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Re-evaluation of the Thermodynamic Activity Quantities in Aqueous Solutions of Uni-univalent Alkali Metal Salts of Aliphatic Carboxylic Acids and Thallium Acetate at 25 °C

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ABSTRACT: The Hückel equation, which was used in this study to correlate the experimental activities of dilute solutions of uni-univalent alkali metal salts of aliphatic carboxylic acids up to a molality of about 1 $\text{mol}\cdot\text{kg}^{-1}$, contains two parameters that are dependent on the electrolyte: B (closely related to the ion-size parameter a^* in the Debye—Hückel equation) and b_1 (the coefficient of the linear term with respect to the molality, related to the hydration numbers of the ions of the electrolyte). For thallium acetate solutions, this equation applies up to a molality of 3.5 $\text{mol}\cdot\text{kg}^{-1}$. In more concentrated solutions of these electrolytes, in the best case up to a molality of about 7.5 $\text{mol}\cdot\text{kg}^{-1}$, 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 lithium, sodium, and potassium acetate were determined from isopiestic data measured by Robinson for solutions of these salts against KCl solutions (*J. Am. Chem. Soc.* **1935**, *57*, 1165—1168), and all parameters for rubidium, cesium and thallium acetate solutions were obtained from the osmotic coefficients reported by Robinson for solutions of these salts (*J. Am. Chem. Soc.* **1937**, *59*, 84—90). All Hückel parameters for sodium formate, propionate, butyrate, and valerate were determined from the results of isopiestic measurements of Smith and Robinson (*Trans. Faraday Soc.* **1942**, *38*, 70—78) in which these salts were measured against KCl solutions, and the parameters for the extended Hückel equation of potassium formate solutions were solved from the recent vapor pressure data of Beyer and Steiger (*J. Chem. Eng. Data* **2010**, *55*, 830—838). The Hückel parameters of primary sodium and potassium salts of malonic, succinic, and adipic acids were determined from the isopiestic data measured by Stokes (*J. Am. Chem. Soc.* **1948**, *70*, 1944—1946) in which these salts were measured against NaCl solutions. The resulting parameter values were tested with the vapor pressure and isopiestic data existing in the literature for the solutions of these organic 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 of the salt solutions considered. Reliable activity and osmotic coefficients for solutions of these electrolytes can therefore be calculated 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: London, 1959), to those calculated using the Pitzer equations with the parameter values of Pitzer and Mayorga (*J. Phys. Chem.* **1973**, *77*, 2300—2308), and to those calculated using the extended Hückel equations of Hamer and Wu (*J. Phys. Chem. Ref. Data* **1972**, *1*, 1047—1099).

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. In these tables, the values of the activity quantities for lithium, sodium, and potassium acetate have been based on the isopiestic data of Robinson[3] for solutions of these salts and KCl as the reference electrolyte. Values are given for molalities of (0.1 up to 4.0, 3.5, and 3.5) $\text{mol}\cdot\text{kg}^{-1}$, respectively. For sodium formate, propionate, butyrate, valerate, caproate, heptylate, caprylate, pelargonate, and caprate solutions, the activity quantities in these tables[2] were based on the isopiestic data of Smith and Robinson[4] in which the solutions of these salts also were measured against KCl solutions. Formates are salts of methanoic acid, acetates salts of ethanoic acid, propionates salts of propanoic acid, butyrates salts of butanoic acid, valerates salts of pentanoic acid, caproates salts of hexanoic acid, heptylates salts of heptanoic acid, caprylates salts of octanoic acid, pelargonates salts of nonanoic acid, and caprates salts of decanoic acid. In the tables of Robinson and Stokes[2] for sodium formate solutions, activity and osmotic coefficients are given from (0.1 to 3.5) $\text{mol}\cdot\text{kg}^{-1}$. For the other sodium salts of these fatty acids, the values are given in the tables for the following molality ranges: sodium propionate, (0.1 to 3.0) $\text{mol}\cdot\text{kg}^{-1}$; sodium butyrate, (0.1 to 3.5) $\text{mol}\cdot\text{kg}^{-1}$; sodium valerate, (0.1 to 3.5) $\text{mol}\cdot\text{kg}^{-1}$; sodium caproate, (0.1 to 4.5) $\text{mol}\cdot\text{kg}^{-1}$; sodium heptylate, (0.1 to 5.0) $\text{mol}\cdot\text{kg}^{-1}$; sodium caprylate, (0.5 to 3.0) $\text{mol}\cdot\text{kg}^{-1}$; sodium pelargonate, (0.3 to 2.5) $\text{mol}\cdot\text{kg}^{-1}$; and sodium caprate, (0.3 to 1.8) $\text{mol}\cdot\text{kg}^{-1}$. Stokes[5] performed isopiestic measurements on solutions of primary sodium and potassium salts of malonic acid ($HOOCCH_2COOH$), succinic acid ($HOOCCH_2CH_2COOH$), and adipic acid ($HOOCCH_2CH_2CH_2CH_2COOH$) against NaCl

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Table 1. Values of the Parameters in the Equations of Hamer and Wu[13] (Equations 7 and 8) for the Organic Electrolytes Considered in This Study at 25 °C

	B^{*a}	$10^3 \cdot \beta$	$10^3 \cdot C$	$10^3 \cdot D$	$10^3 \cdot E$	$10^3 \cdot F$	max $(m/m°)^b$
Na formate	1.50	24.781	−0.54350	0.28402			3.5
Li acetate	1.50	35.673	8.1453	−1.1625			4
Na acetate	1.50	87.320	−4.8128	0.69295			3.5
K acetate	1.50	102.44	−5.1136	0.75650			3.5
Rb acetate	1.50	106.30	−3.6957	0.43613			3.5
Cs acetate	1.50	113.57	−5.2680	0.45087			3.5
Ta acetate	1.25	−87.283	32.612	−7.3907	0.77672	−0.029141	6.0
Na propionate	1.50	114.03	−1.6798	−0.61530			3.0
Na butyrate	1.50	125.47	33.688	−20.442	2.7440		3.5
Na valerate	1.50	129.02	28.803	−13.844	−1.1394		2.0
Na caproate	1.50	130.39	71.752	−64.283			1.2
Na H malonate	1.25	−25.969	5.4455	−0.51150	0.011165		5
Na H succinate	1.25	−13.050	−1.2759	4.2800	−1.0581	0.0801	5
Na H adipate	1.25	63.902	−80.250	46.890			0.7
K H malonate	1.50	−95.652	26.791	−4.4686	0.28346		5
K H succinate	1.39	−58.664	16.865	−1.7901	0.038068		4.5
K H adipate	1.25	38.476	−71.126	43.579			1.0

[a] The unit of B^* is $(\text{mol} \cdot \text{kg}^{-1})^{-1/2}$. [b] The maximum molality up to which the equations apply ($m° = 1\ \text{mol} \cdot \text{kg}^{-1}$).

solutions, and the results from these measurements were used by Robinson and Stokes[2] in their tables. For sodium hydrogen malonate and succinate and for potassium hydrogen malonate solutions, activity and osmotic coefficients were reported up to a molality of 5 $\text{mol} \cdot \text{kg}^{-1}$; for potassium hydrogen succinate, potassium hydrogen adipate, and sodium hydrogen adipate solutions, values were given up to (4.5, 1.0, and 0.7) $\text{mol} \cdot \text{kg}^{-1}$, respectively. For rubidium, cesium, and thallium acetates in these tables,[2] activity and osmotic coefficients have been reported up to molalities of (3.5, 3.5, and 6.0) $\text{mol} \cdot \text{kg}^{-1}$, respectively, and the values were slightly revised from those reported by Robinson.[6]

The importance of the activities in 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[7] for various electrolytes in the famous article[8] on thermodynamics of single electrolytes. From the isopiestic results for the sodium salts of the fatty acids reported by Smith and Robinson,[4] Pitzer and Mayorga[8] considered only the results for sodium formate, acetate, and propionate. The omission of the results for the salts of higher carboxylic acids was probably due to the existence of micelle formation and other complicated chemical equilibria in these salt solutions. For this reason, the isopiestic results from all of the solutions reported by Smith and Robinson will not be considered in the present study.

In the present study, it is shown that reliable thermodynamic activity values for alkali metal and thallium acetate solutions; for sodium formate, propionate, butyrate, valerate, and caproate solutions; and for sodium and potassium hydrogen malonate, succinate, and adipate solutions can also be obtained by such a simple equation as the Hückel equation or the extended Hückel equation with two or three parameters, respectively (see the historical refs 9−12 for the Hückel equation and 13 for the extended versions). In a previous study,[14] it was shown that reliable activity values for NaCl and KCl solutions at 25 °C can also be obtained with these equations. In other previous studies (e.g., see refs 15−20), equations of this type proved to be very useful in the thermodynamic treatment of weak acid solutions (especially of those of pH buffer substances[17,19,20]) and also in the treatment of other strong acid solutions.[21−28] For the carboxylic acid salts considered here, the new values for activity and osmotic coefficients are very important in that they have been tested thoroughly with existing experimental data. Additionally, they are fully transparent and traceable because all of the calculation methods and data sets used in the parameter estimations and tests are presented here in detail. Also, the reliability of the literature data used in the tests was evaluated in this work, and only the best data were used in the parameter estimations.

The form of the Hückel equation used in this investigation (see below and, e.g., ref 21) contains two parameters that are dependent on the electrolyte: B (closely related to the ion-size parameter a^* in the Debye−Hückel equation) and b_1 (the coefficient of the linear term with respect to the molality, related to the hydration numbers of the ions of the electrolyte; see refs 10 and 12). The Hückel parameters needed in the estimations from the isopiestic results for NaCl and KCl solutions were taken from the results of the previous study.[14] The parameters were estimated from the same data sets as those used by Robinson and Stokes.[1,2] The resulting parameter values were tested with the data used in the parameter estimation and with the sodium acetate data measured by Smith and Robinson.[4] The resulting Hückel equations usually apply up to a molality of about 1.5 $\text{mol} \cdot \text{kg}^{-1}$.

Additionally, it is shown here that reliable activity values for lithium acetate, sodium acetate, potassium acetate, thallium acetate, sodium formate, potassium formate, sodium propionate, sodium butyrate, sodium hydrogen malonate, sodium hydrogen succinate, potassium hydrogen malonate, and potassium hydrogen succinate solutions can be obtained up to molalities of about (4.0, 7.5, 3.5, 6.0, 4.5, 5.5, 4.5, 3.5, 5.0, 5.0, 5.0, and 5.0) $\text{mol} \cdot \text{kg}^{-1}$, 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. For each salt, the value of the parameter B used in this extended Hückel equation was the same as that for dilute solutions, except for potassium formate, for which data are not available for dilute solutions. In this case, a reasonable value for B based on other acetate and formate values of this parameter was used. New values of parameters b_1 and b_2 in this extended Hückel equation were then determined for solutions of all of these salts from the same isopiestic set as that used above in the parameter estimation for dilute solutions, but all points were included in the determination for each salt. For potassium formate solutions, these values were determined from the vapor pressure data of Beyer and Steiger,[29] and those for thallium acetate solutions were determined from the osmotic coefficients reported by Robinson.[6] The resulting parameter values were tested with all of the isopiestic results mentioned above, and additionally, the sodium acetate parameters were tested with the isopiestic data of Smith and Robinson,[4] Bonner,[30] Robinson et al.,[31] and Jones and Prue[32] for solutions of this salt and KCl, LiCl, NaCl, and NaCl or KCl as the reference salt, respectively. The sodium formate and acetate parameters were also tested with the vapor pressure data of Beyer and Steiger.[29,33] Bonner[30] also performed isopiestic measurements on sodium formate and propionate solutions against LiCl solutions, and these data were used here in the tests. The Hückel parameters needed in these tests for LiCl solutions were taken from the results of the previous study.[23] Robinson et al.[31] also measured lithium acetate solutions against NaCl solutions, and Jones and Prue[32] measured potassium acetate solutions against NaCl and KCl solutions. All points in these two sets were included in the present tests.

Table 2. Values Recommended by Pitzer and Mayorga[8] for the Parameters in the Pitzer Equations (Equations 9 to 12) for the Organic Electrolytes Considered in This Study at 25 °C

	β^0	β^1	C^ϕ	max $(m/m^\circ)^a$
Na formate	0.0820	0.2872	−0.00523	3.5
Li acetate	0.1124	0.2483	−0.00525	4
Na acetate	0.1426	0.3237	−0.00629	3.5
K acetate	0.1587	0.3251	−0.00660	3.5
Rb acetate	0.1622	0.3353	−0.00551	3.5
Cs acetate	0.1628	0.3605	−0.00555	3.5
Tl acetate	0.0082	0.0131	−0.00127	6.0
Na propionate	0.1875	0.2789	−0.01277	3
NaH malonate	0.0229	0.1600	−0.00106	5
NaH succinate	0.0354	0.1606	0.00040	5
NaH adipate	0.0472	0.3168		0.7
KH malonate	−0.0095	0.1423	0.00167	5
KH succinate	0.0111	0.1564	0.00274	4.5
KH adipate	0.0419	0.2523		1

[a] The maximum molality up to which the equations apply ($m^\circ = 1\ \mathrm{mol \cdot kg^{-1}}$).

As in refs 14 and 21−28, all of the tests in this study were performed on the raw experimental results of appropriate measurements to determine whether these could be predicted using 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 the vapor pressures of water were calculated using the new Hückel equations at rounded molalities of the organic salt solutions, and these values were tabulated as the recommended values. These activity and osmotic coefficients have been compared with those of the previous investigations.

