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Isobaric vapor–liquid equilibria of water–pyridine and water–pyridine–calcium chloride mixtures

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Abstract

Isobaric vapor–liquid equilibrium data at 705 ± 1 mm Hg for the systems water–pyridine and water–pyridine–$CaCl_2$ were obtained using the modified Othmer circulation still. The experimental data for the water–pyridine system exhibited an azeotropic point at a water composition of 75.0 mol% and a temperature of 92.60°C. The isobaric salt-free binary data were compared with predicted vapor–liquid equilibrium (VLE) data using the UNIFAC model. Good agreement between the experimental and the predicted results was obtained, with a root-mean-square-deviation (RMSD) in predicted bubble-point temperature and predicted vapor-phase composition of 0.28 K and 0.007, respectively. In addition to that, the experimental data were correlated with the Wilson, the NRTL and the UNIQUAC models. The calculated VLE data using the parameters found by these models were in good agreement with the experimental results.

The VLE of water–pyridine mixtures in the presence of calcium chloride at different concentrations was found to be dramatically different from that of the salt-free mixtures. Calcium chloride had showed a salting-out effect on water and could eliminate the azeotropic point of the system when used under saturated conditions. In addition, analysis of the data showed that the salt resulted in “splitting” the liquid mixtures into two different liquid phases. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: VLE; Pyridine; Azeotrope; Salt

1. Introduction

In many important chemical processes, there is a need to separate binary mixtures that have azeotropic points or close boiling points. The separation of these mixtures by conventional distillation is either impossible or very expensive. The conventional method for separating these mixtures is to shift the azeotropic composition by altering the column pressure or by using extractive distillation by adding an alien component as a solvent to break the azeotrope [1]. However, separation by altering the column pressure is possible only in cases where pressure has a considerable effect on the azeotropic composition. Moreover, an extra separation step is needed to recover the solvent, if an alien component is added, or to adjust the pressure, which adds extra cost to the separation.

Instead of adding a solvent, a nonvolatile salt could be used as a separating agent to alter the vapor–liquid equilibrium (VLE) of a given mixture. It is envisioned that the ions of the added salt form association complexes more with the molecules of one of the components of a mixture to be separated than with the other components. This association complex “phenomenon” may result in altering the vapor and partial pressures, solubility, thermal conductivity, density, surface tension, etc. These changes, if they occur, also result in altering the VLE of the system, thus altering the “ease” of separation and shifting or eliminating the azeotropic point of a given mixture [2–29].

There are many advantages of adding salts instead of liquids in an extractive distillation process: (i) lower energy consumption since salts are nonvolatile and do not evaporate or condense in the distillation process, (ii) the purity of the over-head product from the extracting agent is high as the salts are nonvolatile, and (iii) the effects of some salts on some systems are very large, so that a small amount of salt will facilitate the required separation. However, the thermodynamic analysis of the VLE of salt-containing mixtures is still not satisfactory due to the lack of a clear mechanism describing the chemistry of the effect of salt addition on the VLE of mixtures. Nevertheless, many empirical and semi-empirical models have been proposed either to correlate or to predict the VLE data of salt-containing mixtures

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Abbreviations: RMSD, root-mean-square-deviation; VLE, vapor–liquid equilibrium

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Nomenclature

a_i	activity of the *i*th component
A_i^{s}	solute–solvent interaction parameter
A_{21}^{s}	ratio of solute–solvent interaction parameters of two components
G	molar Gibbs energy
P	total system pressure (mm Hg)
p_i^{s}	vapor pressure of *i*th component (mm Hg)
T	temperature (K)
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Greek letters

α	relative volatility
ϕ_i	fugacity coefficient of the *i*th component in the mixture
ϕ_i^{s}	fugacity coefficient of pure component
φ	the overall range of boiling points of the system
γ_i	activity coefficient of the *i*th component

Subscript

1	water
2	pyridine
i	*i*th component
s	property evaluated in the presence of salt

Superscript

E	excess property
M	property of mixing
s	saturation

[18–28]. Many of these models are based on the UNIQUAC model, the local volume fraction model and, local molar fraction model (NRTL). Most of the UNIQUAC based models assume that the excess Gibbs energy consists of two contributions: a modified Debye–Hückel term and a UNIQUAC type term. The UNIQUAC type term further consists of two parts: the residual part, which is a function of the salt concentration, and a combinatorial part which is unaffected by the presence of the salt [25–27]. On the other hand, Tan [18,19], Tan and Ng [20] and Tan and Ti [21,22] developed two models based on either the local volume fraction, similar to the Wilson model, or the local molar fraction model which is similar to that of NRTL model. These two models contain two solvent–solvent interaction parameters, which are the same as those obtained by the Wilson or NRTL model for the salt-free system, and two salt–solvent interaction parameters.

