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Phase Equilibria of the Ternary System Water + Propionic Acid + 2-Butanol

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ABSTRACT

Liquid–liquid equilibria for the ternary system water + propionic acid + 2-butanol was measured over a temperature range of 298 to 318 K. The results were used to estimate the interaction parameters between each of the three compounds for the nonrandom, two liquid (NRTL) equilibrium model as a function of temperature. The estimated interaction parameters were successfully used to predict the equilibrium compositions by the NRTL model. Based on this work, the distribution coefficients were also calculated and compared with the experimental values.

INTRODUCTION

Propionic acid is made by the liquid-phase oxidation of propionaldehyde and can also be made by oxidation of propane or hydrocarboxylation of ethylene with carbon monoxide and hydrogen in the presence of rhodium or iridium catalyst (1).

Markets for propionic acid are distributed among antifungal agents, cellulose propionate plastics, herbicides such as 2,2-dichloropropionic acid and 3′,4′-dichloropropionanilide, and in grain preservation which has become a prominant market for propionic acid.

Due to the increasing market demands for propionic acid, its recovery from dilute solutions has become very important. Many solvents have been tried to extract acids from dilute solutions. Moreover, several alco-

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hols, ketones, and esters have been used as solvents for the recovery of propionic acid (2, 3).

Precise liquid–liquid equilibrium data are required for extraction processes. Excess activity models, such as the nonrandom, two liquid (NRTL) model (4), the universal quasi-chemical (UNIQUAC) model (5), and the universal function-group activity coefficients (UNIFAC) model (6), have been successfully applied for the prediction of several liquid–liquid systems.

The objective of this work is to study the liquid–liquid phase equilibria of the ternary system water + propionic acid + 2-butanol at several temperatures and to test the capability of the nonrandom, two liquid model to correlate these data. The compositions were measured at 298, 303, 308, 313, and 318 K and regressed by the NRTL model.

EXPERIMENTAL

Chemicals

Propionic acid and 2-butanol were supplied by Fluka with a purity of 98+%. Water was distilled and demineralized before being used.

Apparatus and Procedure

The equilibrium runs were performed in 60 cm^3 extraction cells surrounded by water jackets. The jackets were thermostatically controlled using a Julabu PC (F18) controller mounted on a water bath. The temperature range for this thermostat was −20 to 100°C with a controller accuracy of ±0.2°C. The cell constituents were prepared by mass, stirred for not less than 30 minutes, and allowed to settle for not less than 2 hours. Longer mixing and settling periods did not result in any sensible change in the phases compositions.

A Chrompack CP9001 gas chromatography equipped with a flame ionization detector was used to measure the concentrations of 2-butanol and propionic acid. A 25 m × 0.32 mm ID WCOT fused silica [coated with the free fatty acid phase (FFAP) with a coating thickness, *df*, of 0.3 μm] capillary column was used isothermally with an FID detector. The oven temperature ranged from 80 to 145°C with a temperature rise of 10°C/min. The injection port temperature was held at 250°C and the detector temperature was 250°C. The accuracy of the measured concentrations was ±0.246% and ±0.634% for 2-butanol and propionic acid, respectively.

The gas chromatograph was calibrated by the internal standard calibration method. This was done by injecting internal standards of acetic acid

(45.22 mg/mL) and 2-pentanol (15.06 mg/mL) as references for propionic acid and 2-butanol in the sample. Calibration solutions of propionic acid and 2-butanol were prepared by weighing different samples of pure compounds and diluting them in a 25 cm^3 volumetric flask to yield solutions of 62.33 and 15.92 mg/mL of 2-butanol and propionic acid, respectively. The accuracy of the balance was ± 0.0001 g and of the volumetric flask was ± 0.03 cm^3. The resulting accuracies in measuring the concentrations of the calibration solutions were $\pm 0.182\%$ and $\pm 0.126\%$ for 2-butanol and propionic acid, respectively.

