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Re-evaluation of the Thermodynamic Activity Quantities in Aqueous Solutions of Silver Nitrate, Alkali Metal Fluorides and Nitrites, and Dihydrogen Phosphate, Dihydrogen Arsenate, and Thiocyanate Salts with Sodium and Potassium Ions at 25 °C

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ABSTRACT: The Hückel equation used in this study to correlate the experimental activities of dilute solutions of silver nitrate, alkali metal fluorides, and sodium and potassium salts with dihydrogen phosphate, dihydrogen arsenate, and thiocyanate ions up to a molality of about 1.5 $\text{mol}\cdot\text{kg}^{-1}$ contains two parameters being dependent on the electrolyte: B [that is related closely to the ion-size parameter (a^*) in the Debye–Hückel equation] and b_1 (this parameter is the coefficient of the linear term with respect to the molality, and this coefficient is related to hydration numbers of the ions of the electrolyte). In more concentrated solutions of these electrolytes and of alkali metal nitrites in the best case up to a molality of 10 $\text{mol}\cdot\text{kg}^{-1}$, an extended Hückel equation was used; it contains additionally a quadratic term with respect to the molality, and the coefficient of this term is the parameter b_2. All parameter values for the Hückel equations of $AgNO_3$ solutions were determined from the isopiestic data measured by Robinson and Tait for solutions of this salt against KCl solutions (*Trans. Faraday Soc.* **1941**, *37*, 569–570). All Hückel parameters for NaSCN and KSCN, those for NaF and KF, and those for RbF and CsF solutions were determined from the isopiestic data of Robinson (*J. Am. Chem. Soc.* **1940**, *62*, 3131–3132), Robinson (*J. Am. Chem. Soc.* **1941**, *63*, 628–629), and Ti Tien (*J. Phys. Chem.* **1963**, *67*, 532–533), respectively, where these salt solutions were measured against KCl solutions. All Hückel parameters for KH_2PO_4, KH_2AsO_4, and NaH_2AsO_4 solutions were determined from the data of Scatchard and Breckenridge (*J. Phys. Chem.* **1954**, *58*, 596–602) where these salts were measured against NaCl. Also the parameters for the Hückel equation of NaH_2PO_4 were determined from these data, but the parameters of the extended Hückel equation for this salt were obtained from the data of Stokes (*Trans. Faraday Soc.* **1945**, *41*, 685–688) against KCl. The Hückel parameters for concentrated $NaNO_2$ and KNO_2 solutions and for concentrated $LiNO_2$, $RbNO_2$, and $CsNO_2$ solutions were determined from the osmotic coefficients reported by Chekhunova and Protsenko (*Russ. J. Phys. Chem.* **1967**, *41*, 1220–1221) and by Chekhunova et al. (*Russ. J. Phys. Chem.* **1969**, *43*, 1158–1161), respectively. The osmotic coefficients for nitrite solutions were based on direct vapor pressure measurements. In the estimations from the isopiestic data, the Hückel parameters determined recently for NaCl and KCl solutions (*J. Chem. Eng. Data* **2009**, *54*, 208–219) were used. The resulting parameter values were tested with the vapor pressure and isopiestic data existing in the literature for the solutions of these salts. Most of these data support well the recommended Hückel parameters at least up to a molality of 3.0 $\text{mol}\cdot\text{kg}^{-1}$ for all salt solutions considered. Reliable activity and osmotic coefficients for solutions of these electrolytes can, therefore, be calculated by using the new Hückel equations, and they have been tabulated at rounded molalities. The activity and osmotic coefficients obtained from these equations were compared to the values suggested by Robinson and Stokes (*Electrolyte Solutions*, 2nd ed.; Butterworths Scientific Publications: London, 1959), to those calculated by using the Pitzer equations (*Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, 2000; pp 100–101), and to those calculated by using the extended Hückel equations of Hamer and Wu (*J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099). The recommended values for alkali metal nitrites were compared to those obtained by the extended Hückel equations of Staples (*J. Phys. Chem. Ref. Data* **1981**, *10*, 765–777).

INTRODUCTION

In 1949, Robinson and Stokes[1,2] presented tables for activity and osmotic coefficients of electrolytes in aqueous solution at 25 °C, and these tables have been widely accepted and used, for example, in chemical literature. The values of the activity quantities of $AgNO_3$ solutions in these tables have been based on the isopiestic data measured by Robinson and Tait[3] for solutions of this salt and KCl as the reference electrolyte. The values are given up to a molality of 6.0 $\text{mol}\cdot\text{kg}^{-1}$. For NaSCN and KSCN solutions, these values were based on the isopiestic data of Robinson[4] against KCl solutions, and activity values are given for NaSCN solutions up to a molality of 4.0 $\text{mol}\cdot\text{kg}^{-1}$ and for KSCN solutions up to 5.0 $\text{mol}\cdot\text{kg}^{-1}$. Isopiestically against KCl solutions, Robinson[5] has also measured NaF and KF solutions, and values of activity quantities for NaF solutions are given up to 1.0 $\text{mol}\cdot\text{kg}^{-1}$ and for KF solutions up to 4.0 $\text{mol}\cdot\text{kg}^{-1}$. For KH_2PO_4 and NaH_2PO_4 solutions, the activity and osmotic coefficients[1,2] were based on the data of Stokes[6] against KCl solutions, and values are given up to 1.8 $\text{mol}\cdot\text{kg}^{-1}$ for the former solutions and up to 6.0 $\text{mol}\cdot\text{kg}^{-1}$ for the latter. In the tables of

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Table 1. Parameter Values of the Equations of Hamer and Wu[32] (see eqs 7 and 8) for the Electrolytes Considered in This Study at 25 °C

	(B^*)[a]	$10^3\,\beta$	$10^3\,C$	$10^3\,D$	$10^6\,E$	$(m_{\max}/m^\circ)$[b]
$AgNO_3$	0.95	−114.93	10.846	−0.68493	18.73	13
NaF	1.28	−18.000				0.983[c]
KF	1.29	27.845	5.0000	−0.25309	2.679	17.5[c]
RbF	1.198	91.52	−17.980	2.1090		3.5
CsF	1.674	39.269	14.799	−2.3270		3.5
NaH_2PO_4	1.275	−131.56	28.874	−3.5926	194.55	6.5
KH_2PO_4	0.95	−128.76	16.212			1.83[c]
NaH_2AsO_4	1.75	−114.24	17.543			1.3
KH_2AsO_4	1.425	−153.14	29.695			1.3
NaSCN	1.60	44.018	2.9953	−0.14925	−1.0518	18
KSCN	1.30	−1.8501	0.85729			5
$LiNO_2$[d]	1.424	86.51	−2.4043	0.014377		19.9[c]
$NaNO_2$[d]	0.9282	39.21	−4.2095	0.24332	−5.4566	12.34[c]
KNO_2[d]	0.8602	−0.437	−0.2036	0.003219		34.12[c]
$RbNO_2$[d]	0.7672	−1.941	−0.32603	0.0076285	−0.05377	62.30[c]
$CsNO_2$[d]	1.016	2.678	−0.70786	0.021896	−0.24619	36[c]

[a] The unit is $(\mathrm{mol \cdot kg^{-1}})^{-1/2}$. [b] The maximum molality to which the equations apply ($m^\circ = 1\ \mathrm{mol \cdot kg^{-1}}$). [c] The molality of the saturated solution. [d] Determined by Staples.[33]

Table 2. Parameter Values Recommended by Pitzer and Mayorga[9] for the Pitzer Equations (see eqs 9 to 12) of the Electrolytes Considered in This Study at 25 °C

	β^0	β^1	C^ϕ	$(m_{\max}/m^\circ)$[a]
$AgNO_3$	−0.0856	0.0025	0.00591	6
NaF	0.0215	0.2107		1
KF	0.08089	0.2021	0.00093	2
RbF	0.1141	0.2842	−0.0105	3.5
CsF	0.1306	0.2570	−0.0043	3.2
$LiNO_2$	0.1336	0.325	−0.0053	6
$NaNO_2$	0.0641	0.1015	−0.0049	5
KNO_2	0.0151	0.015	0.0007	5
$RbNO_2$	0.0269	−0.1553	−0.00366	5
$CsNO_2$	0.0427	0.060	−0.0051	6
NaH_2PO_4	−0.0533	0.0396	0.00795	6
KH_2PO_4	−0.0678	−0.1042		1.8
KH_2PO_4	−0.101[b]	−0.02[b]	0.017[b]	1.83
NaH_2AsO_4	−0.0442	0.2895		1.2
KH_2AsO_4	−0.0584	0.0626		1.2
NaSCN	0.1005	0.3582	−0.00303	4
KSCN	0.0416	0.2302	−0.00252	5

[a] The maximum molality to which the equations apply ($m^\circ = 1\ \mathrm{mol \cdot kg^{-1}}$). [b] Determined by Partanen et al.[34] from the data of Stokes.[6]

Robinson and Stokes[2] are also given activity values for KH_2AsO_4 and NaH_2AsO_4 solutions up to a molality of 1.2 mol·kg^{-1} on the basis of the isopiestic data against NaCl solutions measured by Scatchard and Breckenridge.[7] The importance of the activities of ref 2 is also reflected by the fact that Pitzer and Mayorga mainly used these values when they determined the parameters of the Pitzer equation[8] for various electrolytes in the famous article[9] on thermodynamics of single electrolytes. In the Pitzer tables (see also ref [10]) are also given the parameters for rubidium and cesium fluorides based on the isopiestic data of Ti Tien[11] against KCl solutions up to a molality of about 3.5 mol·kg^{-1} in both cases. Also in the Pitzer parameter tables[9,10] are given values for alkali metal nitrite solutions based on the osmotic coefficients reported by Chekhunova and Protsenko[12] up to the saturated solutions of $NaNO_2$ (up to 12.25 mol·kg^{-1}) and KNO_2 (34.12 mol·kg^{-1}) and by Chekhunova et al.[13] up to the saturated solutions of $LiNO_2$ (19.90 mol·kg^{-1}), $RbNO_2$ (62.3 mol·kg^{-1}), and $CsNO_2$ (36.0 mol·kg^{-1}). These osmotic coefficient data have been measured by using direct vapor pressure measurements.

In the present study, it is shown that reliable thermodynamic activity values for $AgNO_3$, NaF, KF, RbF, CsF, NaH_2PO_4, KH_2PO_4, NaH_2AsO_4, KH_2AsO_4, NaSCN, and KSCN solutions can also be obtained by such a simple equation as the Hückel equation at least up to a molality of about 1 mol·kg^{-1}. The form of the Hückel equation used in this investigation (see below and, e.g., ref 14) contains two parameters dependent on the electrolyte: B [that is closely related to the ion-size parameter (a^*) in the Debye–Hückel equation] and b_1 (this parameter is the coefficient of the linear term with respect to the molality, and this coefficient is related to the hydration numbers of the ions of the electrolyte). The values of B and b_1 for dilute $AgNO_3$, NaF, KF, NaSCN, and KSCN solutions were determined here from the same isopiestic data set as that used by Robinson and Stokes[2] for each salt. For NaH_2PO_4, KH_2PO_4, NaH_2AsO_4, and KH_2AsO_4 solutions, these parameters were determined from the data of Scatchard and Breckenridge[7] and for RbF and CsF solutions from the data of Ti Tien.[11] The Hückel parameters needed in these estimations (from the isopiestic results) for NaCl or KCl solutions (as in all estimations of the present study) were taken from the results of a previous study[15] where these salt solutions are considered. The resulting parameter values were tested with the data used in the parameter estimations. The parameters for NaH_2PO_4 and KH_2PO_4 solutions were also tested with the isopiestic data of Stokes,[6] and the NaF parameters were tested with the cell potential difference data measured by Ivett and de Vries[16] using a sodium amalgam electrode and a lead amalgam–lead fluoride electrode in NaF solutions.

Additionally, it is shown here that reliable activity values for $AgNO_3$, KF, RbF, CsF, KH_2PO_4, NaH_2PO_4, NaSCN, and KSCN solutions are obtained up to the molalities of (6.5, 9, 3.5, 3.2, 1.8, 4.9, 4.0, and 10) mol·kg^{-1}, respectively, by extending the Hückel equation with a quadratic term with respect to the molality. The coefficient multiplying the quantity m^2 in this term is b_2. The same value for parameter B was used in this extended Hückel equation as that for dilute solutions for each salt. New values of parameters b_1 and b_2 in this extended Hückel equation were then determined for KF, RbF, CsF, KH_2PO_4, NaSCN, and KSCN solutions from the same isopiestic set as that used above in the parameter estimation for dilute solutions, but all points in this set were included in the determination. For $AgNO_3$ solutions, however, only the points of Robinson and Tait[3] where the molality is less than 6.5 mol·kg^{-1} could be included from all points extending up to 13.48 mol·kg^{-1}, and for NaH_2PO_4 solutions, the set of Stokes[6] was used in the parameter estimation instead of that of Scatchard and Breckenbridge.[7]

For $NaNO_2$ and KNO_2 the reported osmotic coefficients of Chekhunova and Protsenko,[12] and for $LiNO_2$, $RbNO_2$, and $CsNO_2$ those of Chekhunova et al.[13] were used in the parameter estimation. Hückel equations were estimated for $LiNO_2$, $NaNO_2$, and $CsNO_2$ solutions, and these equations apply up to molalities of (3.0, 5.0, and 7.0) mol·kg^{-1}, respectively. Extended equations were estimated for $LiNO_2$, KNO_2, and $RbNO_2$ solutions, and these equations apply up to (9.0, 5.0, and 7.0) mol·kg^{-1}, respectively.