The objectives of this study are to measure the VLE of water–pyridine mixtures at 705 mm Hg and to investigate the effect of adding calcium chloride on the VLE of this system. The measured VLE data of the water–pyridine salt-free system will be compared with those predicted by the UNIFAC model and will also be correlated with the Wilson, the NRTL and the UNIQUAC models. The measured VLE data in the presence of the salt will be analyzed by Tan and his group approach.

2. Experimental apparatus and procedure

2.1. Chemicals

Distilled water and pyridine (purity: 99.6%, supplier: Sigma) were used in this study. The salt used was calcium chloride (purity: 99%, supplier: Janssen Chimica).

2.2. Procedure

The still used in this study is an 800 ml circulation still similar to that used by Jaques and Furter [8], Subbaiah [14], and Abu Al-Rub [29], which is a modification of the Othmer still. A detailed description of this still can be found in the above references.

The pressure was measured using another ebulliometer containing pure boiling water. By connecting the two stills in parallel, we can obtain an absolute manometer. The pressure was controlled using a vacuum pump and an air compressor connected to the condenser. The experiment was conducted at a pressure of 705 ± 1 mm Hg. Steady state was attained after 30 min, where the temperature was measured, using a calibrated thermometer with a resolution of $\pm 0.01^{\circ}$C.

2.3. Samples analysis

Samples of liquid and condensed vapor were withdrawn and analyzed five times using a Perkin Elmer Auto System Gas Chromatograph with a 6 ft, $\frac{1}{8}$ in., Porapak R column under isothermal conditions at 170°C.

The reproducibility of the salt-free results was checked by performing up to three replicate experiments to obtain deviation of the measured data due to random error and was found to be within 0.01%. It should be mentioned that due to the small volume of the condensed vapor compared to that of the liquid at equilibrium, the difference in the liquid phase composition at equilibrium and the feed composition, in most cases, was within the experimental error.

In the case of salt addition, immiscible regions were obtained. In these regions the samples of both liquid phases were collected using the method of Lin et al. [30]. However, the tabulated data were those corresponding to the overall liquid compositions which were assumed to be similar to those of the feed.

3. Results and discussion

A check on the reliability of the experimental technique, procedure and apparatus was done in other study by Abu Al-Rub [29] by performing VLE measurements for

Table 1
VLE data of water–pyridine mixtures at 705 mm Hg

x_1	y_1	T (°C)
0.0000	0.0000	112.60
0.0495	0.1710	107.70
0.0789	0.2310	105.90
0.1011	0.2856	104.31
0.1305	0.3386	104.00
0.1511	0.3885	102.22
0.2501	0.5182	98.50
0.3051	0.5602	96.80
0.4125	0.6456	94.90
0.5268	0.6853	93.31
0.6156	0.7201	92.90
0.7501	0.7560	92.61
0.8156	0.7742	92.50
0.8756	0.7850	92.45
0.9001	0.8010	92.50
0.9233	0.8150	92.50
0.9501	0.8351	92.70
1.0000	1.0000	97.70

ethanol–water mixtures. The experimental results thus obtained were compared with those reported in the literature [31] and were in a good agreement.

3.1. VLE of water–pyridine–salt-free mixtures

The experimental isobaric VLE data for the water–pyridine–salt-free mixtures at 705 mm Hg are presented in Table 1 and plotted in Fig. 1 as an x–y–T diagram. Fig. 1 indicates that the system water–pyridine at 705 mm Hg has an azeotropic point at 75.0 mol% water and 92.6°C.

