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

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Isobaric vapor−liquid equilibria for the binary water + sodium acetate and acetic acid + sodium acetate systems and ternary mixtures of water, acetic acid, and sodium acetate have been measured at 100 kPa with a recirculating still. The addition of sodium acetate to water + acetic acid mixtures produced an appreciable rise in equilibrium temperature but a small effect on the relative volatility of water, which was augmented at higher water solvent concentrations and decreased at lower concentrations. These effects increased with higher salt concentrations. The experimental binary data sets have been correlated using a modified Mock's electrolyte NRTL model, which takes into account the association of the acetic acid in the vapor phase by means of Marek's Chemical Theory (eNRTL−CT model). The estimated model parameters from binary data have been used to predict the ternary vapor−liquid equilibrium. The values obtained in this way agreed well with the experimental values.

Introduction

The dissolution of a salt in a solvent mixture modifies the boiling point, the mutual solubility of the liquid components, and the equilibrium composition of the vapor phase, because the nondissociated salt 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 this effect is influenced by the nature of the implied species and their concentrations.

The correlative and predictive thermodynamic models for liquid-phase activity, which are very efficient in modeling the vapor−liquid equilibrium of nonelectrolytes, fail when they are applied to electrolyte solutions. In recent decades, much progress has been made, and several models based on the local composition 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.,[1,2] the extended UNIQUAC models of Sander et al.[3] and Macedo et al.,[4] the modified UNIFAC group contribution models of Kikic et al.[5] and Achard et al.,[6] the LIQUAC model of Li et al.,[7] and the thermodynamic models of Zerres and Prausnitz[8] and Kolker and de Pablo.[9]

Moreover, it is known that acetic acid molecules associate with each other to form stable dimers in both liquid and vapor phases.[10] Marek and Standart[11] and Marek[12] derived the Chemical Theory model, regarding the dimerization as a chemical equilibrium reaction and treating the dimer as an individual component. Vercher et al.[13] successfully combined the electrolyte NRTL and the chemical theory models to calculate the vapor−liquid equilibria of the water (1) + acetic acid (2) + lithium acetate (3) ternary system.

Vercher et al.[13] reported bibliographic information from EVLM′2001[14] on vapor−liquid equilibria for water + acetic acid systems containing salt. Among these studies, only the paper of Shiah et al.[15] about the water + acetic acid system saturated with sodium chloride uses a predictive model[16] to calculate the vapor−liquid equilibrium and then compares the predicted results with the experimental values.

Ciparis and Dzekciorius[17] studied the water + acetic acid + sodium acetate system at atmospheric pressure, but the pressure did not remain constant, varying from (740 to 768) mmHg. In addition, Ciparis and Adomas[18] studied the same system at isothermal conditions of (40 and 60) °C. The measured equilibrium pressure values at 40 °C were about (40 to 50) mmHg and (100 to 140) mmHg at 60 °C, but the pressure accuracy was only 1 mmHg.

The aim of this work is to determine the effect of sodium acetate on vapor−liquid equilibria of the water + acetic acid system, to compare these results with those reported for the same system in the previous works,[17,18] and to test the electrolyte NRTL−Chemical Theory (eNRTL−CT) model[13] with another mixed solvent salt system that presents association in the vapor phase.

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 sodium acetate anhydrous (Merck, Fractopur grade, minimum purity 99.5 mass %). The solvents were used directly without further purification, whereas the sodium acetate was kept in an oven held at 453 K for at least for 24 h. The water contents of acetic acid (maximum 0.03 mass %) and desiccated sodium acetate (maximum 0.07 mass %) were determined by the Karl−Fischer method.