The resulting parameters were tested with all isopiestic and vapor pressure data mentioned above, and additionally, the $LiNO_2$, $NaNO_2$, and KNO_2 parameters with the activities of water (see below) reported by Ray and Ogg[17] for solutions of

Table 3. Results from the Parameter Estimation for the Hückel Equations (eqs 1 and 2) of $AgNO_3$, NaSCN, KSCN, NaF, KF, RbF, CsF, KH_2PO_4, NaH_2PO_4, KH_2AsO_4, and NaH_2AsO_4 at 25 °C by Least-Squares Fitting Using eq 13

	$B/(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$	b_1	$s(b_1)$[a]	N[b]	$(m_{\max}/m^{\circ})$[c]	(s_0/Pa)[d]	ref[e]
$AgNO_3$	0.87	−0.2104	0.0013	9	1.275	0.11	3, KCl
NaSCN	1.75	0.0966	0.0014	14	1.374	0.17	4, KCl
KSCN	1.25	0.017	0.003	7	1.035	0.16	4, KCl
NaF	1.25	−0.032	0.003	10	0.9356	0.13	5, KCl
KF	1.16	0.100	0.003	7	1.48	0.27	5, KCl
RbF	1.5	0.1205	0.0014	9	1.052	0.09	11, KCl
CsF	1.6	0.1346	0.0004	9	1.038	0.02	11, KCl
KH_2PO_4	1.0	−0.2814	0.0014	17	0.72163	0.05	7, NaCl
NaH_2PO_4	1.2	−0.249	0.002	13	0.63224	0.06	7, NaCl
NaH_2PO_4	0.89[f]	−0.156[f]	0.002	24	1.16786	0.22	7, NaCl
KH_2AsO_4	0.77	−0.1269	0.0014	25	1.38515	0.21	7, NaCl
NaH_2AsO_4	1.24	−0.137	0.002	24[g]	1.28602	0.24	7, NaCl

[a] The standard deviation of parameter b_1. [b] Number of points included in the estimation. [c] Maximum molality included in the estimation ($m^{\circ} = 1$ mol·kg^{-1}). [d] Standard error between the vapor pressures of water over the tested and reference solutions (see eq 14). [e] The citation number and the reference electrolyte. [f] Recommended value. [g] The point ($m_x = 0.15172$ mol·kg^{-1}, $m_y = 0.11193$ mol·kg^{-1}) was omitted as an outlier.

these salts, the $AgNO_3$, KF, and KSCN parameters with the vapor pressure data of Kangro and Groeneveld,[18] Jakli and Van Hook,[19] and Pearce and Hopson,[20] respectively, the NaH_2PO_4 parameters with the isopiestic data of Scatchard and Breckenridge,[7] the KH_2PO_4 parameters with those of Stokes,[6] the NaSCN parameters with those of Miller and Sheridan[21] against H_2SO_4 solutions, and the KF parameters with those of Tamas and Kosza[22] against H_2SO_4 solutions. Childs et al.[23] have measured isopiestically concentrated NaH_2PO_4 and KH_2PO_4 solutions against NaCl and KCl solutions, and also these data were used in the tests of the NaH_2PO_4 and KH_2PO_4 parameters.

As in ref 15, all tests of this study were performed on the raw experimental results of appropriate measurements to test whether these could be predicted with the Hückel equations. It was observed in these tests that the Hückel equations are very reliable. The activity coefficients of the electrolyte and the osmotic coefficients and vapor pressures of water were calculated using the new Hückel equations at rounded molalities for the electrolyte solutions considered here, and these values are tabulated as recommended values. These activity and osmotic coefficients were compared to those of the previous investigations. Activity coefficient deviations in this comparison are presented as the cell-potential deviations for galvanic cells without a liquid junction (in the same way as in refs 14, 15, and 24), and the osmotic coefficient deviations are presented as vapor pressure deviations (as in refs 15 and 25 to 29).

THEORY

In previous studies, it was found that the following Hückel equations apply very well to the thermodynamic properties of NaCl,[15] KCl,[15] LiCl,[25] RbCl,[26] and CsCl[26] and alkali metal bromide,[27] iodide,[28] and nitrate[29] solutions at least up to the molalities of about 1 mol·kg^{-1}

$$\ln \gamma = -\frac{\alpha\sqrt{m}}{1+B\sqrt{m}} + b_1(m/m^{\circ}) \tag{1}$$

$$\phi = 1 - \frac{\alpha}{B^3 m}\left[(1+B\sqrt{m}) - 2\ln(1+B\sqrt{m}) - \frac{1}{1+B\sqrt{m}}\right] + \frac{1}{2}b_1(m/m^{\circ}) \tag{2}$$

In these equations, m is the molality; γ is the mean activity coefficient on the molality scale; ϕ is the osmotic coefficient of the solvent (symbol 1, water in this case); α is Debye−Hückel parameter [its value at 25 °C is 1.17444 (mol·kg^{-1})$^{-1/2}$; see Archer and Wang[30]]; $m^{\circ} = 1$ mol·kg^{-1}; and the parameters being dependent on the electrolyte are B and b_1. The osmotic coefficient is related to the activity of water (a_1) in pure solutions of a uniunivalent electrolyte by the following thermodynamic identity

$$\ln a_1 = -2mM_1\phi \tag{3}$$

where M_1 is the molar mass of water (= 0.018015 kg·mol^{-1}) and where the activity of water is related to the vapor pressure of water over the solution (p_1) and to the vapor pressure of pure solvent at the temperature under consideration (p_1^*) by the equation

$$a_1 = p_1/p_1^* \tag{4}$$

This equation is not an exact relation, but it is an excellent approximation because, under the studied conditions, the difference between the fugacity and vapor pressure is very small. For water at 25 °C, $p_1^* = 3.1686$ kPa (i.e., 23.766 mmHg, see Kell[31]).

In more concentrated solutions, the following extended Hückel equations were used here as earlier[15,25−29] for the activity and osmotic coefficients

$$\ln \gamma = -\frac{\alpha\sqrt{m}}{1+B\sqrt{m}} + b_1(m/m^{\circ}) + b_2(m/m^{\circ})^2 \tag{5}$$

$$\phi = 1 - \frac{\alpha}{B^3 m}\left[(1+B\sqrt{m}) - 2\ln(1+B\sqrt{m}) - \frac{1}{1+B\sqrt{m}}\right] + \frac{1}{2}b_1(m/m^{\circ}) + \frac{2}{3}b_2(m/m^{\circ})^2 \tag{6}$$

Hamer and Wu[32] suggested the following extended Hückel equations for the activity and osmotic coefficients of uniunivalent electrolytes at 25 °C, and these equations apply often near to the saturated solution of each electrolyte

$$\log(\gamma) = -\frac{A\sqrt{m}}{1+B^*\sqrt{m}} + \beta(m/m^{\circ}) + C(m/m^{\circ})^2 + D(m/m^{\circ})^3 + E(m/m^{\circ})^4 \tag{7}$$

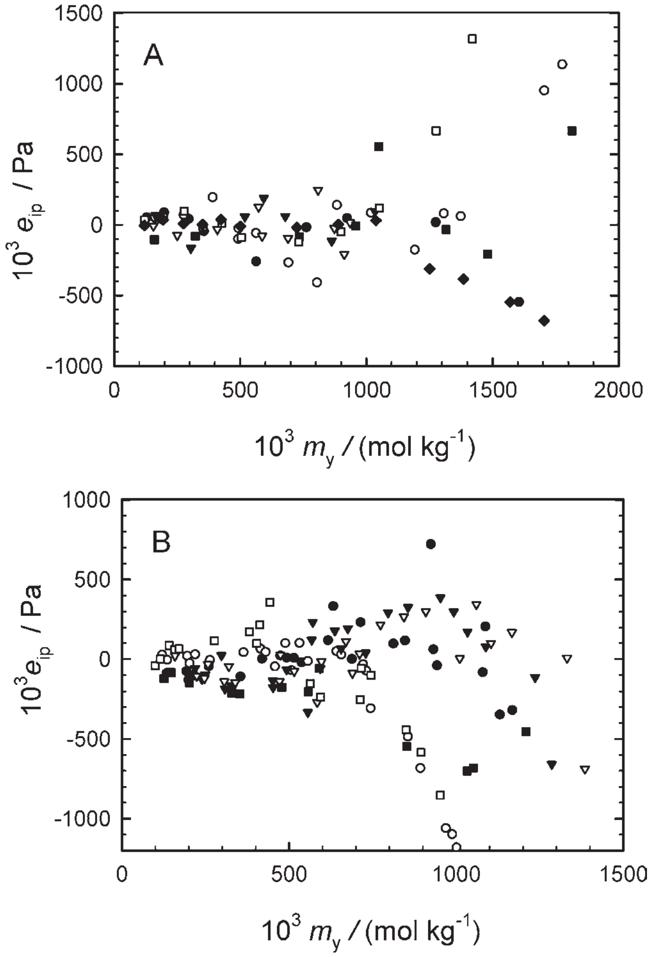

Figure 1. Difference, e_{ip} in eq 15, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the dilute isotonic solutions of NaCl or KCl (x) and of the tested electrolyte (y), see Table 3. The vapor pressures have been calculated by eqs 3 and 4 using eq 2 with $B_{NaCl} = 1.4\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_{1,NaCl} = 0.0716$ or with $B_{KCl} = 1.3\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_{1,KCl} = 0.011$ and with the recommended parameter values shown in Table 3 for the tested electrolytes. Symbols: ●, $AgNO_3$ (graph A), NaH_2PO_4[7] (graph B); ○, NaSCN (A), KH_2PO_4[7] (B); ▼, KSCN (A), NaH_2AsO_4 (B); ▽, NaF (A), KH_2AsO_4 (B); ■, KF (A), NaH_2PO_4[6] (B); □, RbF (A), KH_2PO_4[6] (B); ◆, CsF (A).

$$\phi = 1 - \ln(10)\left\{\frac{A}{(B^*)^3 m}\left[(1 + B^*\sqrt{m}) - 2\ln(1 + B^*\sqrt{m}) - \frac{1}{1 + B^*\sqrt{m}}\right] - \frac{1}{2}\beta(m/m^\circ) - \frac{2}{3}C(m/m^\circ)^2 - \frac{3}{4}D(m/m^\circ)^3 - \frac{4}{5}E(m/m^\circ)^4\right\} \tag{8}$$

where the Debye−Hückel parameter A has a value of 0.5108 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ [$= \alpha/\ln(10)$]. The parameter values of these equations for the electrolytes considered in this study are shown in Table 1. Staples[33] has determined parameter values of alkali metal nitrites for eqs 7 and 8 from the vapor pressure data of Chekhunova and Protsenko,[12] Chekhunova et al.,[13] and Ray and Ogg.[17] These values are also given in Table 1.

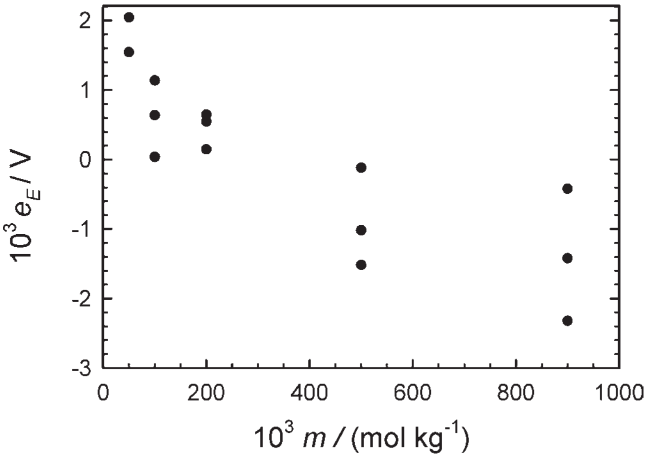

Figure 2. Deviation, e_E in eq 19, between the observed and the predicted cell potential difference (cpd) from the data measured by Ivett and De Vries[16] in NaF solutions on cell 17 (see text) as a function of molality m. The predicted cpd was calculated by using eq 18 where the Hückel equation (eq 1) with the parameter values of $B = 1.25\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.032$ was used for the activity coefficients, and the value of 2.36815 V was used for the standard cpd.

Table 4. Results of the Parameter Estimation for the Extended Hückel Equations (eqs 5 and 6) of $AgNO_3$, NaSCN, KSCN, KF, RbF, CsF, KH_2PO_4, and NaH_2PO_4 at 25 °C by Least-Squares Fitting Using eq 20

	$[B/(m^\circ)^{-1/2}]^a$	b_2	b_1	$s(b_1)^b$	N^c	$(m_{max}/m^\circ)^d$	$(s_0/\text{Pa})^e$	ref
$AgNO_3$	0.87	0.0105	−0.2141	0.0003	33	6.472	1.2	3
NaSCN	1.75	0.0007	0.1033	0.0005	27	3.982	0.7	4
KSCN	1.25	−0.0001	0.0099	0.0004	18	4.925	0.7	4
KF	1.16	0.0037	0.0981	0.0008	18	4.183	0.9	5
RbF	1.5	−0.0105	0.1363	0.0006	23	3.46	0.5	11
CsF	1.6	0.0022	0.1491	0.0007	23	3.175	0.6	11
NaH_2PO_4	0.89	0.0156	−0.1596	0.0004	32	4.868	0.7	6[f]
KH_2PO_4	1.0	0.040	−0.3126	0.0006	28	1.25414	0.09	7

[a] $m^\circ = 1\ \text{mol}\cdot\text{kg}^{-1}$. [b] The standard deviation of parameter b_1. [c] Number of points included in the estimation. [d] The maximum molality of included in the estimation ($m^\circ = 1\ \text{mol}\cdot\text{kg}^{-1}$). [e] Standard error between the vapor pressures of water over the tested and reference solutions (see eq 14). [f] The reference electrolyte is KCl.

