to equilibrium pressure changes, can be written as

$$n_1\,d\mu_1 + n_2\,d\mu_2 + n_w\,d\mu_w = 0 \qquad (A1)$$

where n_1 and n_2 are the number of moles of salts and n_w is the number of moles of water. The corresponding chemical potentials are μ_1, μ_2, and μ_w. The chemical potentials of the salts and water can be written in terms of their activity, and the number of moles can be expressed in terms of ionic strength. Therefore, for the ternary aqueous mixture eq A1 can be written as

$$\frac{I_1}{K_1}\,d\ln a_1 + \frac{I_2}{K_2}\,d\ln a_2 = -55.51\,d\ln a_w \qquad (A2)$$

where

$$K_k = {}^1\!/_2(\nu^+{}_k Z_{+k}{}^2 + \nu^-{}_k Z_{-k}{}^2)$$

the activity of the salt k can be written as (*4*, *7*)

$$a_k = \nu_{\pm k} m^{\nu_k}{}_k \gamma^{\nu_k}{}_{\pm k}$$

thus

$$d\ln a_k = \nu_k\,d\ln(m_k\gamma_{\pm k}) = \nu_k\,d\ln\left(\frac{I_k}{K_k}\gamma_{\pm k}\right) \qquad (A3)$$

With use of eq A3 for both electrolytes and with the assumption that Harned's rule is valid for both salts, then eq A2 yields

$$\left(\frac{\nu_1}{K_1}\alpha'_{12} + \frac{\nu_2}{K_2}\alpha'_{21}\right)Y_1\,dY_1 - \frac{\nu_2}{K_2}\alpha'_{21}\,dY_1 + \left(\frac{\nu_1}{K_1} - \frac{\nu_2}{K_2}\right)\frac{dY_1}{I} = -\frac{55.51}{I^2}\,d\ln a_w \qquad (A4)$$

where $Y_1 = I_1/I$ and $I_2 = (1 - Y_1)I$ with $I = I_1 + I_2$ constant. Equation A4 is then integrated at constant I and T from $Y_1 = 0$ (pure salt 2) to $Y_1 = 1$ (pure salt 1) to give

$$\frac{1}{2}\left(\frac{\nu_1}{K_1}\alpha'_{12} + \frac{\nu_2}{K_2}\alpha'_{21}\right) - \frac{\nu_2}{K_2}\alpha'_{21} + \frac{1}{I}\left(\frac{\nu_1}{K_1} - \frac{\nu_2}{K_2}\right) = -\frac{55.51}{I^2}\ln\left(\frac{a^\circ{}_w(1)}{a^\circ{}_w(2)}\right) \qquad (A5)$$

The activity of water can be written in terms of its osmotic coefficient (*2*), thus, at a total ionic strength I

$$\ln a^\circ{}_w = -\frac{\nu_k m_k}{55.51}\phi^\circ{}_k = -\frac{\nu_k I}{55.51 K_k}\phi^\circ{}_k \qquad (A6)$$

with

$$\phi^\circ{}_k = 1 + \frac{1}{I}\int_0^I d\ln\gamma^\circ{}_{\pm k} \qquad (A7)$$

Thus combining eq A5 with A7 gives

$$\frac{\nu_1}{K_1}\alpha'_{12} - \frac{\nu_2}{K_2}\alpha'_{21} = \frac{2}{I^2}\int_0^I I\,d\ln\left[\frac{(\gamma^\circ{\pm}_1)^{\nu_1/K_1}}{(\gamma^\circ{}_{\pm 2})^{\nu_2/K_2}}\right] = \frac{2}{I}\left[\frac{\nu_1}{K_1}(\phi^\circ{}_1 - 1) - \frac{\nu_2}{K_2}(\phi^\circ{}_2 - 1)\right] \qquad (A8)$$

Registry No. NaCl, 7647-14-5; $NaNO_3$, 7631-99-4; NaBr, 7647-15-6.

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Received for review October 30, 1990. Revised February 1, 1991. Accepted March 26, 1991. Financial support from NSERC, Canada, is gratefully acknowledged.

Low-Pressure Isobaric Vapor–Liquid Equilibria of Ethanol/Water Mixtures Containing Electrolytes

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Experimental vapor–liquid equilibrium data at low pressure are presented for ethanol/water mixtures containing sodium chloride and calcium chloride at constant molalities. In addition, the results for an ethanol/water mixture saturated with sodium chloride are given. The saturation concentrations of ethanol/water mixtures at boiling temperature and 123.1 mbar are reported. The data are compared with the predicted results using an extended UNIQUAC model for electrolyte systems published by Macedo et al.

