

Isobaric Vapor–Liquid Equilibria for 1-Propanol + Water + Calcium Nitrate

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Isobaric vapor–liquid equilibria for all of the binary and ternary mixtures of 1-propanol, water, and calcium nitrate have been measured at 100.00 kPa using a recirculating still. The addition of calcium nitrate to the solvent mixture produced an important salt effect; the azeotrope was removed at salt mole fractions higher than 0.08. The three experimental binary data sets were independently fitted with the electrolyte NRTL model (Mock, B.; Evans, L. B.; Chen, C. C. *AIChE J.* **1986**, *32*, 1655–1664), and the parameters of Mock's model were estimated for each binary system. No ternary parameter was required. These parameters were used to predict the ternary vapor–liquid equilibrium using the same model, and the values so obtained agreed well with the experimental ones.

1. Introduction

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 concentration. This interaction modifies the boiling point, the mutual solubility of the liquid components, and the equilibrium composition of the vapor phase.

This "salt effect" was already known by the Catalan alchemists of the XIII century who used it to get anhydrous ethanol in the distillation of wine. Interest in this topic arose again with the early papers of Furter because of its practical importance to industry (rectification, absorption, precipitation, etc.) and the achievements obtained in the prediction of the thermodynamic behavior of solvent mixtures and, at the same time, because of the difficulty to apply them to electrolyte-containing systems.

Furter (Furter and Cook, 1967; Furter, 1977) summarized the literature on the effects of the salts on vapor–liquid equilibrium; Ciparis (1966) gathered the data of 188 systems containing salt that was later enlarged to 286 (Ciparis, 1973). In addition, Ohe (1991) made an important compilation of vapor–liquid equilibrium data in the presence of salts. The most complete Vapor–Liquid Equilibrium Data Collection (Gmehling et al., 1981) does not present data on electrolyte-containing mixtures; instead, Wichterle et al. (1997) present bibliographical information on these systems. Recently, Yan et al. (1998a,b) have discussed the creation of a database with more than 1800 vapor–liquid equilibrium data sets in the Dortmund Data Bank.

Wichterle et al. (1997) report on the system 1-propanol + water in the presence of the following salts: sodium, potassium, calcium, and barium acetates; lithium, sodium, potassium, ammonium, magnesium, calcium, strontium, barium, cobalt(II), nickel, copper(I), copper(II), zinc, and mercury(II) chlorides; sodium, potassium, magnesium, calcium, strontium, and lead nitrates; sodium, potassium, and ammonium sulfates; and sodium and potassium bro-

mides. The 1-propanol + water + calcium nitrate system was only experimentally studied by Rius and Alvarez (1958). Their study was limited to seven points at saturation conditions and ten points below saturation, but there was variation of the pressure, temperature, solvent composition, and salt content for all of the points.

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. (1984, 1986), the extended UNIQUAC models of Sander et al. (1986) and Macedo et al. (1990), the modified UNIFAC group-contribution model of Kikic et al. (1991), and the LIQUAC model of Li et al. (1994).

The aim of this work is to determine experimentally the effect of calcium nitrate on vapor–liquid equilibria of the 1-propanol + water system at different salt concentrations and to check these results with the predicted ones using the electrolyte NRTL model. Parameters obtained by fitting this model to data for binary systems will be used for this calculation.

2. Experimental Section

2.1. Materials. The chemicals were 1-propanol (Merck, GR grade) with a stated minimum purity of 99.5 mass % (maximum 0.05 mass % water), distilled water (Merck, HPLC grade), and calcium nitrate tetrahydrate (Merck, GR grade, >99.0 mass %). The solvents were used directly without further purification, whereas the calcium nitrate was desiccated in an oven held at 185 °C for at least 24 h.

2.2. Apparatus and Procedure. The equilibrium apparatus was a recirculating still (Labodest model), manufactured by Fisher (Walas, 1985). The vapor–liquid equilibria were obtained at (100.00 ± 0.02) kPa. The accuracy 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 precision of ± 0.0001 g and, afterward, by adding different quantities of 1-propanol, water, or a 1-propanol + water mixture. Each experiment

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Table 1. Experimental Antoine Coefficients and Mean Absolute Deviations for 1-Propanol and Water

component	temp range/K	Antoine coeff ^a			$\Delta P^b/\text{kPa}$
		A	B	C	
1-propanol	320–375	15.8040	3300.22	-75.19	0.03
water	320–375	16.3144	3845.02	-44.42	0.05

^a Antoine equation: $\ln(P^\circ/\text{kPa}) = A - B/(TK) + C$. ^b $\Delta P^\circ = (1/N)\sum|P^\circ_{\text{expt}} - P^\circ_{\text{calc}}|$.

was kept at the boiling point for 15 min or more to ensure a stationary state.

