Activity Coefficients of Strong Electrolytes in Multicomponent Aqueous Solutions

H. P. MEISSNER

Chemical Engineering Department
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

C. L. KUSIK

Arthur D. Little, Inc., Cambridge, Massachusetts 02140

The quantity Γ_{12} here called the reduced activity coefficient is related to γ_{12} the mean activity coefficient of a strong electrolyte 12 as follows:

$$\Gamma_{12} = \gamma_{12}^{1/z_1z_2}$$

where z_1 and z_2 are the charge numbers on the ions. The value of Γ_{12} for electrolyte 12 in an aqueous solution containing the three ions 1, 2, and 3, such as Na^+, Cl^-, and Ba^{++}, is to be calculated as follows:

$$\log \Gamma_{12} = \log \Gamma^\circ_{12} + \tfrac{1}{2}(X_3) \log (\Gamma^\circ_{32}/\Gamma^\circ_{12})$$

Here Γ°_{32} and Γ°_{12} are for the indicated electrolytes, namely NaCl and $BaCl_2$ in this example, at the total ionic strength of the mixture. The term X_3 represents the fraction $m_3z_3^2/(m_1z_1^2 + m_3z_3^2)$ in which m represents the molality of the indicated ion. Fair success is usually attained with this equation in predicting γ, even at high electrolyte concentrations.

Similar equations are proposed for aqueous solutions containing four or more ions.

Values of γ, the mean activity coefficient of an individual strong electrolyte in an aqueous solution of two or more strong electrolytes, are required in calculating the ionic reaction equilibria in aqueous solutions. Of particular interest are γ values in relatively concentrated solutions (brines, waste streams, etc.) such as are encountered in industrial chemistry, in hydrometallurgy, in electrochemistry, in biochemical systems and the like. Experimental data on γ in mixed systems are difficult to obtain and relatively few direct measurements have been published. The object here is to consider a method for approximating the values of such activity coefficients, applicable in all concentrations of mixed aqueous solutions at 25°C.

In the systems under discussions, the cations are designated by the subscripts 1, 3, 5, 7, etc., while the anions are 2, 4, 6, 8, etc., with corresponding ion molalities being m_1, m_2, m_3, etc., and ion charges being z_1, z_2, z_3, etc. The mean activity coefficient of any single electrolyte 12 in solution is designated at γ°_{12}, while its mean activity coefficient in a “mixed’ solution containing more than one anion and one cation is γ_{12}. The total ionic strength μ_T of solutions, regardless of the number of dissolved electrolytes, is then $\tfrac{1}{2}(m_1z_1^2 + m_2z_2^2 + m_3z_3^2 + \ldots)$. Similarly, in ionic strength units, the cationic strength μ_c is $\tfrac{1}{2}(m_1z_1^2 + m_3z_3^2 + m_5z_5^2 + \ldots)$, while the anionic strength μ_a is $\tfrac{1}{2}(m_2z_2^2 + m_4z_4^2 + m_6z_6^2 + \ldots)$. Obviously, μ_c and μ_a are equal only when all ion charges are of equal magnitude. By definition, the total ionic strength is μ_T, where $\mu_T = \mu_c + \mu_a$.

In ionic strength units, the fraction of the cations present represented by cation 1 is X_1, where

$$X_1 = 1/2(m_1z_1^2/\mu_c)$$

Similarly, the fraction of the anions present represented by anion 2 is Y_2, where

$$Y_2 = 1/2(m_2z_2^2/\mu_a)$$

In any solution containing a single electrolyte, X_1 and Y_2 are unity.

For mixed systems, these definitions are conveniently illustrated with a solution containing 1 g.-mole Na_2SO_4 and 1 g.-mole $AlCl_3$ in 1000 g. water. The ions Na^+, $SO_4^=$, Al^{+++} and Cl^- are arbitrarily designated as 1, 2, 3, and 4 respectively; consequently, the molalities m_1, m_2, m_3 and m_4 are respectively 2, 1, 1, and 3, while the corresponding z values are 1, 2, 3, and 1. In ionic strength units, μ_c is $1/2(2 \cdot 1^2 + 1 \cdot 3^2)$ or 5.5, μ_a is $1/2(1 \cdot 2^2 + 3 \cdot 1^2)$ or 3.5, hence μ_T is $(5.5 + 3.5)$ or 9. In these units, the ion fractions are as follows: X_1 is $1/2(2 \cdot 1^2)/5.5$ or 0.18; X_3 is $1/2(1 \cdot 3^2)/5.5$ or 0.82; Y_2 is $1/2(1 \cdot 2^2)/3.5$ or 0.57; and Y_4 is $1/2(3 \cdot 1^2)/3.5$ or 0.43. It is clear that the mixed solution just discussed could have been prepared in many other ways, as by dissolving 2 g.-moles of NaCl, 1/3 g.-mole of $AlCl_3$ and 1/3 g.-mole of $Al_2(SO_4)_3$ in 1000 g. of water, or by dissolving 1 g.-mole NaCl, 1/6 g.-mole of $Al_2(SO_4)_3$, 2/3 g.-moles of $AlCl_3$ and 1/2 g.-mole of Na_2SO_4 in 1000 g. of water, etc. The values of m, μ, X and Y for the individual ions are of course independent of how this solution is prepared.