Table 3. Results of the Parameter Estimation for the Hückel Equations (Equations 1 and 2) for Organic Salts at 25 °C by Least-Squares Fitting Using Equation 16 with the Rubidium, Cesium, and Thallium Acetate Data and Equation 13 with the Other Data Included in the Estimations

	$B/(\mathrm{mol \cdot kg^{-1}})^{-1/2}$	b_1	$s(b_1)^a$	N^b	max $(m/m^\circ)^c$	$s_0{}^d$/Pa	ref^e
Na formate	1.72	0.0356	0.0014	12	1.405	0.13	4, KCl
Li acetate	1.50	0.1111	0.0011	14	1.622	0.20	3, KCl
Na acetate	1.76	0.163	0.002	14	1.390	0.26	3, KCl
K acetate	1.66	0.204	0.002	16	1.245	0.28	3, KCl
Rb acetate	1.65	0.2200	0.0004	11	3.5	0.25^f	6
Cs acetate	1.74	0.2191	0.0004	11	3.5	0.25^f	6
Tl acetate	0.78	−0.0168	0.0003	11	3.0	0.15^f	6
Na propionate	1.76^g	0.220^h		11	1.198	0.2	4, KCl
Na butyrate	1.76^g	0.293^i					4, KCl
Na valerate	1.76^g	0.293^j		11	1.157	0.3	4, KCl
Na caproate	1.76^g	0.293^i					4, KCl
Na heptylate	1.76^g	0.293^i					4, KCl
Na H malonate	1.16	−0.0283	0.0013	5	1.799	0.19	5, NaCl
Na H succinate	1.21	−0.0087	0.0009	5	1.650	0.11	5, NaCl
Na H adipate	1.52	0.0127	0.0010	5	0.6863	0.02	5, NaCl
K H malonate	1.13	−0.088	0.002	6	1.697	0.32	5, NaCl
K H succinate	1.08	−0.0330	0.0013	7	1.823	0.2	5, NaCl
K H adipate	1.31	0.010	0.002	10	0.973	0.13	5, NaCl

[a] The standard deviation of parameter b_1. [b] Number of points included in the estimation. [c] The maximum molality included in the estimation ($m^\circ = 1\ \mathrm{mol \cdot kg^{-1}}$). [d] Unless otherwise noted, s_0 is the standard error between the vapor pressures of water over the tested and reference solutions (eq 14). [e] The citation number and the reference electrolyte are given. [f] Standard error between the reported and predicted vapor pressures of water (eq 17). [g] The recommended value for sodium acetate was used. [h] Optimized value based on the squared-error sum in eq 14. [i] The value obtained for Na valerate solutions was used (see footnote j). [j] Optimized value based on the squared-error sum in eq 14 but with the point ($m_x/m^\circ = 0.8760$, $m_y/m^\circ = 0.7520$) omitted from the estimation as a slightly erroneous point.

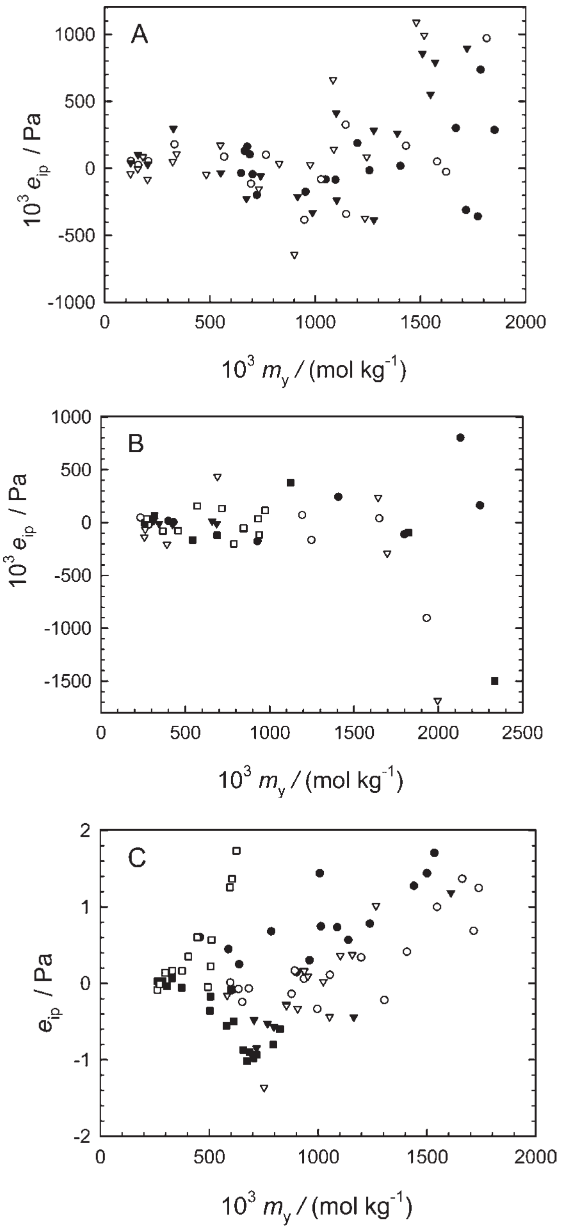

Figure 1. Plot of e_{ip} (eq 15), the difference between the vapor pressure of water over the reference solution (x) and that over the tested solution (y), as a function of the molality of the tested solution (m_y) for dilute isotonic solutions of NaCl or KCl (x) and the tested electrolytes (y) (see Table 3). The vapor pressures were calculated with 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, 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: ●, Na formate (graph A), Na H malonate (B), Na acetate (ref 4, graph C); ○, Li acetate (A), Na H succinate (B), Na propionate (C); ▼, Na acetate (ref 3, A), Na H adipate (B), Na butyrate (C); ▽, K acetate (A), K H malonate (B), Na valerate (C); ■, K H succinate (B); Na caproate (C); □, K H adipate (B), Na heptylate (C). The point (m_x/m° = 0.4810, m_y/m° = 0.4580) was used instead of the point (m_x/m° = 0.1810, m_y/m° = 0.4580) for the Na acetate set of Smith and Robinson.[4]

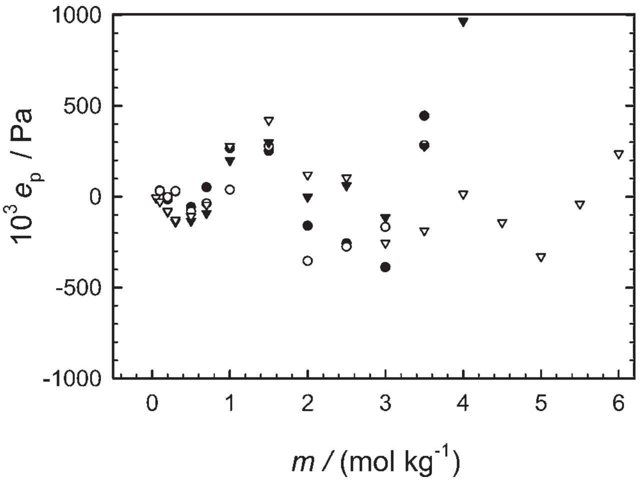

Figure 2. Plot of e_p (eq 18), the difference between the reported and predicted vapor pressures of water over solutions of rubidium acetate (●), cesium acetate (○), and thallium acetate (▼, Hückel equation; ▽, extended Hückel equation) as a function of molality m. The observed vapor pressures were obtained from the reported osmotic coefficients of Robinson.[6] The vapor pressures were predicted with eqs 3 and 4 using eq 2 or 6 with the recommended parameter values shown in Table 3 or 4.

Activity coefficient deviations in this comparison are presented as cell-potential deviations for galvanic cells without a liquid junction (in the same way as in refs 14 and 21−28) and osmotic coefficient deviations as vapor pressure deviations (as in refs 14 and 23−28), allowing the deviation plots to be compared directly with the experimental error plots.

THEORY

In previous studies, it was found that the following Hückel equations apply very well to the thermodynamic properties of NaCl,[14] KCl,[14] LiCl,[23] RbCl,[24] CsCl,[24] AgCl,[28] NaH_2PO_4,[28] KH_2PO_4,[28] NaH_2AsO_4,[28] KH_2AsO_4,[28] NaSCN,[28] and KSCN[28] solutions in addition to alkali metal fluoride,[28] bromide,[25] iodide,[26] nitrate,[27] and nitrite[28] solutions, at least up to molalities of about 1 $\text{mol}\cdot\text{kg}^{-1}$:

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

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

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 (the label 1 refers to the solvent, water in this case); α is the Debye−Hückel parameter [its value at 25 °C and at 101.325 kPa is 1.17444 $(\text{mol}\cdot\text{kg}^{-1})^{-1/2}$; see Archer and Wang[34]]; m° is 1 $\text{mol}\cdot\text{kg}^{-1}$; and the parameters 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 uni-univalent 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 $\text{kg}\cdot\text{mol}^{-1}$). The activity of water is related to the vapor pressure of water over the solution (p_1) and the vapor pressure of pure solvent at the temperature under consideration (p_1^*) by the equation

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

Table 4. Results of the Parameter Estimations for the Extended Hückel Equations (Equations 5 and 6) of Organic Salts at 25 °C by Least-Squares Fitting Using Equation 20 with the Thallium Acetate and Potassium Formate Data and Using Equation 19 for the Other Data Included in the Estimations

	$B/(\mathrm{mol \cdot kg^{-1}})^{-1/2}$	b_2	b_1	$s(b_1)$[a]	N[b]	max (m/m°)[c]	s_0[d]/Pa	ref[e]
Na formate	1.72	0.002	0.0424	0.0004	30	3.373	0.4	4
K formate	1.65[f]	0.0029	0.085	0.002	7	5.5182	3.1[g]	29
Li acetate	1.50[h]	−0.0008[h]	0.1232[h]	0.0004	28	4.091	0.5	3
Li acetate	1.70[i]	−0.00323	0.1273	0.0010	5	6.2568[j]	0.6	31
Na acetate	1.76	−0.00185	0.1752	0.0003	35	3.813	0.4	3
K acetate	1.66	−0.0047	0.2212	0.0004	30	3.475	0.4	3
Tl acetate	0.78	−0.00065	−0.0145	0.00008	17	6.0	0.2[g]	6
Na propionate	1.76	−0.0078	0.2444	0.0007	27	2.784	0.4	4
Na butyrate	1.76	−0.0345	0.3642	0.0010	14[k]	3.478	0.8	4
Na H malonate	1.16	0.0019	−0.0242	0.0005	12	4.765	0.6	5
Na H succinate	1.21	0.0046	−0.0048	0.0004	12	4.935	0.5	5
K H malonate	1.13	0.0054	−0.0847	0.0008	13	5.035	1.4	5
K H succinate	1.08	0.0064	−0.0360	0.0007	13	4.398	0.8	5

[a] The standard deviation of parameter b_1. [b] Number of points included in the estimation. [c] The maximum molality included in the estimation ($m^\circ = 1$ mol·kg^{-1}). [d] Unless otherwise noted, s_0 is the standard error between the vapor pressures of water over the tested and reference solutions (eq 14). [e] The citation number is given. [f] Evaluated on the basis of the B values for potassium acetate, sodium acetate, and sodium formate. [g] Standard error between the reported and predicted vapor pressures of water (eq 17). [h] The recommended value. [i] Evaluated on the basis of the B values for alkali metal salts of formates and acetates. [j] The most dilute point has a molality of 4.904 mol·kg^{-1} for Li acetate. [k] The point ($m_x/m^\circ = 1.899$, $m_y/m^\circ = 1.441$) was omitted as a probable outlier.

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[35]).

In more concentrated solutions, the following extended Hückel equations were used here as well as in earlier work[14,23−28] for the activity and osmotic coefficients:

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

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

Hamer and Wu[13] suggested the following extended Hückel equations for the activity and osmotic coefficients of uni-univalent electrolytes at 25 °C:

$$\log(\gamma) = -\frac{A\sqrt{m}}{1 + B^*\sqrt{m}} + \beta(m/m^\circ) + C(m/m^\circ)^2 + D(m/m^\circ)^3 + E(m/m^\circ)^4 + F(m/m^\circ)^5 \qquad (7)$$

$$\phi = 1 - \ln(10)\left\{\frac{A}{(B^*)^3 m}\left[(1 + B^*\sqrt{m}) - 2\ln(1 + B^*\sqrt{m}) - \frac{1}{1 + B^*\sqrt{m}}\right] - \frac{1}{2}\beta(m/m^\circ) - \frac{2}{3}C(m/m^\circ)^2 - \frac{3}{4}D(m/m^\circ)^3 - \frac{4}{5}E(m/m^\circ)^4 - \frac{5}{6}F(m/m^\circ)^5\right\} \qquad (8)$$

where the Debye−Hückel parameter A has the value of 0.5108 $(\mathrm{mol \cdot kg^{-1}})^{-1/2}$ [$= \alpha/\ln(10)$]. The values of the parameters in eqs 7 and 8 for the electrolytes considered in this study are shown in Table 1.

