

Thermodynamics of Mixed Electrolyte Solutions. VI. An Isopiestic Study of a Pseudo-ternary System: NaCl-KCl-MgCl₂-H₂O at 25°C

D. Saad,¹ J. Padova,^{1,3} and Y. Marcus²

Received May 30, 1975; revised July 21, 1975

Activity coefficients for magnesium chloride in the aqueous pseudo-ternary system sodium chloride-potassium chloride-magnesium chloride were derived from isopiestic measurements at 25°C. The isopiestic data were treated by both McKay-Perring and Scatchard methods, and results obtained agree fairly well over the ionic strength range of 1-6. At constant ionic strength, the activity coefficient of MgCl₂ increased with addition of other salts. Interaction coefficients were obtained from Scatchard's and Friedman's formalisms. The excess free energy of mixing was calculated and compared with similar systems.

KEY WORDS: Osmotic coefficients; activity coefficients; excess free energy of mixing; mixed salt solutions; interaction coefficients; NaCl; KCl; MgCl₂.

1. INTRODUCTION

Many investigations on the thermodynamics of aqueous solutions of mixed electrolytes have been carried out since Harned and Robinson published their book,⁽¹⁾ but relatively fewer studies have been made on multicomponent mixtures by either the isopiestic⁽²⁻⁹⁾ or the emf⁽¹⁰⁻¹³⁾ methods. The present work deals with the NaCl-KCl-MgCl₂-H₂O system at a constant molal ratio of KCl to NaCl. This can be looked upon as a pseudo-binary system and therefore be treated by standard isopiestic methods to yield the excess free energy of mixing.

¹ Soreq Nuclear Research Center, Yavne, Israel.

² Hebrew University, Jerusalem, Israel.

³ To whom correspondence should be addressed.

2. EXPERIMENTAL

Fluka purissimum (A.R.) sodium chloride and potassium chloride certified reagents were recrystallized twice from conductivity water and dried to constant weight at 200°C. Stock solutions of the pure salts were prepared by weight and their concentrations gravimetrically determined by precipitated silver chloride. The constant-salt-ratio mixtures were prepared by weight from the stock solutions and then diluted by the weight dilution method. Baker reagent grade magnesium chloride was purified by several crystallizations from bidistilled water and conductivity water and partially dried under water pump vacuum. A stock solution of about 2 *m* was prepared and then diluted. The final concentrations were gravimetrically checked as precipitated silver chloride. All weights were in vacuo.

The isopiestic apparatus and procedure have been described previously.⁽¹⁴⁾ The osmotic coefficients were isopiastically determined over an ionic strength range of 0.6 to almost 6.5 at 25°C at a constant molality ratio of KCl to NaCl equal to 1.3296.

3. RESULTS

The isopiestic data are given in Table I. The first column gives the molality of the NaCl reference solution and the water activity (in parentheses) obtained from Robinson and Stokes,^(15a) the second column gives *I*, the total ionic strength of the mixed salt solution, and the third column gives the ionic strength fraction of the magnesium chloride, $y_B = I_B/I = 3m_B/m_A + 3m_B$, where m_A is the total molality of the salt (KCl · *n*NaCl) and m_B the molality of MgCl₂ in the mixed salt solution. The quantity Φ is the observed osmotic coefficient of the solution.

4. TREATMENT OF RESULTS

Assuming that the entity (KCl · *n*NaCl) behaves as a single compound, the results reported here were analyzed by two methods to obtain the activity coefficients.