Introduction

In the past few years, local composition models like NRTL and UNIQUAC have been extended for the application to vapor–liquid equilibria of electrolyte systems (*1–3*). The most recent model was presented by Macedo et al. (*1*). For several alcohol/water/salt mixtures, model parameters depending on salt concentration have been published. These parameters were evaluated from previously published experimental data measured at atmospheric pressure. To verify the applicability of the model parameters at other conditions, low-pressure vapor–liquid equilibria were measured.

0021-9568/91/1736-0340$02.50/0

Experimental Method

Vapor-liquid equilibrium compositions were measured by using a Swietoslawski ebulliometer, as described by Rogalski et al. (*4*). The measurements were taken at constant pressures of 123.1 and 199.1 mbar, controlled by a Wallace & Tiernan high-precision mercury gauge with a resolution of 0.1 mbar. The temperature was measured by using a calibrated thermometer with a resolution of 0.01 °C. Because of slight difficulties in establishing a continuous boiling process at higher salt concentrations, the reliability in temperature data is not better than 0.1 °C.

The analysis of the vapor phase was performed by density measurements of a condensed sample with vibrating-tube Anton Paar KG equipment, based on oscillation analysis of a sample-filled glass tube. Densities were obtained with an accuracy of 0.0001 g/cm^3. The liquid-phase composition was analyzed by evaporation of a sample to obtain the dry weight of salt and by density measurement of the condensed vapor. In this way mole fractions of the vapor phase and salt-free mole fractions of the liquid phase were obtained with an accuracy of ±0.001.

Correlation

In the extended UNIQUAC model (*1*), the excess Gibbs energy is given as a sum of three contributions: a Debye–Hückel expression for the electrostatic interactions due to ion formation (*5*), a combinatorial term, which takes into account the form and size of the molecules, and an expression for the interactions between the molecules (*6*). The last term includes adjustable parameters for the interaction energies.

For the calulation of the Debye–Hückel contribution, dielectric constants at 25 °C for water and alcohol were taken from the literature. Thereby it was assumed that the model parameters presented by Macedo et al. have been evaluated with temperature-independent dielectric constants, since experimental values about temperature effects on this property are very rare, but this is not clearly specified in their publication.

Boiling points and vapor-phase compositions were calculated iteratively from the following two equations:

$$x_{i,\mathrm{exp}}\gamma_i(T,x_{i,\mathrm{exp}})P_i^{\circ} = p_i \qquad (1)$$

$$\sum_i p_i = P \qquad i = \text{ethanol, water} \qquad (2)$$

$x_{i,\mathrm{exp}}$'s are the experimental liquid-phase compositions with the presence of salt being taken into account. The model treats every ionic species as a single component so that liquid mole fractions have to be calculated in the following way:

$$x_i = \frac{n_i}{n_{\mathrm{ethanol}} + n_{\mathrm{water}} + n_{\mathrm{cation}} + n_{\mathrm{anion}}} \qquad (3)$$

For the calculation of the vapor-phase composition of the saturated solution, the measured experimental saturation concentrations of NaCl in ethanol/water mixtures were correlated empirically:

$$m_{\mathrm{NaCl,sat.}} = 4.611 - 13.42x_1' + 11.29(x_1')^2 - 0.61(x_1')^3 - 1.87(x_1')^4 \qquad (4)$$

In this equation $m_{\mathrm{NaCl,sat.}}$ is the saturation salt molality in moles per kilogram of solvent mixture at boiling temperature and 123.1 mbar, depending on the salt-free mole fraction of ethanol x_1'.

Results and Discussion

Tables I–III contain the experimental results for the three systems. The boiling temperature, the salt-free mole fraction of ethanol in the liquid phase, and the vapor-phase mole fraction of ethanol are given. For comparison with the calculated data, the differences between experimental and calculated temperatures (ϑ) and y_1 are also listed. Table III also shows the measured saturation concentrations at boiling temperature and the differences in the calculated data by the given correlation.

