Activity and Osmotic Coefficients in Electrolyte Solutions at Elevated Temperatures

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In this article, a numerical procedure is proposed for prediction of activity and osmotic coefficients at elevated temperatures based on the vapor pressure lowering of electrolyte solutions available at room and intermediate temperatures. The vapor pressure lowering of electrolyte solutions can be correlated over a wide temperature range by equation, $\ln \Delta P = A + B/T + C(\ln T - T/2T_c)$, where A, B and C are adjustable parameters and T_c is the critical temperature of pure water. The procedure is illustrated in the cases of KCl, CaCl$_2$ and especially LiCl solutions. An analytical expression for osmotic coefficients in the Meissner approach is derived by an integration of the Bjerrum equation.

Thermodynamic properties of aqueous solutions of strong electrolytes at high temperatures are of considerable importance in many areas of chemical industry, in geochemistry, in desalination and steam power generation. However, with few exceptions, the available experimental data are confined to temperatures which are not far from room temperatures. In recent years, our knowledge about activity and osmotic coefficients comes mainly from isopiestic measurements performed at elevated temperatures by the Holmes and Mesmer group. Unfortunately, these measurements constitute only a small part of industrially important electrolyte-water systems and therefore procedures for prediction of activity and osmotic coefficients must be considered. Since in the case of electrolyte solutions, a linear temperature dependence of the coefficients is rarely observed, ordinary interpolation and extrapolation techniques have rather limited value. For example, if one molal solution is considered, osmotic coefficients as a function of temperature in the 273-573 K range have a distinct maximum for NaCl, KCl and CsCl, they decrease monotonically for LiCl and for CaCl$_2$ remain practically constant up to about temperature of 373 K but after they decrease with temperature increasing (Lindsay and Liu, 1971; Holmes et al., 1978; Holmes and Mesmer, 1981).

In our previous works on the subject, estimation procedures were proposed for activity and osmotic coefficients at elevated temperatures based on data at one or two temperatures (Apelblat et al., 1988) and on the application of the Moriyama rule (Apelblat et al., 1987). In this work, it is considered a new extrapolation technique to predict activity and osmotic coefficients which is based on plentiful data available at room and intermediate temperatures (for example, Robinson and Stokes, 1965; Hamer and Wu, 1972; Goldberg, 1981; Lobo and Quaresma, 1989). The proposed numerical procedure is illustrated in the cases of KCl, CaCl$_2$ and especially LiCl solutions (lithium chloride is very soluble in water).

Representation of Osmotic and Activity Coefficients as a Function of Temperature and Concentration

At temperature T and concentration m, the difference in water vapor pressures

$$\Delta P = P_W(T) - P_S(T) \qquad (1)$$

is called the vapor pressure lowering of the electrolyte solution where $P_W(T)$ denotes the vapor pressure of pure water and $P_S(T)$ is the vapor pressure of water over electrolyte solution at T. The values of $P_W(T)$ are available from a very accurate the Saul and Wagner equation (1987):

$$\ln[P_W(T)/P_c] = \frac{\tau}{1-\tau}[-7.85823 + 1.83991\tau^{0.5} - 11.7811\tau^2$$
$$+ 22.6705\tau^{2/5} - 15.9393\tau^3 + 1.77516\tau^{6.5}] \qquad (2a)$$

$$\tau = 1 - \frac{T}{T_c}; \quad T_c = 647.14 \text{ K}; \quad P_c = 22.064 \text{ MPa} \qquad (2b)$$

where P_c and T_c are critical pressure and temperature of water. Osmotic coefficients $\phi(T)$, can be expressed in terms of vapor pressure lowering ΔP, as:

$$\phi(T) = -\frac{55.508}{\nu m}\left\{\ln\left(1 - \frac{\Delta P}{P_W(T)}\right) - \frac{B_W(T)\Delta P}{RT}\right\} \qquad (3)$$

where ν is the total number of ions of dissociating electrolyte and $B_W(T)$ is the second virial coefficient of water vapors. The viral coefficients are correlated in cm$^3 \cdot$ mol^{-1} from the Dymond and Smith compilation (1980):

$$B_W(T) = -11,766 + 66.962T$$
$$-0.12993T^2 + 0.00008477T^3 \quad (4)$$

Thus, at given T and knowing $B_W(T)$ from Eq. 4, the values of vapor pressure lowering ΔP and osmotic coefficients $\phi(T)$ are interrelated.

