TEACHING ELECTROLYTE THERMODYNAMICS

SIMÃO P. PINHO,* EUGÉNIA A. MACEDO
Universidade do Porto • 4200-465 Porto, Portugal

Electrolyte solutions can be found in many natural and industrial processes. Some examples are the absorption of acid gases, such as carbon dioxide, for removal from effluent gas streams, avoiding atmospheric pollution;[1] the fractional crystallization processes in which several salts are separated as pure phases from a multicomponent mixture; for the production of fertilizers such as ammonium phosphate, ammonium nitrate, or potassium sulfate;[2] for extractive distillation using salt as the extractive agent;[3] and for precipitation of globular proteins from an aqueous solution by the addition of salts.[4]

It is not surprising that during the last few decades, much attention has been devoted to experimental and theoretical studies in this area. At the undergraduate level, however, most of the thermodynamics courses still do not consider these types of mixtures, and as a result the students are not given enough insight into the differences when compared to nonelectrolyte thermodynamics. Nevertheless, several authors have recognized this gap, and recent editions of the books by Prausnitz, et al.,[5] and Tester and Modell[6] include chapters totally devoted to the thermodynamics of electrolyte solutions.

Electrolytes are usually classified according to their degree of dissociation in solution: those undergoing a total dissociation into cations and anions are called strong electrolytes, while the ones that participate in different chemical reactions, such as ion association, are called weak electrolytes. This classification has no definite boundaries because the degree of dissociation depends on, among other things, the type of solvent and solute concentration. For instance, zinc iodide is a strong electrolyte in water only if the concentration is lower than about 0.3 molal.[7]

In this paper, the thermodynamic description of a strong electrolyte solution is illustrated by calculations on the freezing point depression of strong electrolytes in water, emphasizing the differences between electrolyte and nonelectrolyte thermodynamics. In this way, students can gain some knowledge on the physical chemistry of electrolyte solutions.

THE IDEALITY IN ELECTROLYTE SOLUTIONS

Freezing point depression is a colligative property that depends on the number of solute particles but not on its nature. If we consider a solution of a solvent 1 in which a solute A is dissolved, the freezing point depression is defined as the difference between the melting temperature of the pure solvent, T_m, and the freezing temperature of the mixture, T_f, ($\Delta T = T_m - T_f$). This last temperature is lower than the melting point of the pure solvent. It is interesting to observe how the freezing point changes with the amount of solute added to the solvent. The simplest equation for the freezing point depression, which is familiar to the students in a chemical thermodynamics course, can be written as[8]

$$\Delta T = T_m - T_f = \frac{RT_m^2}{\Delta H_f(T_m)} x_A \qquad (1)$$

where ΔH_f is the enthalpy of fusion at T_m, R is the ideal gas constant, and x_A is the solute mole fraction.

The different performance obtained, using Eq. (1), in the

Simão P. Pinho graduated in chemical engineering from the University of Porto in 1992 and received his PhD from the same University in 2000. He became Professor Adjunto at Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, in 2000. His research interests are in chemical thermodynamics and separation processes.

Eugénia A. Macedo graduated in chemical engineering from the University of Porto in 1978 and received her PhD from the same University in 1984. She became Associate Professor in the Chemical Engineering Department at the University of Porto in 1990. Her research interests are in chemical thermodynamics and separation processes.

