Self-Consistent Local Composition Model of Electrolyte Solutions

A self-consistent local composition theory for the excess Gibbs free energy of a multicomponent electrolyte solution is developed. The theory incorporates correct pair counting, assumes that like-charged ions cannot be nearest neighbors of each other, and accounts for the effect of second nearest neighbor interactions.

A perturbation analysis of the model, linear in the interaction parameters, is also carried out. For a given solvent and a given class of electrolyte the perturbed theory yields universal functions of molality, which can be weighted by suitable parameter values and added to give the desired property. The parameters can be expressed in a temperature-independent form. This theory correlates very well the data on osmotic and activity coefficients in single-solute aqueous solutions up to very high concentrations (up to 20 M) as well as over a range of temperatures.

M.S. Ananth
Sunder Ramachandran
Department of Chemical Engineering
Indian Institute of Technology
Madras 600 036, India

General Theory

Introduction

The modeling of the excess Gibbs energy of electrolyte solutions has been an important area in the field of chemical engineering thermodynamics. In the period since the Debye-Huckel theory was established as an exact theory for dilute solutions, significant advances in the theory have been made. The excess Gibbs energy is assumed to be the sum of two parts: a long-range electrostatic part and a short-range interaction part. Among the more successful theories of this kind are those of Pitzer (1973) and Chen et al. (1982). The Debye-Huckel theory is used to describe the electrostatic contribution to the excess Gibbs energy. The theory of Chen et al. reduces to the NRTL theory (Renon and Prausnitz, 1968) to describe the contribution of the short-range forces. This work uses a modified version of the UNIQUAC theory (Abrams and Prausnitz, 1975). Flemr (1976), McDermott and Ashton (1977), and Panayitou and Vera (1980) have pointed out that the UNIQUAC theory with constant coordination number leads to incorrect pair counting. Iwai and Arai (1982) incorporated correct pair counting into the UNIQUAC theory for binary mixtures. Govindan (1984) extended this result to multicomponent nonelectrolyte systems and called the model the self-consistent local composition (SCLC) model. T.P. Ramachandran (1988) extended the SCLC model to include the effect of second nearest neighbor interactions. It is this latter version of the SCLC model that is considered here.

Development of Theory

The Helmoltz free energy A can be written as a sum of two parts $A^{el} + A^{sr}$ where A^{el} is the Helmoltz free energy corresponding to the "primitive" model and A^{sr} is the Helmoltz free energy of the other short-range interactions (Munster, 1974). It is assumed that pressure effects are negligible and therefore A^E and G^E are equal. The excess Gibbs energy is accordingly written as:

$$G^E = G^{Eel} + G^{Esr} \tag{1}$$

and

$$\ln \Gamma_i = \ln \Gamma_i^{el} + \Gamma_i^{sr} \tag{2}$$

Following Chen et al. (1982) it is assumed that G^{Eel} is modeled by the expression of Pitzer (1980) and that G^{Esr} is modeled by a local composition lattice theory. Clearly in $\Gamma_i^{el} = \ln \Gamma_i^{pdh}$ (Chen et al.),

$$\ln \Gamma_i^{pdh} = -\sqrt{(1{,}000/W_s)}\, A_\phi[(2/\rho)(Z_i^2) \ln (1 + \rho\sqrt{I_x}) + \sqrt{I_x}\,(aZ_i^2/b - 2I_x)/(1 + \rho\sqrt{I_x})] \tag{3}$$

Correspondence concerning this paper should be addressed to M.S. Ananth.
The present address of S. Ramachandran is: Department of Chemical Engineering, Colorado State University, Fort Collins, CO, 80521.

The SCLC theory (T.P. Ramachandran, 1988) is used to model A^{sr}:

$$A^{sr} = A^{SCLC} = kT \ln Q_{\text{lattice}} \tag{4}$$

The theory ignores size and shape factors so that the description is made in terms of local composition variables x_{ij}, where x_{ij} denotes the mole fraction of species i in the immediate neighborhood of species j. The assumption of Chen et al. that like ions cannot be nearest neightbors is also adopted:

$$x_{i+j+} = x_{i-j-} = 0 \tag{5}$$

The self-consistent assumption of correct pair counting (Flemr, 1976; McDermott and Ashton, 1977; Panayitou and Vera, 1980) is introduced into the UNIQUAC framework. Correct pair counting requires that:

$$x_{ji}\, x_i = x_{ij}\, x_j \tag{6}$$

Local electroneutrality automatically follows from global electroneutrality and correct pair counting. Normalization results in Eq. 7 below, where the arbitrary paired subscripts i and j are implicitly constrained by Eq. 5:

$$\sum_i x_{ij} = 1 \tag{7}$$

Following Abrams and Prausnitz (1975) the configurational intergral is given by:

$$Q_{\text{lattice}} = \sum_{ij} w(x_{ij}) \exp\left[-U(x_{ij})/kT\right] \tag{8}$$

The combinatorial factor $w(x_{ij})$ is assumed to be the same function of local composition variables as in the quasichemical expression of Abrams and Prausnitz (1975).

$$w = h \prod_i w_i \tag{9}$$

where h is the normalization constant and

$$w_i = \left(\sum_j N_j x_{ij}\right)! \Big/ \prod_j (N_j x_{ij})! \tag{10}$$

The potential energy $U(x_{ij})$ is expressed as a sum of terms representing nearest neighbor pair interactions $U^1(x_{ij})$ as well as next nearest neighbor pair interactions $U^2(x_{ij})$

$$U(x_{ij}) = U^1(x_{ij}) + U^2(x_{ij}) \tag{11}$$

where

$$-U^1(x_{ij}) = (z/2) \sum_i \sum_j N_j x_{ij} u_{ij} \tag{12}$$

$$-U^2(x_{ij}) = [z(z-1)/8] \sum_i \sum_j \sum_k N_j x_{ij} x_{ki} u'_{kj} \tag{13}$$

Equations 9 to 13 are substituted into Eq. 8. The configurational integral is then approximated by substituting the maximum term for the sum. The maximum term is determined by differentiating the typical term $w(x_{ij}) \exp(-U/kT)$ in the sum with respect to the independent sets of local composition mole fractions. This procedure leads to a set of equations for the most probable local composition mole fraction. These are given in Appendix A. $\ln Q_{\text{lattice}}$ can now be calculated and the chemical potential of an arbitrary species can be found by differentiating $\ln Q_{\text{lattice}}$ with respect to N_i (Panayitou and Vera, 1980).

$$\mu_i = -kT \frac{\delta \ln Q_{\text{lattice}}}{\delta N_i}\Bigg|_{T,\, V,\, N_{j\neq i}\, \{x_{m^0n^0}\},\, \{x_{m^+n^0}\},\, \{x_{m^-n^0}\},\, \{x_{m^+n^-}\}} \tag{14}$$

The algebra is tedious and lengthy but fairly straightforward (S. Ramachandran, 1988). The results for the activity coefficients are:

$$\ln \Gamma_{m^0} = \ln\left(x_{m^0m^0}/x_{m^0}\right) + (1/2) \sum_i \sum_k x_{im^0} x_{k^0} (v'_{ki^0} - v'_{m^0i} - v'_{km^0}) \tag{15}$$

$$\begin{aligned}
\ln \Gamma^{sr}_{\pm} = {} & \frac{a}{a+b} \ln\left(\frac{1{,}000\, x_{m^+}}{W_s a m_{M_aN_b}}\right) \\
& + \frac{b}{a+b} \ln\left(\frac{1{,}000\, x_{n^-}}{W_s b m_{M_aN_b}}\right) \\
& + \frac{a}{a+b} \ln\left(\frac{x_{m^+n^-} x_{n^-m^+}}{x_{m^+} x_{n^-}}\right) - \frac{2a}{a+b} v_{m^+n^-} \\
& + \frac{b-a}{b+a} \ln\left(\frac{x_{s^0n^-} x_{n^-s^0}}{x_{s^0s^0} x_{n^-}}\right) + [a/(a+b)] \\
& \cdot \Bigg[\sum_j \sum_k x_{jn^-} x_{kn^-} (v'_{kj} - v'_{s^0j} - v'_{s^0k})/2 \\
& + \sum_j \sum_k x_{jm^+} x_{km^+} (v'_{kj} - v'_{s^0k} - v'_{s^0j})/2 \\
& + \sum_j x_{jn^-} (v'_{s^0j} - v'_{s^0m^+} - v'_{jm^+}) \\
& + \sum_k x_{km^+} (v'_{s^0k} - v'_{s^0n^-} - v'_{kn^-})\Bigg] \\
& + [(b-a)/(b+a)]\Bigg[\sum_j \sum_k x_{j^0n^-} x_{kn^-} \\
& \cdot (v'_{kj} - v'_{ks^0} v'_{s^0j})/2 \\
& + \sum_k x_{ks^0} (v'_{ks^0} - v'_{s^0n^-} - v'_{kn^-})\Bigg]
\end{aligned} \tag{16}$$

Single-solvent single-solute systems

The following equations express the composition dependence of $x_{n^-m^+}$ and the activity coefficients in single-solute single-solvent systems. $x_{n^-m^+}$ is denoted here by just x and $(W_s\, m/1{,}000)$ by just y for the sake of brevity.

$$\begin{aligned}
\frac{x[1-(a+b)y + 2axy]}{(1-x)(b-ax)y} = \exp\{ & v_{m^+n^-} + v'_{m^+s^0} \\
& \cdot [y(3a+b)/2 - 2axy - ax/b] \\
& + v'_{n^-s^0}[y(a+3b)/2 - 2axy - x] \\
& + v'_{m^+n^-}[axy - (a+b)y/2]\}
\end{aligned} \tag{17}$$

$$\ln \Gamma_{s^o} = \sqrt{(1000/W_s)}\, A_\phi (2I_x^{1.5}/(1 + \rho\sqrt{I_x}) + \ln (x_{s^o s^o}/x_{s^o}) - y^2 \{v'_{m^+ s^o}[2a^2x^2 - (3a + b)ax + a(a + b)] + v'_{n^- s^o}[2a^2x^2 - (a + 3b)ax + b(a + b)] + v'_{m^+ n^-}[a^2x^2 - a(a + b)x + ab]\} \quad (18)$$

$$\ln \Gamma_\pm = -\sqrt{(1000/W_s)} A_\phi [(2_a/\rho b)(Z_i^2) \ln (1 + \rho\sqrt{I_x}) + \sqrt{I_x}(aZ_i^2/b - 2I_x)/(1 + \rho\sqrt{I_x})] + \frac{a}{a+b} \ln \left(\frac{ax^2}{bx_{n^-} x_{m^+}} \right) - \frac{2a}{(a+b)} v_{m^+ n^-} + \frac{b-a}{b+a} \ln \left\{ \frac{(1 - ax/b)^2 by}{[1 - (a+b)y + 2ayx]x} \right\} + \frac{a}{a+b} [v'_{n^- s^o}(2x - x^2) + v'_{m^+ s^o}(2ax/b - x^2)] + \frac{b-a}{b+a} \{v'_{m^+ s^o}[ay(1 - x) - a^2x^2/b^2] - v'_{m^+ n^-} ay(1 - x) - v'_{n^- s^o} y\{a(1 - x) + 2(b - ax)]\} \quad (19)$$

There are four distinct parameters in the general case: $v_{m^+ n^-}$, $v'_{m^+ s^o}$, $v'_{n^- s^o}$, and $v'_{m^+ n^-}$. If $a = b$, then the coefficients of the parameters $v'_{m^+ s^o}$ and $v'_{n^- s^o}$ are the same and the system has only three distinct parameters: $v_{m^+ n^-}$, $(v'_{m^+ s^o} + v'_{n^- s^o})$, and $v'_{m^+ n^-}$. It should be noted that for each composition the nonlinear Eq. 17 should be solved. Hence the fitting of the parameters requires a nonlinear minimization algorithm (private communication, A. W. Westerberg, 1969). It is therefore important to minimize the number of parameters required to fit the data. Since the nearest neighbor interactions, characterized by $v_{m^+ n^-}$, are most likely to be dominated by the hard-sphere repulsion energies included in the Pitzer-Debye-Huckel theory, it appears reasonable to set this parameter to zero. This is an arbitrary choice of convenience and it is shown later that the theory still has enough flexibility to fit the data very well.

Results of SCLC theory on 1-1 electrolyte systems

Customarily, different theories have been evaluated for their ability to correlate thermodynamic data of one type alone. In other words, theories of electrolytes in water are evaluated for their correlative rather than predictive ability. In general the "best" parameters determined by fitting the osmotic coefficient differ from those determined by fitting the mean ionic activity coefficient. This is a limitation common to all the theories, including the present one.

In this work the best parameters are determined using one or the other property. Yet the deviations of the calculated values of both properties from experimental data are reported. For the fitted property the standard deviation is an indication of the correlative ability of the theory, while for the other property it is an indication of the predictive ability of the theory. In the literature on other theories this is not done. Hence comparison between theories is restricted to a comparison of their correlative abilities alone.