It was found that the vapor pressure lowering ΔP over a wide range of temperatures can be represented accurately by equation:

$$\ln \Delta P = A + \frac{B}{T} + C\left(\ln T - \frac{T}{2T_c}\right) \quad (5)$$

where the coefficients A, B and C can be evaluated from available low temperature data using a multivariate least-square technique. Since T_c of electrolyte solutions is rarely known, in calculations, its value can be replaced by that of pure water. Thus, at desired temperature ($T > 373$ K) and molality m (for which ΔP is calculated), the osmotic coefficient $\phi(T, m)$ is given by Eqs. 3, 4 and 5. It is worthwhile to note that the temperature dependence of ΔP in Eq. 5 is similar to that of vapor pressure of pure component when the difference in heat capacities of vapor and liquid phases varies linearly with temperature and vanishes at the critical temperature T_c (Moelwyn-Hughes, 1961).

All currently used equations which describe concentration dependence of activity and osmotic coefficients can be written as a sum of two terms. This first term is the Debye-Hückel type term and the second term can be called the correction term, because it is introduced in order to extend the range of concentrations over which equations are valid:

$$\phi = \phi_{DH} + \phi_{corr.} \quad (6a)$$

$$\ln \gamma_\pm = \ln \gamma_{\pm DH} + \ln \gamma_{\pm corr.} \quad (6b)$$

Usually, the first term has the form of the extended limiting Debye-Hückel law, but with different values of the distance of closest approach of two ions in solution (Guggenheim and Stokes, 1969; Horvath, 1985; Zemaitis et al., 1986). The main factor which distinguishes between different equations is a number of adjustable parameters and complexity of the correction term. The simplest form of the correction term is a formal expansion in series of concentration m or in the ionic strength I. Equations with only one, a linear term constitute a group of historically important equations of Brönstead (1922), Guggenheim (1935), Scatchard (1936) and Davies (1938) (Pitzer, 1979; Horvath, 1985). Higher terms were added by Lietzke and Stoughton (1962), Hamer and Wu (1972) and Goldberg (1981). From many equations having a more complex correction term, it is worthwhile to mention frequently used the one-adjustable parameter equations of Bromley and Meissner (Bromley, 1973; Meissner and Tester, 1972; Zemaitis et al., 1986) and the three-adjustable parameter equation of Pitzer (Pitzer and Mayorga, 1973; Pitzer, 1979). The Pitzer equations for an electrolyte dissociating into $\nu = \nu_+ + \nu_-$ ions having charges z_+ and z_- are:

$$\phi_{DH} = 1 - \frac{|z_+ z_-| A_\phi \sqrt{I}}{1 + b\sqrt{I}} \quad (7a)$$

$$\phi_{corr.} = \nu_1[\beta^{(0)} + \beta^{(1)} e^{-\alpha\sqrt{I}}]m + \nu_2 C^\phi m^2 \quad (7b)$$

where $\nu_1 = 2(\nu_+ \nu_-)/\nu$, $\nu_2 = 2(\nu_+ \nu_-)^{3/2}/\nu$, $\alpha = 2.0$ mol$^{-1/2} \cdot$kg$^{1/2}$, $b = 1.2$ mol$^{-1/2} \cdot$kg$^{1/2}$, and A_ϕ is the Debye-Hückel constant.

$$\ln \gamma_{\pm DH} = -\frac{|z_+ z_-| A_\phi \sqrt{I}}{1 + b\sqrt{I}} - \frac{2|z_+ z_-| A_\phi}{b} \ln(1 + b\sqrt{I}) \quad (8a)$$

$$\ln \gamma_{\pm corr.} = 2\nu_1 \left\{ \beta^{(0)} + \beta^{(1)} \left[\frac{1}{\alpha^2 I} - \left(\frac{1}{\alpha^2 I} + \frac{1}{\alpha\sqrt{I}} - \frac{1}{2} \right) e^{-\alpha\sqrt{I}} \right] \right\} m$$
$$+ \frac{3}{2} \nu_2 C^\phi m^2 \quad (8b)$$

