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Isobaric Vapor−Liquid Equilibria for Water + Acetic Acid + Lithium Acetate

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Isobaric vapor−liquid equilibria for all of the binary and ternary mixtures of water, acetic acid, and lithium acetate have been measured at 100.00 kPa using a recirculating still. To take into account the association of the acetic acid in the vapor phase, Marek's chemical theory has been considered. The three experimental binary data sets have been independently correlated using Mock's electrolyte NRTL model, and the binary parameters estimated for each binary system have been used to predict the ternary vapor−liquid equilibrium using the same model. No ternary parameters were required. The ternary equilibrium values obtained in this way agreed well with the experimental values.

Introduction

The aim of this paper is to investigate the effect of the addition of lithium acetate on the vapor−liquid equilibrium of the water + acetic acid system, to correlate the experimental results, and to develop a model capable of predicting the behavior of salt + mixed solvent systems. This work is a part of a broader project to study the salt effect on the thermodynamic properties of solvent mixtures.

Two major difficulties arise for modeling this system. First, it is known that acetic acid molecules associate with each other to form stable dimers in both liquid and vapor phases.[1] Marek and Standart[2] and Marek[3] derived the chemical theory model, regarding the dimerization as a chemical equilibrium reaction and treating the dimer as an individual component. This theory has been commonly used and modified to calculate the vapor−liquid equilibria of systems with associating components and can be applied also to the acetic acid (2) + lithium acetate (3) binary system and to the water (1) + acetic acid (2) + lithium acetate (3) ternary system, where there is dimerized acetic acid in the vapor phase.

On the other hand, when a salt is dissolved in a mixed solvent, the nondissociated molecules, the ions, or both, interact with the solvent molecules in a very complex way, affecting the activity of the liquid phase components. The magnitude of the interaction is influenced by the nature of the implied species and their concentrations. This interaction modifies the boiling point, the mutual solubility of the liquid components, and the equilibrium composition of the vapor phase.

In recent decades much progress has been made, and several correlative and predictive models based on the local composition or group contribution concept have been proposed to calculate the vapor−liquid equilibrium of systems formed by mixed solvents and electrolytes. Among them are the electrolyte NRTL model of Mock et al.,[4,5] the extended UNIQUAC models of Sander et al.[6] and Macedo et al.,[7] the modified UNIFAC group contribution models of Kikic et al.[8] and Achard et al.,[9] the LIQUAC model of Li et al.,[10] the thermodynamic models of Zerres and Prausnitz[11] and Kolker and de Pablo,[12] and the neural network model of Iliuta et al.[13]

The electrolyte NRTL model used to predict the vapor−liquid equilibrium of the ternary system is an extension of the nonrandom two-liquid local composition model of Renon and Prausnitz[14] for liquid phase activity coefficients. Chen et al.[15] derived a model for single-solvent + electrolyte systems, and later Mock et al.[4,5] extended it to mixed-solvent + electrolyte systems while neglecting the long-range interaction contribution term.

The three fundamental assumptions for the mixed-solvent electrolyte NRTL model are that (a) the local composition of cations (anions) around a central cation (anion) is zero, (b) the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero (local electroneutrality condition), and (c) the long-range interaction contribution can be neglected in the calculation of the activity coefficients of solvents. The expressions for the liquid phase activity coefficients of the solvents in a ternary system containing a salt have been derived in a previous work.[16]

Experimental studies for water + acetic acid containing salt are scarce. The bibliographic database EVLM′2000[17] reports literature on the system water + acetic acid in the presence of the following salts: sodium,[18,19] potassium,[18,19] calcium,[18−20] and copper(II)[19] acetates; lithium,[21] sodium,[21−25] potassium,[25−28] magnesium,[23,29,30] calcium,[23,27,29,31,32] and strontium[29] chlorides; potassium[26,27,33] bromide and iodide; sodium nitrate;[23] and sodium and potassium sulfates.[28] All of the salts studied were found to have a salting-out effect for acetic acid, and some (sodium and calcium chlorides) form azeotropes at high concentrations. Among these studies, only the paper of Shiah et al.[24] about the water + acetic acid system saturated with sodium chloride uses a predictive model[34] to calculate the vapor−liquid equilibrium and then compares the predicted results with the experimental values. No experimental study about the water + acetic acid + lithium acetate system has been found.