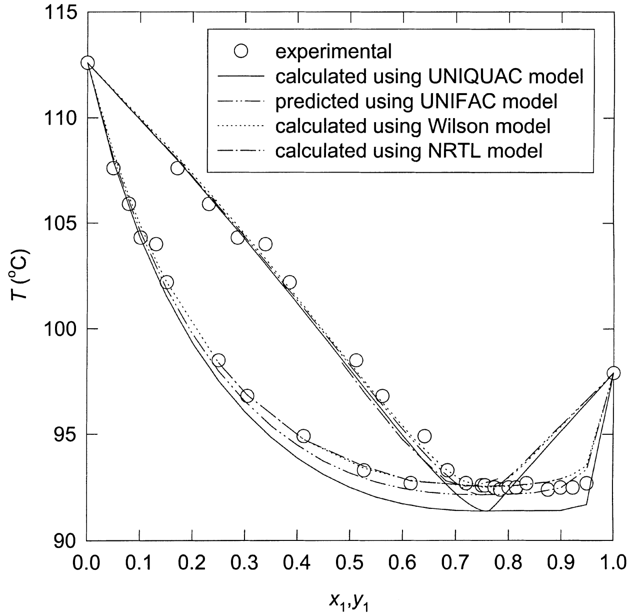

Fig. 1. Isobaric x–y–T data of water–pyridine mixtures at 705 mm Hg.

The general equation governing the VLE of a given mixture is given by

$$y_i \phi_i P = x_i \gamma_i \phi_i^{\mathrm{s}} p_i^{\mathrm{s}} \tag{1}$$

where γ_i is the activity coefficient of the ith component, ϕ_i its fugacity coefficient, y_i its composition in the vapor phase, x_i its composition in the liquid phase, p_i^{s} its vapor pressure, ϕ_i^{s} the fugacity coefficient of it as a pure component evaluated at the system temperature and the corresponding vapor pressure and P the total pressure. For low pressures, the values of the fugacity coefficients can be assumed to be unity, thus Eq. (1) reduces to the simple form

$$y_i P = x_i \gamma_i p_i^{\mathrm{s}} \tag{2}$$

Eq. (2) can be used to calculate the activity coefficient of each component in the mixture provided that there are some x–y–T or x–y–P experimental data available. Hence the calculated activity coefficients can then be used to calculate the molar excess Gibbs energy and the molar Gibbs energy of mixing using the following equations [23]:

$$\frac{G^{\mathrm{E}}}{RT} = x_1 \ln(\gamma_1) + x_2 \ln(\gamma_2) \tag{3}$$

$$\frac{G^{\mathrm{M}}}{RT} = \frac{G^{\mathrm{E}}}{RT} + x_1 \ln(x_1) + x_2 \ln(x_2) \tag{4}$$

Fig. 2 shows the molar excess Gibbs energy of water–pyridine system against the mole fraction of water in the liquid phase. As can be seen from Fig. 2, this system exhibits a positive deviation from ideality ($G^{\mathrm{E}}/RT > 0$). Comparison of the results of this study with other literature results was not possible since this system under the studied

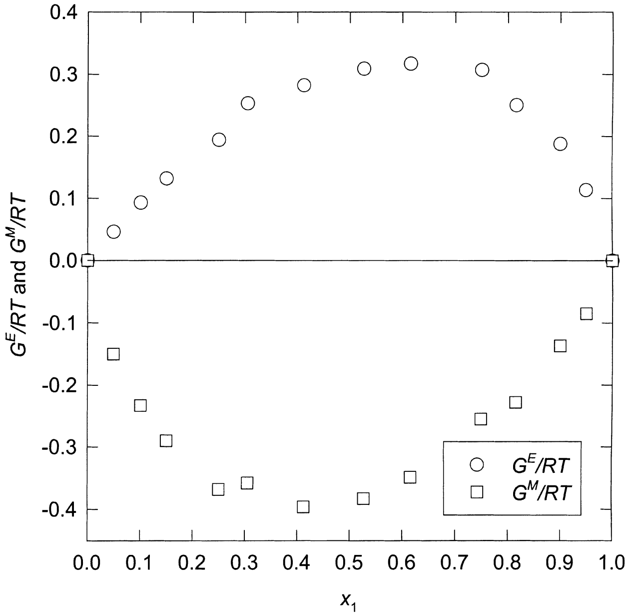

Fig. 2. Molar Gibbs energy of mixing and molar excess Gibbs energy for water–pyridine mixtures at 702 mm Hg.

conditions, according to the best of authors' knowledge, has not been investigated before. Kumar and Rajendran [32] studied the VLE of this system at 760 mm Hg and similar "trend" of the *x–y–T* diagram was obtained.

