Ethanol + 2-Methyl-1-butanol + Calcium Chloride System: Vapor−Liquid Equilibrium Data and Correlation Using the NRTL Electrolyte Model

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Experimental VLE data for the system ethanol (1) + 2-methyl-1-butanol (2) + $CaCl_2$ (3) have been measured at two different pressures (33.3 and 101.3 kPa) and three salt concentrations and have been correlated using the NRTL electrolyte model. From the results obtained, we can conclude that $CaCl_2$ does not significantly affect the relative volatility of the system and that the NRTL electrolyte model is suitable for fitting the equilibrium data for the ethanol (1) + 2-methyl-1-butanol (2) + calcium chloride(3) system with more than sufficient accuracy.

Introduction

Extractive distillation with salts consists of the addition of salts to a system to be separated, thus altering by their presence the relative volatility of the mixture. This produces an alteration of the vapor−liquid equilibrium (VLE) of the system, making it possible to form or to break an azeotrope.[1−3] The cause of these effects on relative volatility and the VLE is not fully known, but it is known that it is closely related to other phenomena that take place simultaneously: the alteration of the boiling points in some cases, the solubilities of components in others, and modification to the composition of the vapor in the equilibrium.

The thermodynamic resolution of the saline effect in the VLE is extraordinarily complex because of the many possible interactions that can take place. These depend as much on the degree of dissociation of the salt as on the composition of the liquid, that is to say, on the reliability of the mixture composition and to a lesser extent on the concentration of the salt. Therefore, it is not surprising that it is an arduous task to correlate and predict the VLE data of saline systems, in which satisfactory and generalizable results are difficult to obtain. In spite of this, in recent decades, the increasing importance of processes of extractive distillation with salts in industry has led many researchers to try and obtain correlation and prediction models for these systems. Thus in the past decade authors such as Hàla,[4] Mock et al.,[5] Sander et al.,[6] Ohe,[7] and Yan et al.[8] have proposed models that utilize thermodynamic equations, improving on currently existing models since each new model can be generalized further and extended to multicomponent systems, that is, those with several solvents and several electrolytes.

The objective of this work was to obtain experimental data on the VLE of the ternary system ethanol (1) + 2-methyl-1-butanol (2) + calcium chloride ($CaCl_2$) (3) at three concentrations of salt (1, 3, and 10 %, approximately) and two working pressures (33.3 and 101.3 kPa). This system is of increasing interest for the composition of the types of flavor that are retained in the fraction of isoamyl alcohol (2-methyl-1-butanol), obtained as a byproduct in the distillation of wine. In addition, the experimental data on this system have been compared with those obtained using the NRTL electrolyte prediction model.[5] Data on the three binary systems[9−11] that comprise the ternary system under study have been used for the development of this model.

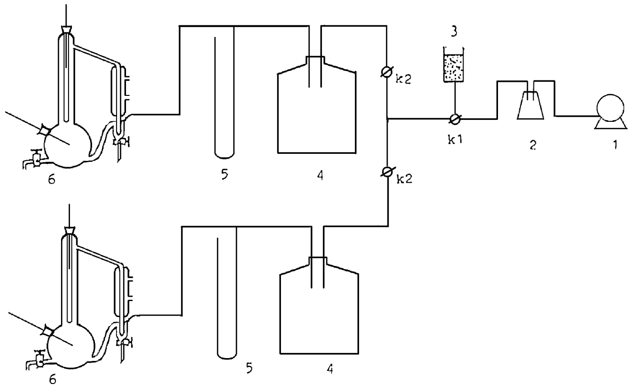

Figure 1. System for the determination of low-pressure VLE: 1, vacuum pump; 2, trap; 3, drying vessel ($CaCl_2$); 4, pressure control vessel; 5, mercury manometer; 6, modified Othmer still.