Computations have been carried out on 27 systems of 1-1 electrolytes in water and the best parameters have been determined for these systems for the purpose of fitting the theory to experimental values of either the mean ionic activity coefficient of the salt or the osmotic coefficient of the solvent. In Table 1 the parameters $(v'_{m^+ s^o} + v'_{n^- s^o})$ and $v'_{m^+ n^-}$ are given for the best fits of ϕ and $\ln \Gamma_\pm$ data, respectively. Figures 1 and 2 compare the theory with experimental data for KCl. The standard deviations σ reported in Table 1 in respect of the osmotic coefficient ϕ are by and large below 2%. All halides are particularly well correlated by the theory (min $\sigma = 0.017$ for NaF, max $\sigma = 1.754$ for CsCl). All nitrates are also well described by the theory with the exception of $AgNO_3$ ($\sigma = 5.163$) and to a lesser extent KNO_3 ($\sigma = 2.306$). The fit of $\ln \Gamma_\pm$ is uniformly good while the RMS deviation for the predicted ϕ is less than would be expected on the basis of the results. Ln $\Gamma_\pm$ varies more strongly with molality than the osmotic coefficient and hence the difference between the two. When the data on $\ln \Gamma_\pm$ and ϕ are simultaneously fitted the results are very similar to those obtained by fitting the data on $\ln \Gamma_\pm$ alone (S. Ramachandran, 1988). The comparison with experiment presented here is limited to a few systems because the perturbation analysis of the SCLC theory developed in the following section yields simpler and better results.

Comparison of SCLC theory with other theories

Table 2 compares the results of the theory with those of other theories. The σ ϕ values for the other theories are those reported by Ball et al. (1985) while for $\ln \Gamma_\pm$ the comparison is made with the values reported by Chen (1982, 1986). It can be seen from the table that the theory compares favorably with the theory of Chen et al., which is the only other theory of comparable statistical mechanical rigor. It should be emphasized that in all the theories mentioned above the parameters that best correlate the data must be found using a nonlinear least-squares algorithm. Fitting experimental data requires good a priori guess values for the parameters and there is no guarantee of uniqueness of the parameters. In the following, the SCLC theory is analyzed using a perturbation technique to yield an elegant first-order theory that eliminates this difficulty and correlates data better than the original theory.

Universal Correlations

All the existing models of electrolyte solutions are nonlinear with respect to their parameters. A perturbation analysis of the SCLC theory to first order in the interaction parameters leads to a linear theory. Such a theory has many engineering advantages. It is simpler to use as a correlative theory. Parameter determination requires no guess values and the set of best parameters is unique. The theory lends itself to a more concise representation of data. For a given solvent and a given class of electrolyte the theory presents universal functions of molality. When weighted suitably by parameter values these functions can simply be added to give the logarithm of the mean ionic activity coefficient or the osmotic coefficient. This linear theory is validated by extensive comparison with experimental data for single-solute single-solvent systems.

General perturbation analysis of SCLC Equations

Each local composition mole fraction x_{ij} can be expressed in terms of perturbation functions x_{ij}^o, x_{ij}^{kl}, and $x_{ij}^{'kl}$ of zero and first

Table 1. SCLC Parameters for 1-1 Electrolyte Systems

		Fit of ϕ Data				Fit of ln $\Gamma_\pm$ Data			
Salt	Max. m	$v'_{m+s^\circ} + v'_{n-s^\circ}$	v'_{m+n^-}	σ % ϕ	σ % ln $\Gamma\pm$	$v'_{m+s^\circ} + v'_{n-s^\circ}$	v'_{m+n^-}	σ % ϕ	σ % ln $\Gamma\pm$
NaCl	6.0	36.1	65.7	0.62	0.877	36.1	65.7	0.64	0.81
NaBr	4.0	18.6	27.9	0.38	0.773	15.5	21.2	0.47	0.54
NaI	3.5	16.6	20.6	0.51	1.220	10.4	6.9	0.60	1.76
NaF	1.0	5.6	11.5	0.02	0.034	9.9	20.3	0.02	0.03
$NaNO_3$	6.0	30.7	6.1	0.17	0.165	3.1	64.7	0.16	0.13
NaOH	6.0	81.8	155.1	1.44	2.195	79.5	150.7	1.49	2.99
LiCl	6.0	163.5	311.7	0.96	1.437	138.8	262.2	0.98	1.47
LiBr	6.0	151.7	284.7	1.65	2.811	197.8	377.1	1.61	2.67
LiI	3.0	23.2	22.7	1.16	3.955	10.7	−4.9	1.63	2.20
$LiNO_3$	6.0	9.3	4.6	0.31	0.894	8.4	2.4	0.38	0.63
HCl	6.0	96.4	175.3	0.36	1.264	69.9	121.7	0.47	1.80
HBr	3.0	66.6	111.1	0.45	1.319	43.8	64.4	0.58	0.90
HI	3.0	20.5	13.1	0.68	2.766	13.8	−2.0	1.04	1.50
HNO_3	3.0	9.7	7.4	0.37	1.717	3.9	−5.4	0.70	0.80
$HClO_4$	6.0	211.1	402.5	2.14	3.609	193.2	366.4	2.15	3.64
KCl	4.5	13.5	24.8	0.09	0.179	8.8	15.0	0.18	0.16
KBr	5.5	6.7	9.8	0.10	0.332	5.4	7.1	0.15	0.19
KI	4.5	1.4	3.2	0.23	0.801	34.5	−5.7	0.38	0.53
KNO_3	3.5	−3.8	4.0	2.31	5.229	−10.6	10.9	3.91	3.28
KOH	6.0	91.9	170.0	0.36	1.465	85.3	157.0	0.55	1.09
$AgNO_3$	6.0	−6.8	−2.9	5.16	10.907	−10.7	−8.7	9.80	6.45
NH_4Cl	6.0	2.0	1.4	0.15	0.190	2.2	1.8	0.16	0.15
NH_4NO_3	6.0	14.3	34.3	0.81	3.962	14.3	35.0	2.28	2.53
RbCl	5.0	68.8	137.1	0.29	0.997	66.5	132.6	0.48	0.69
RbBr	5.0	68.0	136.1	0.18	0.735	65.7	131.6	0.34	0.51
RbI	5.0	53.1	10.6	0.41	1.345	50.8	110.4	0.66	1.95
CsCl	6.0	50.8	102.2	1.75	5.097	50.8	102.9	1.52	3.53

order in the energy parameters v_{kl} and v'_{kl}:

$$x_{ij} = x^\circ_{ij} + \Sigma\ v_{kl}x^{kl}_{ij} + \Sigma\ v'_{kl}x'^{kl}_{ij} \tag{20}$$

where Σ is over distinct admissible pairs kl.

The correct pair counting and normalization requirements for the perturbation functions of arbitrary order follow from Eqs. 20, 6, and 7, respectively:

For all orders

$$x^n_{ij}x_j = x_i x^n_{ji} \tag{21}$$

Zero order

$$\sum_i x^\circ_{ij} = 1 \tag{22}$$

Nonzero order

$$\sum_i x^n_{ij} = 0 \tag{23}$$

The local compositions at each order can be obtained from Eq. 20 and Eqs. A1 to A4 of Appendix A. The equations are obtained by grouping together terms of like order in the energy difference parameters and setting the coefficients of each to zero. This procedure leads to the appropriate equations for the perturbation functions of the zero and first orders (Ramachandran, 1988). For the sake of continuity these equations are presented in Appendix B. The zero-order equations there (Eqs.

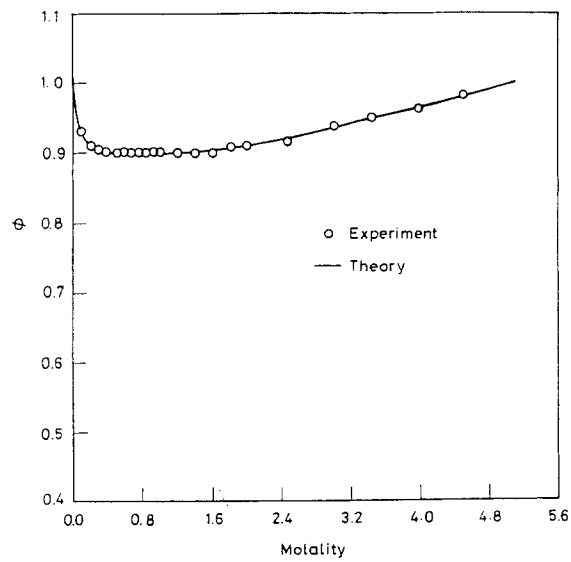

Figure 1. Comparison of two-parameter SCLC model with osmotic coefficient data for KCl-H_2O system at 25°C.

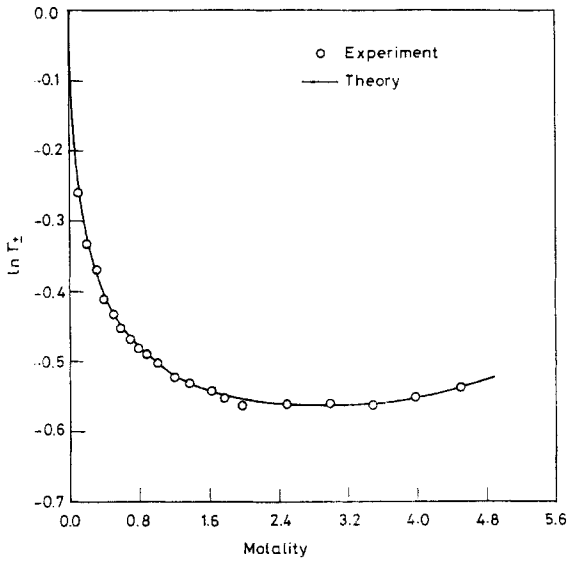

Figure 2. Comparison of two-parameter SCLC model with mean ionic activity coefficient data for KCl-H_2O system at 25°C.

B1–B6) correspond to the equations for the local composition variables in a lattice in the absence of intermolecular interactions but subject to the like-ion repulsion constraint. In the absence of this constraint, as for example in the case of nonelectrolytes, the solutions will simply be those for a random mixture.

Table 2. RMS Deviation for Various Theories of Electrolytes

Salt	Max. m	σ % ϕ SCLC	Chen	Pitzer	Cruz	σ % $\ln\Gamma_\pm$ SCLC	Chen
NaCl	6.0	0.62	1.20	0.30	1.30	0.81	1.80
NaBr	4.0	0.38	0.60	0.10	0.70	0.54	0.90
NaI	3.5	0.51	0.70	0.20	0.60	0.76	1.00
NaF	1.0	0.02	0.02	0.03	0.02	0.02	0.00
$NaNO_3$	6.0	0.17	0.20	0.15	0.70	0.13	0.20
NaOH	6.0	1.44	2.30	1.30	0.90	1.99	2.90
LiCl	6.0	0.96	2.40	0.80	1.20	1.47	4.00
LiBr	6.0	1.65	2.80	1.20	0.60	2.67	5.00
LiI	3.0	1.16	1.50	0.90	1.20	2.20	2.40
$LiNO_3$	6.0	0.31	0.40	0.20	0.20	0.63	1.30
HCl	6.0	0.36	1.90	0.20	0.80	0.80	3.50
HBr	3.0	0.45	0.80	0.40	0.40	0.90	1.50
HI	3.0	0.68	1.00	0.20	0.70	1.50	1.80
HNO_3	3.0	0.37	0.50	0.10	0.30	0.80	0.80
$HClO_4$	6.0	2.14	3.30	1.90	0.80	3.64	6.30
KCl	4.5	0.09	0.20	0.10	0.10	0.16	0.30
KBr	5.5	0.10	0.30	0.30	0.10	0.19	0.40
KI	4.5	0.23	0.20	0.50	0.10	0.53	0.50
KNO_3	3.5	2.31	0.60	0.40	0.60	3.28	0.80
KOH	6.0	0.36	1.50	0.30	0.90	1.10	2.30
$AgNO_3$	6.0	5.16	0.70	1.30	0.90	1.10	1.00
NH_4Cl	6.0	0.15	0.07	0.70	0.30	0.23	0.10
NH_4NO_3	6.0	0.81	0.50	0.10	0.60	1.56	1.20
RbCl	5.0	0.29	0.20	0.20	0.30	0.53	0.30
RbBr	5.0	0.18	0.20	0.20	0.30	0.52	0.20
RbI	5.0	0.41	0.10	0.20	0.40	0.66	0.40
CsCl	3.5	1.75	0.40	0.20	0.80	3.53	0.60

The equations for the activity coefficients Γ_{m° and $\ln\Gamma_\pm$ are given below.

