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Effect of Calcium Chloride on the Isobaric Vapor−Liquid Equilibrium of 1-Propanol + Water

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The effect of calcium chloride at salt mole fractions from 0.02 to saturation on the vapor−liquid equilibrium (VLE) of 1-propanol + water has been studied at 101.32 kPa using a modified Othmer equilibrium still. The salt exhibited a salting-out effect of the alcohol over the whole range of liquid composition, the azeotrope being eliminated at salt mole fractions greater than 0.080. A liquid phase splitting into two immiscible liquid phases on the whole range of salt concentration and over a liquid range of about 0.01−0.54 1-propanol mole fraction (salt-free basis) was observed. The results were compared with the values predicted from the extended UNIQUAC models of Sander et al. and Macedo et al. and the modified UNIFAC group-contribution model of Kikic et al.

1. Introduction

A salt dissolved in a mixed solvent affects the boiling point, the mutual solubilities of the two liquid components, and the equilibrium vapor phase composition. This alteration of phase equilibrium of mixed-solvent mixtures (known as the salt effect) constitutes a possible technique of extractive distillation for the separation of systems of low relative volatility or systems exhibiting azeotropic behavior in composition regions critical to the separation.

Through preferential solvation of the particles of the dissolved salt (nondissociated molecules or ions or both) by the molecules of solvent, the solubility relationship between the two volatile components is altered such that one component is "salted-out" with respect to the other. The effect of the addition of charged particles to binary liquid solutions is a complex phenomenon because of the variety of interactions involved: ion−nonelectrolyte, ion−solvent, and nonelectrolyte−solvent as well as self-interactions of all three components. The complex mechanism that originates this salt effect in vapor−liquid equilibrium (VLE) must be better understood before a sound approach can be made to the design of extractive distillation processes.

Usually, the molecules of the more polar component are preferentially attracted by the electrostatic field of the ions, and hence the vapor composition is enriched in the less polar component in which the salt is less soluble. Also, in general, the selectivity and hence magnitude of the salt effect on vapor composition depends more or less directly on the difference between the solubilities of the salt in both solvents separately. However, three types of behaviors anomalous to the predictions described above have been identified and presented by Meranda and Furter (1974), namely (a) the crossover in the salt effect between salting-in and salting-out, as the liquid composition is varied, even though the salt is clearly more soluble in one component than in the other, (b) the enrichment of vapor composition throughout, in the component in which the salt is more, rather than less, soluble, and (c) the relatively large effect on vapor composition caused by a salt having little difference in solubility between the two solvents. Moreover, a minimum nonazeotropic point in the temperature−composition diagram was observed for some azeotropic systems (Novela and Tarraso, 1952; Gomez and Galan, 1974; Galan et al., 1976; Iliuta and Thyrion, 1995a,b). Iliuta and Thyrion (1995a,b) have shown that the minimum in the temperature−composition diagram corresponds to an apparent intersection point and hence does not represent an azeotropic point. This behavior was predicted for the 1-propanol + water + $CaCl_2$ system at two different salt concentrations by Sander et al. (1986) using the modified UNIQUAC model, but experimental data were needed to prove this prediction.

Gomez and Galan (1974) studied the 1-propanol + water system saturated with cobalt(II) chloride, Morrison et al. (1990) studied the effect of NaCl, NaBr, and KBr at different salt concentrations, and Lin et al. (1993) studied the effect of NaCl and LiBr also at different salt concentrations. The vapor−liquid equilibrium of the 1-propanol + water system in the presence of calcium chloride has been studied by Hashitani et al. (1968) only at saturation, but results at various salt concentrations below saturation were not found in the literature.

To calculate VLE for the mixed-solvent salt systems, local composition models have been modified to take into account the interactions in the electrolytic systems. To represent the long-range contribution, a Debye−Hückel expression is often used. For the short-range contribution, Mock et al. (1986) used the NRTL model, Sander et al. (1986) and Macedo et al. (1990) used the UNIQUAC model, and Kikic et al. (1991) used the UNIFAC group-contribution model.

The aim of this work is to determine the effect of $CaCl_2$ on the VLE of 1-propanol + water at different salt concentrations and to check the prediction results obtained using the extended UNIQUAC models of Sander et al. (1986) and of Macedo et al. (1990) and the modified UNIFAC group-contribution model of Kikic et al. (1991).

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Table 1. Experimental Vapor–Liquid Equilibrium for 1-Propanol (1) + Water (2) at 101.32 kPa

x_1'	y_1	T/K	α_0	x_1'	y_1	T/K	α_0
0.000	0.000	373.15		0.538	0.461	361.00	0.7345
0.053	0.353	362.85	9.7487	0.604	0.485	361.30	0.6174
0.100	0.378	361.85	5.4695	0.650	0.514	361.70	0.5695
0.150	0.387	361.30	3.5775	0.700	0.550	362.10	0.5238
0.200	0.395	361.25	2.6116	0.751	0.585	362.80	0.4674
0.253	0.400	361.20	1.9684	0.800	0.634	363.60	0.4331
0.300	0.403	361.05	1.5751	0.847	0.693	364.65	0.4078
0.347	0.414	361.00	1.3295	0.900	0.770	366.10	0.3720
0.400	0.421	360.95	1.0907	0.952	0.870	368.00	0.3374
0.438	0.438	360.90	1.0000	1.000	1.000	370.40	
0.500	0.447	360.95	0.8083				

2. Experimental Section

2.1. Chemicals. 1-Propanol (Rathburn, HPLC grade) with a stated minimum purity of 99.8 mass % (maximum 0.03 mass % water) and distilled water (LAB-SCAN, HPLC grade) were used. The alcohol was used directly without further purification.