By knowing the initial mass of each component, measuring the volume of each phase, and assuming that the density of the aqueous phase equals that of pure water, the concentration of water in each phase is calculated by material balance. To verify these calculations, random test runs were investigated by measuring the concentration of water using gas chromatography. The gas chromatograph in this case was equipped with a TCD detector. A 25 m × 0.53 mm ID PORAPLOT Q capillary column (coated with PORAPLOT Q) was used isothermally. The temperature of the oven was held at 175°C, the injection port temperature was held at 250°C, and the detector temperature was 300°C. The root-mean-square deviation (RMSD%) between the measured and the calculated concentrations was 3.95%.

MODELS AND PREDICTIONS

If a liquid mixture of a given composition and at a known temperature is separated into two phases (i.e., at equilibrium), the compositions of the two phases can be calculated using the following system of equations:

$$\gamma_i^E x_i^E = \gamma_i^R x_i^R \tag{1}$$

$$z_i = z_i^E + z_i^R \tag{2}$$

where z_i, z_i^E, and z_i^R are the numbers of moles of component i in the system, in the extract (organic) phase, and in the raffinate (aqueous) phase, respectively. γ_i^E and γ_i^R are the corresponding activity coefficients of component i in the extract and the raffinate phases as calculated from the NRTL model.

According to Renon and Prausnitz (4), the NRTL equation is given by

$$\frac{g^E}{RT} = \sum_{i=1}^{C} x_i \left[\sum_{j=1}^{C} x_{ji}\tau_{ji} \right] \tag{3}$$

or

$$\ln \gamma_i = \frac{\sum_{j=1}^{C} (\tau_{ji} G_{ji} x_j)}{\sum_{k=1}^{C} (G_{ki} x_k)} + \sum_{j=1}^{C} \left[\frac{x_j G_{ij}}{\sum_{k=1}^{C} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{k=1}^{C} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{C} G_{kj} x_k} \right) \right] \tag{4}$$

where

$$x_{ji} = \frac{x_j \exp(-\alpha_{ji} \tau_{ji})}{\sum_{k=1}^{C} x_k \exp(-\alpha_{ki} \tau_{ki})} \tag{5}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \tag{6}$$

where α_{ij} is an adjustable parameter related to the degree of randomness of the mixture, and α_{ij} equals α_{ji}.

$$\mathrm{a}_{ij} = \tau_{ij} T = (g_{ij} - g_{jj})/R \tag{7}$$

$$\mathrm{a}_{ji} = \tau_{ji} T = (g_{ji} - g_{ii})/R \tag{8}$$

Gibbs energies of interaction between molecules are identified by g_{ij} where j refers to the central molecule, and mole fractions x_{ij} in the surrounding region are identified in the same way. The values of $\tau_{ii} = \tau_{jj} = 0$ and $\tau_{ij} \neq \tau_{ji}$.

Equations (1) and (2) are solved to calculate the mole fraction (x) for component i in each liquid phase. This method of calculation gives a single tie line.

RESULTS AND DISCUSSION

The measured equilibrium mole percents are shown in Tables 1–5 and plotted in Figs. 1–5. These measurements were used to determine the optimum NRTL interaction parameters between water, propionic acid, and 2-butanol.

The NRTL equation was fitted to experimental data using an iterative computer program developed by Sørensen (7) to minimize the values of the following objective functions:

$$F(a) = \sum^k \sum^i [(a_{ik}^{\mathrm{E}} - a_{ik}^{\mathrm{R}})/(a_{ik}^{\mathrm{E}} + a_{ik}^{\mathrm{R}})]^2 + Q \sum^n P_n^2 \tag{9}$$

$$F(x) = \sum^k \min \sum^i \sum^j (x_{ijk} - x_{ijk}^*)^2 + Q \sum^n P_n^2 \tag{10}$$

The second term in both Eq. (9) and Eq. (10) is called the penalty term and is used to reduce the risk of multiple solutions associated with high