1. Robinson^(15a, b) has shown that if, in a given set of isopiestic measurements on mixed salt solutions, the isopiestic ratio defined as $R = 1.5M_B/m_A + 1.5m_B$, where M_B is the molality of the aqueous magnesium chloride solution in isopiestic equilibrium with the mixed solution, is given by

$$R = 1 + ax_A + bx_A^2 \quad (1)$$

where $x_A = m_A/\Sigma m$, then the activity coefficient calculated by the McKay-Perring transform⁽¹⁶⁾ is

$$\log \gamma_B = \log \Gamma_B + \log R + \frac{x_A^2}{2.303} \int_0^{M_A \Phi_A} \frac{b}{M_A} d(M_A \Phi_A) \quad (2)$$

Table I. Osmotic Coefficients in the System $\text{KCl} \cdot n\text{NaCl} - \text{MgCl}_2 - \text{H}_2\text{O}$

M_r	I	γ_B	Φ
0.5840 (0.9895)	0.596	0.0	0.908
	0.639	0.1393	0.909
	0.762	0.4389	0.909
	0.847	0.5994	0.911
	1.048	0.8678	0.912
	1.178	1.0	0.918
0.9067 (0.9701)	0.934	0.0	0.905
	0.996	0.1393	0.912
	1.179	0.4389	0.918
	1.296	0.5994	0.931
	1.419	0.7350	0.941
	1.576	0.8678	0.947
1.6109 (0.9456)	1.745	1.0	0.968
	1.686	0.0	0.920
	1.790	0.1393	0.932
	1.916	0.2856	0.945
	2.244	0.5994	0.987
	2.422	0.7350	1.013
1.6908 (0.9428)	2.622	0.8678	1.045
	2.853	1.0	1.088
	1.756	0.0	0.930
	1.863	0.1393	0.942
	1.997	0.2856	0.954
	2.329	0.5994	1.001
2.1587 (0.9258)	2.509	0.7350	1.029
	2.950	1.0	1.107
	2.268	0.0	0.944
	2.392	0.1393	0.962
	2.545	0.2856	0.982
	2.722	0.4389	1.008
2.8543 (0.8991)	3.139	0.7350	1.079
	3.357	0.8678	1.127
	3.601	1.0	1.189
	3.041	0.0	0.971
	3.398	0.3076	1.027
	3.677	0.5094	1.078
	3.911	0.6576	1.125
	4.117	0.7880	1.184
	4.259	0.8588	1.216
	4.525	1.0	1.306

Table I. Continued

M_r	I	γ_B	Φ
3.0070 (0.8930)	3.210	0.0	0.979
	3.582	0.3076	1.037
	3.870	0.5094	1.090
	4.097	0.6576	1.143
	4.313	0.7880	1.202
	4.713	1.0	1.334
3.1222 (0.8882)	3.338	0.0	0.986
	3.484	0.1359	1.013
	4.009	0.5094	1.101
	4.238	0.6576	1.157
	4.458	0.7880	1.218
	4.854	1.0	1.356
3.5077 (0.8724)	5.782	0.0	1.001
	3.961	0.1359	1.026
	4.181	0.3076	1.071
	4.473	0.5094	1.136
	4.716	0.6576	1.197
	4.929	0.7880	1.268
	5.069	0.8588	1.309
	5.332	1.0	1.421
4.3027 (0.8381)	4.694	0.0	1.044
	4.884	0.1359	1.077
	5.135	0.3076	1.128
	5.449	0.5094	1.207
	5.680	0.6576	1.286
	5.891	0.7880	1.373
	6.007	0.8588	1.430
	6.256	1.0	1.567

where γ_B and Γ_B are the activity coefficients of MgCl_2 in the mixed and pure solutions in isopiestic equilibrium, respectively. Values of a and b are listed in Table II as well as a_w , the activity of water at which the experiments were carried out, and σ , the standard deviation.