Electrolytes are often characterized by their ion charges, in that a salt like NaCl or KBr is a 1:1 electrolyte, $CaCl_2$ is a 2:1 electrolyte, $CuSO_4$ is a 2:2 electrolyte, etc. For any electrolyte, it has been found useful (5) to designate the “reduced” activity coefficient, namely (γ_{12}^{1/z_1z_2}), as Γ^*_{12} in a “pure” solution and Γ_{12} in a “mixed” solution. For a 1:1 electrolyte, γ is identical with Γ, and γ° with Γ°, but these equalities obviously do not hold for electrolytes containing ions having charges greater than unity.

Γ° IN PURE SYSTEMS

In this development it will become evident that to predict γ for a strong electrolyte in a mixed solution of any given ionic strength, it is necessary to know the value of Γ° or of γ° for this same electrolyte in a pure solution of the same total ionic strength and the same temperature. Sometimes the only experimental Γ° or γ° values available are at ionic strengths other than that of interest, in which case extrapolation is undertaken with the aid of Figure 1. This extrapolation is based on the finding (*5*) that curves of Γ° versus μ for most strong electrolytes fall fairly well into the curve family of Figures 1 and 2, with only one known point required to locate a curve. Thus experimental values of Γ° for $Pb(NO_3)_2$ are 0.50 and 0.31 at ionic strengths of 1.0 and 6.0 respectively (*6*). Locating the point where μ is unity and Γ° is 0.5 on Figure 1 and following the curve thus identified to where μ is 6, Γ° is found to be 0.29, or within 10% of the experimental value. To establish a value for Γ° in the supersaturated region, it is merely necessary to follow this same curve out to the desired ionic strength. In general, errors in extrapolation become greater as extrapolation from low μ values to values in excess of 10 is undertaken. To minimize such errors, the range of μ involved in an extrapolation should be kept as small as possible.

Often, no known values for Γ° or γ° are available at any concentration for the strong electrolyte under study. In this event, methods of prediction for Γ° outlined elsewhere (*5*), or in later paragraphs of this paper may be useful.

Γ IN MIXTURES

The limited direct experimental measurements available in the literature on activity coefficients in mixed solutions are reviewed and methods of correlations are discussed by Hala et al. (*2*) as well as by Harned and Robinson (*4*). Most of these studies involve solutions of two electrolytes having a common ion, such as HCl and NaCl. These solutions are usually made by adding μ_{12} ionic strength units of electrolyte 12 and μ_{32} ionic strength units of electrolyte 32 to 1000 g. of water, in such proportions that the total ionic strength μ_T, namely $(\mu_{12} + \mu_{32})$, is constant at some value. In such systems, Harned showed that as a first approximation at a constant total ionic strength, experimental data on γ can be correlated as follows:

$$\log\gamma_{12} = \log\gamma^\circ_{12} + \alpha\mu_{32}/\mu_T \quad (1)$$

$$\log\gamma_{32} = \log\gamma^\circ_{32} - \alpha\mu_{12}/\mu_T \quad (2)$$

Here α is constant at any fixed value of μ_T, but can vary with μ_T, while γ°_{12} and γ°_{32} are the activity coefficients for the pure electrolytes at μ_T.