3.2. Thermodynamic consistency of the experimental data

The thermodynamic consistency of the data was tested using the "modified" integral (area) test. According to Herington's method [33], for the experimental data to be consistent, the following criterion should be satisfied:

$$|D - J| < 10 \tag{5}$$

where D, the percentage deviation of the integral $\int_0^1 \ln(\gamma_1/\gamma_2)\,\mathrm{d}x_1$ from zero, is calculated from

$$D = \frac{100\left|\int_0^1 \ln(\gamma_1/\gamma_2)\,\mathrm{d}x_1\right|}{\Sigma} \tag{6}$$

where Σ is the sum of the absolute values of the areas under the curve $\ln(\gamma_1/\gamma_2)$ vs. x_1.

The term J in Eq. (5) is a function of the overall boiling point range of the system and is found using the equation

$$J = \frac{150|\varphi|}{T_{\min}} \tag{7}$$

where φ is the overall range of boiling points of the system and $T_{\min}$ the lowest measured boiling point of the system in degree Kelvin.

Upon applying of the above equations to the system under investigation, it was found that $|D - J| = 3.5$. Thus, as per Eq. (5), the experimental data of this study can be assumed to be thermodynamically consistent.

3.3. Thermodynamic analysis of the experimental data

The experimental data of the VLE of the water–pyridine salt-free mixtures are next compared with those predicted by the UNIFAC model [34]. The predicted VLE results are shown in Fig. 1 which indicates that the predicted results from this model are in a good agreement with the experimental data. This result is more evident in Figs. 3 and 4 which show plots of the difference in either deviations in predicted bubble-point temperatures (Fig. 3) or deviations in predicted vapor-phase composition (Fig. 4) against the composition of water in the liquid phase. A comparison in terms of root-mean-square-deviation (RMSD) is given in Table 2.

Next the experimental data are correlated using the Wilson [35], the NRTL [36] and the UNIQUAC [37] models for liquid phase activity coefficients. The parameters of these equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{j=1}^{n}\left(\frac{\gamma_{1,j,\mathrm{exp}} - \gamma_{1,j,\mathrm{cal}}}{\gamma_{1,j,\mathrm{exp}}}\right)^2 + \left(\frac{\gamma_{2,j,\mathrm{exp}} - \gamma_{2,j,\mathrm{cal}}}{\gamma_{2,j,\mathrm{exp}}}\right)^2 \tag{8}$$

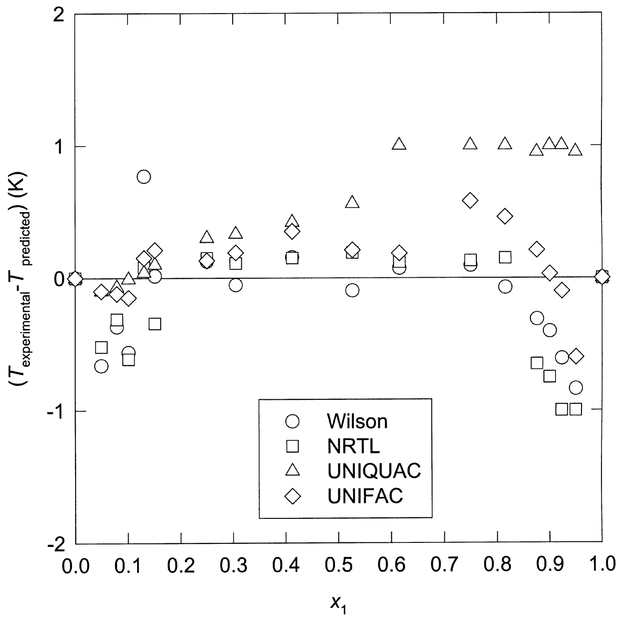

Fig. 3. Comparison of the bubble-point temperature deviations of the system water–pyridine at 705 mm Hg.