2. The second method of analysis used is the neutral-electrolyte treatment of Scatchard⁽¹⁷⁻¹⁹⁾ which leads to the expressions for the Gibbs free energy of mixing. For a mixture of salt A ($\text{KCl} \cdot n\text{NaCl}$), a 1-1 electrolyte, with a salt B of the 1-2 charge type (MgCl_2), the osmotic coefficient Φ is written as

$$(\gamma_A + 1)\Phi = 2\gamma_A\Phi_A^\circ + \gamma_B\Phi_B^\circ + \Delta \quad (3)$$

where

$$\Delta = \beta_0\gamma_A\gamma_B + \beta_1\gamma_A\gamma_B(\gamma_A - \gamma_B) \quad (4)$$

Table II. Constants of Eq. (1)

a	$-b$	a_w	$\sigma \times 10^3$
0.3725	0.0367	0.8381	1.2
0.3209	0.0243	0.8724	1.1
0.3047	0.0326	0.8882	1.4
0.2962	0.0293	0.8930	0.8
0.2817	0.0254	0.8991	1.3
0.2317	0.0265	0.9258	1.1
0.1777	0.0168	0.9428	1.3
0.1721	0.0180	0.9456	0.4
0.0754	0.0124	0.9701	3.2
0.0174	0.0079	0.9895	1.6

in which

$$\beta_0 = b_{01}I + b_{02}I^2 + b_{03}I^3 \quad (5)$$

$$\beta_1 = b_{12}I^2 + b_{13}I^3 \quad (6)$$

The values of the Scatchard coefficient b_{ij} which best reproduced the observed osmotic coefficients of the mixed aqueous solutions of $\text{KCl} \cdot n\text{NaCl} - \text{MgCl}_2$ are $b_{01} = 0.0879$, $b_{02} = -0.0299$, $b_{03} = 0.0031$, $b_{12} = 0.0006$, and $b_{13} = 0$. The standard deviation of Φ is 0.0028.

The mean activity coefficient of MgCl_2 in the mixture is given by the expression⁽¹⁹⁾

$$\ln(\gamma_B/\gamma_B^\circ) = [2(\Phi_A^\circ - 1) - (\Phi_B^\circ - 1) + \beta_0 - \beta_1]y_B + [(B_0 - \beta_0) - 3(B_1 - \beta_1)]y_B^2 + 2(2B_1 - \beta_1)y_B^3 \quad (7)$$

and the calculated values are shown in Table III.

Table III. Calculated Values of Osmotic and Mean Activity Coefficients and Excess Free Energy

I	y_B	Φ	$-\log \gamma$	$\Delta G^E/RT$
1.0	0.0	0.910	0.328	0.0
	0.2	0.914	0.328	0.012
	0.4	0.917	0.328	0.018
	0.6	0.917	0.327	0.018
	0.8	0.913	0.326	0.012
	1.0	0.902	0.324	0.0
1.5	0.0	0.919	0.322	0.0
	0.2	0.929	0.323	0.024
	0.4	0.937	0.323	0.037
	0.6	0.943	0.323	0.037
	0.8	0.947	0.321	0.025
	1.0	0.946	0.319	0.0

Table III. Continued

I	y_B	Φ	$-\log \gamma$	$\Delta G^E/RT$
2.0	0.0	0.933	0.305	0.0
	0.2	0.947	0.308	0.040
	0.4	0.961	0.308	0.060
	0.6	0.974	0.308	0.060
	0.8	0.986	0.306	0.040
	1.0	0.902	0.302	0.0
2.5	0.0	0.950	0.283	0.0
	0.2	0.968	0.286	0.057
	0.4	0.988	0.287	0.085
	0.6	1.008	0.286	0.086
	0.8	1.029	0.283	0.057
	1.0	1.052	0.278	0.0
3.0	0.0	0.970	0.251	0.0
	0.2	0.992	0.255	0.075
	0.4	1.017	0.257	0.113
	0.6	1.044	0.255	0.113
	0.8	1.075	0.251	0.076
	1.0	1.111	0.245	0.0
3.5	0.0	0.992	0.219	0.0
	0.2	1.018	0.223	0.093
	0.4	1.048	0.225	0.141
	0.6	1.082	0.223	0.142
	0.8	1.123	0.218	0.096
	1.0	1.172	0.210	0.0
4.0	0.0	1.014	0.184	0.0
	0.2	1.045	0.189	0.112
	0.4	1.080	0.189	0.170
	0.6	1.122	0.186	0.172
	0.8	1.173	0.180	0.116
	1.0	1.237	0.170	0.0
4.5	0.0	1.035	0.148	0.0
	0.2	1.070	0.151	0.132
	0.4	1.112	0.150	0.200
	0.6	1.163	0.145	0.202
	0.8	1.225	0.137	0.137
	1.0	1.305	0.125	0.0
5.0	0.0	1.051	0.114	0.0
	0.2	1.094	0.114	0.152
	0.4	1.144	0.110	0.231
	0.6	1.204	0.102	0.234
	0.8	1.279	0.091	0.159
	1.0	1.376	0.077	0.0

