A Comparison of Thermodynamic Models for VLE Data in Electrolyte Systems

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A considerable body of theoretical and experimental work has been completed on the molality mean ionic activity coefficients for aqueous electrolyte solutions. Chen et al. (1982) use an extended Debye-Huckel equation given by Pitzer (1980) and a local composition model to give the excess Gibbs functions as,

$$\frac{g^*}{RT} = \frac{g^*_{PDH}}{RT} + \frac{g^*_{LC}}{RT} \qquad (1)$$

The liquid-phase activity coefficient is given by,

$$\ln \gamma_i = \ln \gamma_{PDH,i} + \ln \gamma_{LC,i} \qquad (2)$$

Haghtalab and Vera (1988) use a Debye-Huckel expression and a nonrandom factor (NRF) into a modified nonrandom two-liquid (NRTL) expression to give the excess Gibbs function as,

$$\frac{g}{RT} = \frac{g_{DH}}{RT} + \frac{g_{NRTL\text{-}NRF}}{RT} \qquad (3)$$

This work on single-solvent systems has provided the basis for multiple-solvent systems.

Multiple-Solvent Electrolyte Systems

Multiple-solvent electrolyte systems are important in the distillation of binary and multicomponent mixtures in the presence of one or more electrolytes. The phase equilibria is normally at constant pressure and the temperature covers the bubble-point temperature range of the mixture. Results for single-solvent, single-electrolyte systems are often at 298K, which is considerably lower than the usual bubble-point temperatures in distillation.

Bekerman and Tassios (1976) correlated vapor-liquid equilibria (VLE) data using the NRTL model and obtained good results for the methanol-water-LiCl and methanol-water-$CaCl_2$ systems. However, other systems gave poor results. Boone et al. (1976) and Li et al. (1986) have used a pseudobinary solution to estimate infinite dilution activity coefficients with the Wilson model. New Wilson parameters must be used for each electrolyte concentration, which severely limits its range of application. Rousseau and Boone (1976) use pseudobinaries and the UNIQUAC model with both binary- and ternary-solvent systems such as ethanol-water-LiCl and methanol-1-propanol-water-LiCl. Very good agreement was obtained for binary solvent VLE data but this quality was reduced for ternary systems. An unfavorable aspect of this method is the need to use different UNIQUAC parameters over different electrolyte concentration ranges. Gulga and Sax (1985) used pure component vapor depression data to estimate the UNIQUAC parameters for electrolyte systems up to 2 molar. Using these parameters, binary and ternary VLE were predicted with electrolytes, but were seriously restricted by the maximum electrolyte concentration of 2 molar. Tan (1985) used a modified Wilson equation to correlate experimental VLE data of the 2-propanol-water system, with saturated potassium and calcium nitrates. Significant errors exist between the experimental and predicted VLE data for the calcium nitrate electrolyte. Hala (1983) also discusses the effect of strong electrolytes.

Mock et al. (1986) present phase equilibria for mixed-solvent electrolyte systems based on the NRTL method and identified as the NRTLE method. This method is an extension of the models of Chen et al. (1982) and Chen and Evans (1986). The model takes into account solvent-solvent, ion-solvent, and ion-ion interactions. The two basic assumptions are that the local composition of cations around a central cation is zero, and that the distribution of cations and anions around a central molecule leaves the net local ionic charge as zero. It was found that the contribution due to the extended Debye-Huckel term was small and could be eliminated, leaving only the local interactions due to the NRTL electrolyte model.

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The expression for the excess Gibbs function is given by,

$$g^E/RT = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_j X_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}} + \sum_a X_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}} \quad (4)$$

The activity coefficient of the solvent species is given by,

$$\ln \gamma_n = \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_m \frac{X_{m'} G_{mm'}}{\sum_k X_k G_{km'}} \left(\tau_{mm'} - \frac{\sum_k X_k G_{km} \tau_{km}}{\sum_k X_k G_{km}} \right) + \sum_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{X_c G_{mca'c}}{\sum_k X_k G_{kc,a'c}} \left(\tau_{mca'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right) + \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{mac'a}}{\sum_k X_k G_{ka,c'a}} \left(\tau_{mac'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right) \quad (5)$$

Nine binary parameters are required for a system composed of two solvents and one salt. Extensive tabulated data of these parameters is provided for both binary- and ternary-solvent systems with numerous electrolytes, up to saturation. A good agreement with experimental VLE data was obtained for methanol-water-$CaCl_2$ and the 2-propanol-water-LiCl systems. Other systems showed more variation.

