

# Liquid–liquid equilibria of ternary mixtures of water + 2-propanol with ethyl acetate, isopropyl acetate, or ethyl caproate

Gui-Bing Hong, Ming-Jer Lee\*, Ho-mu Lin

*Department of Chemical Engineering, National Taiwan University of Science and Technology,  
43 Keelung Road, Section 4, Taipei 106-07, Taiwan*

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## Abstract

Liquid–liquid equilibrium (LLE) data were measured for the ternary mixtures of water + 2-propanol + ethyl acetate, water + 2-propanol + isopropyl acetate, and water + 2-propanol + ethyl caproate at atmospheric pressure over a temperature range of 283.15–323.15 K. All these three ternary systems exhibit the type-1 behavior of LLE. The areas of two-phase region decrease with increasing temperature for each ternary system and decrease in the order of the mixtures containing ethyl caproate > isopropyl acetate > ethyl acetate. Ethyl caproate is a preferable entrainer for separation of 2-propanol from aqueous solutions. The UNIQUAC model with the model parameters determined from the constituent binaries qualitatively predicted the binodal locus. By adjusting six parameters simultaneously, the NRTL and the UNIQUAC models correlated well the LLE data.

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## 1. Introduction

2-Propanol (or isopropyl alcohol, IPA) is widely used as a cleaning agent in the production of many electronic devices. Since the mixture of 2-propanol and water forms a minimum boiling azeotrope at  $T^{\text{aze}} = 353.27$  K and  $x_{\text{IPA}}^{\text{aze}} = 0.68$  [1], the separation of 2-propanol from the spent aqueous solutions becomes economically infeasible by using traditional distillation method. Heterogeneous extractive distillation is one of alternative methods to separate such azeotropic mixtures. Phase equilibrium data of the aqueous mixtures with entrainer are fundamentally important for simulation and design of the separation processes [2]. The focus of this study is placed on the phase behavior of LLE for the mixtures of water + 2-propanol with one of three potential entrainers: ethyl acetate, isopropyl acetate, and ethyl caproate. The phase compositions of the two coexistent liquid-phases are measured at temperatures from 283.15 to 323.15 K. These new LLE data are correlated with the solution models of the NRTL [3] and of the UNIQUAC [4].

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\* Corresponding author. Tel.: +886-2-2737-6626; fax: +886-2-2737-6644.

E-mail address: mjl@ch.ntust.edu.tw (M.-J. Lee).

## 2. Experimental section

The schematic diagram of the LLE apparatus is similar to that of Peschke and Sandler [5]. The equilibrium cell is made of glass (internal volume about 30 cm<sup>3</sup>) with a jacket, in which thermostatic water is circulated to control the temperature of cell within  $\pm 0.1$  K. The cell temperature was measured by a precision thermometer (Model-1506, Hart Scientific, USA) with a platinum RTD probe to an accuracy of  $\pm 0.02$  K. The liquid mixture in the cell was agitated vigorously by a magnetic stirrer. For each run, the agitation was continued at least 4 h to sufficiently mix the compounds. The mixture was then settled at least 8 h to completely separate the two liquid phases. The sample of organic-rich phase was taken with a syringe from the top opening of the cell and that of water-rich phase from a sampling port at the bottom of the cell. This method can avoid cross contamination by the other phase during the sampling procedure.

The composition of sample was analyzed by a gas chromatography (GC) (Model: 8700, China Chromatography Co., Taiwan) with thermal conductivity detector (TCD). High purity helium (99.99%) was used as a carrier gas. A stainless steel column packed with 10% Porapak Qs 80/100 (2 m  $\times$  1/8 in.) can clearly separate the constituent compounds of the samples. Four to five samples were replicated for each phase at a fixed experimental condition. In general, the repeatability of the area fractions is about  $\pm 0.2\%$ . The averaged area fraction was converted into mole fraction by the calibration equations. Calibrations were made with gravimetrically prepared samples in two composition ranges, in accordance with those in the organic-rich and the water-rich phases for each aqueous binary system. The calibration coefficients were determined by fitting a polynomial equation to the calibration results for each composition range. The uncertainties of sample analysis for the minor components are tabulated in Table 1.