2.3. Sample Analysis. Compositions of the condensed vapor phase (1-propanol + water) 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 \times 1/8 in.) was packed with Porapak QS. The carrier gas was helium flowing at 50 cm³·min⁻¹, and the column temperature was 458 K. The injector and detector temperatures were 473 and 493 K, respectively. The calibration was carried out with gravimetrically prepared standard solutions. The accuracy of the measured vapor-phase mole fraction was ± 0.002 . This procedure was also used for the liquid-phase analysis of the 1-propanol + water binary system.

The liquid phase of the ternary system was composed of 1-propanol, water, and calcium nitrate. The salt mass fraction was gravimetrically determined after the volatile components were separated from a known mass of sample by evaporation to dryness. On the other hand, the density of the liquid phase was determined with a vibrating tube densimeter (Anton Paar DMA 58) with proportional temperature control that kept the samples at (298.15 \pm 0.01) K. The densimeter was calibrated with purified water and dry air. The accuracy of the density values was ± 0.08 kg·m⁻³. Previously, the density of a set of standard solutions with known quantities of 1-propanol, water, and salt was measured, and a correlation that allowed determination of the mass fraction of 1-propanol in the sample, given the density and the salt mass fraction in the solution, was obtained. The mass fractions were then translated into mole fractions. The accuracy in the measurement of the 1-propanol, water, and calcium nitrate mole fractions in the liquid phase was ± 0.004 . This method of analyzing the composition of salt-containing mixtures was found to be reproducible and of consistent accuracy, as described in a previous work (Vercher et al., 1994).

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 ± 0.00005 .

3. Results and Discussion

3.1. Experimental Data. To test the equilibrium apparatus and to dispose of suitable data of pure solvents, the 1-propanol and water vapor pressures were measured in the range 320–375 K. Antoine coefficients for both solvents, obtained from our experimental data, and mean absolute deviations between experimental and calculated vapor pressure data are shown in Table 1.

Moreover, vapor–liquid equilibria for the three binary systems 1-propanol (1) + water (2), 1-propanol (1) + calcium nitrate (3), and water (2) + calcium nitrate (3) were obtained at 100.00 kPa. The results are reported in Tables 2–4. Also, vapor–liquid equilibria for the 1-propanol (1) + water (2) + calcium nitrate (3) ternary system was

Table 2. Vapor–Liquid Equilibrium Data for 1-Propanol (1) + Water (2) at 100.00 kPa

x_1	y_1	T/K	x_1	y_1	T/K
0.019	0.239	365.90	0.418	0.429	360.40
0.027	0.296	364.20	0.460	0.439	360.40
0.036	0.330	363.15	0.487	0.447	360.45
0.047	0.351	362.35	0.517	0.457	360.50
0.060	0.366	361.90	0.550	0.467	360.60
0.062	0.367	361.80	0.585	0.483	360.70
0.086	0.378	361.35	0.626	0.502	360.95
0.111	0.383	361.10	0.659	0.520	361.20
0.145	0.390	360.95	0.697	0.549	361.60
0.172	0.395	360.80	0.749	0.587	362.30
0.208	0.401	360.70	0.786	0.617	362.90
0.237	0.402	360.70	0.824	0.666	363.65
0.264	0.404	360.60	0.866	0.711	364.60
0.296	0.407	360.55	0.902	0.783	365.90
0.328	0.411	360.50	0.950	0.874	367.60
0.355	0.416	360.45	1.000	1.000	369.90
0.382	0.422	360.40			

Table 3. Vapor–Liquid Equilibrium Data for 1-Propanol (1) + Calcium Nitrate (3) at 100.00 kPa

x_3	T/K	x_3	T/K	x_3	T/K
0.0056	369.90	0.0580	370.80	0.1115	372.00
0.0099	369.95	0.0664	370.95	0.1216	372.25
0.0160	370.05	0.0747	371.10	0.1263	372.40
0.0235	370.15	0.0806	371.25	0.1295	372.50
0.0326	370.35	0.0892	371.40	0.1324	372.65
0.0415	370.45	0.0968	371.60	0.1391	372.75
0.0496	370.65	0.1044	371.80	0.1448	372.85