5. DISCUSSION

The good agreement between the two methods of treating the isopiestic results is illustrated in Table IV. The average deviation in γ^{trace} is 0.007, which is reasonable and within the uncertainty in the McKay-Perring integral term.

Friedman⁽²⁰⁾ has extended Mayer's ionic solution theory⁽²¹⁾ and derived the excess free energy of mixing

$$\Delta G^E(y, I) = RTI^2 y_A y_B [g_0 + g_1(y_A - y_B) + \cdots] \quad (8)$$

where R and T have their usual meaning and the g_i are interaction parameters. On the other hand, the excess free energy of mixing is usually defined as

$$\Delta G^{\text{ex}}(y, I) = G^{\text{ex}}(y, I) - y_A G^{\text{ex}}(0, I) - y_B G^{\text{ex}}(1, I) \quad (9)$$

where $G^{\text{ex}}(0, I)$ and $G^{\text{ex}}(1, I)$ refer to the excess free energy of solutions of the pure salts. It may be shown that Friedman's interaction parameters are given in terms of Scatchard's parameters by

$$g_0 = b_{01} + \frac{1}{2}b_{02}I + \frac{1}{3}b_{03}I^2 \quad (10)$$

$$g_1 = \frac{1}{2}b_{12}I + \frac{1}{3}b_{13}I^2 \quad (11)$$

which permit the calculation of the values of the excess free energies from Eq. (8), which are listed in Table III.

A more direct way of calculating the ΔG^{ex} of our systems makes use of Eq. (16.22) from ref. 20 whereby

$$[\partial(\Delta G^{\text{ex}}/I)/\partial(1/I)]_{p,T,y} = \Delta G_w^{\text{ex}} \quad (12)$$

and ΔG_w^{ex} is the solvent contribution to the excess free energy of mixing and is obviously defined by

$$\Delta G_w^{\text{ex}} = G_w^{\text{ex}}(y, I) - y_A G_w^{\text{ex}}(0, I) - y_B G_w^{\text{ex}}(1, I) \quad (13)$$

Table IV. Values of the Mean Activity Coefficient of MgCl_2 as Obtained by the Scatchard (S) and McKay-Perring (M.P.) Methods

y_B	$I = 1.0$		$I = 2.5$		$I = 4.0$	
	$-\log \gamma$ (S)	$-\log \gamma$ (M.P.)	$-\log \gamma$ (S)	$-\log \gamma$ (M.P.)	$-\log \gamma$ (S)	$-\log \gamma$ (M.P.)
0.0	0.328	0.337	0.283	0.287	0.184	0.174
0.2	0.328	0.335	0.286	0.188	0.188	0.177
0.4	0.328	0.332	0.287	0.285	0.189	0.179
0.6	0.327	0.330	0.286	0.284	0.186	0.179
0.8	0.326	0.329	0.283	0.281	0.180	0.175
1.0	0.324	0.328	0.278	0.278	0.170	0.168

The integration of Eq. (12), at constant y , yields⁽²⁰⁾

$$\Delta G^{\text{ex}}(y, I) = I \int_0^I \Delta G_w^{\text{ex}}(y, I') d(1/I') \quad (14)$$