Calcium chloride dihydrate (pa grade, minimum 99 mass %, Across) was desiccated in a microwave oven before use and was shown to contain less than 0.2 mass % water as analyzed by the Karl–Fisher method.

2.2. Apparatus and Procedure. VLE was measured with a modified recirculation Othmer type still previously used by Sada et al. (1975). The description of the still and the experimental procedure have been described previously (Iliuta and Thyrion, 1995a,b).

Results were obtained at 101.32 kPa. Atmospheric pressure was measured by a mercury column barometer with an accuracy of ±0.066 kPa. The boiling temperature was measured using a calibrated thermometer with an accuracy of ±0.05 K.

2.3. Samples Analysis. The liquid and vapor compositions were analyzed by gas chromatography using a TCD detector and a 2.4 × 3.2 mm OD Poropak Q column. The optimum operating conditions were the following: carrier gas, hydrogen; flow rate, of 30 cc/min; oven temperature, 453 K; injection temperature, 473 K; detector temperature, 453 K. In the immiscible range, the samples of both liquid phases were collected using the method of Lin et al. (1993) to ensure that both the immiscible liquid phase samples were collected with minimum error and the alteration of the equilibrium state of the two immiscible liquid phases was avoided because the salt solubilities in solvents are dependent on the temperature. Calibration and analysis were carried out in molar fractions by means of the internal standard technique. The chromatographic measurements showed a good reproducibility, the mole fractions of alcohol and water being calculated from the peak area ratio of the samples with an accuracy of ±0.002 in mole fraction. On the removal of the solvent by evaporation of a known mass of the liquid sample, it was possible to measure the mass of salt in the sample using a Mettler balance with a resolution of ±0.0001 g.

3. Results and Discussion

3.1. Experimental Data. Vapor–liquid equilibrium results for 1-propanol (1) + water (2) at 101.32 kPa are presented in Table 1. The experimental results are shown in Figure 1 and compared with the results reported by Kojima et al. (Gmehling and Onken, 1977), Morrison et al. (1990), and Lin et al. (1993). The graphical representation shows good agreement between our results and those in the literature. The azeotropic point was found at $x_1 = 0.438$ and $T = 360.90$ K.

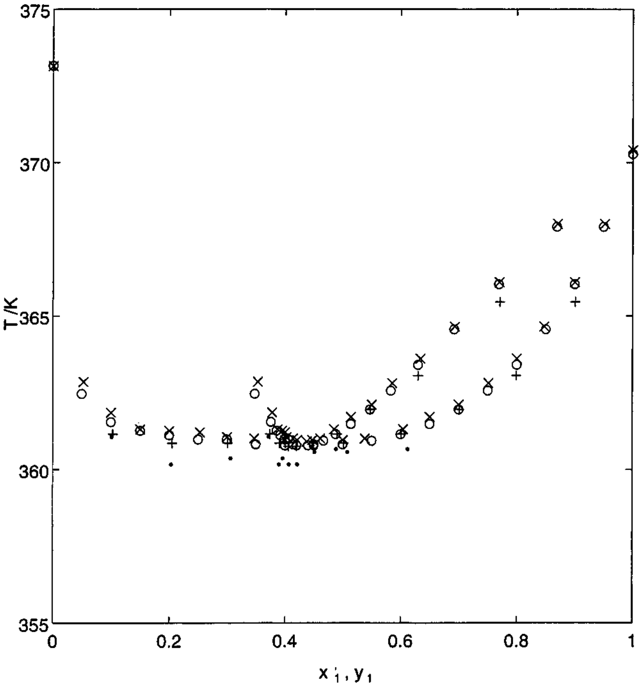

Figure 1. Temperature–composition diagram for the 1-propanol (1) + water (2) at 101.32 kPa: ×, this work; ○, Kojima et al. (1968); •, Morrison et al. (1990); +, Lin et al. (1993).

Isobaric VLE data at 101.32 kPa were measured at $x_3 =$ 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, and 0.14 and at saturation for the system 1-propanol (1) + water (2) + $CaCl_2$ (3), and the results are presented in Table 2. The liquid concentration is presented on a salt-free basis in order to render more visible the salt effect on the VLE of the mixed solvent. Our results at saturation agree well with those given by Hashitani et al. (1968).

To point out the modifications in the vapor phase concentration, the results are presented in Figure 2 at various salt concentrations. The salt is preferentially more soluble in water than in propanol as shown by the solubility values in the boiling mixtures (Table 2). In this context the 1-propanol is expected to be salted-out from the mixed solvent over the whole range of liquid concentration. Moreover, the salting-out effect should increase with increasing salt concentration over the whole range of mixed-solvent composition as predicted by the relative volatility plots of Johnson and Furter (1960):

$$\ln(\alpha_S/\alpha_0) = K_S x_3 \tag{1}$$

where α_S and α_0 are the relative volatilities with and without salt, respectively, K_S is the salt parameter, and x_3 is the salt mole fraction.