Table 4. Vapor–Liquid Equilibrium Data for Water (2) + Calcium Nitrate (3) at 100.00 kPa

x_3	T/K	x_3	T/K	x_3	T/K
0.0051	373.15	0.0422	376.50	0.0711	380.15
0.0129	373.75	0.0434	376.65	0.0731	380.45
0.0156	373.95	0.0449	376.85	0.0767	380.95
0.0179	374.15	0.0469	377.05	0.0793	381.30
0.0200	374.35	0.0484	377.25	0.0831	381.85
0.0221	374.50	0.0501	377.45	0.0844	382.35
0.0244	374.70	0.0514	377.65	0.0879	382.65
0.0270	375.00	0.0535	377.85	0.0913	383.35
0.0299	375.25	0.0553	378.05	0.0963	384.05
0.0327	375.50	0.0570	378.25	0.1014	384.65
0.0353	375.80	0.0595	378.60	0.1048	385.45
0.0380	376.10	0.0632	379.00	0.1069	385.75
0.0393	376.25	0.0658	379.35		
0.0407	376.35	0.0688	379.75		

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 1-propanol in the liquid phase expressed on a salt-free basis, y_1 is the mole fraction of 1-propanol in the vapor phase, and T is the equilibrium temperature.

The experimental data obtained for the 1-propanol (1) + water (2) system show a minimum boiling point azeotrope at $x_1 = 0.435$ and $T = 360.4$ K, obtained for the x_1 value that makes the function $(y_1 - x_1) = f(x_1)$ equal zero. These results agree well with those reported by Gabaldón et al. (1996) working at the same pressure.

The experimental results of the 1-propanol (1) + water (2) system were tested for thermodynamic consistency using the point-to-point tests of Van Ness et al. (1973), modified by Fredenslund et al. (1977) and Wisniak (1993). The Vann Ness test gave a mean absolute deviation between calculated and measured mole fractions of 1-propanol in the vapor phase of $\delta(y) = 0.0078$, and the Wisniak test gave $1.00 \leq L_i/W_i \leq 1.01$ for all the points, which shows that the values are thermodynamically consistent. No consistency test was used for salt-containing systems.

3.2. Calculation of Phase Equilibrium. The electrolyte NRTL model used to predict the vapor–liquid equilibrium of the ternary system is an extension of the