Modeling Section

Marek's model[3] assumes that in both liquid and vapor phases there exist monomers and dimers of acetic acid

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molecules. The equilibrium constant of vapor phase dimerization is defined by

$$K^{V} = \frac{y^{*}_{2D}}{(y^{*}_{2M})^{2}P} \tag{1}$$

and the equilibrium constant of liquid phase dimerization is defined by

$$K^{L} = \frac{x^{*}_{2D}}{(x^{*}_{2M})^{2}} \tag{2}$$

In these equations, y^{*}_{2D} and x^{*}_{2D} are the mole fractions of dimer acetic acid in vapor and liquid phases, y^{*}_{2M} and x^{*}_{2M} are the mole fractions of monomer acetic acid in vapor and liquid phases, and P is the system pressure. The vapor phase equilibrium constant of dimerization, K^{V}, can be calculated by using the temperature-dependent expression obtained by Marek[3] and popularized by Gmehling et al.[35]

$$K^{V} = \exp\left(\frac{7290}{T} - 21.980\right) \tag{3}$$

where K^{V} was expressed in kPa^{-1} and T in K.

The acetic acid dimerization modifies the vapor and liquid phase compositions, and therefore in the water (1) + acetic acid (2) system there are not two but three components, water (1) + monomer acetic acid (2M) + dimer acetic acid (2D), in the mixture. The actual mole fractions of these components are y^{*}_{1}, y^{*}_{2M}, y^{*}_{2D}, x^{*}_{1}, x^{*}_{2M}, x^{*}_{2D}.

The vapor–liquid equilibrium relations for the actual components are

$$Py^{*}_{1}\Phi_{1} = P^{\circ}_{1}x^{*}_{1}\gamma_{1} \tag{4}$$

$$Py^{*}_{2M}\Phi_{2M} = P^{\circ}_{2M}x^{*}_{2M}\gamma_{2M} \tag{5}$$

$$Py^{*}_{2D}\Phi_{2D} = P^{\circ}_{2D}x^{*}_{2D}\gamma_{2D} \tag{6}$$

On the other hand, the actual mole fractions can be related to the apparent mole fraction of analytically measured components (y_1, y_2, x_1, and x_2) by means of mass balances and equilibrium relations. Similarly, the actual vapor pressures of monomer and dimer acetic acid (P°_{2M}, P°_{2D}) can be related to the experimentally determined apparent vapor pressure of acetic acid (P°_{2}). Thus, by replacing the actual compositions and vapor pressures by the apparent ones, we obtain for the nonassociating component, water (1)

$$Py_{1}Z_{1}\Phi_{1} = P^{\circ}_{1}x_{1}\Gamma_{1}\gamma_{1} \tag{7}$$

where

$$Z_{1} = \frac{2}{(2 - y_{2})}\,\frac{1 - y_{2} + \sqrt{1 + 4K^{V}Py_{2}(2 - y_{2})}}{1 + \sqrt{1 + 4K^{V}Py_{2}(2 - y_{2})}} \tag{8}$$

$$\Gamma_{1} = \frac{2}{(2 - x_{2})}\,\frac{1 - x_{2} + \sqrt{1 + 4K^{L}x_{2}(2 - x_{2})}}{1 + \sqrt{1 + 4K^{L}x_{2}(2 - x_{2})}} \tag{9}$$

and for the associating component, acetic acid (2)

$$Py_{2}Z_{2}\Phi_{2} = P^{\circ}_{2}\Pi^{\circ}_{2}x_{2}\Gamma_{2}\gamma_{2} \tag{10}$$

where

$$Z_{2} = \frac{2}{1 + \sqrt{1 + 4K^{V}Py_{2}(2 - y_{2})}} \tag{11}$$

$$\Gamma_{2} = \frac{2}{1 + \sqrt{1 + 4K^{L}x_{2}(2 - x_{2})}} \tag{12}$$

$$\Pi^{\circ}_{2} = \frac{1 + \sqrt{1 + 4K^{L}}}{1 + \sqrt{1 + 4K^{V}P^{\circ}_{2}}} \tag{13}$$