For activity coefficients of a uniunivalent electrolyte, the Pitzer equation[8,9] has the form

$$\ln\gamma = f^\gamma + B^\gamma(m/m^\circ) + (3/2)C^\phi(m/m^\circ)^2 \tag{9}$$

where

$$f^\gamma = -\frac{\alpha}{3}\left[\frac{\sqrt{m}}{1 + 1.2\sqrt{m/m^\circ}} + \frac{2\sqrt{m^\circ}}{1.2}\ln(1 + 1.2\sqrt{m/m^\circ})\right] \tag{10}$$

$$B^\gamma = 2\beta^0 + \frac{\beta^1 m^\circ}{2m}\left[1 - e^{-2\sqrt{m/m^\circ}}\left(1 + 2\sqrt{m/m^\circ} - 2\frac{m}{m^\circ}\right)\right] \tag{11}$$

In eqs 9 and 11, β^0, β^1, and C^ϕ are the parameters being dependent on the electrolyte. Pitzer and Mayorga[9] have determined the values

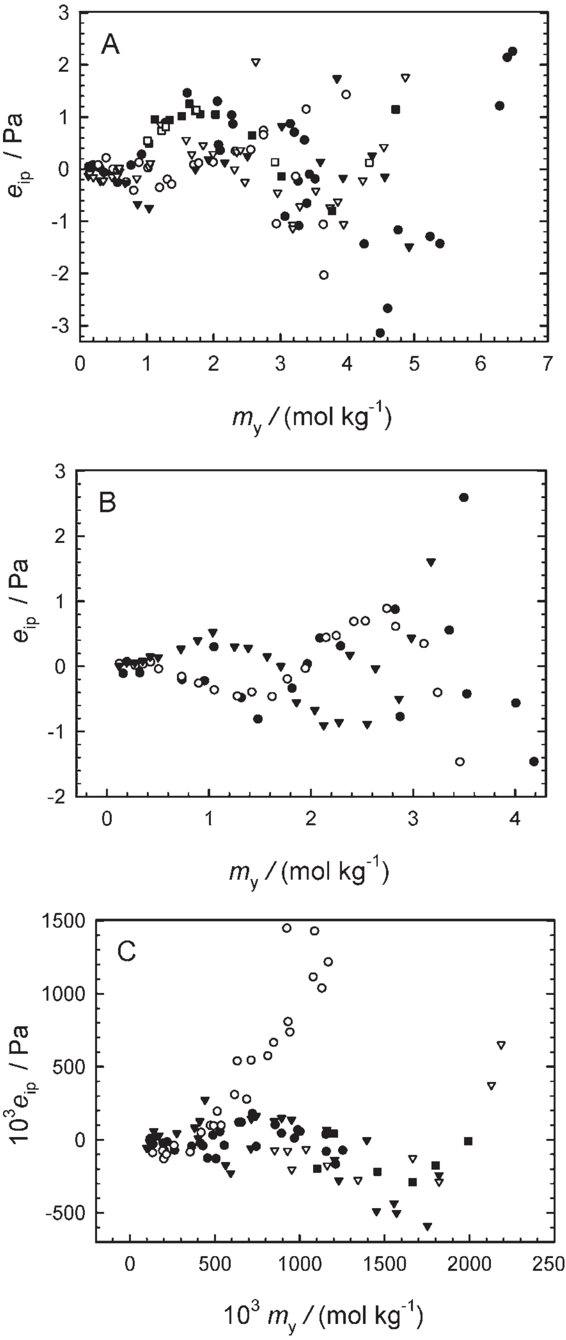

Figure 3. Difference, e_{ip} in eq 15, between the vapor pressure of water over the reference solution (x) and that over the tested solution (y) as a function of the molality of the tested solution (m_y) in the isotonic solutions of NaCl or KCl (x) and of the tested electrolyte (y); see Table 4. The vapor pressures have been calculated by eqs 3 and 4 using eq 6 with $B_{NaCl} = 1.4\ (mol \cdot kg^{-1})^{-1/2}$, $b_{1,NaCl} = 0.0699$, $b_{2,NaCl} = 0.0062$, $B_{KCl} = 1.3\ (mol \cdot kg^{-1})^{-1/2}$, $b_{1,KCl} = 0.01324$, and $b_{2,KCl} = 0.0036$ and with the recommended parameter values shown in Table 4 for the tested electrolytes. For the KH_2PO_4 sets[6,7,23] and for the NaH_2PO_4 set,[7] however, the values of $B_{NaCl} = 1.4\ (mol \cdot kg^{-1})^{-1/2}$, $b_{1,NaCl} = 0.0716$, $B_{KCl} = 1.3\ (mol \cdot kg^{-1})^{-1/2}$, and $b_{1,KCl} = 0.011$ were used. Symbols: ●, $AgNO_3$ (graph A), KF (graph B), KH_2PO_4[7] (graph C); ○, NaSCN (A), RbF (B), NaH_2PO_4[7] (C); ▼, KSCN (A), CsF (B), KH_2PO_4[6] (C); ▽, NaH_2PO_4[6] (A), KH_2PO_4[23] (reference electrolyte KCl, graph C); ■, NaH_2PO_4[23] (NaCl, graph A), KH_2PO_4[23] (NaCl, graph C); □, NaH_2PO_4[23] (KCl, graph A).

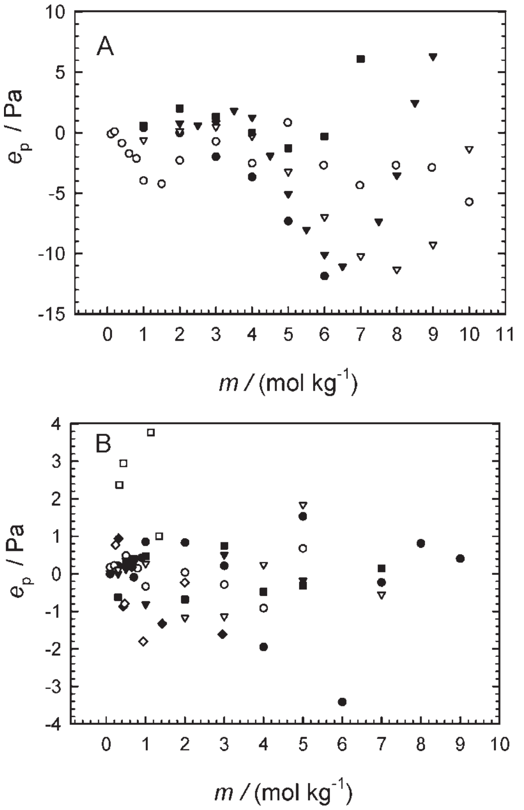

Figure 4. Difference, e_p in eq 21, between the reported and the predicted vapor pressure of water over $AgNO_3$, KF, NaSCN, KSCN, and alkali metal nitrite solutions as a function of the molality m of the solution. The reported vapor pressures were obtained from the data of Pearce and Hopson[20] for KSCN (symbol ○, graph A) solutions and from the data of Kangro and Groenefeld[18] for $AgNO_3$ solutions (■, A), from osmotic coefficients of Miller and Sheridan[21] for NaSCN solutions (symbol ●, graph A), Tamas and Kosza,[22] and Jakli and Van Hook[19] for KF solutions (▼ and ▽, respectively, A), Chekhunova and Protsenko[12] for $NaNO_2$ (○, B) and KNO_2 solutions (▼, B), and Chekhunova et al.[13] for $LiNO_2$ (●, B), $RbNO_2$ (▽, B), and $CsNO_2$ (■, B) solutions, and from the activities of water reported by Ray and Ogg[17] for $LiNO_2$, (□, B), $NaNO_2$ (◆, B), and KNO_2 (◇, B) solutions. The vapor pressures were predicted using eqs 3 and 4 with eq 6 with the recommended parameter values shown in Tables 4 and 6. The points where $m = 0.470\ mol \cdot kg^{-1}$ and $a_1 = 0.9815$ and where $m = 4.640\ mol \cdot kg^{-1}$ and $a_1 = 0.8740$ from the set of Ray and Ogg[17] for KNO_2 solutions were omitted as probable outliers (the errors of these points are −12.7 and 6.4 Pa, respectively).

shown in Table 2 for these parameters for the electrolytes considered here. In this table are also included the values determined in ref 34 for the three-parameter Pitzer equations of KH_2PO_4 from the data of Stokes.[6] For all of these electrolytes, Kim and Frederick[35] and Marshall et al.[36] have also presented Pitzer parameters. These values are not considered here because they were based on the activity and osmotic coefficients tabulated by Hamer and Wu[32] (or on those of Staples[33] for the nitrites) which are included in the present tests. In a very recent study,[37] all of these Pitzer parameter values were tested up to the saturated solutions with several uniunivalent electrolytes, including KH_2PO_4 from the electrolytes considered here. For this electrolyte, the new extended Hückel equation was used in the tests with the parameter values determined here in detail. For osmotic coefficients of water in solutions of a

Table 5. Mean Activity Coefficient Obtained from the Solubility Data for the Saturated Solution of NaF, KH_2PO_4, and KH_2AsO_4 at 25 °C (γ_{obs}) and That Obtained by the Hückel or Extended Hückel Equations with the Recommended Parameter Values (γ_{pred}) for This Solution

	$\Delta_f G^o(\text{cr})$[a]	$\Delta_f G^o(\text{aq})$[b]				$e_{E,GC}$[d]
electrolyte	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	(m_s/m^o)[c]	γ_{obs}	γ_{pred}	mV
NaF	−543.490	−540.680	0.983	0.577	0.576	−0.09
KH_2PO_4	−1415.85	−1413.55	1.8239	0.345	0.329	−2.4
KH_2AsO_4	−1035.90	−1036.45	1.6914	0.66	0.38	−28.9

[a] The standard molar Gibbs energy of formation for the crystalline state. [b] The standard molar Gibbs energy of formation for aqueous solutions at infinite dilution. [c] The molality of the saturated solution ($m^o = 1\ mol\cdot kg^{-1}$). [d] Galvanic cell deviation that has been calculated from equation $e_{E,GC} = -(2RT/F)\ln(\gamma_{obs}/\gamma_{pred})$.

Table 6. Results of the Parameter Estimation for the Hückel or Extended Hückel Equations of Alkali Metal Nitrites at 25 °C by Least-Squares Fitting Using eq 23

	$[B/(m^o)^{-1/2}]$[a]	b_2	b_1	$s(b_1)$[b]	N[c]	(m_{max}/m^o)[d]	(s_0/Pa)[e]	ref
$LiNO_2$	1.6	0	0.1631	0.0005	8	3	0.23	13
$LiNO_2$	1.6	−0.00323[f]	0.1763[f]	0.0003	14	9	1.3	13
$NaNO_2$	1.18	0	0.0324	0.0004	9	5	0.5	12
KNO_2	0.81	0.0012	−0.0111	0.0004	7	5	0.5	12
$RbNO_2$	0.63	−0.0025	0.0258	0.0004	9	7	1.0	13
$CsNO_2$	1.15	0	−0.0078	0.0002	9	7	0.6	13

[a] $m^o = 1\ mol\cdot kg^{-1}$. [b] The standard deviation of parameter b_1. [c] Number of points included in the estimation. [d] The maximum molality of alkali metal nitrite solution included in the estimation ($m^o = 1\ mol\cdot kg^{-1}$). [e] Standard error between the reported and predicted vapor pressures of water (see eq 24). [f] Recommended value.

Table 7. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Silver Nitrate Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
$mol\cdot kg^{-1}$	γ	ϕ	kPa
0.1	0.732	0.904	3.1583
0.2	0.657	0.873	3.1487
0.3	0.607	0.850	3.1396
0.4	0.569	0.832(0.831)	3.1308(3.1309)
0.5	0.539(0.538)	0.816(0.815)	3.1224
0.6	0.513(0.512)	0.801(0.800)	3.1142(3.1143)
0.7	0.490(0.489)	0.787(0.785)	3.1063(3.1065)
0.8	0.470(0.468)	0.775(0.772)	3.0986(3.0989)
0.9	0.452(0.449, −0.27[b])	0.763(0.759)	3.0912(3.0916)
1.0	0.435(0.432, −0.35[b])	0.751(0.746)	3.0840(3.0846)
1.2	0.406(0.402, −0.55[b])	0.730(0.722)	3.0702(3.0712)
1.4	0.381	0.709	3.0572
1.6	0.360	0.691	3.0449
1.8	0.340	0.673	3.0334
2.0	0.323	0.655	3.0224
2.5	0.286	0.616	2.9975
3.0	0.257	0.581	2.9756
3.5	0.233	0.551	2.9561
4.0	0.213	0.524	2.9383
4.5	0.197	0.500	2.9216
5	0.183	0.481	2.9057
5.5	0.171	0.465	2.8897
6.0	0.161	0.452	2.8733
6.5	0.153	0.444	2.8559

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 0.87\ (mol\cdot kg^{-1})^{-1/2}$ and $b_1 = -0.2104$, and the other activity values with the extended Hückel equation with $B = 0.87\ (mol\cdot kg^{-1})^{-1/2}$, $b_1 = -0.2141$, and $b_2 = 0.0105$. [b] Galvanic cell deviation in mV that has been calculated from equation $e_{E,GC} = -(2RT/F)\ln(\gamma(\text{eq } 5)/\gamma(\text{eq } 1))$.

uniunivalent electrolyte, the Pitzer equation has the form

$$\phi = 1 - \frac{\alpha}{3}\frac{\sqrt{m}}{1 + 1.2\sqrt{m/m^o}} + (\beta^0 + \beta^1 e^{-2\sqrt{m/m^o}})(m/m^o) + C^{\phi}(m/m^o)^2 \qquad (12)$$

RESULTS AND DISCUSSION

Determination of Parameters B and b_1 for Dilute Solutions of the Present Electrolytes and Tests of the Resulting Values. The parameter values suggested in ref 15 for the Hückel equation of NaCl [i.e., those of $B = 1.4\ (mol\cdot kg^{-1})^{-1/2}$ and $b_1 = 0.072$] and KCl [$B = 1.3\ (mol\cdot kg^{-1})^{-1/2}$ and $b_1 = 0.011$] seem to apply well up to a molality of about 1.5 $mol\cdot kg^{-1}$. These values together with equation

$$\begin{aligned} f_1 &= \ln a_{1,x} + 2M_1 m_y \\ &\quad - \frac{2\alpha M_1}{B_y^3}\left[(1 + B_y\sqrt{m_y}) - 2\ln(1 + B_y\sqrt{m_y}) - \frac{1}{1 + B_y\sqrt{m_y}}\right] = f_0 - b_{1,y}M_1(m_y^2/m^o) \\ &= f_0 + k_1 m_y^2 \end{aligned} \qquad (13)$$

where $k_1 = -b_{1,y}\,M_1/m^o$ were used in the present study for the estimation of the Hückel parameters for dilute solutions of the electrolytes considered here from the experimental data introduced above. In these determinations, either NaCl or KCl is the reference electrolyte (x) because the activities in its solutions are known. The activity of water in the NaCl or KCl solutions can be calculated from the isopiestic molality of this solution (m_x) using eqs 2 and 3. The other salt is the tested electrolyte (y), and the molality of its isotonic solution with the reference solution is thus regarded as the response variable (m_y). The details of the estimations have been presented in the previous alkali metal bromide paper[27] (see eq 13 and the text associated with this equation in that study). The results of the present estimations are shown in Table 3. The standard error s_0 in this table is defined by the equation

$$s_0 = \sqrt{\sum_{i=1}^{N}(p_{x,i} - p_{y,i})^2/(N - P)} \qquad (14)$$

where N is the number of points and P the number of estimated parameters (now 2).