Table 5. Vapor–Liquid Equilibrium Data for 1-Propanol (1) + Water (2) + Calcium Nitrate (3) at 100.00 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
0.009	0.518	0.483	360.90	0.033	0.879	0.823	367.45	0.066	0.767	0.766	367.15
0.009	0.449	0.464	360.80	0.033	0.899	0.845	367.90	0.067	0.780	0.778	367.40
0.010	0.950	0.900	368.35	0.034	0.276	0.480	361.50	0.067	0.823	0.811	368.00
0.010	0.376	0.447	360.70	0.035	0.759	0.712	365.40	0.068	0.694	0.714	366.40
0.011	0.705	0.588	362.65	0.035	0.394	0.512	361.95	0.070	0.850	0.843	368.55
0.011	0.583	0.519	361.50	0.035	0.701	0.660	364.45	0.071	0.591	0.666	365.50
0.011	0.479	0.479	361.00	0.036	0.557	0.575	363.00	0.071	0.520	0.631	364.80
0.011	0.399	0.457	360.80	0.036	0.461	0.535	362.35	0.071	0.909	0.899	369.60
0.011	0.221	0.422	360.80	0.036	0.187	0.468	361.40	0.073	0.636	0.700	366.25
0.011	0.138	0.410	360.90	0.036	0.092	0.447	361.40	0.074	0.730	0.748	367.10
0.012	0.675	0.571	362.35	0.036	0.947	0.922	369.30	0.076	0.814	0.803	368.05
0.012	0.307	0.436	360.75	0.037	0.808	0.776	366.65	0.077	0.468	0.625	364.80
0.012	0.959	0.897	368.35	0.038	0.730	0.689	365.10	0.077	0.938	0.926	370.15
0.013	0.889	0.796	366.45	0.039	0.879	0.837	367.85	0.078	0.554	0.661	365.55
0.013	0.843	0.730	365.25	0.040	0.666	0.649	364.35	0.078	0.825	0.819	368.35
0.014	0.591	0.533	361.85	0.040	0.350	0.509	362.00	0.078	0.839	0.837	368.70
0.014	0.527	0.503	361.35	0.040	0.247	0.484	361.65	0.080	0.753	0.772	367.60
0.014	0.164	0.420	360.90	0.040	0.063	0.444	361.60	0.080	0.851	0.845	368.90
0.014	0.122	0.412	360.95	0.042	0.716	0.691	365.15	0.081	0.599	0.691	366.35
0.015	0.940	0.873	367.95	0.042	0.143	0.468	361.50	0.081	0.672	0.718	366.80
0.015	0.433	0.475	361.10	0.042	0.840	0.803	367.20	0.081	0.725	0.752	367.35
0.016	0.089	0.410	361.15	0.042	0.760	0.723	365.80	0.081	0.743	0.767	367.70
0.017	0.686	0.598	362.95	0.043	0.793	0.762	366.45	0.084	0.517	0.652	365.60
0.017	0.938	0.874	368.05	0.043	0.525	0.577	363.20	0.084	0.862	0.855	369.20
0.018	0.848	0.757	365.85	0.043	0.435	0.542	362.60	0.086	0.760	0.785	368.10
0.018	0.784	0.683	364.45	0.044	0.937	0.916	369.35	0.087	0.560	0.686	366.45
0.018	0.248	0.439	360.90	0.045	0.307	0.509	362.00	0.089	0.938	0.924	370.50
0.018	0.053	0.399	361.75	0.045	0.211	0.488	361.75	0.091	0.839	0.842	369.20
0.018	0.937	0.874	368.05	0.045	0.842	0.812	367.45	0.092	0.721	0.759	367.90
0.019	0.915	0.849	367.60	0.045	0.797	0.760	366.60	0.092	0.795	0.806	368.55
0.019	0.506	0.510	361.60	0.046	0.610	0.629	364.15	0.092	0.779	0.802	368.60
0.019	0.404	0.478	361.20	0.046	0.861	0.830	367.90	0.093	0.627	0.712	367.10
0.019	0.322	0.460	361.05	0.047	0.473	0.564	363.05	0.094	0.775	0.800	368.60
0.020	0.558	0.531	361.95	0.048	0.767	0.746	366.35	0.095	0.523	0.680	366.55
0.020	0.146	0.428	361.00	0.048	0.371	0.531	362.50	0.097	0.687	0.744	367.75
0.020	0.537	0.528	361.90	0.048	0.085	0.467	361.60	0.099	0.936	0.921	370.70
0.021	0.224	0.443	361.00	0.048	0.859	0.832	367.80	0.099	0.796	0.820	369.10
0.021	0.929	0.866	368.00	0.049	0.267	0.508	362.10	0.100	0.764	0.800	368.75
0.023	0.880	0.828	367.35	0.049	0.172	0.486	361.75	0.101	0.688	0.754	368.10
0.023	0.801	0.723	365.30	0.049	0.851	0.826	367.85	0.103	0.891	0.887	370.40
0.023	0.715	0.639	363.75	0.050	0.779	0.752	366.55	0.104	0.584	0.706	367.40
0.023	0.639	0.586	362.90	0.051	0.051	0.460	361.85	0.106	0.823	0.837	369.60
0.023	0.362	0.477	361.30	0.051	0.880	0.851	368.35	0.109	0.824	0.831	369.60
0.023	0.110	0.427	361.10	0.052	0.341	0.534	362.65	0.110	0.759	0.798	369.15
0.023	0.913	0.848	367.70	0.052	0.842	0.820	367.80	0.111	0.929	0.912	370.70
0.024	0.535	0.536	362.15	0.053	0.732	0.734	366.25	0.112	0.649	0.747	368.50
0.024	0.463	0.509	361.70	0.053	0.542	0.603	364.00	0.113	0.953	0.931	371.20
0.024	0.289	0.464	361.20	0.053	0.131	0.486	361.85	0.113	0.895	0.882	370.40
0.024	0.909	0.849	367.75	0.053	0.806	0.784	367.10	0.115	0.739	0.796	369.25
0.024	0.595	0.566	362.55	0.054	0.927	0.908	369.40	0.115	0.940	0.919	370.95
0.026	0.906	0.849	367.80	0.054	0.763	0.743	366.50	0.116	0.845	0.858	370.30
0.027	0.169	0.444	361.10	0.055	0.836	0.820	367.90	0.119	0.812	0.831	369.90
0.027	0.082	0.427	361.30	0.056	0.625	0.658	364.90	0.121	0.953	0.927	371.40
0.028	0.857	0.811	367.05	0.056	0.811	0.796	367.40	0.121	0.896	0.882	370.80
0.028	0.314	0.475	361.35	0.059	0.676	0.687	365.55	0.122	0.726	0.789	369.50
0.028	0.631	0.597	363.15	0.059	0.837	0.816	367.90	0.124	0.882	0.880	370.70
0.029	0.798	0.735	365.75	0.059	0.861	0.848	368.40	0.125	0.729	0.798	369.75
0.029	0.488	0.530	362.15	0.059	0.741	0.737	366.50	0.128	0.711	0.787	369.30
0.029	0.426	0.509	361.80	0.060	0.705	0.723	366.25	0.128	0.915	0.897	371.10
0.029	0.955	0.924	369.20	0.060	0.482	0.597	363.95	0.129	0.873	0.874	370.95
0.030	0.592	0.581	362.90	0.062	0.823	0.813	367.95	0.130	0.946	0.923	371.70
0.030	0.060	0.423	361.70	0.062	0.724	0.727	366.40	0.130	0.791	0.834	370.35
0.031	0.236	0.466	361.30	0.063	0.568	0.642	364.80	0.132	0.690	0.786	370.10
0.032	0.832	0.794	366.85	0.064	0.916	0.903	369.55	0.135	0.793	0.833	370.70
0.032	0.120	0.445	361.25	0.065	0.429	0.587	363.85	0.136	0.907	0.897	371.55
0.032	0.679	0.638	364.00	0.065	0.710	0.721	366.40	0.141	0.867	0.873	371.50
0.033	0.727	0.676	364.75	0.066	0.672	0.711	366.20	0.142	0.905	0.891	371.60
0.033	0.878	0.828	367.50	0.066	0.637	0.678	365.50	0.144	0.927	0.896	371.80