Sander et al. (1986) provide a comprehensive treatment for mixed solvents in electrolyte systems using a Debye-Huckel term for the long range electrostatic interactions between ions, and an extended UNIQUAC expression with concentration dependent parameters for ion-solvent and solvent-solvent interactions. The method simplifies the Debye-Huckel term for mixed solvents by setting the Debye-Hukel parameters, A and b, to the constants, 2 $(kg/mol)^{1/2}$ and 1.5 $(kg/mol)^{1/2}$, respectively. The concentration dependence of the interaction energy parameters between ion, i, and solvent, m, for the extended UNIQUAC model is linear with tabulated values of the parameters, $\delta_{ij,m}$. A special feature of the table is the identification of the δ parameters with ions rather than salts. The method has many characteristics of group contribution methods, whereby a large number of salts can be studied from a short list of group parameters and hence, is identified as the UNIFE method for electrolytes. The following ions have been investigated: Li^+, Na^+, K^+, Ca^{2+}, Cl^-, Br^-, NO_3^-, and CH_3COO^-. The solvents studied are limited to water, methanol, ethanol, 1-propanol and 2-propanol. The UNIFE parameters have been obtained from an extensive data base of experimental data of VLE information. Unfortunately, this data cannot be subjected to a thermodynamic consistency test. The maximum salt concentrations for the UNIFE model are 10 mol/kg for 1:1 salts, and 6.5 mol/kg for 2:1 salts. The values of the volume and surface area parameters, r and q, are tabulated for the ions, which have special values obtained by minimizing an objective function. The UNIFE method is capable of handling a large number of mixed solvents together with a large number of salts to predict VLE data.

The activity coefficient for a solvent, n, is given by,

$$\ln \gamma_n = \ln \gamma_n^{D-H} + \ln \gamma_n^R + \ln \gamma_n^C \quad (6)$$

where the Debye-Huckel term is

$$\ln \gamma_n^{DH} = M_n (2A/b^3)(1 + b\sqrt{I} - 1/(1 + b\sqrt{I}) - 2 \ln (1 + b\sqrt{I}) \quad (7)$$

The combinatorial term is

$$\ln \gamma_n^C = \ln \phi_n/x_n + 1 - \phi_n/x_n - \tfrac{1}{2} z q_n (\ln \phi_n/\theta_n + 1 - \phi_n/\theta_n) \quad (8)$$

where

$$z = 10 \quad \text{and} \quad \phi_n \text{ is the volume fraction} \quad (9)$$

$$\phi_n = \frac{X_n r_n}{\sum_k X_k r_k} \quad (10)$$

The residual term is

$$\ln \gamma_n^R = q_n \left(1 - \ln \left(\sum_k \theta_k \Psi_{kn} \right) - \sum_l \frac{\theta_l \Psi_{nl}}{\sum_k \theta_k \Psi_{kl}} \right) - 2q_n/T \cdot \sum_i \sum_m \theta_i^2 \theta_m \sum_{j \neq i} \delta_{ij,m} \theta_j \cdot \left(\frac{\Psi_{mi}}{\sum_k \theta_k \Psi_{ki}} + \frac{\Psi_{im}}{\sum_k \theta_k \Psi_{km}} \right) \quad (11)$$

A comparison between experimental and predicted vapor-phase compositions is quoted with an overall absolute deviation of 0.012 vapor-phase mole fraction. The UNIFE method is capable of estimating the salt concentration necessary to break azeotropes in the ethanol-water system. The method also predicts the appearance of a second azeotrope in the system, 1-propanol-water-$CaCl_2$. For the ternary solvent system, methanol-ethanol-water-$CaCl_2$, the VLE absolute deviations are 0.029, 0.018 and 0.015 vapor mole fraction for the respective solvents. Further efforts to improve the simplifications in the Debye-Huckel term have been given by Marcio et al. (1987).