Apparatus and Procedure. The equilibrium apparatus used in this work is an all-glass dynamic recirculating still manufactured by Fischer (Labodest model) and equipped with a Cottrell pump,[19] which ensures that both liquid and vapor phases are in intimate contact. The still is capable of handling pressures from (0.25 to 400) kPa and temperatures up to 523 K. The apparatus pressure was kept constant by means of a vacuum pump and an electrovalve controlled by a pressure sensor. The equilibrium pressure

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Table 1. Vapor−Liquid Equilibrium Data for Water (1) + Sodium Acetate (3) at 100 kPa

x_3	T/K	x_3	T/K	x_3	T/K
0.0060	373.05	0.0570	376.55	0.0945	379.95
0.0105	373.35	0.0632	377.05	0.0986	380.25
0.0179	373.75	0.0688	377.45	0.1030	380.65
0.0247	374.15	0.0744	378.05	0.1076	381.15
0.0312	374.65	0.0793	378.45	0.1112	381.45
0.0377	375.05	0.0844	378.95	0.1153	381.85
0.0439	375.55	0.0898	379.55	0.1197	382.25
0.0504	376.05				

was measured with a digital manometer with a standard uncertainty of 0.01 kPa. The standard uncertainty of the boiling point temperature measurement 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 standard uncertainty of 0.0001 g and, afterward, by adding different quantities of water or acetic acid. Equilibrium conditions were assumed when temperature and pressure remained constant for 30 min or more.

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 $\mathrm{cm^3 \cdot min^{-1}}$, 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 combined standard uncertainty of the measured vapor-phase mole fraction was 0.001.

The liquid phase of the ternary system was composed of water, acetic acid, and sodium acetate. The salt mass fraction was gravimetrically determined after separating the volatile components 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 $\mathrm{cm^3}$ steps of reagent. The weight of the analyzed sample was varied according to its water content in order 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, which was modified by the presence of acetic acid in the sample. The combined standard uncertainty of the water, acetic acid, and sodium acetate mole fractions in the liquid phase was 0.0010.

In the solvent + salt binary systems, the liquid phase was analyzed gravimetrically by evaporation to dryness and the vapor phase was not analyzed. The combined standard uncertainty of the salt mole fraction in the liquid phase was 0.0001.

Results and Discussion

Experimental Data. Vapor−liquid equilibria for the binary systems water (1) + sodium acetate (3), and acetic acid (2) + sodium acetate (3) have been obtained at 100 kPa. The results are reported in Tables 1 and 2. Also, the vapor−liquid equilibrium for the water (1) + acetic acid (2) + sodium acetate (3) ternary system was obtained at 100 kPa, and the results are reported in Table 3. In these tables, x_3 is the mole fraction of salt 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 apparent mole fraction of water in the vapor phase, and T is the equilibrium temperature. These data cannot be directly compared with those of Ciparis and Dzekciorius,[17] because they have been obtained at different experimental conditions.

Table 2. Vapor−Liquid Equilibrium Data for Acetic Acid (2) + Sodium Acetate (3) at 100 kPa

x_3	T/K	x_3	T/K	x_3	T/K
0.0008	390.55	0.0469	392.95	0.0817	395.55
0.0028	390.65	0.0493	393.05	0.0841	395.65
0.0056	390.75	0.0517	393.25	0.0849	395.55
0.0091	390.95	0.0546	393.45	0.0862	395.95
0.0131	391.15	0.0569	393.65	0.0877	395.75
0.0175	391.35	0.0598	393.75	0.0900	396.05
0.0222	391.55	0.0621	393.95	0.0931	396.35
0.0270	391.75	0.0652	394.15	0.0961	396.55
0.0316	391.95	0.0669	394.25	0.0987	396.75
0.0358	392.15	0.0690	394.45	0.1030	397.15
0.0387	392.35	0.0712	394.65	0.1061	397.45
0.0412	392.45	0.0740	394.85	0.1102	397.75
0.0439	392.65	0.0775	395.25		

Calculation of Phase Equilibrium. The nonideality of the gas phase has been modeled using the Marek's Chemical Theory model,[12] which only requires knowing the variation of association equilibrium constant with temperature. On the other hand, the nonideality of the liquid phase is due not only to the interactions between solvent molecules and salt ions but also to the association of acetic acid in the liquid phase. Usually, it is accepted that all of the liquid-phase nonideality causes are included in the activity coefficients γ_1 and γ_2.[12] Hence, although in this work the electrolyte NRTL model of Mock et al.[1,2] is used for γ_1 and γ_2, the physical sense of their parameters has been lost, and their values can be different from those usual for a mixture of nonassociating solvents.