For NaH_2PO_4 solutions, two equations were estimated here from the data of Scatchard and Breckenridge.[7] The latter equation [with the parameter values of $B = 0.89\ (mol\cdot kg^{-1})^{-1/2}$ and $b_1 = -0.156$] applies quite well to all of these data (i.e., up to molalities of 1.2 $mol\cdot kg^{-1}$), but the fit is not complete for the most

Table 8. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Sodium Thiocyanate Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.796(0.795)	0.942	3.1579
0.2	0.760(0.759)	0.939(0.938)	3.1472(3.1473)
0.3	0.743(0.741)	0.940(0.939)	3.1366
0.4	0.733(0.731)	0.943(0.942)	3.1258(3.1259)
0.5	0.727(0.724)	0.947(0.945)	3.1150(3.1151)
0.6	0.723(0.720, −0.22[b])	0.952(0.950)	3.1041(3.1042)
0.7	0.722(0.718, −0.26[b])	0.957(0.954)	3.0931(3.0933)
0.8	0.722(0.717, −0.30[b])	0.962(0.959)	3.0820(3.0822)
0.9	0.722(0.718, −0.34[b])	0.967(0.964)	3.0708(3.0711)
1.0	0.724(0.719, −0.38[b])	0.973(0.969)	3.0495(3.0599)
1.2	0.729(0.722, −0.46[b])	0.984(0.979)	3.0367(3.0373)
1.4	0.736(0.728,−0.55[b])	0.995(0.989)	3.0135(3.0144)
1.6	0.744	1.006	2.9901
1.8	0.754	1.017	2.9663
2.0	0.764	1.029	2.9422
2.5	0.794	1.058	2.8807
3.0	0.828	1.086	2.8175
3.5	0.866	1.115	2.7528
4.0	0.907	1.145	2.6868

[a] The activity values in parentheses have been calculated with the Hückel equation with B = 1.75 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.966, and the other activity values with the extended Hückel equation with B = 1.75 (mol·kg^{-1})$^{-1/2}$, b_1 =0.1033, and b_2 = 0.0007. [b] Galvanic cell deviation in mV that has been calculated from equation $e_{\mathrm{E,GC}} = -(2RT/F)\ln(\gamma(\text{eq }5)/\gamma(\text{eq }1))$.

dilute points. Therefore, the former equation [with the parameter values of B = 1.2 (mol·kg^{-1})$^{-1/2}$ and b_1 = −0.249] was estimated from these dilute points (i.e., up to 0.63 mol·kg^{-1}). Because the differences in the vapor pressures predicted by these two Hückel equations are very small, the equation with B = 0.89 (mol·kg^{-1})$^{-1/2}$ and b_1 = −0.156 is only considered further here. Dihydrogen and hydrogen phosphate salts are important pH buffer substances, and thus the former values can be more useful for the pH calculations where nowadays often only dilute solutions are considered.

The new Hückel equations suggested in Table 3 can first be tested by predicting the vapor pressures of water over the isotonic solutions of NaCl or KCl and of the tested electrolyte in this table. The vapor pressures of both solutions in every point were calculated by using eqs 2, 3, and 4 with the suggested activity parameters. The results are shown in the two graphs of Figure 1 where the isopiestic vapor pressure error (e_{ip}) is defined by

$$e_{\mathrm{ip}} = p_{\mathrm{x}} - p_{\mathrm{y}} \qquad (15)$$

and presented as a function of the molality m_{y}. In graph A of this figure are given the results for $AgNO_3$, NaSCN, KSCN, NaF, KF, RbF, and CsF solutions. The largest absolute error in these tests is at molalities smaller than 1.4 mol·kg^{-1} less than 0.7 Pa (= 0.005 mmHg). The errors form for all sets a random pattern, and thus the results from these dilute solutions support well the suggested parameter values for all of these electrolytes. In graph B are given the results for NaH_2PO_4, KH_2PO_4, NaH_2AsO_4, and KH_2AsO_4 solutions. In this graph are given, additionally, the results from the sets of Stokes[6] for NaH_2PO_4 and KH_2PO_4 solutions with the recommended parameter values. According to this graph, the parameter values of KH_2PO_4 apply well to the data up to a molality of 0.8 mol·kg^{-1} and the parameter values of the other electrolytes up to a molality of 1.4 mol·kg^{-1}.

Table 9. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Potassium Thiocyanate Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.767(0.768)	0.926	3.1580
0.2	0.715(0.716)	0.912(0.913)	3.1478
0.3	0.685(0.686)	0.905(0.906)	3.1377
0.4	0.663(0.665)	0.901(0.903)	3.1277(3.1276)
0.5	0.647(0.649)	0.899(0.900)	3.1177(3.1176)
0.6	0.634(0.636, +0.21[b])	0.897(0.899)	3.1078(3.1076)
0.7	0.623(0.626, +0.25[b])	0.896(0.898)	3.0978(3.0976)
0.8	0.614(0.617, +0.29[b])	0.895(0.898)	3.0879(3.0877)
0.9	0.606(0.610, +0.32[b])	0.895(0.898)	3.0780(3.0777)
1.0	0.599(0.603, +0.36[b])	0.894(0.898)	3.0681(3.0677)
1.2	0.588(0.593, +0.43[b])	0.895(0.899)	3.0484(3.0478)
1.4	0.579(0.584, +0.51[b])	0.895(0.900)	3.0287(3.0280)
1.6	0.571	0.896	3.0091
1.8	0.565	0.897	2.9895
2.0	0.560	0.898	2.9670
2.5	0.549	0.902	2.9215
3.0	0.541	0.905	2.8733
3.5	0.535	0.909	2.8256
4.0	0.531	0.912	2.7783
4.5	0.527	0.916	2.7314
5	0.525	0.919	2.6851
5.5	0.522	0.923	2.6392
6.0	0.521	0.926	2.5938
6.5	0.519	0.929	2.5490
7.0	0.518	0.932	2.5047
7.5	0.518	0.935	2.4610
8.0	0.517	0.938	2.4178
8.5	0.517	0.941	2.3751
9.0	0.516	0.944	2.3330
9.5	0.516	0.947	2.2915
10.0	0.516	0.950	2.2505

[a] The activity values in parentheses have been calculated with the Hückel equation with B = 1.25 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.0168, and the other activity values with the extended Hückel equation with B = 1.25 (mol·kg^{-1})$^{-1/2}$, b_1 = 0.0099, and b_2 = −0.0001. [b] Galvanic cell deviation in mV that has been calculated from equation $e_{\mathrm{E,GC}} = -(2RT/F)\ln(\gamma(\text{eq }5)/\gamma(\text{eq }1))$.

The estimated Hückel parameters for NaF [i.e., those of B = 1.25 (mol·kg^{-1})$^{-1/2}$ and b_1 = −0.032] can also be tested with cell potential difference (= cpd) data. Ivett and De Vries[16] have measured directly NaF solutions on amalgam cells of the following type

$$\mathrm{Na(Hg}, x)|\mathrm{NaF(aq}, m)|\mathrm{PbF_2(s)}|\mathrm{Pb(Hg, two\ phases)} \qquad (16)$$

where Na(Hg, x) refers to the sodium amalgam electrode. The data consist of five series of measurements, and the mole fraction (x) of sodium in the amalgam was constant in each series and the molality of NaF (m) varied. Altogether 14 points were measured in the molality range from (0.05 to 0.9) mol·kg^{-1}. On the basis

Table 10. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Sodium Fluoride Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.764	0.924	3.1581
0.2	0.709	0.908	3.1479
0.3	0.676	0.899	3.1380
0.4	0.652	0.893	3.1281
0.5	0.633	0.888	3.1183
0.6	0.618	0.884	3.1086
0.7	0.605	0.881	3.0990
0.8	0.594	0.878	3.0894
0.9	0.584	0.876	3.0799
0.983^b	0.576	0.874	3.0720

[a] The activity values have been calculated with the Hückel equation with B = 1.25 (mol·kg^{-1})$^{-1/2}$ and b_1 = −0.032. [b] The molality of the saturated solution.

Table 11. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Potassium Fluoride Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.770	0.928	3.1580
0.2	0.722	0.918	3.1477
0.3	0.695	0.914	3.1374
0.4	0.678	0.914	3.1271
0.5	0.666	0.915	3.1168
0.6	0.658(0.657)	0.918(0.917)	3.1063(3.1064)
0.7	0.652(0.651)	0.921(0.920)	3.0958(3.0959)
0.8	0.647	0.925(0.924)	3.0852(3.0853)
0.9	0.645(0.643)	0.929(0.928)	3.0746(3.0747)
1.0	0.643(0.641)	0.934(0.932)	3.0638(3.0640)
1.2	0.642(0.639)	0.943(0.940)	3.0420(3.0423)
1.4	0.643(0.640, −0.27^b)	0.954(0.950)	3.0198(3.0204)
1.6	0.647(0.642, −0.37^b)	0.965(0.959)	2.9972(2.9981)
1.8	0.652(0.646, −0.49^b)	0.976(0.969)	2.9743(2.9756)
2.0	0.658	0.988	2.9509
2.5	0.679	1.018	2.8909
3.0	0.706	1.051	2.8285
3.5	0.738	1.084	2.7637
4.0	0.774	1.119	2.6966
4.5	0.816	1.156	2.6273
5.0	0.863	1.193	2.5558
5.5	0.915	1.232	2.4824
6.0	0.973	1.272	2.4071
6.5	1.038	1.313	2.3300
7.0	1.110	1.355	2.2514
7.5	1.190	1.398	2.1714
8.0	1.278	1.443	2.0903
8.5	1.377	1.489	2.0083
9.0	1.486	1.536	1.9255

[a] The activity values in parentheses have been calculated with the Hückel equation with B = 1.16 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.100, and the other activity values with the extended Hückel equation with B = 1.16 (mol·kg^{-1})$^{-1/2}$, b_1 =0.0981, and b_2 = 0.0037. [b] Galvanic cell deviation in mV that has been calculated from equation $e_{\mathrm{E,GC}} = -(2RT/F)\ln(\gamma(\text{eq } 5)/\gamma(\text{eq } 1))$.

Table 12. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Rubidium Fluoride Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.788(0.787)	0.938	3.1579
0.2	0.750(0.748)	0.934(0.933)	3.1473(3.1474)
0.3	0.731(0.728)	0.935(0.933)	3.1367(3.1368)
0.4	0.720(0.717, −0.24^b)	0.938(0.936)	3.1261
0.5	0.714(0.710, −0.27^b)	0.942(0.940)	3.1153(3.1154)
0.6	0.710(0.706, −0.29^b)	0.947(0.945)	3.1044(3.1045)
0.7	0.708(0.704, −0.30^b)	0.952(0.950)	3.0934(3.0936)
0.8	0.707(0.703, −0.30^b)	0.957(0.956)	3.0824(3.0825)
0.9	0.708(0.704, −0.29^b)	0.963(0.961)	3.0712(3.0714)
1.0	0.709(0.705, −0.27^b)	0.968(0.967)	3.0600(3.0601)
1.2	0.713(0.710, −0.20^b)	0.979	3.0373(3.0372)
1.4	0.719(0.717)	0.989(0.992)	3.0144(3.0140)
1.6	0.725(0.726)	0.999(1.004)	2.9913(2.9904)
1.8	0.732(0.736, +0.29^b)	1.008(1.017)	2.9681(2.9664)
2.0	0.740	1.017	2.9447
2.5	0.759	1.037	2.8860
3.0	0.778	1.053	2.8276
3.5	0.795	1.066	2.7700

[a] The activity values in parentheses have been calculated with the Hückel equation with B = 1.5 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.1205, and the other activity values with the extended Hückel equation with B = 1.5 (mol·kg^{-1})$^{-1/2}$, b_1 =0.1363, and b_2 = −0.0105. [b] Galvanic cell deviation in mV that has been calculated from equation $e_{\mathrm{E,GC}} = -(2RT/F)\ln(\gamma(\text{eq } 5)/\gamma(\text{eq } 1))$.

Table 13. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Cesium Fluoride Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.793(0.792)	0.941	3.1579
0.2	0.759(0.756)	0.939(0.937)	3.1472(3.1473)
0.3	0.742(0.739, −0.23^b)	0.942(0.939)	3.1365(3.1366)
0.4	0.734(0.730, −0.32^b)	0.946(0.943)	3.1257(3.1258)
0.5	0.730(0.724, −0.40^b)	0.952(0.948)	3.1147(3.1149)
0.6	0.729(0.722, −0.49^b)	0.959(0.954)	3.1036(3.1039)
0.7	0.730(0.722, −0.58^b)	0.966(0.960)	3.0923(3.0928)
0.8	0.732	0.973	3.0809
0.9	0.736	0.981	3.0694
1.0	0.741	0.989	3.0577
1.2	0.752	1.005	3.0339
1.4	0.765	1.021	3.0096
1.6	0.781	1.037	2.9847
1.8	0.798	1.054	2.9593
2.0	0.817	1.070	2.9334
2.5	0.870	1.113	2.8665
3.0	0.930	1.155	2.7966
3.5	0.999	1.199	2.7239

[a] The activity values in parentheses have been calculated with the Hückel equation with B = 1.6 (mol·kg^{-1})$^{-1/2}$ and b_1 = 0.1346, and the other activity values with the extended Hückel equation with B = 1.6 (mol·kg^{-1})$^{-1/2}$, b_1 = 0.1491, and b_2 = 0.0022. [b] Galvanic cell deviation in mV that has been calculated from equation $e_{\mathrm{E,GC}} = -(2RT/F)\ln(\gamma(\text{eq } 5)/\gamma(\text{eq } 1))$.