Experimental Section

Apparatus, Procedure, and Chemicals. A modified Othmer still was used for the acquisition of VLE data at atmospheric pressure. For a study at low pressure, a vacuum device was coupled to the previously cited still (Figure 1). The operating method has been described in previous papers.[10,12] Auxiliary equipment includes a Crison 621 digital thermometer with six thermowells and an uncertainty of ± 0.1 °C; two mercury manometers with an uncertainty of ± 1 mmHg; two heaters with a magnetic stirrer system from Selecta Agimatic; and a cryothermostatic bath from Hetofrig. The 2-methyl-1-butanol (99 mass %) was purchased from Aldrich. Ethanol (99.8 mass %) and 1-butanol (95 mass %) were obtained from Merck. Anhydrous calcium chloride (95 mass %) was obtained from Panreac. All chemicals were used without further purification. $CaCl_2$ was previously dried at 120 °C in an oven and removed. The water used was bi-distilled.

Analytical Methods. The equilibrium composition of the vapor phase was determined by gas chromatography (GC) using 1-butanol as an internal standard. The chromatographic equip-

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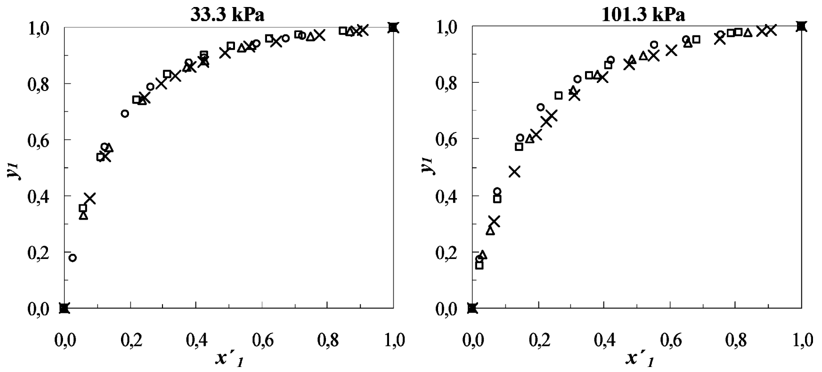

Figure 2. VLE of the ethanol (1) + 2-methyl-1-butanol (2) + $CaCl_2$ (3) system at two working pressures (33.3 and 101.3 kPa) and three salt concentrations. ×, △, □, and ○ (0, 1, 3, and 10% salt, respectively). x'_1 is the mole fraction of ethanol on a free salt basis.

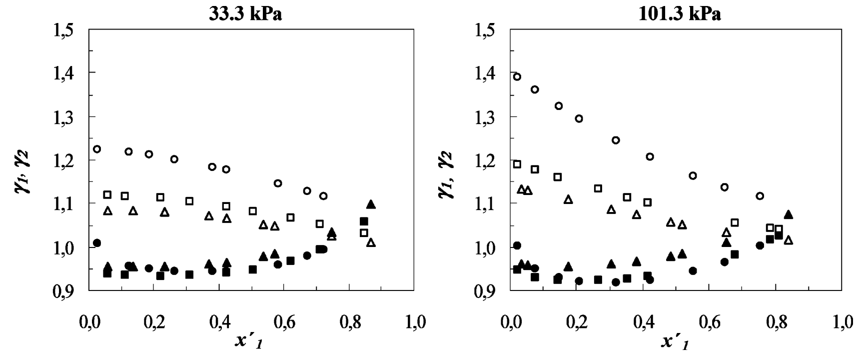

Figure 3. Activity coefficients of the solvents for the NRTL electrolyte model in the ethanol (1) + 2-methyl-1 butanol (2) + $CaCl_2$ (3) system (1, 3, and 10 mass %) at two working pressures (33.3 and 101.3 kPa). x'_1 is the ethanol molar fraction on a free salt basis. △, □, and ○ (γ ethanol: 1, 3, and 10 % salt, respectively) and ▲, ■, and ● (γ 2-methyl-1-butanol, 1, 3, and 10 % salt, respectively).