The Bromley equations with one-adjustable parameter B, (Bromley, 1973) are:

$$\phi_{DH} = 1 - |z_+ z_-| A_\phi \sqrt{I} \sigma(\sqrt{I}) \quad (9a)$$

$$\phi_{corr.} = \frac{\ln 10}{2} \left[BI + |z_+ z_-| (0.06 + 0.6B) |\psi\left(\frac{3I}{2|z_+ z_-|} \right) \right] \quad (9b)$$

where the functions $\sigma(Y)$ and $\psi(Y)$ are defined by:

$$\sigma(Y) = \frac{3}{Y^3} \left[1 + Y - 2\ln(1 + Y) - \frac{1}{1 + Y} \right] \quad (10a)$$

$$\psi(Y) = \frac{2}{Y} \left[\frac{1 + 2Y}{(1 + Y)^2} - \frac{1}{Y} \ln(1 + Y) \right] \quad (10b)$$

and

$$\ln \gamma_{\pm DH} = -\frac{3|z_+ z_-| A_\phi \sqrt{I}}{1 + \sqrt{I}} \quad (11a)$$

$$\ln \gamma_{\pm corr.} = \ln 10 \left[BI + \frac{|z_+ z_-|(0.06 + 0.6B)I}{\left(1 + \frac{3I}{2|z_+ z_-|}\right)^2} \right] \quad (11b)$$

The Bromley equations correlate data to an ionic strengths of about six.

Meissner proposed an alternative equation with one-adjustable q parameter, but only for activity coefficients (Meissner and Tester, 1972; Zemaitis et al., 1986):

$$\ln \gamma_{\pm DH} = -\frac{3|z_+ z_-| A_\phi \sqrt{I}}{1 + C(q,I)\sqrt{I}} \quad (12a)$$

$$\ln \gamma_{\pm corr.} = |z_+ z_-| \ln\{1 + B(q)[(1 + 0.1I)^q - 1]\} \quad (12b)$$

where $B(q)$ and $C(q, I)$ are empirical expressions defined by:

$$B(q) = 0.75 - 0.065q \quad (13a)$$

$$C(q,I) = 1 + 0.055q e^{-0.023 I^3} \quad (13b)$$

In the Meissner approach, the water activities and osmotic coefficients are estimated graphically from the Gibbs-Duhem equation (Meissner and Kusik, 1973; Meissner, 1978; Meissner, 1980). However, it is possible to perform analytical integration of the Bjerrum equation:

$$\phi = 1 + \frac{1}{m} \int_0^m m \, d \ln \gamma_\pm \qquad (14)$$

By introducing Eq. 12 into 14, a closed expression for the Meissner osmotic coefficients can be derived. The integration is tedious but rather elementary, and therefore only the final results are presented here.

The Debye-Hückel type term has an usual form:

$$\phi_{DH} = 1 - |z_+ z_-| A_\phi \sqrt{I} \sigma(C^* \sqrt{I}) \qquad (15a)$$

$$C(q,I) < C^* < 1 + 0.055q \qquad (15b)$$

where $\sigma(Y)$ is defined in Eq. 10a. The correction term is expressed in terms of the hypergeometric functions (Abramowitz and Stegun, 1965):

$$\phi_{corr.} = \frac{|z_+ z_-|}{0.1 I} \left\{ q(1 + 0.1 I)_2 F_1 \left[1, -\frac{1}{q}; 1 - \frac{1}{q}; -\frac{1 - B(q)}{B^*(q)} \right] \right.$$
$$- q_2 F_1 \left[1, -\frac{1}{q}; 1 - \frac{1}{q}; -\frac{1 - B(q)}{B(q)} \right]$$
$$\left. - \ln\left[1 + B^*(q) - B(q)\right] \right\} \qquad (16a)$$

$$B^*(q) = B(q)(1 + 0.1 I)^q \qquad (16b)$$

where the hypergeometric function in this case is given by:

$$_2 F_1 \left(1, -\frac{1}{q}; 1 - \frac{1}{q}; -Y \right) = \sum_{n=0}^{\infty} \frac{(-1)^{n+1} Y^n}{nq - 1} \qquad (17)$$
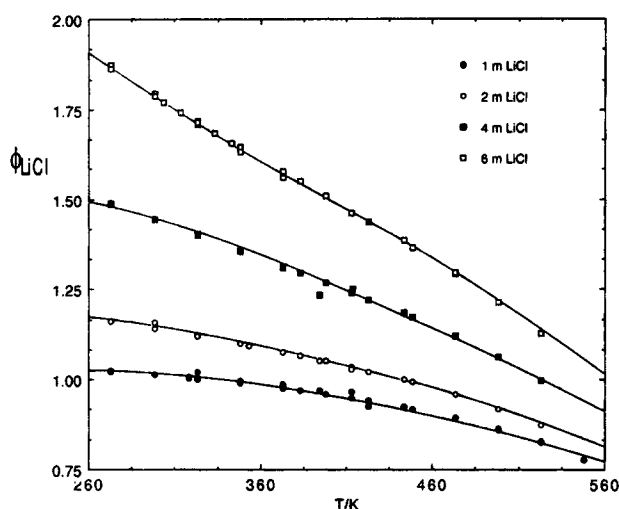
The series converges rapidly because values of $[1 - B(q)]/B^*(q)$ and $[1 - B(q)]/B(q)$ are less than unity. At given T, parameters in the Bromley and Pitzer equations (B and $\beta^{(0)}$, $\beta^{(0)}$, C^ϕ) can be determined from calculated osmotic coefficients $\phi(T, m)$ by the linear regression technique after a suitable transformation of these equations. In the case of the Meissner equation, q-parameter can be determined by a rather simple "trial and error" method. The Debye-Hückel constant A_ϕ as a function of temperature is given by Silvester and Pitzer (1977) and Ananthaswamy and Atkinson (1985).

Numerical Results

The proposed procedure for prediction of activity and osmotic coefficients is here illustrated for a number of electrolyte-water systems. The vapor pressure lowering ΔP were evaluated from known osmotic coefficients of one molal solutions of KCl (Patterson et al., 1960; Hellams et al., 1965; Lindsay and Liu, 1971; Moore et al., 1972; Herrington and Jackson, 1973; Snipes et al., 1975; Davies et al., 1985; Patil et al., 1991) and CaCl$_2$ (Ananthaswamy and Atkinson, 1985; Davies et al., 1986;

Table 1. Vapor Pressure Lowering ΔP and Boiling Point Elevations ΔT of LiCl Solutions: Coefficients of Eqs. 5 and 19

m mol·kg^{-1}	A	$-B$ K	$-C$	$-a$ K	b
1.0	79.973	7,368.8	9.230	1.40	0.00646
2.0	83.468	7,465.0	9.677	2.70	0.01322
4.0	86.690	7,516.9	10.076	5.19	0.02828
5.0	84.233	7,396.2	9.648	6.53	0.03707
6.0	88.916	7,552.8	10.363	7.06	0.04434
8.0	89.276	7,532.4	10.376	8.27	0.06042
10.0	99.537	7,906.2	11.978	4.46	0.06332
12.0	94.005	7,687.5	11.071	6.04	0.08181
15.0	97.152	7,811.5	11.544	1.67	0.08834
18.0	95.692	7,776.3	11.285	2.34	0.10706

Patil et al., 1991) for temperatures less than 373 K. They are correlated: $\ln \Delta P = 87.684 - 7739.4/T - 10.446$ ($\ln T - 0.0007726 2T$) for KCl and $\ln \Delta P = 100.99 - 8137.4/T - 12.536$ ($\ln T - 0.0007726 2T$) for CaCl$_2$. Using these equations, the osmotic coefficients for $T > 373$ K were calculated from Eqs. 3 and 4 and compared with experimental values at high temperatures for KCl (Soldano and Patterson, 1962; Soldano and Meek, 1963; Lindsay and Liu, 1971; Holmes et al., 1978; Palaban and Pitzer, 1988) and for CaCl$_2$ (Holmes et al., 1978). A very nice agreement between the calculated and experimental osmotic coefficients was observed.