A second possible source of activity coefficient values in mixed solutions is from solubility product calculations in saturated solutions. That is, the solubility product of any 1:1 electrolyte 12 in its pure saturated solution is $(\gamma^\circ_{12}m^\circ_{12})^2$, where m_{12} is the molality and γ°_{12} is its corresponding activity coefficient determined experimentally or by estimation (*5*). The solubility product of 12 in a mixed system saturated with 12 is γ^2_{12} (m_1m_2), where m_1 and m_2 are the ion molalities. Equating these two solubility product expressions and rearranging

$$\gamma_{12} = \frac{\gamma^\circ_{12}m^\circ_{12}}{(m_1m_2)^{1/2}} \quad (3)$$

Thus a pure saturated solution of KNO_3 is 3.79 molal, for which γ° is 0.24 (*6*). In a solution saturated with both KNO_3 and $NaNO_3$ the respective molalities of these two salts are 4.65 and 11.8, hence with ions K^+, NO_3^- and Na^+ designated as 1, 2, and 3, m_1 is 4.65 and m_2 is (4.65 + 11.8) or 16.45. Substituting into Equation (3), the value of γ_{KNO_3} based upon solubility products is $(3.79 \times 0.24)/(4.65 \times 16.45)^{1/2}$ or 0.122. Since this solution happens also to be saturated with $NaNO_3$, its activity coefficient can be determined in an analogous way.

A similar calculation using solubility data usually cannot be carried out to test the success in predicting γ for electrolytes containing ions with z values greater than unity. That is, the solubility product relation of Equation (3) applies only when the electrolyte involved exists as a pure solid, containing no water of crystallization. Unfortunately, solid salts whose ions carry more than a single charge are almost invariably hydrated when in contact with their saturated solutions. Thus Equation (3) applies primarily

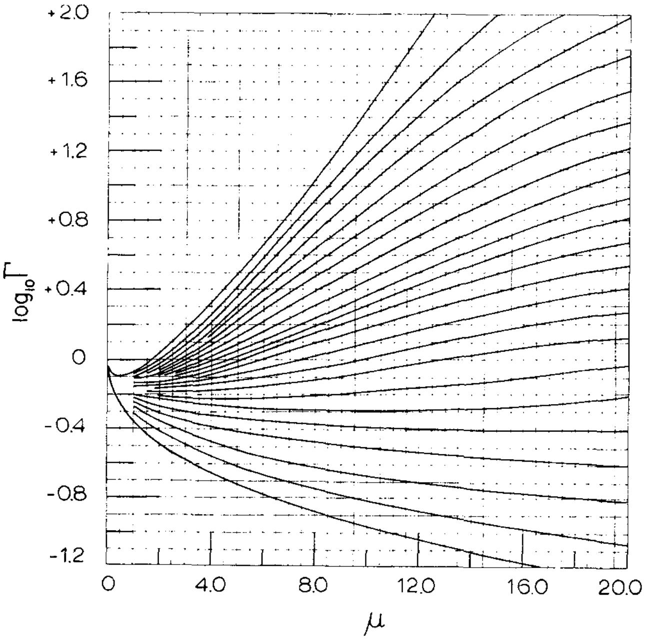

Fig. 1. Generalized plot of the reduced activity coefficient Γ versus ionic strength μ over the ionic strength range of 1.0 to 20.

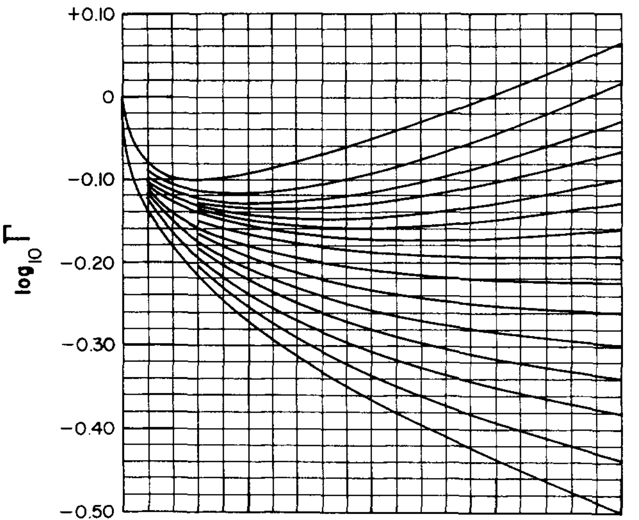

Fig. 2. Generalized plot of Γ versus μ over the ionic strength range of 0.1 to 2.0. This graph supplements the information on Figure 1.

to 1:1 salts, since most of these as solids do not contain water of hydration. Similarly, Equation (3) cannot be used for testing when the solid electrolyte exists in solid solution or as a double salt.