$$\ln\Gamma_{m^\circ} = \ln\left(x^\circ_{m^\circ m^\circ}/x_{m^\circ}\right) + \sum_{kl}\left(x^{kl}_{m^\circ m^\circ}/x_{m^\circ m^\circ}\right)v_{kl} + \sum_{kl}\left(x'^{kl}_{m^\circ m^\circ}/x_{m^\circ m^\circ}\right)v'_{kl} + \frac{1}{2}\sum_i\sum_k x^\circ_{im^\circ}x^\circ_{km^\circ}\left(v'_{ki} - v'_{m^\circ i} - v'_{km^\circ}\right) \quad (24)$$

$$\begin{aligned}\ln\Gamma^{sr}_\pm = {} & \frac{a}{a+b}\ln\left(\frac{1{,}000\,x_{m^+}}{W_s a m_{MaNb}}\right) + \frac{b}{a+b}\ln\frac{1{,}000\,x_{n^-}}{W_s b m_{MaNb}} \\ & + \frac{a}{a+b}\ln\frac{x^\circ_{m^+n^-}x^\circ_{n^-m^+}}{x_{m^+}x_{n^-}} + \frac{b-a}{b+a}\ln\frac{x^\circ_{s^\circ n^-}x^\circ_{n^-s^\circ}}{x_{s^\circ s^\circ}x^\circ_{n^-}} \\ & + \frac{a}{a+b}\left[\sum_{kl}\left(\frac{x^{kl}_{m^+n^-}}{x^\circ_{m^+n^-}} + \frac{x^{kl}_{n^-m^+}}{x^\circ_{n^-m^+}}\right)v_{kl} - 2v_{m^+n^-}\right. \\ & \left. + \sum_{kl}\left(\frac{x'^{kl}_{m^+n^-}}{x^\circ_{m^+n^-}} + \frac{x'^{kl}_{n^-m^+}}{x^\circ_{n^-m^+}}\right)v'_{kl}\right] \\ & + \frac{b-a}{a+b}\left[\sum_{kl}\left(\frac{x^{kl}_{s^\circ n^-}}{x^\circ_{sn^-}} + \frac{x^{kl}_{n^-s^\circ}}{x^\circ_{n^-s^\circ}} - \frac{x^{kl}_{s^\circ s^\circ}}{x_{s^\circ s^\circ}}\right)v_{kl}\right. \\ & \left. + \sum_{kl}\left(\frac{x'^{kl}_{s^\circ n^-}}{x^\circ_{sn^-}} + \frac{x'^{kl}_{n^-s^\circ}}{x^\circ_{n^-s^\circ}} - \frac{x'^{kl}_{s^\circ s^\circ}}{x_{s^\circ s^\circ}}\right)v_{kl}\right] \\ & + \frac{a}{2(a+b)}\left[\sum_j\sum_k x^\circ_{jn^-}x^\circ_{kn^-}\left(v'_{kj} - v'_{s^\circ j} - v'_{s^\circ k}\right)\right. \\ & + \frac{1}{2}\sum_j\sum_k x^\circ_{jm^+}x^\circ_{km^+}\left(v'_{kj} - v'_{s^\circ k} - v'_{s^\circ j}\right) \\ & + \sum_j x^\circ_{jn^-}\left(v'_{s^\circ j} + v'_{s^\circ m^+} - v'_{jm^+}\right) \\ & \left. + \sum_k x^\circ_{km^+}\left(v'_{s^\circ k} + v'_{s^\circ n^-} - v'_{kn^-}\right)\right] \\ & + \frac{(b-a)}{1(b+a)}\left[\sum_j\sum_k x^\circ_{jn^-}x^\circ_{kn^-}\left(v'_{kj} - v'_{ks^\circ} - v'_{s^\circ j}\right)\right. \\ & \left. + \sum_k x^\circ_{ks^\circ}\left(v'_{ks^\circ} + v'_{s^\circ n^-} - v'_{kn^-}\right)\right] \end{aligned} \quad (25)$$

The sum Σ_{kl} in these equations is over all distinct pairs kl.

Single-electrolyte single-solvent systems

The general perturbation equations can be solved easily for the specific case of a single salt *MaNb* dissolved in a solvent. Such a system is characterized by four parameters: $v_{m^+n^-}$, $v'_{m^+s^\circ}$, $v'_{n^-s^\circ}$, and $v'_{m^+n^-}$. The local compositions are:

Zero order

$$x^\circ = \frac{-1 + \sqrt{(1 + 4aby^2)}}{2ay} \quad (26)$$

First order

$$x^{m^+n^-} = \left[\frac{1}{x^\circ} + \frac{2ay}{1 - (a+b)y + 2ax^\circ y} + \frac{1}{1 - x^\circ} + \frac{a}{(b - ax^\circ)}\right]^{-1} \quad (27)$$

$$x'^{m^+s^o} = [(1.5a + 0.5b)y - ax^o(1/b + 2y)]x^{m^+n^-} \quad (28)$$

$$x'^{n^-s^o} = [(0.5a + 1.5b)y - x^o - 2ayx^o]x^{m^+n^-} \quad (29)$$

$$x'^{m^+n^-} = [ayx^o - (a + b)y/2]x^{m^+n^-} \quad (30)$$

where $x^n = x^n_{n^-m^+}$.

The other local composition mole fractions can be obtained using the self-consistent pair counting and normalization equations. In the case of symmetric electrolytes ($a = b$), $x^{m^+s^o} = x^{n^-s^o}$. Equations 24 and 26—30 lead to the following equation for the osmotic coefficient:

$$\phi = A_\phi \phi^{DHP} + \phi^o + \phi_{m^+n^-}v_{m^+n^-} + \phi'_{m^+s^o}v'_{m^+s^o} + \phi'_{n^-s^o}v'_{n^-s^o} + \phi'_{m^+n^-}v'_{m^+n^-} \quad (31)$$

where

$$\phi\text{DHP} = -\sqrt{[(1{,}000/W_s)(2Ix)]^3}/[m(a + b)(1 + \rho\sqrt{Ix})] \quad (32)$$

$$\phi^o = -[1/(a + b)y] \ln x^o_{s^os^o} \quad (33)$$

$$\phi_{m^+n^-} = -[2a/(a + b)]x^{m^+n^-}/x^o_{s^os^o} \quad (34)$$

$$\phi'_{m^+s^o} = -[2ax'^{m^+s^o}/x^o_{s^os^o} - ay(1 - x^o)(a + b - 2ax^o)]/(a + b) \quad (35)$$

$$\phi'_{n^-s^o} = -[2ax'^{n^-s^o}/x^o_{s^os^o} - y(b - ax^o)(a + b - 2ax^o)]/(a + b) \quad (36)$$

$$\phi'_{m^+n^-} = -[2ax'^{m^+n^-}/x^o_{s^os^o} + ay(1 - x^o)(b - ax^o)]/(a + b) \quad (37)$$

where

$$x^o_{s^os^o} = 1 - (a + b)y + 2ax^o y \quad (38)$$

Similarly, substitution of the perturbation solutions for the local mole fractions into Eq. 24 gives for $\ln \Gamma_\pm$:

$$\ln \Gamma_\pm = A_\phi f^{PDH} + f^o + f_{m^+n^-}v_{m^+n^-} + f'_{m^+s^o}v'_{m^+s^o} + f'_{n^-s^o}v'_{n^-s^o} + f'_{m^+n^-}v'_{m^+n^-} \quad (39)$$

where

$$f^{PDH} = -\sqrt{(1{,}000/W_s)}[2aZ_m^2 \ln(1 + \rho\sqrt{Ix})/b\rho + (aZ_m^2/b - 2Ix)\sqrt{Ix}/(1 + \rho\sqrt{Ix})] \quad (40)$$

$$f^o = -\ln[1 + (a + b)y] + (a/(a + b)] \ln(ax^{o2}/bx_{m^+}x_{n^-}) + (b - a)/(b + a) \ln(x^o_{s^on^-}x^o_{n^-s^o}/x^o_{s^os^o}x_{n^-}) \quad (41)$$

$$f_{m^+n^-} = [2a/(a + b)](fcom\, x^{m^+n^-} - 1) \quad (42)$$

$$f'_{m^+s^o} = [a/(a + b)][2\, fcom\, x^{m^+s^o} + (ax^o/b)(2 - ax^o/b) + (b - a)y(1 - x^o)] \quad (43)$$

$$f'_{n^-s^o} = [1/(a + b)]\{2a\, fcom\, x^{n^-s^o} + ax^o(2 - x^o) + (b - a)[(a + 2b)y - 3ayx^o]\} \quad (44)$$

$$f'_{m^+n^-} = [a/(a + b)][2\, fcom\, x'^{m^+n^-} + (a - b)y(1 - x^o)] \quad (45)$$

where

$$fcom = \left[\frac{1}{x^o} + (a - b)\left(\frac{1}{b - ax^o} + \frac{y}{1 - (a + b)y + 2ayx^o}\right)\right] \quad (46)$$

The format chosen in Eq. 31 for ϕ and in Eq. 39 for $\ln \Gamma_\pm$ emphasizes the structure of the solutions and highlights the different contributions to ϕ and $\ln \Gamma_\pm$ from different independent energetic interactions. Thus the leading term represents the Pitzer-Debye-Huckel result for the contribution of electrostatic and hardcore repulsive forces to ϕ and $\ln \Gamma_\pm$. The second term represents the entropic (combinatorial) contribution to ϕ and $\ln \Gamma_\pm$. These effects are expected to be very small in the absence of size and shape factors (Sayegh and Vera, 1980). The third term represents the contribution to ϕ and $\ln \Gamma_\pm$ from nearest neighbor interactions while the remaining three terms represent the different contributions from independent second nearest neighbor interaction energy terms to ϕ and $\ln \Gamma_\pm$. Each term in Eqs. 31 and 39 is of the form: interaction parameter times a function that represents the contribution to ϕ or $\ln \Gamma_\pm$ per unit value of the parameter. Each such function is a "universal" function of molality, the nature of the solvent, the stoichiometry, and the valency of the ions in the electrolyte. It is universal in the sense of being independent of the chemical nature of the ions into which the electrolyte dissociates in solution. For a given solvent (for example, water) and for a given class of electrolytes (for example, 1 + 1) these terms are universal functions of molality and can be computed as such once and for all. As explained earlier, $v_{m^+n^-}$ is set to zero in order to reduce the number of parameters. The resulting theory describes experimental data satisfactorily with this choice.

Comparison of Perturbation Theory with SCLC Theory

Considering the different assumptions involved in deriving the SCLC theory, the use of the first-order perturbation expansion can be treated as one more approximation. The perturbation theory can then be treated as an independent theory whose validity can be established by direct comparison with experiment. However, in this section the perturbation theory is numerically compared with the SCLC theory for the same values of the energy difference parameters. Figure 3 shows such a comparison for ϕ for 1 − 1 electrolytes for a typical set of parameter values: $(v'_{m^+s^o} + v'_{n^-s^o}) = 13.5$ and $v'_{m^+n^-} = 24.75$. The two theories are identical up to a molality of 1.2 and differ only slightly even at a molality of 5. Figure 4 shows similar results for $\ln \Gamma_\pm$: $(v'_{m^+s^o} + v'_{n^-s^o}) = 8.76$ and $v'_{m^+n^-} = 15.02$. These figures suggest that the first-order theory is a valid approximation to the SCLC theory.

Virial type expansions

The functions of the perturbation theory can be expanded in powers of molality to examine their behavior for low values of m.

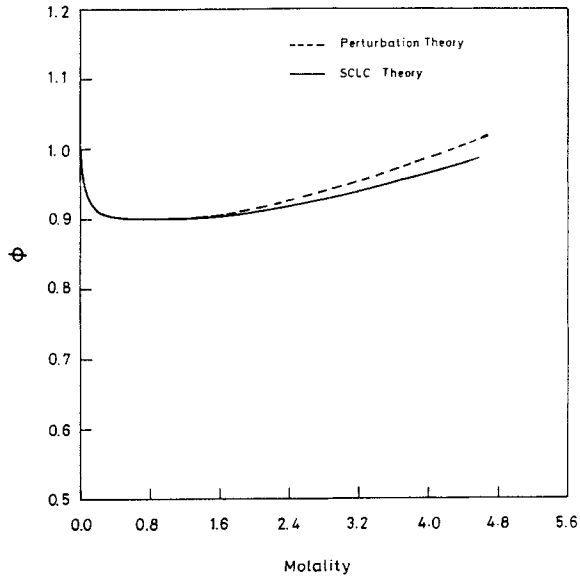

Figure 3. Comparison of perturbation theory with SCLC theory for osmotic coefficient using the same values of energy difference parameters.

