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Multiphase Coexistence for Aqueous System with Hydrophilic Agent

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***Abstract*—**Liquid-Liquid Equilibrium (LLE) data are measured for the ternary mixtures of water + 1-butanol + butyl acetate and quaternary mixtures of water + 1-butanol + butyl acetate + glycerol at atmospheric pressure at 313.15 K. In addition, isothermal vapor–liquid–liquid equilibrium (VLLE) data are determined experimentally at 333.15 K. The region of heterogeneity is found to increase as the hydrophilic agent (glycerol) is introduced into the aqueous mixtures. The experimental data are correlated with the NRTL model. The predicted results from the solution model with the model parameters determined from the constituent binaries are also compared with the experimental values.

***Keywords*—**LLE, VLLE, hydrophilic agent, NRTL.

I. Introduction

BUTYL ACETATE is an organic compound commonly used as a solvent in the production of many products and also as a synthetic fruit flavoring in foods. Due to its powerful solvency, high volatility and mild odor, butyl acetate is widely used in the manufacture of paints, coatings, adhesives and in the printing industry. Butyl acetate can be synthesized by the esterification of 1-butanol and acetic acid with acidic ion-exchange resins via a reactive distillation process. The products of the esterification are water and butyl acetate, which are partially miscible; thus, the product mixtures containing water, butyl acetate and 1-butanol may form two-liquid phases in a certain range of compositions. While the solubility of butyl acetate is very low in the aqueous phase, a substantial amount of water dissolves in the organic-rich phase. Separation may be economically feasible if the heterogeneity region can be increased. As evidenced from previous experimental results, such as [1]-[3], adding a salt and/or a hydrophilic agent into the liquid mixtures could be an effective method. Pai and Rao [1] measured the mutual solubilities of water + ethanol + ethyl acetate without salt and with saturated salt of potassium acetate, sodium acetate, potassium chloride, sodium chloride, potassium sulfate and sodium sulfate at 303.15 K. The results indicated that potassium acetate yielded the highest solubility depression of water in the organic phase. The focus of this study was to investigate the enhancement of phase splitting of the liquid mixtures of water + 1-butanol + butyl acetate in the presence of a hydrophilic agent (glycerol). The phase compositions of the two coexistenting liquid phases were measured at temperatures from 313.15 K to 333.15 K. The new LLE and VLLE data were correlated and predictions made using the NRTL model.

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II. Experimental Section

A. Materials

1-Butanol (99+ mass%) and butyl acetate (99+ mass%) were purchased from Acros, USA. Glycerol (98.5+ mass%) was supplied from Yakuri, Japan. The chemicals were used without further purification. Deionized distilled water was prepared in our laboratory. The purity of the organic compounds was checked and no impurity peak was detected by the chromatographic analysis for any of chemicals.

B. Apparatus and Procedures

The schematic diagram shows the glass-made LLE apparatus with an internal volume of about 30 cm^3 similar to that of [4]. Thermostatic water is circulated through the jacket of the equilibrium cell to control the cell's temperature to within ±0.1 K. The equilibrium cell's temperature is controlled by the thermostatic water through the jacket to within ±0.1 K. The cell temperature is measured with a precision thermometer (Model-1506, Hart Scientific, USA) with an uncertainty of ±0.02 K. The liquid mixture in the cell is agitated vigorously by a magnetic stirrer for more than 4 hours in order to thoroughly mix the compounds for each run. The two-liquid phases will separate completely after settling for at least 8 hours. To avoid contamination by the other phase during the sampling procedure, the sample of the organic-rich phase is taken from the top opening of the cell with a syringe, and that of the water-rich phase is taken from a sampling port at the bottom of the cell. A static VLLE apparatus similar to that of Lee et al. [5] was employed in the present study to measure the VLLE data. The center of the apparatus is the visual equilibrium cell that is immersed in a visibility thermostatic bath (Model TV 4000, stability, ±0.03 K, Neslab, USA). The phase behavior in the equilibrium cell can be observed through the transparent windows. A pressure transducer (Model PDCR-912, 0–1000 kPa, Druck, UK) with a digital indicator (Model DPI-261, Druck, UK) measures the equilibrium pressure. The accuracy of the pressure measurement is about ±0.1%. This apparatus is equipped with both liquid and vapor circulation loops to promote the attainment of equilibrium. A four-port liquid-sampling valve (Model 7410, Rheodyne, USA) with a 1 μl loop disc is installed in the liquid circulation loop to trap the liquid sample, while a pre-heater is used to reheat the returned liquid to the cell if a sample is not taken. A switch valve is utilized to select one of the coexistent liquid phases to be circulated. The gas circulation loop consists of a six-port