The difficulty caused by the lower limit of the integral has been overcome,⁽²²⁾ and Friedman's interaction parameters g_i are thus directly obtained from Eq. (14) and compared in Table V with those obtained by Scatchard's procedure. The values of g_0 obtained by the use of both formalisms are in good agreement, but a deviation trend may be seen which increases toward the lower concentration range. The deviation is probably due to the fact that the Scatchard formalism does not take into account the limiting law for asymmetric mixtures⁽²³⁾ where dg_0/dI is positive and which also requires that as $I \rightarrow 0$, g_0 goes to $-\infty$ as $\ln I$, and $g_1 \rightarrow 0$ as \sqrt{I} .⁽²⁴⁾ Model calculations for aqueous MgCl_2 - NaCl mixtures⁽²⁵⁾ have shown that only when $I < 10^{-4} m$ is the asymptotic behavior of the g_i close to their limiting law, but unfortunately there does not seem to be any data for solutions dilute enough to make a comparison of these results.

It should be stressed at this point that the ΔG^{ex} obtained for the excess free energy of the aqueous mixture NaCl - KCl - MgCl_2 were calculated using the pure components MgCl_2 and $(\text{KCl} \cdot n\text{NaCl})$ as reference solutions. In other words, the interaction parameters obtained express the changes incurred when MgCl_2 is added to an aqueous solution of $(\text{KCl} \cdot n\text{NaCl})$.

It has been reported⁽²⁶⁾ that in aqueous mixtures of KCl and NaCl , potassium-potassium and sodium-sodium interactions tend to be replaced by potassium-sodium interactions, as indicated by a negative g_0 . In the

Table V. Values of Friedman's Interaction Parameter g_0 Obtained by Direct Integration (F) and from Scatchard's Coefficient (S)

I	$g_0(\text{S})$	$g_0(\text{F})$	$-g_1(\text{S})$
1.0	0.080	0.099	0.0003
1.5	0.072	0.085	0.0004
2.0	0.066	0.075	0.0006
2.5	0.060	0.067	0.0007
3.0	0.054	0.060	0.0008
3.5	0.050	0.055	0.0010
4.0	0.046	0.050	0.0011
4.5	0.043	0.047	0.0013
5.0	0.041	0.044	0.0014

present case, this leads to strengthening the concept of the pseudo-binary system, which consists of a mixture of a 1-1 electrolyte (characterized by the pair interactions Na-K and Cl-Cl) with a 2-1 electrolyte, MgCl_2 .

The interactions between two ions which contribute to a charge-asymmetric mixture with a common ion has been calculated by Friedman⁽²⁰⁾

$$\begin{aligned}
 -g_{02}/2 = & \left(\frac{B(1, 0, 0)}{Z_1 Z_2 (Z_1 - Z_3)(Z_2 - Z_3)} \right) - \left(\frac{B(2, 0, 0)}{Z_1^2 (Z_1 - Z_2)^2} \right) \\
 & - \left(\frac{B(0, 2, 0)}{Z_2^2 (Z_2 - Z_3)^2} \right) + \frac{Z_1 - Z_2}{Z_3 (Z_1 - Z_3)(Z_2 - Z_3)} \\
 & \times \left| \left(\frac{B(0, 1, 1)}{Z_2 (Z_2 - Z_3)} \right) - \left(\frac{B(1, 0, 1)}{Z_1 (Z_1 - Z_3)} \right) - \left(\frac{(Z_1 - Z_2)B(0, 0, 1)}{Z_3 (Z_1 - Z_3)(Z_2 - Z_3)} \right) \right|
 \end{aligned} \quad (15)$$

where, for a MCl-MgCl_2 mixture,

$$Z_1 = Z(\text{Mg}^{2+}) = +2$$

$$Z_2 = Z(\text{M}^+) = +1$$

$$Z_3 = Z(\text{Cl}^-) = -1$$

The cluster integrals $B(i, j, k)$ are integrals involving (*i*) magnesium ions, (*j*) sodium or potassium ions, and (*k*) chloride ions. Thus, for this kind of mixture all possible pairs contribute.⁽²⁷⁾ For a charge-symmetric mixture, $Z_1 = Z_2$ and only cation-cation pair terms are left, as can be seen in Eq. (15). The effect of triplet formation is more complicated since in general they contribute to both g_1 and g_0 . The values of g_0 as seen in Table V are all positive but decrease with increasing ionic strength I and reflect the increasing effect of the triplet formation contribution and possibly the (+ -) pair association.