Table 14. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Sodium Dihydrogen Phosphate Solutions at 25 °C as a Function of the Molality (m)[a]

m / $\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p / kPa
0.1	0.737	0.907	3.1583
0.2	0.666	0.879	3.1486
0.3	0.619	0.860	3.1393
0.4	0.585(0.584)	0.845(0.844)	3.1303
0.5	0.557(0.556)	0.832(0.830)	3.1215(3.1216)
0.6	0.533(0.532)	0.821(0.818)	3.1129(3.1131)
0.7	0.513(0.511, −0.25[b])	0.810(0.807)	3.1045(3.1048)
0.8	0.495(0.492, −0.35[b])	0.801(0.796)	3.0963(3.0967)
0.9	0.479(0.475, −0.47[b])	0.792(0.786)	3.0882(3.0889)
1.0	0.465(0.460, −0.60[b])	0.784(0.776)	3.0803(3.0812)
1.2	0.440	0.770	3.0649
1.4	0.419	0.757	3.0499
1.6	0.401	0.746	3.0353
1.8	0.385	0.736	3.0210
2.0	0.371	0.727	3.0069
2.5	0.342	0.709	2.9726
3.0	0.320	0.697	2.9386
3.5	0.304	0.691	2.9041
4.0	0.291	0.691	2.8683
4.5	0.282	0.696	2.8306
5.0	0.276	0.706	2.7901

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 0.89\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.1557$, and the other activity values with the extended Hückel equation with $B = 0.89\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = -0.1596$, and $b_2 = 0.0156$. [b] Galvanic cell deviation in mV that has been calculated from equation $e_{\text{E,GC}} = -(2RT/F)\ln(\gamma(\text{eq } 5)/\gamma(\text{eq } 1))$.

Table 15. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Potassium Dihydrogen Phosphate Solutions at 25 °C as a Function of the Molality (m)[a]

m / $\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p / kPa
0.1	0.731(0.733)	0.903(0.904)	3.1583
0.2	0.655(0.658, +0.24[b])	0.870(0.872)	3.1488(3.1487)
0.3	0.603(0.607, +0.30[b])	0.846(0.848)	3.1398(3.1397)
0.4	0.563(0.567, +0.31[b])	0.825(0.827)	3.1311
0.5	0.531(0.534, +0.29[b])	0.807(0.808)	3.1229(3.1228)
0.6	0.504(0.506, +0.22[b])	0.791(0.790)	3.1149
0.7	0.480(0.481)	0.776(0.774)	3.1072(3.1074)
0.8	0.459	0.762(0.757)	3.0998(3.1002)
0.9	0.440(0.438, −0.22[b])	0.749(0.741)	3.0926(3.0933)
1.0	0.423(0.420, −0.45[b])	0.737(0.726)	3.0856(3.0868)
1.2	0.394	0.715	3.0721
1.4	0.369	0.696	3.0593
1.6	0.349	0.680	3.0468
1.8	0.331	0.666	3.0346
1.83[c]	0.328	0.664	3.0328

[a] The activity values in parentheses have been calculated with the Hückel equation with $B = 1.00\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.2814$, and the other activity values with the extended Hückel equation with $B = 1.00\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = -0.3126$, and $b_2 = 0.0400$. [b] Galvanic cell deviation in mV that has been calculated from equation $e_{\text{E,GC}} = -(2RT/F)\ln(\gamma(\text{eq } 5)/\gamma(\text{eq } 1))$. [c] The molality of the saturated solution.

Table 16. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Sodium Dihydrogen Arsenate Solutions at 25 °C as a Function of the Molality (m)[a]

m / $\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p / kPa
0.1	0.755	0.918	3.1581
0.2	0.694	0.897	3.1482
0.3	0.654	0.883	3.1385
0.4	0.624	0.871	3.1291
0.5	0.600	0.861	3.1198
0.6	0.579	0.852	3.1108
0.7	0.561	0.844	3.1019
0.8	0.545	0.836	3.0932
0.9	0.530	0.828	3.0847
1.0	0.516	0.820	3.0763
1.2	0.492	0.806	3.0601
1.4	0.470	0.792	3.0445

[a] The activity values have been calculated with the Hückel equation with $B = 1.24\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.1366$.

of their data, Ivett and De Vries reported also the calculated cpd value for each experimental point for the following cell

$$\text{Na(s)}|\text{NaF(aq}, m)|\text{PbF}_2\text{(s)}|\text{Pb(Hg, two phases)} \tag{17}$$

Because only a few points were measured in each sodium amalgam series, the cpd values for cell 17 were used in the present study (despite the fact they are not actual experimental data). The cpd of cell 17 can be calculated from the following equation

$$E = E^{\circ} - (2RT/F)\ln(\gamma m/m^{\circ}) \tag{18}$$

where E° is the standard cpd and it is now independent of x. These data were predicted with the new Hückel equation for NaF, and the resulting error plot is shown in Figure 2. In this plot, the cpd errors were calculated by equation

$$e_{\text{E}} = E(\text{observed}) - E(\text{predicted}) \tag{19}$$

and are presented as a function of the molality. The best value of E° was used in the calculation of the errors, and this value is 2.36815 V. According to this figure, the lead−lead fluoride electrode data support at least satisfactorily the suggested Hückel equation for NaF solutions.

Determination of Parameters b_1 and b_2 for More Concentrated Solutions of the Present Electrolytes and Tests of the Resulting Values. The parameter values suggested in ref 15 for the extended Hückel equation of NaCl [i.e., those of $B = 1.4\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.0699$, and $b_2 = 0.0062$] and KCl [$B = 1.3\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.01324$, and $b_2 = 0.0036$] seem to apply well up to the saturated solutions (i.e., up to 6.14 and 4.80

Table 17. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Potassium Dihydrogen Arsenate Solutions at 25 °C as a Function of the Molality (m)[a]

m $\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p kPa
0.1	0.732	0.905	3.1583
0.2	0.660	0.876	3.1487
0.3	0.612	0.856	3.1394
0.4	0.577	0.840	3.1305
0.5	0.548	0.826	3.1218
0.6	0.524	0.814	3.1133
0.7	0.503	0.803	3.1051
0.8	0.485	0.793	3.0970
0.9	0.469	0.783	3.0891
1.0	0.454	0.774	3.0814
1.2	0.427	0.757	3.0665
1.4	0.405	0.741	3.0523

[a] The activity values have been calculated with the Hückel equation with $B = 0.77\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.1269$.

$\text{mol}\cdot\text{kg}^{-1}$, respectively). These values together with equation

$$f_2 = \ln a_{1,x} + 2M_1 m_y - \frac{2\alpha M_1}{{B_y}^3}\left[(1 + B_y\sqrt{m_y}) - 2\ln(1 + B_y\sqrt{m_y}) - \frac{1}{1 + B_y\sqrt{m_y}}\right] + \frac{4M_1 b_{2,y} {m_y}^3}{3(m^\circ)^2} = f_0 - b_{1,y}M_1(m_y^2/m^\circ) = f_0 + k_2 m_y^2 \tag{20}$$

where $k_2 = -b_{1,y}M_1/m^\circ$ were used in the present study for the estimation of the Hückel parameters for more concentrated $AgNO_3$, NaSCN, KSCN, KF, RbF, CsF, NaH_2PO_4, and KH_2PO_4 solutions. In these determinations, NaCl or KCl is again the reference electrolyte (x), and the values of parameter B_y were taken from Table 3. When parameter $b_{2,y}$ has been fixed, eq 20 represents an equation of a straight line f_2 versus m_y^2. The straight line should go through the origin, and therefore, parameter $b_{2,y}$ must be determined again so that the value of intercept f_0 is zero.

For NaH_2PO_4 solutions, the isopiestic data of Stokes[6] up to a molality of 4.868 $\text{mol}\cdot\text{kg}^{-1}$ were used in the parameter estimation. Thus 32 (out of 37) points could be included in this estimation. For the other electrolytes the same isopiestic sets were used in these parameter estimations as those used for eq 13 (see Table 3), but all data were included in the estimation, except for the $AgNO_3$ solutions where only the molalities less than 6.5 $\text{mol}\cdot\text{kg}^{-1}$ could be included. In the calculation of the KH_2PO_4 parameters, the Hückel equation with parameters $B = 1.4\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0716$ was used for the reference electrolyte (NaCl) because this set[7] consists of only dilute solutions. The results of all calculations are shown in Table 4. The resulting parameter values were first tested by predicting the vapor pressures in the sets used in the estimations. The vapor pressures of both solutions in each isotonic point of these sets can be calculated using eqs 3, 4, and 6 with the recommended activity parameters (in the KH_2PO_4 calculations, eq 2 was used instead of eq 6 for the NaCl solutions). The results are shown in three graphs of Figure 3 where the isopiestic vapor pressure error (defined by eq 15) is presented as a function of the molality m_y. In graph A are shown the results for $AgNO_3$, NaSCN, KSCN, and NaH_2PO_4 solutions, in graph B for KF, RbF, and CsF solutions, and in graph C for KH_2PO_4 solutions. Almost all absolute errors in these tests are less than 2.7 Pa (= 0.02 mmHg), and the experimental data thus support well the recommended parameter values.

Table 18. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Lithium Nitrite Solutions at 25 °C as a Function of the Molality (m)[a]

m $\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	p kPa
0.1	0.795	0.943	3.1579
0.2	0.763	0.941	3.1472
0.3	0.748	0.945	3.1364
0.4	0.741	0.951	3.1255
0.5	0.739	0.958	3.1144
0.6	0.740	0.966	3.1031
0.7	0.742	0.974	3.0917
0.8	0.746	0.982	3.0802
0.9	0.751	0.990	3.0685
1.0	0.757	0.999	3.0566
1.2	0.771	1.016	3.0325
1.4	0.787	1.033	3.0078
1.6	0.805	1.049	2.9826
1.8	0.824	1.066	2.9569
2.0	0.844	1.083	2.9307
2.5	0.900	1.124	2.8635
3.0	0.961	1.164	2.7941
3.5	1.028	1.202	2.7228
4.0	1.099	1.240	2.6501
4.5	1.175	1.276	2.5763
5	1.255	1.311	2.5019
5.5	1.340	1.345	2.4270
6.0	1.429	1.378	2.3522
6.5	1.522	1.410	2.2775
7.0	1.619	1.441	2.2033
7.5	1.721	1.470	2.1298
8.0	1.827	1.498	2.0573
8.5	1.936	1.526	1.9859
9.0	2.050	1.552	1.9158

[a] The activity values have been calculated with the extended Hückel equation with $B = 1.6\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.1763$, and $b_2 = -0.00323$.

The recommended NaH_2PO_4 and KH_2PO_4 parameters in Table 4 can further be tested with the isopiestic data reported by Scatchard and Breckenbridge[7] for solutions of NaH_2PO_4, by Stokes[6] for solutions of KH_2PO_4 and by Childs et al.[23] for solutions of both of these electrolytes. In the last study, both NaCl and KCl were used as the reference electrolytes. The tests with these data are shown as e_{ip} error plots (see eq 15) in graphs A (the results from ref 23 for NaH_2PO_4) and C (the other results) of Figure 3, and these plots correspond exactly with the other plots in this figure. Again in the calculation of the KH_2PO_4 results and the NaH_2PO_4 results from ref 7, the two-parameter Hückel equations were used for NaCl and KCl. In graph A for the NaH_2PO_4 data of Childs et al.,[23] four points for the most con-

Table 19. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Sodium Nitrite Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.765	0.925	3.1581
0.2	0.714	0.912	3.1479
0.3	0.683	0.905	3.1377
0.4	0.662	0.902	3.1277
0.5	0.646	0.900	3.1177
0.6	0.634	0.899	3.1076
0.7	0.624	0.898	3.0976
0.8	0.616	0.899	3.0876
0.9	0.609	0.899	3.0776
1.0	0.603	0.900	3.0675
1.2	0.593	0.902	3.0474
1.4	0.586	0.905	3.0273
1.6	0.580	0.908	3.0071
1.8	0.576	0.911	2.9869
2.0	0.573	0.914	2.9666
2.5	0.567	0.923	2.9158
3.0	0.565	0.932	2.8649
3.5	0.565	0.941	2.8139
4.0	0.566	0.951	2.7629
4.5	0.568	0.961	2.7118
5.0	0.571	0.969	2.6609

[a] The activity values have been calculated with the Hückel equation with $B = 1.18\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = 0.0324$.

Table 20. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Potassium Nitrite Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.743	0.912	3.1582
0.2	0.679	0.890	3.1484
0.3	0.638	0.876	3.1387
0.4	0.609	0.866	3.1293
0.5	0.587	0.859	3.1199
0.6	0.568	0.853	3.1107
0.7	0.553	0.849	3.1015
0.8	0.539	0.845	3.0924
0.9	0.528	0.842	3.0833
1.0	0.517	0.839	3.0743
1.2	0.500	0.834	3.0564
1.4	0.485	0.830	3.0386
1.6	0.473	0.828	3.0210
1.8	0.462	0.825	3.0035
2.0	0.453	0.823	2.9861
2.5	0.434	0.820	2.9429
3.0	0.419	0.819	2.9003
3.5	0.408	0.818	2.8580
4.0	0.398	0.818	2.8161
4.5	0.390	0.819	2.7745
5.0	0.383	0.821	2.7331

[a] The activity values have been calculated with the extended Hückel equation with $B = 0.81\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $b_1 = -0.0111$, and $b_2 = 0.0012$.

Table 21. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Rubidium Nitrite Solutions at 25 °C as a Function of the Molality (m)[a]

m			p
mol·kg^{-1}	γ	ϕ	kPa
0.1	0.736	0.907	3.1583
0.2	0.667	0.882	3.1485
0.3	0.625	0.867	3.1390
0.4	0.594	0.856	3.1297
0.5	0.570	0.848	3.1205
0.6	0.551	0.842	3.1114
0.7	0.534	0.837	3.1024
0.8	0.521	0.833	3.0934
0.9	0.509	0.829	3.0845
1.0	0.498	0.826	3.0756
1.2	0.480	0.822	3.0580
1.4	0.465	0.819	3.0404
1.6	0.453	0.816	3.0230
1.8	0.442	0.814	3.0057
2.0	0.433	0.813	2.9884
2.5	0.414	0.810	2.9456
3.0	0.399	0.808	2.9035
3.5	0.387	0.807	2.8620
4.0	0.377	0.806	2.8213
4.5	0.368	0.804	2.7814
5.0	0.359	0.802	2.7425
5.5	0.352	0.799	2.7046
6.0	0.344	0.796	2.6678
6.5	0.337	0.792	2.6323
7.0	0.331	0.787	2.5980

[a] The activity values have been calculated with the extended Hückel equation with $B = 0.63\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $b_1 = 0.0258$, and $b_2 = -0.0025$.

centrated solutions (i.e., above the molality of 5.5733 mol·kg^{-1}) do not support the model, and these errors lay outside the range of the graph. In graph C it can be seen that the parameters for the extended Hückel equation of NaH_2PO_4 do not explain very well the data of Scatchard and Breckenbridge[7] (used above in the estimation of the Hückel parameters for dilute solutions, see Table 3). Otherwise, all new results in these graphs support quite well the recommended parameter values, and the KH_2PO_4 parameters apply thus up to the saturated solution where m = 1.83 mol·kg^{-1}. The set of Childs et al.[23] contains also some data from supersaturated solutions, and the new parameters apply also to these data.