PROPOSED RELATIONS

Brønsted (*1*) proposed that the value of the mean activity coefficient for electrolyte 12 in a mixed solution depends primarily upon the interaction between cation 1 and each anion present, namely ions 2, 4, 6, etc., and on the interaction between anion 2 and each cation present, namely cations 1, 3, 5, etc. As a first approximation the interaction of ions with like charge is small and can be neglected. To extend this reasoning, assume:

1. The energy of interaction between cation 1 and the anions present is measured by F_1, where F_1 is defined as

$$F_1 = \tfrac{1}{2}(Y_2 \log\Gamma^\circ_{12} + Y_4 \log\Gamma^\circ_{14} + Y_6 \log\Gamma^\circ_{16} + \ldots) \tag{4}$$

All Γ° are at the total ionic strengths of the mixture.

2. The energy of interaction between anion 2 and the cations present is F_2, where

$$F_2 = \tfrac{1}{2}(X_1 \log\Gamma^\circ_{12} + X_3 \log\Gamma^\circ_{32} + X_5 \log\Gamma^\circ_{52} + \ldots) \tag{5}$$

where the Γ° values are again taken at the total ionic strengths of the mixture.

3. The mean activity coefficients of 12 in the mixture is then related to F_1 and F_2 as follows:

$$\log \Gamma_{12} = F_1 + F_2 \tag{6}$$

Thus substitution of Equations (4) and (5) into Equation (6) leads directly to values of the reduced activity coefficient Γ_{12} in mixed solutions.

Similar relations are presented below for calculating activity coefficients of electrolytes formed by other possible combinations of ions. Thus in a system containing ions 3, 4, 5 and 6 in addition to ions 1 and 2:

$$F_3 = \tfrac{1}{2}(Y_2 \log \Gamma^\circ_{32} + Y_4 \log \Gamma^\circ_{34} + Y_6 \log \Gamma^\circ_{36} + \ldots) \tag{7}$$

$$F_4 = \tfrac{1}{2}(X_1 \log \Gamma^\circ_{14} + X_3 \log \Gamma^\circ_{34} + X_5 \log \Gamma^\circ_{54} + \ldots) \tag{8}$$

$$F_5 = \tfrac{1}{2}(Y_2 \log \Gamma^\circ_{52} + Y_4 \log \Gamma^\circ_{54} + Y_6 \log \Gamma^\circ_{56} + \ldots) \tag{9}$$

$$F_6 = \tfrac{1}{2}(X_1 \log \Gamma^\circ_{16} + X_3 \log \Gamma^\circ_{36} + X_5 \log \Gamma^\circ_{56} + \ldots) \tag{10}$$

Using the convention of numbering the cation first, the reduced activity coefficients for various ion combinations then are of the form:

$$\log \Gamma_{32} = F_3 + F_2 \tag{11}$$

$$\log \Gamma_{34} = F_3 + F_4 \tag{12}$$

$$\log \Gamma_{14} = F_1 + F_4 \tag{13}$$

$$\log \Gamma_{52} = F_5 + F_2\text{, etc.} \tag{14}$$

The extensions of these equations to systems containing more than six ions is obvious. The equations proposed above are presumed to apply to saturated as well as unsaturated solutions. For saturated solutions, unlike Equation (3), they apply regardless of what forms may be taken by the solid phases. That is, these solid phases may be unhydrated or hydrated salts, double salts, solid solutions, etc.

Errors to be expected in using these equations are indicated by comparing calculated values of the activity coefficient with corresponding experimental values for various systems. In the typical cases now discussed, solubility data on pure and mixed solutions are from Seidell-Linke (*7*), while experimental values for activity coefficients are from the appendices of Harned and Owen (*3*) and from Robinson and Stokes (*6*). It is often necessary to estimate γ° and Γ° values for pure supersaturated solutions, which is done by extrapolating known values of Γ° using Figure 1. All examples presented here involve aqueous solutions at 25°C.

THREE ION SYSTEMS

Two cations and one anion. Only the three ions, 1, 2, and 3 are present when dissolving electrolytes 12 and 32 in water. Obviously, Equations (6) and (11) apply here, with all terms other than those involving X_1, Y_2, and X_3 in Equations (4), (5), and (7) being zero. Substituting Equations (4), (5), and (7) into Equations (6) and (11):

$$\log \Gamma_{12} = \tfrac{1}{2}(X_1 \log \Gamma^\circ_{12} + Y_2 \log \Gamma^\circ_{12} + X_3 \log \Gamma^\circ_{32}) \tag{15}$$

$$\log \Gamma_{32} = \tfrac{1}{2}(X_1 \log \Gamma^\circ_{12} + Y_2 \log \Gamma^\circ_{32} + X_3 \log \Gamma^\circ_{32}) \tag{16}$$