nonrandom two liquid (NRTL) local composition model of Renon and Prausnitz (1968) for liquid-phase activity coefficients. Chen et al. (1982) derived a model for single-solvent + electrolyte systems, and later Mock et al. (1984, 1986) 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 as follows: (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 when calculating the activity coefficients of solvents.

From the molar excess Gibbs energy expression proposed by Mock et al. (1984, 1986), the following expressions for the liquid-phase activity coefficients of 1-propanol (1) and water (2) in a ternary system containing calcium nitrate (3) can be derived.

$$\ln \gamma_1 = \left[\frac{G_{3,1}\tau_{3,1}(X_a + X_c) + X_2G_{2,1}\tau_{2,1}}{G_{3,1}(X_a + X_c) + X_1 + X_2G_{2,1}} \right] - X_1 \left[\frac{G_{3,1}\tau_{3,1}(X_a + X_c) + X_2G_{2,1}\tau_{2,1}}{(G_{3,1}(X_a + X_c) + X_1 + X_2G_{2,1})^2} \right] + \left[\frac{X_2G_{1,2}\tau_{1,2}}{G_{3,2}(X_a + X_c) + X_2 + X_1G_{1,2}} \right] - X_2G_{1,2} \left[\frac{G_{3,2}\tau_{3,2}(X_a + X_c) + X_1G_{1,2}\tau_{1,2}}{(G_{3,2}(X_a + X_c) + X_2 + X_1G_{1,2})^2} \right] + \left[\frac{X_cG_{1,3}\tau_{1,3}}{X_a + X_1G_{1,3} + X_2G_{2,3}} \right] - X_cG_{1,3} \left[\frac{X_1G_{1,3}\tau_{1,3} + X_2G_{2,3}\tau_{2,3}}{(X_a + X_1G_{1,3} + X_2G_{2,3})^2} \right] + \left[\frac{X_aG_{1,3}\tau_{1,3}}{X_c + X_1G_{1,3} + X_2G_{2,3}} \right] - X_aG_{1,3} \left[\frac{X_1G_{1,3}\tau_{1,3} + X_2G_{2,3}\tau_{2,3}}{(X_c + X_1G_{1,3} + X_2G_{2,3})^2} \right] \quad (1)$$