The recommended parameters for NaSCN were additionally tested with the osmotic coefficients reported by Miller and Sheridan[21] for concentrated NaSCN solutions and by Tamas and Kosza[22] and Jakli and Van Hook[19] for concentrated KF solutions. The NaSCN data start at a molality of 1 mol·kg^{-1} and extend up to 18 mol·kg^{-1}, and the former KF data start at 2 mol·kg^{-1} and extend up to the molality of the saturated solution (i.e., to 17.5 mol·kg^{-1}). Both data sets were based on isopiestic measurements against H_2SO_4 solutions. The osmotic coefficients for KF solutions reported by Jakli and Van Hook[19] were based on vapor pressure measurements at various temperatures from (3.404 to 84.182) °C at molalities of (3, 6, 9, and 12)

Table 22. Recommended Activity Coefficient (γ), Osmotic Coefficient (ϕ), and Vapor Pressure of Water (p) in Aqueous Cesium Nitrite Solutions at 25 °C as a Function of the Molality (m)[a]

m mol·kg^{-1}	γ	ϕ	p kPa
0.1	0.761	0.922	3.1581
0.2	0.706	0.906	3.1480
0.3	0.672	0.898	3.1380
0.4	0.648	0.892	3.1281
0.5	0.630	0.886	3.1183
0.6	0.615	0.885	3.1086
0.7	0.603	0.882	3.0989
0.8	0.592	0.880	3.0892
0.9	0.583	0.879	3.0796
1.0	0.575	0.877	3.0700
1.2	0.561	0.875	3.0509
1.4	0.549	0.874	3.0320
1.6	0.539	0.872	3.0132
1.8	0.531	0.872	2.9945
2.0	0.523	0.871	2.9759
2.5	0.507	0.869	2.9299
3.0	0.495	0.868	2.8847
3.5	0.485	0.868	2.8402
4.0	0.476	0.867	2.7965
4.5	0.468	0.866	2.7535
5.0	0.461	0.865	2.7112
5.5	0.455	0.865	2.6697
6.0	0.449	0.864	2.6288
6.5	0.444	0.863	2.5887
7.0	0.439	0.862	2.5493

[a] The activity values have been calculated with the Hückel equation with $B = 1.15\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.0078$.

mol·kg^{-1} and smoothed values at 25 °C are reported from a molality of (1 to 12) mol·kg^{-1}. The NaSCN and KF parameters were tested with these data by predicting the observed vapor pressures (calculated from the reported osmotic coefficients by using eqs 3 and 4) with these parameter values. The results are shown in graph A of Figure 4 where the vapor pressure error (e_p) is defined by

$$e_p = p(\text{observed}) - p(\text{predicted}) \tag{21}$$

and presented as function of the molality m. The points of the NaSCN set support quite well the recommended parameter values up to 4 mol·kg^{-1}. For KF solutions, the points from both sets support well the suggested parameter values up to 5 mol·kg^{-1} and satisfactorily up to 9 mol·kg^{-1}. The recommended parameters for KSCN were additionally tested with the vapor pressure data of Pearce and Hopson.[20] These data extend up to a molality of 10 mol·kg^{-1}. The older value of 23.752 mmHg was used in this case for the vapor pressure of pure water (i.e., the same as that in the original paper). The results of these tests are shown as vapor pressure errors (see eq 21) in graph A of Figure 4. All of these data support quite well the suggested parameter values for KSCN solutions. The recommended parameters for $AgNO_3$ were finally tested with the vapor pressure data of Kangro and Groeneveld.[18] These data extend up to a molality of 15 mol·kg^{-1}. The older value of 23.756 mmHg was used in this case for the vapor pressure of pure water (i.e., the same value as that in the original paper). Also these results are shown as vapor pressure errors (see eq 21) in graph A of Figure 4. These data support well the suggested parameter values for $AgNO_3$ solutions up to a molality of 6 mol·kg^{-1}.

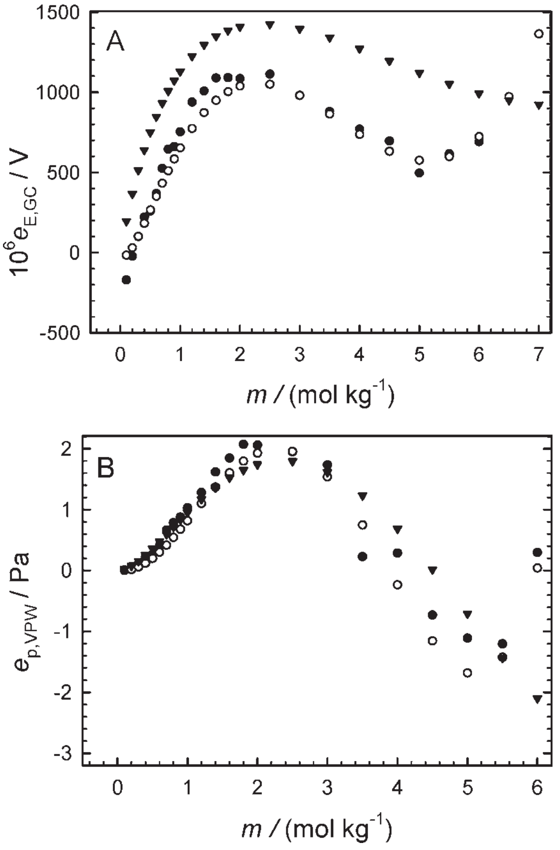

Figure 5. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for $AgNO_3$ solutions as a function of the molality m (see Table 7). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[32] ▼, Pitzer and Mayorga.[9]

The new parameter values for the Hückel equations of NaF, KH_2PO_4, and KH_2AsO_4 probably apply up to the saturated solutions. Therefore, these values can also be tested with solubility data. The NBS tables of thermodynamic properties[38] give the values shown in Table 5 for the standard molar Gibbs energy of formation for the crystalline state [$\Delta_f G^\circ(\text{cr})$] and for aqueous solutions at infinite dilution [$\Delta_f G^\circ(\text{aq})$] at 25 °C for these three salts. These values are related to the solubility product (K_{sp}), to the molality of the saturated solution (m_s), and to the mean activity coefficient of that solution by equation

$$-RT \ln K_{sp} = -2RT \ln(\gamma m_s/m^\circ) = \Delta_f G^\circ(\text{aq}) - \Delta_f G^\circ(\text{cr}) \tag{22}$$

In this table are shown the observed activity coefficients (obtained using eq 22) and those predicted with the new Hückel equations for NaF and KH_2AsO_4 solutions and with the extended Hückel equation for KH_2PO_4 solutions. The molalities of

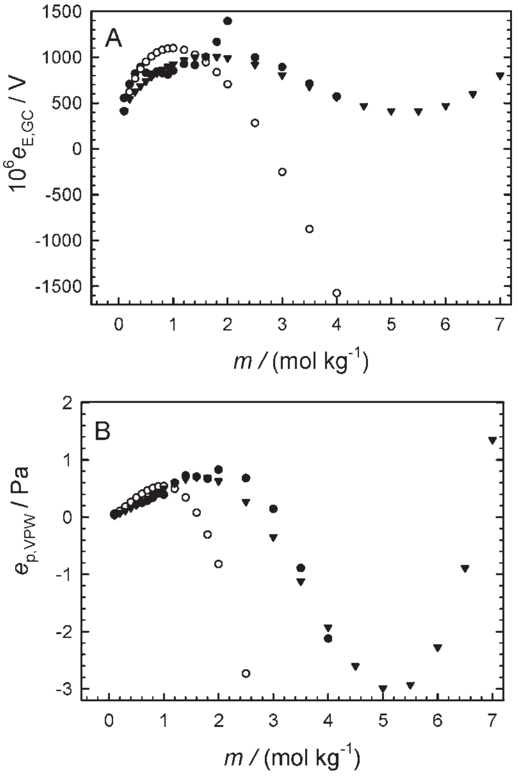

Figure 6. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for NaSCN solutions as a function of the molality m (see Table 8). The deviations where m is greater than 2.5 mol·kg^{-1} lie outside the scale of graph B for the equation of Hamer and Wu. At molalities of (3, 3.5, and 4) mol·kg^{-1}, their values are (−5.6, −9.4, and −14.1) Pa, respectively. Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[32] ▼, Pitzer and Mayorga.[9]

the saturated solution of these salts were taken from ref 39. The observed and predicted activity coefficients correspond well to each other for NaF solutions, satisfactorily for KH_2PO_4 solutions, but poorly for KH_2AsO_4 solutions. In the last case, the predicted value seems to be more reliable because of the experimental evidence obtained with the reported osmotic coefficients of Scatchard and Breckenbridge[7] (see Figure 1B).

In Table 6 are shown the parameter values for the Hückel equations that were obtained from the experimental osmotic coefficients reported by Chenkunova et al. for $LiNO_2$,[13] $NaNO_2$,[12] KNO_2,[12] $RbNO_2$,[13] and $CsNO_2$[13] solutions. These values were estimated from the following equation:

$$f_3 = \ln a_{1,\mathrm{exptl}} + 2M_1 m - \frac{2\alpha M_1}{B^3}\left[(1+B\sqrt{m}) - 2\ln(1+B\sqrt{m}) - \frac{1}{1+B\sqrt{m}}\right] + \frac{4M_1 b_2 m^3}{3(m^\circ)^2} = f_0 - b_1 M_1 (m^2/m^\circ) \qquad (23)$$

where $a_{1,\mathrm{exptl}}$ was calculated from the reported osmotic coefficient using eq 3 and otherwise this equation was used as eq 13 or 20 except that both parameters B and b_2 were estimated from the same set. Parameter B was first estimated using eq 23 without the term containing parameter b_2 from the data of dilute solutions,

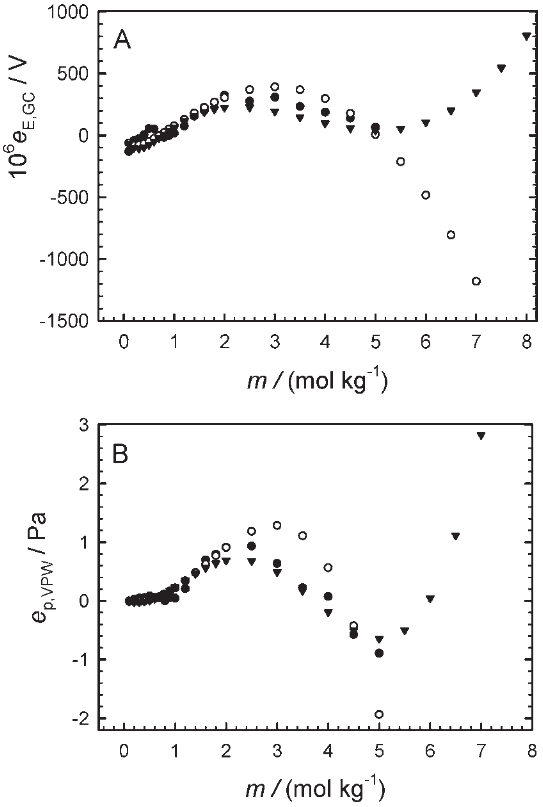

Figure 7. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for KSCN solutions as a function of the molality m (see Table 9). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[32] ▼, Pitzer and Mayorga.[9]

and parameter b_2 was then estimated with this B value by using the full eq 23 from all data that could be used in the estimation. The standard error s_0 in this table for the alkali metal nitrite sets was calculated from equation

$$s_0 = \sqrt{\sum_{i=1}^{N} (p_{i,\mathrm{obsd}} - p_{i,\mathrm{pred}})^2/(N-P)} \qquad (24)$$

which corresponds to eq 14 and where the observed vapor pressure was calculated from the reported osmotic coefficient. For $LiNO_2$, two sets of parameter values are shown in Table 6. In the first set, the value of parameter b_2 was thus set equal to zero, and the resulting two-parameter Hückel equation applies up to a molality of 3.0 mol·kg^{-1}. In the second set, the value obtained in this first parameter estimation for B [= 1.6 (mol·kg^{-1})$^{-1/2}$] was accepted, and new values for b_1 and b_2 were determined for the three-parameter extended Hückel equation. The resulting equation applies up to a molality of 9.0 mol·kg^{-1}. In the subsequent consideration, the extended Hückel equation for $LiNO_2$ was only used. It was observed in the parameter estimations for $NaNO_2$ and $CsNO_2$ that parameter b_2 can be omitted, and the resulting Hückel equations apply to very concentrated solutions, that is, up to (5 and 7) mol·kg^{-1}, respectively.

