosen, f_j^{rL} is easily obtained from the saturation pressure. In the present work, the saturation pressure data are taken from Haase et al. (1963):

$$P^s_{H_2O}(298.15^\circ K) = 3.166 \text{ kN/m}^2$$

$$\text{and} \quad P^s_{HCl}(298.15^\circ K) = 4.793 \text{ MN/m}^2$$

For the present data, it appears that the fugacity coefficients in the vapor phase Φ_j^V, calculated by the Nothnagel et al. (1973) correlations, differ from unity by less than 1%. The exponential Poynting correction in Equation (37) is close to one.

The optimization program is described by Renon et al. (1971). The minimization is carried out on the sum of squares:

$$S_{LV} = \sum_{i=1}^{n} (y_{i\,HCl}^{cal} - y_{i,HCl}^{exp})^2 + \sum_{i=1}^{n} \left(\frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \right)^2 \qquad (38)$$

Table 6. Representation of the Vapor-Liquid Equilibrium of the System H_2O-HCl at 298.15 K

	Parameters							
	$Z_{\pm S}$ kJ/(g-mole)	$G_{\pm S}$	$10^{-2}\,\Delta_D$	D_{AB}	$C_{AB,S}$ kJ/(g-mole)	$C_{S,AB}$	$\delta P/P$	δy_{HCl}
Table (V)	27.223	1.66763	−0.69848	10.155	−10.745	12.478	1.11	0.35
Table (VI)	26.382	1.67740	−0.71372	10.103	−10.791	11.502	0.99	0.34

The apparent activity coefficients γ_j^a are calculated by simultaneous use of Equations (33) to (35), (37), and (2) with $pK^*_{HCl} = -3.8$. The results of the adjustments are shown in Figure 7 and, respectively, in Tables 4 and 5 for the data of Haase et al. and Vega and Vera at 298.15°K. The calculated parameters for these data are given in Table 6.

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NOTATION

$\overset{\circ}{a}$ = distance of closest approach of opposite signed ions, cm
a'_{AB} = true activity of undissociated AB in pure electrolyte
b_j = polynomial parameters in Equation (B1), g/cm^3
c°_{AB} = stoichiometric molarity of electrolyte AB, (g-mole)/dm^3
C_{ki} = NRTL parameters, J/(g-mole)
D = macroscopic static dielectric constant of the solution
D_{AB} = adjustable parameter in Equation (12)
D_S = dielectric constant of pure liquid solvent
f_j = fugacity of j, N/m^2
g_{ki} = Gibbs energy of interaction between components k and i, J/(g-mole)
g^E = molar excess Gibbs energy of the system, J/(g-mole)
G^E = total excess Gibbs energy, J
G^I and G^{II} = long and short range contributions to G^E, J
G_{ki} = NRTL parameter
I = ionic strength, (g-mole)/dm^3
k = Boltzmann constant, 1.3805410^{-23} J/K (molecule)
K° = reciprocal Debye length, cm^{-1}
$K(T)$ = dissociation equilibrium constant
m°_{AB} = stoichiometric molality of electrolyte AB, (g-mole)/(kg of solvent)
M_j = molecular weight of component j, g/(g-mole)
n = number of experimental determinations
N = Avogadro number, 6.02252 10^{23}(molecule)/(g-mole)
N_j = number of moles of j in the total volume V
N°_j = initial number of moles of j
p = number of adjusted parameters
pK = cologarithm of dissociation constant
P_j^s = saturation pressure of component j, N/m^2
r_i^P and r_i^N = Pauling and Nightingale ionic radii, cm
r_i' = ionic saturated cavity radius, cm
R = gas constant, 8.3143 J/K·(g-mole)
$\bar{s}_i^*$ = partial molar entropy of hydration of i at infinite dilution J/K·(g-mole)
S_γ, S_ϕ, S_{LV} = sums of squares defined by Equations (25), (26), and (38)
T = absolute temperature, °K
v_j^c = molar volume of the saturated cavity around the ions j, cm^3/(g-mole)
v°_j = molar volume of pure component j, cm^3/(g-mole)
$\bar{v}_j$ = partial molar volume of component j, cm^3/(g-mole)
v^c_{AB} = molar volume of the average cavity around AB, cm^3/(g-mole)
V = total volume of the system, cm^3
w = wt % of electrolyte
x_{AB} = apparent mole fraction of electrolyte AB
x_j = apparent mole fraction of j in the liquid phase, $N^\circ_j \Big/ \sum_i N^\circ_i$
y_j = mole fraction of j in the vapor phase
z_+ and z_- = charge and sign of charge of ions
Z_{ki} = NRTL parameter defined by Equation (18), J/(g-mole)