* *Instituto Politécnico de Bragança, 5301-857 Bragança, Portugal.*

calculation of ΔT for nonelectrolyte and electrolyte solutions can be easily compared. The relative percent deviations obtained for the representation of freezing point depression for aqueous solutions of D-fructose, ethylene glycol, NaCl, and $AgNO_3$, can be seen in Figure 1. Despite the fact that the maximum mole fraction is around 0.01, for the NaCl and $AgNO_3$ aqueous solutions the deviations are much more pronounced than for the nonelectrolyte systems, with errors higher than 4% even at very low concentrations ($\cong 5 \times 10^{-4}$). It should be mentioned that for those calculations, $\Delta H_f(T_m) = 6010.0$ J/mol and $T_m = 273.15$ K were used.[9]

One main assumption in the derivation of Eq. (1) is that the solute is very dilute and forms an ideal solution. When, for instance, NaCl is dissolved in water, the solution essentially contains sodium and chloride ions. At this point it is important to call the students' attention to the different nature of forces depending on the kind of solutes: the ions interact with each other through coloumbic potential, which varies as 1/r. For neutral solute molecules (nonelectrolytes) such as D-fructose, the interactions vary something like $1/r^6$. So the interaction between ions in solution is effective over a much greater distance than the interaction between neutral solute particles and, unlike what happens in nonelectrolyte solutions, even in very dilute solutions the long-range nature of the electrostatic forces between the ions is responsible for strong deviation from ideal behavior. Thus, while Eq. (1) is widely used for nonelectrolyte solutions, it cannot give reliable results for electrolyte solutions since they are ideal at concentrations too low to produce a measurable ΔT.

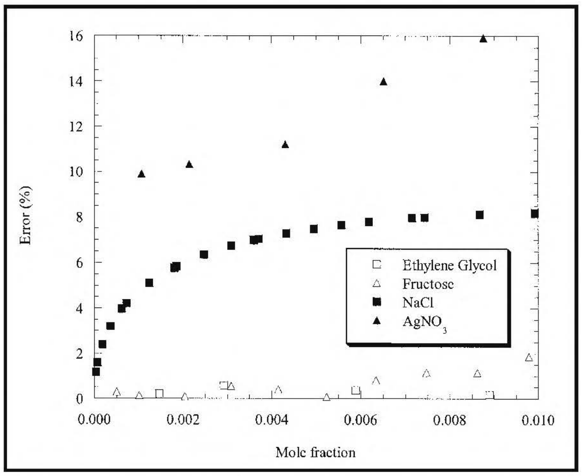

Figure 1. *Comparison of the relative percentage deviations in the calculation of the ideal freezing point depression for aqueous nonelectrolyte and electrolyte solutions.*[9,10]

Figure 1 is a fine way of showing students the different perspective that should be taken regarding the concept of ideality at high dilution in electrolyte and nonelectrolyte solutions. Another important difference that arises in the thermodynamics of electrolytes is the concentration scale used. In electrolyte, it is common to use the molality scale instead of the mole fraction scale. Moreover, in order to properly account for the number of solute particles in solution, due to the dissociation of the electrolyte, the mole fraction of solute A used in Eq. (1) should be calculated as

$$x_A = \frac{\nu n_A}{\nu n_A + n_1} \qquad (2)$$

where n_A and n_1 are the solute and solvent mole numbers, respectively, and ν is the sum of the stoichiometric coefficients of the anion and the cation.

THE DEBYE-HÜCKEL THEORY AS THE PATH FOR NON-IDEALITY IN ELECTROLYTE SOLUTIONS

So far, the students have learned that, for electrolyte solutions, assuming ideality may introduce significant errors in the calculation of the properties of the solution, even at high dilution. Thus, in order to obtain trustworthy values of ΔT, corrections to the ideal behavior should be introduced using the activity coefficient. From the thermodynamic condition for equilibrium and after some reasonable assumptions, it is possible to obtain[8]

$$\ell n\, \gamma_1 x_1 = \frac{\Delta H_f(T_m)}{R}\left(\frac{1}{T_m} - \frac{1}{T_f}\right) \qquad (3)$$

where γ_1 is the solvent activity coefficient and x_1 is its mole fraction. Now, ΔT can be calculated by solving Eq. (3) for T_f.