To represent the phase equilibrium of mixed-solvent electrolyte systems, it is necessary to determine the binary adjustable parameters of Mock's model 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 taken from Vercher et al.[13] The 1−3 and 2−3 binary solvent−salt parameters were determined independently from the experimental vapor−liquid equilibrium data given in Tables 1 and 2 by minimization of the objective function

$$F = \sum_j |T_{\mathrm{exptl}} - T_{\mathrm{calcd}}| \tag{1}$$

In eq 1, T is the equilibrium temperature. The indices exptl and calcd denote the experimental and calculated values. The summation is extended to all data points. The values of binary parameters and mean absolute deviations in vapor-phase compositions and equilibrium temperatures are reported in Table 4.

Equilibrium temperatures and vapor-phase compositions were calculated by solving the equilibrium condition for solvents of the eNRTL−CT model[13]

$$Py_1Z_1 = X_1\gamma_1P_1^\circ \tag{2}$$

$$Py_2Z_2 = X_2\gamma_2P_2^\circ\Pi_2^\circ \tag{3}$$

In eqs 2 and 3, P is the total pressure in the system, y_i is the apparent vapor-phase mole fraction of solvent i,

Table 3. Vapor−Liquid Equilibrium Data for Water (1) + Acetic Acid (2) + Sodium Acetate (3) at 100 kPa

