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Effect of Calcium Nitrate on the Vapor–Liquid Equilibria of Ethanol + Water and 2-Propanol + Water

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The effect of calcium nitrate on the vapor–liquid equilibria of ethanol + water and 2-propanol + water was studied using a Swietoslawski ebulliometer. The measurements were performed for two constant salt molalities (1 and 2 mol·kg^{-1}) under isobaric conditions at 50.66 kPa. Strong salting-out of the alcohol was observed in all cases, leading to a complete elimination of the azeotropic point at relatively low salt concentrations. The results were correlated using an extension of the NRTL equation for mixed solvent electrolyte systems proposed by Mock, Evans, and Chen.

Introduction

The vapor–liquid equilibrium (VLE) behavior of solvent mixtures may be strongly influenced by the presence of salts. In water + alcohol systems usually an increase of the concentration of the alcohol component in the vapor phase compared to the salt-free system is observed (salting-out), which in many cases results in a shifting or complete elimination of azeotropic points. Therefore, salts have been used as separating agents in extractive distillation as an interesting alternative to solvents (*1, 2*). For the design of separation processes involving salt components an accurate description of the VLE behavior is necessary. However, in many cases the required experimental information is not available. Little is known about the effect of calcium nitrate on the VLE equilibrium of alcohol + water systems. The data of Rius Miro and Alvarez Gonzales (*3, 4*) were measured only for the salt-saturated system and do not cover the whole range of liquid composition in the case of the system 2-propanol + water + calcium nitrate. In order to decide to what extent the azeotropic point is shifted at lower salt concentrations, the VLE equilibrium of the systems ethanol + water + calcium nitrate and 2-propanol + water + calcium nitrate was measured at constant salt molalities of 1.0 and 2.0 mol·kg^{-1}.

Table 1. Interaction Parameters and Nonrandomness Factors for the NRTL Electrolyte Model

solvent + solvent (salt) pair	$\alpha_{1,2}$[a]	$\tau_{1,2}$[a]	$\tau_{2,1}$[a]
ethanol (1) + water (2)	0.3	−0.134	1.822
2-propanol (1) + water (2)	0.3	−0.131	2.587
water (1) + Ca $(NO_3)_2$ (2)	0.2	9.159	−4.892
ethanol (1) + $Ca(NO_3)_2$ (2)	0.888 (f)	1.936 (f)	6.530 (f)
2-propanol (1) + $Ca(NO_3)_2$ (2)	0.734 (f)	2.361 (f)	1.760 (f)

[a] f = fitted.

Experimental Section

Equipment and Procedures. Equilibrium compositions and boiling points were measured using a modified Swietoslawski ebulliometer. A detailed description of the apparatus is given by Rogalski et al. (*5, 6*). The pressure was maintained constant at 50.66 kPa controlled by a Vacuubrand vacuum controller CVC 24 and a Wallace & Tiernan mercury gauge with a resolution of ±0.01 kPa. Equilibrium temperatures were measured using a calibrated thermometer with an accuracy of ±0.1 K.

At the beginning of each experimental series, the ebulliometer was charged with an aqueous solution of calcium nitrate of the desired molality. The change of the liquid-phase composition was achieved by gradually adding an