It is easy to show that:

$$(\phi - \phi^{\circ} - A\phi^{DHP}) = -K_o(a+b)y + \lambda_o(a+b)^2y^2 \quad (47)$$

$$(\ln \Gamma_{\pm} - f^{\circ} - Af^{DHP}) = -K_a(a+b)y + \lambda_a(a+b)^2y^2 \quad (48)$$

where K and λ are combinations of the energy parameters as well as the stoichiometric numbers:

$$K_o = \frac{2ab}{(a+b)^2}v_{m^+n^-} - \frac{av'_{m^+s^\circ} + bv'_{n^-s^\circ}}{a+b} + \frac{ab}{(a+b)^2}v'_{m^+n^-} \quad (49)$$

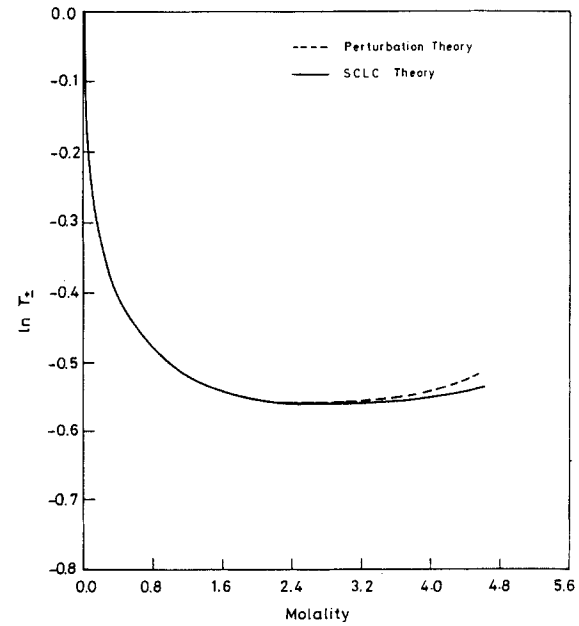

Figure 4. Comparison of perturbation theory with SCLC theory for ln $\Gamma_{\pm}$ using the same values of energy difference parameters.

$$\lambda_o = -\frac{2ab}{(a+b)^3}[(2a+b)v'_{m^+s^\circ} + (2b+a)v'_{n^-s^\circ}] + \frac{2ab}{(a+b)^2}v'_{m^+n^-} \quad (50)$$

$$K_a = \frac{4ab}{(a+b)^2}v_{m^+n^-} - \frac{2}{a+b}(av'_{m^+s^\circ} + bv'_{n^-s^\circ}) + \frac{2a^2}{(a+b)^2}v'_{m^+n^-} \quad (51)$$

$$\lambda_a = \frac{2ab(2b-a)}{(a+b)^3}v_{m^+n^-} - \frac{1}{(a+b)^2}[a(5ab+3b^2+a^2)v'_{m^+s^\circ} + 3ab(a+2b)v'_{n^-s^\circ}] + \frac{3ab^2}{(a+b)^3}v'_{m^+m^-} \quad (52)$$

The linear terms dominate at low molalities (m < 2), explaining the surprising success of Pitzer's theory.

Universal correlations

The parameter A_ϕ is a function of solvent and temperature alone (Chen et al., 1982):

$$\begin{aligned} A_\phi = &-61.44534 \exp[(T-273.15)/273.15] \\ &+ 2.864468 \exp[(T-273.15)/273.15]^2 \\ &+ 183.5379 \ln(T/273.15) \\ &- 0.6820223(T-273.15) \\ &+ 0.0007875695[T^2 - (273.15)^2] \\ &+ 58.95788(273.15/T) \end{aligned} \quad (53)$$

The parameters v and v' are system and temperature dependent. It is clear from these equations that the perturbation functions are functions of composition, solvent nature, stoichiometry of the dissociation of the solute, and ion valency. Hence, for a given solvent (e.g., water) and a given class of solutes (e.g., l = 1) the perturbation functions become universal functions of composition. As in the previous part, the perturbation functions that accompany the parameter v can be disregarded as this parameter has been set to zero for engineering convenience. In this paper attention is focused on electrolytes dissolved in water alone and the universal correlations resulting from the perturbation analysis are discussed separately for each class of solutes.

Symmetric Systems

In symmetric electrolyte systems ($a = b$) it is clear from the equations above that the following equalities hold:

$$\phi'_{m^+s^\circ} = \phi'_{n^-s^\circ} \quad (54)$$

$$f'_{m^+s^\circ} = f'_{n^-s^\circ} \quad (55)$$

There are two important groups of symmetric electrolyte systems: 1 – 1 systems and 2 – 2 systems. The variation of ϕ°, $\phi'_{m^+s^\circ}$, $\phi'_{m^+n^-}$ and of f°, $f'_{m^+s^\circ}$, $f'_{m^+n^-}$ with molality is the same for both types of systems whereas the variations of both ϕ^{DHP} and

f^{DHP} with respect to molality are different for the two groups. In Figure 5 the functions ϕ^{DHP}, $\phi°$, $\phi'_{m^+s°}$, and $\phi'_{m^+n^-}$ are plotted as functions of molality to give an easy and universal method to determine osmotic coefficients. In Figure 6 the functions f^{DHP}, $f°$, $10f'_{m^+s°}$, and $10f'_{m^+n^-}$ are plotted as functions of molality. The functions ϕ^{DHP} *and* f^{DHP} represent the effect of electrostatic interactions, which vary significantly at low concentrations and become relatively constant at higher concentrations. The functions $\phi°$ and $f°$ represent the combinatorial contributions including the effects of like-ion repulsion to the respective functions. Clearly, like-ion repulsion does not introduce significant nonrandomness in this case. Functions $\phi_{m^+n^-}$ and $f_{m^+n^-}$ are disregarded since $v_{m^+n^-}$ has been set to zero for engineering convenience. Functions $\phi'_{m^+s°}$, $\phi'_{m^+n^-}$, $f'_{m^+s°}$, $f'_{m^+n^-}$ represent the effect of second nearest neighbor interactions. It can be seen from the figures that at low concentrations the functions are linear with respect to molality.

Unsymmetric systems

For unsymmetric systems functions $\phi'_{n^-s°}$ and $f'_{n^-s°}$ have to be additionally plotted as Eqs. 54 and 55 do not hold. Figures 7 and 8 display perturbation functions for ϕ and $\ln \Gamma_\pm$, respectively, for both 1 – 2 and 2 – 1 electrolytes. In these graphs, the $m^+s°$ functions for a 1 – 2 electrolyte are the same as the $n^-s°$ functions for a 2 – 1 electrolyte and vice versa. Similar curves can be plotted for 3 – 1, 3 – 2, and 4 – 1 electrolyte systems as well (Ramachandran, 1988). It is only in the case of 4 – 1 electrolyte systems that there are there any significant combinatorial contributions.

Results of Perturbation Theory

In this section a comparison of the perturbation theory with experiment is presented. The tables of this section report the "best" parameters that are determined using one or the other property. Yet the percent root mean square (RMS) deviations of the calculated values of both properties from experimental data are reported. Hence the reported RMS deviations must be interpreted differently: for the fitted property the RMS deviation is

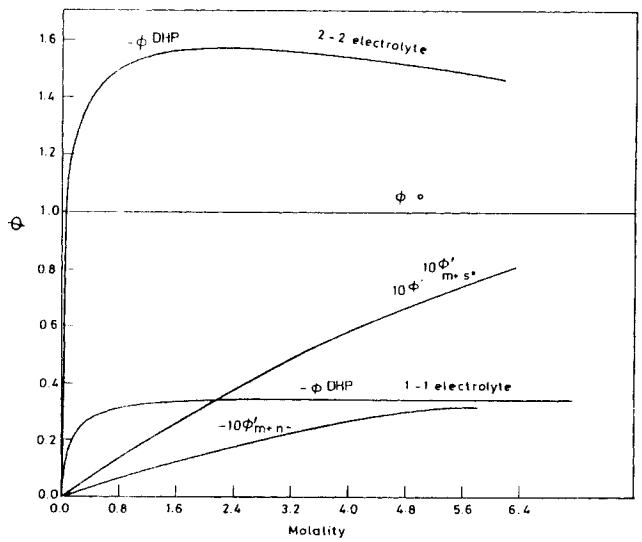

Figure 5. Universal correlations for ϕ for single electrolytes in water (symmetric case, 1-1, 2-2).

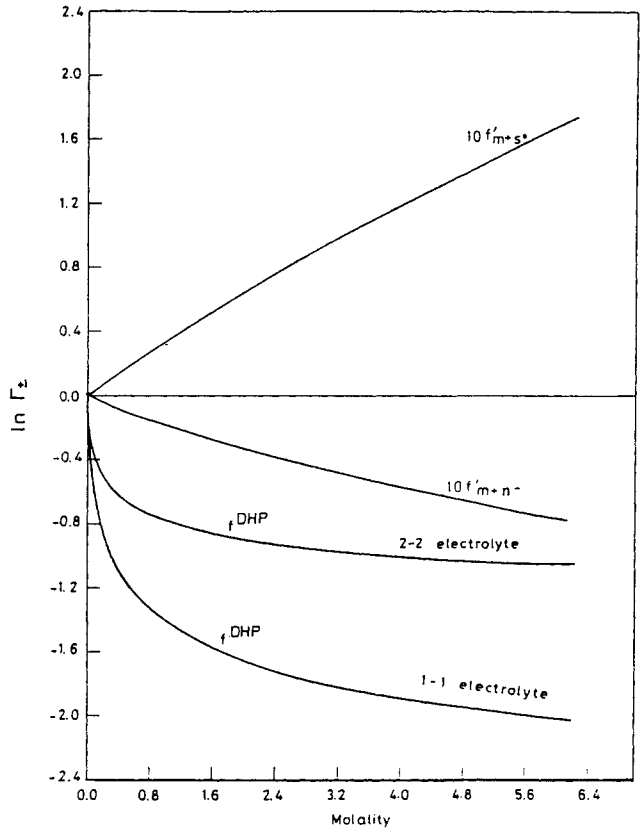

Figure 6. Universal correlations for ln $\Gamma_\pm$ for single electrolytes in water (symmetric case, 1-1, 2-2).

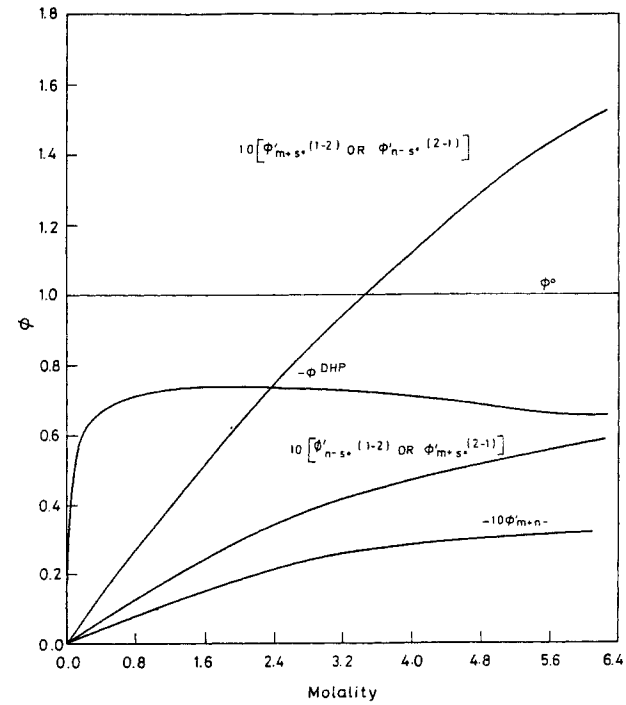

Figure 7. Universal correlations for ϕ for single electrolytes in water (unsymmetric case, 2-1, 1-2).

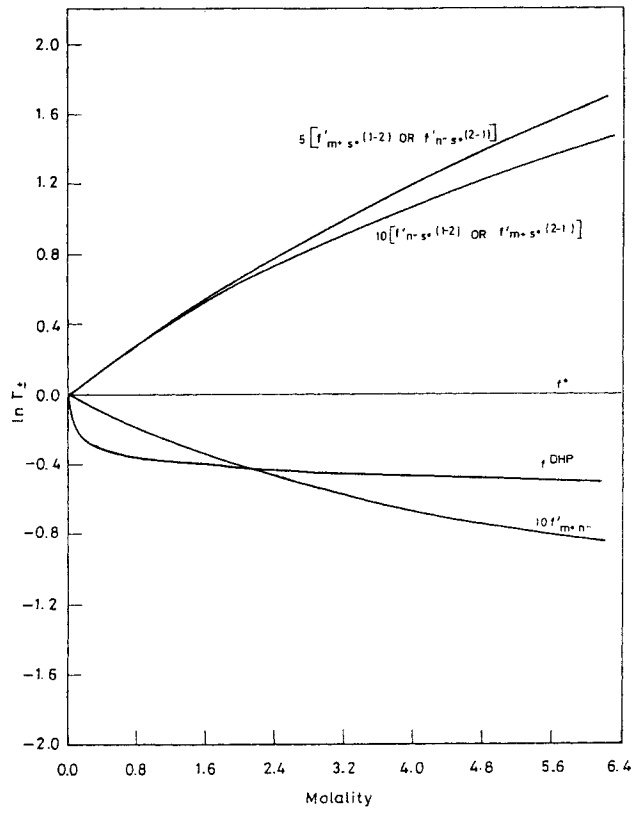

Figure 8. Universal correlations for ln $\Gamma_\pm$ of single electrolytes in water (unsymmetric case, 1-2, 2-1).

an indication of the correlative ability of the theory while, for the other property it is an indication of the predictive ability of the theory. In the literature on other theories this is not done. Hence comparison between theories is restricted to a comparison of their correlative abilities alone. In conformity with the usual practice in the literature in this area, relative RMS deviations for ϕ and absolute ones for ln $\Gamma_\pm$ are calculated.

Symmetrical systems

Table 3 gives the best values of these parameters for 1 – 1 electrolytes dissolved in water when the theory is fitted to ϕ or to ln $\Gamma_\pm$ data (Robinson and Stokes, 1965). The table demonstrates the excellent correlative ability (σ = 0.5%) for ϕ and the simultaneously good predictive ability for ln $\Gamma_\pm$ (σ = 1.5%). When ln $\Gamma_\pm$ is correlated the figures are even more impressive (σ ln $\Gamma_\pm$ = 0.83% and $\sigma\,\phi$% = 0.76%). It appears that for the simultaneous prediction of both properties it is better to use values that fit ln $\Gamma_\pm$ well. This has been confirmed by fitting the theory simultaneously to data on both properties.