In these equations, Z_1 and Z_2 can be viewed as correction factors for nonideality in the vapor phase because of association and, compared with them, the fugacity coefficients Φ_1 and Φ_2 are negligible. On the other hand, Π°_{2} can be seen as a correction factor for the vapor pressure of the associating component. Finally, Γ_1 and Γ_2 express the nonideality in the liquid phase because of the existence of association, and γ_1 and γ_2 represent the nonideality in this phase due to other factors. It is not suitable to separately evaluate these two nonideality correction factors[3] and, usually, it is accepted that all of the liquid phase nonideality causes are included in the activity coefficients. In this work, this treatment has been made, and eqs 7 and 10 become

$$Py_{1}Z_{1} = P^{\circ}_{1}x_{1}\gamma_{1} \tag{14}$$

$$Py_{2}Z_{2} = P^{\circ}_{2}\Pi^{\circ}_{2}x_{2}\gamma_{2} \tag{15}$$

Experimental Section

Materials. The chemicals were acetic acid (glacial) 100% (Merck, PA grade) with a stated minimum purity of 99.8 mass %, distilled water (Merck, HPLC grade), and lithium acetate dihydrate (Aldrich, 98.0 mass %). The solvents were used directly without further purification, whereas the lithium acetate was desiccated in an oven held at 150 °C at least for 24 h.

Apparatus and Procedure. The equilibrium apparatus was a recirculating still (Labodest model), manufactured by Fisher.[36] The vapor–liquid equilibria were obtained at (100.00 ± 0.02) kPa. The accuracy of boiling point temperature measurements was ±0.1 K.

Every experimental point was obtained from an initial sample prepared gravimetrically by using a Mettler AE 200 analytical balance with a precision of ±0.0001 g and, afterward, by adding different quantities of water, acetic acid, or water + lithium acetate mixture. Each experiment was kept at the boiling point for 15 min or more to ensure a stationary state.

Sample Analysis. Compositions of the condensed vapor phase (water + acetic acid) were analyzed using a Varian STAR 3400 CX gas chromatograph with a thermal conductivity detector. The GC response was treated with a Star chromatography station. The chromatographic column (2 m × $^{1}/_{8}$ in.) was packed with Porapak QS. The carrier gas was helium flowing at 40 $cm^{3}\cdot min^{-1}$, and the column temperature was 478 K. The injector and detector temperatures were 493 and 513 K, respectively. The calibration was carried out with gravimetrically prepared standard solutions. The accuracy of the measured vapor phase mole fraction was ±0.001. This procedure was also used for the liquid phase analysis of the water + acetic acid binary system.

The liquid phase of the ternary system was composed of water, acetic acid, and lithium acetate. The salt mass fraction was gravimetrically determined after the volatile

Table 1. Experimental Antoine Coefficients and Mean Absolute Deviations for Water and Acetic Acid

component	temp range/K	Antoine coefficients[a]			$\Delta P°$/kPa[b]
		A	B	C	
water	320−375	16.3144	3845.02	−44.42	0.05
acetic acid	320−395	14.8311	3424.04	−55.64	0.04

[a] Antoine equation: $\ln P°/\text{kPa} = A - B/(T/\text{K} + C)$. [b] $\Delta P° = (1/N) \sum |P°_{\text{exptl}} - P°_{\text{calcd}}|$.

Table 2. Vapor−Liquid Equilibrium Data for Water (1) + Acetic Acid (2) at 100.00 kPa

x_1	y_1	T/K	x_1	y_1	T/K	x_1	y_1	T/K
0.000	0.000	390.55	0.341	0.483	379.85	0.774	0.851	374.45
0.015	0.036	389.55	0.371	0.513	379.35	0.807	0.872	374.15
0.034	0.076	388.45	0.407	0.550	378.75	0.839	0.894	373.95
0.060	0.123	387.25	0.450	0.591	378.15	0.868	0.913	373.75
0.091	0.175	385.95	0.486	0.624	377.65	0.891	0.925	373.55
0.121	0.221	384.85	0.519	0.654	377.15	0.914	0.942	373.45
0.149	0.261	383.95	0.556	0.688	376.75	0.935	0.955	373.25
0.177	0.298	383.25	0.595	0.719	376.25	0.954	0.967	373.15
0.204	0.331	382.55	0.631	0.748	375.85	0.974	0.981	373.05
0.242	0.376	381.75	0.667	0.777	375.45	1.000	1.000	372.80
0.279	0.417	380.95	0.703	0.802	375.05			
0.312	0.452	380.35	0.738	0.830	374.75			

Table 3. Vapor−Liquid Equilibrium Data for Water (1) + Lithium Acetate (3) at 100.00 kPa

x_3	T/K	x_3	T/K	x_3	T/K
0.0092	373.25	0.0511	375.65	0.0982	378.85
0.0131	373.40	0.0553	375.90	0.1043	379.25
0.0173	373.65	0.0594	376.15	0.1086	379.55
0.0216	373.85	0.0642	376.50	0.1118	379.85
0.0260	374.15	0.0693	376.80	0.1173	380.15
0.0307	374.40	0.0749	377.25	0.1202	380.35
0.0353	374.65	0.0789	377.60	0.1243	380.75
0.0395	374.90	0.0841	377.85	0.1293	380.95
0.0433	375.15	0.0896	378.15	0.1333	381.25
0.0467	375.35	0.0929	378.50	0.1368	381.55