TABLE 1
Comparing Experimental and Predicted LLE Data for the System Water (1) + Propionic Acid (2) + 2-Butanol (3) at 298 K (α = 0.25)

Aqueous phase				Organic phase			
x_1		x_2		x_1		x_2	
Exp.	NRTL	Exp.	NRTL	Exp.	NRTL	Exp.	NRTL
0.9494	0.9499	0.0000	0.0000	0.6449	0.6458	0.0000	0.0000
0.9445	0.9449	0.0039	0.0044	0.6924	0.6908	0.0172	0.0195
0.9410	0.9389	0.0061	0.0081	0.7215	0.7183	0.0239	0.0280
0.9396	0.9384	0.0075	0.0084	0.7211	0.7206	0.0282	0.0287
0.9266	0.9274	0.0145	0.0139	0.7507	0.7537	0.0401	0.0356
[a]RMS%	0.12		0.10		0.21		0.29

[a] RMS% = (100%) $\left\{\left[\sum_k (x^{\mathrm{I}}_{k,\mathrm{exp}} - x^{\mathrm{I}}_{k,\mathrm{calcd}})^2_j\right]/n\right\}^{1/2}$, k = 1, 2, . . . , n (tie lines).

parameter values. $F(a)$ is an activity residual function, a is the activity obtained directly from the equilibrium model by insertion of experimental concentrations, Q is a constant in the penalty term, P is the parameter value in the penalty term, $F(x)$ is a concentration residual function, x is the experimental fraction of the liquid phase, and x^* is the mole fraction

TABLE 2
Comparing Experimental and Predicted LLE Data for the System Water (1) + Propionic Acid (2) + 2-Butanol (3) at 303 K (α = 0.37)

Aqueous phase				Organic phase			
x_1		x_2		x_1		x_2	
Exp.	NRTL	Exp.	NRTL	Exp.	NRTL	Exp.	NRTL
0.9469	0.9496	0.0000	0.0000	0.6543	0.6555	0.0000	0.0000
0.9476	0.9440	0.0049	0.0059	0.6901	0.6862	0.0217	0.0256
0.9425	0.9398	0.0079	0.0090	0.7024	0.7008	0.0324	0.0337
0.9373	0.9367	0.0106	0.0110	0.7087	0.7099	0.0394	0.0377
0.9208	0.9237	0.0186	0.0184	0.7387	0.7409	0.0494	0.0475
[a]RMS%	0.27		0.07		0.23		0.22

[a] RMS% = (100%) $\left\{\left[\sum_k (x^{\mathrm{I}}_{k,\mathrm{exp}} - x^{\mathrm{I}}_{k,\mathrm{calcd}})^2_j\right]/n\right\}^{1/2}$, k = 1, 2, . . . , n (tie lines).

TABLE 3
Comparing Experimental and Predicted LLE Data for the System Water (1) + Propionic Acid (2) + 2-Butanol (3) at 308 K (α = 0.41)

Aqueous phase				Organic phase			
x_1		x_2		x_1		x_2	
Exp.	NRTL	Exp.	NRTL	Exp.	NRTL	Exp.	NRTL
0.9597	0.9580	0.0000	0.0001	0.6509	0.6503	0.0000	0.0004
0.9516	0.9490	0.0046	0.0070	0.6809	0.6756	0.0225	0.0275
0.9480	0.9481	0.0076	0.0077	0.6727	0.6777	0.0346	0.0293
0.9428	0.9426	0.0100	0.0114	0.6883	0.6908	0.0427	0.0399
0.9255	0.9259	0.0175	0.0214	0.7234	0.7226	0.0538	0.0550
[a] RMS%	0.14		0.21		0.35		0.35

[a] RMS% = $(100\%)\left\{\left[\sum_k (x^1_{k,\text{exp}} - x^1_{k,\text{calcd}})^2_j\right]/n\right\}^{1/2}$, $k = 1, 2, \ldots, n$ (tie lines).