For activity coefficients of a uni-univalent electrolyte, the Pitzer equation[8,36] has the form

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

where

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

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

In eqs 9 and 11, β^0, β^1, and C^ϕ are parameters that depend on the electrolyte. Pitzer and Mayorga[8] determined the values of these parameters shown in Table 2 for the electrolytes considered here. For all of these electrolytes, Kim and Frederick[37] and Marshall et al.[38] have also presented Pitzer parameters. These values were not considered here because they were based on the activity and osmotic coefficients tabulated by Hamer and Wu,[13] which are included in the present tests. For the osmotic coefficient of water in solutions of a uni-univalent electrolyte, the Pitzer equation has the form

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

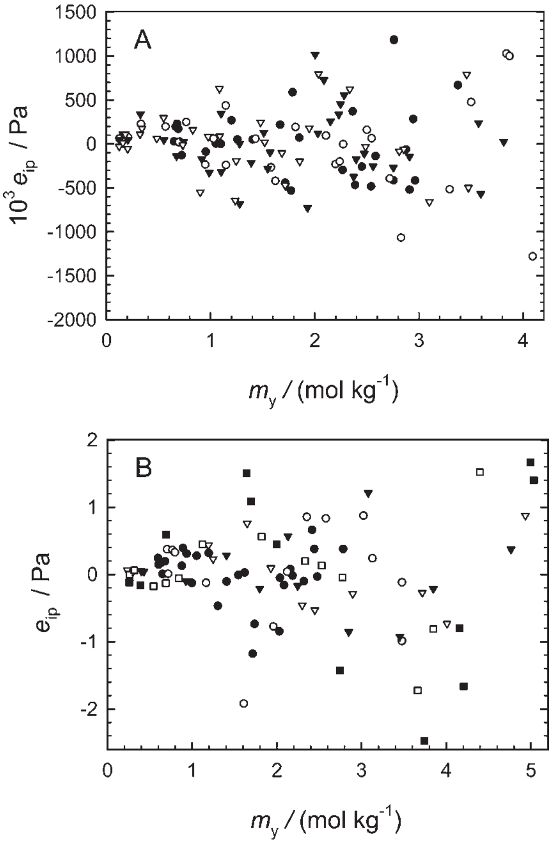

Figure 3. Plot of e_{ip} (eq 15), the difference between the vapor pressure of water over the reference solution (x) and that over the tested solution (y), as a function of the molality of the tested solution (m_y) in the isotonic solutions of NaCl or KCl (x) and the tested electrolyte (y) (see Table 4). The vapor pressures were calculated with eqs 3 and 4 using eq 6 with $B_{NaCl} = 1.4\ (mol \cdot kg^{-1})^{-1/2}$, $b_{1,NaCl} = 0.0699$, and $b_{2,NaCl} = 0.0062$; $B_{KCl} = 1.3\ (mol \cdot kg^{-1})^{-1/2}$, $b_{1,KCl} = 0.01324$, and $b_{2,KCl} = 0.0036$; and the recommended parameter values shown in Table 4 for the tested electrolytes. Only the results for the sets used in the parameter estimation are shown. Symbols: ●, Na formate (graph A), Na propionate (graph B); ○, Li acetate (A), Na butyrate (B); ▼, Na acetate (A), Na H malonate (B); ▽, K acetate (A), Na H succinate (B); ■, K H malonate (B); □, K H succinate (B).

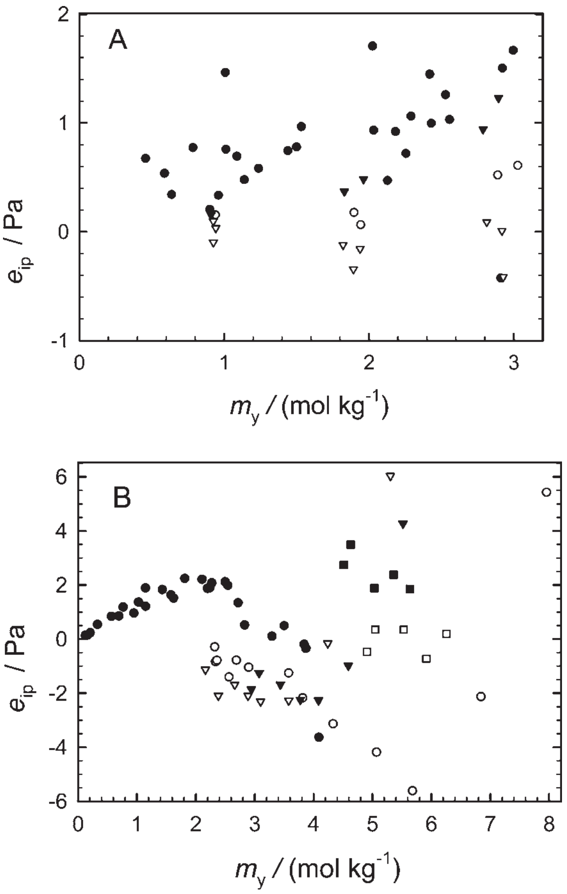

Figure 4. Plot of e_{ip} (eq 15), the difference between the vapor pressure of water over the reference solution (x) and that over the tested solution (y), as a function of the molality of the tested solution (m_y) in the isotonic solutions of NaCl, KCl, or LiCl (x) and the solutions of the tested electrolyte (y) (see Table 4). The vapor pressures were calculated with eqs 3 and 4 using eq 6 with $B_{NaCl} = 1.4\ (mol \cdot kg^{-1})^{-1/2}$, $b_{1,NaCl} = 0.0699$, and $b_{2,NaCl} = 0.0062$; $B_{KCl} = 1.3\ (mol \cdot kg^{-1})^{-1/2}$, $b_{1,KCl} = 0.01324$, and $b_{2,KCl} = 0.0036$; $B_{LiCl} = 1.5\ (mol \cdot kg^{-1})^{-1/2}$, $b_{1,LiCl} = 0.2028$, and $b_{2,LiCl} = 0.0117$; and with the suggested parameter values shown in Table 4 for the tested electrolytes. Symbols: ●, Na acetate (Smith and Robinson,[4] KCl reference electrolyte, graph A), Li acetate (Robinson,[3] KCl, parameter values from ref 31, B); ○, Na acetate (Jones and Prue,[32] NaCl, A), Na acetate (Bonner,[30] LiCl, B); ▼, Na acetate (Jones and Prue,[32] KCl, A), Na formate (Bonner,[30] LiCl, B); ▽, K acetate (Jones and Prue,[32] NaCl, A), Na propionate (Bonner,[30] LiCl, B); ■, Na acetate (Robinson et al.,[31] NaCl, B); □, Li acetate (Robinson et al.,[31] NaCl, parameter values from ref 31, B). The point ($m_x/m^\circ = 0.4810$, $m_y/m^\circ = 0.4580$) was used instead of the point ($m_x/m^\circ = 0.1810$, $m_y/m^\circ = 0.4580$) for the Na acetate set of Smith and Robinson.[4]

■ 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 14 for the Hückel equations for NaCl [i.e., $B = 1.4\ (mol \cdot kg^{-1})^{-1/2}$ 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·kg^{-1}. These values, together with the equation

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

where $k_1 = -b_{1,y}M_1/m^\circ$, were used in the present study for the estimation of the Hückel parameters for dilute solutions of the organic electrolytes considered here from the experimental isopiestic data introduced above. In these determinations, either NaCl or KCl was the reference electrolyte (x) because the activities in its solutions are known. The activity of water in the NaCl or KCl solution can be calculated from the isopiestic molality of this solution (m_x) using eqs 2 and 3. The organic 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[25] (see eq 13 and the text

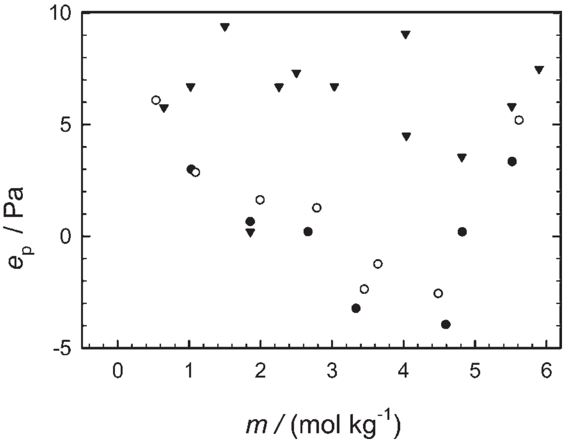

Figure 5. Plot of e_p (eq 18), the difference between the measured and predicted vapor pressures of water over solutions of K formate (●), Na formate (○), and Na acetate (▼) as a function of molality m. The vapor pressures were measured by Beyer and Steiger (for K and Na formate data, see ref 29; for Na acetate data, see ref 33). The vapor pressures were predicted with eqs 3 and 4 using eq 6 with the recommended parameter values shown in Table 4.

Table 5. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Sodium Formate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.790 (0.789)	0.939 (0.938)	3.1579
0.2	0.750 (0.748)	0.932 (0.931)	3.1473 (3.1474)
0.3	0.727 (0.726)	0.930 (0.929)	3.1369 (3.1370)
0.4	0.713 (0.711)	0.930 (0.928)	3.1264 (3.1265)
0.5	0.703 (0.700, −0.20[b])	0.931 (0.929)	3.1159 (3.1160)
0.6	0.695(0.692, −0.25[b])	0.932 (0.930)	3.1054 (3.1055)
0.7	0.689(0.685, −0.29[b])	0.934 (0.931)	3.0948 (3.0950)
0.8	0.685 (0.680, −0.35[b])	0.937 (0.933)	3.0842 (3.0845)
0.9	0.681 (0.676, −0.40[b])	0.939 (0.935)	3.0736 (3.0740)
1.0	0.679 (0.673, −0.45[b])	0.942 (0.937)	3.0629 (3.0634)
1.2	0.675 (0.668, −0.56[b])	0.947 (0.941)	3.0415 (3.0423)
1.4	0.674	0.952	3.0200
1.6	0.674	0.958	2.9983
1.8	0.675	0.964	2.9766
2.0	0.676	0.970	2.9547
2.5	0.683	0.985	2.8995
3.0	0.693	1.001	2.8436
3.5	0.706	1.018	2.7869
4.0	0.721	1.035	2.7295
4.5	0.737	1.053	2.6715

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.72$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.0356$ and the other activity values using the extended Hückel equation with $B = 1.72$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.0424$, and $b_2 = 0.002$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,GC} = -(2RT/F)\ \ln[\gamma(\text{eq 5})/\gamma(\text{eq 1})]$.

Table 6. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Potassium Formate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.790	0.939	3.1579
0.2	0.752	0.934	3.1473
0.3	0.732	0.934	3.1368
0.4	0.720	0.936	3.1262
0.5	0.712	0.939	3.1155
0.6	0.707	0.942	3.1047
0.7	0.703	0.946	3.0939
0.8	0.702	0.951	3.0830
0.9	0.701	0.955	3.0720
1.0	0.701	0.960	3.0609
1.2	0.703	0.970	3.0385
1.4	0.708	0.980	3.0158
1.6	0.713	0.990	2.9929
1.8	0.720	1.000	2.9696
2.0	0.729	1.011	2.9460
2.5	0.753	1.038	2.8857
3.0	0.782	1.067	2.8236
3.5	0.815	1.096	2.7597
4.0	0.852	1.126	2.6941
4.5	0.894	1.157	2.6268
5.0	0.939	1.188	2.5579
5.5	0.990	1.221	2.4876

[a] The activity values were calculated using the extended Hückel equation with $B = 1.65$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.085$, and $b_2 = 0.0029$.

associated with this equation in that study). The results from the present estimations are shown in Table 3. The standard error s_0 in this table is defined by the equation

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

where N is the number of points and P is the number of estimated parameters (now 2). For sodium salts of the carboxylic acids other than formic acid and acetic acid, the sodium acetate value of 1.76 (mol·kg^{-1})$^{-1/2}$ was accepted in this table for the parameter B. For sodium propionate and valerate, new values for parameter b_1 were estimated using the minimization of the squared-error sum in eq 14. For sodium butyrate (not enough data were available for its own value), caproate, and heptylate, the b_1 value for sodium valerate (0.293) was recommended in Table 3 for this parameter.

All of the suggested parameter values for the Hückel equations given in Table 3 based on the isopiestic data can be tested by predicting the vapor pressures of water over isotonic solutions of NaCl or KCl and the tested electrolyte and comparing the resulting values. The vapor pressures of both solutions at every point were calculated using eqs 2, 3, and 4 with the recommended activity parameters. The results are shown in the three graphs in Figure 1, where the isopiestic vapor pressure error (e_{ip}), defined as

$$e_{ip} = p_x - p_y \qquad (15)$$

is presented as function of the molality m_y. Graph A contains the results for sodium formate and lithium, sodium, and potassium acetate, and graph B shows those for the hydrogen salts of the

Table 7. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Lithium Acetate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.787 (0.786)	0.938 (0.937)	3.1579
0.2	0.748 (0.747)	0.933 (0.932)	3.1474
0.3	0.729 (0.726)	0.934 (0.932)	3.1368
0.4	0.717 (0.714, −0.24[b])	0.937 (0.934)	3.1261 (3.1262)
0.5	0.711 (0.706, −0.30[b])	0.941 (0.938)	3.1154 (3.1155)
0.6	0.707 (0.702, −0.36[b])	0.945 (0.942)	3.1045 (3.1047)
0.7	0.705 (0.699, −0.42[b])	0.951 (0.947)	3.0935 (3.0938)
0.8	0.704 (0.698, −0.47[b])	0.956 (0.952)	3.0824 (3.0828)
0.9	0.705 (0.698, −0.53[b])	0.962 (0.957)	3.0713 (3.0718)
1.0	0.707 (0.699, −0.58[b])	0.968 (0.962)	3.0600 (3.0606)
1.2	0.712	0.980	3.0371
1.4	0.719	0.992	3.0139
1.6	0.728	1.005	2.9903
1.8	0.738	1.017	2.9663
2.0	0.749	1.030	2.9420
2.5	0.781	1.061	2.8798
3.0	0.816	1.092	2.8159
3.5	0.856	1.123	2.7504
4.0	0.898	1.153	2.6836

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.50$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.1111$ and the other activity values using the extended Hückel equation with $B = 1.50$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.1232$, and $b_2 = -0.0008$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,\mathrm{GC}} = -(2RT/F) \ln[\gamma(\text{eq } 5)/\gamma(\text{eq } 1)]$.