Table 4. Vapor−Liquid Equilibrium Data for Acetic Acid (2) + Lithium Acetate (3) at 100.00 kPa

x_3	T/K	x_3	T/K	x_3	T/K
0.0065	390.75	0.0490	392.65	0.0929	394.65
0.0097	390.85	0.0521	392.75	0.0973	394.85
0.0132	391.00	0.0551	392.95	0.1022	395.05
0.0173	391.15	0.0588	393.10	0.1062	395.25
0.0214	391.35	0.0624	393.25	0.1115	395.55
0.0261	391.65	0.0662	393.45	0.1168	395.75
0.0305	391.85	0.0704	393.65	0.1198	396.05
0.0350	392.05	0.0747	393.75	0.1251	396.25
0.0386	392.25	0.0792	393.95	0.1300	396.45
0.0422	392.40	0.0834	394.15	0.1332	396.65
0.0455	392.55	0.0889	394.45	0.1378	396.85

components were separated from a known mass of sample by evaporation to dryness. On the other hand, the water content of the liquid phase was determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino). This titrator performs 0.001 cm^3 steps of reagent. The weight of the analyzed sample was varied according to its water content to improve the accuracy of the method. The one-component reagent used was Hydranal-Composite (Riedel-de Haën). Methanol dried (Riedel-de Haën, maximum 0.005 mass % water) was used as solvent, and Hydranal-Puffer (Riedel-de Haën) was used to stabilize the pH of the system, modified by the presence of acetic acid in the sample. The accuracy in the measurement of the water, acetic acid, and lithium acetate mole fractions in the liquid phase was ±0.001.

In the solvent + salt binary systems, the liquid phase was analyzed gravimetrically by evaporation to dryness and the vapor phase was not analyzed. The accuracy in the measurement of the solvent and salt mole fractions in the liquid phase was ±0.00007.

Results and Discussion

Experimental Data. To test the equilibrium apparatus and to dispose of suitable data of pure solvents, the acetic acid vapor pressure was measured in the range 320−395 K. Antoine coefficients for acetic acid, obtained from our experimental data, and mean absolute deviations between experimental and calculated vapor pressure data are shown in Table 1, together with the Antoine coefficients for water from Vercher et al.[16] used in this work.

In addition, vapor−liquid equilibria for the three binary systems water (1) + acetic acid (2), water (1) + lithium acetate (3), and acetic acid (2) + lithium acetate (3) were obtained at 100.00 kPa. The results are reported in Tables 2−4. The experimental results of the water (1) + acetic acid (2) system agree well with those reported by Marek[3] and Ellis and Bahari[37] working at the same temperature. Vapor−liquid equilibrium for the water (1) + acetic acid (2) + lithium acetate (3) ternary system was obtained at 100.00 kPa, and the results are reported in Table 5. In these tables, x_i is the mole fraction of component i in the liquid phase, x'_1 is the mole fraction of water in the liquid phase expressed on a salt-free basis, y_1 is the mole fraction of water in vapor phase, and T is the equilibrium temperature. As can be observed in Table 5, the experimental values for the ternary system were obtained trying to maintain the x_3 value constant in each series.

The experimental results of the water (1) + acetic acid (2) system were tested for thermodynamic consistency using the point-to-point tests of Van Ness et al.,[38] as modified by Fredenslund et al.,[39] and the activity coefficients defined by eqs 14 and 15. This test gave a mean absolute deviation between calculated and measured mole fractions of water in the vapor phase of $\delta(y) = 0.0028$, which shows that the values are thermodynamically consistent. No consistency test was used for salt-containing systems.

Calculation of Phase Equilibrium. To represent the phase equilibrium of mixed-solvent electrolyte systems, it is necessary to determine the binary adjustable parameters for each of the solvent−solvent, solvent−salt, and salt−salt pairs in the system. In our system (two solvents and one salt) nine binary adjustable parameters for three pairs must be determined. Of them, six are energy parameters ($\Delta g_{1,2}$, $\Delta g_{2,1}$, $\Delta g_{1,3}$, $\Delta g_{3,1}$, $\Delta g_{2,3}$, and $\Delta g_{3,2}$) and three are nonrandomness factors ($\alpha_{1,2} = \alpha_{2,1}$, $\alpha_{1,3} = \alpha_{3,1}$, and $\alpha_{2,3} = \alpha_{3,2}$).