x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K
0.0038	0.661	0.768	375.75	0.0231	0.843	0.895	375.15	0.0519	0.450	0.592	381.25	0.0853	0.262	0.396	387.25
0.0040	0.822	0.881	374.15	0.0235	0.752	0.838	375.85	0.0529	0.919	0.946	376.75	0.0868	0.116	0.186	391.45
0.0045	0.597	0.717	376.45	0.0239	0.915	0.936	374.75	0.0532	0.948	0.967	376.65	0.0869	0.455	0.616	383.95
0.0051	0.774	0.848	374.75	0.0248	0.643	0.755	377.05	0.0546	0.200	0.305	386.25	0.0873	0.050	0.085	393.75
0.0052	0.534	0.656	377.45	0.0250	0.448	0.581	379.65	0.0552	0.533	0.673	380.35	0.0892	0.520	0.683	383.15
0.0058	0.879	0.913	373.95	0.0276	0.880	0.914	375.25	0.0558	0.615	0.745	379.35	0.0899	0.222	0.347	388.65
0.0059	0.959	0.972	373.35	0.0281	0.384	0.508	380.95	0.0575	0.393	0.534	382.55	0.0899	0.946	0.969	379.55
0.0060	0.460	0.588	378.45	0.0282	0.703	0.801	376.65	0.0587	0.146	0.231	388.05	0.0908	0.588	0.745	382.45
0.0064	0.714	0.809	375.25	0.0287	0.585	0.708	377.95	0.0601	0.602	0.732	379.95	0.0918	0.063	0.104	393.75
0.0066	0.929	0.950	373.65	0.0289	0.762	0.840	376.25	0.0604	0.486	0.633	381.35	0.0932	0.650	0.796	381.95
0.0069	0.386	0.516	379.65	0.0296	0.801	0.868	375.95	0.0615	0.671	0.790	379.35	0.0947	0.179	0.288	390.15
0.0076	0.323	0.450	380.75	0.0307	0.843	0.892	375.75	0.0621	0.568	0.713	380.35	0.0952	0.326	0.483	386.55
0.0077	0.655	0.764	375.95	0.0313	0.316	0.438	382.35	0.0625	0.096	0.159	389.95	0.0955	0.709	0.840	381.55
0.0080	0.828	0.882	374.45	0.0327	0.528	0.659	378.95	0.0634	0.730	0.835	378.85	0.0966	0.085	0.136	393.35
0.0083	0.260	0.380	381.95	0.0327	0.896	0.928	375.55	0.0634	0.329	0.468	384.05	0.0971	0.768	0.874	381.25
0.0087	0.942	0.957	373.65	0.0331	0.650	0.764	377.55	0.0646	0.785	0.869	378.45	0.0977	0.873	0.929	380.75
0.0091	0.187	0.295	383.65	0.0341	0.255	0.368	383.75	0.0647	0.447	0.593	382.35	0.0979	0.823	0.905	380.95
0.0092	0.589	0.710	376.85	0.0344	0.945	0.957	375.35	0.0653	0.048	0.084	391.95	0.0980	0.271	0.411	388.05
0.0099	0.124	0.207	385.65	0.0355	0.705	0.804	377.15	0.0660	0.883	0.925	378.05	0.0999	0.115	0.190	392.55
0.0101	0.894	0.925	374.05	0.0364	0.753	0.840	376.75	0.0661	0.833	0.899	378.25	0.1001	0.324	0.478	387.15
0.0103	0.775	0.847	375.05	0.0365	0.914	0.940	375.65	0.0669	0.285	0.417	385.25	0.1004	0.915	0.952	380.75
0.0107	0.051	0.093	388.45	0.0366	0.470	0.606	379.95	0.0676	0.918	0.947	377.95	0.1011	0.131	0.220	391.95
0.0107	0.524	0.646	377.85	0.0375	0.185	0.285	385.55	0.0689	0.949	0.968	377.95	0.1023	0.950	0.971	380.85
0.0125	0.448	0.578	378.85	0.0377	0.597	0.724	378.45	0.0694	0.515	0.669	381.55	0.1023	0.382	0.551	386.35
0.0127	0.913	0.940	374.05	0.0381	0.880	0.917	376.05	0.0713	0.388	0.534	383.75	0.1036	0.446	0.624	385.35
0.0128	0.719	0.809	375.65	0.0396	0.427	0.558	380.85	0.0714	0.231	0.353	386.75	0.1046	0.056	0.089	395.25
0.0139	0.854	0.899	374.55	0.0398	0.122	0.198	387.55	0.0715	0.465	0.614	382.55	0.1052	0.512	0.691	384.55
0.0140	0.380	0.505	380.15	0.0406	0.658	0.772	377.95	0.0742	0.521	0.674	381.95	0.1058	0.247	0.392	389.15
0.0144	0.924	0.942	374.15	0.0409	0.841	0.894	376.45	0.0749	0.190	0.301	388.05	0.1071	0.577	0.750	383.85
0.0151	0.668	0.768	376.35	0.0432	0.051	0.087	390.45	0.0759	0.347	0.491	384.85	0.1089	0.643	0.802	383.25
0.0156	0.310	0.435	381.45	0.0433	0.538	0.677	379.45	0.0762	0.584	0.734	381.25	0.1098	0.713	0.846	382.85
0.0167	0.758	0.840	375.45	0.0433	0.704	0.808	377.65	0.0779	0.650	0.787	380.65	0.1110	0.773	0.880	382.55
0.0170	0.249	0.367	382.65	0.0434	0.796	0.867	376.95	0.0786	0.147	0.237	389.65	0.1113	0.221	0.349	390.75
0.0175	0.882	0.920	374.55	0.0435	0.370	0.498	382.05	0.0788	0.719	0.832	380.25	0.1124	0.826	0.908	382.25
0.0182	0.600	0.715	377.25	0.0460	0.613	0.738	378.75	0.0792	0.778	0.868	379.85	0.1127	0.190	0.315	391.25
0.0183	0.805	0.870	375.15	0.0471	0.500	0.638	380.25	0.0797	0.446	0.610	383.15	0.1131	0.076	0.123	395.35
0.0184	0.184	0.287	384.35	0.0478	0.738	0.834	377.65	0.0808	0.301	0.440	386.05	0.1135	0.873	0.933	382.15
0.0199	0.120	0.202	386.25	0.0480	0.301	0.424	383.65	0.0812	0.826	0.899	379.55	0.1146	0.913	0.955	382.15
0.0200	0.888	0.920	374.75	0.0485	0.797	0.869	377.25	0.0820	0.876	0.925	379.35	0.1151	0.265	0.414	389.75
0.0206	0.701	0.801	376.25	0.0498	0.656	0.778	378.45	0.0830	0.099	0.165	391.55	0.1168	0.319	0.485	388.85
0.0208	0.947	0.956	374.45	0.0501	0.844	0.898	377.05	0.0837	0.913	0.949	379.25	0.1173	0.949	0.972	382.15
0.0214	0.051	0.092	389.05	0.0510	0.884	0.923	376.85	0.0849	0.391	0.543	384.75	0.1179	0.376	0.559	387.85
0.0216	0.524	0.652	378.35	0.0515	0.252	0.369	384.85	0.0851	0.400	0.556	384.55	0.1185	0.139	0.220	393.85
0.0225	0.817	0.873	375.45												