Table 8. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Sodium Acetate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.802 (0.801)	0.946 (0.945)	3.1578
0.2	0.772 (0.770)	0.946 (0.945)	3.1471
0.3	0.759 (0.757)	0.951 (0.949)	3.1362 (3.1363)
0.4	0.754 (0.751, −0.23[b])	0.958 (0.955)	3.1252 (3.1253)
0.5	0.754 (0.749, −0.28[b])	0.965 (0.962)	3.1140 (3.1141)
0.6	0.755 (0.750, −0.34[b])	0.973 (0.970)	3.1026 (3.1028)
0.7	0.759 (0.753, −0.39[b])	0.981 (0.978)	3.0911 (3.0914)
0.8	0.764 (0.758, −0.43[b])	0.990 (0.986)	3.0795 (3.0798)
0.9	0.770 (0.763, −0.48[b])	0.999 (0.994)	3.0676 (3.0681)
1.0	0.777 (0.769, −0.52[b])	1.007 (1.002)	3.0557 (3.0562)
1.2	0.793 (0.784, −0.60[b])	1.025 (1.019)	3.0313 (3.0320)
1.4	0.811	1.042	3.0063
1.6	0.831	1.060	2.9808
1.8	0.853	1.077	2.9548
2.0	0.875	1.095	2.9282
2.5	0.938	1.137	2.8600
3.0	1.007	1.180	2.7893
3.5	1.082	1.221	2.7164
4.0	1.164	1.262	2.6418
4.5	1.252	1.302	2.5658
5	1.347	1.341	2.4887
5.5	1.448	1.379	2.4108
6.0	1.557	1.417	2.3325
6.5	1.674	1.454	2.2540
7.0	1.798	1.491	2.1756
7.5	1.930	1.527	2.0976

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.76$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.163$ and the other activity values using the extended Hückel equation with $B = 1.76$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.1752$, and $b_2 = -0.00185$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,\mathrm{GC}} = -(2RT/F) \ln[\gamma(\text{eq } 5)/\gamma(\text{eq } 1)]$.

three dicarboxylic acids considered here. The largest absolute error in these graphs at molalities smaller than 1.5 mol·kg^{-1} is less than 0.7 Pa (0.005 mmHg), and for all sets the errors form a random pattern. Thus, the results from these dilute solutions support well the suggested parameter values for all electrolytes. In graph C are presented the results for the heavier carboxylic acids in Table 3 and, additionally, the results from the data of Smith and Robinson[4] for the recommended sodium acetate parameters. The latter data in this graph support only satisfactorily the recommended parameter values. On the other hand, the sodium propionate values apply well to the experimental data up to a molality of 1.5 mol·kg^{-1}, and the sodium valerate values apply up to 1.2 mol·kg^{-1}. The latter values apply well to sodium butyrate, caproate, and heptylate solutions up to (1.2, 0.6, and 0.5) mol·kg^{-1}, respectively.

In Table 3 are also shown the parameter values obtained for rubidium, cesium, and thallium acetate solutions from the osmotic coefficients reported Robinson.[6] The original isopiestic data on which these osmotic coefficients were based are not available in the literature. The parameter values for these three acetates were estimated using the following equation:

$$f_2 = \ln a_{1,\mathrm{exptl}} + 2M_1 m - \frac{2\alpha M_1}{B^3}\left[\left(1 + B\sqrt{m}\right) - 2\ln(1 + B\sqrt{m}) - \frac{1}{1 + B\sqrt{m}}\right] = f_0 - b_1 M_1 (m^2/m^\circ) \qquad (16)$$

where $a_{1,\mathrm{exptl}}$ was calculated from the reported osmotic coefficient using eq 3 and otherwise this equation was used as eq 13. The standard error s_0 in Table 3 for these acetate data was calculated using the equation

$$s_0 = \sqrt{\sum_{i=1}^{N} \frac{(p_{i,\mathrm{obsd}} - p_{i,\mathrm{pred}})^2}{N - P}} \qquad (17)$$

where the observed vapor pressure was calculated from the reported osmotic coefficient. It was observed in these estimations that the simple Hückel equation applies to all points in the data sets of rubidium and cesium acetates and also in the set of thallium acetate values up to the same molality of 3.5 mol·kg^{-1}. The parameters for these three acetates were tested by predicting the observed vapor pressures (calculated from the reported osmotic coefficients) using these recommended values. The results are shown in Figure 2, in which the vapor pressure error (e_p), defined as

$$e_p = p(\text{reported}) - p(\text{predicted}) \qquad (18)$$

is presented as a function of the molality m. The largest absolute error in these tests at the molalities used in the estimations is less

Table 9. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Potassium Acetate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.801 (0.800)	0.946 (0.945)	3.1578
0.2	0.773 (0.771)	0.948 (0.946)	3.1470 (3.1471)
0.3	0.763 (0.759, −0.24[b])	0.954 (0.952)	3.1361 (3.1362)
0.4	0.760 (0.755, −0.31[b])	0.963 (0.960)	3.1249 (3.1251)
0.5	0.761 (0.756, −0.37[b])	0.972 (0.968)	3.1136 (3.1138)
0.6	0.766 (0.759, −0.43[b])	0.982 (0.978)	3.1021 (3.1023)
0.7	0.772 (0.765, −0.49[b])	0.992 (0.988)	3.0903 (3.0907)
0.8	0.780 (0.771, −0.54[b])	1.002 (0.998)	3.0784 (3.0788)
0.9	0.789 (0.779, −0.58[b])	1.013 (1.008)	3.0662 (3.0667)
1.0	0.799 (0.789, −0.62[b])	1.023 (1.018)	3.0539 (3.0545)
1.2	0.821	1.044	3.0387
1.4	0.845	1.066	3.0028
1.6	0.872	1.086	2.9762
1.8	0.900	1.107	2.9491
2.0	0.930	1.127	2.9213
2.5	1.011	1.178	2.8497
3.0	1.101	1.226	2.7754
3.5	1.199	1.273	2.6988

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.66$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.204$ and the other activity values using the extended Hückel equation with $B = 1.66$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.2212$, and $b_2 = -0.0047$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,GC} = -(2RT/F)\ln[\gamma(\text{eq }5)/\gamma(\text{eq }1)]$.

than about 0.5 Pa (= 0.004 mmHg), and therefore, the results support very well the suggested Hückel equations.

Determination of the 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 14 for the extended Hückel equation of NaCl [i.e., $B = 1.4$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.0699$, and $b_2 = 0.0062$] and KCl [$B = 1.3$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.01324$, and $b_2 = 0.0036$] apply well up to the molalities of the saturated solutions [i.e., (6.14 and 4.80) mol·kg^{-1}, respectively]. These values, together with equation

$$f_3 = \ln a_{1,x} + 2M_1 m_y - \frac{2\alpha M_1}{B_y^3}\left[(1 + B_y\sqrt{m_y}) - 2\ln(1 + B_y\sqrt{m_y}) - \frac{1}{1 + B_y\sqrt{m_y}}\right] + \frac{4M_1 b_{2,y} {m_y}^3}{3(m^\circ)^2} = f_0 - b_{1,y}M_1({m_y}^2/m^\circ) = f_0 + k_3 {m_y}^2 \qquad (19)$$

where $k_3 = -b_{1,y}M_1/m^\circ$, were used in the present study for the estimation of the Hückel parameters for more concentrated lithium, sodium, and potassium acetate; sodium formate, propionate and butyrate; and sodium and potassium hydrogen malonate and hydrogen succinate solutions. In these determinations, NaCl or KCl was again the reference electrolyte (x), and the values of the parameter B_y were taken from Table 3. When parameter $b_{2,y}$ is fixed, eq 19 represents an equation of a straight line for f_3 versus ${m_y}^2$. The straight line should go through the origin, and therefore, parameter $b_{2,y}$ must be determined again to ensure that the value of the intercept f_0 is equal to zero. For each organic salt, the same isopiestic set as that used for eq 13 was used in the new parameter estimations, but all of the data were included in the estimations. For lithium

Table 10. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Rubidium Acetate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.801	0.946	3.1579
0.2	0.772	0.947	3.1470
0.3	0.762	0.954	3.1361
0.4	0.759	0.962	3.1250
0.5	0.761	0.972	3.1136
0.6	0.765	0.982	3.1020
0.7	0.772	0.993	3.0903
0.8	0.780	1.003	3.0783
0.9	0.790	1.014	3.0661
1.0	0.800	1.025	3.0537
1.2	0.823	1.048	3.0283
1.4	0.850	1.070	3.0021
1.6	0.879	1.093	2.9751
1.8	0.910	1.116	2.9475
2.0	0.943	1.138	2.9191
2.5	1.036	1.195	2.8452
3.0	1.142	1.252	2.7676
3.5	1.262	1.308	2.6867

[a] The activity values were calculated using the Hückel equation with $B = 1.65$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.2200$.

Table 11. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Cesium Acetate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.804	0.948	3.1578
0.2	0.778	0.950	3.1470
0.3	0.768	0.957	3.1360
0.4	0.766	0.966	3.1248
0.5	0.769	0.976	3.1134
0.6	0.774	0.986	3.1018
0.7	0.781	0.997	3.0899
0.8	0.790	1.007	3.0779
0.9	0.800	1.018	3.0657
1.0	0.811	1.029	3.0532
1.2	0.835	1.052	3.0277
1.4	0.863	1.074	3.0014
1.6	0.893	1.097	2.9744
1.8	0.925	1.120	2.9467
2.0	0.959	1.142	2.9182
2.5	1.054	1.199	2.8442
3.0	1.162	1.255	2.7665
3.5	1.285	1.312	2.6855

[a] The activity values were calculated using the Hückel equation with $B = 1.74$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.2191$.

Table 12. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Thallium Acetate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.741	0.911	3.1582
0.2	0.675	0.888	3.1484
0.3	0.634	0.873	3.1388
0.4	0.605 (0.604)	0.863	3.1294 (3.1295)
0.5	0.581	0.855	3.1202
0.6	0.562 (0.561)	0.849 (0.848)	3.1110
0.7	0.546 (0.545)	0.843	3.1019 (3.1020)
0.8	0.532 (0.531)	0.839 (0.838)	3.0929 (3.0930)
0.9	0.520 (0.519)	0.835 (0.834)	3.0840
1.0	0.509 (0.508)	0.832 (0.831)	3.0751 (3.0752)
1.2	0.491 (0.490)	0.826 (0.825)	3.0575 (3.0576)
1.4	0.475 (0.474)	0.821 (0.820)	3.0040 (3.0402)
1.6	0.462 (0.461)	0.817 (0.816)	3.0229 (3.0230)
1.8	0.450 (0.449)	0.813 (0.812)	3.0059 (3.0060)
2.0	0.440 (0.439)	0.810 (0.809)	2.9890 (2.9892)
2.5	0.418 (0.417)	0.802	2.9477
3.0	0.401 (0.400)	0.796 (0.797)	2.9073 (2.9072)
3.5	0.386	0.790 (0.792)	2.8680 (2.8675)
4.0	0.373 (0.374)	0.785 (0.787)	2.8296 (2.8287)
4.5	0.362 (0.363)	0.780 (0.783)	2.7923 (2.7907)
5.0	0.351 (0.353)	0.774 (0.779)	2.7560 (2.7535)
5.5	0.342 (0.344)	0.769 (0.776)	2.7208 (2.7171)
6.0	0.333 (0.336)	0.763 (0.772)	2.6865 (2.6815)

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 0.78$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = -0.0168$ and the other activity values using the extended Hückel equation with $B = 0.78$ (mol·kg^{-1})$^{-1/2}$, $b_1 = -0.0145$, and $b_2 = -0.00065$.

Table 13. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Sodium Propionate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.807 (0.805)	0.949 (0.948)	3.1578
0.2	0.782 (0.779, −0.23[b])	0.953 (0.951)	3.1469 (3.1470)
0.3	0.775 (0.770, −0.34[b])	0.961 (0.958)	3.1359 (3.1360)
0.4	0.775 (0.768, −0.44[b])	0.971 (0.967)	3.1246 (3.1248)
0.5	0.779 (0.771, −0.53[b])	0.981 (0.977)	3.1131 (3.1133)
0.6	0.786 (0.777, −0.61[b])	0.992 (0.987)	3.1013 (3.1017)
0.7	0.794 (0.784, −0.68[b])	1.004 (0.998)	3.0894 (3.0899)
0.8	0.804 (0.793, −0.75[b])	1.015 (1.009)	3.0772 (3.0778)
0.9	0.816 (0.803, −0.80[b])	1.026 (1.020)	3.0649 (3.0655)
1.0	0.828 (0.814, −0.85[b])	1.038 (1.031)	3.0523 (3.0531)
1.2	0.854	1.061	3.0266
1.4	0.883	1.083	3.0002
1.6	0.914	1.105	2.9731
1.8	0.947	1.127	2.9453
2.0	0.982	1.148	2.9171
2.5	1.074	1.199	2.8442
3.0	1.174	1.248	2.7688
3.5	1.281	1.293	2.6917
4.0	1.395	1.337	2.6134
4.5	1.515	1.377	2.5346

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.76$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.220$ and the other activity values using the extended Hückel equation with $B = 1.76$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.2444$, and $b_2 = -0.0078$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,GC} = -(2RT/F)\ln[\gamma(\text{eq } 5)/\gamma(\text{eq } 1)]$.

acetate solutions, the other parameter values were also estimated from the isopiestic data of Robinson et al.,[31] where the reference salt was NaCl. This set consists of five points in a molality range of (4.9 to 6.3) mol·kg^{-1}, and these data cannot be predicted using the parameter values recommended here for lithium acetate solutions on the basis of the data in ref 3. The results for all of the estimations are shown in Table 4.