The 1−2 binary solvent−solvent parameters were determined from the vapor−liquid equilibrium data of the water (1) + acetic acid (2) binary system given in Table 2. The 1−3 and 2−3 binary solvent−salt parameters were determined independently from the vapor−liquid equilibrium data of the water (1) + lithium acetate (3) system given in Table 3 and the acetic acid (2) + lithium acetate (3) system given in Table 4.

For each binary system, the three corresponding parameters were estimated by minimization of the objective function

$$F = \sum_j h|y_{1,\text{exptl}} - y_{1,\text{calcd}}| + \sum_j k|T_{\text{exptl}} - T_{\text{calcd}}| \quad (16)$$

where T is the equilibrium temperature and y_1 the water apparent mole fraction in the vapor phase. The indices exptl and calcd denote the experimental and calculated

Table 5. Vapor−Liquid Equilibrium Data for Water (1) + Acetic Acid (2) + Lithium Acetate (3) at 100.00 kPa

x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K
0.022	0.052	0.089	389.05	0.021	0.617	0.707	377.35
0.022	0.125	0.199	386.25	0.022	0.659	0.758	376.65
0.022	0.204	0.297	384.15	0.022	0.720	0.804	376.05
0.022	0.279	0.383	382.45	0.021	0.781	0.845	375.55
0.022	0.358	0.467	381.00	0.021	0.832	0.882	375.05
0.021	0.426	0.535	379.95	0.021	0.887	0.919	374.65
0.021	0.489	0.594	379.05	0.021	0.939	0.957	374.25
0.021	0.554	0.655	378.15				
0.043	0.053	0.083	390.15	0.045	0.605	0.701	378.85
0.044	0.137	0.205	387.15	0.045	0.656	0.745	378.25
0.044	0.205	0.293	385.35	0.045	0.719	0.799	377.55
0.044	0.276	0.370	383.85	0.045	0.779	0.840	377.00
0.044	0.347	0.452	382.50	0.045	0.829	0.880	376.50
0.045	0.417	0.522	381.35	0.044	0.888	0.916	376.05
0.045	0.481	0.587	380.45	0.044	0.939	0.958	375.65
0.045	0.540	0.644	379.65				
0.065	0.054	0.080	391.25	0.066	0.616	0.708	380.15
0.065	0.142	0.203	388.25	0.066	0.674	0.757	379.55
0.066	0.223	0.300	386.30	0.066	0.727	0.801	378.95
0.066	0.291	0.379	384.95	0.065	0.786	0.843	378.35
0.066	0.362	0.455	383.65	0.065	0.841	0.883	377.85
0.066	0.428	0.527	382.65	0.065	0.895	0.920	377.40
0.066	0.492	0.590	381.70	0.063	0.950	0.957	376.90
0.066	0.549	0.646	380.95				
0.087	0.053	0.078	392.45	0.091	0.608	0.704	381.95
0.088	0.128	0.181	390.05	0.091	0.667	0.756	381.25
0.088	0.207	0.281	388.15	0.091	0.728	0.805	380.60
0.090	0.284	0.371	386.55	0.092	0.779	0.845	380.05
0.090	0.348	0.446	385.35	0.091	0.831	0.880	379.65
0.091	0.415	0.518	384.35	0.090	0.887	0.916	379.25
0.091	0.485	0.588	383.45	0.089	0.942	0.954	378.75
0.091	0.545	0.648	382.65				
0.103	0.053	0.075	393.35	0.106	0.596	0.702	382.85
0.104	0.123	0.172	391.15	0.106	0.658	0.755	382.25
0.106	0.196	0.268	389.35	0.106	0.722	0.803	381.55
0.106	0.271	0.357	387.75	0.107	0.779	0.849	381.05
0.106	0.336	0.434	386.60	0.106	0.834	0.885	380.55
0.106	0.408	0.514	385.45	0.106	0.891	0.921	380.10
0.106	0.477	0.585	384.35	0.105	0.948	0.958	379.75
0.106	0.534	0.644	383.65				
0.121	0.055	0.076	394.25	0.126	0.595	0.705	384.25
0.123	0.174	0.237	390.95	0.127	0.691	0.785	383.15
0.124	0.283	0.374	388.65	0.127	0.778	0.848	382.35
0.125	0.394	0.503	386.95	0.127	0.863	0.904	381.75
0.126	0.500	0.614	385.45	0.124	0.949	0.958	381.05