The behavior of this salt system is in agreement with this prediction. From Figure 2, a considerable increase of the alcohol concentration in the vapor phase by the addition of the salt was observed. For $CaCl_2$, the azeotropic point was changed to about $x_1' = 0.530$, 0.690, and 0.895 at $x_3 =$ 0.02, 0.04, and 0.06, respectively. Moreover, the azeotrope of the mixed solvent system disappears at $x_3 > 0.08$. This result may be explained by the clustering of water (the more polar component of solvent mixtures) being much more pronounced than with alcohol over the whole range of liquid concentration.

The modifications in bubble points are illustrated by the results presented in Figures 3 and 4. In these $T-x'-y$ plots the systems present a nonazeotropic minimum in the temperature. As shown previously (Iliuta and Thyrion,

Table 2. Experimental Results for 1-Propanol (1) + Water (2) + $CaCl_2$ (3) at 101.32 kPa

	$x_3 = 0.02$			$x_3 = 0.04$			$x_3 = 0.06$			$x_3 = 0.08$		
x_1'	y_1	T/K	$\alpha_S{}^a$	y_1	T/K	$\alpha_S{}^a$	y_1	T/K	$\alpha_S{}^a$	y_1	T/K	$\alpha_S{}^a$
0.000	0.000	374.95		0.000	377.50		0.000	381.30		0.000	386.10	
0.053^b	0.436	361.55		0.483	361.65		0.547	362.55		0.609	363.95	
0.100^b	0.437	361.35		0.494	361.95		0.558	362.95		0.620	364.60	
0.200^b	0.451	361.25		0.510	362.10		0.597	363.55		0.640	365.45	
0.300^b	0.470	361.50		0.530	362.65		0.612	364.35		0.666	366.15	
0.438^b	0.518	361.85		0.565	363.25		0.633	365.15		0.681	366.70	
0.538^b	0.547	362.60		0.617	364.40		0.675	366.45		0.716	368.35	
0.604	0.590	362.90	0.9435	0.660	365.30	1.2727	0.715	367.25	1.6448	0.754	369.15	2.0095
0.650	0.613	363.20	0.8529	0.680	366.10	1.1442	0.737	368.00	1.5089	0.773	369.70	1.8336
0.700	0.650	364.45	0.7959	0.715	366.45	1.0752	0.762	368.70	1.3721	0.790	369.95	1.6122
0.800	0.734	366.00	0.6898	0.784	367.85	0.9074	0.817	369.40	1.1161	0.837	370.80	1.2837
0.900	0.835	368.10	0.5623	0.867	369.55	0.7243	0.895	370.55	0.9471	0.917	371.55	1.2276
1.000	1.000	370.85		1.000	371.40		1.000	372.15		1.000	372.65	

	$x_3 = 0.10$			$x_3 = 0.12$			$x_3 = 0.14$			saturation			
x_1'	y_1	T/K	$\alpha_S{}^a$	y_1	T/K	$\alpha_S{}^a$	y_1	T/K	$\alpha_S{}^a$	x_3	y_1	T/K	$\alpha_S{}^a$
0.000	0.000	391.80		0.000	396.70		0.000	402.10		0.270	0.000	438.25	
0.053^b	0.655	365.60		0.705	366.80		0.737	368.70		0.220	0.750	400.00	
0.100^b	0.660	366.35		0.707	367.95		0.754	369.65		0.177	0.757	375.25	
0.200^b	0.690	367.30		0.727	368.90		0.755	370.55		0.160	0.756	374.70	
0.300^b	0.700	367.85		0.735	369.60		0.756	371.30		0.170	0.757	374.85	
0.438^b	0.722	368.80		0.752	370.45		0.756	372.15		0.149	0.756	374.60	
0.538^b	0.755	370.25		0.770	371.90		0.770	373.70		0.147	0.758	374.80	
0.604	0.791	370.95	2.4814	0.800	372.50	2.6225	0.800	374.05	2.6225	0.145	0.777	374.95	2.2844
0.650	0.794	371.50	2.0754	0.815	373.00	2.3721	0.815	374.50	2.3721	0.157	0.817	376.05	2.4040
0.700	0.823	371.60	1.9927	0.830	373.20	2.0924	0.835	374.80	2.1688	0.172	0.837	378.70	2.2007
0.800	0.865	372.25	1.6019	0.880	373.75	1.8333	0.895	375.45	2.1310	0.219	0.912	385.00	2.5909
0.900	0.935	372.85	1.5983	0.940	374.15	1.7407	0.947	375.70	1.9853	0.176	0.950	378.30	2.1111
1.000	1.000	373.40		1.000	374.20		1.000	375.80		0.187	1.000	377.70	

[a] Calculated for the miscible region using relation 2. [b] Immiscible region (overall liquid composition).