Table 4. 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[c]	3047[c]	1464[c]	0.003	0.03
water	sodium acetate	7.283	−747.3	1632		0.23
acetic acid	sodium acetate	0.167	−14677	34081		0.41

[a] $\Delta y = (1/N)\Sigma|y_{\mathrm{exptl}} - y_{\mathrm{calcd}}|$. [b] $\Delta T = (1/N)\Sigma|T_{\mathrm{exptl}} - T_{\mathrm{calcd}}|$. [c] Taken from Vercher et al.[13]

Table 5. Mean Absolute Deviations and Standard Deviations between Experimental and Calculated Values of the Vapor-Phase Mole Fractions and the Equilibrium Temperatures

	δy^a	σy^b	δT^c	σT^d
this work	0.014	0.018	0.32	0.38
Ciparis and Dzekciorius[17] (atm. press.)	0.011	0.025	0.42	0.30
Ciparis and Adomas[18] (T = 60 °C)	0.017	0.014	0.67	0.75
Ciparis and Adomas[18] (T = 40 °C)	0.052	0.025	0.68	0.76

[a] $\delta y = (1/N)\Sigma|y_{\mathrm{exptl}} - y_{\mathrm{calcd}}|$. [b] $\sigma y = (1/N - 1)[\Sigma(y_{\mathrm{exptl}} - y_{\mathrm{calcd}})^2]^{1/2}$. [c] $\delta T = (1/N)\Sigma|T_{\mathrm{exptl}} - T_{\mathrm{calcd}}|$. [d] $\sigma T = (1/N - 1)[\Sigma(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})^2]^{1/2}$.

X_i is the liquid-phase mole fraction of solvent i based on the assumption of total dissociation of electrolytes, γ_i is the activity coefficient of component i in the liquid phase, and P_i° is the vapor pressure of solvent i at the equilibrium temperature, calculated by the Antoine equation using the parameters obtained from experimental vapor pressure values measured with the same recirculating still.[13] In these equations, Z_i and Π_2° can be viewed as correction factors for nonideality in the vapor phase and for the acetic acid vapor pressure, respectively, to take into account the acetic acid association, as described by Vercher et al.[13]

The nine binary parameters obtained were used to predict the vapor−liquid equilibrium of the water (1) + acetic acid (2) + sodium acetate (3) ternary system. To make a comparison with the experimental ternary data reported in Table 3, we have calculated the vapor-phase compositions and equilibrium temperatures for the same conditions of the experimental points. The mean absolute deviations and standard deviations between experimental and calculated values of the vapor-phase mole fraction and the equilibrium temperature are reported in Table 5.

The eNRTL−CT model was also used to reproduce Ciparis and Dzekciorius[17] and Ciparis and Adomas[18] data. In Table 5 the deviations between experimental and calculated values are also reported. This comparison seems to indicate that the model reproduces well the Ciparis and Dzekciorius[17] data at atmospheric pressure, but it fails when trying to reproduce the isothermal data of Ciparis and Adomas,[18] especially at 40 °C.