Table 1. Vapor−Liquid Equilibrium Experimental Data for the Ethanol (1) + 2-Methyl-1-butanol (2) + $CaCl_2$ (3) System at Two Different Operating Pressures (33.3 and 101.3 kPa) and Three Salt Concentrations (1, 3, and 10 mass %)

33.3 kPa						101.3 kPa					
x_1	x_2	x_3	y_1	y_2	t/°C	x_1	x_2	x_3	y_1	y_2	t/°C
					≈ 1 % $CaCl_2$						
0.059	0.933	0.008	0.330	0.670	93.7	0.032	0.960	0.008	0.189	0.811	126.3
0.136	0.857	0.007	0.575	0.425	85.8	0.052	0.940	0.008	0.277	0.723	123.4
0.233	0.760	0.007	0.741	0.259	77.6	0.174	0.819	0.007	0.603	0.397	110.6
0.369	0.624	0.007	0.857	0.143	70.0	0.304	0.689	0.007	0.772	0.228	101.2
0.423	0.571	0.006	0.882	0.118	68.2	0.378	0.615	0.007	0.829	0.171	97.7
0.534	0.460	0.006	0.926	0.074	63.6	0.483	0.511	0.006	0.881	0.119	93.2
0.568	0.426	0.006	0.937	0.063	62.6	0.516	0.478	0.006	0.894	0.106	91.5
0.745	0.250	0.005	0.969	0.031	58.1	0.651	0.344	0.005	0.939	0.061	87.3
0.864	0.131	0.005	0.986	0.014	55.2	0.835	0.160	0.005	0.977	0.023	82.0
					≈ 3 % $CaCl_2$						
0.058	0.919	0.023	0.353	0.647	94.8	0.023	0.953	0.024	0.149	0.851	129.2
0.110	0.867	0.023	0.536	0.464	89.0	0.075	0.902	0.023	0.385	0.615	122.2
0.217	0.762	0.021	0.742	0.258	80.1	0.141	0.837	0.022	0.568	0.432	115.0
0.306	0.674	0.020	0.833	0.167	74.3	0.260	0.719	0.021	0.749	0.251	105.4
0.417	0.564	0.019	0.898	0.102	68.8	0.349	0.631	0.020	0.822	0.178	100.1
0.498	0.484	0.018	0.931	0.069	65.7	0.408	0.573	0.019	0.859	0.141	97.0
0.612	0.371	0.017	0.957	0.043	61.9	0.670	0.314	0.016	0.952	0.048	87.1
0.701	0.283	0.016	0.972	0.028	59.4	0.776	0.209	0.015	0.972	0.028	84.2
0.838	0.148	0.014	0.987	0.013	55.7	0.799	0.186	0.015	0.976	0.024	83.5
					≈ 10 % $CaCl_2$						
0.024	0.896	0.080	0.178	0.822	101.2	0.023	0.897	0.080	0.171	0.829	131.3
0.116	0.807	0.077	0.572	0.428	90.1	0.071	0.851	0.078	0.412	0.588	124.9
0.172	0.754	0.074	0.691	0.309	84.9	0.137	0.787	0.076	0.602	0.398	116.8
0.246	0.682	0.072	0.788	0.212	79.3	0.195	0.731	0.074	0.709	0.291	111.2
0.354	0.579	0.067	0.872	0.128	72.9	0.298	0.632	0.070	0.811	0.189	104.3
0.398	0.536	0.066	0.893	0.107	70.7	0.394	0.540	0.066	0.876	0.124	98.3
0.549	0.391	0.060	0.939	0.061	64.4	0.521	0.418	0.061	0.930	0.070	93.0
0.637	0.307	0.056	0.961	0.039	61.5	0.613	0.330	0.057	0.949	0.051	89.5
0.686	0.259	0.055	0.970	0.030	60.2	0.715	0.232	0.053	0.970	0.030	86.1

ment was from Perkin-Elmer, Sigma 3D model with FID detector, stainless steel column 3 m by 2 mm i.d., and stationary phase 5 % Carbowax-1500 on Carbopack 80-100 mesh. Analytical operating conditions were as follows: injector temperature 200 °C; detector 200 °C; oven 110 °C; carrier gas (nitrogen) 30 mL·min^{-1}. The sample analyses were carried out twice. The uncertainty of measured mole fraction was ± 0.002.