of the calculated tie line lying close to the considered experimental tie line. The counter i represents the number of components, j represents the two liquid phases, k represents the number of tie lines, and n represents the number of parameters. All the experimental tie lines were considered

TABLE 4
Comparing Experimental and Predicted LLE Data for the System Water (1) + Propionic Acid (2) + 2-Butanol (3) at 313 K (α = 0.33)

Aqueous phase				Organic phase			
x_1		x_2		x_1		x_2	
Exp.	NRTL	Exp.	NRTL	Exp.	NRTL	Exp.	NRTL
0.9606	0.9566	0.0000	0.0000	0.6616	0.5760	0.0000	0.0000
0.9542	0.9527	0.0045	0.0051	0.6503	0.6463	0.0257	0.0312
0.9495	0.9522	0.0074	0.0055	0.6451	0.6503	0.0395	0.0324
0.9454	0.9430	0.0099	0.0111	0.7000	0.6980	0.0411	0.0437
0.9274	0.9280	0.0173	0.0185	0.7454	0.7463	0.0506	0.0492
[a]RMS%	0.25		0.12		3.84		0.42

[a] RMS% = $(100\%)\left\{\left[\sum_k (x^1_{k,\text{exp}} - x^1_{k,\text{calcd}})^2_j\right]/n\right\}^{1/2}$, $k = 1, 2, \ldots, n$ (tie lines).

TABLE 5
Comparing Experimental and Predicted LLE Data for the System Water (1) + Propionic Acid (2) + 2-Butanol (3) at 318 K ($\alpha = 0.41$)

Aqueous phase				Organic phase			
x_1		x_2		x_1		x_2	
Exp.	NRTL	Exp.	NRTL	Exp.	NRTL	Exp.	NRTL
0.9620	0.9601	0.0000	0.0005	0.6530	0.6499	0.0000	0.0032
0.9563	0.9566	0.0043	0.0038	0.6719	0.6736	0.0229	0.0210
0.9524	0.9544	0.0069	0.0056	0.6800	0.6850	0.0334	0.0278
0.9479	0.9447	0.0094	0.0117	0.7223	0.7185	0.0369	0.0413
0.9326	0.9337	0.0162	0.0177	0.7462	0.7469	0.0490	0.0484
[a]RMS%	0.20		0.14		0.32		0.36

[a] RMS% = (100%) $\left\{\left[\sum_k (x^{I}_{k,\text{exp}} - x^{I}_{k,\text{calcd}})^2_j\right]/n\right\}^{1/2}$, $k = 1, 2, \ldots, n$ (tie lines).