In this system, Y_2 is unity and X_1 equals $(1 - X_3)$, hence the above equations become

$$\log \Gamma_{12} = \log \Gamma^\circ_{12} + 0.5X_3 \log(\Gamma^\circ_{32}/\Gamma^\circ_{12}) \tag{17}$$

$$\log \Gamma_{32} = \log \Gamma^\circ_{32} - 0.5X_1 \log(\Gamma^\circ_{32}/\Gamma^\circ_{12}) \tag{18}$$

These equations, in which $\log \Gamma_{12}$ is linear in X_3 and $\log \Gamma_{32}$ is linear in X_1, have the following characteristics:

1. The slopes of these equations are both numerically equal to $\log\Gamma^\circ_{32}/\Gamma^\circ_{12}$, but are of opposite sign.
2. The obvious requirement that Γ must become equal to Γ° in pure solution is satisfied, in that $\log \Gamma_{12}$ equals $\log \Gamma^\circ_{12}$ when X_1 is unity and X_3 is zero, and $\log \Gamma_{32}$ equals $\log \Gamma^\circ_{32}$ when X_1 is zero and X_3 is unity.
3. When a solution of electrolyte 32 contains only a trace of 12 for a given value of μ_T, that is, X_1 is zero while Y_2 and Y_3 are both unity, Equation (15) becomes:

$$\Gamma_{12}^{tr} = (\Gamma^\circ_{12} \cdot \Gamma^\circ_{32})^{1/2} \tag{19}$$

Similarly, for a trace of 32 in 12, from Equation (16)

$$\Gamma_{32}^{tr} = (\Gamma^\circ_{12} \cdot \Gamma^\circ_{32})^{1/2} \tag{20}$$

Thus, for a given μ_T, Γ_{12}^{tr} and Γ_{32}^{tr} are equal hence

$$(\gamma_{12}^{tr})^{1/z_1z_2} = (\gamma_{32}^{tr})^{1/z_2z_3} \tag{21}$$

It is interesting to note that Equation (21) is in agreement with the equation developed by Harned and Robinson (*4*) using a different line of reasoning. Calculated values of γ_{12}^{tr} and γ_{32}^{tr} from Equations (19) and (20) are compared with experimental values in the upper part of Table 1. Inspection indicates that in general errors of not over 10% are encountered in predicting γ_{HCl}^{tr} and γ_{NaCl}^{tr} in various three-ion systems with chloride as the common anion. Agreement, however, is poor for $AlCl_3$ and $LaCl_3$ in their trace solutions in aqueous HCl.

4. For mixtures of two 1:1 salts, X_3 obviously equals $\mu_{32}/(\mu_{12} + \mu_{32})$; consequently, Equation (17) becomes similar to Equation (1) and Equation (18) becomes similar to Equation (2). It follows that the slope α in the Harned equation equals $\tfrac{1}{2}\log(\gamma^\circ_{32}/\gamma^\circ_{12})$. In a mixture of two electrolytes having unlike charges, such as when both a 1:1 and a 2:1 salt are present, X_3 is obviously no longer identical with $\mu_{23}/(\mu_{12} + \mu_{23})$. For such systems,

success in correlating experimental data using Equation (17) is nevertheless reasonable, as indicated by the following few paragraphs.

Equations (15) through (21) deal with three-ion systems having a common anion. An analogous set of equations can be written for three ion systems involving ions 1, 2 and 4, with ion 1 as the common cation. Examples here are mixtures of NaCl with $NaClO_3$, with Na_2SO_4, etc. The errors to be expected can again be judged from the data presented in the bottom half of Table 1.

A further test of these relations involves comparing values for γ in saturated solutions calculated by Equation (3) from solubility products, with values of γ calculated by Equation (17):