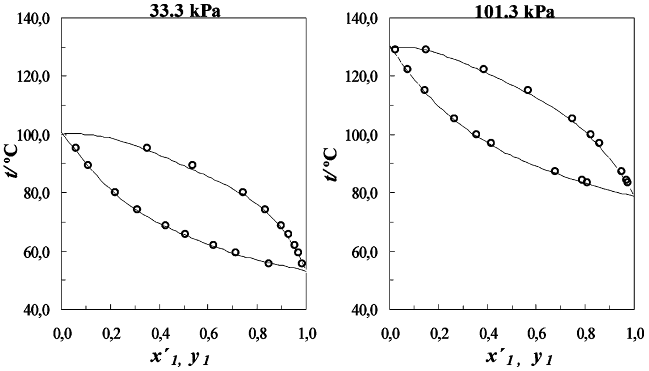

Figure 4. VLE ($t-xy$) of the ethanol (1) + 2-methyl-1-butanol (2) + $CaCl_2$ system (3 mass %) at two working pressures (33.3 and 101.3 kPa): ○, experimental values; - - -, NRTL electrolyte model.

Table 2. Parameter Values of the NRTL Electrolyte Model for Each Binary System at Two Working Pressures (33.3 and 101.3 kPa)[a]

binary systems	P/kPa	$\tau_{i,j}$	$\tau_{j,i}$	α
ethanol (1) + calcium chloride (3)	33.3	1.898	1.701	1.614
	101.3	1.870	0.408	1.575
2-methyl-1-butanol (2) + calcium chloride (3)	33.3	2.425	8.985	1.143
	101.3	2.093	9.110	1.168
ethanol (1) + 2-methyl-1-butanol (2)	33.3	0.985	−0.596	0.389
	101.3	0.760	−0.464	0.382

[a] i and j are the two components of each binary system.

Table 3. Activity Coefficients of the Ethanol (1) + 2-Methyl-1-butanol (2) + $CaCl_2$ (3) Ternary System at Pressures of (33.3 and 101.3) kPa Obtained According to the NRTL Electrolyte Model

1 % $CaCl_2$			3 % $CaCl_2$			10 % $CaCl_2$		
x'_1	γ_1	γ_2	x'_1	γ_1	γ_2	x'_1	γ_1	γ_2
				33.3 kPa				
0.059	1.0957	1.0130	0.060	1.1358	1.0541	0.027	1.2934	1.2030
0.137	1.0902	1.0131	0.112	1.1306	1.0528	0.126	1.2694	1.1883
0.235	1.0823	1.0143	0.222	1.1186	1.0513	0.186	1.2550	1.1806
0.371	1.0690	1.0189	0.313	1.1077	1.0516	0.265	1.2364	1.1723
0.426	1.0630	1.0224	0.425	1.0928	1.0552	0.380	1.2091	1.1642
0.537	1.0500	1.0335	0.507	1.0812	1.0610	0.426	1.1984	1.1627
0.572	1.0457	1.0384	0.622	1.0640	1.0766	0.584	1.1613	1.1675
0.749	1.0236	1.0822	0.713	1.0504	1.0978	0.675	1.1405	1.1806
0.868	1.0106	1.1413	0.850	1.0315	1.1563	0.725	1.1295	1.1925
				101.3kPa				
0.033	1.1326	1.0119	0.023	1.1800	1.0527	0.025	1.3661	1.2195
0.053	1.1292	1.0119	0.077	1.1689	1.0512	0.078	1.3439	1.2092
0.175	1.1082	1.0131	0.144	1.1549	1.0501	0.148	1.3153	1.1972
0.306	1.0860	1.0182	0.266	1.1303	1.0508	0.211	1.2912	1.1882
0.381	1.0737	1.0234	0.356	1.1123	1.0541	0.320	1.2513	1.1768
0.486	1.0569	1.0343	0.416	1.1007	1.0579	0.422	1.2171	1.1714
0.519	1.0517	1.0388	0.681	1.0546	1.0966	0.555	1.1766	1.1737
0.655	1.0325	1.0639	0.788	1.0398	1.1275	0.650	1.1506	1.1833
0.839	1.0122	1.1232	0.811	1.0370	1.1359	0.755	1.1257	1.2036

For the analysis of the liquid phase, it was necessary to eliminate and to determine the salt concentration before the chromatographic analysis. The exact amount of salt ($CaCl_2$) present in the liquid phase was determined gravimetrically by weighing a sample taken from the reboiler. After evaporation of the solvents and drying of the salt, the sample was weighed again. Each determination was carried out three times. The estimated concentration error was found to be ± 0.15 %. Then the salt-free base concentration in the liquid phase was obtained in the same way as in the vapor phase.