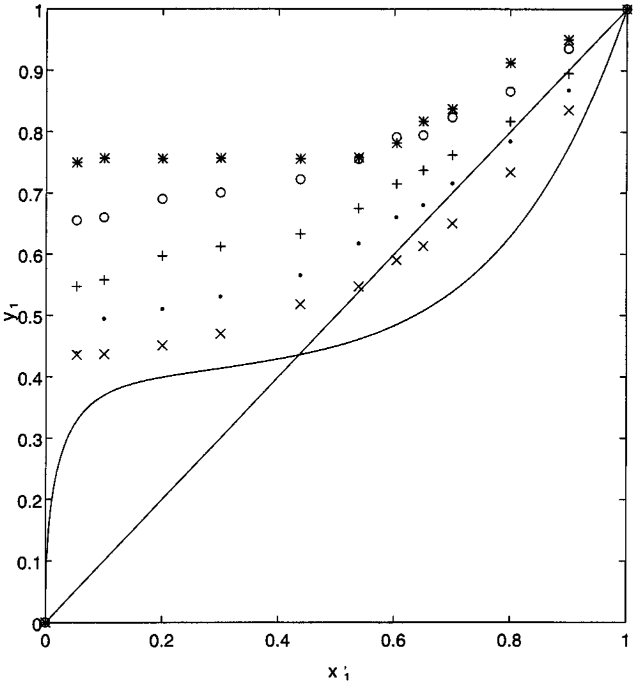

Figure 2. Effect of $CaCl_2$ on the VLE of the 1-propanol (1) + water (2), y_1 versus x_1': —, salt-free system; ×, $x_3 = 0.02$; •, $x_3 = 0.04$; +, $x_3 = 0.06$; ○, $x_3 = 0.10$; *, saturation.

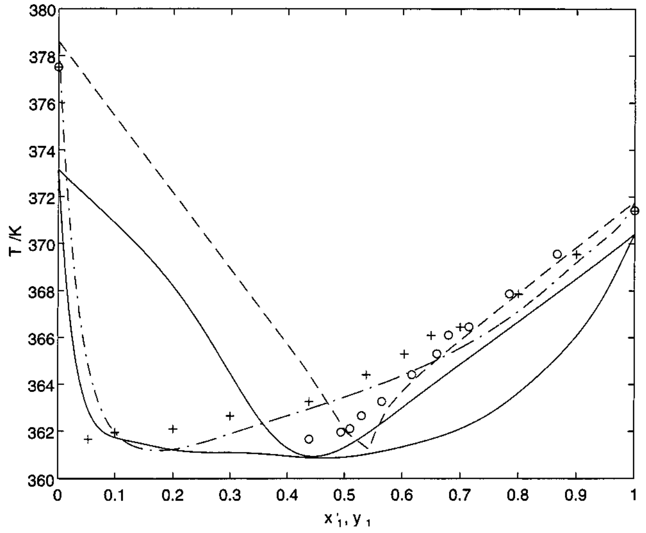

Figure 3. Experimental and calculated $T-x'-y$ diagram for 1-propanol (1) + water (2) + $CaCl_2$ (3) at $x_3 = 0.04$ (calculation based on the extended UNIQUAC model of Macedo et al., 1990): +, $T-x'$ (exp); – • –, $T-x'$ (pred); ○, $T-y$ (exp); – – –, $T-y$ (pred).

1995b), a better examination of the curves for the salt systems points out an apparent crossing point in the salt-free system azeotropic range. For $x_3 = 0.04$, the experimental data show that the azeotropic intersection points do not correspond to the minimum in the temperature. Moreover, Figure 4 shows the existence of a minimum in the $T-x'-y$ curves in a case where the azeotrope is completely eliminated. At molar fractions greater than the apparent intersection points, the $T-x'$ curve lies above the $T-y$ curve. This type of apparent intersection (minimums in the $T-x'-y$ curves) reported for acetone + methanol in the presence of NaI and NaSCN (Iliuta and Thyrion, 1995a,b) was shown to be less evident than for 1-propanol + water. The same behavior was observed in the graphical representations of results for 2-propanol + water + calcium nitrate at two salt molalities (1.038 and 2.073) and at 50.66 kPa (Polka and Gmehling, 1994). It seems that the lower the x_1'(az) value (where x_1'(az) represents the molar fraction of the less volatile solvent in the salt-free system at the azeotropic point) the more evident appears this phenomenon (Iliuta et al., 1996).

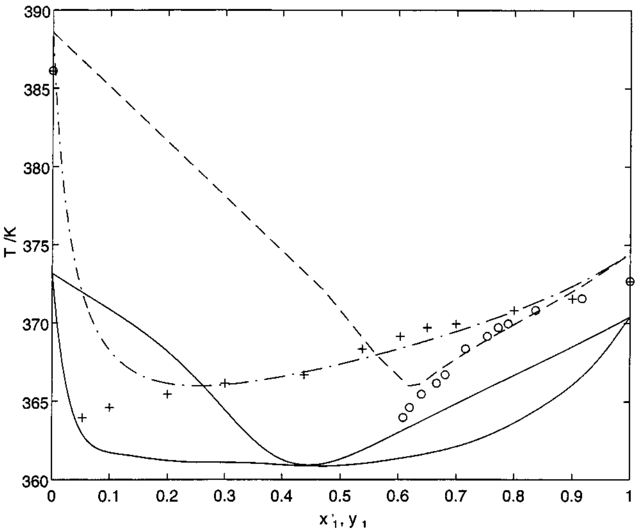

Figure 4. Experimental and calculated $T-x'-y$ diagram for 1-propanol (1) + water (2) + $CaCl_2$ (3) at $x_3 = 0.08$ (calculation based on the extended UNIQUAC model of Macedo et al., 1990): +, $T-x'$ (exp); – · –, $T-x'$ (pred); ○, $T-y$ (exp); – – –, $T-y$ (pred).

For the saturated systems, the presence of an extremum in the boiling points could be linked to the solubility data. For 1-propanol + water saturated with calcium chloride, the minimum is followed by a maximum in the $T-x'$ curve (Figure 5a) and the same behavior was observed in the solubility data representation (Figure 5b). An identical behavior was reported for ethanol + water saturated with copper(II) chloride (Novela and Tarraso, 1952 and Galan et al., 1976) and 1-propanol + water + cobalt(II) chloride (Gomez and Galan, 1974). Regarding the ethanol + water saturated with copper(II) chloride, Novela and Tarraso (1952) have supposed the formation of complexes with the dissolved copper salt.