Table 4 presents the corresponding results for 2 = 2 electrolyte systems (Robinson and Stokes, 1965). It is clear that the theory is a useful tool for correlating ϕ. The average relative RMS deviation is 2.48%. However the theory has poor predictive ability for ln $\Gamma_\pm$. The values of the RMS deviation are large, ranging from 17% to 25%. The theory does not correlate ln $\Gamma_\pm$ data as well as it does ϕ data and the average RMS deviation for ln $\Gamma_\pm$ is 7.22%.

Unsymmetrical systems

In unsymmetric sytsems Eqs. 54 and 55 do not hold and there are three independent parameters, $v'_{m^+s^\circ}$, $v'_{n^-s^\circ}$, and $v'_{m^+n^-}$, which can be used to fit the data. It is noteworthy that the value of $v'_{m^+n^-}$ is very close to zero.

1-2 electrolytes

Table 5 presents the results for 1-2 electrolyte systems (Robinson and Stokes, 1965). The ϕ data are very well correlated by the theory, with an average relative RMS deviation of 0.89% for 11 systems. The average RMS deviation for the prediction of ln $\Gamma_\pm$ for the 11 systems is 4.4%. The table also illustrates the good correlative ability of the theory for ln $\Gamma_\pm$ (average RMS deviation is 1.64%) as well as the good predictive ability of the theory for ϕ (average relative RMS deviation is 3.04%).

2-1 electrolytes

Table 6 summarizes the results for 2-1 electrolytes in water at 25°C. (Robinson and Stokes, 1965). The table shows good correlation of ϕ, with an average relative RMS deviation of 2.04%. The table indicates that the prediction of ln $\Gamma_\pm$ is fair for barium, cobalt, and strontium salts and poor for calcium, magnesium, and zinc salts. The average RMS deviation for ln $\Gamma_\pm$ in these systems is 5%. Oddly, the table predicts ϕ data (average relative RMS deviation of 3.88%) better than it correlates ln $\Gamma_\pm$. Perhaps this is an indication of the experimental uncertainty in the measurement of ln $\Gamma_\pm$.

3-1 electrolytes

Table 7 reports the results for 3-1 electrolyte systems (Robinson and Stokes, 1965). The average relative RMS deviation for the ϕ correlation is 3.74% while the prediction of ln $\Gamma_\pm$ is poor. The average RMS deviation for the correlation of ln $\Gamma_\pm$ is poor. The average RMS deviation for the correlation of ln $\Gamma_\pm$ for these 11 systems is 6.57% while the prediction of ϕ is to the same degree of accuracy (5.15%).

3-2 electrolytes

The results for two 3-2 electrolyte systems dissolved in water at 25°C are given in Table 8 (Robinson and Stokes, 1965). The correlation of ϕ data is fair while the prediction of ln $\Gamma_\pm$ is poor and vice-versa.

The general correlative ability of the present theory is displayed graphically for two typical systems: one symmetric and the other unsymmetric. Figure 9 demonstrates the strong ability of the theory to correlate ϕ and ln $\Gamma_\pm$ data of $CdSO_4$–H_2O at 25°C. Figure 10 demonstrates the fit of the theory for ϕ and ln $\Gamma_\pm$ data of $Mg(CH_3COO)_2$–H_2O at 25°C.

Solutions at high concentrations

Most of the data in the literature are reported only up to a molality of 6. For a few systems data are reported to much higher concentrations. Table 9 shows the values of the parameters that fit ϕ and ln $\Gamma_\pm$ data of ten 1 = 1 electrolyte systems dissolved in water. (Robinson and Stokes, 1965). Table 9 shows that the theory correlates ϕ extremely well over the wide concentration range (σ = 2.44%). Figure 11 compares the theory with ϕ and ln $\Gamma_\pm$ data of the system NH_4NO_3–H_2O up to 20m at 25°C. This comaprison is extremely impressive, with a near perfect fit

Table 3. Parameters of 1-1 Systems at 25°C

System	Max. m	Fit of ϕ Data				Fit of $\ln \Gamma_\pm$ Data			
		$v'_{m+s^e} + v'_{n-s^e}$	v'_{m+n^-}	σ % ϕ	σ % $\ln \Gamma_\pm$	$v'_{m+s^e} + v'_{n-s^e}$	v'_{m+n^-}	σ % ϕ	σ % $\ln \Gamma_\pm$
$AgNO_3$	6.0	9.53	34.22	1.53	3.45	16.08	48.91	2.77	1.94
$Cs(CH_3COO)$	3.5	0.66	−16.76	0.53	1.94	−9.76	−38.96	0.76	1.02
CsBr	5.0	17.21	37.72	1.01	2.46	23.84	51.69	1.36	1.48
CsCl	6.0	13.30	28.11	1.27	3.10	19.04	41.00	1.58	1.77
CsI	3.0	19.96	44.16	0.67	1.73	32.46	70.54	0.97	0.90
$CsNO_3$	1.4	113.07	247.47	0.41	0.82	132.44	287.29	0.55	0.40
CsOH	1.0	193.89	209.82	2.10	4.84	−145.15	−312.08	2.79	0.79
HBr	3.0	47.74	73.61	0.38	1.54	36.35	49.65	0.53	0.91
HCl	6.0	34.83	51.59	0.26	1.12	33.32	48.13	0.36	0.67
$HClO_4$	6.0	59.93	102.43	0.49	2.69	55.16	91.65	0.79	1.42
HI	3.0	24.83	22.14	0.69	3.02	6.01	−17.74	1.02	1.52
HNO_3	3.0	10.87	9.86	0.36	1.75	−12.58	−15.78	0.67	0.82
$K(CH_3COO)$	3.5	0.35	−16.22	0.41	1.52	−7.19	−32.34	0.59	0.82
KBr	5.5	5.92	8.33	0.08	0.30	5.35	7.07	0.12	0.23
$KBrO_3$	0.5	−84.24	−153.56	0.08	0.23	−156.29	−298.59	0.13	0.14
KCl	4.5	8.20	14.08	0.05	0.20	7.76	13.13	0.06	0.18
$KClO_3$	0.7	−54.95	−98.05	0.06	0.22	−88.22	−165.69	0.18	0.22
KCNS	5.0	−0.05	−2.04	0.17	0.23	−0.46	−2.92	0.18	0.22
KF	4.0	20.10	36.03	0.09	0.20	20.94	36.02	0.09	0.19
KH_2PO_4	1.8	92.08	204.64	0.40	1.25	117.22	256.54	0.73	0.43
KH adipate	1.0	−14.93	−33.19	0.12	0.42	−38.74	−81.56	0.17	0.30
KH malonate	5.0	7.28	19.60	0.67	0.64	7.96	21.06	0.68	0.63
KH succinate	4.5	15.00	32.64	0.34	0.47	16.34	35.52	0.36	0.39
KI	4.5	−0.07	−6.13	0.21	0.83	−2.72	−1.19	0.34	0.53
KNO_3	3.5	19.97	54.80	0.80	1.97	30.61	77.47	1.32	1.04
KOH	6.0	30.40	46.75	0.22	1.30	32.47	51.47	0.42	0.59
KTol	3.5	−8.97	−8.60	1.17	2.68	−23.32	−39.17	1.79	1.50
$Li(CH_3COO)$	4.0	4.07	−2.07	0.16	0.47	3.35	−3.55	0.18	0.46
LiBr	6.0	51.56	86.04	0.43	1.38	49.18	80.68	0.54	0.91
LiCl	6.0	39.25	63.65	0.49	1.50	36.56	57.63	0.56	0.94
$LiClO_4$	4.0	28.01	33.72	0.74	3.36	14.13	38.21	1.13	1.75
$LiNO_3$	6.0	9.25	4.72	0.31	0.94	7.67	1.16	0.37	0.65
LiI	3.0	31.15	39.18	1.18	4.31	0.92	−2.47	1.61	2.20
LiOH	4.0	18.01	37.84	1.45	6.62	45.66	97.44	2.98	3.19
LiTol	4.5	6.21	10.37	1.02	1.81	0.10	−2.83	1.18	1.25
$Na(CH_3COO)$	3.5	−1.93	−1.90	0.42	1.17	−8.22	−32.34	0.52	0.71
NaBr	4.0	18.55	28.06	0.30	1.00	14.45	19.24	0.42	0.55
$NaBrO_3$	2.5	16.99	39.69	0.14	0.19	17.13	40.00	0.14	0.19
Na butyrate	3.5	−46.35	−118.21	0.30	0.72	−43.19	−114.19	0.36	0.36
NaCl	6.0	18.22	30.23	0.33	1.15	16.095	25.46	0.47	0.67

of the data perhaps because the model represents well the short-range interactions that are predominant at high concentrations. The prediction of $\ln \Gamma_\pm$ from the parameters given in Table 9 is fair, with an average RMS deviation of 7.01%. The average RMS deviation for correlating $\ln \Gamma_\pm$ for the ten systems is 4.97%. The parameters that best correlate $\ln \Gamma_\pm$ predict ϕ data well, with an average relative RMS deviation of 2.66%, very close to that of the best correlation of ϕ data.

Solutions at different temperatures

The parameters v' are dimensionless. They can be put in the form θ'/T where the θ's are formally temperature-independent. The θ's have the dimensions of temperature. They have been determined to fit the available data for 1-1 electrolytes over a wide range of temperatures: ϕ for NaOH (0–100°C) (Perry and Chilton, 1973) and ϕ and $\ln \Gamma_\pm$ for NaCL and KBr (60 to 100°C) (Robinson and Stokes, 1965). The data for NaOH in particular extend to concentrations of 300/100 g water. The parameters, $(\theta'_{m^+s^e} + \theta'_{n^-s^e})$ K and $\theta'_{m^+n^-}$ K obtained are: 1,470 and 266 for NaOH, 1,894 and 1,312 for NaCl, and −1,542 and −5,127 for KBr. The corresponding RMS values are given in Table 10. Figure 12 illustrates the fit of the theory for ϕ and for $\ln \Gamma_\pm$ for NaCl solutions at 60°C. The fit is remarkably good for NaCl and KBr, and is reasonably good for NaOH.

The relative lowering of the vapor pressures over solutions of 47 salts in water at 100°C has been evaluated using the parameters reported at 25°C and compared with experiment over a wide range of concentrations (Weast, 1976). The predicted values agree with the experiment to within the normal uncertainty of 10 mm Hg for most of the systems. Details of the calculations are available elsewhere (Ramachandran, 1988).

Table 3. (Continued)

System	Max. m	Fit of ϕ Data				Fit of $\ln \Gamma_\pm$ Data			
		$v'_{m+s^o} + v'_{n-s^o}$	v'_{m+n^-}	σ % ϕ	σ % $\ln \Gamma_\pm$	$v'_{m+s^o} + v'_{n-s^o}$	v'_{m+n^-}	σ % ϕ	σ % $\ln \Gamma_\pm$
$NaClO_3$	3.5	29.15	5.37	0.18	1.02	−2.622	−6.43	0.43	0.53
$NaClO_4$	6.0	5.62	7.27	0.35	1.34	3.217	1.85	0.56	0.75
NaCNS	4.0	−0.87	−12.53	0.60	2.05	−9.124	−30.31	0.86	1.14
NaF	1.0	6.35	13.29	0.02	0.20	−0.265	−0.04	0.06	0.20
Na(HCOO)	3.5	−7.40	−22.46	0.33	0.68	−11.434	−30.94	0.39	0.52
NaH_2PO_4	6.0	21.18	53.45	1.18	2.44	25.726	63.65	1.67	1.44
NaH adipate	0.7	−100.39	−208.30	0.05	0.22	−116.004	−239.76	0.07	0.21
NaH malonate	5.0	4.55	10.27	0.29	0.56	6.049	13.54	0.36	0.40
NaH succinate	5.0	11.84	23.45	0.27	0.49	13.168	26.34	0.31	0.38
NaI	3.5	16.41	19.92	0.50	1.21	10.543	7.41	0.58	0.77
$NaNO_3$	6.0	1.63	6.06	0.22	0.42	1.337	7.64	0.26	0.30
NaOH	6.0	28.14	48.68	0.95	1.01	27.331	46.87	0.93	0.96
Na propianate	3.0	−10.14	−39.71	0.25	1.23	−18.671	−57.69	0.43	0.72
Na valerate	3.5	−15.51	−34.08	0.10	2.79	−14.429	−31.74	1.22	1.61
NH_4Cl	6.0	2.02	1.40	0.16	0.31	2.428	2.31	0.18	0.23
NH_4NO_3	6.0	0.84	7.60	0.59	3.17	6.592	20.59	1.55	1.56
$Rb(CH_3COO)$	3.5	3.42	−10.67	0.44	1.47	−4.245	−27.00	0.59	0.84
RbBr	5.0	7.29	14.00	0.28	1.03	10.109	20.19	0.48	0.52
RbCl	5.0	9.82	18.63	0.30	0.99	12.482	24.47	0.47	0.53
RbI	5.0	9.50	18.68	0.38	1.20	12.821	25.97	0.58	0.66
$RbNO_3$	4.5	16.32	48.10	1.28	3.17	27.323	71.98	2.28	1.70
$Tl(CH_3OO)$	6.0	5.30	15.03	1.20	3.22	11.057	28.00	1.80	1.81
$TlClO_4$	0.5	383.43	793.24	0.13	0.43	217.018	458.21	0.35	0.22
$TlNO_3$	0.4	1227.78	2507.24	0.13	1.26	708.673	1463.13	0.51	0.49