Results and Discussion

Experimental data on the VLE of the ternary system ethanol (1) + 2-methyl-1-butanol (2) + $CaCl_2$ (3) at two operating pressures are presented in Table 1 and represented in Figure 2. As can be observed in Figure 2, salt does not notably affect the relative volatility of the system, not even at concentrations near saturation. The concentrations of about 3 % by weight are the most effective at both pressures, since at those concentrations more separation is obtained between ethanol and 2-methyl-1-butanol in addition to being more economical.

In respect of the diminution of working pressure, this factor does not represent a significant increase in the effectiveness of the separation, although it does give a significant reduction in the temperature of boiling of the system.

The usefulness of the NRTL electrolyte model for the determination of equilibrium data of the ethanol (1) + 2-methyl-1-butanol (2) + calcium chloride (3) system has also been studied. For this study, the experimental VLE data on the three binary systems that compose the ternary system are needed, and these data have been taken from the literature.[9−11]

NRTL Electrolyte Model. When the NRTL electrolyte model is used with systems constituted by two solvents plus a salt, the equilibrium condition refers only to the solvents since they are the only species present in both phases. For pressures equal to or less than atmospheric, the following expressions are applied:

$$y_1P = \gamma_1 P_1^\circ x'_1 \tag{1}$$

$$y_2P = \gamma_2 P_2^\circ x'_2 \tag{2}$$

where P_1° and P_2° are the vapor pressures of the pure solvents; γ_1 and γ_2 are the activity coefficients of solvents; and x'_1 and x'_2 are mole fractions of solvents in the liquid phase on a salt-free basis.

The vapor pressure of ethanol and 2-methyl-1-butanol are given by the Antoine equation, whose coefficients are given in a previous paper.[10] The activity coefficients for the solvents 1 and 2, according to the NRTL electrolyte model, are given by the expressions:

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

Table 4. Experimental and Calculated (Using the NRTL Electrolyte Model) VLE Data of the Ethanol (1) + 2-Methyl-1-butanol (2) + $CaCl_2$ (3) System[a]