To illustrate the salt effect in the salt-containing mixture, the relative volatility of 1-propanol (1) to water (2), α, defined as

$$\alpha = y_1 x_2'/y_2 x_1' \qquad (2)$$

was used. The variation of the relative volatility is plotted in Figure 6 against x_1' in the absence of salt, α_0 (Table 1), and for various salt molar fractions, α_S, under the miscible range of the liquid mixtures (Table 2). An increase of the relative volatility with the salt concentration can be observed, the alcohol being the salted-out component of the mixture.

At all salt compositions, the liquid phase separates into two immiscible phases in a liquid phase range of about $x_1' = 0.05-0.54$ except at $x_3 = 0.02$ where the immiscibility range extended from about $x_1' = 0.10$ to 0.54. An identical behavior was reported by Hashitani et al. (1968) for the same system at saturation. In this immiscibility range, the compositions of both liquid phases at equilibrium were analyzed separately. Due to the high viscosity of the lower layer, especially in the water-rich region at high salt concentration and the difficulty of analysis, only the results obtained at $x_1' = 0.200$, 0.438, and 0.538 in the presence of salt at $x_3 = 0.02$, 0.04, 0.06, and 0.08 (12 data) were presented (Table 3). From the analysis of the liquid phase compositions at equilibrium, it is found that the upper layer was the alcohol-rich, salt-poor phase and the lower layer was the water-rich, salt-rich phase. The same behavior was observed by Lin et al. (1993) for the 1-propanol (1) + water (2) + NaCl (3) and 1-propanol (1) + water (2) + KCl (3) systems, although these salts are less soluble in the alcohol than $CaCl_2$.

3.2. Calculation of Phase Equilibrium. Experimental data for 1-propanol + water were correlated using the Wilson (1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) models for liquid phase activity coefficients. The bubble point temperature, T, and vapor composition, y, under isobaric conditions were calculated from the models using a Newton–Raphson iterative method. The pure solvent vapor pressures were obtained from the Antoine constants reported by Reid et al. (1977). Model parameter values, mean absolute deviations in the vapor phase composition, and bubble points are presented in Table 4. Good results are obtained especially using the NRTL model.

In the case of a mixed-solvent–salt system, the calculation of VLE is generally more difficult due to the great complexity of interactions (long-range electrostatic interactions between ions and short-range interactions among the solvent, salt molecules, and ions) and to associations between anions and cations. Due to the presence of a large miscibility gap, a correlation of the results for the salt systems was not performed. The results were only compared with the predicted data obtained using three reliable

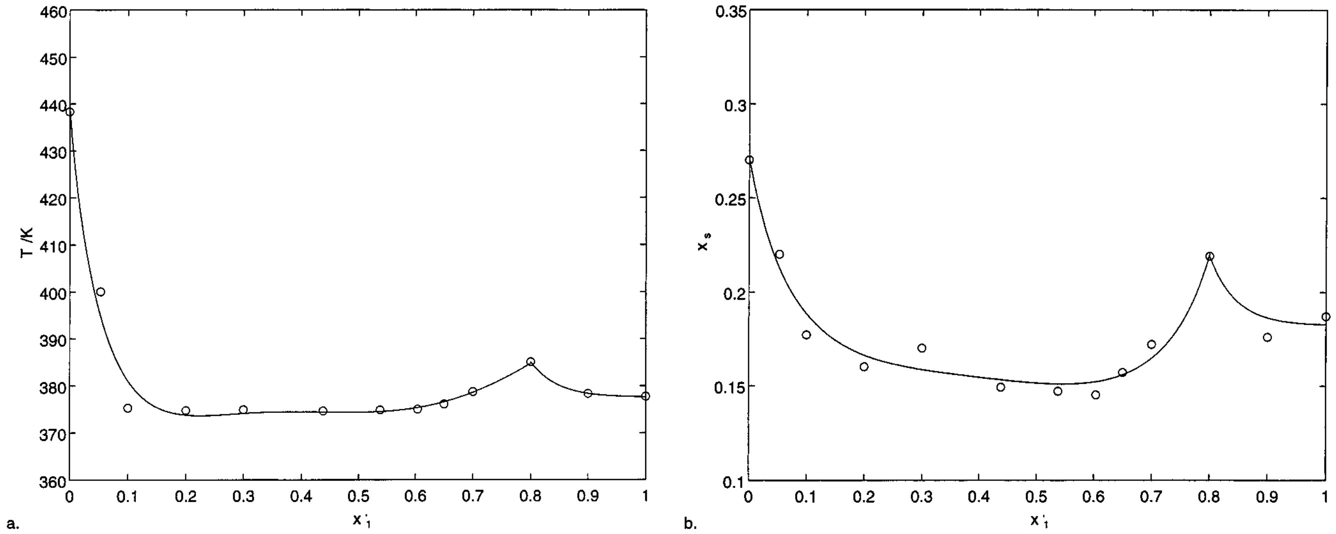

Figure 5. Experimental data for 1-propanol (1) + water (2) + $CaCl_2$ (3) at saturation: (a) temperature–liquid mole fraction (salt-free basis) diagram; (b) salt mole fraction–liquid mole fraction (salt-free basis) diagram.