The resulting new parameters in Table 4 were then tested by predicting the vapor pressures of the data sets used in the estimations. The vapor pressures of both solutions at each isotonic point of these sets were calculated using eqs 3, 4, and 6 with the recommended activity parameters. The results are shown in the two graphs in Figure 3, where the isopiestic vapor pressure error (eq 15) is presented as a function of the molality m_y. In graph A are shown the results for sodium formate and lithium, sodium, and potassium acetate solutions. Almost all of the absolute errors are less than 1 Pa (= 0.008 mmHg), and the experimental data thus support well the recommended parameter values. In graph B are shown the other results for the sets used in the estimations. These data are not as good as the acetate data in graph A, but the error plots also seem to be random for the parameter values used this graph and thus support these values quite well. The least precise data are those of Stokes[5] for potassium hydrogen malonate solutions.

The recommended sodium acetate parameters in Table 4 were further tested using the isopiestic data reported by Smith and Robinson,[4] Robinson et al.,[31] Jones and Prue,[32] and Bonner.[30] The potassium acetate parameters were tested using the isopiestic data of Jones and Prue,[32] where NaCl was the reference electrolyte, and the sodium formate and propionate parameters were tested using the data of Bonner[30] against LiCl solutions. For LiCl solutions, the parameter values $B = 1.5$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.2028$, and $b_2 = 0.0117$ determined in ref 23 were used. The test results using these data are shown as plots of the errors e_{ip} (eq 15) in the two graphs in Figure 4, which correspond exactly to the plots in Figure 3. Figure 4A shows that the results using the data of Jones and Prue[32] support very well the suggested Hückel parameters for both sodium and potassium acetate solutions up to a molality of 3 mol·kg^{-1} and that the sodium acetate parameters are supported quite well by the data of Smith and Robinson.[4] The sodium formate, acetate, and propionate parameters are supported very satisfactorily by the data of Bonner[30] for these salts and LiCl up to a molality of 5 mol·kg^{-1}, as shown in Figure 4B. Figure 4B also shows that the parameter values suggested in Table 4 for lithium acetate solutions on the basis of the results from the concentrated solutions of Robinson et al.[31] do not apply well to the data of Robinson from the dilute solutions.[3] Therefore, the values based on the latter data[3] are recommended here. As can be seen in Figure 4B, however, the values based on the data of Robinson et al.[31] apply well to the lithium acetate data used in the estimation. The recommended sodium acetate parameters in Table 4 explain quite well the data measured by Robinson et al.[31] for the concentrated solutions of this electrolyte and NaCl.

Table 14. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Sodium Butyrate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.817 (0.811, −0.35[b])	0.955 (0.952)	3.1577 (3.1578)
0.2	0.801 (0.790, −0.66[b])	0.964 (0.958)	3.1467 (3.1468)
0.3	0.801 (0.787, −0.94[b])	0.977 (0.969)	3.1353 (3.1356)
0.4	0.809	0.992	3.1236
0.5	0.822	1.007	3.1116
0.6	0.836	1.022	3.0994
0.7	0.853	1.037	3.0868
0.8	0.870	1.052	3.0740
0.9	0.889	1.066	3.0609
1.0	0.909	1.080	3.0477
1.2	0.949	1.107	3.0205
1.4	0.991	1.132	2.9928
1.6	1.035	1.155	2.9645
1.8	1.078	1.177	2.9358
2.0	1.121	1.196	2.9069
2.5	1.226	1.238	2.8343
3.0	1.323	1.267	2.7630
3.5	1.405	1.285	2.6945

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.76$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.293$ (estimated from the Na valerate data) and the other activity values using the extended Hückel equation with $B = 1.76$ (mol·kg^{-1})$^{-1/2}$, $b_1 = 0.3642$, and $b_2 = -0.0345$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,\mathrm{GC}} = -(2RT/F)\ln[\gamma(\text{eq }5)/\gamma(\text{eq }1)]$.

Table 15. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Sodium Valerate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.811	0.952	3.1578
0.2	0.790	0.958	3.1468
0.3	0.787	0.969	3.1356
0.4	0.791	0.981	3.1241
0.5	0.800	0.995	3.1123
0.6	0.811	1.009	3.1002
0.7	0.825	1.023	3.0879
0.8	0.841	1.038	3.0752
0.9	0.858	1.053	3.0623
1.0	0.876	1.067	3.0491
1.2	0.916	1.097	3.0218

[a] The activity values were calculated using the Hückel equation with $B = 1.76$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = 0.293$.

Table 16. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Sodium Hydrogen Malonate Solutions at 25 °C as Functions of the Molality (m)[a]

m / mol·kg^{-1}	γ	ϕ	p / kPa
0.1	0.760	0.922	3.1581
0.2	0.704	0.905	3.1480
0.3	0.670 (0.669)	0.896 (0.895)	3.1381
0.4	0.645 (0.644)	0.889 (0.888)	3.1282 (3.1283)
0.5	0.626 (0.625)	0.885 (0.883)	3.1185 (3.1186)
0.6	0.611 (0.609)	0.881 (0.879)	3.1088 (3.1089)
0.7	0.598 (0.595)	0.878 (0.876)	3.0992 (3.0994)
0.8	0.586 (0.584, −0.23[b])	0.875 (0.873)	3.0897 (3.0899)
0.9	0.577 (0.574, −0.27[b])	0.873 (0.870)	3.0802 (3.0804)
1.0	0.568 (0.564, −0.31[b])	0.871 (0.868)	3.0707 (3.0711)
1.2	0.553 (0.549, −0.39[b])	0.868 (0.864)	3.0519 (3.0524)
1.4	0.540 (0.535, −0.49[b])	0.866 (0.860)	3.0332 (3.0340)
1.6	0.529 (0.523, −0.59[b])	0.864 (0.857)	3.0147 (3.0158)
1.8	0.520	0.862	2.9963
2.0	0.512	0.861	2.9781
2.5	0.495	0.858	2.9330
3.0	0.481	0.856	2.8885
3.5	0.470	0.856	2.8445
4.0	0.461	0.855	2.8011
4.5	0.454	0.856	2.7580
5.0	0.447	0.857	2.7152

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.16$ (mol·kg^{-1})$^{-1/2}$ and $b_1 = -0.0283$ and the other activity values using the extended Hückel equation with $B = 1.16$ (mol·kg^{-1})$^{-1/2}$, $b_1 = -0.0242$, and $b_2 = 0.0019$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,\mathrm{GC}} = -(2RT/F)\ln[\gamma(\text{eq }5)/\gamma(\text{eq }1)]$.

In Table 4 are also shown the parameter values for potassium formate and thallium acetate solutions obtained using vapor pressures measured by Beyer and Steiger[29] for more concentrated potassium formate solutions at 25 °C and osmotic coefficients reported by Robinson[6] for thallium acetate solutions. These values were estimated using equation

$$\begin{aligned} f_4 &= \ln a_{1,\mathrm{exptl}} + 2M_1 m - \frac{2\alpha M_1}{B^3}\left[\left(1 + B\sqrt{m}\right) - 2\ln(1 + B\sqrt{m}) - \frac{1}{1 + B\sqrt{m}}\right] + \frac{4b_2 M_1 m^3}{3(m^\circ)^2} \\ &= f_0 - b_1 M_1 (m^2/m^\circ) \end{aligned} \qquad (20)$$

which corresponds to eq 16 and was used in the same way as eq 19. Because no data are available for dilute solutions of potassium formate, the value of B for this salt was chosen to be 1.65 (mol·kg^{-1})$^{-1/2}$ on the basis of the B values for potassium acetate and sodium formate. This value was used in the regression analysis with eq 20. The parameter values resulting from this analysis were tested by predicting the vapor pressures of the data sets used in the estimation. For the thallium acetate solutions, the vapor pressure errors (eq 18) are shown in Figure 2, and they support very well the suggested Hückel parameters up to a molality of 6.0 mol·kg^{-1}. For potassium acetate solutions, these errors are shown in Figure 5, and they satisfactorily support the estimated parameters up to a molality of 5.5 mol·kg^{-1}. Beyer and Steiger also measured vapor pressures in concentrated solutions of sodium formate[29] and acetate.[33] These data were used in the tests of the new parameter values for the two electrolytes. The results are shown in Figure 5, in which the error plots were obtained in the same way as for potassium formate solutions. The

Table 17. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Potassium Hydrogen Malonate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.754	0.918	3.1581
0.2	0.694 (0.693)	0.898	3.1482
0.3	0.656 (0.654)	0.885 (0.884)	3.1384 (3.1385)
0.4	0.627 (0.626)	0.876 (0.874)	3.1289
0.5	0.605 (0.603)	0.868 (0.866)	3.1194 (3.1195)
0.6	0.586 (0.584, −0.22[b])	0.861 (0.859)	3.1102 (3.1103)
0.7	0.570 (0.567, −0.27[b])	0.855 (0.852)	3.1010 (3.1012)
0.8	0.556 (0.553, −0.33[b])	0.850 (0.846)	3.0919 (3.0923)
0.9	0.544 (0.539, −0.40[b])	0.845 (0.840)	3.0829 (3.0834)
1.0	0.532 (0.527, −0.47[b])	0.841 (0.835)	3.0741 (3.0747)
1.2	0.512 (0.506, −0.63[b])	0.832 (0.825)	3.0566 (3.0576)
1.4	0.495	0.825	3.0395
1.6	0.480	0.818	3.0226
1.8	0.467	0.812	3.0061
2.0	0.455	0.806	2.9898
2.5	0.430	0.794	2.9500
3.0	0.409	0.783	2.9114
3.5	0.392	0.775	2.8737
4.0	0.378	0.768	2.8365
4.5	0.366	0.764	2.7997
5.0	0.356	0.761	2.7628

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.13\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = -0.088$ and the other activity values using the extended Hückel equation with $B = 1.13\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $b_1 = -0.0847$, and $b_2 = 0.0054$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,\mathrm{GC}} = -(2RT/F)\ln[\gamma(\text{eq }5)/\gamma(\text{eq }1)]$.

Table 18. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Sodium Hydrogen Succinate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.764	0.924	3.1581
0.2	0.711 (0.710)	0.909	3.1479
0.3	0.678 (0.677)	0.901	3.1379
0.4	0.656 (0.654)	0.896 (0.895)	3.1279
0.5	0.638 (0.636)	0.893 (0.891)	3.1180 (3.1181)
0.6	0.624 (0.622, −0.21[b])	0.891 (0.889)	3.1082 (3.1083)
0.7	0.613 (0.610, −0.26[b])	0.889 (0.886)	3.0983 (3.0986)
0.8	0.603 (0.600, −0.31[b])	0.888 (0.885)	3.0885 (3.0888)
0.9	0.595 (0.591, −0.37[b])	0.887 (0.883)	3.0787 (3.0791)
1.0	0.588 (0.583, −0.44[b])	0.887 (0.882)	3.0689 (3.0695)
1.2	0.576 (0.569, −0.58[b])	0.887 (0.880)	3.0494 (3.0503)
1.4	0.566	0.887	3.0299
1.6	0.558	0.889	3.0104
1.8	0.552	0.890	2.9908
2.0	0.547	0.892	2.9713
2.5	0.538	0.899	2.9222
3.0	0.533	0.907	2.8727
3.5	0.531	0.917	2.8225
4.0	0.531	0.929	2.7717
4.5	0.534	0.942	2.7199
5.0	0.539	0.956	2.6671

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.21\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$ and $b_1 = -0.0087$ and the other activity values using the extended Hückel equation with $B = 1.21\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$, $b_1 = -0.0048$, and $b_2 = 0.0046$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,\mathrm{GC}} = -(2RT/F)\ln[\gamma(\text{eq }5)/\gamma(\text{eq }1)]$.

error plots satisfactorily support the new extended Hückel equations for sodium formate and acetate up to a molality of 6 mol·kg^{-1}.

Recommended Activity and Osmotic Coefficients at 25 °C. On the basis of the experimental evidence provided by the tests in the present study (Figures 1 to 5), the new Hückel equations for dilute solutions and the new extended Hückel equations for more concentrated solutions are reliable. New tables for the activity and osmotic coefficients of the present electrolytes at 25 °C were calculated using these equations. The new values are given in Tables 5 to 21 as follows: sodium formate, Table 5; potassium formate, Table 6; lithium acetate, Table 7; sodium acetate, Table 8; potassium acetate, Table 9; rubidium acetate, Table 10; cesium acetate, Table 11; thallium acetate, Table 12; sodium propionate, Table 13; sodium butyrate, Table 14; sodium valerate, Table 15; sodium hydrogen malonate, Table 16; potassium hydrogen malonate, Table 17; sodium hydrogen succinate, Table 18; potassium hydrogen succinate, Table 19; sodium hydrogen adipate, Table 20; potassium hydrogen adipate, Table 21. The vapor pressures of water are also included in these tables.