Table 6. Estimated Values of Energy Parameters, $\Delta g_{i,j}$ and $\Delta g_{j,i}$, and Nonrandomness Factors, $\alpha_{i,j}$, for the Electrolyte NRTL Model and Mean Absolute Deviations, Δy and ΔT, in Binary Systems

i component	j component	$\alpha_{i,j}$	$\Delta g_{i,j}$ J·mol^{-1}	$\Delta g_{j,i}$ J·mol^{-1}	Δy^a	ΔT^b
water	acetic acid	1.476	3047	1464	0.003	0.03
water	lithium acetate	0.384	−6409	12856		0.12
acetic acid	lithium acetate	1.250	26219	7265		0.19

[a] $\Delta y = (1/N) \sum |y_{\text{exptl}} - y_{\text{calcd}}|$. [b] $\Delta T = (1/N) \sum |T_{\text{exptl}} - T_{\text{calcd}}|$.

values, and h and k are the weighting factors. The summations are extended to all data points. Equilibrium temperatures and vapor phase compositions were calculated by solving the equilibrium condition for solvents given by eqs 14 and 15.

The estimated values of binary parameters and mean absolute deviations in vapor phase compositions and equilibrium temperatures are reported in Table 6. It can be observed that the electrolyte NRTL model satisfactorily represents the experimental vapor−liquid equilibrium data for the three binary systems.

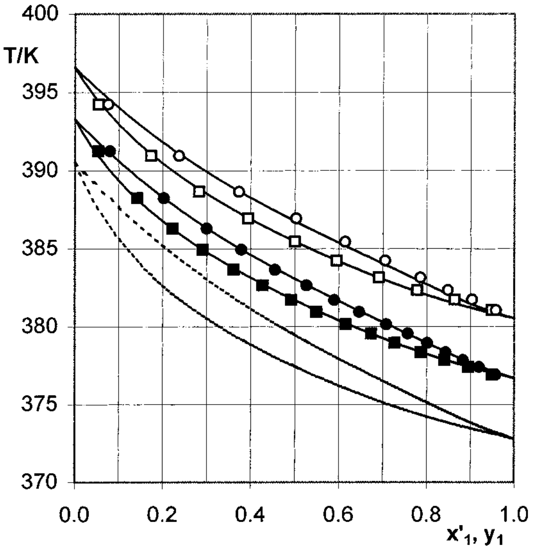

Figure 1. Experimental and calculated $T-x'_1-y_1$ diagram for water (1) + acetic acid (2) + lithium acetate (3) at 100.00 kPa: (salt mole fraction, $x_3 = 0.066$) ■, $T-x'_1$ experimental, and ●, $T-y_1$ experimental; (salt mole fraction, $x_3 = 0.125$) □, $T-x'_1$ experimental, and ○, $T-y_1$ experimental; solid line, $T-x'_1-y_1$ calculated; dotted line, $T-x'_1-y_1$ calculated salt-free system (calculation based on electrolyte NRTL model with the parameters from Table 6).

The nine parameters obtained from binary systems were used to predict the vapor−liquid equilibrium of the water (1) + acetic acid (2) + lithium acetate (3) ternary system. To make a comparison with the experimental ternary data reported in Table 5, we have calculated the vapor phase compositions and equilibrium temperatures for the same conditions of the experimental points. The mean absolute deviation between experimental and calculated values of the vapor phase mole fraction was 0.006, and its standard deviation was 0.008. The mean absolute deviation between experimental and calculated values of the equilibrium temperature was 0.13 K, and its standard deviation was 0.16 K. The predictive ability of the model can be seen in Figure 1, where the calculated and experimental vapor−liquid equilibria of the water + acetic acid + lithium acetate ternary system are plotted on a $T-x'_1-y_1$ diagram for x_3 = 0, 0.066, and 0.125. Similar results have been obtained for all of the composition ranges studied.

Conclusions

The addition of lithium acetate to water + acetic acid systems produces a very small salting-out effect for the acetic acid, although the equilibrium temperature is appreciably changed.

The electrolyte NRTL model of Mock et al.,[4,5] together with the chemical theory of Marek[3] to take into account the acetic acid association in the vapor phase, proved to be suitable to predict the vapor−liquid equilibrium of the water + acetic acid + lithium acetate system, using the parameters obtained by applying the same model to the three binary systems. Experimental data agree very well with the values predicted from the model in the entire range of compositions.

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