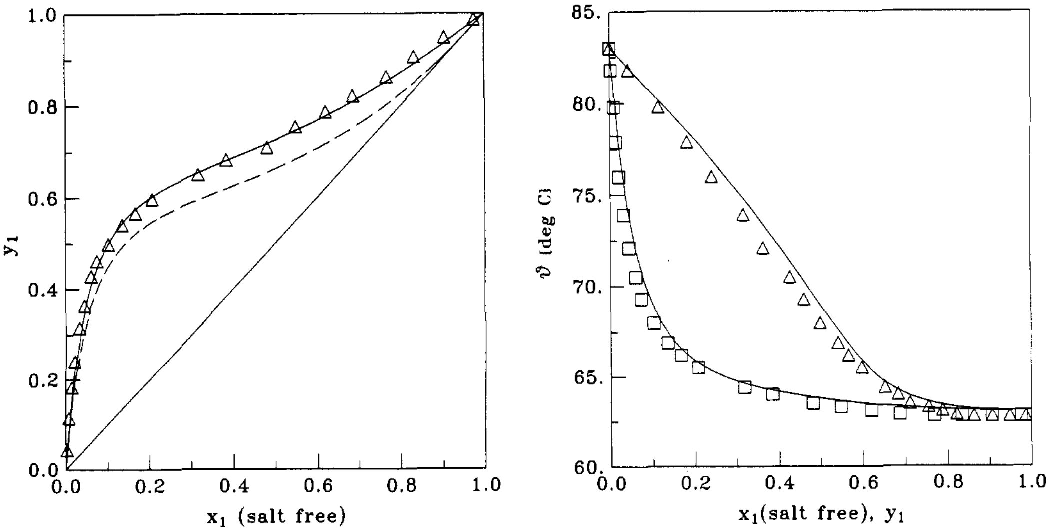

Figure 1. Experimental and calculated x'–y and ϑ–x',y diagrams for ethanol + water + calcium nitrate at 50.66 kPa (salt molality m = 1.038 mol·kg^{-1}): (△, □), experimental, (—) calculated, (- - -) salt-free system (calculation based on the UNIQUAC equation; parameters taken from Gmehling (*10*)).

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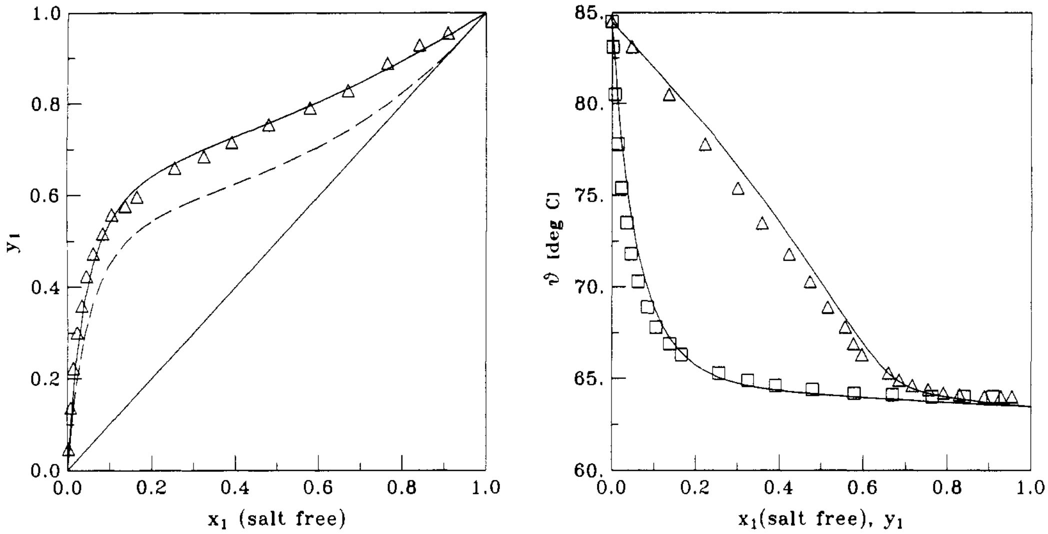

Figure 2. Experimental and calculated x'–y and ϑ–x',y diagrams for ethanol + water + calcium nitrate at 50.66 kPa (salt molality m = 2.049 mol·kg^{-1}): (△, □), experimental, (—) calculated, (- - -) salt-free system (calculation based on the UNIQUAC equation; parameters taken from Gmehling (*10*)).