The parameter values shown in Table 6 were first tested by predicting the experimental vapor pressures (calculated from the reported osmotic coefficients) used in the estimations by using

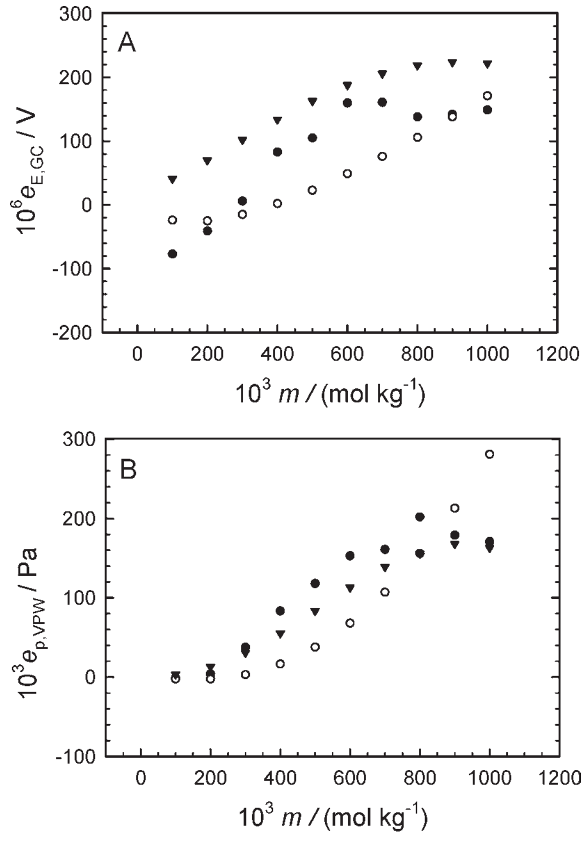

Figure 8. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 1, graph A) and deviation, expressed as vapor pressure error $e_{p,VDW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 2, graph B) for NaF solutions as a function of the molality m (see Table 10). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[32] ▼, Pitzer and Mayorga.[9]

these values. The results are in graph B of Figure 4 where the vapor pressure error (see eq 21) is presented for each set as a function of the molality m. The largest absolute error in these tests at the molalities used in the estimations is less than about 2.7 Pa (= 0.02 mmHg). The errors form for all sets a random pattern, and thus the results from these alkali metal nitrite solutions support well the suggested parameter values. The new Hückel parameters for $LiNO_2$, $NaNO_2$, and KNO_2 in Table 6 were then tested with the activities of water (see eq 4) reported by Ray and Ogg[17] for the solutions of these salts. These activities were based on direct vapor pressure measurements. The results are shown in graph B of Figure 4. From the reported activities, the vapor pressures of water were calculated using eq 4, and the vapor pressure errors were then obtained using eq 21 and presented in this figure as a function of the molality. All vapor pressures from the data of Ray and Ogg[17] for $NaNO_2$ and KNO_2 solutions support quite well the suggested Hückel equations for these electrolytes up to a molality of 3 mol·kg^{-1}, but for $LiNO_2$ solutions, a satisfactory agreement is obtained only up to 1.3 mol·kg^{-1}. This $LiNO_2$ set contains additionally five points from (2.74 to 8.76) mol·kg^{-1}, but these points do not support at all the new models determined from the data of ref 13.

Recommended Activity and Osmotic Coefficients at 25 °C. Because of the experimental evidence indicated in the tests of the present study (see Figures 1 to 4), the new Hückel equations for dilute solutions and the new extended Hückel equations for more concentrated solutions are very reliable. New tables for the activity and osmotic coefficients of the present electrolytes at 25 °C have been calculated on the basis of these equations. For $AgNO_3$ the new values are given in Table 7, for NaSCN in Table 8, for KSCN in Table 9, for NaF in Table 10, for KF in Table 11, for RbF in Table 12, for CsF in Table 13, for NaH_2PO_4 in Table 14, for KH_2PO_4 in Table 15, for NaH_2AsO_4 in Table 16, for KH_2AsO_4 in Table 17, for $LiNO_2$ in Table 18, for $NaNO_2$ in Table 19, for KNO_2 in Table 20, for $RbNO_2$ in Table 21, and for $CsNO_2$ in Table 22. Also the vapor pressures of water are included in the tables.

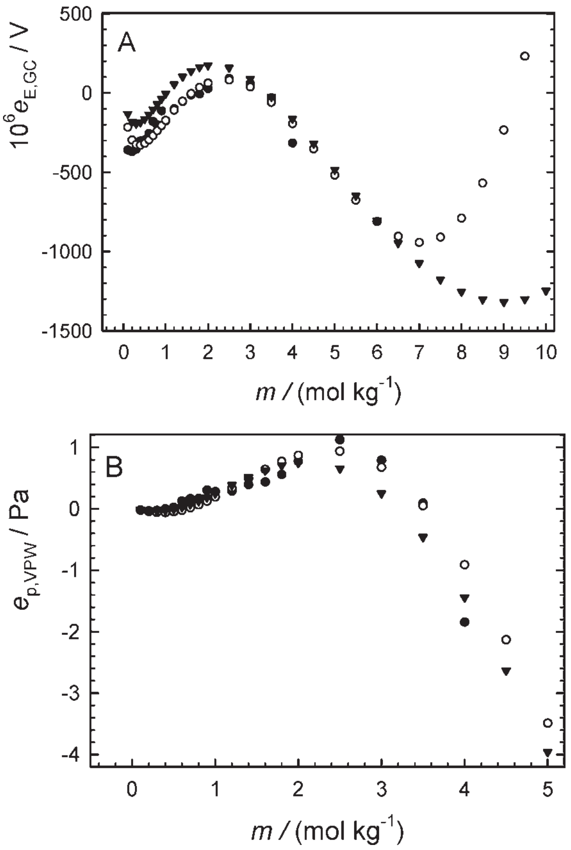

Figure 9. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for KF solutions as a function of the molality m (see Table 11). The deviations for graph B for the equation of Hamer and Wu at the molalities of (6, 7, 8, 9, and 10) mol·kg^{-1} are (−6.0, −6.9, −4.7, +2.1, and +7.6) Pa, respectively. Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[32] ▼, Pitzer and Mayorga.[9]

The values of the activity quantities in these tables have been calculated by using the parameter values suggested for the extended Hückel equations except for those electrolytes for which only the Hückel equation was determined. In dilute solutions (i.e., in most cases when m is less than about 1.5 mol·kg^{-1}), the values obtained with the suggested Hückel equations are given in parentheses when they differ from those presented in the tables. The absolute difference between these two values is always quite small. It is less than 0.6 mV for the galvanic cell deviation for γ (the definition will be given below) and less than

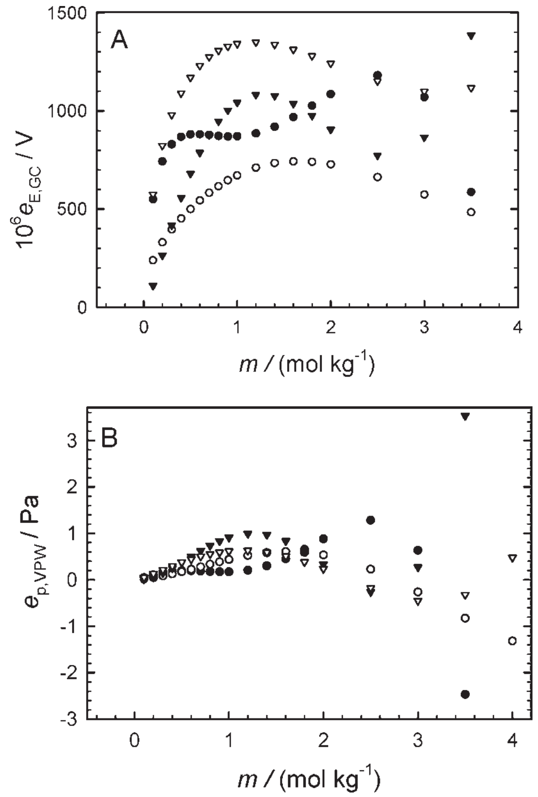

Figure 10. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure errors $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for RbF and CsF solutions (see Tables 12 and 13). Symbols: ●, RbF, Hamer and Wu;[32] ○, RbF, Pitzer and Mayorga;[9] ▼, CsF, Hamer and Wu;[32] ▽, CsF, Pitzer and Mayorga.[9]

1.2 Pa (= 0.009 mmHg) for the vapor pressure deviation for ϕ. Also these deviations for γ are given in the critical cases in the tables.

Comparison of the Recommended Activity Values to Literature Values. The values in Tables 7 to 22 were compared to the activity and osmotic coefficients presented by Robinson and Stokes,[2] Hamer and Wu,[32] and Pitzer and Mayorga.[9] The comparison of the activity coefficients are shown in graphs A of Figures 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 for $AgNO_3$; NaSCN; KSCN; NaF; KF; RbF and CsF; NaH_2AsO_4; KH_2PO_4; NaH_2AsO_4 and KH_2AsO_4; $LiNO_2$ and $NaNO_2$; KNO_2, $RbNO_2$, and $CsNO_2$, respectively. The results for the osmotic coefficients are presented correspondingly in graph B of these figures. The quantity presented on the y-axis in these graphs is the cell potential deviation (graph A, $e_{E,GC}$) or the vapor pressure deviation (graph B $e_{p,VPW}$). Details from these quantities are presented, for example, in ref 29 (see eqs 22 and 23 in that study). They are defined by equations

$$e_{E,GC} = -\frac{2RT}{F} \ln \frac{\gamma(\text{literature})}{\gamma(\text{recd})} \tag{25}$$

and

$$e_{p,VPW} = p(\text{literature}) - p(\text{recd}) \tag{26}$$

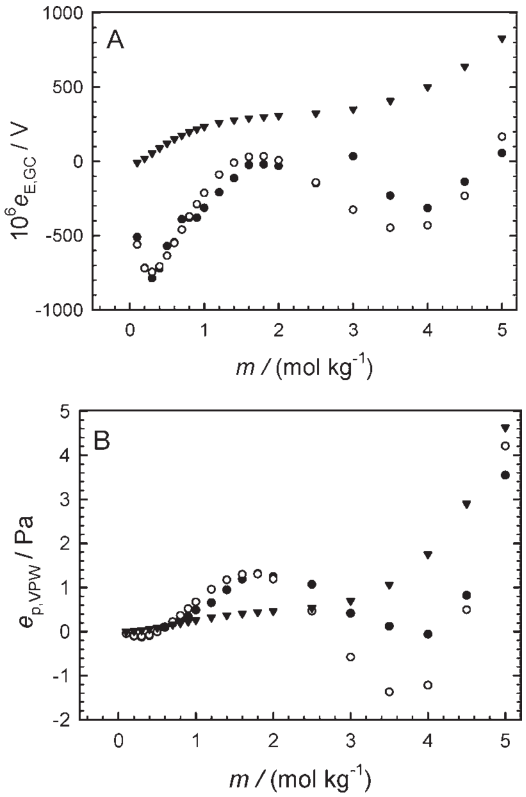

Figure 11. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for NaH_2PO_4 solutions as a function of the molality m (see Table 14). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[32] ▼, Pitzer and Mayorga.[9]

For the recommended activity values, the values obtained from eqs 5 and 6 were used when available, but the values from eqs 1 and 2 were used in the other cases.

The activity and osmotic coefficients suggested in the literature for $AgNO_3$ solutions agree satisfactorily in Figure 5 with those recommended in Table 7 up to a molality of 6.0 mol·kg^{-1}. The values from the equations of Hamer and Wu and of Pitzer and Mayorga follow accurately the values determined by Robinson and Stokes which are slightly different from those recommended in Table 7. The latter values seem to be more reliable because they are strongly supported by the isopiestic data of Robinson and Tait[3] (Figure 3A) and the vapor pressure data of Kangro and Groenefeld[18] (Figure 4A).

The activity quantities suggested by Robinson and Stokes for NaSCN solutions agree satisfactorily in Figure 6 with those recommended in Table 8 up to a molality of 4 mol·kg^{-1}. Above 2 mol·kg^{-1}, the values from Hamer and Wu are considerably different from the other values. The former values are mainly determined from the vapor pressure data of Sheridan and Miller,[21] which do not agree well with the isopiestic data of Robinson[4] used in the present parameter estimation. It seems that the isopiestic data are more reliable. In Figure 6 it is shown that the activity values in Table 8 agree satisfactorily with those of the equations of Pitzer and Mayorga up to a molality of 7.0 mol·kg^{-1}, but there are no experimental data to verify the values above 4 mol·kg^{-1}. In Figure 7, the activity and osmotic coefficients suggested in Table 9 for KSCN solutions agree well with the literature values up to a

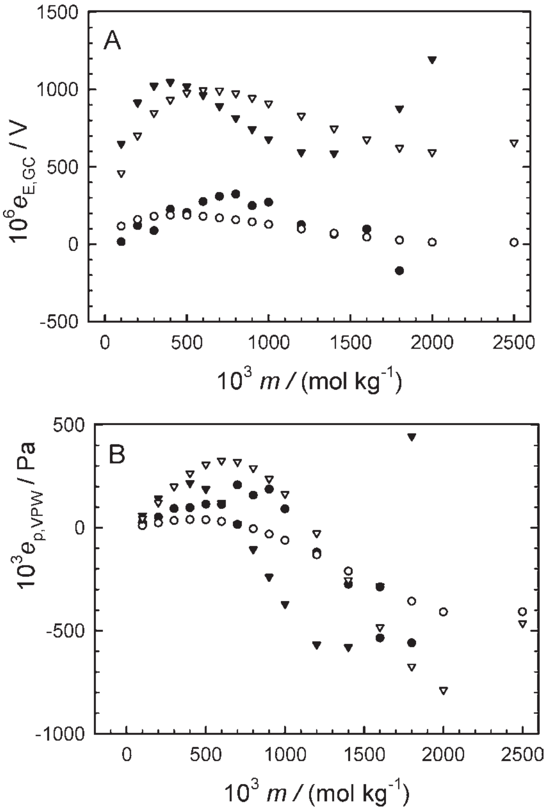

Figure 12. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 5, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 6, graph B) for KH_2PO_4 solutions as a function of the molality m (see Table 15). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[32] ▼, Pitzer and Mayorga;[9] ▽, Partanen et al.[34]

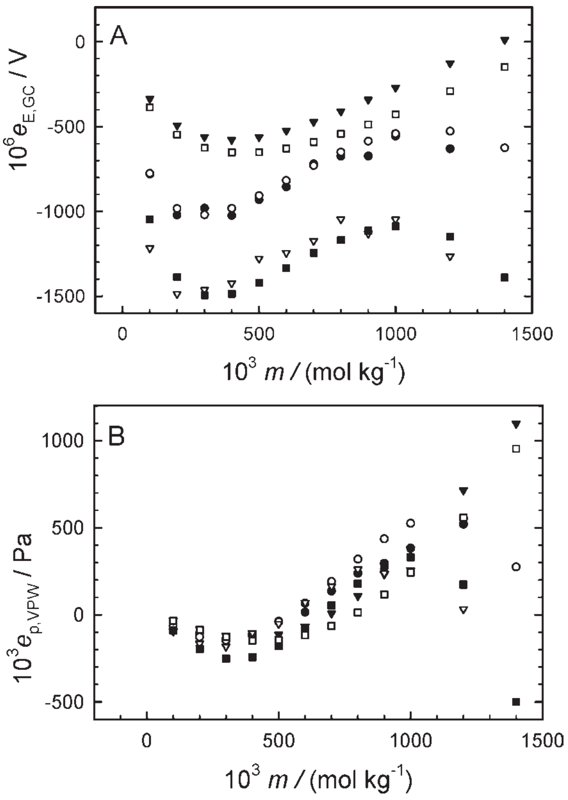

Figure 13. Deviation, expressed as galvanic cell error $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 1, graph A) and deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 2, graph B) for NaH_2AsO_4 and KH_2AsO_4 solutions as a function of the molality m (see Tables 16 and 17). Symbols: ●, NaH_2AsO_4, Robinson and Stokes;[2] ○, NaH_2AsO_4, Hamer and Wu;[32] ▼, NaH_2AsO_4, Pitzer and Mayorga;[9] ▽, KH_2AsO_4, Robinson and Stokes;[2] ■, KH_2AsO_4, Hamer and Wu;[32] □, KH_2AsO_4, Pitzer and Mayorga.[9]

molality of about 5 mol·kg^{-1}. For the Pitzer equations, a quite good agreement extends up to 7 mol·kg^{-1}.