Taking into account only the electrostatic forces, assuming ions to be charged points in a continuous medium of uniform relative permittivity, and using well-established concepts from classical electrostatics, Peter Debye and Erich Hückel[11] derived the following expression for the mean ionic molal activity coefficient of an electrolyte ($\gamma_\pm^*$)

$$\ell n\, \gamma_\pm^* = -\frac{A|z_+ z_-|\sqrt{I}}{1 + Ba\sqrt{I}} \qquad (4)$$

In Eq. (4), A and B are parameters related to the density and dielectric constant of the solvent,[5,12,13] and a is the so-called distance of closest approach between ions (usually taken as 4 Å), z_+ and z_- are the charges of the cation and the anion, respectively, and I is the ionic strength defined by

$$I = 0.5 \sum_{i=1}^{N_{ions}} m_i z_i^2 \qquad (5)$$

being m_i the molality of the ion i and N_{ions} the number of types of ions in the solution.

The ionic strength is a very common measure of concentration in electrolyte solutions. In fact, it takes into account not only the concentration of the ion but also the magnitude of its charge. A big difference comes from the fact that using this model, the freezing point depression is now not only dependent upon the solute concentration, but also on its charges.

So the characterization of the electrolytes, in terms of its ions valences, is fundamental to establish differences that occur when applying the proposed methodology for the study of the freezing point depression of different types of electrolytes. Depending on the charge of the cation and the anion, the electrolytes can be classified as 1:1, 2:1, 1:2, 2:2, etc. For example, a 2:1 type has a cation of double charge and an anion of unit charge.

From Eq. (4), taking into consideration the Gibbs-Duhem equation, the activity of the solvent can be calculated as

$$\ell n\,\gamma_1 x_1 = -M_1 \nu m\left(1 - A|z_+ z_-|\sqrt{I}\,\sigma\left(Ba\sqrt{I}\right)\right) \qquad (6)$$

where M_1 is the molar mass of the solvent (kg/mol), and s(y) is the function

$$\sigma(y) = \frac{1}{y^3}\left(1 + y - 2\,\ell n(1+y) - \frac{1}{1+y}\right) \qquad (7)$$

The full understanding of the thermodynamic concepts that makes possible the derivation of Eq. (6) from Eq. (4) is far beyond the scope of this paper, but it is important to refer to some of the most relevant points such as the definition of the activity coefficients in different concentration scales, the standard states and the normalization of the activity coefficients, and the need for defining mean ionic properties, which are calculated based on the properties of the ions.[5-7] These concepts introduce significant changes to the nonelectrolyte thermodynamics and should be carefully discussed with the students.

Inserting the result for $\ell n\,\gamma_1 x_1$ given by Eq. (6) into Eq. (3), it is possible to obtain better estimates for ΔT in electrolyte solutions. Fixing $A = 1.130\ kg^{0.5}/mol^{0.5}$ and $B = 3.246 \times 10^9\ kg^{0.5}/(m\ mol^{0.5})$, obtained by using values of the solvent density and dielectric constant for water at 273.15 K,[9] one can calculate, for comparison with the previous results shown, new values of ΔT for aqueous NaCl solutions.

The errors obtained assuming ideal behavior and using the Debye-Hückel equation are compared in Figure 2. Using this new methodology, the errors in calculated values of ΔT are only higher than 4% for x_A around 0.05. In fact, the Debye-Hückel theory gives an exact expression for the activity coefficients of the electrolyte and of the solvent for very dilute solutions, and as can be seen, the errors for ΔT at very low solute mole fraction are near zero.