Table 2. Vapor–Liquid Equilibrium Data for Ethanol (1) + Water (2) + Ca(NO$_3$)$_2$ at 50.66 kPa (m = 1.038 ● 0.001 mol·kg^{-1})

$x_1'^{a}$	y_1	ϑ/°C	Δy_1^{b}	$\Delta\vartheta^{c}$/°C
0.000	0.000	83.0	0.000	−0.03
0.003	0.044	81.8	0.003	−0.27
0.008	0.114	79.8	0.013	−0.81
0.014	0.183	77.9	0.022	−1.19
0.021	0.241	76.0	0.022	−1.55
0.032	0.316	73.9	0.026	−1.66
0.045	0.364	72.1	0.011	−1.59
0.061	0.429	70.5	0.019	−1.40
0.075	0.462	69.3	0.014	−1.38
0.102	0.499	68.0	−0.002	−0.93
0.135	0.541	66.9	−0.004	−0.60
0.167	0.566	66.2	−0.009	−0.37
0.207	0.597	65.5	−0.006	−0.27
0.317	0.651	64.4	−0.004	−0.22
0.384	0.682	64.0	0.001	−0.24
0.481	0.710	63.5	0.008	−0.35
0.548	0.754	63.3	0.008	−0.34
0.620	0.787	63.1	0.010	−0.35
0.686	0.821	62.9	0.012	−0.41
0.768	0.862	62.8	0.010	−0.38
0.833	0.906	62.8	0.016	−0.32
0.905	0.948	62.8	0.013	−0.29
0.975	0.986	62.8	0.004	−0.31
mean absolute deviation			0.011	0.66

[a] Mole fraction based on the salt-free system: $x_1' = n_1/(n_1 + n_2)$. n_1, n_2 = number of moles of solvents 1 and 2. [b] $\Delta y_1 = y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}$. [c] $\Delta\vartheta = \vartheta_{\mathrm{exp}} - \vartheta_{\mathrm{calc}}$.

Table 3. Vapor–Liquid Equilibrium Data for Ethanol (1) + Water (2) + Ca(NO$_3$)$_2$ at 50.66 kPa (m = 2.049 ● 0.004 mol·kg^{-1})[a]

x_1'	y_1	ϑ/°C	Δy_1	$\Delta\vartheta$/°C
0.000	0.000	84.5	0.000	0.03
0.002	0.047	83.1	0.012	−0.54
0.008	0.136	80.5	0.027	−1.33
0.014	0.223	77.8	0.036	−2.03
0.023	0.301	75.4	0.041	−2.40
0.034	0.359	73.5	0.023	−2.06
0.046	0.424	71.8	0.031	−2.01
0.062	0.473	70.3	0.022	−1.58
0.085	0.517	68.9	0.006	−0.98
0.106	0.558	67.8	0.010	−0.82
0.138	0.577	66.9	−0.013	−0.33
0.166	0.597	66.3	−0.019	−0.12
0.256	0.660	65.3	−0.011	0.24
0.325	0.685	64.9	−0.016	0.29
0.392	0.716	64.6	−0.009	0.24
0.480	0.754	64.4	−0.003	0.24
0.579	0.790	64.2	−0.006	0.21
0.669	0.829	64.1	−0.005	0.24
0.764	0.888	64.0	0.012	0.28
0.840	0.928	64.0	0.014	0.37
0.909	0.954	64.0	0.005	0.46
mean absolute deviation			0.016	0.80

[a] See footnotes *a*–*c* in Table 2.

alcoholic solution of calcium nitrate of the same molality. In this way the molality of the liquid phase was kept constant over the whole range of solvent composition. However, the withdrawal of salt-free vapor-phase samples results in an increase of the salt to solvent ratio. To maintain a constant salt molality, the mass of each vapor-phase sample was determined using an analytical balance and a corresponding mass of pure alcohol was added to compensate the solvent loss. To obtain results in the alcohol-rich region, the reverse procedure was carried out, adding the aqueous solution to an alcohol + calcium nitrate solution of the same molality. In the case of insufficient solubility of the salt in the pure alcohol, a small quantity of water was added to ensure complete dissolution of the salt.

Measurement of Sample Composition. Liquid- and vapor-phase samples were analyzed using a HP 5890 gas chromatograph with the capillary column technique and thermal conductivity detector. As the stationary phase of the chromatographic column (25 m × 0.32 mm) Permabond CW20M (polyethylene glycol 20000) was used. The mesurements were made under isothermal conditions at a column temperature of 70 °C. Hydrogen was used as the carrier gas. In this way vapor- and liquid-phase mole fractions were obtained with an accuracy of ±0.01.