1. By Equation (17): A solution 5.27 molal in $Ca(NO_3)_2$ and 5.3 molal in $NaNO_3$ is saturated with $NaNO_3$ but not $Ca(NO_3)_2$. The ionic strength of the anions in this solution is $\frac{1}{2}(5.3 \times 1^2 + 2 \times 5.27 \times 1^2)$ or 7.9. The ionic strength of the cations is $\frac{1}{2}(5.3 \times 1^2 + 5.27 \times 2^2)$ or 13.2; the total ionic strength is $(7.92 + 13.2)$ or 21.1. Ionic strengths at which experimental activity coefficient data are available are 18 for $Ca(NO_3)_2$ where $\Gamma°$ is 0.77, and 6 for $NaNO_3$, where $\Gamma°$ is 0.37. Using Figure 1 to extrapolate to a μ_T of 21.1, $\Gamma°$ is 0.85 for $Ca(NO_3)_2$ and 0.25 for $NaNO_3$. The value of $X_{Ca^{++}}$ in this solution is $(5.27 \times 2^2)/(2 \times 13.2)$ or 0.8. Substituting into Equation (17), Γ and γ for $NaNO_3$ are found to be 0.40.
2. The ionic strength of a pure saturated solution of $NaNO_3$ at 25°C. is 10.8, where $\gamma°$ by Figure 1 for $NaNO_3$ is found to be 0.32. Substituting into Equation (3), γ for $NaNO_3$ in the mixed solution described above is $(0.32 \times 10.8)/[(5.3)(5.3 + 2 \times 5.27)]^{1/2}$ or 0.38. This is within 10% of the value calculated above from Equation (17).

Using the procedure just illustrated, solubility data have been used to test the extent to which the equations proposed here can be used to predict γ values of 1:1 electrolytes in saturated mixed solutions of high as well as lower ionic strength. In most cases, at ionic strengths from perhaps 10 to 30, agreement between predicted values and those based upon solubility product calculations lies within 25%, with an average error of about 15%. Errors are generally smaller at lower total ionic strengths. When the proper solubility data are available, it is suggested calculated values from Equation (17), etc., on a given system be tested by comparing results with those calculated from Equation (3).

ESTIMATING $\Gamma°$ IN PURE SYSTEMS

In the absence of direct measurements, values of $\gamma°$ and $\Gamma°$ for an electrolyte 32 can be estimated by Equations (3) and (17), given suitable solubility data for a 1:1 electrolyte like NaCl or KNO_3 in mixed solution with electrolyte 32. To illustrate, the value of $\Gamma°_{32}$ will be estimated for $Ca(NO_3)_2$ in a solution known to be saturated with $NaNO_3$ (6.1 molal) and 3.40 molal in $Ca(NO_3)_2$. Since in a pure saturated solution, $NaNO_3$ is 10.8 molal, with $\gamma°$ and $\Gamma°$ values of 0.32, then in the mixed solution by Equation (3):

$$\gamma_{NaNO_3} = 10.8 \times 0.32/[(6.1)(6.1 + 2 \times 3.40)]^{1/2} = 0.39$$

The total ionic strength of this mixed solution is 16.3, at which $\Gamma°_{12}$ for $NaNO_3$ is 0.29 while X for Ca^{++} is 0.69. Substituting these values into Equation (17), $\Gamma°$ for electrolyte 32 is found to be about 0.69, versus an experimental value (3) of 0.735.

FOUR ION SYSTEMS

Two types of four-ion systems exist: those containing two cations and two anions, and those containing three cations and one anion, or one cation and three anions.

Two cations and two anions. These solutions are made by dissolving electrolytes 12 and 34 in water after which 32 or 34 may or may not be added. In all cases, four different ion pairs are identifiable, namely 12, 32, 34, and 14, respectively involving Equations (6), (11), (12), and (13). Remembering that both $(X_1 + X_3)$ and $(Y_2 + Y_4)$ equal unity, then by combining Equations (4), (5), and

Table 1. Experimental Versus Predicted Values of γ^{tr}

Cl^- as Common Anion

12	32	μ_T	$\gamma_{12}°$	$\gamma_{32}°$	γ_{12}^{tr} exptl.*	γ_{12}^{tr} calc.**	γ_{32}^{tr} exptl.*	γ_{32}^{tr} calc.**
HCl	LiCl	2	1.009	0.921	0.986	0.96	—	0.96
HCl	NaCl	2	1.009	0.668	0.878	0.82	—	0.82
HCl	KCl	2	1.009	0.573	0.781	0.76	—	0.76
HCl	CsCl	2	1.009	0.496	0.641	0.71	—	0.71
HCl	$CaCl_2$	0.3	0.588	0.326	0.578	0.58	0.334	0.34
NaCl	$MgCl_2$	3	0.714	0.569	0.77	0.73	0.636	0.54
NaCl	$CaCl_2$	6	0.965	0.79	0.935	0.93	—	0.86
NaCl	$SrCl_2$	3	0.714	0.465	0.705	0.70	0.536	0.49
HCl	$AlCl_3$	3	1.318	0.33	0.85	0.95	0.45	0.87
HCl	$AlCl_3$	12	7.25	3.37	3.96	3.30	—	—
HCl	$LaCl_3$	1	0.809	0.282	0.655	0.73	0.256	0.38
HCl	$ThCl_4$	3	1.318	0.14	0.895	0.90	—	0.65