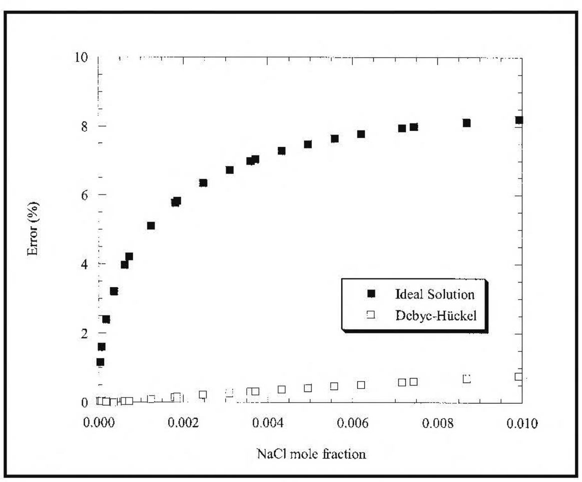

Figure 2. *Comparison of the relative percentage deviations in the calculation of the freezing point depression: ideal behavior and the Debye-Hückel equation. NaCl/water system.*[9,10]

In Figures 3 and 4, the freezing point depressions are shown for different types of electrolytes at low molality in water assuming ideality and using the Debye-Hückel equation. In all cases the assumption of ideality agrees only with the experimental values at very low concentrations, and the molality range of applicability of this equation decreases as the valences of the ions increase. This is evident in Figure 3 since the ideal

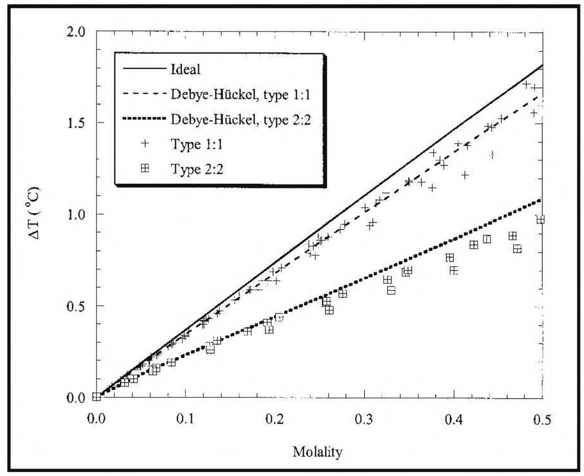

Figure 3. *Comparison of the freezing point depression for 1:1 (HNO_3, LiCl, NaCl, NaBr, NaOH, $NaNO_3$, KCl, KBr, KI, KOH, KNO_3, CH_3COOH, NH_4Cl, and $AgNO_3$) and 2:2 ($MgSO_4$, $MnSO_4$, $ZnSO_4$, and $CuSO_4$) electroclytes:*[9,10] *ideal behavior and the Debye-Hückel equation*

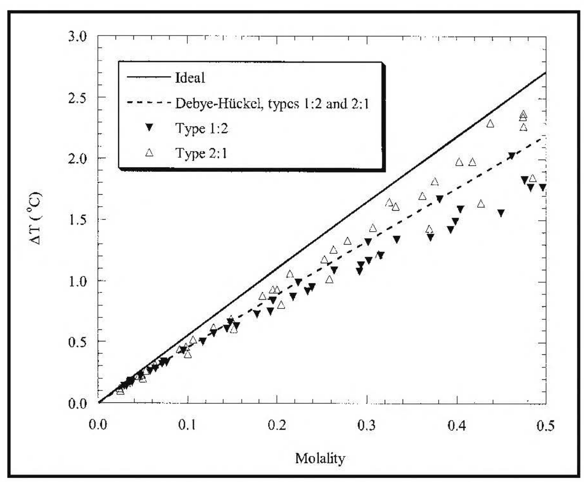

Figure 4. *Comparison of the freezing point depression for 1:2 (Na_2CO_3, Na_2SO_4, $Na_2S_2O_3$, K_2CO_3, K_2SO_4, and $(NH_4)_2SO_4$) and 2:1 ($BaCl_2$, $CsCl_2$, $MgCl_2$, $SrCl_2$, and $CaCl_2$) electrolytes:*[9] *ideal behavior and the Debye-Hückel equation.*

curve in terms of molality is the same for 1:1 and 2:2 electrolytes, while the experimental data are different. The improvement observed upon using a simple model such as the Debye-Hückel model is even more evident for 1:2, 2:1, or 2:2 electrolytes than for 1:1 electrolytes. Nevertheless, the Debye-Hückel model allows more accurate calculation of the freezing point depression to higher concentrations for all types of electrolytes.