The available activity and osmotic coefficients of lithium chloride at temperatures other than 298.15 K (solubility of LiCl in water at 298.15 K is more than 19.0 mol·kg^{-1}, Hamer and Wu, 1972) are with few exceptions, confined to a limited range of temperatures and concentrations. They are reported for $T \leq 373$ K by Patterson et al. (1960), $T = 372.75$ K, $m = 0.8$-4.0 mol·kg^{-1}; Hellams et al. (1965), $T = 318.15$ K, $m = 0.7$-2.5 mol·kg^{-1}; Hamer and Wu (1972), $T = 298.15$ K, $m = 0$-19.2 mol·kg^{-1}; Moore et al. (1972), $T = 353.15$ K, $m = 1.2$-3.5 mol·kg^{-1}; Gibbard and Scatchard (1973), $T = 298.15$-373.15 K, $m = 1.0$-18.5 mol·kg^{-1}; Davis et al. (1985), $T = 318.15$ K, $m = 0.5$-4.5 mol·kg^{-1}; Davies et al. (1986), $T = 323.15$ K, $m = 0.3$-4.5 mol·kg^{-1}; Patil et al. (1990), $T = 303.15$-343.15 K, $m = 3.0$-18.5 mol·kg^{-1}; and for $T > 373$ K by Soldano and Meek (1963), $T = 413.45$ K, $m = 0.35$-4.0 mol·kg^{-1}; Lindsay and Liu (1971), $T = 273.15$-573.15 K, $m = 1.0$ mol·kg^{-1}; Campbell and Bhatnagar (1979), $T = 323.15$-423.15 K, $m = 0.45$-3.2 mol·kg^{-1}, Holmes and Mesmer 1981, 1983, $T = 273.15$-573.15 K, $m = 0$-6.0 mol·kg^{-1}. Most of information about thermodynamic properties of aqueous solutions of LiCl is presented in the Lobo compilation (1989). In Table 1 are reported coefficients A, B and C of Eq. 5 for the vapor pressure lowerings ΔP which were evaluated for selected concentrations of LiCl. They were calculated using known osmotic coefficients of LiCl at temperatures less than 373 K by solving Eqs. 3 and 4 and by applying a multivariate least-square method to fit ΔP values in Eq. 5. Using these coefficients and the second virial coefficients of water, the osmotic coefficients of LiCl were calculated over the 273-573 K temperature range and they are compared in Figure 1 with the available experimental results ($m \leq 6.0$ mol·kg^{-1}). As can be seen, the calculated and experimental are in an excellent agreement. Since the coefficients A, B, and C (Table 1) are determined for a number of concentrations in the 1.0-18.0 mol·kg^{-1} range, it is possible to predict ϕ and $\gamma_\pm$ values at high temperatures for

Figure 1. Calculated (curve) and experimental osmotic coefficients ϕ of LiCl solutions as a function of temperature T at the indicated concentrations.

more concentrated than six molal lithium chloride solutions. This is illustrated for LiCl solutions at 473.15 K. The adjustable parameters of the Pitzer, Bromley and Meissner equations were evaluated and they are: $\beta^{(0)} = 0.1314$ $\text{mol}^{-1} \cdot \text{kg}$, $\beta^{(1)} = 0.3836$ $\text{mol}^{-1} \cdot \text{kg}$ and $C^{\phi} = -0.00383$ $\text{mol}^{-2} \cdot \text{kg}^2$; $B = 0.07734$ $\text{mol}^{-1} \cdot \text{kg}$ and $q = 3.0$ and the Debye-Hückel constant at 473.15 K is $A_{\phi} = 0.6212$ $\text{mol}^{-1/2} \cdot \text{kg}^{1/2}$ (Silvester and Pitzer, 1977). The Pitzer parameters given by Holmes and Mesmer (1981) at this temperature are: $\beta^{(0)} = 0.1190$ $\text{mol}^{-1} \cdot \text{kg}$, $\beta^{(1)} = 0.4439$ $\text{mol}^{-1} \cdot \text{kg}$ and $C^{\phi} = -0.00142$ $\text{mol}^{-2} \cdot \text{kg}^2$, but the corresponding relations cover results for $m \leq 6.0$ $\text{mol} \cdot \text{kg}^{-1}$ only. The available parameters of the Bromley and Meissner equations at other temperatures are: B (298.15 K) $= 0.1283$ $\text{mol}^{-1} \cdot \text{kg}$ (Bromley, 1973), B (373.15 K) $= 0.1089$ $\text{mol}^{-1} \cdot \text{kg}$ (Rastogi and Tassios, 1980) and q (298.15 K) $= 5.62$ (Kusik and Meissner, 1978). Once again, it is observed an excellent agreement (Table 2) between the calculated and determined osmotic coefficients (Holmes