Na^+ as Common Cation

12	14	μ_T	$\gamma_{12}°$	$\gamma_{14}°$	γ_{12}^{tr} exptl.*	γ_{12}^{tr} calc.**	γ_{14}^{tr} exptl.*	γ_{14}^{tr} calc.**
NaCl	Na_2SO_4	6	0.985	0.154	0.62	0.62	—	0.39
NaCl	Na_2SO_4	1	0.655	0.31	0.60	0.60	—	0.36
NaCl	NaAcetate	3	0.714	0.99	0.833	0.84	—	0.84
NaCl	$NaNO_3$	6	0.985	0.37	0.61	0.60	—	0.60
NaCl	$NaClO_3$	6	0.985	0.675	0.815	0.82	—	0.82

* *Primarily from (3) and (6).*
** *Calculated from Equations (19) and (20).*

(6) and rearranging

$$\log\Gamma_{12} = \log\Gamma^\circ_{12} + \tfrac{1}{2} X_3(\log\Gamma^\circ_{32} - \log\Gamma^\circ_{12}) + \tfrac{1}{2} Y_4(\log\Gamma^\circ_{14} - \log\Gamma^\circ_{12}) \quad (22)$$

As an illustration, consider the solution containing the ions Na^+, Cl^-, NH_4^+, and $SO_4^=$, respectively designated as 1, 2, 3, and 4, with molalities of 5.04, 7.76, 5.18, and 1.23. Under these conditions, the solution is known to be saturated with NaCl, NH_4Cl and $Na_2SO_4\cdot 10\ H_2O$. As discussed earlier, Equation (3) may be applied without modification to NaCl and NH_4Cl but not to $Na_2SO_4\cdot 10\ H_2O$. A pure saturated solution of NaCl is 6.14 molar, with values for γ° and Γ° of unity, consequently in the mixed solution by Equation (3):

$$\gamma_{NaCl} = 6.14 \times 1/(5.04 \times 7.76)^{1/2} = 0.98$$

Alternatively, γ_{NaCl} may be calculated from Equation (22). At the total ionic strength of this solution of 11.5, Γ° values are found to be 1.75 for NaCl, by extrapolation using Figure 1, 0.56 for NH_4Cl, and 0.36 for Na_2SO_4. By Equation (22), Γ and γ for NaCl in this mixture are 0.97, which is in good agreement with the results of Equation (3).

Since this solution is also saturated with NH_4Cl, calculations similar to those just presented for the activity coefficient of NaCl can be repeated for NH_4Cl. The values of γ for NH_4Cl are found to be 0.67 by Equation (3) and 0.64 by Equation (22), which again represents fair agreement.

Three cations and one anion. Such a solution is prepared by adding electrolytes 12, 32 and 52 such as KCl, $CaCl_2$ and $MgCl_2$ to water. Values of Γ for these ion pairs can be calculated from Equations (6), (11) and (14). For electrolyte 12, by combining Equations (4), (5), and (6)

$$\log\Gamma_{12} = \tfrac{1}{2}(X_1 \log\Gamma^\circ_{12} + X_3 \log\Gamma^\circ_{32} + X_5 \log\Gamma^\circ_{52} + Y_2 \log\Gamma^\circ_{12}) \quad (23)$$

where Y_2 is, of course, unity. Analogous equations for Γ can of course be written for electrolytes 32 and 52. An example here is a solution containing $CaCl_2$, which is in equilibrium with both solid KCl and solid Carnallite, namely $KMgCl_3\cdot 6\ H_2O$. This solution is 0.67 molal in KCl, 2.54 molal in $CaCl_2$ and 1.97 molal in $MgCl_2$ corresponding to a total ionic strength of 14.2. A pure saturated solution of KCl is 4.9 molal, where Γ° is 0.59, consequently by Equation (3):

$$\gamma_{KCl} = 0.59 \times 4.9/[0.67(0.67 + 2 + 1.97 + 2 \times 2.54)]^{1/2} = 1.13$$

Alternatively, at this total ionic strength, Γ° for KCl (by extrapolation using Figure 1) is 0.65, for $CaCl_2$ is 1.9 and for $MgCl_2$ is 3.3. Similarly, X values for K^+, Ca^{++}, and Mg^{++} are respectively 0.036, 0.544 and 0.42, while Y for Cl^- is unity. Substituting into Equation (23), γ for KCl is found to be 1.22, which again compares reasonably with the value found by Equation (3).