The values of all of the activity quantities in Tables 5 to 21 were calculated using the parameter values suggested for the extended Hückel equations except for rubidium acetate, cesium acetate, sodium valerate, sodium hydrogen adipate, and potassium hydrogen adipate solutions (for which only the Hückel equation parameters were determined). In dilute solutions (i.e., in most cases for m less than about 1.2 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 differences between these two values for most salts are quite small [for γ, less than 0.6 mV for galvanic cell deviations (as defined in the tables); for ϕ, less than 1 Pa for vapor pressure deviations]. Exceptions are solutions of sodium propionate (Table 13) and sodium butyrate (Table 14). For the former, the activity and osmotic coefficients from the normal Hückel equation and the extended one agree satisfactorily up to 0.6 mol·kg^{-1}. For the latter, they agree up to only 0.2 mol·kg^{-1}. In the latter case, however, only the extended Hückel equation was determined from the data for the salt, as for the potassium formate solutions in Table 6 (see above; this point will be discussed below).

Comparison of the Recommended Activity Values to Literature Values. The values in Tables 5 to 21 were compared with the activity and osmotic coefficients presented by Robinson and Stokes,[2] Hamer and Wu,[13] and Pitzer and Mayorga.[8] The comparisons with the literature values are shown in Figure 6 for sodium formate, Figure 7 for lithium acetate, Figure 8 for sodium acetate, Figure 9 for potassium acetate, Figure 10 for rubidium acetate, Figure 11 for cesium acetate, Figure 12 for thallium acetate, Figure 13 for sodium propionate, Figure 14 for sodium butyrate and sodium valerate, Figure 15 for sodium hydrogen malonate, Figure 16 for potassium hydrogen malonate,

Table 19. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Potassium Hydrogen Succinate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.755 (0.756)	0.919	3.1581
0.2	0.697	0.901	3.1481
0.3	0.661	0.890	3.1383
0.4	0.635	0.882	3.1286
0.5	0.614	0.877 (0.876)	3.1190
0.6	0.598 (0.597)	0.872	3.1094 (3.1095)
0.7	0.584 (0.583)	0.869 (0.878)	3.0999 (3.1000)
0.8	0.572 (0.571)	0.866 (0.864)	3.0905 (3.0907)
0.9	0.561 (0.560)	0.863 (0.861)	3.0812 (3.0814)
1.0	0.552 (0.550)	0.861 (0.858)	3.0718 (3.0721)
1.2	0.536 (0.533, −0.29[b])	0.857 (0.853)	3.0533 (3.0539)
1.4	0.523 (0.519, −0.43[b])	0.855 (0.849)	3.0348 (3.0358)
1.6	0.512 (0.506, −0.59[b])	0.853 (0.845)	3.0165 (3.0180)
1.8	0.503	0.852	2.9982
2.0	0.495	0.852	2.9800
2.5	0.479	0.853	2.9344
3.0	0.468	0.856	2.8886
3.5	0.461	0.862	2.8423
4.0	0.456	0.870	2.7953
4.5	0.454	0.880	2.7472
5.0	0.454	0.893	2.6980

[a] The activity values in parentheses were calculated using the Hückel equation with $B = 1.08\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = -0.033$ and the other activity values using the extended Hückel equation with $B = 1.08\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = -0.036$, and $b_2 = 0.0064$. [b] Galvanic cell deviation in mV calculated using the equation $e_{E,\text{GC}} = -(2RT/F)\ \ln[\gamma(\text{eq 5})/\gamma(\text{eq 1})]$.

Table 20. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Sodium Hydrogen Adipate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.779	0.933	3.1580
0.2	0.733	0.922	3.1476
0.3	0.707	0.918	3.1373
0.4	0.688	0.915	3.1271
0.5	0.674	0.914	3.1168
0.6	0.664	0.914	3.1066
0.7	0.655	0.913	3.0964

[a] The activity values were calculated using the Hückel equation with $B = 1.52\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0127$.

Table 21. Recommended Activity Coefficients (γ), Osmotic Coefficients (ϕ), and Vapor Pressures of Water (p) in Aqueous Potassium Hydrogen Adipate Solutions at 25 °C as Functions of the Molality (m)[a]

m/mol·kg^{-1}	γ	ϕ	p/kPa
0.1	0.770	0.928	3.1580
0.2	0.720	0.915	3.1478
0.3	0.690	0.908	3.1376
0.4	0.669	0.905	3.1276
0.5	0.653	0.902	3.1175
0.6	0.641	0.901	3.1075
0.7	0.630	0.900	3.0975
0.8	0.622	0.900	3.0875
0.9	0.614	0.899	3.0775
1.0	0.608	0.899	3.0675

[a] The activity values were calculated using the Hückel equation with $B = 1.31\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$ and $b_1 = 0.0103$.

Figure 17 for sodium hydrogen succinate, Figure 18 for potassium hydrogen succinate, and Figure 19 for sodium hydrogen adipate and potassium hydrogen adipate. In each figure, the comparison of the activity coefficients is shown in graph A and the comparison of the osmotic coefficients in graph B. The quantities presented on the y axes in these graphs are the cell potential deviation $e_{E,\text{GC}}$ (graph A) and the vapor pressure deviation $e_{p,\text{VPW}}$ (graph B). Details for these quantities are presented, for example, in ref 27 (see eqs 22 and 23 in that study). They are defined by equations

$$e_{E,\text{GC}} = -\frac{2RT}{F}\ln\left[\frac{\gamma(\text{literature})}{\gamma(\text{recommended})}\right] \tag{21}$$

$$e_{p,\text{VPW}} = p(\text{literature}) - p(\text{recommended}) \tag{22}$$

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

In Figure 6, the osmotic coefficients suggested by Robinson and Stokes[2] and by Pitzer and Mayorga[8] agree quite well with those recommended in Table 5 for sodium formate solutions up to a molality of 3.0 mol·kg^{-1}, but those of Hamer and Wu[13] do not agree as well. The activity coefficient deviations in graph A of this figure are quite large (most of the absolute errors are larger than 1 mV), and these deviations are much larger than the usual experimental error of, for example, the galvanic cell data with hydrogen and Ag/AgCl electrodes (see ref 22) or with alkali metal amalgam and Ag/AgCl electrodes (see refs 14 and 24). The agreement of the literature activity coefficients with the values in Table 5 is thus not good. Also, as shown in Figure 7, the osmotic coefficients suggested by Robinson and Stokes[2] and by Pitzer and Mayorga[8] agree well with those recommended in Table 7 for lithium acetate solutions up to a molality of 4.0 mol·kg^{-1}, but those of Hamer and Wu[13] do not agree as well. The activity coefficient deviations in graph A of this figure are smaller than those of Figure 6 (the absolute errors are on the order of 1 mV), and the agreement is thus better than in Table 5 for sodium formate solutions. In this figure are also included the deviations for the other extended Hückel equation presented in Table 4 on the basis of the concentrated data points of Robinson et al.[31] According to both graphs, this model does not agree well with the recommended model based on the data of Robinson.[3] Almost the same comments as those for Figure 6 apply to the activity and osmotic coefficients of sodium acetate solutions in Figure 8. In this case, the recommended activity and osmotic coefficients in Table 8 apply probably quite well up to a molality of 7.5 mol·kg^{-1} on the basis of the results in Figure 4B (see the error plot for the data of Bonner[30]).

All literature activity and osmotic coefficients for potassium, rubidium, and cesium acetate solutions (Figures 9, 10, and 11,

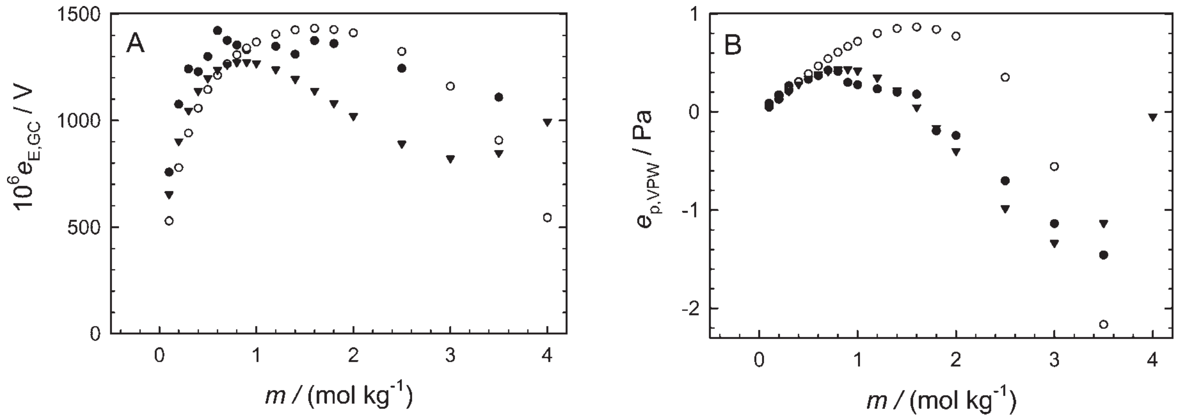

Figure 6. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for sodium formate solutions (see Table 5). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

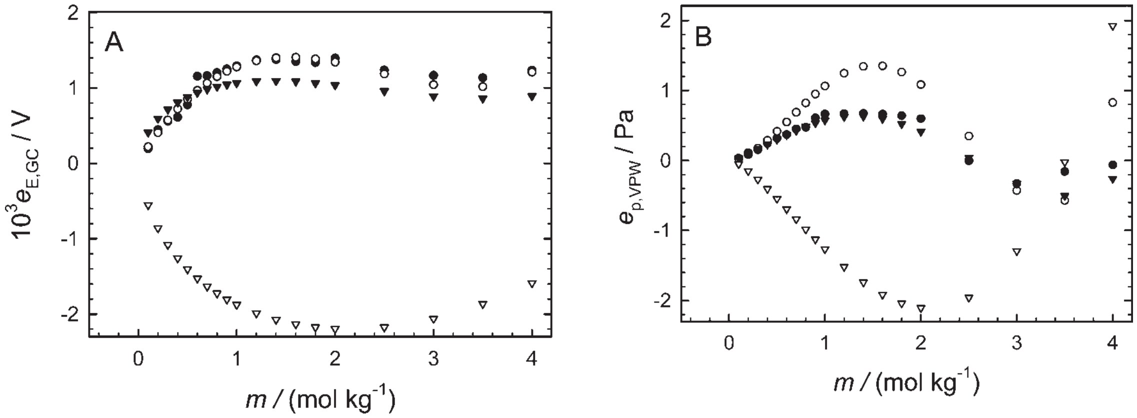

Figure 7. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for lithium acetate solutions (see Table 7). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga;[8] ▽, extended Hückel equation with $B = 1.7\ (\text{mol}\cdot\text{kg}^{-1})^{-1/2}$, $b_1 = 0.1273$, and $b_2 = -0.00323$ (see the text and Table 4).

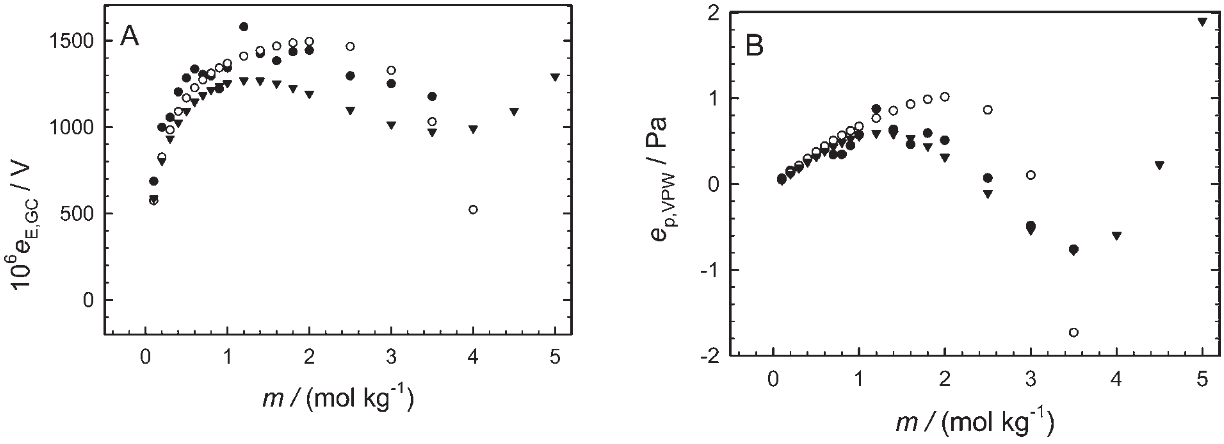

Figure 8. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for sodium acetate solutions (see Table 8). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

respectively) agree at least satisfactorily with those recommended in Tables 9, 10, and 11, respectively, for solutions of these salts.