The salt concentration of each liquid phase sample was measured by evaporating the solvent and weighing the dried residue using an analytical balance with a resolution of ±0.0001 g. The salt molalities proved to be constant within ±0.004 mol·kg^{-1}. The mean value was found to slightly exceed the concentration of the solution filled into the ebulliometer, which is due to the evaporation of a part of the liquid phase during the operation of the ebulliometer.

Materials. Ethanol and 2-propanol with a guaranteed purity greater than 99.8% were used without further purification. Deionized water was distilled twice. Calcium nitrate tetrahydrate of reagent grade was dried in an electric oven

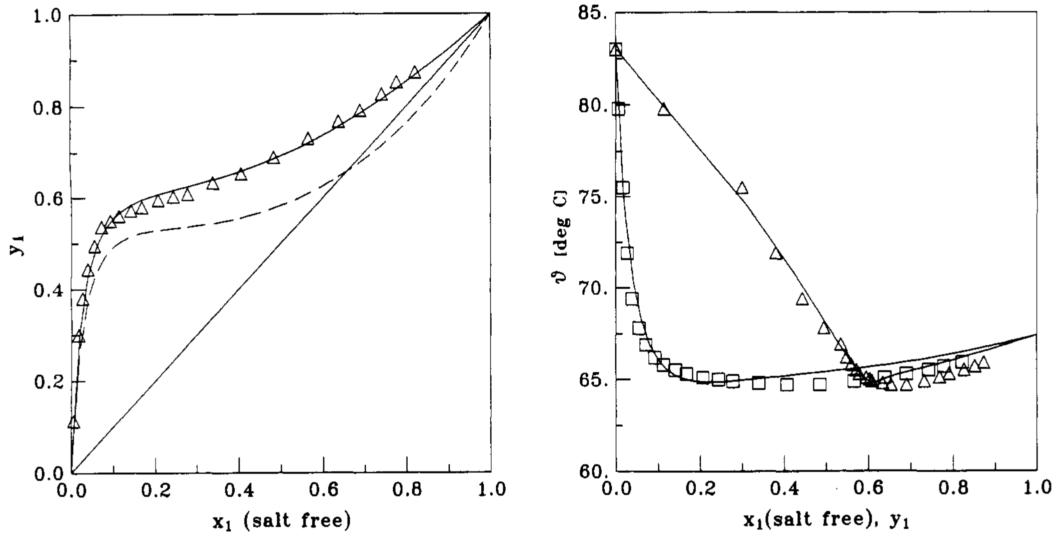

Figure 3. Experimental and calculated x'–y and ϑ–x',y diagrams for 2-propanol + water + calcium nitrate at 50.66 kPa (salt molality m = 1.038 mol·kg^{-1}): (△, □), experimental, (—) calculated, (- - -) salt-free system (calculation based on the UNIQUAC equation; parameters taken from Gmehling (*10*)).