This brief discussion alerts the students to the changes that must be made for the description of electrolyte systems. Also, there can be significant differences when comparing the behavior of aqueous solutions of electrolytes of different valences, which is explored in the next section by extending the calculations to concentrated solutions.

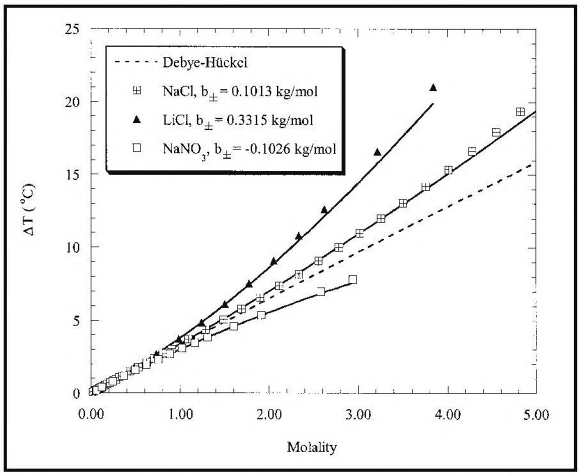

Figure 5. *Analysis of the Guggenheim equation in the description of the freezing point depression of aqueous solutions with 1:1 electrolytes.*[9,10] *Improvement to the Debye-Hückel equation.*

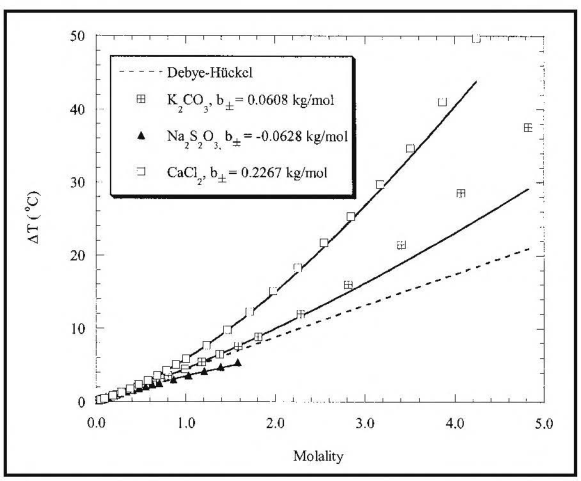

Figure 6 *Analysis of the Guggenheim equation in the description of the freezing point depression of aqueous solutions with 1:2 or 2:1 electrolytes.*[9] *Improvement to the Debye-Hückel equation.*

EXTENDING THE FREEZING POINT CALCULATION FOR CONCENTRATED SOLUTIONS

The main assumption of the Debye-Hückel theory is that deviations from ideality are only due to electrostatic forces between the ions, which is physically reasonable at high dilution but unreal when the ionic concentration increases so the ions more closely approach each other and short-range forces become dominant. Guggenheim suggested the use of a power series in electrolyte concentration to better describe the physical chemistry of electrolyte solutions, leading to the virial expansion models. To do so, Guggenheim added a new specific electrolyte empirical interaction parameter ($b_{\pm}$), proposing the following equation for the mean ionic molal activity coefficient:[13]

$$\ell n\ \gamma_{\pm}^{*} = -\frac{A\left|z_{+}z_{-}\right|\sqrt{I}}{1+\sqrt{I}} + b_{\pm}I \qquad (8)$$

From Eq. (8), the activity of the solvent is given by

$$\ell n\ \gamma_1 x_1 = -M_1 \nu m\left[1 - A\left|z_{+}z_{-}\right|\sqrt{I}\,\sigma\left(\sqrt{I}\right) + \frac{b_{\pm}I}{2}\right] \qquad (9)$$

It is interesting for the students to evaluate how this change makes possible a much better quantitative description of the freezing point depression at high concentrations. Thus, using an experimental value of the freezing temperature at a concentration around 1 molal, it is possible to obtain a value for the empirical parameter $b_{\pm}$. For instance, the experimental value for an aqueous NaCl solution of 0.90 molal is T_f = 270.11 K; from this, $b_{\pm}$ = 0.1013 kg/mol is calculated. Now, combining Eqs. (3) and (9) makes it possible to study the usefulness of the equation proposed by Guggenheim for calculation of the freezing point depression.