$$\ln \gamma_2 = \left[\frac{G_{3,2}\tau_{3,2}(X_a + X_c) + X_1G_{1,2}\tau_{1,2}}{G_{3,2}(X_a + X_c) + X_2 + X_1G_{1,2}} \right] - X_2 \left[\frac{G_{3,2}\tau_{3,2}(X_a + X_c) + X_1G_{1,2}\tau_{1,2}}{(G_{3,2}(X_a + X_c) + X_2 + X_1G_{1,2})^2} \right] + \left[\frac{X_1G_{2,1}\tau_{2,1}}{G_{3,1}(X_a + X_c) + X_1 + X_2G_{2,1}} \right] - X_1G_{2,1} \left[\frac{G_{3,1}\tau_{3,1}(X_a + X_c) + X_2G_{2,1}\tau_{2,1}}{(G_{3,1}(X_a + X_c) + X_1 + X_2G_{2,1})^2} \right] + \left[\frac{X_cG_{2,3}\tau_{2,3}}{X_a + X_1G_{1,3} + X_2G_{2,3}} \right] - X_cG_{2,3} \left[\frac{X_1G_{1,3}\tau_{1,3} + X_2G_{2,3}\tau_{2,3}}{(X_a + X_1G_{1,3} + X_2G_{2,3})^2} \right] + \left[\frac{X_aG_{2,3}\tau_{2,3}}{X_c + X_1G_{1,3} + X_2G_{2,3}} \right] - X_aG_{2,3} \left[\frac{X_1G_{1,3}\tau_{1,3} + X_2G_{2,3}\tau_{2,3}}{(X_c + X_1G_{1,3} + X_2G_{2,3})^2} \right] \quad (2)$$

In eqs 1 and 2, X_1 and X_2 are the liquid-phase mole fraction of 1-propanol (1) and water (2) based on the assumption of total dissociation of electrolyte components. X_c and X_a ($X_c = X_a$) are the liquid-phase mole fractions of cation and anion multiplied by the absolute value of its ionic charge, based on the assumption of total dissociation of electrolyte components. In the absence of salt ($X_a = X_c = 0$), eqs 1 and 2 are reduced to the original NRTL expressions for nonelectrolyte systems (Renon and Prausnitz, 1968). The G_{ij} and τ_{ij} parameters are defined as

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad \tau_{ij} = \Delta g_{ij}/RT \quad (3)$$

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 $\alpha_{2,3} = \alpha_{3,2}$). Taking Δg_{ij} as adjustable parameters instead of τ_{ij} , the temperature effect is taken into account.

The 1-2 binary solvent-solvent parameters were first determined from the vapor-liquid equilibrium data of the 1-propanol (1) + water (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 1-propanol (1) + calcium nitrate (3) system given in Table 3 and the water (2) + calcium nitrate (3) system given in Table 4.

For each binary system, the three corresponding parameters were estimated by minimization of the objective function F given in eq 4, using the SOLVER tool of the Microsoft Excel 97 spreadsheet. No parameters were arbitrarily set to predetermined values.

$$F = \sum_j h|y_{1,\text{expt}} - y_{1,\text{calc}}| + \sum_j k|T_{\text{expt}} - T_{\text{calc}}| \quad (4)$$

In eq 4, T is the equilibrium temperature and y_1 , the 1-propanol mole fraction in the vapor phase. The indices expt and calc denote the experimental and calculated values, and h and k are the weighting factors. The summations are extended to all data points. Equilibrium temperatures and vapor-phase compositions were calcu-

lated assuming ideal behavior of the vapor phase and solving iteratively the equilibrium condition for solvents

$$y_i P = X_i \gamma_i P_i^\circ \quad (5)$$

where P_i° is the vapor pressure of solvent i at equilibrium temperature ($i = 1, 2$), y_i is the vapor phase mole fraction, X_i is the liquid-phase mole fraction based on the assumption of total dissociation of electrolytes, γ_i is the activity coefficient of component i obtained from eq 1 or 2, and P is the total pressure in the system.