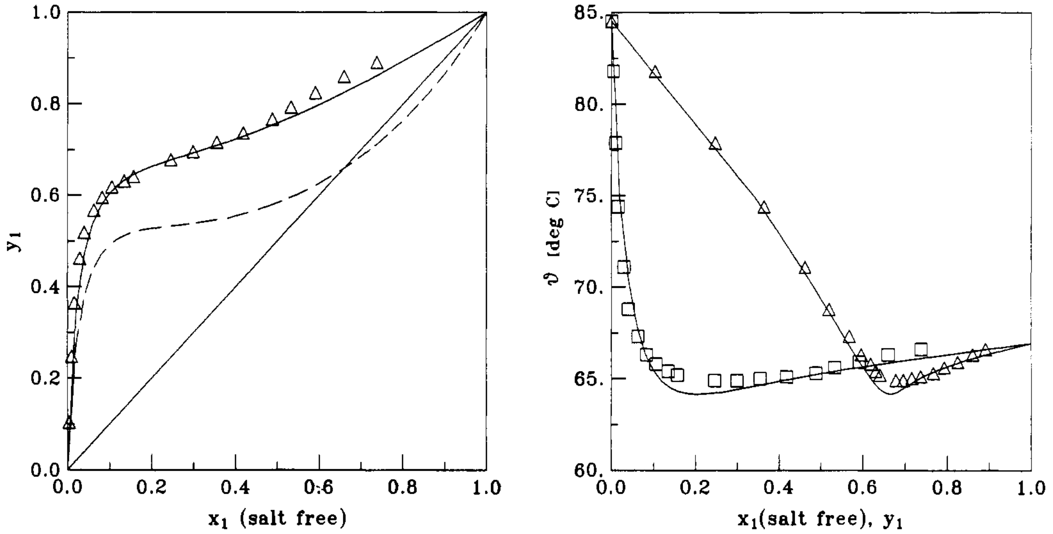

Figure 4. Experimental and calculated x'–y and ϑ–x',y diagrams for 2-propanol + water + calcium nitrate at 50.66 kPa (salt molality m = 2.073 mol·kg^{-1}): (△, □), experimental, (—) calculated, (- - -) salt-free system (calculation based on the UNIQUAC equation; parameters taken from Gmehling (*10*)).

at 170 °C. The complete removal of water was checked by weighing.

Correlation. The G^E model used to correlate the VLE data is an extension of Chen's previously published method for single solvent electrolyte systems to mixed solvent systems (*7, 8*). The basic assumptions about the local composition of an electrolyte solution are (1) repulsion of ions of the same sign, which results in a local mole fraction of zero for cations (anions) surrounding a central cation (anion) and (2) local electroneutrality (the sum of the charges of cations and anions surrounding a central molecule is zero).

The model parameters are specific for solvent–solvent and solvent–salt pairs. For a system containing two solvents, m and w, and one salt, ca, six interaction parameters, $\tau_{m,w}$, $\tau_{w,m}$, $\tau_{m,ca}$, $\tau_{w,ca}$, $\tau_{ca,m}$, and $\tau_{ca,w}$, and three nonrandomness factors, $\alpha_{m,w}$, $\alpha_{ca,m}$, and $\alpha_{ca,w}$, are required. The parameters for the three binary systems ethanol + water, 2-propanol + water, and water + calcium nitrate were taken directly from Mock et al. (*8*). The remaining parameters for the binary pairs ethanol + calcium nitrate and 2-propanol + calcium nitrate were estimated by minimization of the following objective function Z using the Simplex–Nelder–Mead method (*9*): where

$$Z = 100\sum_i g_i\left\{\frac{\vartheta_{\mathrm{exp}} - \vartheta_{\mathrm{calc}}}{\vartheta_{\mathrm{exp}}}\right\}^2 + \sum_i g_i\left\{\frac{y_{\mathrm{exp}} - y_{\mathrm{calc}}}{y_{\mathrm{exp}}}\right\}^2 \qquad (1)$$

$$i = 1, ..., N_{\mathrm{dp}}$$

ϑ is the temperature (°C) and y the vapor-phase mole fraction. The indices exp and calc denote the experimental and calculated values. N_{dp} is the number of experimental data points and g_i the weighting factor. Boiling points and vapor-phase compositions were calculated assuming ideal behavior of the vapor phase and solving the following equilibrium condition iteratively: where x_i is the mole fraction of solvent

$$y_i P = x_i \gamma_i P_i^{\mathrm{s}} \qquad (2)$$

i in the liquid phase based on the assumption of total dissociation of the electrolyte component In eq 3 the

$$x_i = n_i/(\sum n_{\mathrm{sol}} + \sum n_{\mathrm{ion}}) \qquad (3)$$

summation includes the number of moles of solvents and ions present in the liquid phase. The expression for the