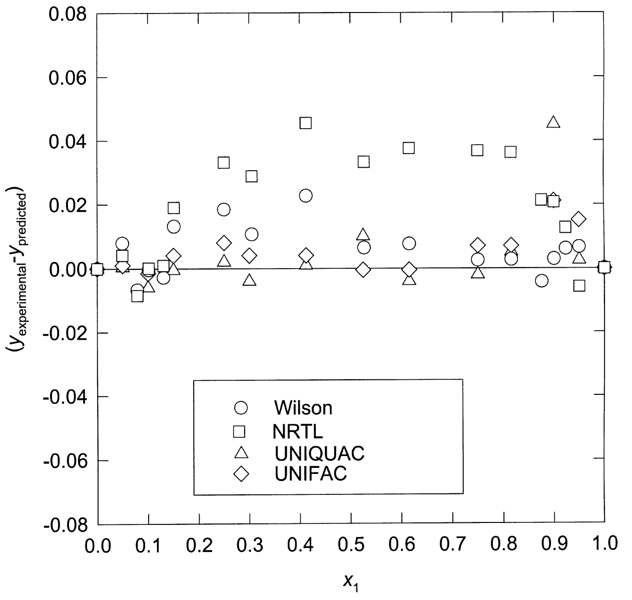

Fig. 4. Comparison of deviations of vapor-phase composition of the system water–pyridine at 705 mm Hg.

Table 2
RMSD of the models used to analyze the VLE of water–pyridine mixtures at 705 mm Hg

Model	Model parameters (J/mol)	*T*-RMSD	y_1-RMSD
Wilson	$\Delta\lambda_{12} = 4505.1$, $\Delta\lambda_{21} = 4352.9$	0.43	0.009
NRTL	$\Delta g_{12} = 7403.3$, $\Delta g_{21} = -765.7$, $\alpha = 0.30$	0.49	0.024
UNIQUAC	$\Delta u_{12} = 1409.6$, $\Delta u_{21} = -756.5$	0.67	0.012
UNIFAC	–	0.28	0.007

Table 3
VLE data of water–pyridine–0.04 M calcium chloride mixtures at 705 mm Hg

x_1	y_1	T (°C)
0.0000	0.0000	118.00
0.0501	0.9320	106.10
0.1053	0.9351	103.20
0.1821	0.9400	99.40
0.2895	0.9449	96.71
0.3894	0.9499	94.90
0.4987	0.9471	93.25
0.6567	0.9483	92.80
0.8251	0.9490	92.00
0.9044	0.9521	92.20
0.9556	0.9551	93.10
1.0000	1.0000	101.90

where n is the number of data points. The parameters found by minimizing the above OF, and the corresponding RMSD are given in Table 2. The calculated VLE results using these models are shown in Figs. 1, 3 and 4. The results tabulated in Table 2 and presented in Figs. 1, 3 and 4 show that the three models can adequately represent the VLE of the water–pyridine mixtures. It is clear from these figures that the Wilson model gave the best calculation of bubble-point temperature and vapor-phase composition with a maximum absolute deviation in temperature of 0.84 K and a maximum absolute deviation in vapor-phase composition of 0.022.

3.4. VLE of water–pyridine–calcium chloride system

The effect of calcium chloride on the VLE of the water–pyridine system was studied at the following different salt concentrations: 0.04, 0.08 M, and under saturation conditions. The experimental results are presented in Tables 3–5 and plotted as *x*–*y* diagram in Fig. 5. Fig. 5 shows that the addition of calcium chloride to the water–pyridine mixtures resulted in a dramatic altering of the VLE of the mixtures and the water was salted-out. In fact, the effect was so strong that it resulted in phase “splitting” of the liquid phase into two liquid phases. Similar results were obtained by Kumar and Rajendran [32] at a pressure of 760 mm Hg and with different salt concentration. Phase-splitting can be analyzed using the stability criterion which requires that for a stable phase the following criterion should be satisfied [38]:

$$\frac{\mathrm{d}\ln(x_i\gamma_i)}{\mathrm{d}x_i} = \frac{\mathrm{d}\ln(a_i)}{\mathrm{d}x_i} > 0 \qquad (9)$$

where a_i is the activity of the ith component. Calculated values of a_1 are shown in Fig. 6. It can be noticed that the stability criterion is violated in the system water–pyridine–calcium chloride which suggests liquid phase-splitting, in accordance with the experimental results.