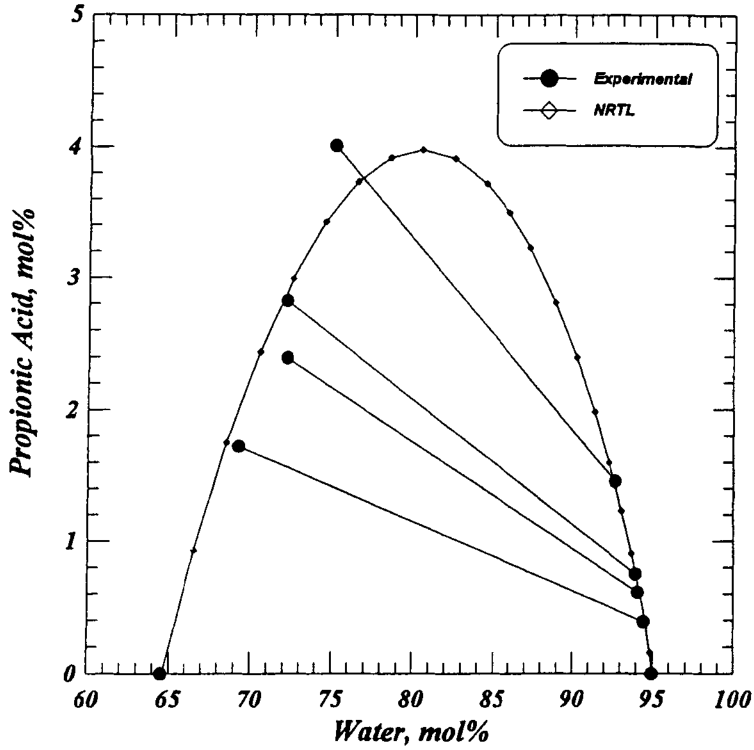

FIG. 1 LLE of the ternary system water (1) + propionic acid (2) + 2-butanol (3) at 25°C.

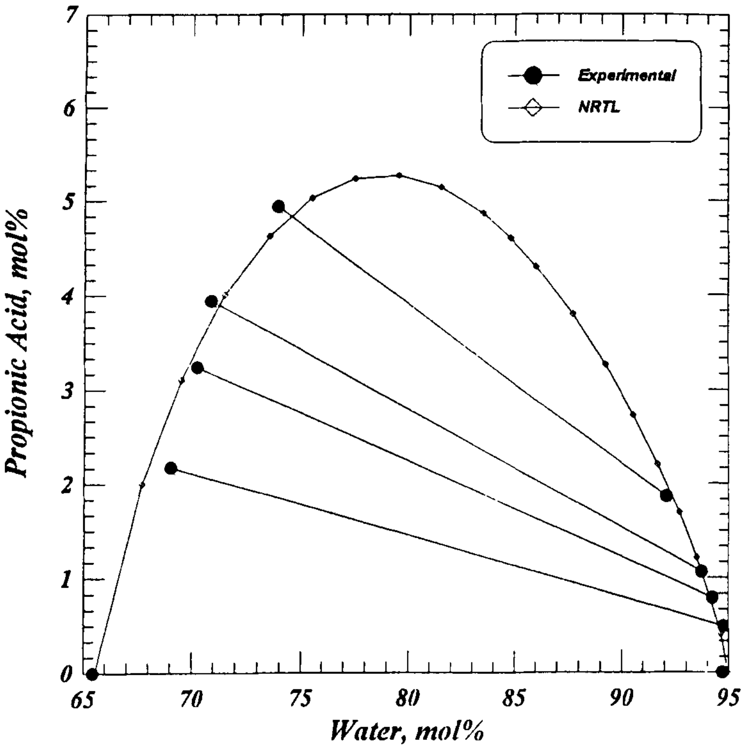

FIG. 2 LLE of the ternary system water (1) + propionic acid (2) + 2-butanol (3) at 30°C.

in correlating the data to the NRTL model at each temperature except the binary tie line at 40°C where an erroneous estimation of the organic phase was noticed.

The values of the adjustible parameter, α, was fixed at each temperature as shown in Tables 1–5. Generally, α is independent of temperature and depends on the molecule's properties. Its values usually lie between 0.2 and 0.47 (8). In this work the effect of changing α was noticed at each temperature, and we adopted the value that yielded the best correlation of the experimental data using the NRTL model.

The NRTL equation is fitted to the experimental compositions by optimizing the interaction parameters a_{ij} and a_{ji} between each pair of molecules. The resulting values of the interaction were fitted linearly with the temperature according to the following equation:

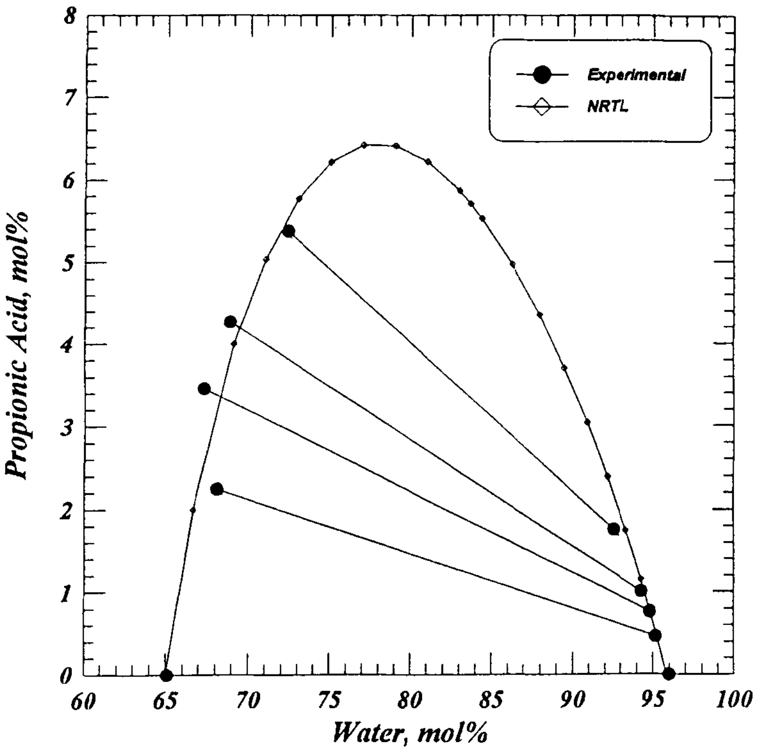

FIG. 3 LLE of the ternary system water (1) + propionic acid (2) + 2-butanol (3) at 35°C.

$$a_{ij} = a_{ij}^0 + b_{ij}[T\,(\mathrm{K}) - 273.15] \tag{11}$$

where a_{ij} is the interaction parameter between the molecules i and j in Kelvin and (a_{ij}^0 and b_{ij}) are the correlation constants between each two compounds in the system. The values of the correlation constants are shown in Table 6. The corresponding calculated tie lines are shown in Tables 1–5.

The root-mean-square deviations (RMSD) were calculated from the difference between the experimental data and the predictions of the NRTL model at each temperature according to the following formula:

$$\mathrm{RMSD} = \left\{\sum\nolimits_k \left[\sum\nolimits_i \sum\nolimits_j (x_{i,\mathrm{exp}} - x_{i,\mathrm{calcd}})_j^2\right]/4n\right\}^{1/2} \tag{12}$$