vapor-sampling valve (Model 7010, Rheodyne, USA) with a 100μl sample loop, a magnetic gear pump and a pre-heater. A proper amount of solution is loaded into the degassing unit at the beginning of an experiment. The degassing procedure used here was similar to that of [6]. The degassed solution is then transferred into the equilibrium cell, in which the levels of the vapor–liquid–liquid interfaces should be adjusted properly such that the upper liquid phase can be circulated. Both liquid and vapor mixtures are circulated alternately by the circulation pumps to promote equilibration. When the system reaches equilibrium, the pressure reading of the cell approaches a constant. Five replicated samples for each phase are implemented to determine the equilibrium compositions. The composition of LLE and VLLE samples in each phase is analyzed by a gas chromatography (Model 8700, China Chromatography Co., Taiwan) with a thermal conductivity detector (TCD). A stainless steel column packed with 10% Porapak Qs 80/100 (2m of length) which can clearly separate the constituent compounds of the samples is employed for the sample analysis. High purity helium (99.99%) is used as a carrier gas. Calibrations are made with gravimetrically prepared samples in two composition ranges, in accordance with those in the organic-rich and the water-rich phases.

III. Experimental Results

A glass-made and static VLLE apparatus was employed to measure the LLE and VLLE data of water + 1-butanol + butyl acetate at 313.15 and 333.15 K. Tables I, II report the experimental results, which show the mutual solubilities of water and butyl acetate. Since the system of water + 1-butanol + butyl acetate behaves as a type-II LLE, the effects of adding an auxiliary agent on the mutual solubilities of water + butyl acetate can provide useful indications for the liquid phase-splitting enhancement. The experimental results showed that the immiscibility gaps were substantially enlarged as glycerol was introduced into the aqueous solutions. The composition of the auxiliary compounds in the initial feed was 20 wt% in each run. Tables III, IV present the LLE and VLLE experimental results for water + 1-butanol + butyl acetate + glycerol. In this aqueous system, no glycerol was detected in the organic-rich and vapor phases. Glycerol was found to be sparingly soluble in the organic phase; that is, most of the auxiliary agents dissolved in the aqueous phase.

TABLE I
LLE Data for Water (1) + 1-Butanol (2) + Butyl acetate (3) at 313.15K

Organic phase		Aqueous phase	
x_2^I	x_3^I	x_2^{II}	x_3^{II}
-	0.8828	-	0.0012
0.0809	0.7810	0.0025	0.0007
0.1267	0.7168	0.0035	0.0008
0.2535	0.5174	0.0062	0.0013
0.2826	0.4478	0.0064	0.0006
0.3532	0.3092	0.0081	0.0007
0.3834	0.2467	0.0092	0.0008
0.4215	0.1736	0.0114	0.0009
0.4869	-	0.0142	-

TABLE II
VLLE Data for Water (1) + 1-Butanol (2) + Butyl Acetate (3) at 333.15K

	Organic phase		Aqueous phase		Vapor phase	
P(kPa)	x_2^I	x_3^I	x_2^{II}	x_3^{II}	y_2	y_3
24.4	0.435	-	0.015	-	0.243	-
27.0	0.417	0.182	0.008	0.0005	0.189	0.127
27.7	0.356	0.317	0.006	0.0007	0.164	0.172
27.9	0.299	0.428	0.004	0.0008	0.109	0.238
28.2	0.152	0.669	0.002	0.0009	0.045	0.280
28.3	-	0.877	-	0.0010	-	0.313

TABLE III
LLE Data for Water (1) + 1-Butanol (2) + Butyl Acetate (3) + Glycerol (4) at 313.15 K

Organic phase			Aqueous phase		
x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}
0.074	-	0.927	0.843	-	0.0011
0.116	0.089	0.795	0.890	0.003	0.0009
0.147	0.162	0.692	0.903	0.002	0.0005
0.190	0.266	0.544	0.860	0.008	0.0013
0.301	0.381	0.318	0.898	0.011	0.0013
0.351	0.449	0.200	0.883	0.013	0.0006
0.448	0.513	0.039	0.865	0.017	0.0013
0.480	0.520	-	0.873	0.023	-