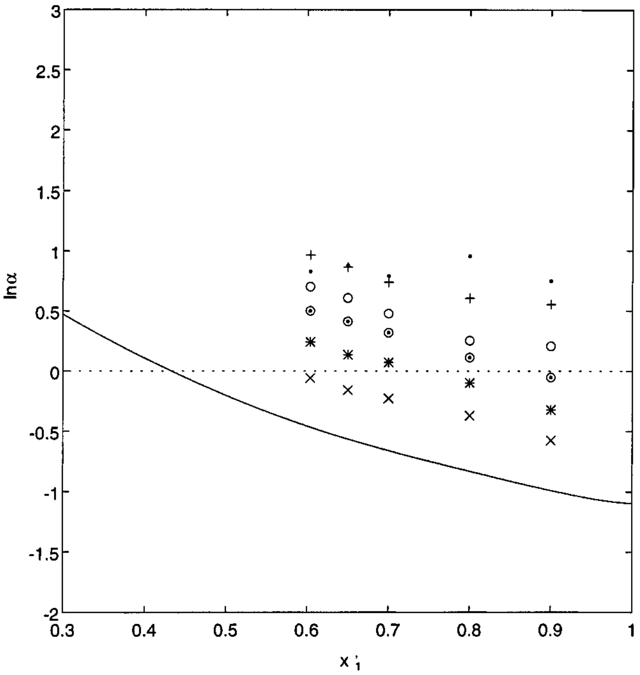

Figure 6. Relative volatility of 1-propanol (1) + water (2) + $CaCl_2$ (3) in the miscible range of liquid at different salt mole fractions: —, salt-free system; ×, $x_3 = 0.02$; *, $x_3 = 0.04$; ⊙, $x_3 = 0.06$; ○, $x_3 = 0.08$; +, $x_3 = 0.12$; •, saturation.

Table 3. Selected Experimental Vapor−Liquid−Liquid Equilibrium for 1-Propanol (1) + Water (2) + $CaCl_2$ (3) at 101.32 kPa

	upper layer			lower layer				
x_3[a]	x_1	x_3	α_S[b]	x_1	x_3	α_S[b]	y_1	T/K
	0.334	0.008	1.9788	0.062	0.031	14.6942	0.451	361.25
0.02	0.522	0.010	0.9478	0.038	0.075	25.0855	0.518	361.85
	0.551	0.015	0.9511	0.031	0.091	34.1997	0.547	362.60
	0.516	0.012	0.9521	0.035	0.054	27.0910	0.510	362.10
0.04	0.544	0.017	1.0481	0.023	0.107	49.1304	0.565	363.25
	0.558	0.035	1.1750	0.018	0.148	74.6414	0.617	364.40
	0.557	0.020	1.1250	0.025	0.077	53.2115	0.597	363.55
0.06	0.560	0.047	1.2104	0.018	0.116	82.9818	0.633	365.15
	0.570	0.048	1.3919	0.015	0.172	112.5693	0.675	366.45
	0.549	0.039	1.3341	0.039	0.098	39.3390	0.640	365.45
0.08	0.556	0.061	1.4705	0.014	0.127	130.9850	0.681	366.70
	0.572	0.070	1.5779	0.012	0.198	165.9742	0.716	368.35

[a] Global salt mole fraction. [b] Calculated using the relation $\alpha_S = y_1x_2/y_2x_1$, where x_i represents the mole fraction of the solvent i calculated on a salt-basis.

Table 4. Results of the Correlation with the NRTL, UNIQUAC, and Wilson Models

model type	ΔT[a]/K	Δy[b]	model parameters	units
NRTL	0.07	0.003	$g_{12} - g_{22} = 163.680$	K
			$g_{21} - g_{11} = 912.580$	K
			$\alpha_{12} = \alpha_{12} = 0.4548$	
UNIQUAC	0.15	0.005	$u_{12} - u_{22} = 90.210$	K
			$u_{21} - u_{11} = 144.557$	K
Wilson	0.14	0.006	$\lambda_{12} - \lambda_{12} = 661.261$	K
			$\lambda_{21} - \lambda_{11} = 644.396$	K

[a] $\Delta T = (1/N)\sum_i^N |T_i^{\text{exp}} - T_i^{\text{calc}}|$ where N represents the number of data points. [b] $\Delta y = (1/N)\sum_i^N |y_{1,i}^{\text{exp}} - y_{1,i}^{\text{calc}}|$ where N represents the number of data points.

Table 5. Results of the Prediction with the Extended UNIQUAC Model of Macedo et al. (1990)

system	N	x_3	ΔT/K[a]	Δy[a]	ΔT/K[b]	Δy[b]
propanol (1) + water (2) + $CaCl_2$ (3)	13	0.02	0.52	0.020	0.47	0.019
	13	0.04	0.86	0.020	0.80	0.019
	13	0.06	1.35	0.019	1.29	0.019
	13	0.08	1.56	0.026	1.49	0.026
	13	0.10	2.47	0.035	2.41	0.034
average deviation			1.35	0.023	1.29	0.023

[a] Using the solvent−solvent interaction parameters given by Macedo et al. (1990). [b] Using the solvent−solvent interaction parameters obtained from actual experimental data.

electrolytic models for which necessary interaction parameters exist in the literature.