NRTLE and UNIFE Methods

The predicted VLE data for constant total pressure conditions as shown by Furzer (1986) require the estimation of the bubble-point temperature of the electrolyte system, followed by the solvent K values and finally, the vapor phase composition for

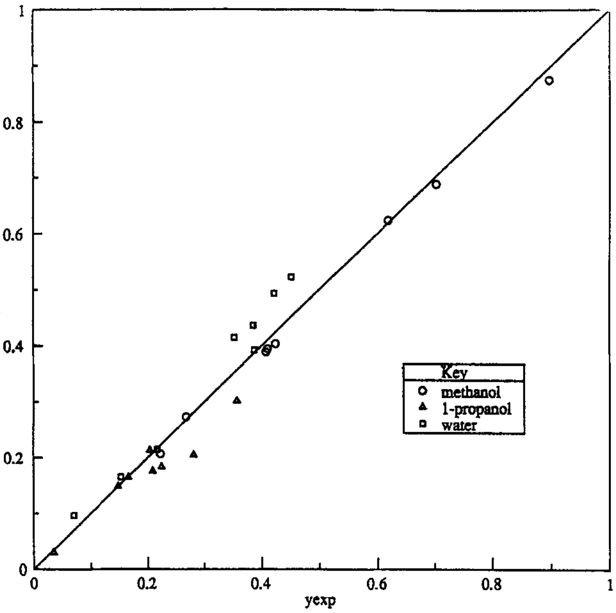

Figure 1. Experimental vs. predicted vapor phase composition for methanol-1-propanol-water with lithium chloride.
Method used is NRTLE.

a given x, the liquid composition. Activity coefficients calculated by both the NRTLE and UNIFE methods have been programmed and the calculated VLE data are in good agreement with the many examples provided by Moch et al. (1986) and Sander et al. (1986).

Extensive experimental VLE data for salt systems is given by Meranda and Furter (1972) and Furter (1977). Rousseau and Boone (1978) have presented experimental VLE data for the systems, methanol-1-propanol-water-LiCl and ethanol-1-propanol-water-LiCl. Figures 1 and 2 show a comparison between the three-solvent experimental and predicted compositions using the NRTLE method. There are significant deviations of over 0.030 vapor mole fraction for many points in these figures; the user of this type of VLE data for distillation should bear in mind these limitations. A comparison with the UNIFE method can not be made, due to present gaps in the parameter tables. It should be noted that Rousseau and Boone (1978) could obtain improved

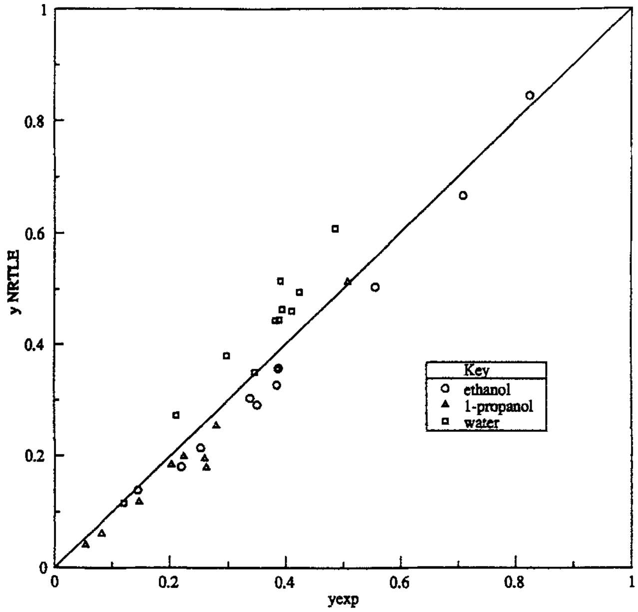

Figure 2. Experimental vs. predicted vapor phase composition for ethanol-1-propanol-water with lithium chloride.
Method used is NRTLE.