TABLE IV
VLLE Data for Water (1) + 1-Butanol (2) + Butyl Acetate (3) + Glycerol (4) at 333.15 K

	Organic phase			Aqueous phase			Vapor phase		
P(kPa)	x_2^I	x_3^I	x_4^I	x_2^{II}	x_3^{II}	x_4^{II}	y_2	y_3	y_4
24.1	0.506	-	-	0.019	-	0.158	0.287	-	-
24.4	0.458	0.158	-	0.013	0.0007	0.191	0.220	0.113	-
24.8	0.356	0.373	-	0.011	0.0012	0.214	0.155	0.206	-
25.2	0.290	0.504	-	0.007	0.0012	0.212	0.102	0.259	-
26.0	0.164	0.687	-	0.004	0.0013	0.212	0.068	0.293	-
26.2	-	0.902	-	-	0.0013	0.169	-	0.337	-

IV. LLE and VLLE Data Correlation and Prediction

At LLE or VLLE, the compositions of the two coexisting liquid phases can be calculated from the criteria of LLE (equality of the constituent fugacities between the coexisting liquid phases) together with the material balance equation. The calculation procedure is detailed in [7]. Based on 1 mole of feed with a total composition of z_i, the compositions of the coexisting liquid phases are solved simultaneously from:

$$1-\sum_{i=1}^{n_c}\frac{z_i}{\beta+K_i(1-\beta)}=0 \tag{1}$$

with

$$K_i = x_i^{II}/x_i^{I} = \gamma_i^{I}/\gamma_i^{II} \tag{2}$$

where is the fraction of the total material that is present in the first liquid phase (the organic-rich phase, denoted as superscript I), n_c is the number of components, the superscript II represents the second liquid phase (the aqueous phase) and K_i is the distribution ratio for component i. The activity coefficient γ_i is calculated from a solution model. Among several others, the

NRTL model is commonly chosen to implement LLE or VLLE calculation. For the VLLE calculation, the equilibrium pressures and the vapor pressures of the constituent compounds were not sufficiently higher than the investigated conditions, and the Poynting pressure correction factor and the fugacity coefficient of vapor phase were negligible in the calculation. The vapor composition (y_i) and the bubble-point pressure (P) can be calculated from:

$$y_i = \frac{\gamma_i^I x_i^I P_i^s}{P} = \frac{\gamma_i^{II} x_i^{II} P_i^s}{P} \tag{3}$$

and

$$P = \sum_{i=1}^{n_c} y_i P = \sum_{i=1}^{n_c} \gamma_i^I x_i^I P_i^s = \sum_{i=1}^{n_c} \gamma_i^{II} x_i^{II} P_i^s \tag{4}$$

where P_i^s is the saturated vapor pressure of component i. In the LLE and VLLE calculation, there are two parameters, a_{12} and a_{21}, in the NRTL model (with α= 0.2) for each constituent binary. Theoretically, the LLE and VLLE behavior of ternary and quaternary systems may be estimated from a solution model, with the model parameters determined from the phase-equilibrium data of the constituent binaries. Tables V-VIII give the binary parameters of the NRTL (with α=0.2) for the related pairs. While the parameters of water + esters at a specific temperature were determined from the mutual solubility (LLE) data, those of the other binary systems were obtained from the vapor-liquid equilibrium (VLE) binary data [8]. The predicted results are listed in Tables V-VIII and illustrated in Figs. 1 and 2, indicating that the NRTL model is qualitatively described for the LLE and VLLE ternary systems, except for the quaternary system.

TABLE V
LLE PREDICTED RESULTS FROM THE NRTL MODEL FOR WATER (1) + 1-BUTANOL (2) + BUTYL ACETATE (3) AT 313.15 K

i-j	α_{ij}	a_{ij}[a] (K)	a_{ji}[a] (K)	Grand AAD (Δ)
1-2	0.4518	1217.443	325.540	
1-3	0.2911	1900.217	471.749	0.0086
2-3	0.3011	105.917	89.141	

[a] *aij* = (*gij* −*gjj*)/*R*, where *gij* is the interaction energy between the *i–j* pair and *R* is the gas constant