Table 2. Predicted and Experimental Osmotic Coefficients of LiCl Solutions at 473.15 K

m $\text{mol} \cdot \text{kg}^{-1}$	ϕ^{*}	ϕ^{**}	$\phi^{\dagger}$	$\phi^{\dagger\dagger}$	$\phi^{\dagger\dagger\dagger}$
1.0	0.895	0.899	0.897	0.882	0.887
2.0	0.959	0.960	0.967	0.953	0.970
4.0	1.121	1.127	1.127	1.128	1.126
5.0	1.208	1.234	1.206	1.219	1.202
6.0	1.297	1.306	1.281	1.311	1.280
8.0		1.464	1.417	1.496	1.429
10.0		1.504	1.528		1.562
12.0		1.636	1.623		1.682
15.0		1.648	1.686		1.838
18.0		1.687	1.693		

*Osmotic coefficients determined at 473.15 K by Holmes and Mesmer (1981).
**Osmotic coefficients calculated using the vapor pressure lowerings from Table 1.
†Osmotic coefficients correlated using the Pitzer parameters: $\beta^{(0)} = 0.1314$ $\text{mol}^{-1} \cdot \text{kg}$, $\beta^{(1)} = 0.3836$ $\text{mol}^{-1} \cdot \text{kg}$, and $C^{\phi} = -0.00383$ $\text{mol}^{-2} \cdot \text{kg}^2$.
††Osmotic coefficients correlated using the Bromley parameter $B = 0.07734$ $\text{mol}^{-1} \cdot \text{kg}$.
†††Osmotic coefficients correlated using the Meissner parameter $q = 3.0$.

Table 3. Predicted and Experimental Activity Coefficients of LiCl Solutions at 473.15 K

m $\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}^{*}$	$\gamma_{\pm}^{**}$	$\gamma_{\pm}^{\dagger}$	$\gamma_{\pm}^{\ddagger}$
1.0	0.489	0.489	0.495	0.500
2.0	0.496	0.501	0.499	0.511
4.0	0.604	0.611	0.604	0.586
5.0	0.687	0.690	0.687	0.645
6.0	0.789	0.780	0.790	0.725
8.0		0.992	1.065	0.929
10.0		1.236		1.186
12.0		1.495		1.496
15.0		1.864		2.073
18.0		2.133		

*Activity coefficients determined at 473.15 K by Holmes and Mesmer (1981).
**Activity coefficients correlated using the Pitzer parameters: $\beta^{(0)} = 0.1314$ $\text{mol}^{-1} \cdot \text{kg}$, $\beta^{(1)} = 0.3836$ $\text{mol}^{-1} \cdot \text{kg}$ and $C^{\phi} = -0.00383$ $\text{mol}^{-2} \cdot \text{kg}^2$.
†Activity coefficients correlated using the Bromley parameter $B = 0.07734$ $\text{mol}^{-1} \cdot \text{kg}$.
‡Activity coefficients correlated using the Meissner parameter $q = 3.0$.

and Mesmer, 1981). Evidently, the Pitzer equation with three-adjustable parameters represents ϕ (473.15 K, m) much better than one-adjustable parameter equation of Meissner. If limited to the ionic strength of six, the Bromley equation is also satisfactory, this means that it can serve for many electrolytes which are considerably less soluble in water than lithium chloride. The Meissner equation which covers successfully the concentration range up to about 12.0 $\text{mol} \cdot \text{kg}^{-1}$ (Table 2) is recommended to use when our knowledge about electrolyte-water system at lower temperatures is limited. In this case, in determination of the parameters, we need less equations of ΔP than for the corresponding Pitzer equation. The evaluated parameters of the osmotic coefficient equations permit calculation of activity coefficients of LiCl at 473.15 K (Table 3) from the Pitzer (Eq. 8), Bromley (Eq. 11) and Meissner (Eq. 12) equations. As can be seen in Table 3, the representation of activity coefficients by different equations is similar to that observed for osmotic coefficients.

It is worthwhile to note that it should be expected even better agreement between experimental and predicted values of ϕ and $\gamma_{\pm}$ in the case of KCl, CaCl$_2$ and LiCl solutions than is reported here. This results from the fact that in calculation of A, B and C coefficients of the vapor pressure lowering equations (Eq. 5), only osmotic coefficients at temperatures less than 373 K were included. Osmotic coefficients at high temperatures served only as an indication of efficiency of the proposed method. Evidently, all available data should be included in calculations, to ensure a maximal accuracy and reliability of ΔP equations as a function of temperature. These equations are the basis for a successful prediction of osmotic and activity coefficients at desired temperature T and concentration m.