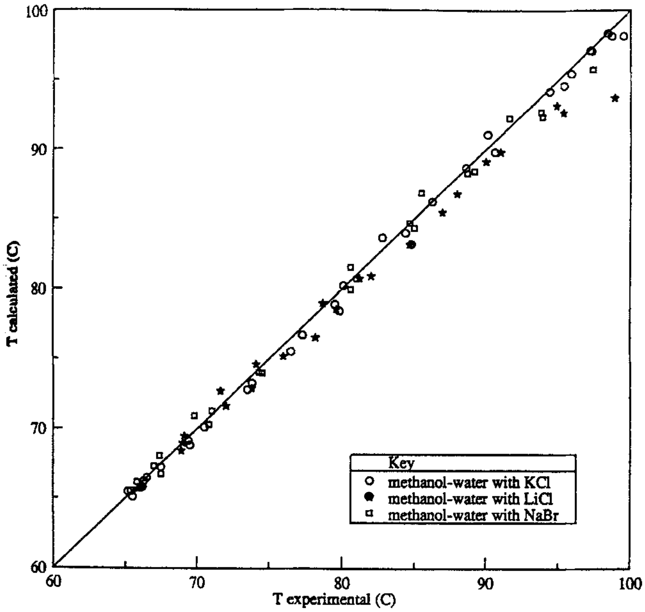

Figure 3. Calculated vs. experimental bubble-point temperatures.
Calculated values from NRTLE.

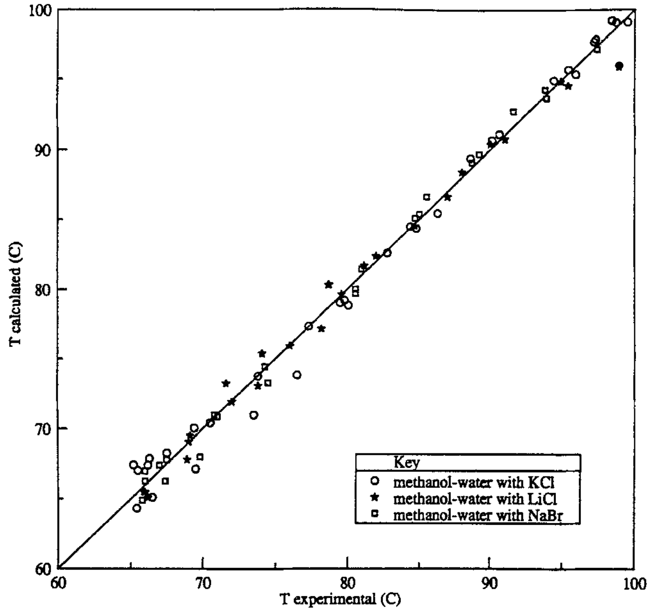

Figure 4. Calculated vs. experimental bubble-point temperatures.
Calculated values from UNIFE.

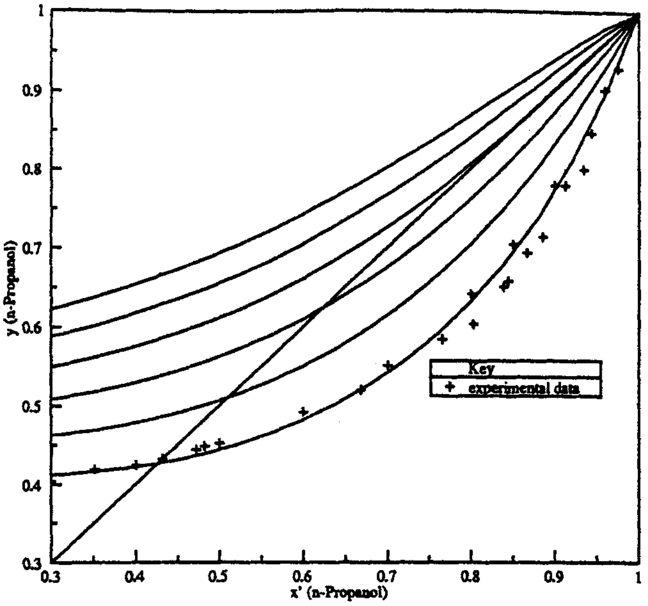

Figure 5. Vapor-liquid equilibria for 1-propanol-water with $CaCl_2$.
Salt concentration: 0.0–2.0 molal.