TABLE VI
VLLE PREDICTED RESULTS FROM THE NRTL MODEL FOR WATER (1) + 1-BUTANOL (2) + BUTYL ACETATE (3) AT 333.15 K

i-j	α_{ij}	a_{ij}[a] (K)	a_{ji}[a] (K)	ΔP/P (%)	Δx^{II}_1	Δx^{II}_1	Δy
1-2	0.4518	1217.443	325.540				
1-3	0.2911	1900.217	471.749	1.88	0.0104	0.0013	0.0232
2-3	0.3011	105.917	89.141				

[a] *aij* = (*gij* −*gjj*)/*R*, where *gij* is the interaction energy between the *i–j* pair and *R* is the gas constant

TABLE VII
LLE PREDICTED RESULTS FROM THE NRTL MODEL FOR WATER (1) + 1-BUTANOL (2) + BUTYL ACETATE (3) + GLYCEROL (4) AT 313.15 K

i-j	α_{ij}	a_{ij}[a] (K)	a_{ji}[a] (K)	Grand AAD (Δ)
1-2	0.4518	1217.443	325.540	
1-3	0.2911	1900.217	471.749	
1-4	0.2000	336.437	974.595	
2-3	0.3011	105.917	89.141	0.0425
2-4	0.2000	-446.541	1302.426	
3-4	0.2000	894.676	305.220	

[a] *aij* = (*gij* −*gjj*)/*R*, where *gij* is the interaction energy between the *i–j* pair and *R* is the gas constant

TABLE VIII
VLLE PREDICTED RESULTS FROM THE NRTL MODEL FOR WATER (1) + 1-BUTANOL (2) + BUTYL ACETATE (3) + GLYCEROL (4) AT 333.15 K

i-j	α_{ij}	a_{ij}[a] (K)	a_{ji}[a] (K)	ΔP/P (%)	Δx^{II}_1	Δx^{II}_1	Δy
1-2	0.4518	1217.443	325.540				
1-3	0.2911	1900.217	471.749				
1-4	0.2000	336.437	974.595				
2-3	0.3011	105.917	89.141	3.92	0.0707	0.0682	0.0351
2-4	0.2000	-446.541	1302.426				
3-4	0.2000	894.676	305.220				

[a] *aij* = (*gij* −*gjj*)/*R*, where *gij* is the interaction energy between the *i–j* pair and *R* is the gas constant

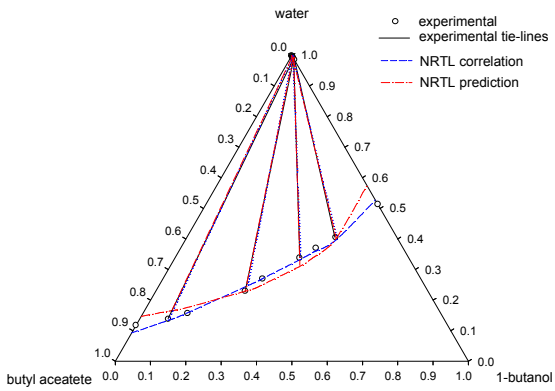

Fig. 1 Comparison of calculated results with LLE experimental values for water + 1-butanol + butyl acetate at 313.15 K

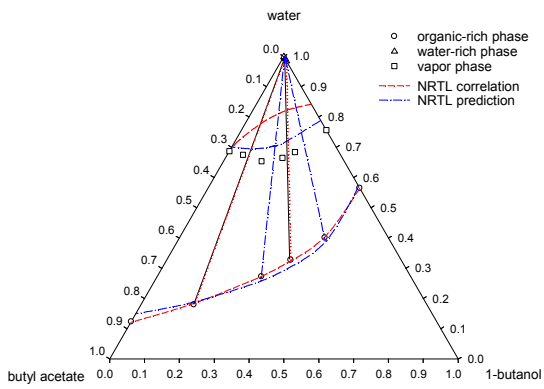

Fig. 2 Comparison of calculated results with VLLE experimental values for water + 1-butanol + butyl acetate at 333.15 K

To improve the representation of the binodal locus, the

ternary LLE and VLLE data were correlated with the NRTL model by adjusting six model parameters simultaneously. The objective function of the parameter determination is defined as:

$$\Delta = \left(\sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} \left| (\hat{x}_{ijk} - x_{ijk}) \right| \right) / 6n \quad (5)$$

where x_{ijk} and $\hat{x}_{ijk}$ are the observed and the calculated mole fractions of component i in phase j on tie-line k, respectively, and n is the number of tie-lines. Tables IX, X present the correlated results. Figs. 1, 2 show a comparison of the calculated binodal locus and tie-lines from the NRTL model with the experimental results. The accuracy of the data correlation was much better than that of the predicted results with the model parameters obtained from the constituent binaries. However, the accuracy was still inadequate for the vapor phase and the bubble-point pressure for VLLE behavior.