Sander et al. (1986) proposed a local composition model where the solvent activity coefficients are calculated as a sum of a long-range interaction contribution given by a generalized Debye−Hückel equation for the mixed solvents and a short-range interaction contribution given by an extended UNIQUAC equation with concentration-dependent parameters. The model parameters are ion specific ones, and no ternary parameters are required. To ensure a more correct representation of long-range forces, Macedo et al. (1990) modified only the Debye−Hückel term of Sander's model according to the McMillan−Mayer solution theory (Cardoso and O'Connell, 1987). The results of Table 2 were compared with the corresponding predicted values obtained using these models. For a binary solvent−salt system, 14 parameters are needed to describe VLE: 2 solvent−solvent interaction parameters, 2 ion−ion interaction parameters, 8 ion−solvent reference interaction parameters, and 2 salt−solvent interaction parameters. Because the results obtained using Sander's model have the same accuracy as those using Macedo's model, these results are not presented. The results of calculations using Macedo's model are presented in Table 5 for $x_3 \leq 0.10$, the maximum salt concentration for the data points included in the database of the original paper being 6.5 mol/kg for 2:1 electrolytes. The UNIQUAC volume (r_k) and surface area (q_k), and reference interaction (a_{kl}^*) parameters and the $\delta_{ij,m}$ parameters were taken from the original paper of Macedo et al. (1990). The calculation was also performed using the solvent−solvent UNIQUAC parameters obtained by correlating our experimental data for the salt-free system (Table 4). For two salt molar fractions (0.04 and 0.08) the experimental and predictive results obtained using Macedo's paper parameters are shown in Figures 3 and 4. Rather high deviations exist in the two-phase liquid range. Hence, the incorrect predictions for this system are mainly due to the use of ion−ion, salt−solvent, and ion−solvent parameters which were estimated from VLE data, without taking into account the presence of the vapor−liquid−liquid equilibrium (VLLE) region. The disagreement between experimental and predicted behavior for this system reflects the difficulty in describing the systems exhibiting partial solubility only in the presence of salt. However, in the alcohol-rich region ($x_1' > 0.540$), where the liquid phase is homogeneous, the prediction results are rather good. The results show that the calculations must consider VLLE instead of VLE in the heterogeneous regions.

Kikic et al. (1991) substituted the UNIQUAC equation in the original model of Sander et al. (1986) by the original UNIFAC group-contribution model (Fredenslund et al., 1977) with concentration independent group-interaction parameters, and the Debye−Hückel term was calculated according to the McMillan−Mayer solution theory as described by Cardoso and O'Connell (1987). The UNIFAC group-interaction parameters between solvent groups and between ions and solvent groups were taken from the original paper of Kikic et al. (1991). Considering that UNIFAC is a group-contribution method and the group-

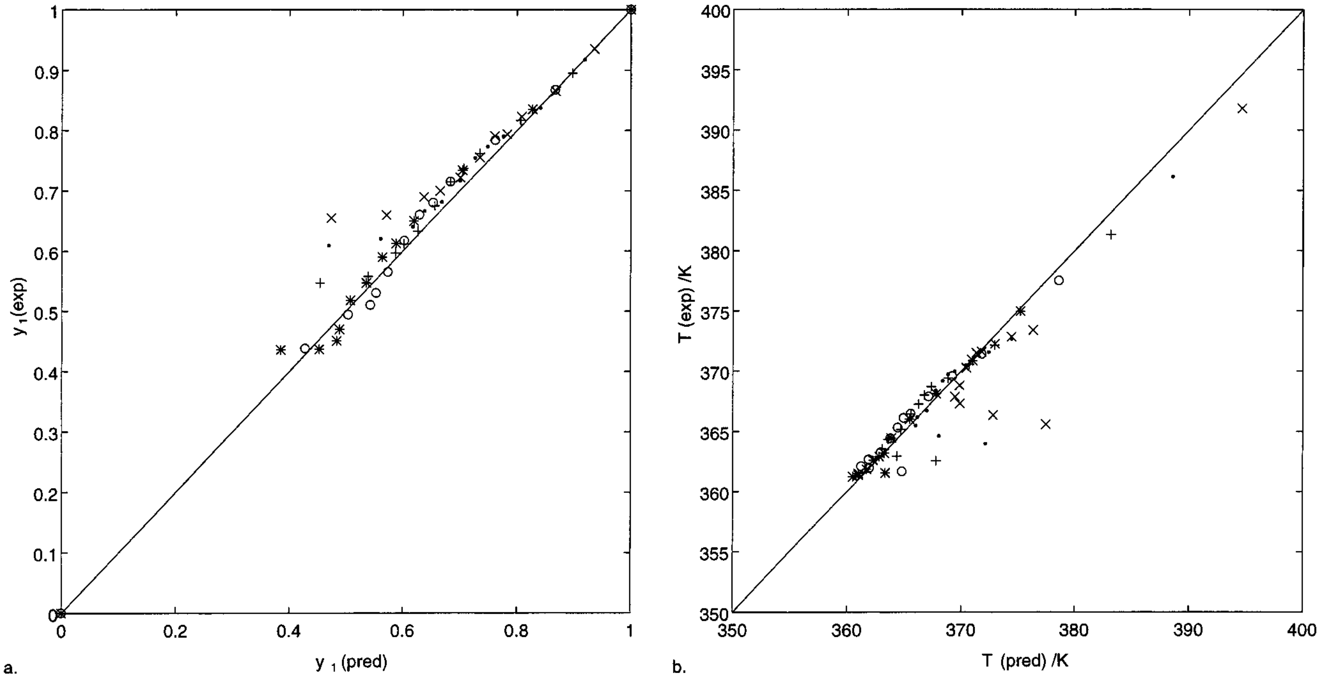

Figure 7. Results of calculation using the extended UNIQUAC model of Macedo et al. (1990): *, $x_3 = 0.02$; ○, $x_3 = 0.04$; +, $x_3 = 0.06$; • $x_3 = 0.08$; ×, $x_3 = 0.10$; (a) experimental vs predicted vapor composition; (b) experimental vs predicted bubble points.