It has generally been accepted that in 1-1 electrolyte mixtures like-charge triplet interactions are less important than those of mixed-charge triplets.⁽²⁸⁾ However, for charge-asymmetric mixtures all triplets contribute to the skewness. Since triplet interactions become relatively more important as the concentration increases^(20,29) it is expected that g_1 should be more important at higher ionic strength, and indeed this is the trend presented in Table V. At low concentrations g_1 may be neglected, while starting from $I = 3.0$, it becomes of the same order of magnitude as g_0 .

The values of the excess Gibbs free energies at $I = 1, 3$, and 5 m are approximately given as $\Delta G^{\text{ex}} = 11.8, 68$, and $137\text{ cal}\cdot\text{kg}^{-1}\text{ water}$, respectively. These relatively large values are consistent with those obtained in the systems $\text{H}_2\text{O-NaCl-MCl}_2$, where M represents Ba ,^(15b) Ca ,⁽³⁾ and Mg ,⁽³⁰⁾ and in the

systems $\text{H}_2\text{O}-\text{KCl}-\text{MCl}_2$, where M represents Ca ,⁽³¹⁾ Sr ,⁽³²⁾ and Ba .⁽³³⁾ For the system $\text{H}_2\text{O}-\text{KCl}-\text{MgCl}_2$, however, there are serious discrepancies between the newer data⁽³⁴⁾ and those of Robinson and Stokes as regards the osmotic coefficients of both pure MgCl_2 solutions^(15a) and the mixed electrolyte.⁽³⁵⁾ Consequently, a quantitative comparison of the present data with the predictions of various proposed equations⁽³⁶⁾ is not justified at the moment.

An isopiestic study of the system $\text{H}_2\text{O}-\text{KCl}-\text{MgCl}_2$ is now planned in order to resolve the discrepancies, complement the present study, and permit a comparison with theory. It will be interesting to see then whether mixed triplet interactions $\text{K}^+-\text{Mg}^{2+}-\text{Cl}^-$ are predominant in solutions also containing Na^+ ions, which may culminate in the precipitation of carnallite $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ in saturated solutions. In the present industrial process for the production of carnallite, sodium chloride is first removed, since the Na^+-K^+ interactions may interfere with the precipitation of carnallite.