Table 4. Parameters of 2-2 Systems at 25°C

System	Max. m	Fit of ϕ Data				Fit of $\ln \Gamma_\pm$ Data			
		$v'_{m+s^o} + v'_{n-s^o}$	v'_{m+n^-}	σ % ϕ	σ % $\ln \Gamma_\pm$	$v'_{m+s^o} + v'_{n-s^o}$	v'_{m+n^-}	σ % ϕ	σ % $\ln \Gamma_\pm$
$BeSO_4$	4.0	90.7	163.8	2.17	19.80	172.9	341.5	11.51	7.56
$CdSO_4$	3.5	950.4	187.1	1.16	18.55	197.7	406.4	13.60	7.16
$CuSO_4$	1.4	47.1	88.2	0.88	19.30	636.4	129.7	14.02	5.51
$MgSO_4$	3.0	54.3	94.5	3.36	19.57	261.4	527.9	13.36	6.36
$MnSO_4$	4.0	98.3	191.0	2.74	17.83	172.3	351.1	12.51	6.78
$NiSO_4$	2.5	123.7	244.3	2.59	17.74	312.0	638.1	13.34	5.84
$ZnSO_4$	3.5	137.4	271.1	2.82	17.90	234.2	477.9	13.01	6.67
UO_2SO_4	6.0	37.0	61.2	5.02	24.97	82.3	163.7	12.41	11.93

Table 5. Parameters of 1-2 Systems at 25°C

System	Max. m	Fit of ϕ Data					Fit of $\ln \Gamma_\pm$ Data				
		v'_{m+s^o}	v'_{n-s^o}	$v'_{m+n^-} \times 1{,}000$	σ % ϕ	σ % $\ln \Gamma_\pm$	v'_{m+s^o}	v'_{n-s^o}	$v'_{m+n^-} \times 1{,}000$	σ % ϕ	σ % $\ln \Gamma_\pm$
Cs_2SO_4	1.8	46.94	−9.893	0.05	0.42	1.67	−0.86	19.80	0.04	0.74	0.83
K_2CrO_4	3.5	11.11	−23.35	0.25	0.73	3.85	9.66	−19.55	0.25	2.08	1.33
K_2SO_4	0.7	48.71	−104.40	0.01	0.42	1.92	134.40	−278.90	0.03	1.27	0.62
Li_2SO_4	3.0	11.22	−18.92	0.26	0.81	4.31	6.05	−71.85	0.24	1.77	1.59
Na_2CrO_4	4.0	22.39	−45.65	1.14	1.91	10.60	19.56	−37.73	0.84	5.19	3.45
Na fumarate	2.0	5.446	−2.18	−0.05	0.37	0.85	12.77	−17.43	−0.03	0.72	0.45
Na maleate	3.0	18.73	−37.24	−0.55	1.81	7.22	46.71	−96.80	−0.55	5.26	3.64
$Na_2S_2O_3$	3.5	17.43	−36.68	−0.33	0.88	5.33	17.87	−36.54	−0.30	3.32	1.58
Na_2SO_4	4.0	16.41	−38.61	0.07	0.33	4.26	21.22	−48.06	0.09	4.83	0.54
$(NH_4)_2SO_4$	4.0	11.47	−28.30	−0.80	1.65	6.16	27.14	−62.22	−0.76	7.31	3.24
Rb_2SO_4	1.8	10.99	−24.81	0.06	0.44	1.96	5.42	−12.78	0.05	0.95	0.75

Table 6. Parameters of 2-1 Systems at 25°C

System	Max. m	Fit of ϕ Data v'_{m+s^o}	v'_{n-s^o}	$v'_{m+n^-} \times 1{,}000$	σ % ϕ	σ % ln $\Gamma_\pm$	Fit of ln $\Gamma_\pm$ Data v'_{m+s^o}	v'_{n-s^o}	$v'_{m+n^-} \times 1{,}000$	σ % ϕ	σ % ln $\Gamma_\pm$
Ba acetate	3.5	79.07	−33.71	0.94	1.76	4.28	89.73	−39.10	0.24	3.91	1.46
$BaBr_2$	2.0	31.75	−6.27	0.22	1.30	5.80	96.40	−36.82	0.19	2.18	2.52
$BaCl_2$	1.8	51.99	−18.36	0.16	1.15	4.68	120.3	−50.90	0.12	2.07	2.12
$Ba(ClO_4)_2$	5.0	13.26	3.06	1.55	2.05	9.05	36.24	7.01	1.60	3.06	4.88
BaI_2	2.0	52.23	10.81	0.45	1.84	7.50	96.14	−32.22	0.24	2.59	3.05
$Ba(NO_3)_2$	0.4	−155.70	71.02	0.01	0.26	1.10	−415.6	199.40	0.05	0.62	0.16
$CaBr_2$	6.0	−93.40	56.39	−4.88	2.65	22.59	−87.66	55.14	3.54	4.41	7.09
$CaCl_2$	6.0	−47.83	32.89	−1.54	1.69	12.23	−44.27	32.01	−0.93	3.21	4.13
$Ca(ClO_4)_2$	6.0	−45.04	36.87	−1.82	1.98	15.35	−35.94	33.66	−1.36	3.40	5.67
CaI_2	2.0	−11.94	20.86	0.32	1.69	9.42	74.21	−19.58	0.29	2.72	3.77
$Ca(NO_3)_2$	6.0	−13.30	4.48	2.43	1.92	7.15	−9.36	0.022	1.78	2.74	3.71
$Cd(NO_3)_2$	2.5	58.31	−20.63	−0.48	1.63	6.81	118.9	−49.07	0.44	2.91	3.33
$CoBr_2$	5.0	−22.19	25.40	−1.73	1.40	7.72	−13.61	21.97	0.24	2.26	3.36
$CoCl_2$	4.0	60.24	8.03	−0.53	1.31	5.44	22.84	0.54	0.32	2.04	2.83
CoI_2	6.0	−14.33	26.29	−14.74	3.69	9.73	−15.99	27.23	−3.56	3.86	9.24
$Co(NO_3)_2$	5.0	−21.19	19.45	1.06	1.68	10.14	−5.69	12.99	1.36	2.74	4.32
$CuCl_2$	5.0	38.48	−12.13	2.56	2.21	7.67	63.86	−23.50	1.75	4.55	4.55
$Cu(NO_3)_2$	6.0	−11.69	13.72	0.55	1.67	8.97	−13.74	9.55	1.49	2.52	4.10
$FeCl_2$	2.0	2.83	8.85	0.19	1.23	5.95	61.88	−18.95	0.18	2.05	2.50
Mg acetate	4.0	0.00	4.26	−0.12	0.49	2.22	−6.91	7.33	−0.22	9.36	9.81
$MgBr_2$	5.0	−78.10	52.16	1.50	1.90	16.02	−67.54	48.42	1.71	3.33	5.28
$MgCl_2$	5.0	−74.34	47.29	0.96	1.81	14.63	−65.45	44.23	1.44	3.48	4.77
$Mg(ClO_4)_2$	4.0	−97.13	64.63	1.24	2.48	19.01	−65.28	51.29	1.63	4.09	7.19
MgI_2	5.0	103.60	66.94	1.94	2.10	21.55	−88.27	61.43	2.28	3.96	6.95
$Mg(NO_3)_2$	5.0	−25.25	22.35	2.03	2.17	11.51	−7.75	15.06	1.75	2.99	5.02
$MnCl_2$	6.0	26.09	−3.43	0.45	1.10	5.39	40.31	−9.70	1.14	2.73	3.14
$NiCl_2$	5.0	−8.98	15.68	−2.26	1.61	5.69	−1.60	12.64	−0.07	2.24	3.12
$Pb(ClO_4)_2$	6.0	−17.74	18.66	0.11	1.67	10.59	−7.03	14.42	1.43	2.70	4.56
$Pb(NO_3)_2$	2.0	−105.00	44.85	−0.22	2.01	6.99	−199.2	89.56	−0.23	6.59	3.07
$SrBr_2$	2.0	−13.52	17.38	−0.29	1.57	7.56	56.49	−15.50	0.24	2.50	3.10
$SrCl_2$	4.0	−39.49	27.59	0.89	1.77	9.95	−19.27	18.92	0.96	2.99	4.11
$Sr(ClO_4)_2$	6.0	−14.05	20.33	−1.36	1.29	6.94	−79.43	17.96	0.59	1.87	3.16
SrI_2	2.0	−14.12	20.76	0.35	1.81	16.44	76.94	−22.02	0.29	2.90	3.90
$Sr(NO_3)_2$	4.0	7.22	−2.42	1.05	1.87	5.73	26.44	−11.02	0.78	3.31	2.98
UO_2Cl_2	3.0	53.11	−13.42	0.85	1.77	8.05	105.4	−37.69	0.74	2.75	4.12
$UO_2(ClO_4)_2$	5.5	−90.50	67.93	−5.51	2.25	19.09	−87.43	67.74	0.07	3.82	6.74
$UO_2(NO_3)_2$	5.5	80.63	−24.53	−1.29	1.41	7.45	101.7	−34.36	0.22	4.45	3.03
$ZnBr_2$	6.0	30.94	−8.50	14.93	8.74	27.00	81.36	−30.09	0.85	12.38	16.23
$ZnCl_2$	6.0	−14.88	8.61	6.22	5.78	22.67	16.62	−4.42	5.13	9.70	11.18
$Zn(ClO_4)_2$	4.0	−108.40	70.34	0.75	2.04	16.83	−86.66	61.56	1.22	3.65	5.85
ZnI_2	6.0	71.36	−23.68	20.65	9.72	28.36	132.7	−50.42	10.27	14.23	18.68
$Zn(NO_3)_2$	6.0	−15.98	17.69	1.67	1.95	12.12	−2.26	12.17	2.22	2.92	5.40

Table 7. Parameters of 3-1 Systems at 25°C

System	Max. m	Fit of ϕ Data v'_{m+s^o}	v'_{n-s^o}	$v'_{m+n^-} \times 1{,}000$	σ % ϕ	σ % ln $\Gamma_\pm$	Fit of ln $\Gamma_\pm$ Data v'_{m+s^o}	v'_{n-s^o}	$v'_{m+n^-} \times 1{,}000$	σ % ϕ	σ % ln $\Gamma_\pm$
$AlCl_3$	1.8	−60.09	35.41	1.10	4.21	20.5	46.63	39.40	0.85	5.88	8.06
$CeCl_3$	2.0	3.06	11.38	1.16	3.91	15.6	79.04	−10.92	0.83	5.19	6.69
$CrCl_3$	1.2	109.10	−18.73	0.35	3.28	13.0	279.50	−71.54	0.28	4.54	5.40
$Cr(NO_3)_3$	1.4	93.47	−15.37	0.55	3.31	12.6	220.20	−54.21	0.39	4.48	5.44
$EuCl_3$	2.0	−3.69	14.13	1.10	3.98	17.4	79.56	−10.26	0.87	5.57	7.24
$LaCl_3$	2.0	8.46	9.64	1.00	3.84	16.1	87.20	−13.46	0.80	5.38	6.78
$NdCl_3$	2.0	−1.29	12.84	0.97	3.72	15.4	72.23	−8.70	0.77	5.11	6.46
$PrCl_3$	2.0	1.18	11.84	0.93	3.77	15.7	77.00	−10.38	0.76	5.30	6.55
$ScCl_3$	1.8	8.57	12.22	0.78	3.50	14.9	96.01	−13.77	0.63	4.75	6.17
$SmCl_3$	2.0	−0.26	12.90	1.01	3.85	16.3	78.18	−10.10	0.80	5.32	6.82
YCl_3	2.0	−16.87	18.79	1.06	3.75	16.2	58.09	−3.12	0.81	5.08	6.69

Table 8. Parameters of 3-2 Systems at 25°C

System	Max. m	Fit of ϕ Data					Fit of $\ln \Gamma_\pm$ Data				
		v'_{m+s^o}	v'_{n-s^o}	$v'_{m+n^-} \times 1{,}000$	σ % ϕ	σ % $\ln \Gamma_\pm$	v'_{m+s^o}	v'_{n-s^o}	$v'_{m+n^-} \times 1{,}000$	σ % ϕ	σ % $\ln \Gamma_\pm$
$Al_2(SO_4)_3$	1.0	62.82	−23.2	0.62	13.8	12.2	281.1	−164.6	0.25	13.8	6.8
$Cr_2(SO_4)_3$	1.2	51.35	−16.6	1.10	14.8	42.5	599.5	−369.1	0.89	24.0	15.6

Comparison of Present Theory with Other Theories

In this section the perturbation theory is briefly compared with the theories of Pitzer (1973), Cruz and Renon (1978), and Chen et al. (1982). The comparison of theory for fit of ϕ data is based on the values of RMS reported by Ball et al. (1985) for the other theories. Comparison of the theory for $\ln \Gamma_\pm$ is done only with the theory of Chen et al. In the paper of Chen et al. standard deviation values for $\ln \Gamma_\pm$ are reported. These values are converted to RMS values and compared. In all cases comparision is restricted to those systems and to those properties, ϕ or $\ln \Gamma_\pm$, for which calculations using other theories have already been reported in the literature.