Greek Letters

α = dissociation coefficient of the electrolyte
α_{ki} = NRTL parameter
β = adjustable parameter in extended Debye-Hückel Equation (32)
γ_j = activity coefficient of j in a mole fraction scale
$\bar{\delta}$ and δ_i = Hasted depressions, dm^3/(g-mole)
$\delta P/P$ = relative error on P, in percentage

$$100\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{P_i^{\text{cal}} - P_i^{\text{exp}}}{p_i^{\text{exp}}}\right)^2\right]^{1/2}$$

δy_j = absolute error on y, in percentage

$$100\left[\frac{1}{n}\sum_{i=1}^{n}(y_{ji}^{\text{cal}} - y_{ji}^{\text{exp}})^2\right]^{1/2}$$

Δ_D = dielectric nonideality parameter
ϵ = charge of the electron, 4.80298 10^{-10} ues-cgs
μ_j = chemical potential of j, J/(g-mole)
ν_+ and ν_- = stoichiometric numbers of ions in the dissociation equation
ν = $\nu_+ + \nu_-$
ξ_j = true mole fraction of j, $N_j \Big/ \sum_i N_i$
ρ = density of solution, g/cm^3
σ_γ and σ_ϕ = square roots of the estimation variances
τ_{ki} = NRTL parameter defined by Equation (16)
ϕ_{AB} = osmotic coefficient of a solution of electrolyte AB
Φ_j = fugacity coefficient of component j
ω_j = apparent volume fraction of component j in the liquid phase ($\omega_{AB} = N^\circ_{AB}v^\circ_{AB}/V$)
ω_c = volume fraction of saturated cavities

Subscripts

$\pm$ = mean ionic
m = molality scale

Superscripts

$*$ = infinite dilution reference state (or at infinite dilution)
a = apparent
L = in the liquid phase
r = in the reference state
s = saturated
V = in the vapor phase

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APPENDIX A

From the relation (Renon and Prausnitz, 1968) between local mole fractions ξ_{ki} of molecules k which are in the immediate neighborhood of a central molecule i

$$\frac{\xi_{ki}}{\xi_{ii}} = \frac{\xi_k}{\xi_i}\,\frac{\exp(-\alpha_{ki}g_{ki}/RT)}{\exp(-\alpha_{ki}g_{ii}/RT)} = \frac{\xi_k}{\xi_i}G_{ki}$$

$$g_{ki} = g_{ik}$$

with

$$C_{ki} = g_{ki} - g_{ii}$$

it is clear that molecules k will be excluded from the vicinity of i as g_{ki} increases to infinity, g_{ii} remaining finite.

In the present electrolytic system, recalling that the α_{ki} are finite, a scale of values of g_{ki} can be roughly defined which leads to values of ξ_{ki} consistent with assumptions of this work and the knowledge of ionic solvation. The energy parameter g_{ki} increases from low to large numerical values in the following order: (solvent-ion) < (solvent or AB) — (solvent or AB) << (AB-ion) or (ion-ion of opposite signs) < (ion-ion of same signs).

On the right side of the sign <<, very large values of g_{ki} are found, and true local mole fractions are taken equal to zero. Equivalent results are formally obtained by assuming G_{ki} equal to zero. In applications, the following assumptions are made: $G_{AB,A}$, $G_{AB,B}$, $G_{A,AB}$, $G_{B,AB}$, $G_{A,B}$, and $G_{B,A}$ are zero, and the true local mole fractions $\xi_{S,A}$ and $\xi_{S,B}$ are one. This last assumption eliminates parameters $G_{S,A}$ and $G_{S,B}$ from Equation (19).