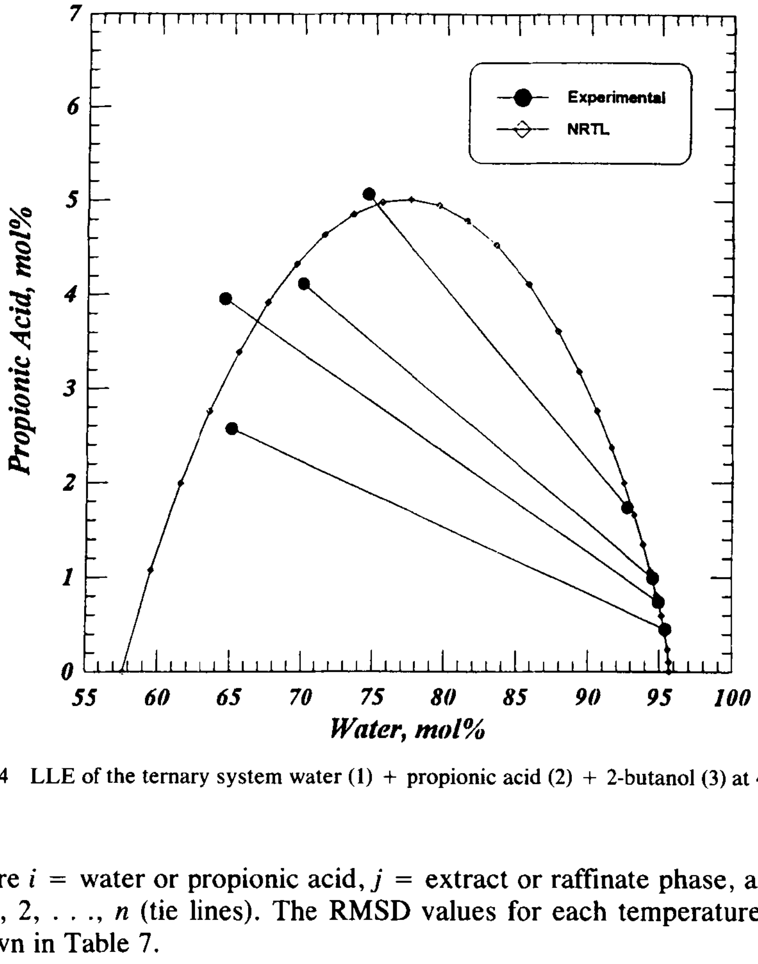

FIG. 4 LLE of the ternary system water (1) + propionic acid (2) + 2-butanol (3) at 40°C.

where i = water or propionic acid, j = extract or raffinate phase, and k = 1, 2, . . ., n (tie lines). The RMSD values for each temperature are shown in Table 7.

The average distribution coefficient, K, of propionic acid was calculated according the following equation:

TABLE 6

Optimum Interaction Parameters According the Equation $a_{ij} = a_{ij}^0 + b_{ij}[T\,(\mathrm{K}) - 273.15]$

i	j	a_{ij}^0 (K)	b_{ij}	a_{ji}^0 (K)	b_{ji}
H_2O	Propionic acid	−652.961	15.777	−423.796	10.603
H_2O	2-Butanol	1598.290	−15.629	−707.066	20.792
Propionic acid	2-Butanol	−952.468	10.870	889.807	−22.304

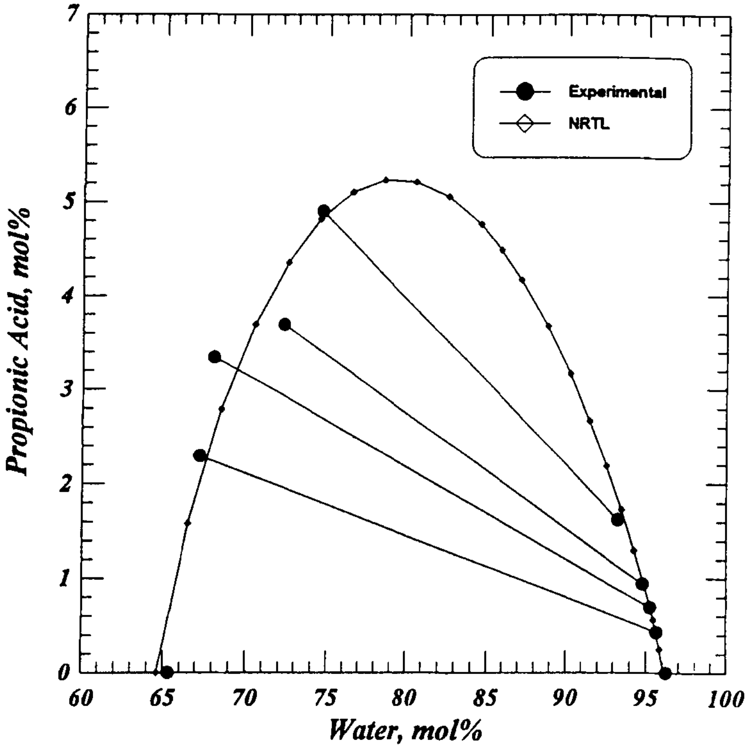

FIG. 5 LLE of the ternary system water (1) + propionic acid (2) + 2-butanol (3) at 45°C.

$$K = \frac{1}{n}\sum^{n} \frac{x^{E}_{\text{propionic acid}}}{x^{R}_{\text{propionic acid}}} \tag{13}$$

The temperature effect on the distribution coefficients was found to be moderate but positive. The predictions were fitted according to the follow-