Table 4
VLE data of water–pyridine–0.08 M calcium chloride mixtures at 705 mm Hg

x_1	y_1	T (°C)
0.0753	0.9456	104.20
0.1570	0.9500	100.10
0.2234	0.9555	98.40
0.3045	0.9571	96.35
0.4001	0.9553	94.50
0.5234	0.9571	93.25
0.6134	0.9582	92.10
0.8045	0.9540	91.90
0.9011	0.9520	92.20
0.9489	0.9560	92.90

Table 5
VLE data of water–pyridine–saturated calcium chloride mixtures at 705 mm Hg

x_1	y_1	T (°C)
0.0671	0.9810	105.10
0.1043	0.9868	102.80
0.1456	0.9854	99.92
0.2121	0.9821	98.40
0.3675	0.9821	94.50
0.5431	0.9805	92.62
0.6754	0.9841	91.90
0.7895	0.9850	91.70
0.8992	0.9850	91.95
0.9456	0.9853	92.60

The effect of the salt on the VLE of binary mixtures can be analyzed using the solute–solvent interaction parameter, A_i^{s}, which is defined by [18,19,22]

$$A_i^{\mathrm{s}} \equiv \frac{p_i^{\mathrm{s}}}{P} \text{ evaluated at } T_{\mathrm{salt},i} \qquad (10)$$

where $T_{\mathrm{salt},i}$ is the bubble point of the solvent component i saturated with dissolved solute or having the same solute

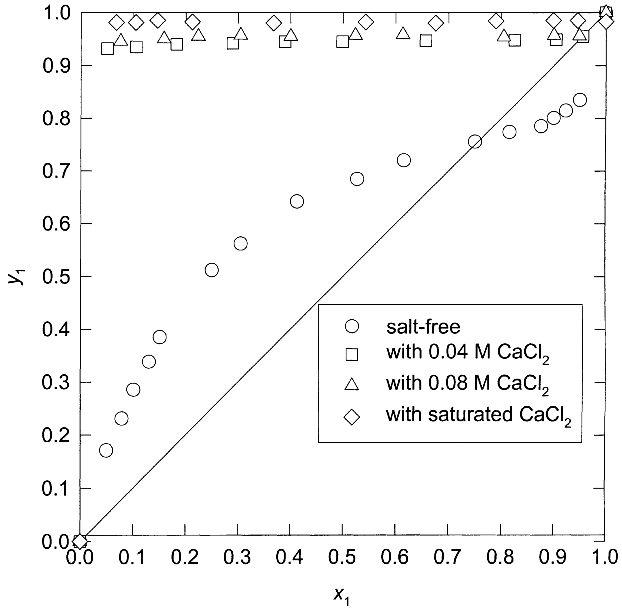

Fig. 5. Isobaric VLE of water–pyridine–calcium chloride system at 705 mm Hg.

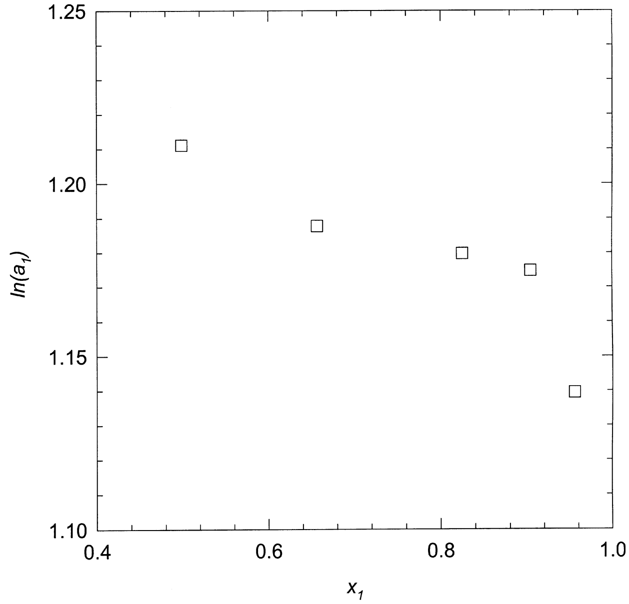

Fig. 6. Test for phase stability.