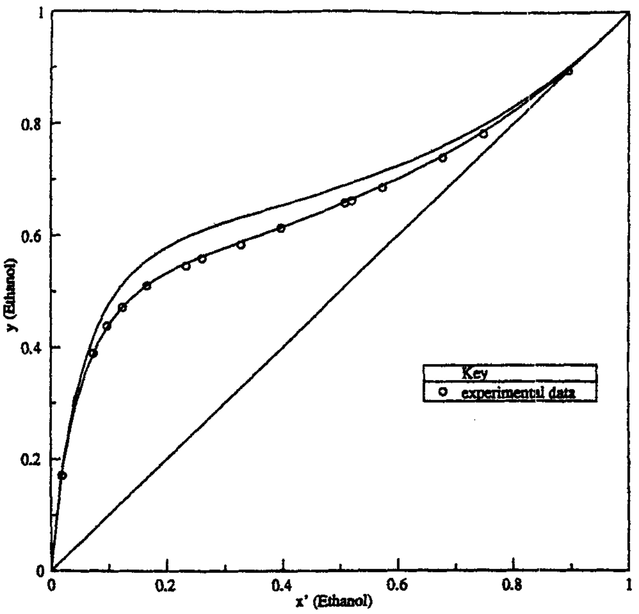

Figure 7. Vapor-liquid equilibria for ethanol-water with NaCl.
Saturated salt and no salt at $P = 101$ kPa.

predicted VLE data, but at the expense of having model parameters change in different concentration ranges.

Boone et al. (1976) have presented experimental bubble-point temperatures for the systems, methanol-water-KCl, methanol-water-LiCl, and methanol-water-NaBr. Figures 3 and 4 show a comparison between experimental and predicted bubble-point temperatures for the NRTLE and UNIFE methods, respectively. Both methods provide good predictions over the full bubble-point temperature range.

Figure 5 shows the good agreement between the predicted and experimental azeotrope for the 1-propanol-water system with no salt. The effect of $CaCl_2$ on the azeotrope for concentrations from 0 to 2 in steps of 0.4 molal, is predicted by the UNIFE method in Figure 5. The azeotrope is predicted to be removed at a concentration of about 1.6 molal. The inverted volatility of 1-propanol at concentrations greater than the azeotrope is well described by the UNIFE method. Figure 6 shows a similar effect of $Ca(NO_3)_2$ on the azeotrope.

Experimental data on salt solubility in binary or multiple solvents is limited, and some caution should be used in predicting VLE data that might be outside salt solubility limits. In some

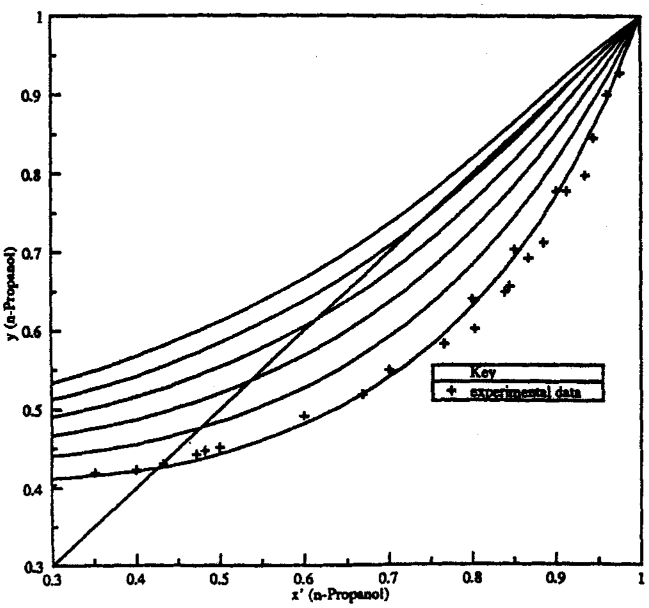

Figure 6. Vapor-liquid equilibria for 1-propanol-water with $Ca(NO_3)_2$.
Salt concentration changes from 0.0 to 2.0 molal.