Table 4. Vapor–Liquid Equilibrium Data for 2-Propanol (1) + Water (2) + $Ca(NO_3)_2$ at 50.66 kPa (m = 1.038 ± 0.002 mol·kg^{-1})[a]

x_1'	y_1	ϑ/°C	Δy_1	$\Delta\vartheta$/°C
0.000	0.000	83.0	0.000	−0.03
0.006	0.114	79.8	−0.018	0.10
0.017	0.300	75.5	0.020	0.02
0.027	0.380	71.9	0.019	−0.99
0.039	0.444	69.4	0.019	−1.31
0.055	0.495	67.8	0.016	−0.97
0.072	0.536	66.9	0.021	−0.53
0.093	0.549	66.2	0.005	−0.19
0.113	0.560	65.8	−0.002	0.02
0.141	0.572	65.5	−0.007	0.20
0.167	0.579	65.3	−0.010	0.22
0.206	0.595	65.1	−0.005	0.13
0.243	0.603	65.0	−0.005	0.03
0.278	0.609	64.9	−0.005	−0.12
0.339	0.634	64.8	0.007	−0.33
0.407	0.654	64.7	0.009	−0.55
0.485	0.690	64.7	0.020	−0.69
0.567	0.732	64.9	0.028	−0.65
0.639	0.768	65.1	0.029	−0.63
0.690	0.791	65.3	0.024	−0.59
0.742	0.826	65.5	0.027	−0.57
0.778	0.852	65.7	0.029	−0.52
0.822	0.873	65.9	0.019	−0.52
mean absolute deviation			0.016	0.43

[a] See footnotes a–c in Table 2.

Table 5. Vapor–Liquid Equilibrium Data for 2-Propanol (1) + Water (2) + $Ca(NO_3)_2$ at 50.66 kPa (m = 2.073 ± 0.003 mol·kg^{-1})[a]

x_1'	y_1	ϑ/°C	Δy_1	$\Delta\vartheta$/°C
0.000	0.000	84.5	0.000	0.00
0.004	0.104	81.8	−0.003	0.01
0.010	0.248	77.9	−0.027	−0.73
0.016	0.365	74.4	0.063	−1.80
0.029	0.462	71.1	0.050	−1.38
0.040	0.519	68.8	0.049	−1.57
0.063	0.568	67.3	0.026	−0.31
0.083	0.596	66.3	0.018	0.06
0.106	0.619	65.8	0.014	0.50
0.135	0.631	65.4	0.005	0.74
0.157	0.641	65.2	0.004	0.78
0.246	0.678	64.9	0.014	0.56
0.299	0.696	64.9	0.019	0.37
0.355	0.716	65.0	0.025	0.24
0.418	0.737	65.1	0.028	0.09
0.488	0.767	65.3	0.035	0.03
0.533	0.793	65.6	0.044	0.17
0.591	0.825	65.9	0.052	0.27
0.660	0.860	66.3	0.056	0.43
0.738	0.891	66.6	0.047	0.46
mean absolute deviation			0.031	0.53

[a] See footnotes a–c in Table 2.

activity coefficient of the solvent components γ_i is given by Mock et al. (*8*). The saturation vapor pressures of the pure solvent components P_i^s were calculated by the Antoine equation using Antoine constants from the literature (*10*). Table 1 contains the fitted interaction parameters and nonrandomness factors together with the parameters taken from the literature.

Results and Discussion

The experimental results are listed in Tables 2–5 together with deviations between experimental and calculated vapor-phase mole fractions and temperatures. As can be seen from Figures 1–4 the addition of calcium nitrate results in a considerable increase of the mole fraction of the alcohol in the vapor phase compared to the salt-free systems. For ethanol + water + calcium nitrate no azeotrope exists even at the lower salt concentration of 1.04 mol·kg^{-1}. The solubility of calcium nitrate in 2-propanol was not sufficient to obtain results at high alcohol content in the case of the 2-propanol + water + calcium nitrate system. The calculated curve for the vapor-phase mole fraction indicates a complete elimination of the azeotropic point.

The calculated vapor-phase mole fractions show satisfactory agreement with the experimental values. However, the errors for the boiling temperatures are rather systematic, leading to greater deviations for the boiling points of the alcohol + salt systems compared to the water + salt systems. It may be assumed that this is partly due to model deficiencies (for example, the assumption of total dissociation of the electrolyte over the whole range of liquid composition) and partly due to the use of interaction parameters taken from the literature, which were originally obtained for a different temperature range. Since the nonrandom two-liquid (NRTL) electrolyte model does not regard any temperature dependence, extrapolation to a different temperature may lead to erroneous results.

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