Figures 1–3 show the phase equilibrium diagrams of the system. All calculated properties are in good agreement with the experimental data, although for the system ethanol/water/calcium chloride the predicted boiling points are systematically too low and at the same time the vapor-phase mole fractions of ethanol too high. Nevertheless the results are quite satisfying, which demonstrates the capability of the model and the quality of the given parameters. A temperature extrapolation of the extended UNIQUAC model was successfully performed.

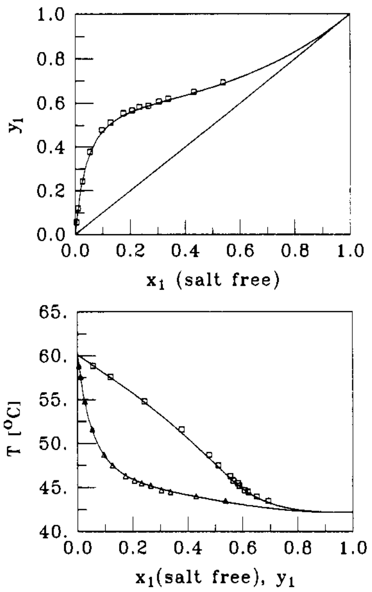

Figure 1. Vapor-liquid equilibrium data for the system ethanol (1)/water (2) with 0.122 mol of NaCl/kg of solvent mixture at 199.1 mbar: (□) vapor data; (Δ) liquid data; (—) calculated result.

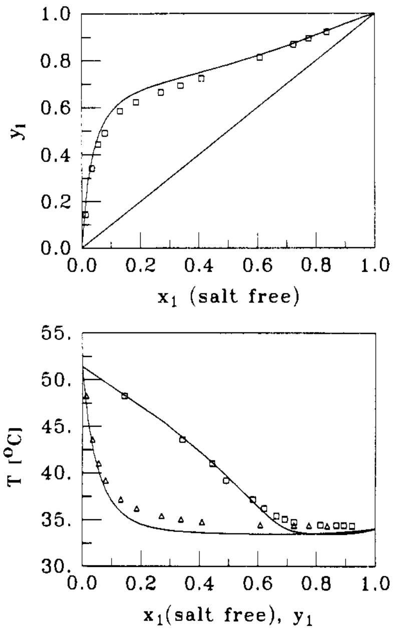

Figure 2. Vapor-liquid equilibrium data for the system ethanol (1)/water (2) with 0.974 mol of CaCl$_2$/kg of solvent mixture at 123.1 mbar: (□) vapor data; (Δ) liquid data (—) calculated result.

Table I. Vapor–Liquid Equilibrium Data for the System Ethanol (1)/Water (2) with 0.122 mol of NaCl/kg of Solvent Mixture at 199.1 mbar

boiling point ϑ, °C	x_1'[a]	y_1	$\Delta\vartheta$,[b] °C	Δy_1[c]
43.5	0.537	0.693	0.13	0.006
44.0	0.431	0.651	0.04	0.005
44.5	0.337	0.620	−0.08	0.007
44.7	0.304	0.607	−0.14	0.006
45.2	0.265	0.588	0.02	0.001
45.5	0.232	0.583	−0.03	0.009
45.8	0.206	0.566	−0.06	0.005
46.3	0.174	0.555	−0.07	0.012
47.5	0.127	0.512	0.00	0.007
48.7	0.096	0.478	0.03	0.012
51.6	0.054	0.378	0.20	0.007
54.8	0.027	0.243	0.25	−0.008
57.6	0.011	0.120	0.18	−0.009
58.9	0.005	0.056	0.09	−0.009
mean absolute deviation			0.094	0.0074

[a] Salt-free mole fraction. [b] Difference between experimental and calculated temperatures, $\Delta\vartheta = \vartheta_{exp} - \vartheta_{cal}$. [c] Difference between experimental and calculated vapor-phase compositions, $\Delta y_1 = y_{1,exp} - y_{1,cal}$.

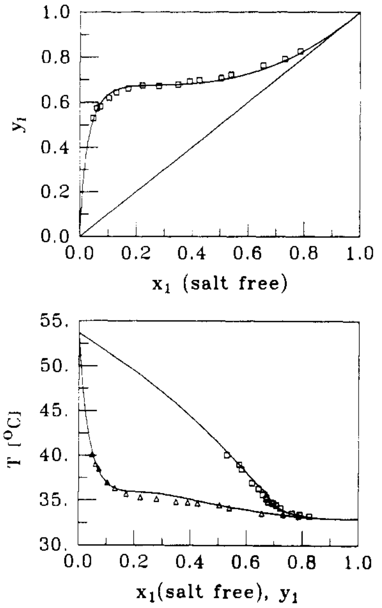

Figure 3. Vapor–liquid equilibrium data for the system ethanol (1)/water (2) saturated with NaCl at 123.1 mbar: (□) vapor data; (△) liquid data; (—) calculated result.