REFERENCES

1. H. S. Harned and R. A. Robinson, *Multicomponent Electrolyte Solutions* (Pergamon Press, Oxford, 1968).
2. R. A. Robinson, *J. Mar. Biol. Assoc. U.K.* **33**, 449 (1954).
3. R. A. Robinson and J. E. Bower, *J. Res. Nat. Bur. Stand.* **A69**, 365 (1965).
4. R. M. Rush and J. S. Johnson, *J. Chem. Eng. Data* **11**, 590 (1966).
5. A. N. Kirgintsev and A. V. Lukyanov, *Russ. J. Phys. Chem.* **41**, 54 (1967).
6. P. J. Reilly, R. H. Wood, and R. A. Robinson, *J. Phys. Chem.* **75**, 1305 (1971).
7. C. C. Briggs, R. Charlton, and T. H. Lilley, *J. Chem. Thermodyn.* **5**, 445 (1973).
8. R. F. Platford, *J. Solution Chem.* **3**, 771 (1974).
9. R. F. Platford, *J. Solution Chem.* **4**, 37 (1975).
10. R. F. Platford, *J. Mar. Res.* **23**, 55 (1965); R. F. Platford, *J. Fish. Res. Board Can.* **22**, 113 (1965); R. F. Platford and T. Dafoe, *J. Mar. Res.* **23**, 63 (1961).
11. J. M. T. M. Gieskes, *Z. Phys. Chem. N.F.* **50**, 78 (1966).
12. A. Lerman and A. Shatkay, *Earth Planet. Sci. Lett.* **5**, 63 (1968).
13. M. H. Lietzke, R. Shea, and R. W. Stoughton, *J. Tenn. Acad. Sci.* **42**, 122 (1967); M. H. Lietzke, H. B. Hupf, and R. W. Stoughton, *J. Inorgan. Nucl. Chem.* **31**, 3481 (1969); M. H. Lietzke and R. J. Herdclotz, *J. Inorgan. Nucl. Chem.* **33**, 1649 (1971); M. H. Lietzke and C. Daugherty, *J. Inorgan. Nucl. Chem.* **34**, 2233 (1972); M. H. Lietzke and M. D. Danford, *J. Inorgan. Nucl. Chem.* **34**, 3789 (1972).
14. S. Amdur, J. Padova, and A. Schwartz, *J. Chem. Eng. Data* **15**, 47 (1970).
- 15a. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed. (Butterworths, London, 1965).
- 15b. R. A. Robinson and V. E. Bower, *J. Res. Nat. Bur. Stand.* **A69**, 19 (1965).
16. H. A. C. McKay and J. K. Perring, *Trans. Faraday Soc.* **49**, 163 (1953).
17. G. Scatchard, *J. Am. Chem. Soc.* **83**, 2636 (1961).
18. R. M. Rush and J. S. Johnson, *J. Phys. Chem.* **72**, 767 (1968).
19. R. M. Rush, Oak Ridge Nat. Lab. Rep. ORNL-4402 (1969).
20. H. L. Friedman, *Ionic Solution Theory* (Interscience, New York, 1962).
21. J. E. Mayer, *J. Chem. Phys.* **18**, 1426 (1950).
22. D. Rosenzweig and D. Saad, to be published.

23. H. L. Friedman, *Ionic Solution Theory* (Interscience, New York, 1962), p. 246.
24. H. L. Friedman and C. V. Krishnan, *J. Phys. Chem.* **78** 1927 (1974).
25. H. L. Friedman, A. Smitherman, and R. De Santis, *J. Solution Chem.* **2**, 59 (1973).
26. R. A. Robinson, A. K. Covington, and C. P. Bezboruah, *J. Chem. Thermodyn.* **2**, 431 (1970).
27. R. H. Wood, J. D. Patton, and M. Ghamkar, *J. Phys. Chem.* **73**, 346 (1969).
28. H. L. Anderson and R. H. Wood, in *Water, A Comprehensive Treatise*, F. Franks, ed. (Plenum Press, London, 1973), Vol. 3, Chap. 2, p. 119.
29. P. J. Reilly and R. H. Wood, *J. Phys. Chem.* **73**, 4992 (1969); P. J. Reilly and R. H. Wood, *J. Phys. Chem.* **76**, 3473 (1972).
30. R. F. Platford, *J. Phys. Chem.* **72**, 4053 (1968).
31. R. A. Robinson and A. K. Covington, *J. Res. Nat. Bur. Stand.* **72A**, 239 (1968).
32. C. J. Downes, *J. Chem. Thermodyn.* **6**, 317 (1974).
33. R. A. Robinson and V. E. Bower, *J. Res. Nat. Bur. Stand.* **69A**, 439 (1965).
34. A. N. Kirgintsev and A. Lukyanov, *Russ. J. Phys. Chem.* **40**, 686 (1966).
35. R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.* **41**, 752 (1945).
36. G. Scatchard, R. M. Rush, and J. S. Johnson, *J. Phys. Chem.* **74**, 3786 (1970); P. J. Reilly, R. H. Wood, and R. A. Robinson, *J. Phys. Chem.* **75**, 1305 (1971); K. S. Pitzer and J. J. Kim, *J. Am. Chem. Soc.* **96**, 570 (1974); K. S. Pitzer, *J. Solution Chem.* **4**, 250 (1975).