Figure 8 shows that the literature activity and osmotic coefficients agree well with those suggested in Table 10 for NaF solutions up to the molality of the saturated solutions (i.e., up to 0.983 mol·kg^{-1}). In Figure 9 is shown a good agreement between the literature activity and osmotic coefficients and suggested in Table 11 for KF solutions up to the molality of 4 mol·kg^{-1}. The equations of Pitzer and Mayorga and of Hamer and Wu apply satisfactorily to the activity and osmotic coefficients of KF solutions up to a molality of 10 mol·kg^{-1} (for the osmotic coefficients, see also the caption of this figure). Figure 10 shows that the osmotic coefficients from the equations of Hamer and Wu and of Pitzer and Mayorga for RbF and CsF solutions (graph B) agree well with those suggested in Tables 12 and 13 up to a molality of 3 mol·kg^{-1}, but the activity coefficients do not agree as well (graph A). In the latter case, almost all errors are larger than 0.5 mV.

For the NaH_2PO_4 solutions in Figure 11, the activity quantities from the Pitzer equation agree well with those in Table 14 up to a molality of 4 mol·kg^{-1}. For the other literature values, the agreement is not as good. For KH_2PO_4, NaH_2AsO_4, and KH_2AsO_4 in graphs B of Figures 12 and 13, the osmotic coefficients presented in the literature agree quite well with those shown in Tables 15, 16, and 17 up to (1.8, 1.2, and 1.2) mol·kg^{-1}, respectively. The recommended activity values for KH_2PO_4 solutions were tested in Figure 3C with the isopiestic data of Childs et al.[23] that contain some points also from supersaturated solutions. Figure 12 shows that the equation of Hamer and Wu and the Pitzer equation with the parameter values suggested in ref 34 apply also quite well to these supersaturated solutions. Graph A in this figure shows, additionally, that the activity coefficients from the Pitzer equations of KH_2PO_4 are not in line with the values in Table 14 as well as those suggested by Robinson and Stokes and Hamer and Wu. To the contrary, the activity coefficients from the Pitzer equations agree better for NaH_2AsO_4 and KH_2AsO_4 solutions in Figure 13A with the values in Tables 16 and 17 than with the other literature values.

In the alkali metal nitrite plots of Figures 14 and 15, the agreement between the activity values from the extended Hückel equations of Staples, those from the Pitzer equations, and those recommended in Tables 18 to 22 is even in the best case only satisfactory. With the parameter values suggested by Staples[33] for KNO_2 solutions (shown in Table 1 of the present study), the activity values recommended in Table 12 of that paper[33] (for rounded molalities up to 34 mol·kg^{-1}) cannot be reproduced. The values in that table (Table 12[33]) are probably erroneous, and the values calculated from the extended Hückel equation (with the parameter values shown in Table 1) were used here.

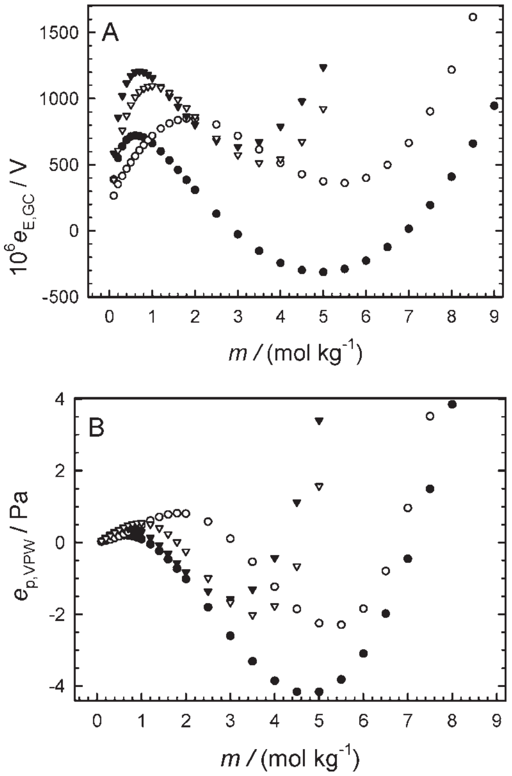

Figure 14. Deviation, expressed as galvanic cell errors $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 1 or 5, graph A) and deviation, expressed as vapor pressure errors $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 2 or 6, graph B) for $LiNO_2$ and $NaNO_2$ solutions as a function of the molality m (see Tables 18 and 19). The deviations for the equation of Staples at molalities of (8.5 and 9) $mol \cdot kg^{-1}$ for $LiNO_2$ solutions lie outside the scale of graph B; their values are (6.6 and 9.7) Pa, respectively. Symbols: ●, $LiNO_2$, Staples;[33] ○, $LiNO_2$, Pitzer and Mayorga;[9] ▼, $NaNO_2$, Staples;[33] ▽, $NaNO_2$, Pitzer and Mayorga.[9]

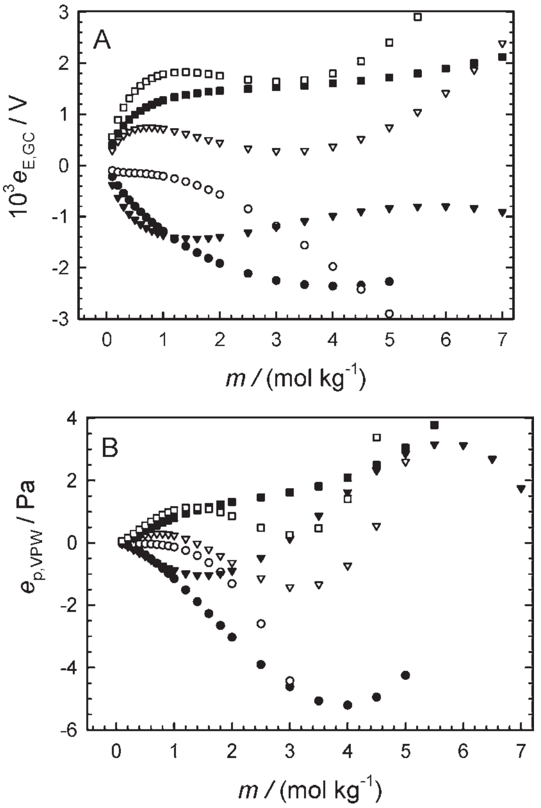

Figure 15. Deviation, expressed as galvanic cell errors $e_{E,GC}$ in eq 25, between the literature activity coefficients and those recommended in this study (eq 1 or 5, graph A) and deviation, expressed as vapor pressure errors $e_{p,VPW}$ in eq 26, between the literature osmotic coefficients and those recommended in this study (eq 2 or 6, graph B) for KNO_2, $RbNO_2$, and $CsNO_2$ solutions as a function of the molality m (see Tables 20, 21, and 22). The deviations for the equation of Pitzer and Mayorga at molalities of (6, 6.5, and 7) $mol \cdot kg^{-1}$ for $CsNO_2$ solutions lie outside the scale of graph A; their values are (3.6, 4.3, and 5.3) mV, respectively. Also the deviations for the equation of Pitzer and Mayorga at molalities of (3.5, 4, 4.5, and 5) $mol \cdot kg^{-1}$ for KNO_2 solutions lie outside the scale of graph B; their values are (−6.8, −9.8, −13.3, and − 17.4) Pa, respectively. Finally, the deviations for the equation of Staples at molalities of (6, 6.5, and 7) $mol \cdot kg^{-1}$, and that for the Pitzer equations at (5, 5.5, and 6.0) $mol \cdot kg^{-1}$ for $CsNO_2$ solutions lie outside the scale of graph B; their values are (4.7, 5.9, 7.2, 6.6, 11.5, and 18.2) Pa, respectively. Symbols: ●, KNO_2, Staples;[33] ○, KNO_2, Pitzer and Mayorga;[9] ▼, $RbNO_2$, Staples;[33] ▽, $RbNO_2$, Pitzer and Mayorga;[9] ■, $CsNO_2$, Staples;[33] □; $CsNO_2$, Pitzer and Mayorga.[9]

The vapor pressure of water in the solutions of the electrolytes considered here is compared to that of potassium chloride solutions (as the reference electrolyte) in Figure 16. The difference is also in this case presented as the vapor pressure deviation defined by

$$e_{p,\mathrm{VPW}} = p_{\mathrm{MX}} - p_{\mathrm{KCl}} \qquad (27)$$

where MX is the tested electrolyte, and this deviation is presented as a function of the molality. The recommended vapor pressures were taken for KCl solutions from ref 15. In graph A are shown the results for silver nitrate and sodium and potassium thiocyanate, dihydrogen phosphate, and dihydrogen arsenate solutions. Graph B shows the results for the tested fluoride solutions, and for comparison, additionally, the results for the corresponding chloride solutions. The recommended vapor pressures were taken for NaCl solutions from ref 15 and for RbCl and CsCl solutions from ref 26. Graph C shows the results for the alkali metal nitrite solutions and for comparison also the results from the alkali metal nitrate solutions (the vapor pressures were taken from ref 29). The deviation plots are interesting: The vapor pressure of silver nitrate and sodium and potassium dihydrogen phosphate and arsenate solutions is always closer to that of pure water than the vapor pressure of the potassium chloride solutions at the same molality. These results show that water molecules in aqueous solutions of these electrolytes are less thermodynamically stabilized than in KCl solutions. In graph A, the vapor pressures of potassium and sodium thiocyanate solutions are, on the other hand, rather close to those of KCl and NaCl solutions (see also graph B), respectively. Graph B shows that fluoride ions stabilize the solutions of potassium, rubidium, and cesium ions when compared to the solutions of chloride ions. This trend is most pronounced in the case of cesium ions, and the vapor pressure of a CsF solution is always considerably smaller than that of the corresponding CsCl solution. The vapor pressure of KF solutions is close to that of NaCl solutions, and the vapor pressure of NaF solutions is close to that of RbCl solutions at the same molality (the latter result cannot be clearly seen in graph B because only dilute solutions are available for NaF). In graph C can be seen, that only the vapor pressures on $LiNO_2$ solutions are close to those of $LiNO_3$ solutions. Otherwise, an alkali metal nitrite solution has a

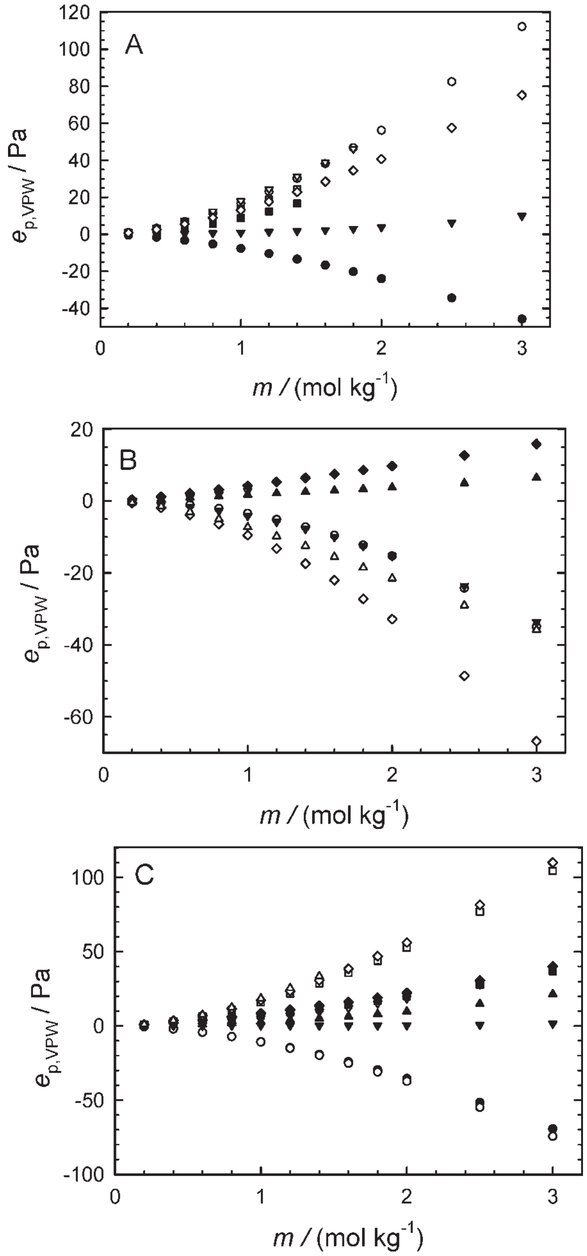

Figure 16. Deviation, expressed as vapor pressure error $e_{p,VPW}$ in eq 27, between the osmotic coefficients of solutions of the electrolytes considered in this study or of some related electrolytes[15,26,29] and of potassium chloride solutions[15] as a function of the molality m. The osmotic coefficients have been calculated using the Hückel or extended Hückel equation (eqs 2 or 6) with the recommended parameter values (see Tables 3, 4, and 6). Symbols: ●, NaSCN (graph A), $LiNO_2$ (C); ○, $AgNO_3$ (A), KF (B), $LiNO_3$ (C); ▼, KSCN (A), NaCl (B), $NaNO_2$ (C); ▽, KH_2PO_4 (A), NaF (B), $NaNO_3$ (C); ■, NaH_2AsO_4 (A), KNO_2 (C); □, KH_2AsO_4 (A), KNO_3 (C); ♦, CsCl (B), $RbNO_2$ (C); ◊, NaH_2PO_4 (A), CsF (B), $RbNO_3$ (C); ▲, RbCl (B), $CsNO_2$ (C); △, RbF (B), $CsNO_3$ (C).

smaller vapor pressure than that of the corresponding alkali metal nitrate solution. Thus, nitrite ions are usually more thermodynamically stabilized in aqueous solutions than nitrate ions.

■ AUTHOR INFORMATION

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