Glossary

$m_{sat.}$	saturation molality
n_i	mole number of component i
p_i	partial pressure of component i
P_i^s	saturation vapor pressure of pure component i
P	total pressure
x_i'	salt-free liquid-phase mole fraction of component i
$x_{i,exp}$	experimental liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
γ_i	activity coefficient of component i
ϑ	temperature

Table II. Vapor–Liquid Equilibrium Data for the System Ethanol (1)/Water (2) with 0.974 mol of $CaCl_2$/kg of Solvent Mixture at 123.1 mbar

boiling point ϑ, °C	x_1'[a]	y_1	$\Delta\vartheta$,[b] °C	Δy_1[c]
34.4	0.837	0.922	0.77	−0.004
34.4	0.775	0.893	0.89	−0.003
34.4	0.724	0.868	0.92	−0.005
34.5	0.608	0.814	0.97	−0.010
34.8	0.409	0.723	1.14	−0.027
35.1	0.337	0.692	1.32	−0.034
35.4	0.270	0.664	1.43	−0.038
36.2	0.185	0.622	1.49	−0.040
37.2	0.131	0.584	1.34	−0.036
39.2	0.079	0.491	1.01	−0.052
41.0	0.056	0.444	0.91	−0.036
43.6	0.035	0.342	0.79	−0.042
48.3	0.014	0.144	1.19	−0.066
mean absolute deviation			1.09	0.030

[a] Salt-free mole fraction. [b] Difference between experimental and calculated temperatures, $\Delta\vartheta = \vartheta_{exp} - \vartheta_{cal}$. [c] Difference between experimental and calculated vapor-phase compositions, $\Delta y_1 = y_{1,exp} - y_{1,cal}$.

Table III. Vapor-Liquid Equilibrium Data for the System Ethanol (1)/Water (2) Saturated with NaCl at 123.1 mbar

boiling point ϑ, °C	x_1'[a]	y_1	$m_{sat.}$, mol/kg	$\Delta m_{sat.}$,[b] mol/kg	$\Delta\vartheta$,[c] °C	Δy_1[d]
33.2	0.786	0.825	0.06	0.032	0.02	0.005
33.4	0.731	0.790	0.08	−0.018	0.05	0.005
33.5	0.654	0.763	0.12	−0.031	−0.14	0.019
34.2	0.539	0.722	0.36	−0.044	−0.10	0.018
34.5	0.504	0.707	0.56	0.044	−0.04	0.006
34.7	0.425	0.697	0.79	−0.049	−0.27	0.014
34.8	0.391	0.692	0.95	−0.060	−0.39	0.014
34.9	0.348	0.679	1.25	−0.005	−0.59	0.000
35.2	0.280	0.672	1.79	0.076	−0.63	−0.008
35.3	0.222	0.674	2.34	0.163	−0.47	−0.010
35.7	0.171	0.659	2.72	0.078	−0.24	−0.014
36.3	0.130	0.643	2.96	−0.095	−0.16	−0.006
37.0	0.103	0.620	3.19	−0.158	−0.19	−0.006
38.5	0.072	0.582	3.40	−0.303	−0.34	0.008
39.0	0.060	0.573	3.84	−0.006	−0.30	0.008
40.1	0.048	0.529	4.34	0.347	0.09	−0.020
mean absolute deviation				0.09	0.25	0.01

[a] Salt-free mole fraction. [b] Difference between experimental and correlated saturation concentrations, $\Delta m_{sat.} = m_{sat.,exp} - m_{sat.,cal}$. [c] Difference between experimental and calculated temperatures, $\Delta\vartheta = \vartheta_{exp} - \vartheta_{cal}$. [d] Difference between experimental and calculated vapor-phase compositions, $\Delta y_1 = y_{1,exp} - y_{1,cal}$.

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Received for review October 12, 1990. Accepted February 27, 1991. We acknowledge the financial support of the Bundesministerium für Forschung und Technologie (BMFT), FRG.