Until now, electrolyte solutions were characterized by values of the vapor pressure lowering ΔP, but it is possible to express their properties also in terms of the boiling point elevations:

$$\Delta T = T_S - T_W \qquad (18)$$

where T_S denotes the boiling point of electrolyte solution and T_W is the boiling point of pure water at the pressure P_S. The boiling point elevation of electrolyte solutions is important
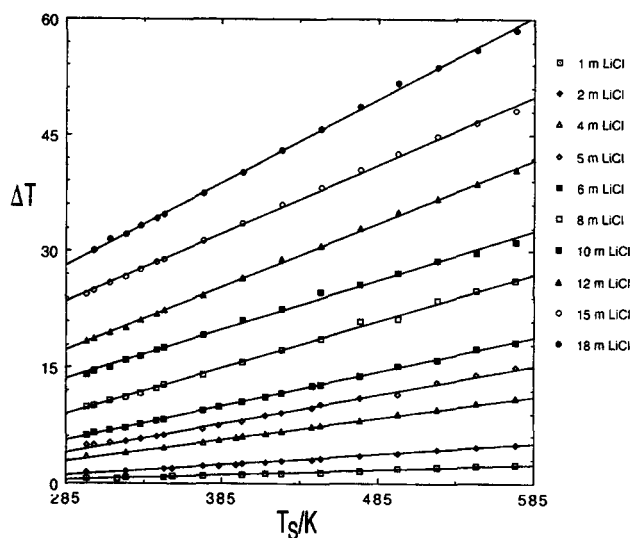
Figure 2. Calculated (curve, Eq. 19) boiling point elevations ΔT of LiCl solutions as a function of the solution temperature T_S at the indicated concentrations.

when design and control of industrial evaporators is considered.

Since for lithium chloride solutions, $\Delta P = P_W(T) - P_S(T)$ are known as a function of temperature (Table 1) and $P_W(T)$ are available from the Saul and Wagner equation (1987) it is possible to calculate the boiling point elevations ΔT of these solutions. They can be approximated by the straight line relationship (Figure 2):

$$\Delta T = a + bT_S \tag{19}$$

which is frequently observed for electrolyte solutions (Horvath, 1985). The coefficients a and b are reported in Table 1. In principle, the linear relationship (Eq. 19) permits prediction of osmotic coefficients as a function of temperature at a specified concentration m because two values of ΔT at different temperatures are sufficient to establish the corresponding relation for ΔP. However, the validity of Eq. 19 for any electrolyte system is *a priori* questionable and therefore it should be used only when existing experimental data is very limited.

Notation

a = constant, Eq. 19
A = constant, Eq. 5
A_ϕ = the Debye-Hückel constant, Eqs. 7a, 8a, 9a, 11a, 12a and Eq. 15a
b = constant, Eqs. 7a and 8a
b = constant, Eq. 19
B = constant, Eq. 12b
B = the Bromley parameter, Eqs. 9b and 11b
$B(q)$ = constant, Eq. 13a
B^* = function, Eq. 16b
$B_W(T)$ = second virial coefficient of water, Eqs. 3 and 4
C = constant, Eq. 5
$C(q,I)$ = function, Eq. 13b and 15b
C^* = constant, Eq. 15b
C^ϕ = constant, Eqs. 7b and 8b
I = ionic strength
m = molality of electrolyte

P = pressure
ΔP = vapor pressure lowering of electrolyte solution, Eqs. 1, 3 and 5
q = the Meissner parameter, Eqs. 12b, 13, 15 and 16
T = temperature
ΔT = boiling point elevation of electrolyte solution, Eqs. 18 and 19
Y = variable, Eqs. 10 and 19
z_+, z_- = positive and negative charges of ions

Greek letters

α = constant, Eqs. 7b and 8b
$\beta^{(0)}$ = constant, Eqs. 7b and 8b
$\beta^{(1)}$ = constant, Eqs. 7b and 8b
$\gamma_\pm$ = mean molal activity coefficient of electrolyte
ν = $\nu_+ + \nu_-$ total number of positive and negative ions
ν_1, ν_2 = constants, Eqs. 7b and 8b
σ = function, Eq. 10
τ = variable, Eq. 2
ϕ = osmotic coefficient of electrolyte
ψ = function, Eq. 10

Subscripts

c = critical temperature
corr. = correction term
DH = the Debye-Hückel term
S = electrolyte solution
W = pure water

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