The activity and osmotic coefficients for thallium acetate solutions in Table 12 are quite different from those of the alkali metal

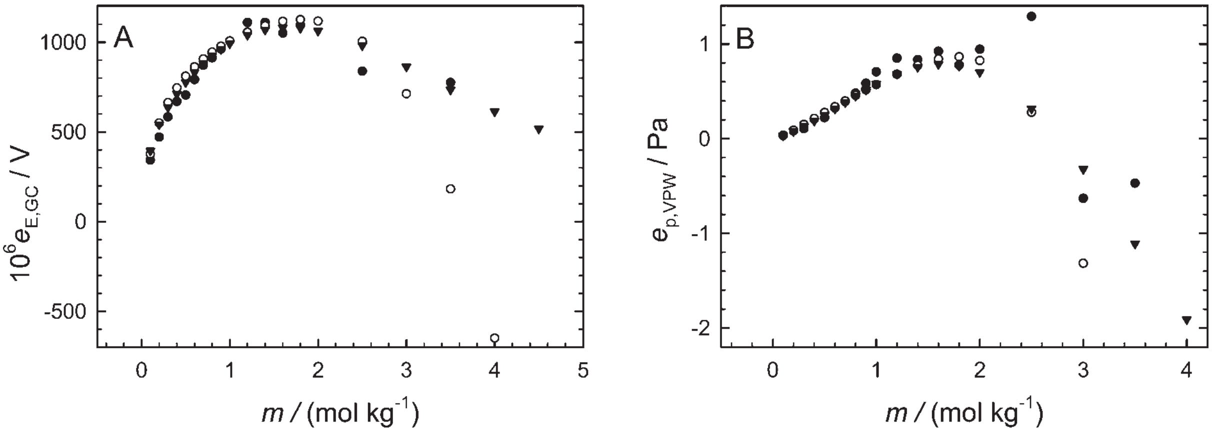

Figure 9. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for potassium acetate solutions (see Table 9). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

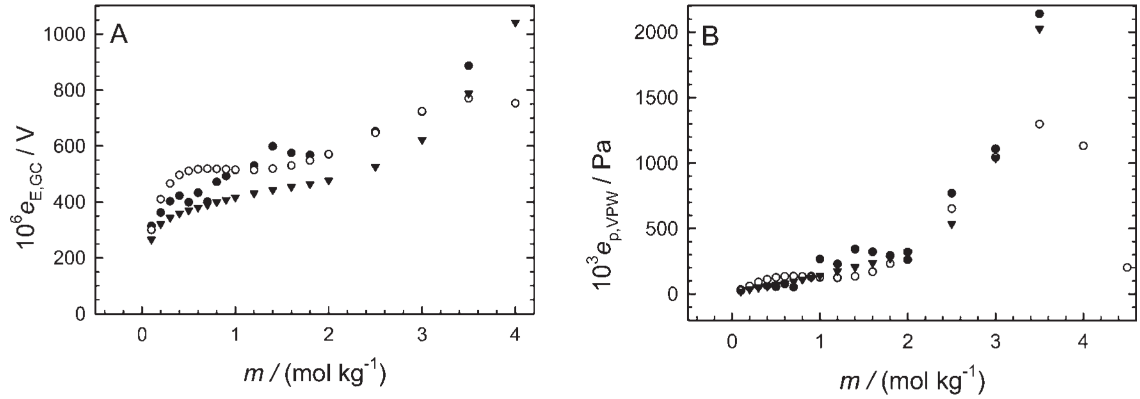

Figure 10. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 1) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 2) for rubidium acetate solutions (see Table 10). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

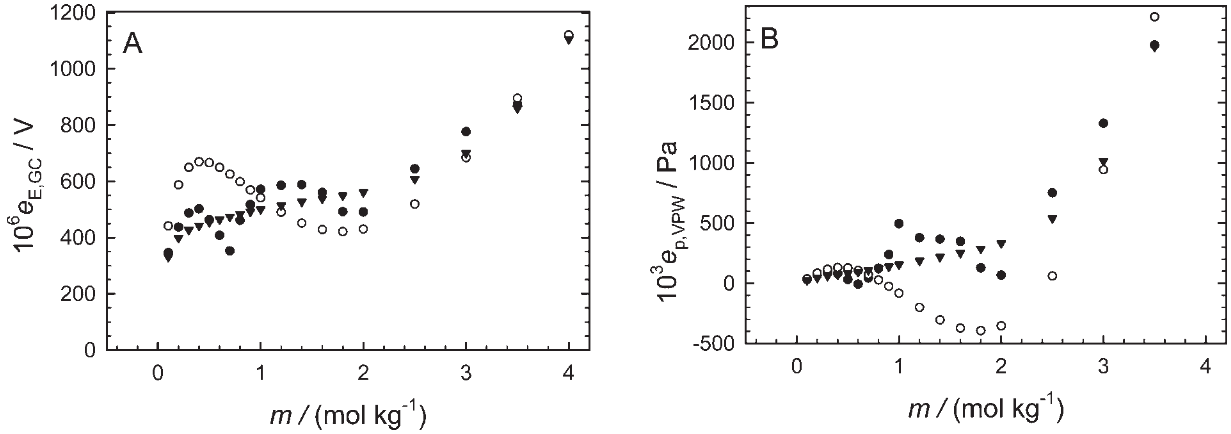

Figure 11. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 1) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 2) for cesium acetate solutions (see Table 11). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

acetates (see Tables 7 to 11). The literature osmotic coefficients in Figure 12B for solutions of this electrolyte agree quite well with those recommended in Table 12, and the best agreement is again obtained with the values of Robinson and Stokes[2] and Pitzer and

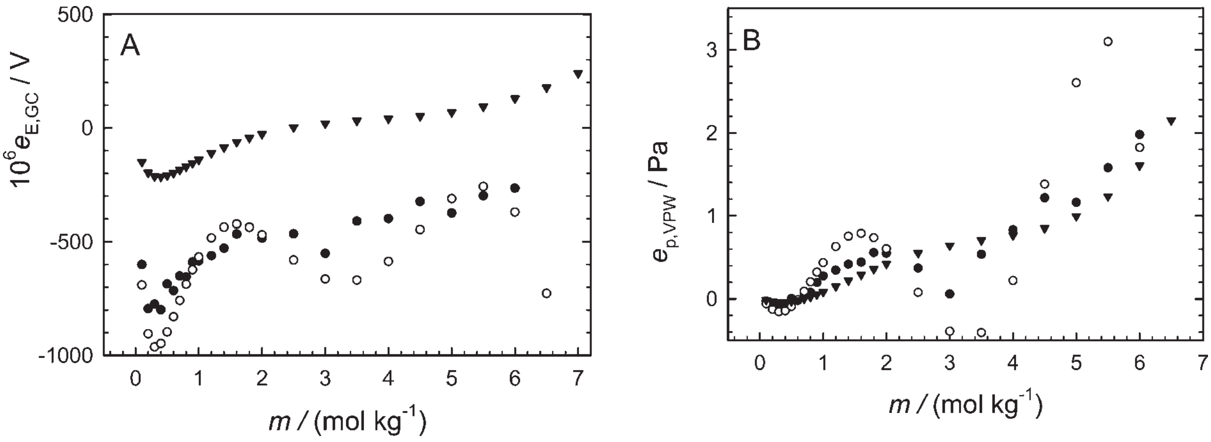

Figure 12. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for thallium acetate solutions (see Table 12). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

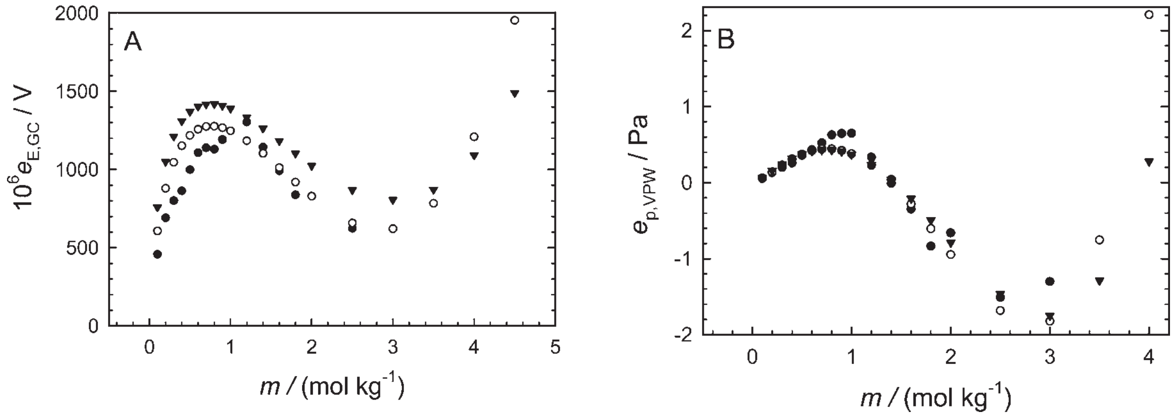

Figure 13. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for sodium propionate solutions (see Table 13). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

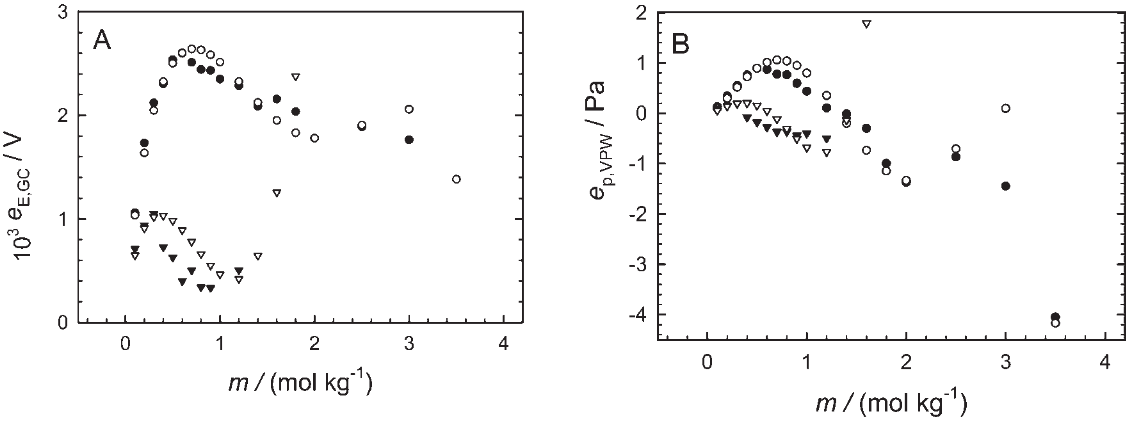

Figure 14. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eqs 5 and 1, respectively) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eqs 6 and 2, respectively) for sodium butyrate and sodium valerate solutions (see Tables 14 and 15, respectively). Symbols: ●, Na butyrate, Robinson and Stokes;[2] ○, Na butyrate, Hamer and Wu;[13] ▼, Na valerate, Robinson and Stokes;[2] ▽, Na valerate; Hamer and Wu.[13]

Mayorga.[8] In Figure 12A, the Pitzer activity coefficients are almost the same as those recommended in this table up to a molality of 6 mol·kg^{-1}. Also, a very satisfactory agreement for the other literature activity coefficients can be observed in this graph.

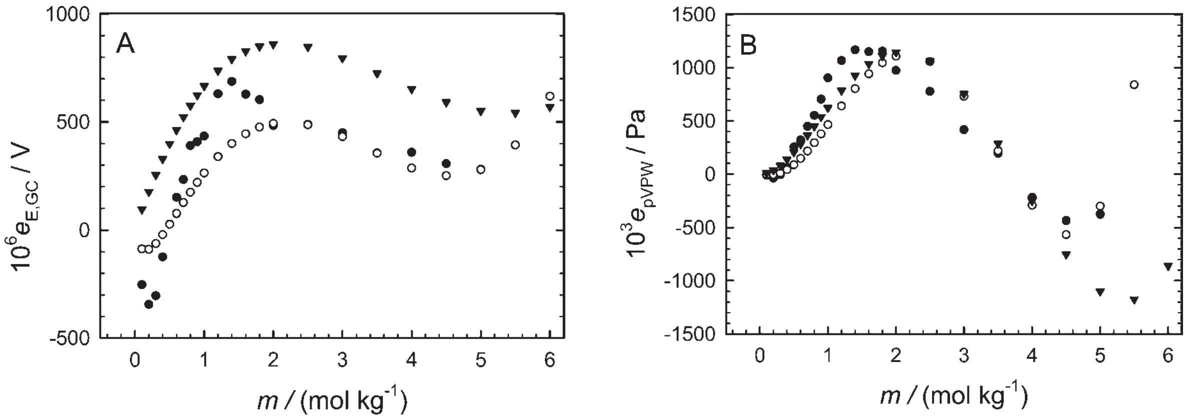

Figure 15. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for sodium hydrogen malonate solutions (see Table 16). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

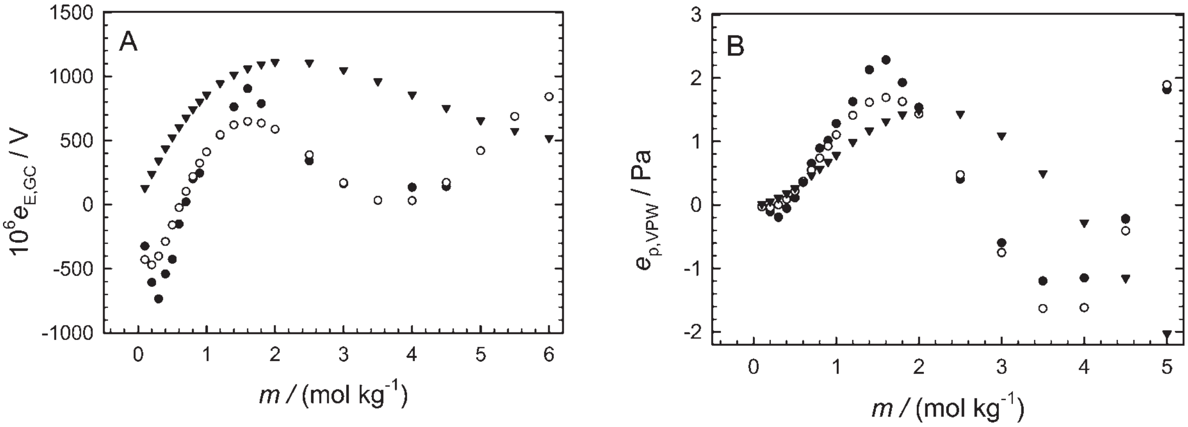

Figure 16. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for potassium hydrogen malonate solutions (see Table 17). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