A purely numerical approach for the comparison of alternative theories would be misleading. The present theory (perturbation theory) distinguishes itself from all other theories for the following reasons:

1. It is linear in the parameters while all the other theories are nonlinear. No guess values are required in the present theory for parameter estimation.

2. It has the unique feature of presenting universal graphs to estimate the ϕ and $\ln \Gamma_\pm$. The practicing engineer needs only these graphs for each class with a table of parameter values.

3. It correlates high concentration data remarkably well. Other theories have not been tested for their ability to do so.

4. It can be parameterized in terms of simple temperature-independent parameters which correlate the data remarkably well.

5. It has a sound theoretical basis for accounting for short-range interactions. The Pitzer form for short-range interactions is an empirical form based on chemical intution. The theory of Cruz and Renon (1978) uses the Debye-McAulay model for accounting for the effect of dielectric constant changes introcuced by the solute on the excess Gibbs energy. The model requires a knowledge of the change of dielectric constant with concentration, for which another approximate theory has to be used. Further, in the estimation of these terms varying values are taken for the ionic sizes while the Gibbs-Duhem equation requires a constant value of 4Å. The theory of Cruz and Renon thus carries several empirical features, unlike the present theory. The theory of Chen et al. alone is of a degree of rigor comparable with the present theory. Its demerits are the demerits of the NRTL theory and the neglect of second nearest neighbor interactions.

The average % RMS values for different types of electrolytes in solution are compared in Table 11 for the present theory, Chen's theory, Pitzer's theory, and the theory of Cruz and Renon. The present theory is superior to all others for 2-1 electrolytes, with the an average RMS value of 1.84%. The theories

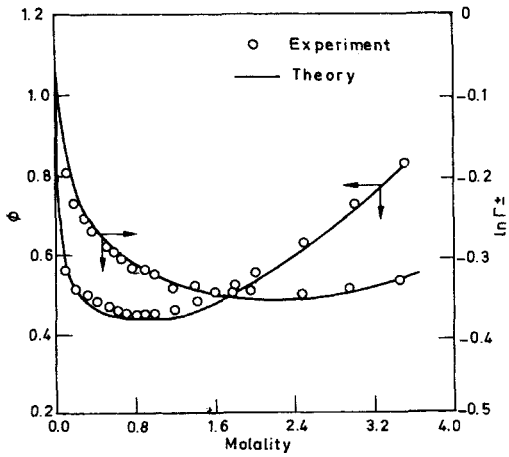

Figure 9. Comparison of perturbation theory with data for $CdSO_4$–H_2O system at 25°C.

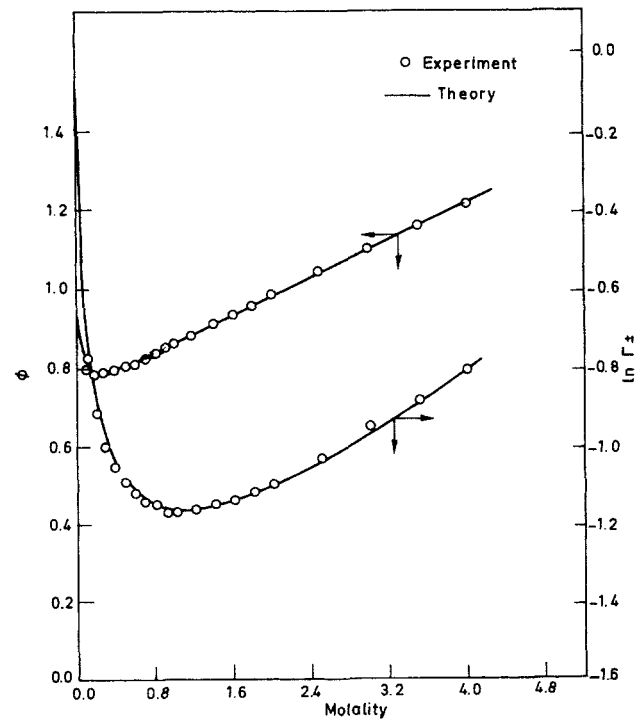

Figure 10. Comparison of perturbation theory with data for $Mg(CH_3COO)$–H_2O system at 25°C.

Table 9. Fit of Data Over Large Range of Concentrations at 25°C

System	Max. m	Fit of ϕ Data $v'_{m+s^e} + v'_{n-s^e}$	v'_{m+n^-}	σ % ϕ	σ % $\ln \Gamma_\pm$	Fit of $\ln \Gamma_\pm$ Data $v'_{m+s^e} + v'_{n-s^e}$	v'_{m+n^-}	σ % ϕ	σ % $\ln \Gamma_\pm$
$AgNO_3$	13.0	−0.61	11.60	3.6	6.9	1.30	17.03	6.6	3.9
CsCl	11.0	5.45	10.73	1.9	5.4	7.79	16.86	2.5	3.1
HCl	16.0	26.71	32.78	1.7	4.6	27.40	34.91	1.4	3.3
$HClO_4$	16.0	33.03	86.20	1.8	3.9	33.43	87.47	1.3	3.4
KOH	16.0	26.34	37.07	1.3	4.8	27.16	39.63	1.2	3.2
LiBr	20.0	38.88	54.65	4.4	16.4	40.05	59.34	3.5	11.9
LiCl	20.0	24.32	27.14	4.9	16.0	25.57	32.09	4.1	10.8
$LiNO_3$	13.0	9.04	4.22	0.3	0.8	8.90	3.80	0.3	0.7
NaOH	20.0	22.85	34.55	3.9	10.8	23.64	37.69	3.3	7.8
NH_4NO_3	20.0	−2.13	0.83	1.0	0.5	−1.73	2.44	2.4	2.4

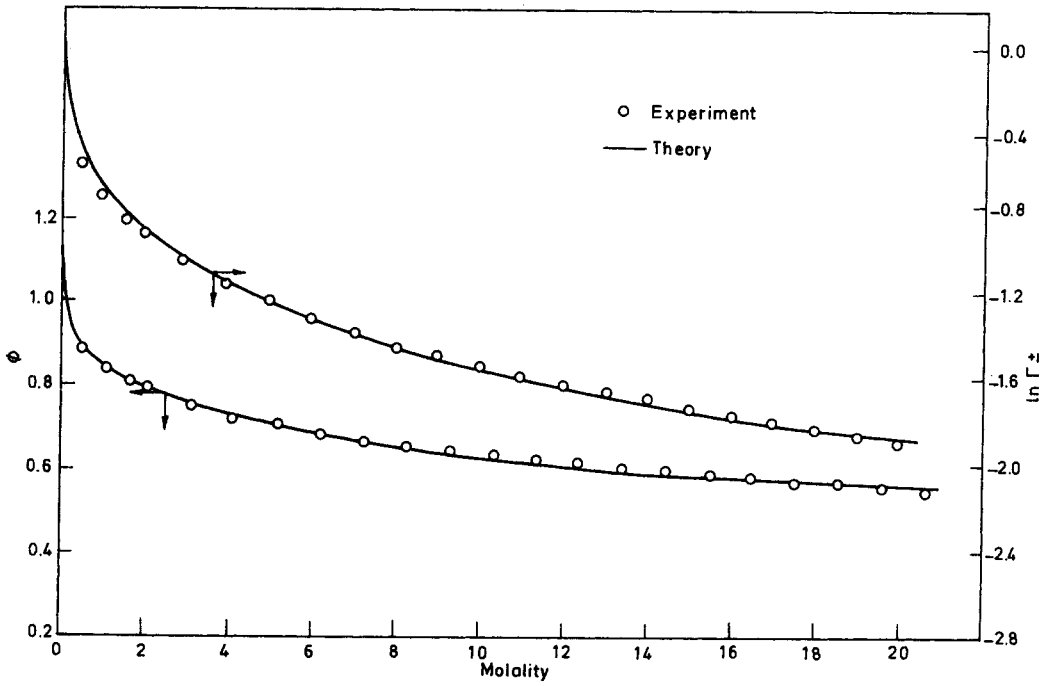

Figure 11. Perturbation theory vs. experiment for NH_4NO_3–H_2O system up to a concentration of 20m at 25°C.

Table 10. RMS % for ϕ and $\ln \Gamma_\pm$ at Various Temperatures Using Temperature-Independent Parameters

T, K	NaOH ϕ	NaCl ϕ	NaCl $\ln \Gamma_\pm$	KBr ϕ	KBr $\ln \Gamma_\pm$
273	5.38	—	—	—	—
293	9.94	—	—	—	—
313	5.46	—	—	—	—
333	2.30	0.82	1.23	1.23	4.41
343	—	0.44	1.32	0.54	2.72
353	6.51	0.37	1.77	2.59	1.43
363	—	0.55	2.46	0.71	1.33
373	11.10	0.77	3.08	1.20	2.25

of Cruz and Pitzer appear to fit ϕ data for 3-1 systems the best while the present theory fits the data better than the theory of Chen. Table 11 also compares the present theory with the theory of Chen et al. for its ability to correlate $\ln \Gamma_\pm$. In general the present theory correlates the data better than the theory of Chen et al. Systemwise comparison is available elsewhere (Ramachandran 1988).

Conclusions

From an engineering point of view one of the most attractive aspects of the theory is the fact that the linearized version yields "universal" functions that quantify the effect of different interactions in solution. The theory is compared with experiment in an exhaustive manner for the special case of a single solute dissolved in water. The theory correlates data for different classes of solutes dissolved in water satisfactorily.

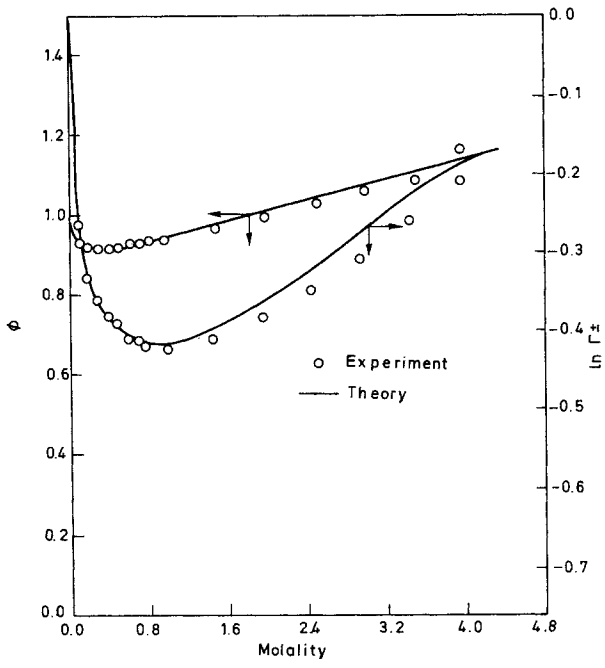

Figure 12. Comparison of perturbation theory with experiment for NaCl-H_2O system at 60° using temperature-independent parameters.

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Notation

a = stoichiometric coefficient of M in $MaNb$
$A\phi$ = Debye-Huckel constant for the osmotic coefficient
b = stoichimetric coefficient of N in $MaNb$
$fcom$ = defined in Eq. 46
I_x = ionic strength on mole fraction basis $I_x = 0.5\Sigma_i Z_i^2 x_i$
k = Boltzmann's constant
m = molality of $MaNb$
$m°$ = an arbitrary neutral molecule
m^+ = an arbitrary cation
m^- = an arbitrary anion
$n°$ = an arbitrary neutral molecule
n^+ = an arbitrary cation
n^- = an arbitrary anion
Q = canonical partition function
PDH = Pitzer-Debye-Huckel
$s°$ = reference solvent
u = nearest neighbor pair energy
u' = next nearest neighbor pair energy
w = number of configurations
W_s = molecular weight
x = mole fraction
z = coordination number
Z = charge

Greek letters

$\beta = 1/kT$
Γ = activity coefficient
μ = chemical potential
σ = RMS deviation
$\sigma_\phi = \Sigma_i [(\phi_{exp} - \phi_{theory})/\phi_{exp}]^2$
$\sigma \ln \Gamma_\pm = \Sigma i(\ln \Gamma_{i\pm theory} - \ln \Gamma_{i\pm exp})^2$
ϕ = osmotic coefficient, defined in single-solute single-solvent systems as: $\phi = (1{,}000 \ln \Gamma_{s°} x_{s°})/[W_s \cdot (a + b)m]$
ρ = closest approach parameter of the Pitzer-Debye-Huckel equation = 14.9

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Table 11. Comparison of Various Models at 25°C

		σ % ϕ					σ % $\ln \Gamma_\pm$	
Type of Electrolyte	No. of Systems	Present Theory	Chen	Pitzer	Cruz	No. of Systems	Present Theory	Chen
1-1	27	0.47	0.91	0.46	0.56	56	0.86	1.09
2-2	1	3.36	5.00	—	1.40	7	7.35	3.73
1-2	1	0.33	2.20	1.4	1.20	11	1.64	1.96
2-1	8	1.84	7.20	2.34	3.26	35	4.79	12.64
3-1	3	3.78	4.83	1.50	2.33	11	6.57	8.04
3-2						2	7.12	12.30

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Appendix A

The equations for the local composition mole fractions in the SCLC theory are given in this appendix.