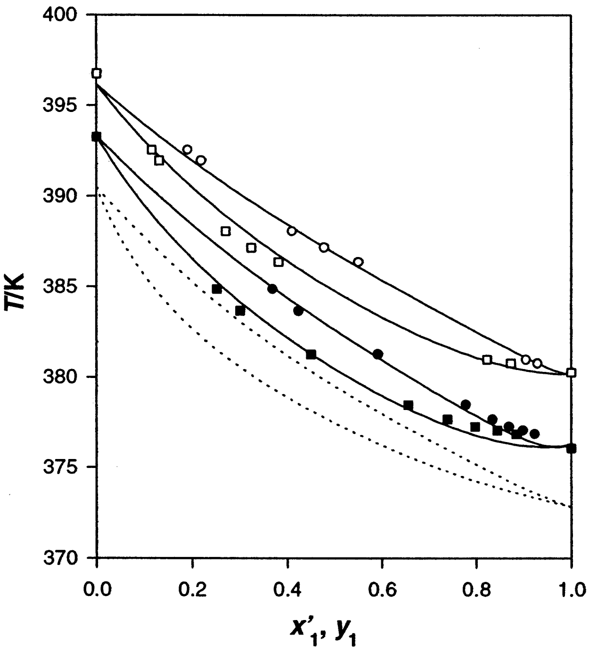

Figure 1. Experimental and calculated $T-x'_1-y_1$ diagram for water (1) + acetic acid (2) + sodium acetate (3) at 100 kPa: (salt mole fraction, $x_3 = 0.050$) ■, $T-x'_1$ experimental, and ●, $T-y_1$ experimental; (salt mole fraction, $x_3 = 0.100$) □, $T-x'_1$ experimental, and ○, $T-y_1$ experimental; solid line, $T-x'_1-y_1$ calculated; dotted line, $T-x'_1-y_1$ calculated salt-free system (calculation based on the electrolyte NRTL model with the parameters from Table 4).

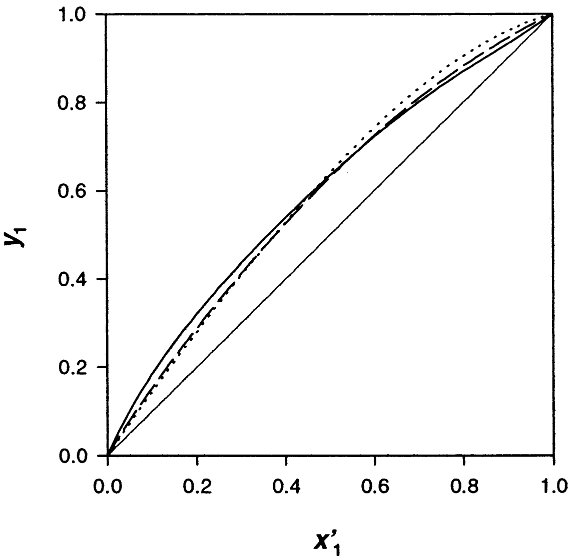

Figure 2. Calculated $y_1-x'_1$ diagram for water (1) + acetic acid (2) + sodium acetate (3) at 100 kPa: solid line, salt-free system; dashed line, salt mole fraction, $x_3 = 0.050$; dotted line, salt mole fraction, $x_3 = 0.100$.

The predictive ability of the model is shown in Figure 1, where the calculated and experimental vapor−liquid equilibria of the water + acetic acid + sodium acetate ternary system are plotted on a $T-x'_1-y_1$ diagram for $x_3 = 0$, 0.050, and 0.100. Similar results have been obtained for all salt contents studied. A $y_1-x'_1$ diagram for $x_3 = 0$, 0.050, and 0.100 has been plotted in Figure 2. These figures show that the addition of sodium acetate produces an appreciable rise in equilibrium temperature but a small effect on relative volatility of water, which augments at higher water solvent concentrations and decreases at lower concentrations. This behavior is different from that observed with lithium acetate,[13] which produces a decrease of the relative volatility of water at all solvent concentrations.

Conclusions

The addition of sodium acetate to the water + acetic acid system produces an appreciable rise in equilibrium temperature but a small effect on the relative volatility of water.

The eNRTL−CT model has proved to be suitable to correlate the vapor−liquid equilibrium of the water + acetic acid + sodium acetate system. Experimental data agree well with the values obtained from the model throughout the range of compositions.

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