APPENDIX B

Calculation of Volumetric Quantities

Density data of the mixture vs. electrolyte concentration are used. Table 7 gives the values of adjustable polynomial parameters, in Equation (B1), obtained from literature density data at 298.15°K for the electrolytic systems studied in this work (Perry, 1963; Weast, 1970):

$$\rho = \sum_{i=1}^{6} b_i(w)^{i-1} \tag{B1}$$

The density of pure water b_1 at 298.15°K is 0.99707 g/cm^3, and the parameters b_i are such that the value of $v°_{AB}$ is recovered for $w = 1$.

When data are missing, it is supposed that

$$V = N°_{AB}v°_{AB} + N°_S v°_S$$

Estimation of Ionic Depressions δ_i and Ionic Radii r_i'

According to the work of Hasted et al. (1948), the mean dielectric depression $\overline{\delta}$ is assumed to be equal to

$$\overline{\delta} = 1/2(\nu_+\delta_+ + \nu_-\delta_-) \tag{B2}$$

Table 8 gives individual values δ_i recommended for the use of Equation (12).

Following an assumption of Beutier (1978), δ_i is expected to be related to the volume of solution dielectrically saturated around an ion. Indeed, the depression of the macroscopic static dielectric constant is in relation with the amount of solvent molecules which are not free to rotate because of the effect of the electrical charge density of the ion.

The relation between individual depression δ_i towards cristallographic radii r_i^P, from Pauling (1940), is shown for monovalent ions in Figure 8*a*. When no dielectric constant measurements are available, a correlation was sought between δ_i and two variables, recommended by Franks (1973) for their relation with the structure of solvated ion in solution.

Figure 8*c* illustrates the linear correlation between δ_i and $\bar{v}_i^*$ for positive and negative monovalent ions at 298.15°K. Later, δ_i values are needed for NH_4^+, NO_3^-, $H_2PO_4^-$, and ClO_4^-. For NH_4^+, the correlation of positive ions is used because it is known that its properties are similar to those of alkali ions. For the negative ions, the correlation of negative ions is tentatively used; indeed, the correlation between

TABLE 7. DENSITY ADJUSTMENT RESULTS FOR H_2O-AB MIXTURES

	b_2	b_3	b_4	b_5	b_6	Weight per cent range	M_{AB} g/(g-mole)	$v°_{AB}$ cm³/(g-mole)
HCl	0.4368	0.4181	−0.3888	−0.7969	0.1213	0-0.63	36.465	46.34
HBr	0.6565	0.6041	0.5499	−1.0417	1.0041	0-0.66	80.92	29.22
HI							127.91	44.88
$HClO_4$	0.4887	0.1094	0.4149	2.3361	−2.5820	0-0.70	100.46	56.95
HNO_3	0.5266	0.2091	0.4789	−1.4854	0.7776	0-0.90	63.01	41.89
H_2SO_4	0.5860	1.0669	−3.4737	5.8955	−3.2456	0-0.90	98.08	53.73
H_3PO_4	0.5375	0.0743	0.5666	−0.4095	0.1000	0-0.75	98.00	52.52
NaOH	1.0804	0.1613	−0.1749	−1.1668	1.2329	0-0.48	40.00	18.78
KOH	0.9599	−0.1500	0.7636	−0.1187	−0.4078	0-0.52	56.11	27.45
NaCl	0.6988	0.1588	0.2364	0.1946	−0.1207	0-0.26	58.44	26.99
LiCl	0.5755	−0.0887	0.6212	−0.1295	0.0146	0-0.46	42.39	21.30
LiBr							86.85	25.07
$CaCl_2$	0.8073	0.3781	0.2392	−0.0255	−0.2462	0-0.40	110.95	51.60
$CaBr_2$							199.90	59.62
NH_4NO_3	0.3908	0.2065	−0.4161	0.4429	−0.1038	0-0.50	84.04	46.40
H_2O							18.015	18.068