Figure 5 presents a comparison between the Debye-Hückel and Guggenheim equations for the estimation of ΔT in aqueous solutions of electrolytes of type 1:1 at concentrations up to 5 molal. It can be easily observed that the use of the Guggenheim equation, with a new empirical parameter regressed from a unique experimental freezing point measurement, introduces a significant improvement in the representa-

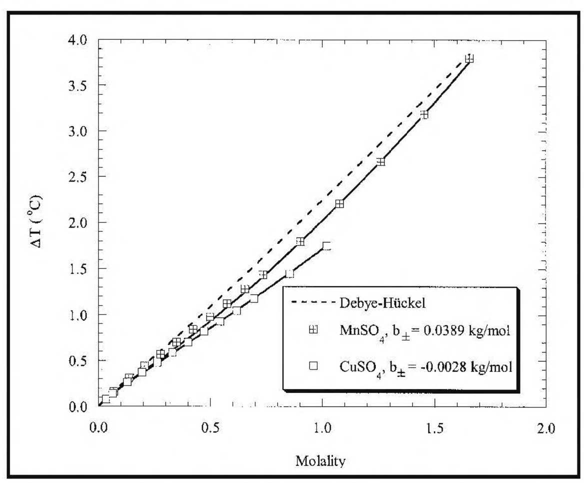

Figure 7. *Analysis of the Guggenheim equation in the description of the freezing point depression of aqueous solutions with 2:2 electrolytes.*[9] *Improvement to the Debye-Hückel equation.*

tion of ΔT for all systems shown. Compared with the previous results shown for the NaCl/water system, the application of this equation results only in a percentage deviation higher than 4% for solute mole fraction around 0.15 ($\cong$5 molal), which is a 3-times-higher concentration than the results achieved using the Debye-Hückel equation. The use of the Guggenheim equation for the systems of water/LiCl and water/$NaNO_3$ shows an even greater improvement over the Debye-Hückel equation.

In Figures 6 and 7, the same kind of comparison is presented for, respectively, 1:2 and 2:1, and 2:2 electrolytes in water. The results obtained provide a very reasonable correlation of the experimental data and only for the system of water/K_2CO_3 are there big discrepancies relative to the experimental results for solute mole fractions higher than 0.15 ($\cong$3.4 molal), which is, nonetheless, a very good result. Moreover, the Guggenheim equation makes it possible to calculate a freezing point depression up to 40°C ($CaCl_2$ system, Figure 6).

TABLE 1
Comparison of Different Approaches for Calculation of the Freezing Point Depression in Aqueous Electrolyte Systems.

Salt Type	*Data Sets*	*Maximum Molality*	*Error (%)* *Ideal*	*Debye-Hückel*	*Guggenheim*
1:1	14	5.1	10.00	6.89	1.19
2:1	5	4.2	22.51	18.56	2.77
1:2	6	4.8	34.55	13.59	2.71
2:2	4	1.7	81.85	11.86	4.02

Table 1 summarizes the deviations obtained in the representation of the freezing points of different aqueous electrolyte solutions. It gives a more comprehensive comparison between all methodologies considered here and the type of electrolyte. First, one sees that the deviations from ideality increase as the valences of the ions increase. The Debye-Hückel equation introduces improvements for all types of systems, which are especially evident for the 2:2 electrolytes. In that case, the maximum molality is much lower than in the other cases, and that is certainly a contributing factor in the big improvements obtained. Finally, it is important to stress that based solely on one experimental data point for each salt, a simple model like the Guggenheim equation makes it possible to calculate the freezing point for all systems with average error of about 2.10%.