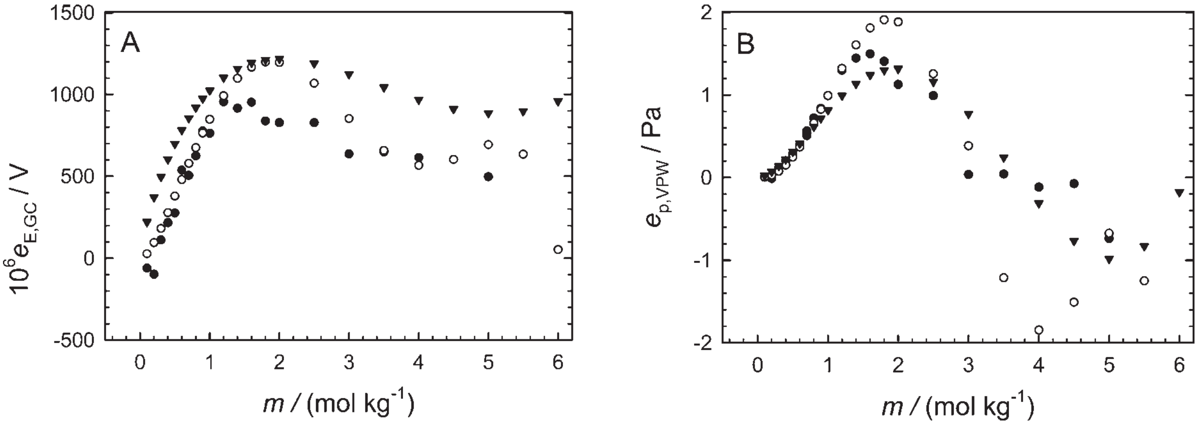

Figure 17. (A) Deviation, expressed as galvanic cell error $e_{E,GC}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,VPW}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for sodium hydrogen succinate solutions (see Table 18). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

In Figure 13B, the literature osmotic coefficients agree quite well with the values recommended in Table 13 for sodium propionate solutions up to a molality of 3.5 mol·kg^{-1}. In Figure 13A, the agreement for the activity coefficients is not as good. Pitzer and

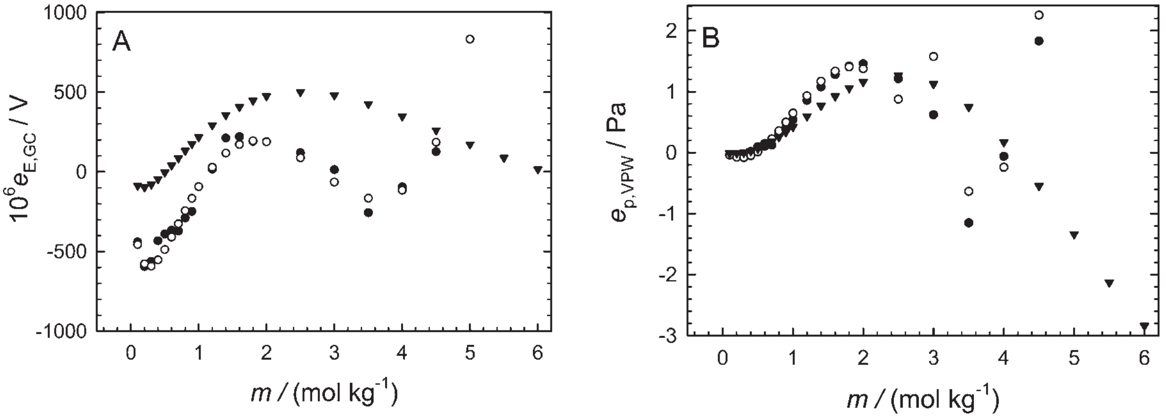

Figure 18. (A) Deviation, expressed as galvanic cell error $e_{E,\mathrm{GC}}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 5) and (B) deviation, expressed as vapor pressure error $e_{p,\mathrm{VPW}}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 6) for potassium hydrogen succinate solutions (see Table 19). Symbols: ●, Robinson and Stokes;[2] ○, Hamer and Wu;[13] ▼, Pitzer and Mayorga.[8]

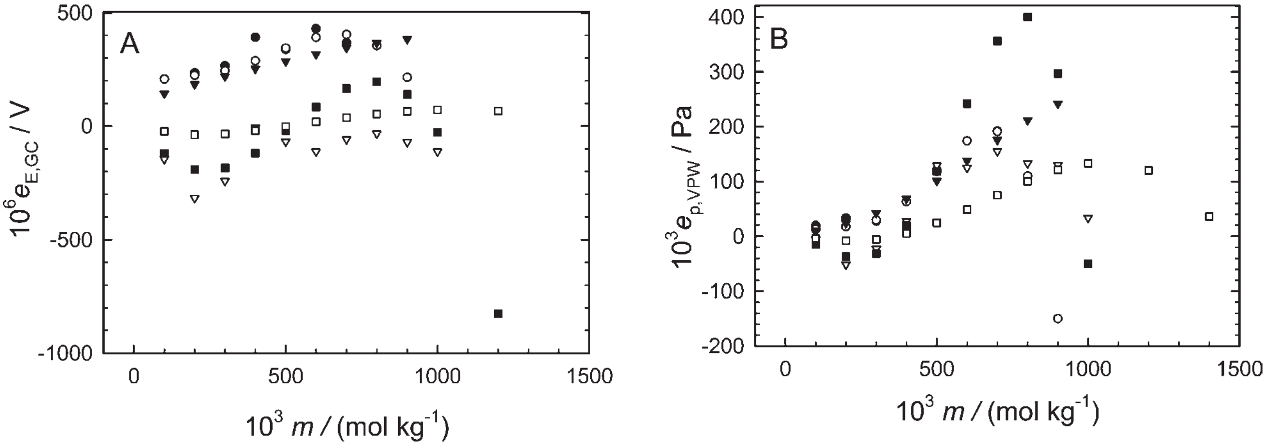

Figure 19. (A) Deviation, expressed as galvanic cell error $e_{E,\mathrm{GC}}$ (eq 21), between the literature activity coefficients and those recommended in this study (eq 1) and (B) deviation, expressed as vapor pressure error $e_{p,\mathrm{VPW}}$ (eq 22), between the literature osmotic coefficients and those recommended in this study (eq 2) for sodium hydrogen adipate and potassium hydrogen adipate solutions (see Tables 20 and 21, respectively). Symbols: ●, Na H adipate, Robinson and Stokes;[2] ○, Na H adipate, Hamer and Wu;[13] ▼, Na H adipate, Pitzer and Mayorga;[8] ▽, K H adipate, Robinson and Stokes;[2] ■, K H adipate, Hamer and Wu;[13] □, K H adipate, Pitzer and Mayorga.[8]

Mayorga[8] did not present activity values for sodium butyrate and valerate solutions, and Figure 14 therefore shows only the results for the values of Robinson and Stokes[2] and Hamer and Wu.[13] For the osmotic coefficients of sodium butyrate solutions, the quite good agreement in Figure 14B extends up to a molality of 3 mol·kg^{-1}, and the agreement for those of sodium valerate solutions extends up to 1.2 mol·kg^{-1}. Also, the literature activity coefficients for sodium valerate in Figure 14A agree quite well with the recommended values in Table 15, but the literature values for sodium butyrate are different from those recommended in Table 14. It seems that the recommended activity coefficients up to a molality of 1.2 mol·kg^{-1} are not in this case completely reliable, and the values presented for sodium valerate solutions in Table 15 (calculated with the Hückel equation recommended also for dilute sodium butyrate solutions in Table 3) may be more reliable because no data from dilute solutions were available for the parameter estimation for the extended Hückel equation of sodium butyrate in ref 4.

In Figures 15 to 19, the activity coefficients sodium and potassium salts of hydrogen malonate, hydrogen succinate, and hydrogen adipate are considered. In these figures, the agreement between the literature activity and osmotic coefficients and those recommended in this study (see Tables 16 to 21) is in all cases at least satisfactory. The best agreement is observed for the data of dilute solutions of sodium and potassium hydrogen adipate in Figure 19. The equation of Hamer and Wu[13] contains many parameters (see Table 1) for the hydrogen salts of the dicarboxylic acids. Rapid oscillations in the osmotic coefficient values can therefore be clearly seen in the deviation plot for sodium hydrogen succinate solutions (Figure 17 B).

In Figure 20, the vapor pressures of water in the solutions of the organic electrolytes considered here are compared with those in potassium chloride solutions (as the reference electrolyte). The difference is also in this case presented as the vapor pressure deviation, defined by

$$e_{p,\mathrm{VPW}} = p_{\mathrm{MX}} - p_{\mathrm{KCl}} \qquad (23)$$

where MX is the tested electrolyte, and this deviation is presented as a function of the molality. The recommended vapor pressures

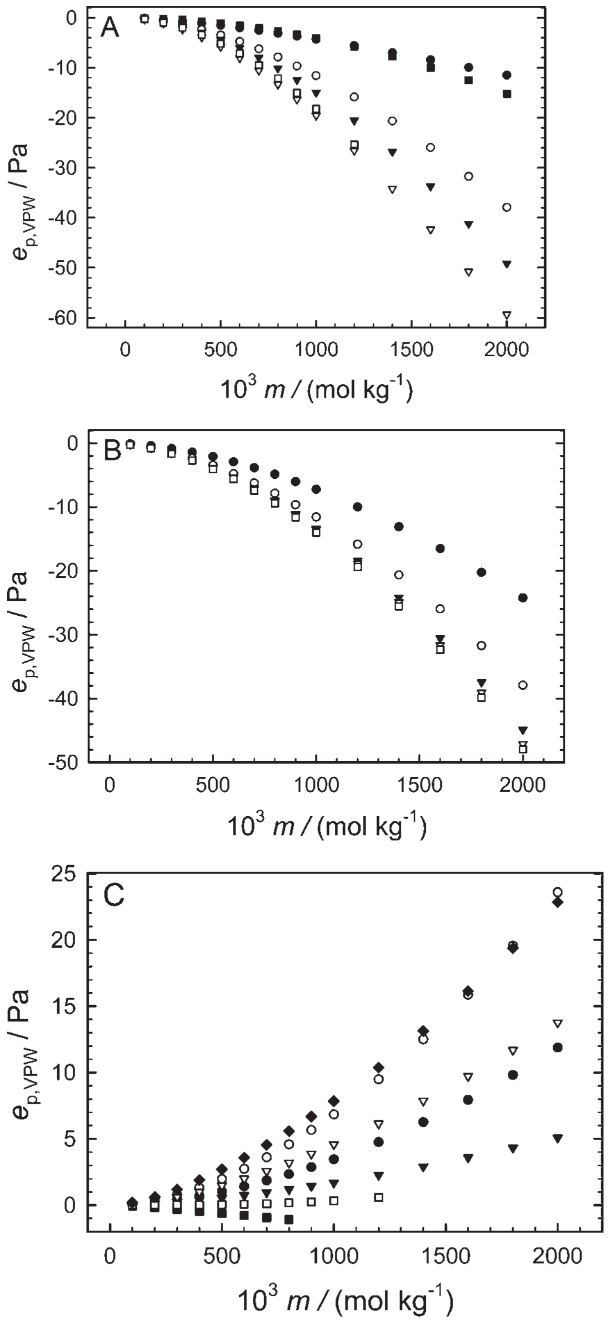

Figure 20. Deviation, expressed as vapor pressure error $e_{p,\mathrm{VPW}}$ (eq 23), between the osmotic coefficients of the electrolytes considered in this study or sodium chloride[14] and those of potassium chloride solutions[14] as a function of the molality m. The osmotic coefficients were calculated using the Hückel or extended Hückel equation (eq 2 or 6) with the recommended parameter values (Tables 3 and 4). Symbols: ●, Na formate (graph A), Li acetate (B), Na H malonate (C); ○, Na acetate (A and B), K H malonate (C); ▼, Na propionate (A), K acetate (B), Na H succinate (C); ▽, Na butyrate (A), Rb acetate (B), K H succinate (C); ■, NaCl (A), Na H adipate (C); □, Na valerate (A), Cs acetate (B), K H adipate (C); ◆, Tl acetate (C).

for KCl solutions were taken from ref 14. In Figure 20A are shown the results for sodium formate, acetate, propionate, butyrate, and valerate solutions and, for comparison, sodium chloride[14] solutions. Figure 20B shows the results for the alkali metal acetate solutions, and Figure 20C displays the results for solutions of the hydrogen salts of the dicarboxylic acids considered in the present study and of thallium acetate. The deviation plots are interesting. In Figure 20A, the vapor pressure of sodium salts of aliphatic carboxylic acids at the same molality decreases as the length of the carbon chain of the acid increases. All vapor pressures are smaller than that of potassium chloride, and the vapor pressure of sodium formate is close to that of sodium chloride; for the other salts tested, it is appreciably smaller. For sodium valerate and butyrate solutions, the vapor pressures are already close to each other. In Figure 20B, the vapor pressure of lithium acetate at the same molality is larger than that of the other acetates of the alkali metals, and the vapor pressure of sodium acetate solution is larger than the approximately same vapor pressures of potassium, rubidium, and cesium acetate solutions. In Figure 20C, the vapor pressures in the solutions of the sodium salts of hydrogen malonate, hydrogen succinate, and hydrogen adipate are always smaller than those of the corresponding potassium salts. For malonates, the vapor pressures are higher than for succinates, and the lowest vapor pressures are observed for the adipates, which are then close to those of potassium chloride solutions. The vapor pressure for thallium acetate solutions is close to that for potassium hydrogen malonate solutions.

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