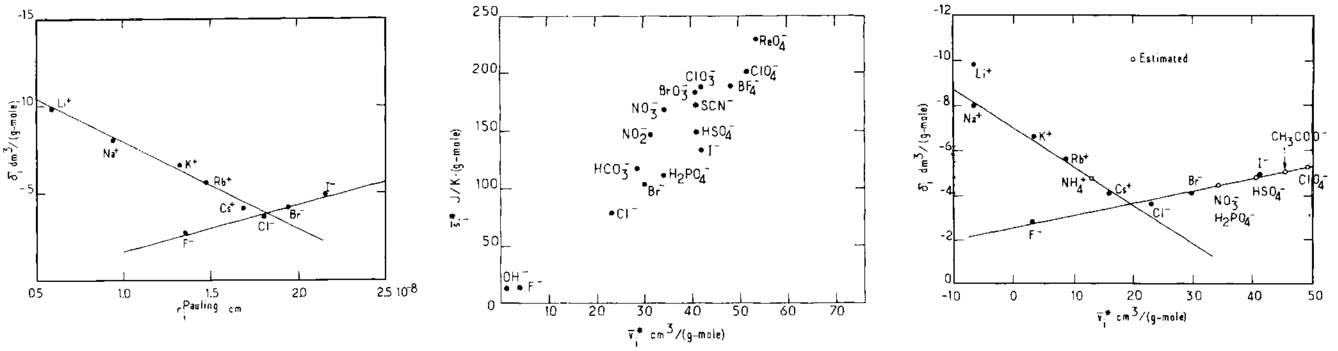

Fig. 8a, 8b and 8c. Correlations between ionic quantities used for the determination of Hasted depressions.

TABLE 8. INDIVIDUAL IONIC PROPERTIES (e = ESTIMATED VALUE)

	δ_i, dm³/(g-mole)	$\bar{v}_i^*$ cm³/(g-mole)	$10^8\, r_i^P$, cm	$10^8\, r_i'$ cm	$10^8\, r_i^N$, cm
Li^+	−9.8	−6.3	0.60	3.21	3.82
Na^+	−8.0	−6.6	0.95	3.00	3.58
K^+	−6.6	3.6	1.33	2.81	3.31
Rb^+	−5.6	8.7	1.48	2.66	3.29
Cs^+	−4.1	15.9	1.69	2.40	3.29
NH_4^+	-4.8^e	13.0	1.48	2.53	3.31
F^-	−2.8	4.2	1.36	2.11	3.52
Cl^-	−3.6	23.2	1.81	2.29	3.32
Br^-	−4.1	30.1	1.95	2.40	3.30
I^-	−4.9	41.6	2.16	2.55	3.31
H^+	−16.4	−5.4		3.81	
OH^-	−13.0	1.4		3.53	
Mg^{2+}	−22.8	−32.0	0.65	4.25	4.28
Ba^{2+}	−20.8	−23.3	1.35	4.13	4.04
Ca^{2+}	-21.4^e	−28.6	0.99	4.20	4.12
La^{3+}	−36.8	−55.3	1.15	4.99	4.52
NO_3^-	-4.4^e	34.5		2.46	3.35
$H_2PO_4^-$	-4.4^e	34.5		2.46	
HSO_4^-	-4.8^e	41.1		2.53	
ClO_4^-	-5.2^e	49.5		2.59	3.38
$SO_4^=$	−6.0	24.8		2.73	3.79

$\bar{v}_i^*$ and $\bar{s}_i^*$ implies a similarity of properties with halide ions (Figure 8*b*).

Note that a group of ion, H^+, OH^- and Li^+, known for their strong hydration are outside the correlation in Figure 8*c*. The values obtained for δ_i are given in Table 8.