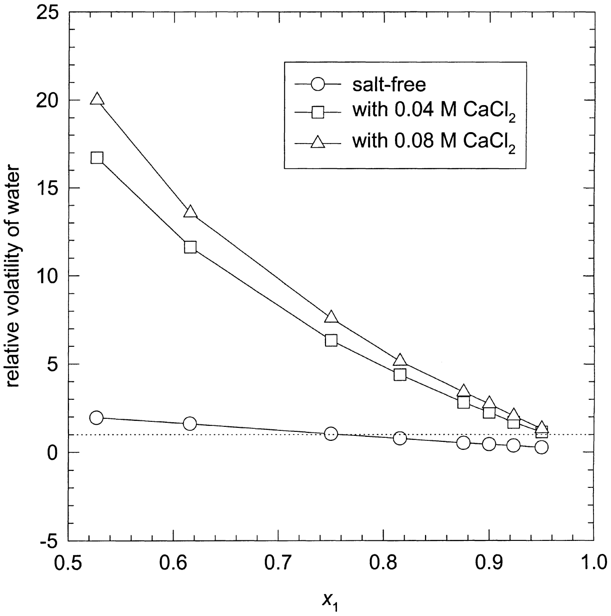

Fig. 7. Relative volatility of water–pyridine mixtures at 705 mm Hg.

concentration at the given system according to whether the system is saturated or unsaturated but containing a constant solute concentration over the whole mole fraction range [18–22]. The values of the salt–solvent interaction parameters were calculated for water and pyridine at a salt concentration of 0.04 M and were found to be 1.167 and 1.2632, respectively. An effective measure of the solute effect on the solvent mixture can be obtained by using the ratio of the solute–solvent interaction parameter for both solvents [18–22], A_{21}^{s}, where

$$A_{21}^{s} \equiv \frac{A_2^{s}}{A_1^{s}} \tag{11}$$

values of A_{21}^{s} greater than 1 indicate salting-out effect of the lighter component. The value of A_{21}^{s} for our system was found to be 1.082 which indicates salting-out of water. This is in accordance with the experimental results. However, although the values of A_{21}^{s} in the presence of calcium chloride could explain the salting-out effect of water, it could not explain the phase-splitting. Moreover, the attempts to predict the VLE of water–pyridine–calcium chloride using either the modified Tan–Wilson or the modified Tan–NRTL models were not successful, probably due to phase-splitting phenomenon.

Kumar and Rajendran [32] attributed the phase “splitting” to the formation of a possible pyridine–calcium-ions complex due to stronger intermolecular forces between them than between either water–pyridine or water–calcium-ions. These intermolecular interactions were so strong that they were effective even at low salt concentrations.

The relative volatility defined as

$$\alpha_{12} \equiv \frac{y_1/x_1}{y_2/x_2} \tag{12}$$

was also calculated for both the cases namely, in the absence and the presence of the salt. The results show that the relative volatility of water in the presence of calcium chloride was much greater than that in its absence. This is especially noticeable at low composition of water in the liquid phase, where the relative volatility of water in the presence of calcium chloride increases more than 200 times of that in the absence of calcium chloride. Fig. 7 shows the relative volatility of water against water composition in the liquid phase at high water compositions. It is clear from Fig. 7 that the relative volatility of water increases in the presence of the salt and this increase is a function of both salt concentration and liquid composition. The azeotropic point can be identified in this figure by noting the point at which the relative volatility equals unity. As it can be seen from Fig. 7, the azeotropic point of this system occurs at a mole fraction of about 0.75 water and it is shifted in the presence of 0.04 M calcium chloride to about 96.0 mol% water. These results show clearly the usefulness of using calcium chloride in shifting or eliminating the azeotropic composition of water–pyridine mixtures, and thus enhancing the separation in these mixtures.

4. Conclusion

The VLE of water–pyridine mixtures at 705 mm Hg was studied in the absence as well as in the presence of calcium chloride with different concentrations using a modified Othmer equilibrium still. The results showed that the system water–pyridine has an azeotropic point at about 75.0 mol% water and 92.6°C. The UNIFAC model was used to analyze the experimental data of the salt-free system. The predicted results from these models were found to be in a good agreement with the experimental ones. Moreover the experimental data were correlated with the Wilson, the NRTL and the UNIQUAC models and calculated VLE data using these models were in a good agreement with the experimental ones. The addition of calcium chloride was found to dramatically alter the VLE of water–pyridine mixtures whence water was salted-out, the azeotropic point was eliminated, and liquid phase-splitting resulted.

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