FIVE ION SYSTEMS

Only limited solubility data are available on solutions containing five or more ions. The following relation, developed by combining Equations (4), (5), and (6) applies to a five-ion system involving the cations 1 and 3, and the anions 2, 4, and 6:

$$\log\Gamma_{12} = \tfrac{1}{2}(X_1 \log\Gamma^\circ_{12} + X_3 \log\Gamma^\circ_{32} + Y_2 \log\Gamma^\circ_{12} + Y_4 \log\Gamma^\circ_{14} + Y_6 \log\Gamma^\circ_{16}) \quad (24)$$

An example here is a solution which is 5.4 molal in NaCl, 0.22 molal in $KClO_4$ and 2.4 molal in $NaNO_3$ (these salts being respectively designated as 12, 34, and 16). This solution is saturated with both NaCl and $KClO_4$. At this solution's total ionic strength of 8.0, Γ° values are as follows: 1.20 for salt 12, 0.63 for salt 32, 0.34 for salt 16 and 0.74 for salt 14. Substituting into Equation (24) and using the appropriate X and Y values the activity coefficient γ_{12} is found to be 0.96, which compares with 0.95 found by solubility product calculations based on Equation (3).

PRECISION

The errors to be expected in predicting γ values by the equations proposed here become larger at higher values of μ_T. Further errors are introduced when Γ° values are predicted as discussed earlier and when extrapolating Γ° over large ranges of μ_T by use of Figure 1. The relations proposed here for estimating activity coefficients for strong electrolytes should therefore not be used when direct experimental data are available.

NOTATION

F = interaction term in Equations (4), (5), (7), etc.
m = molality, g.-moles/1,000 g. water
X_1 = for cation 1, $X_1 = m_1 z_1^2/\mu_c$
Y_2 = for anion 2, $Y_2 = m_2 z_2^2/\mu_a$
z = ion charge; 1 for Na^+, 2 for SO_4^{--}, 3 for Al^{+++}, etc.
α = constant, Equations (1) and (2)
γ = mean activity coefficient of an electrolyte in a multicomponent solution
γ° = mean activity coefficient of an electrolyte in a pure solution
γ^{tr} = activity coefficient of an electrolyte present in trace communications in a multicomponent solution
Γ = $\gamma^{1/z_1 z_2}$
Γ° = $(\gamma^\circ)^{1/z_1 z_2}$
μ_a = ionic strength of anions, namely $\tfrac{1}{2}(m_2 z_2^2 + m_4 z_4^2 + \ldots)$
μ_c = ionic strength of cations, namely $\tfrac{1}{2}(m_1 z_1^2 + m_3 z_3^2 + m_5 z_5^2 + \ldots)$
μ_T = total ionic strength, namely $(\mu_a + \mu_c)$

Subscripts

Cations are indicated by 1, 3, 5, etc., anions are indicated by 2, 4, 6, etc. Electrolytes are identified by subscripts such as 34, indicating cation 3 and anion 4.

LITERATURE CITED

1. Brønsted, J. N., *J. Am. Chem. Soc.*, **42**, 761, (1920); **45**, 2898 (1923).
2. Hala, E., J. Pick, V. Fried, O. Vicini, "Vapor Liquid Equilibrium," 2nd ed., Pergamon Press, New York (1968).
3. Harned, H. S., and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd ed., Appendix A, Rheinhold, New York (1958).
4. Harned, H. S., and R. A. Robinson, "Multicomponent Electrolyte Solutions," p. 17, Pergamon Press, New York (1968).
5. Meissner, H. P., and J. W. Tester, "Activity Coefficients of Strong Electrolytes in Aqueous Solution," *Ind. Eng. Chem. Process Design Develop.*, **11**, 128 (1972).
6. Robinson, R. A., and R. H. Stokes, "Electrolyte Solutions," Appendix 8.1, Butterworth's, London (1955).
7. Seidell, A., and W. F. Linke, "Solubilities, Inorganic and Metal-Organic Compounds," 4th ed., Vol. I & II, Am. Chem. Soc., Washington, D.C. (1965).

Manuscript received June 10, 1971; revision received August 27, 1971; paper accepted September 10, 1971.