Neutral molecule–neutral molecule

$$\frac{x_{m^\circ n^\circ} x_{n^\circ m^\circ}}{x_{n^\circ n^\circ} x_{m^\circ m^\circ}} = \exp\left\{v_{m^\circ n^\circ} + \left[\sum_k (x_{km^\circ} - x_{kn^\circ})(v'_{kn^\circ} - v'_{km^\circ})\right]\right\} \quad \text{(A1)}$$

Cation–neutral molecule

$$\frac{x_{s^\circ s^\circ} x_{n^\circ m^+} x_{m^- n^\circ}}{x_{n^\circ n^\circ} x_{s^\circ m^+} x_{m^- s^\circ}} = \exp\left\{v_{m^+ n^\circ} + \left[\sum_k (x_{ks^\circ} - x_{kn^\circ})(v'_{ks^\circ} - v'_{km^+}) + (x_{km^+} - x_{kn^\circ})(v'_{kn^\circ} - v'_{ks^\circ})\right]\right\} \quad \text{(A2)}$$

Anion–neutral molecule

$$\frac{x_{n^\circ m^-} x_{m^- n^\circ} x_{s^\circ s^\circ}}{x_{s^\circ m^-} x_{n^\circ n^\circ} x_{m^- s^\circ}} = \exp\left\{v_{m^- n^\circ} + \left[\sum_k (x_{kn^\circ} - x_{ks^\circ})(v'_{km^-} - v'_{ks^\circ}) + (x_{km^-} - x_{kn^\circ})(v'_{kn^\circ} - v'_{ks^\circ})\right]\right\} \quad \text{(A3)}$$

Cation–anion

$$\frac{x_{m^+ n^-} x_{n^- m^+} x_{s^\circ s^\circ} x_{s^\circ s^\circ}}{x_{s^\circ m^+} x_{s^\circ n^-} x_{m^+ s^\circ} x_{n^- s^\circ}} = \exp\left(\left\{2v_{m^+ n^-} + \left[\sum_k (x_{ks^\circ} - x_{km^+}) \cdot (v'_{ks^\circ} - v'_{kn^-}) + (x_{ks^\circ} - x_{kn^-})(v'_{ks^\circ} - v'_{km^+})\right]\right\}\right) \quad \text{(A4)}$$

The energy differences v and v' are defined below:

$$v_{m^\circ n^\circ} = \frac{\beta z}{2}(2u_{m^\circ n^\circ} - u_{m^\circ m^\circ} - u_{n^\circ n^\circ}) \quad \text{(A5)}$$

$$v_{m^+ n^\circ} = \frac{\beta z}{2}(2u_{m^+ n^\circ} - 2u_{m^+ s^\circ} + u_{s^\circ s^\circ} - u_{n^\circ n^\circ}) \quad \text{(A6)}$$

$$v_{m^- n^\circ} = \frac{\beta z}{2}(2u_{m^- n^\circ} - 2u_{m^- s^\circ} + u_{s^\circ s^\circ} - u_{n^\circ n^\circ}) \quad \text{(A7)}$$

$$v_{m^+ n^-} = \frac{\beta z}{2}(u_{m^+ n^-} + u_{s^\circ s^\circ} - u_{m^+ s^\circ} - u_{n^- s^\circ}) \quad \text{(A8)}$$

$$v'_{ij} = \frac{\beta z(z-1)}{8}(2u'_{ij} - u'_{ii} - u'_{jj}) \quad \text{(A9)}$$

Equation A1 reduces to the quasichemical form when second nearest neighbor interactions are ignored ($v' = 0$); Eqs. 2–4 do not so reduce because of the assumption that like ions cannot be nearest neighbors.

Appendix B

This appendix contains the equations required for calculating the local composition mole fractions corresponding to the zero and first orders in the perturbation analysis in the sections on universal correlation.

Zero order

(a) Normalization equations:

$$\sum_i x^\circ_{ij} = 1 \quad \text{(B1)}$$

(b) Pair conservation equations for each distinct pair ij $(i = j)$:

$$x^\circ_{ij} x_j = x^\circ_{ji} x_i \quad \text{(B2)}$$

(c) Equations which determine the most probable local compositions for distinct pairs $m^\circ n^\circ$, $m^+ n^\circ$ and $m^- n^\circ$ $(n^\circ \neq s^\circ)$ and $m^+ n^-$ are:

$$\frac{x^\circ_{m^\circ n^\circ} x^\circ_{n^\circ m^\circ}}{x^\circ_{n^\circ n^\circ} x^\circ_{m^\circ m^\circ}} = 1 \quad \text{(B3)}$$

$$\frac{x^\circ_{m^+ n^\circ} x^\circ_{n^\circ m^+} x^\circ_{s^\circ s^\circ}}{x^\circ_{n^\circ n^\circ} x^\circ_{s^\circ m^+} x^\circ_{m^+ s^\circ}} = 1 \quad \text{(B4)}$$

$$\frac{x^\circ_{m^- n^\circ} x^\circ_{n^\circ m^-} x^\circ_{s^\circ s^\circ}}{x^\circ_{n^\circ n^\circ} x^\circ_{s^\circ m^-} x^\circ_{m^- s^\circ}} = 1 \quad \text{(B5)}$$

$$\frac{x^\circ_{n^- m^+} x^\circ_{s^\circ s^\circ}}{x^\circ_{s^\circ m^+} x^\circ_{n^- s^\circ}} = 1 \quad \text{(B6)}$$

First order in v_{kl}

(a) $$\sum_i x^{kl}_{ij} = 0 \quad \text{(B7)}$$

(b) $$x^{kl}_{ij} x_j = x^{kl}_{ji} x_i \quad \text{(B8)}$$

(c) $$\frac{x^{kl}_{m^\circ n^\circ}}{x^\circ_{m^\circ n^\circ}} + \frac{x^{kl}_{n^\circ m^\circ}}{x^\circ_{n^\circ m^\circ}} - \frac{x^{kl}_{n^\circ n^\circ}}{x^\circ_{n^\circ n^\circ}} - \frac{x^{kl}_{m^\circ m^\circ}}{x^\circ_{m^\circ m^\circ}} = \delta_{km^\circ}\delta_{ln^\circ} + \delta_{kn^\circ}\delta_{lm^\circ} \quad \text{(B9)}$$

$$\frac{x^{kl}_{m^+ n^\circ}}{x^\circ_{m^+ n^\circ}} + \frac{x^{kl}_{n^\circ m^+}}{x^\circ_{n^\circ m^+}} + \frac{x^{kl}_{s^\circ s^\circ}}{x^\circ_{s^\circ s^\circ}} - \frac{x^{kl}_{m^+ s^\circ}}{x^\circ_{m^+ s^\circ}} - \frac{x^{kl}_{s^\circ m^+}}{x^\circ_{s^\circ m^+}} - \frac{x^{kl}_{n^\circ n^\circ}}{x^\circ_{n^\circ n^\circ}} = \delta_{km^+}\delta_{kn^\circ} + \delta_{lm^+}\delta_{kn^\circ} \quad \text{(B10)}$$

$$\frac{x^{kl}_{m^- n^\circ}}{x^\circ_{m^- n^\circ}} + \frac{x^{kl}_{n^\circ m^-}}{x^\circ_{n^\circ m^-}} + \frac{x^{kl}_{s^\circ s^\circ}}{x^\circ_{s^\circ s^\circ}} - \frac{x^{kl}_{m^- s^\circ}}{x^\circ_{m^- s^\circ}} - \frac{x^{kl}_{s^\circ m^-}}{x^\circ_{s^\circ m^-}} - \frac{x^{kl}_{n^\circ n^\circ}}{x^\circ_{n^\circ n^\circ}} = \delta_{km^-}\delta_{ln^\circ} + \delta_{ln^\circ}\delta_{lm^-} \quad \text{(B11)}$$

$$\frac{x^{kl}_{n^- m^+}}{x^\circ_{n^- n^+}} + \frac{x^{kl}_{s^\circ s^\circ}}{x^\circ_{s^\circ s^\circ}} - \frac{x^{kl}_{s^\circ m^+}}{x^\circ_{s^\circ m^+}} - \frac{x^{kl}_{n^- s^\circ}}{x^\circ_{n^- s^\circ}} = \delta_{kn^-}\delta_{lm^+} + \delta_{km^+}\delta_{ln^-} \quad \text{(B12)}$$

First order in v'_{kl}

(a) $$\sum_i x'^{kl}_{ij} = 0 \quad \text{(B13)}$$

(b) $$x'^{kl}_{ij} x_j = x'_{ji} x^{kl}_i \quad \text{(B14)}$$

(c) $$\frac{x'^{kl}_{m^\circ n^\circ}}{x^\circ_{m^\circ n^\circ}} + \frac{x'^{kl}_{n^\circ m^\circ}}{x^\circ_{n^\circ m^\circ}} - \frac{x'^{kl}_{n^\circ n^\circ}}{x^\circ_{n^\circ n^\circ}} - \frac{x'^{kl}_{m^\circ m^\circ}}{x^\circ_{m^\circ m^\circ}}$$
$$= (x^\circ_{kn^\circ} - x^\circ_{km^\circ})(\delta_{lm^\circ} - \delta_{ln^\circ}) + (x^\circ_{ln^\circ} - x^\circ_{lm^\circ})(\delta_{km^\circ} - \delta_{kn^\circ}) \quad \text{(B15)}$$

$$\frac{x'^{kl}_{m^+ n^\circ}}{x^\circ_{m^+ n^\circ}} + \frac{x'^{kl}_{n^\circ m^+}}{x^\circ_{n^\circ m^+}} + \frac{x'^{kl}_{s^\circ s^\circ}}{x^\circ_{s^\circ s^\circ}} - \frac{x'^{kl}_{s^\circ m^+}}{x^\circ_{s^\circ m^+}} - \frac{x'^{kl}_{m^+ s^\circ}}{x^\circ_{m^+ s^\circ}} - \frac{x'^{kl}_{n^\circ n^\circ}}{x^\circ_{n^\circ n^\circ}}$$
$$= (x^\circ_{km^+} - x^\circ_{kn^\circ})(\delta_{ln^\circ} - \delta_{lm^+}) + (x^\circ_{lm^+} - x^\circ_{ln^\circ})(\delta_{kn^\circ} - \delta_{km^+})$$
$$+ (x^\circ_{ks^\circ} - x^\circ_{km^+})(\delta_{ls^\circ} - \delta_{lm^+}) + (x^\circ_{ls^\circ} - x^\circ_{lm^+})(\delta_{ks^\circ} - \delta_{km^+}) \quad \text{(B16)}$$

$$\frac{x'^{kl}_{m^- n^\circ}}{x^\circ_{m^- n^\circ}} + \frac{x'^{kl}_{n^\circ m^-}}{x^\circ_{n^\circ m^-}} + \frac{x'^{kl}_{s^\circ s^\circ}}{x^\circ_{s^\circ s^\circ}} - \frac{x'^{kl}_{s^\circ m^-}}{x^\circ_{s^\circ m^-}} - \frac{x'^{kl}_{m^- s^\circ}}{x^\circ_{m^- s^\circ}} - \frac{x'^{kl}_{n^\circ n^\circ}}{x^\circ_{n^\circ n^\circ}}$$
$$= (x^\circ_{km^-} - x^\circ_{kn^\circ})(\delta_{ln^\circ} - \delta_{lm^-}) + (x^\circ_{lm^-} - x^\circ_{ln^\circ})(\delta_{kn^\circ} - \delta_{km^-})$$
$$+ (x^\circ_{ks^\circ} - x^\circ_{km^-})(\delta_{ls^\circ} - \delta_{lm^-}) + (x^\circ_{ls^\circ} - x^\circ_{lm^-})(\delta_{ks^\circ} - \delta_{km^-}) \quad \text{(B17)}$$

$$\frac{x'^{kl}_{s^\circ s^\circ}}{x^\circ_{s^\circ s^\circ}} + \frac{x'^{kl}_{n^- m^+}}{x^\circ_{n^- m^+}} - \frac{x'^{kl}_{s^\circ m^+}}{x^\circ_{s^\circ m^+}} - \frac{x'^{kl}_{n^- s^\circ}}{x^\circ_{m^- s^\circ}}$$
$$= [(x^\circ_{lm^+} - x^\circ_{ls^\circ})(\delta_{kn^-} - \delta_{ks^\circ}) + (x^\circ_{km^+} - x^\circ_{ks^\circ})(\delta_{ln^-} - \delta_{ls^\circ})$$
$$+ (x^\circ_{ln^-} - x^\circ_{ls^\circ})(\delta_{km^+} - \delta_{ks^\circ}) + (x^\circ_{kn^-} - x^\circ_{ks^\circ})(\delta_{lm^+} - \delta_{ls^\circ})] \quad \text{(B18)}$$

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