33.3 kPa					101.3 kPa				
x'_1	t_{exp}	t_{calcd}	$y_{1,\ exp}$	$y_{1,\ calcd}$	x'_1	t_{exp}	t_{calcd}	$y_{1,\ exp}$	$y_{1,\ calcd}$
				≈ **1** % $CaCl_2$					
0.059	93.7	93.3	0.330	0.336	0.033	126.3	126.0	0.189	0.185
0.137	85.8	85.4	0.575	0.582	0.053	123.4	123.3	0.277	0.274
0.235	77.6	78.0	0.741	0.745	0.175	110.6	110.6	0.603	0.604
0.371	70.0	70.4	0.857	0.861	0.306	101.2	101.6	0.772	0.767
0.426	68.2	68.0	0.882	0.889	0.381	97.7	97.6	0.829	0.823
0.537	63.6	63.9	0.926	0.929	0.486	93.2	93.0	0.881	0.879
0.572	62.6	62.8	0.937	0.938	0.519	91.5	91.7	0.894	0.893
0.749	58.1	58.0	0.969	0.972	0.655	87.3	87.2	0.939	0.936
0.868	55.2	55.4	0.986	0.987	0.839	82.0	82.1	0.977	0.976
σ^b	0.306		0.0046		σ^b	0.201		0.0034	
				≈ **3** % $CaCl_2$					
0.060	94.8	94.5	0.353	0.347	0.023	129.2	129.0	0.149	0.145
0.112	89.0	88.7	0.536	0.530	0.077	122.2	121.8	0.385	0.379
0.222	80.1	79.5	0.742	0.738	0.144	115.0	114.4	0.568	0.562
0.313	74.3	73.9	0.833	0.828	0.266	105.4	104.8	0.749	0.741
0.425	68.8	68.5	0.898	0.893	0.356	100.1	99.5	0.822	0.817
0.507	65.7	65.3	0.931	0.923	0.416	97.0	96.5	0.859	0.853
0.622	61.9	61.6	0.957	0.952	0.681	87.1	86.7	0.952	0.946
0.713	59.4	59.2	0.972	0.968	0.788	84.2	83.7	0.972	0.968
0.850	55.7	56.0	0.987	0.985	0.811	83.5	83.1	0.976	0.972
σ^b	0.366		0.0053		σ^b	0.484		0.0056	
				≈ **10** % $CaCl_2$					
0.027	101.2	101.0	0.178	0.180	0.025	131.3	131.5	0.171	0.163
0.126	90.1	89.6	0.572	0.575	0.078	124.9	124.3	0.412	0.409
0.186	84.9	84.2	0.691	0.695	0.148	116.8	116.2	0.602	0.598
0.265	79.3	78.9	0.788	0.793	0.211	111.2	110.6	0.709	0.699
0.380	72.9	72.1	0.872	0.876	0.320	104.3	103.1	0.811	0.807
0.426	70.7	70.0	0.893	0.897	0.422	98.3	97.8	0.876	0.867
0.584	64.4	64.1	0.939	0.946	0.555	93.0	92.3	0.930	0.917
0.675	61.5	61.3	0.961	0.964	0.650	89.5	89.0	0.949	0.942
0.725	60.2	60.0	0.970	0.971	0.755	86.1	85.8	0.970	0.964
σ^b	0.519		0.0041		σ^b	0.631		0.0080	

[a] The temperature is expressed in °C and salt concentration in mass %. x'_1 is the ethanol molar fraction on a free salt basis. [b] $\sigma = (\sum(x_{\text{exp}} - x_{\text{calcd}})^2/N)^{1/2}$, where N = number of data points and x is the temperature or the mole fraction of the ethanol in the phase vapor.

$$\ln \gamma_2 = \left[\frac{G_{3,2}\tau_{3,2}(X_a + X_c) + X_1G_{1,2}\tau_{1,2}}{G_{3,2}(X_a + X_c) + X_2 + X_1G_{1,2}}\right] - X_2 \times \left[\frac{G_{3,2}\tau_{3,2}(X_a + X_c) + X_2G_{1,2}\tau_{1,2}}{(G_{3,2}(X_a + X_c) + X_2 + X_1G_{1,2})^2}\right] + \left[\frac{X_1G_{2,1}\tau_{2,1}}{G_{3,1}(X_a + X_c) + X_2G_{2,1} + X_1}\right] - X_1G_{2,1} \times \left[\frac{G_{3,1}\tau_{3,1}(X_a + X_c) + X_2G_{2,1}\tau_{2,1}}{(G_{3,1}(X_a + X_c) + X_2G_{2,1} + X_1)^2}\right] + \left[\frac{X_cG_{2,3}\tau_{2,3}}{X_a + X_1G_{1,3} + X_2G_{2,3}}\right] - X_cG_{2,3}\left[\frac{X_1G_{1,3}\tau_{1,3} + X_2G_{2,3}\tau_{2,3}}{(X_a + X_1G_{1,3} + X_2G_{2,3})^2}\right] + \left[\frac{X_aG_{2,3}\tau_{2,3}}{X_c + X_1G_{1,3} + X_2G_{2,3}}\right] - X_aG_{2,3}\left[\frac{X_1G_{1,3}\tau_{1,3} + X_2G_{2,3}\tau_{2,3}}{(X_c + X_1G_{1,3} + X_2G_{2,3})^2}\right] \quad (4)$$

where the subscripts c and a represent the cation and anion, respectively; τ are the binary interaction parameters; X are effective mole fractions; and G are the Gibbs free energy.