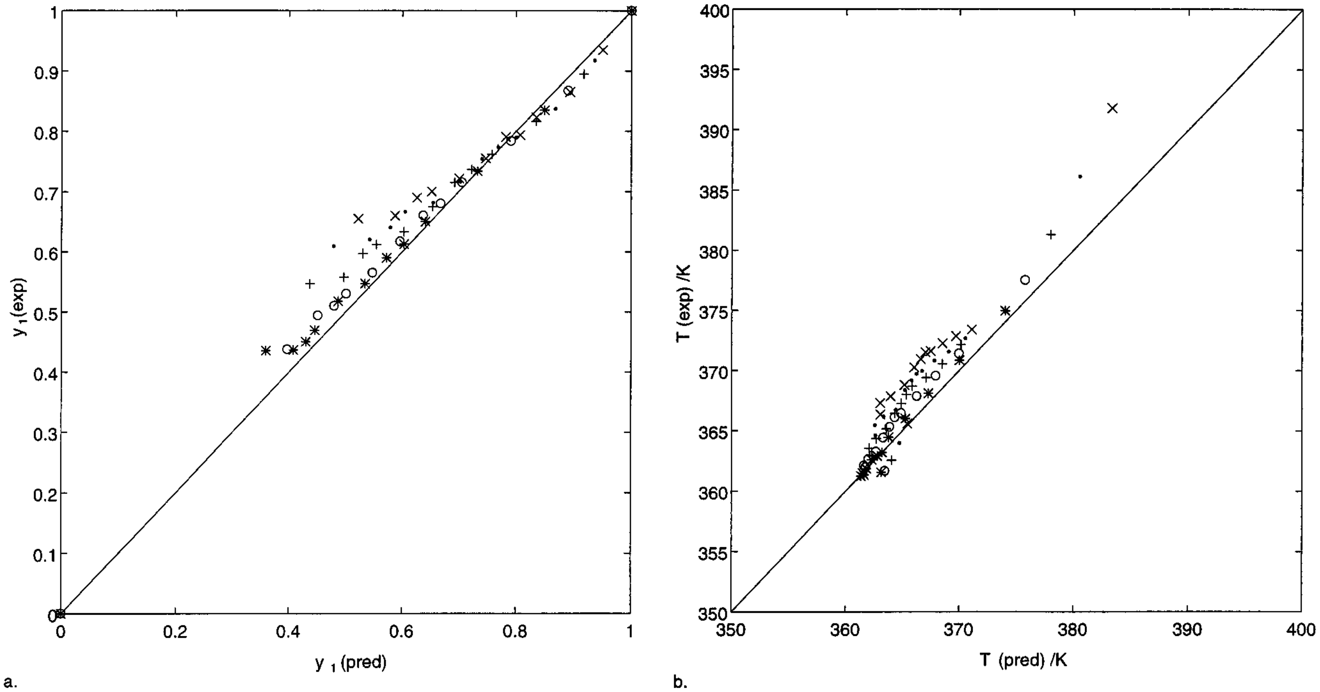

Figure 8. Results of calculation using the modified UNIFAC model of Kikic et al. (1991): *, $x_3 = 0.02$; ○, $x_3 = 0.04$; +, $x_3 = 0.06$; •, $x_3 = 0.08$; ×, $x_3 = 0.10$; (a) experimental vs predicted vapor composition; (b) experimental vs predicted bubble points.

Table 6. Results of the Prediction with the Modified UNIFAC Model of Kikic et al. (1991)

system	N	x_3	ΔT/K	Δy
propanol (1) + water (2) +$CaCl_2$ (3)	13	0.02	0.49	0.019
	13	0.04	1.23	0.023
	13	0.06	2.05	0.032
	13	0.08	2.84	0.034
	13	0.10	3.85	0.033
average deviation			2.09	0.028

interaction parameters are concentration independent, we conclude that the results presented in Table 6 are quite good, although the deviations in bubble points at high salt concentrations are rather high. However, the deviations in vapor phase composition calculations are very close to those obtained using the extended UNIQUAC models. Figures 7 and 8 ensure a better comparison between the capacity of models used in the prediction of vapor phase mole fractions (a) and bubble points (b).

4. Conclusions

At atmospheric pressure, 1-propanol + water + calcium chloride at salt mole fractions between 0.02 and saturation displayed a salting-out effect of the alcohol. In the entire range of salt concentration, a liquid phase splitting into two immiscible liquid phases was observed. In the immiscible region the compositions of the two liquid phases should be considered for the reason of better design and operation of separation processes.

Experimental data agree with the values predicted from the extended UNIQUAC models of Sander et al. and Macedo et al., as well as with the modified UNIFAC group-contribution model of Kikic et al., especially in the presence of a single liquid phase. The incorrect predictions in the immiscibility range are mainly due to the use of parameters estimated from VLE data.

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