Onsager (cited by Pottel, 1973) proposed a saturated cavity model to explain dielectric properties. A saturated cavity is a volume of solution, surrounding an ion, in which the solvent molecules have lost their orientational polarizability. These cavities are introduced into a continuous dielectric medium. A simple formula, tested for a volume fraction of saturated cavities ω_c up to about 0.3 with aqueous tetraalkylammonium bromide solutions, is obtained for monovalent ions:

$$D = D_S \frac{1 - \omega_c}{1 + 0.5\omega_c}$$

In Equation (11), r_i' represents the radius of the cavity around the ion i. Assuming, for high dilutions, no variation of r_i' when electrolyte concentration varies

$$D_S(1 - 1.5\,\omega_c) \simeq D_S + 2\bar{\delta} c°_{AB} = D$$

then the molar volume of the average cavity around AB is

$$v^c_{AB} = -\frac{2\,000\,\bar{\delta}}{1.5\,D_S}$$

In water at 298.15°K, $D_S = 78.30$

$$v^c_{AB} \simeq -17.0\,\bar{\delta}$$

Values of ionic contributions to this volume are therefore related to individual ionic Hasted depressions δ_i by

$$v^c_i \simeq -17.0\,\frac{\delta_i}{2}$$

and if we assume a spherical cavity in water, at 298.15°K, the following expressions are obtained:

$$r_i' = 0.735(v^c{}_i)^{1/3} = 1.5|\delta_i|^{1/3} \quad \text{(B3)}$$

The calculated values of r_i', from δ_i are given in Table 8. In the same table, the values of cristallographic radii from Pauling's data and the hydrated radii of Nightingale (1959) are reported for comparison. These are kinetic values obtained from Stokes law and a correction factor for small radii ions. It appears that r_i' values are generally included in the range (r_i^P, r_i^N).

Applications of the model to various electrolytic systems show that the quality of adjustments is not much affected by the choice of δ_i and r_i'. For instance, similar results are obtained for the system water-sulfuric acid at 298.15°K with

$$\begin{cases} \delta_{H^+} = -17.0 \text{ dm}^3/(\text{g-mole}) & r'_{H^+} = 3.70\ 10^{-8} \text{ cm} \\ \delta_{SO_4^=} = -7.0 \text{ dm}^3/(\text{g-mole}) & r'_{SO_4^=} = 3.70\ 10^{-8} \text{ cm} \end{cases}$$

and

$$\begin{cases} \delta_{H^+} = -16.4 \text{ dm}^3/(\text{g-mole}) & r'_{H^+} = 3.81\ 10^{-8} \text{ cm} \\ \delta_{SO_4^=} = -6.0 \text{ dm}^3/(\text{g-mole}) & r'_{SO_4^=} = 2.73\ 10^{-8} \text{ cm} \end{cases}$$

Therefore, Equation (B3) was used even for polyvalent ions.

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A Sparse Computation System for Process Design and Simulation:

Part I. Data Structures and Processing Techniques

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As an alternative to tearing, symbolic permutation may be used to facilitate data processing rather than dimensional reduction in equation solving, permitting a reduction in computing effort without introducing any deleterious effects on the numerical convergence. Data structures and processing techniques suitable for this purpose have been successfully devised and tested. A program incorporating these techniques has been implemented on a CDC 6400 computer and used to solve irreducible systems of up to 551 linear and nonlinear equations.

SCOPE

The development of process technology is marked by continual improvements in the efficiency of energy and raw material utilization. In recent years, the need for such efficiency enhancement has become ever more compelling because of escalating fuel and raw material costs. One of the ramifications of enhancing process efficiencies is a greater degree of process integration. Our attempts to minimize waste heat and improve product yield lead inexorably to more heat exchanges and more recycle streams, which in turn increase the dimensions of the computing problems. Another consequence of fine tuning the process design and operation is that more accurate and more comprehensive thermophysical and transport properties are needed in process computation. This requirement is usually met by lengthier computational procedures for estimating those properties. The upshot of these two effects is an escalation of the dimension and complexity of realistic process computation which poses many challenging problems in spite of the considerable upgrading of data processing capabilities over the past two decades.

By its very nature, a large system of equations tends to be sparse in the sense that not all variables occur in every equation. The development of efficient computation schemes must capitalize on the sparsity pattern (or structure) of these equations. An approach widely used in computer aided process design is to generate a precedence ordering of equations and variables through partitioning and tearing. The underlying objective of this approach is to minimize the number of variables which must be treated simultaneously in each subsystem. This strategy leads to the minimal recycle or breakpoint criterion used to guide tearing.

Although minimizing the number of iterates seems to be a simple and attractive criterion at first, it does not automatically guarantee computational efficiency. For succes-

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