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

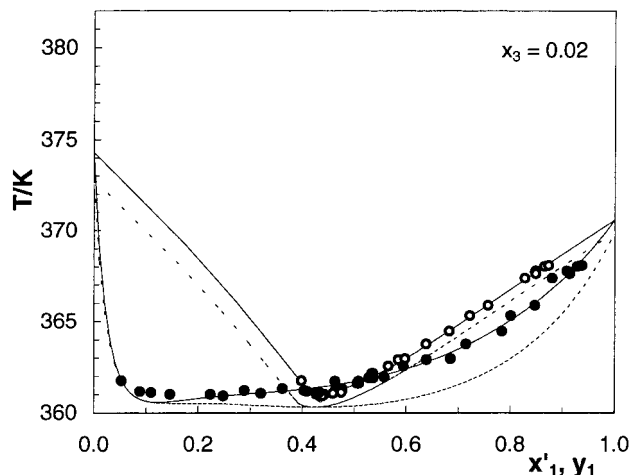
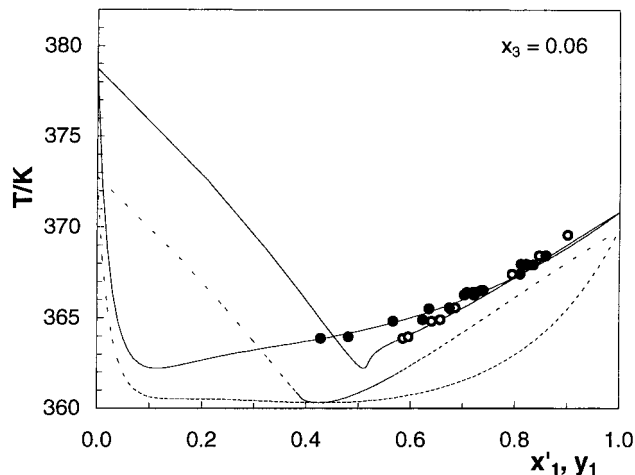
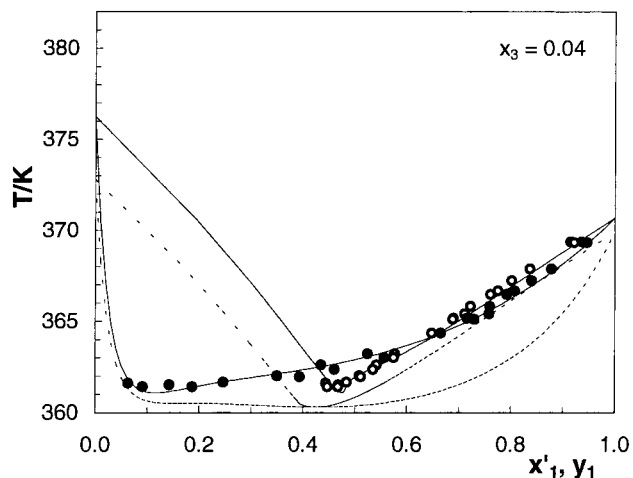
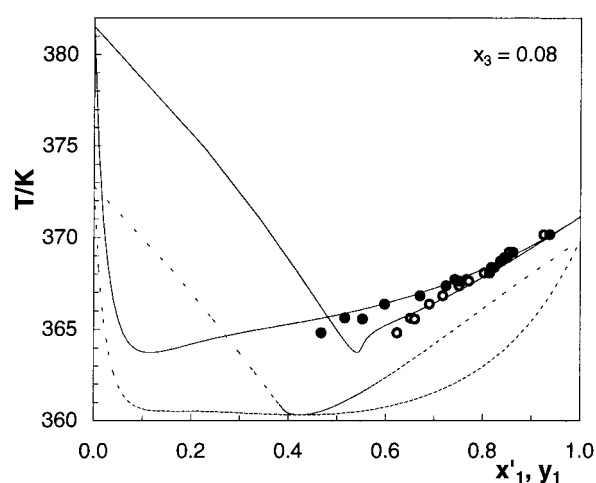
The nine parameters obtained from binary systems were used together to predict the vapor-liquid equilibria of the 1-propanol (1) + water (2) + calcium nitrate (3) ternary system. To make a comparison with the experimental ternary data reported in Table 5, we have calculated the vapor-phase compositions 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 0.014, and its standard deviation was 0.011. The mean absolute deviation between experimental and calculated values of the equilibrium temperature was 0.21 K, and its standard deviation was 0.20 K. The predictive ability of the model can be seen in Figures 1-4, where the predicted and experimental vapor-liquid equilibria of the 1-propanol + water + calcium nitrate ternary system are plotted on a $T-x'_1-y_1$ diagram for $x_3 = 0.02, 0.04, 0.06$, and 0.08.