TABLE IX
LLE CORRELATED RESULTS FROM THE NRTL MODEL FOR WATER (1) + 1-BUTANOL (2) + BUTYL ACETATE (3) AT 313.15 K

i-j	α_{ij}	a_{ij}[a] (K)	a_{ji}[a] (K)	Grand AAD (Δ)
1-2	0.2	2070.013	-437.919	
1-3	0.2	2431.358	319.413	0.0055
2-3	0.2	246.351	-864.939	

[a] *aij* = (*gij* −*gjj*)/*R*, where *gij* is the interaction energy between the *i–j* pair and *R* is the gas constant

TABLE X
VLLE CORRELATED RESULTS FROM THE NRTL MODEL FOR WATER (1) + 1-BUTANOL (2) + BUTYL ACETATE (3) AT 333.15 K

i-j	α_{ij}	a_{ij}[a] (K)	a_{ji}[a] (K)	ΔP/P (%)	Δx^{II}_1	Δx^{II}_1	Δy
1-2	0.2	1843.830	-446.534				
1-3	0.2	2157.993	207.426	6.32	0.0015	0.0004	0.0622
2-3	0.2	1342.648	-952.242				

[a] *aij* = (*gij* −*gjj*)/*R*, where *gij* is the interaction energy between the *i–j* pair and *R* is the gas constant

V. CONCLUSIONS

Liquid–liquid equilibrium and vapor-liquid–liquid equilibrium data were measured for a ternary system of water + 1-butanol + butyl acetate and a quaternary system of water + 1-butanol + butyl acetate + glycerol at temperatures of 313.15K and 333.15K, respectively. The binodal locus could be predicted qualitatively from the NRTL model with the parameters determined from the phase equilibrium data of the constituent binaries. The binodal locus of the LLE and VLLE data could be correlated accurately with the NRTL model, when the six model parameters were adjusted simultaneously. However, the accuracy was still inadequate for the vapor phase and the bubble-point pressure for VLLE behavior.

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REFERENCES

[1] M. U. Pai, and K. M. Rao, "Automatic equalization for digital communication," *J. Chem. Eng. Data*, vol. 11, no. 3, pp. 353–356, Jul. 1966.
[2] J. J. Malinowski, and A. J. Daugulis, "Salt effects in extraction of ethanol, 1-butanol and acetone from aqueous solutions," *AIChE J.*, vol. 40, no. 9, pp. 1459–1465, Sep. 1994.
[3] G. Saravanan, and D. Srinivasan, "Liquid-liquid equilibria for the system ethyl acetate-acetic acid-water in the presence of dissolved inorganic salts," *J. Chem. Eng. Data*, vol. 30, no. 2, pp. 166–171, Apr. 1985.
[4] N. Peschke, and S.I. Sandler, "Liquid-Liquid Equilibria of Fuel Oxygenate + Water + Hydrocarbon Mixtures. 1," *J. Chem. Eng. Data*, vol. 40, no. 1, pp. 315–320, Jan. 1995.
[5] M. J. Lee, L. H. Tsai, G. B. Hong, and H. M. Lin, "Multiphase Coexistence for Aqueous Systems with Amyl Alcohol and Amyl Acetate," *Ind. Eng. Chem. Res.*, vol. 41, no. 13, pp. 3247–3252, Jun. 2002.
[6] M. J. Lee, and C. H. Hu, "Multiphase Coexistence for Aqueous Systems with Amyl Alcohol and Amyl Acetate," *Fluid Phase Equilib.*, vol. 109, no. 1, pp. 83–98, Aug. 1995.
[7] S. M. Walas, *Phase Equilibria in Chemical Engineering*, Butterworth, Boston, MA, 1985.
[8] J. Gmehling, and U. Onken, *Vapor-Liquid Equilibrium Data Collection-Aqueous–Organic Systems*; Chemistry Data Series, Vol. 1, DECHEMA: Frankfurt, Germany, 1977.

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