TABLE 7
Values of RMSD% at Different Temperatures

T (K)	RMSD%
298	0.20
303	0.21
308	0.28
313	1.94
318	0.27
Average	0.58

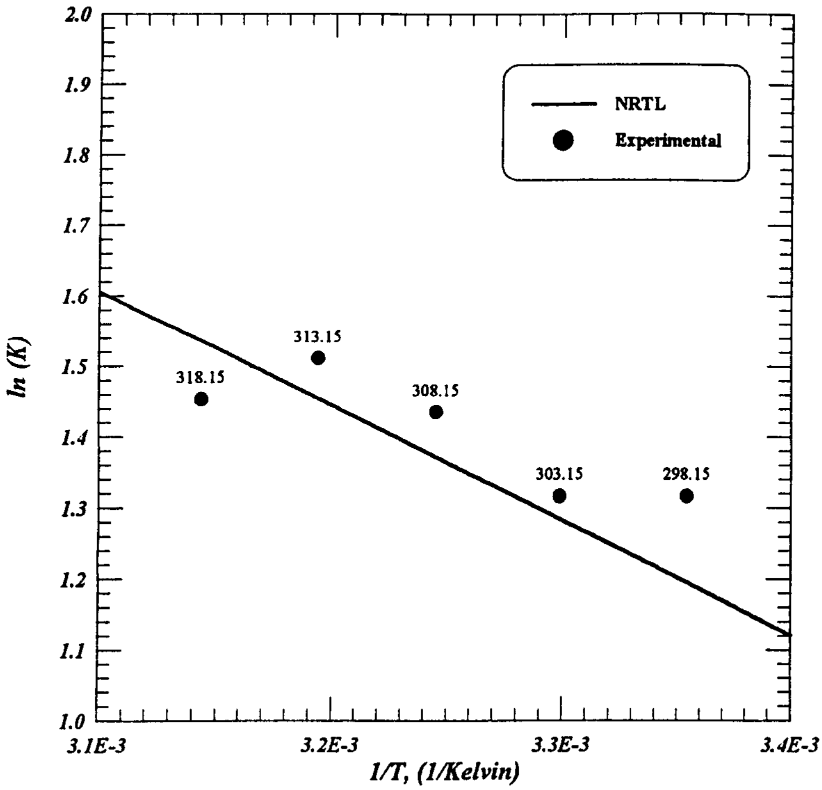

FIG. 6 The effect of temperature on the distribution coefficients of propionic acid.

ing equation:

$$K = A \exp(-E/RT) \tag{14}$$

where A is a constant, E is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. The experimental points

TABLE 8
The Fitting Constants of the Distribution Coefficients According Eq. (14)

Method	A	E (J·mol^{-1})
Experimental	74.41	7,433.81
NRTL model	744.56	13,428.94

and the predicted trend are shown in Fig. 6. The fitted values of *A* and *E* for each method are shown in Table 8.

CONCLUSIONS

The NRTL model was successfully used to regress the experimental equilibrium compositions of the studied system. The average RMSD value between the predicted and the experimental values was 0.58%.

The fitted activation energy has a value of 7,434 J/mol from the experimental data and 13,429 J/mol from the predictions of the NRTL model.

SYMBOLS

a	interaction parameter
a	activity
A	fitting parameter
b	fitting parameter
C	number of components
E	activation energy
g	Gibbs energy of interaction (per mole)
G	Gibbs energy of interaction
i	counter
j	counter
k	counter
K	distribution coefficient of propionic acid
n	number of tie lines
P	parameter value in the penalty terms
Q	penalty constant
R	universal gas constant
RMSD	root-mean-square deviation
T	temperature (K)
x	mole fraction
z	number of moles

Greek

α	adjustable parameter for the NRTL model
γ	activity coefficient
τ	binary interaction parameter

Superscripts

E	extract phase
R	raffinate phase

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