In Figures 1-4 it can be observed that the addition of calcium nitrate results in a considerable increase of the mole fraction of 1-propanol in the vapor phase and the displacement of the azeotropic point to higher x'_1 values. The azeotrope disappears at $x_3 \geq 0.08$. In the same figures, it can also be observed that the salt-containing systems present a minimum temperature. This temperature does not fall on the azeotropic point and remains even though the azeotrope has been eliminated. Table 7 shows the experimental value of azeotropic points of the 1-propanol + water system and those estimated from the electrolyte NRTL model for salt-containing mixtures, together with the minimum temperature of these systems. Similar

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>i</i> component	<i>j</i> component	$\alpha_{i,j}$	$\Delta g_{i,j}(\text{J}\cdot\text{mol}^{-1})$	$\Delta g_{j,i}(\text{J}\cdot\text{mol}^{-1})$	Δy^a	ΔT^b
1-propanol	water	0.477	1 648.8	7 896.7	0.005	0.19
1-propanol	calcium nitrate	0.961	6 739.9	11 369.7		0.15
water	calcium nitrate	0.206	27 580.1	-13 052.8		0.09

$$^a \Delta y = (1/N)\sum|y_{\text{expt}} - y_{\text{calc}}|, \quad ^b \Delta T = (1/N)\sum|T_{\text{expt}} - T_{\text{calc}}|.$$

**Figure 1.** Experimental and calculated T - x' - y diagram for 1-propanol (1) + water (2) + calcium nitrate (3) at 100.00 kPa: salt mole fraction, $x_3 = 0.02$ (●) T - x' experimental values; (○) T - y experimental values; (—) T - x' - y calculated values; (---) T - x' - y calculated salt-free system (calculation based on electrolyte NRTL model; parameters from Table 6).**Figure 3.** Experimental and calculated T - x' - y diagram for 1-propanol (1) + water (2) + calcium nitrate (3) at 100.00 kPa: salt mole fraction, $x_3 = 0.06$; (●) T - x' experimental values; (○) T - y experimental values; (—) T - x' - y calculated values; (---) T - x' - y calculated salt-free system (calculation based on electrolyte NRTL model; parameters from Table 6).**Figure 2.** Experimental and calculated T - x' - y diagram for 1-propanol (1) + water (2) + calcium nitrate (3) at 100.00 kPa: salt mole fraction, $x_3 = 0.04$; (●) T - x' experimental values; (○) T - y experimental values; (—) T - x' - y calculated values; (---) T - x' - y calculated salt-free system (calculation based on electrolyte NRTL model; parameters from Table 6).**Figure 4.** Experimental and calculated T - x' - y diagram for 1-propanol (1) + water (2) + calcium nitrate (3) at 100.00 kPa: salt mole fraction, $x_3 = 0.08$; (●) T - x' experimental values; (○) T - y experimental values; (—) T - x' - y calculated values; (---) T - x' - y calculated salt-free system (calculation based on electrolyte NRTL model; parameters from Table 6).

behavior has been reported by Iliuta et al. (1996) for the 1-propanol + water + calcium chloride system at 101.32 kPa and by Polka and Gmehling (1994) for the 2-propanol + water + calcium nitrate system at 50.66 kPa.

4. Conclusions

The addition of calcium nitrate to 1-propanol + water systems produces an important salting-out effect of the alcohol, and the azeotrope disappears at salt mole fractions higher than 0.08. This effect is strong, but smaller than that produced by calcium chloride on this system (Iliuta et al., 1996).

The electrolyte NRTL model of Mock et al. (1984, 1986) has proved to be suitable to predict the vapor-liquid equilibrium of the 1-propanol + water + calcium nitrate 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. The model also predicts the existence of a minimum in equilibrium temperature that does not coincide with the azeotrope composition and remains even when the azeotrope disappears at high salt concentrations.

Table 7. Effect of Calcium Nitrate Mole Fraction (x_3) on the Azeotropic Point ($x'_{1\text{ az}}$ and T_{az}) and the Minimal Temperature, T_{min} , of 1-Propanol (1) + Water (2) Mixtures

x_3	azeotropic point		T_{min}/K
	$x'_{1\text{ az}}$	T_{az}/K	
0.00 ^a	0.435	360.4	360.4
0.02 ^b	0.527	361.8	360.6
0.04 ^b	0.656	364.2	361.1
0.06 ^b	0.812	367.4	362.2
0.08 ^b	1.000	371.1	363.7

^a Experimental value. ^b Estimated from electrolyte NRTL model.

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