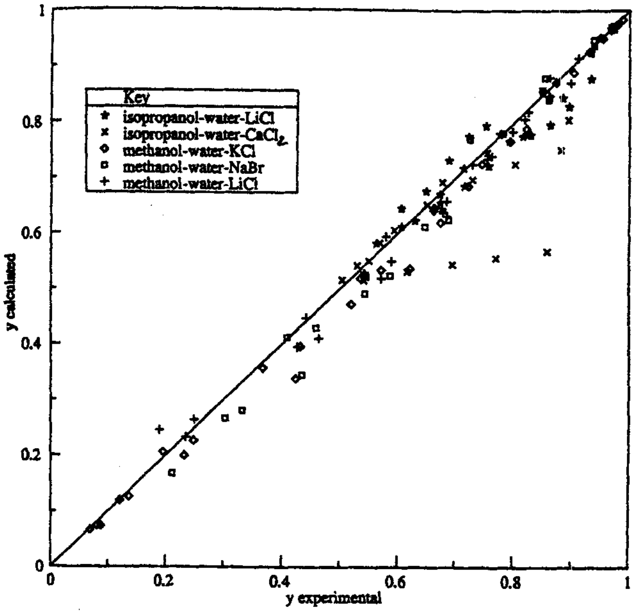

Figure 8. Calculated vs. experimental values of mole fractions for vapor phase.
Calculated values from NRTLE.

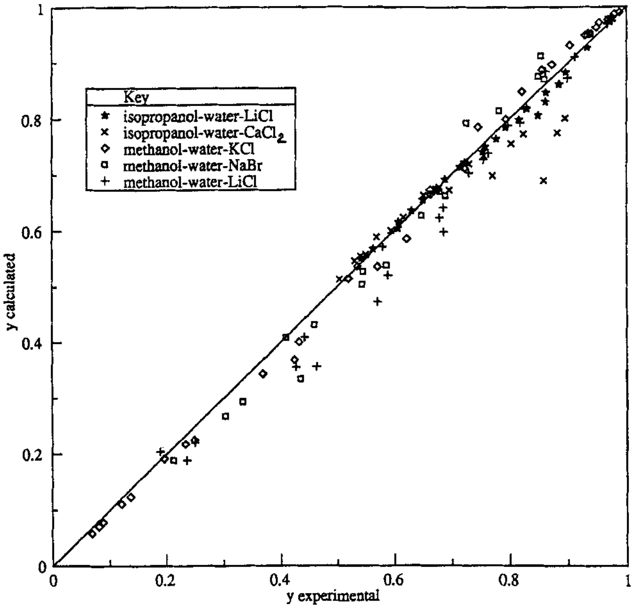

Figure 9. Calculated vs. experimental values of mole fractions for vapor phase.
Calculated values from UNIFE.

binary systems the concentration of the saturated salt solubity is reduced by the presence of nonaqueous components. This can be significant when the azeotrope is at a high concentration of the nonaqueous components. Figure 7 shows the predicted VLE data, using UNIFE for saturated NaCl conditions. The region near the azeotrope is not significantly affected by the presence of these saturated salt conditions with NaCl. The VLE data is dependent on knowing the saturated solubility of salt in solutions at the bubble-point temperatures. The effectiveness of a particular salt requires both saturated solubility data in mixed solvents and the use of the NRTLE or UNIFE models to predict solvent activity coefficients.

A comprehensive examination of the predictive VLE methods for the binary solvent pairs, 2-propanol-water, and methanol-water, for the salts, LiCl, $CaCl_2$, KCl, and NaBr, over the full concentration range, has been made. Figure 8 shows the predicted VLE data using the NRTLE method and Figure 9, using the UNIFE method. There are a number of major deviations from the experimental data for the system, 2-propanol-water-$CaCl_2$, with the NRTLE method, as shown in Figure 8. These deviations are reduced for the UNIFE method, shown in Figure 9. The deviations in both methods of over 0.03 vapor mole fraction over considerable composition ranges, is of some concern for distillation design. The individual VLE data set for a particular salt should be compared with experimental data whenever possible. The least-square error for the NRTLE method is 0.059, and for the UNIFE method, 0.058 vapor mole fraction. A similar sensitivity test for the thermodynamic models, NRTL, UNIQUAC, ASOG, and UNIFAC, has been given for the methanol-acetone-chloroform system, by Cairns and Furzer (1988).

Notation

A, b = Debye-Huckel parameter
g = excess Gibbs function
g^* = excess Gibbs function (asymmetric)
G = variable in NRTLE method
I = ionic strength
LC = local composition
PDH = Pitzer-Debye-Huckel
R = gas constant
T = absolute temperature
x = variable in NRTLE method

Greek letters

γ = liquid phase activity coefficient
δ = UNIFE parameter
τ = interaction parameter in NRTLE method
ρ = Debye-Huckel, closest approach parameter
ϕ = volume fraction in UNIFE method
ψ = variable in UNIFE method

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