Their expressions are as follows:

$$G_{3,i} = \exp(-\alpha_{3i}\cdot\tau_{3,i}) \quad (5a)$$

$$G_{i,3} = \exp(-\alpha_{3i}\cdot\tau_{i,3}) \quad (i = 1, 2) \quad (5b)$$

$$G_{1,2} = \exp(-\alpha_{1,2}\cdot\tau_{1,2}) \quad (5c)$$

$$G_{2,1} = \exp(-\alpha_{1,2}\cdot\tau_{2,1}) \quad (5d)$$

$$X_1 = \frac{x_1}{x_1 + x_2 + x_3(r_a + r_c)} \quad (6)$$

$$X_2 = \frac{x_2}{x_1 + x_2 + x_3(r_a + r_c)} \quad (7)$$

$$X_a = X_c = \frac{r_a\cdot Z_a\cdot x_3}{x_1 + x_2 + x_3(r_a + r_c)} = \frac{r_c\cdot Z_c\cdot x_3}{x_1 + x_2 + x_3(r_a + r_c)} \quad (8)$$

where r indicates the number of ions (cations or anions) that are present in $CaCl_2$; Z is the charge of the ion; and α is the disorder factor, in this model does not have the same physical meaning as that in NRTL model,[13] for that reason that it has been considered as a third adjustable parameter.

This model needs a total of 9 parameters to calculate the coefficients of activity of solvents in the system ethanol (1) + 2-methyl-1-butanol (2) + $CaCl_2$ (3):

(i) six parameters for the solvent + salt binary systems: $\tau_{1,3}$, $\tau_{3,1}$, $\tau_{2,3}$, $\tau_{3,2}$, $\alpha_{3,1}$, $\alpha_{3,2}$

(ii) another three for the ethanol + 2-methyl-1-butanol system: $\tau_{1,2}$,$\tau_{2,1}$, $\alpha_{1,2}$

These parameters have been obtained from experimental data of corresponding binary systems and published in previous articles.[9−11] Table 2 shows these parameters for the two working pressures. Once the nine parameters of the model are known, it is possible to calculate the coefficients of activity of solvents in the ternary system. Table 3 gives the coefficients of activity obtained with the NRTL electrolyte model, and Figure 3 shows the variation of these coefficients with the mole fraction of ethanol on a salt-free basis, x'_1.

It can be observed in all the cases γ_1 decreases as the mole fraction of ethanol increases, whereas γ_2 increases; in addition, almost all the values of these latter parameters are below unity, whereas the coefficients of activity of the ethanol present a positive deviation from the ideal values. It is also notable, as could be expected, that the deviations with respect to unity are greater for γ_1 than for γ_2, when the salt concentration increases. This finding becomes serious more when the pressure is 101.3 kPa, and the diminution of γ_1 with x'_1 also becomes more pronounced.

Having obtained the activity coefficients, the VLE data can be reproduced. Adding the equations eq 1 and eq 2 gives

$$P = \gamma_1 P_1{}^{\circ} x'_1 + \gamma_2 P_2{}^{\circ} x'_2 \tag{9}$$

With eq 9, the temperature (implicit in the vapor pressure of pure solvent) of the ternary system at a given pressure and composition can be obtained. Later, with the eqs 1 and 2, the composition of the vapor phase is calculated (y_1 and y_2).

In Table 4, the experimental data are compared with the values obtained for the composition of the vapor phase (expressed as mole fraction of ethanol, y_1) and the equilibrium temperature (in °C) applied to the NRTL electrolyte model, for each of the concentrations of salt used and the two working pressures. The results for a salt concentration of 3 mass % are shown graphically in Figure 4, in the $T-xy$ diagram.

As can be seen in the previously cited tables and graphs, the differences between the results obtained and the experimental ones are within the values accepted for this type of system, with the mean standard errors being $\sigma_m = 0.417$ °C and $\sigma_m = 0.005$ for temperature and composition of vapor phase, respectively. Therefore, it can be concluded that the NRTL electrolyte model is valid for predicting the behavior of the system under study.

Summary

According to the results obtained, we can conclude that the NRTL electrolyte model is suitable to fit the equilibrium data for ethanol + 2-methyl-1-butanol + calcium chloride system with great precision. This is the reason why we can use either model to predict this system behavior for any operating condition as well as for any salt concentration within the interval studied.

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