Since colligative properties depend on the number of particles in solution, the freezing point data can be analyzed in terms of the physical chemistry of the electrolyte solutions. That is, it might give indications of the degree of dissociation, solvation, and ion-pairing. The students can also be asked to consider other hypotheses that could be made or improved for electrolyte solutions in the development of the models studies here, and further to consider more complex models such as the Pitzer model in the representation of thermodynamic properties of electrolyte solutions.

CONCLUSIONS

The differences that must be taken into account when studying aqueous electrolyte systems rather than nonelectrolyte systems have been pointed out in this paper. Specifically, we have shown that even at very high dilutions, one must use the Debye-Hückel type limiting law to properly represent the freezing point depression. In this way, the students can compare the experimental data with values assuming the ideal behavior and using the Debye-Hückel equation. Finally, the students are also challenged to understand the need for more elaborate expressions in the representation of that property at high concentrations. To do this, we suggest obtaining an empirical parameter of the Guggenheim equation using an experimental data of the freezing point depression at a concentration around 1 molal.

This simple analysis of electrolyte solutions is certainly a nice starting point to motivate students to get some knowledge of electrolyte thermodynamics. It can be introduced in a thermodynamic or a physical-chemistry course, which could be even more attractive if it can be combined with a laboratory experiment for measurement of the freezing point depression of an aqueous electrolyte solution.

REFERENCES

1. Maurer, G., "Electrolyte Solutions," *Fluid Phase Equilibria,* **13**, 269 (1983)
2. Thomsen, K., "Aqueous Electrolytes: Model Parameters and Process Simulation," PhD Thesis, Department of Chemical Engineering, Technical University of Denmark, Lyngby (1997)
3. Furter, W.F., "Extractive Distillation by Salt Effect," *Chem. Eng. Comm.,* **116**, 35 (1992)
4. Prausnitz, J.M., "Some New Frontiers in Chemical Engineering Thermodynamics," *Fluid Phase Equilibria,* **104**, 1 (1995)
5. Prausnitz, J.M., R.N. Lichenthaler, and E.G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria,* 3rd ed., Prentice-Hall, Englewood Cliffs, NJ (1998)
6. Tester, J.W., and M. Modell, *Thermodynamics and Its Applications,"* 3rd ed., Prentice-Hall, Englewood Cliffs, NJ (1977)
7. Robinson, R.A., and R.H. Stokes, *Electrolyte Solutions,* 2nd ed., Butterworths, London, UK (1970)
8. Sandler, S.I., *Chemical and Engineering Thermodynamics,* 3rd ed., John Wiley & Sons, New York, NY (1999)
9. Lide, D.R., (Ed.), *CRC Handbook of Chemistry and Physics,* 79th ed., CRC Press, Boca Raton, FL (1999)
10. Clarke, E.C.W., and D.N. Glew, "Evaluation Functions for Aqueous Sodium Chloride from Equilibrium and Calorimetric Measurements Below 154°C," *J. Phys. Chem. Ref. Data,* **14**, 489 (1985)
11. Debye, P., and E. Hückel, "Zur Theorie der Elektrolyte I. Gefrierpunktserniedrigung und Verwandte Erscheinungen," *Phys. Z.,* **24**, 185 (1923)
12. Pinho, S.P., "Phase Equilibria in Electrolyte Systems," PhD Thesis, Department of Chemical Engineering, University of Porto, Porto, Portugal (2000)
13. Zemaitis, Jr., J.F., D.M. Clark, M. Rafal, and N.C. Scrivner, *Handbook of Aqueous Electrolyte Thermodynamics: Theory and Application,"* AIChE, New York, NY (1986) ❐