2-Propanol (99.5 mass%), ethyl acetate (99.8 mass%), and ethyl caproate (>99 mass%) were purchased from Aldrich, USA. Isopropyl acetate (>99 mass%) was supplied by Acros, USA. Deionized distilled water was prepared in our laboratory. No impurity peak was detected by the chromatographic analysis for any of the chemicals. These chemicals were used without further purification.

Table 1  
Average deviations of GC calibration

| Mixture                        | Phase   | Average deviation <sup>a</sup> |
|--------------------------------|---------|--------------------------------|
| Ethyl acetate + water          | Organic | 0.0026                         |
|                                | Aqueous | 0.00012                        |
| Isopropyl acetate + water      | Organic | 0.0020                         |
|                                | Aqueous | 0.00011                        |
| Ethyl caproate + water         | Organic | 0.0027                         |
|                                | Aqueous | 0.00005                        |
| 2-Propanol + ethyl acetate     | Organic | 0.0005                         |
|                                | Aqueous | 0.0005                         |
| 2-Propanol + isopropyl acetate | Organic | 0.0006                         |
|                                | Aqueous | 0.0006                         |
| 2-Propanol + ethyl caproate    | Organic | 0.0014                         |
|                                | Aqueous | 0.0014                         |

<sup>a</sup> Average deviation =  $1/n_p \sum_{j=1}^{n_p} (|x^{\text{calb}} - x^{\text{act}}|)_j$ , where  $n_p$  is the number of calibration points and  $x$  the mole fraction of the minor constituent compound. The superscript “calb” represents the calibrated values and “act” refers to the actual values.

### 3. Experimental results

The LLE measurements were made at temperatures from 283.15 to 323.15 K under atmospheric pressure. Tables 2–4 list the experimental results for water + 2-propanol with ethyl acetate, isopropyl acetate, or ethyl caproate, respectively. The superscript *i* represents the organic-rich phase and II, the aqueous phase. Figs. 1–4 are the phase diagrams for the ternary systems of water + 2-propanol + ethyl acetate, water + 2-propanol + isopropyl acetate, and water + 2-propanol + ethyl caproate, respectively. Because water/esters is the only pair that is partially miscible, all the investigated ternary systems behave as a type-1 of LLE. Small amounts of the organic compounds were detected in the aqueous phase, while water dissolved appreciably in the organic-rich phase, especially near the plait point. As seen from the figures, the area of the two-phase region obviously depends on the mutual solubilities of water and the esters (the edge of water/ester binary). The experimental results show that the solubilities of water in the esters increase with an increase of temperature. Also, the magnitude of solubility of water in the esters follows

Table 2

LLE data for water (1) + 2-propanol (2) + ethyl acetate (3) at atmospheric pressure

| <i>T</i> (K) | Organic phase |         |         | Aqueous phase |            |            |
|--------------|---------------|---------|---------|---------------|------------|------------|
|              | $x_1^I$       | $x_2^I$ | $x_3^I$ | $x_1^{II}$    | $x_2^{II}$ | $x_3^{II}$ |
| 283.15       | 0.111         | 0.000   | 0.889   | 0.981         | 0.000      | 0.019      |
|              | 0.140         | 0.032   | 0.828   | 0.969         | 0.011      | 0.020      |
|              | 0.179         | 0.065   | 0.756   | 0.959         | 0.020      | 0.021      |
|              | 0.234         | 0.100   | 0.666   | 0.949         | 0.030      | 0.021      |
|              | 0.282         | 0.124   | 0.594   | 0.943         | 0.036      | 0.021      |
|              | 0.337         | 0.145   | 0.518   | 0.935         | 0.042      | 0.023      |
|              | 0.409         | 0.162   | 0.429   | 0.926         | 0.050      | 0.024      |
|              | 0.432         | 0.165   | 0.403   | 0.924         | 0.051      | 0.025      |
|              | 0.539         | 0.168   | 0.293   | 0.909         | 0.061      | 0.030      |
|              | 0.674         | 0.149   | 0.177   | 0.876         | 0.080      | 0.044      |
| 308.15       | 0.161         | 0.000   | 0.839   | 0.985         | 0.000      | 0.015      |
|              | 0.200         | 0.032   | 0.768   | 0.979         | 0.006      | 0.015      |
|              | 0.226         | 0.058   | 0.716   | 0.976         | 0.008      | 0.016      |
|              | 0.276         | 0.089   | 0.635   | 0.970         | 0.016      | 0.014      |
|              | 0.330         | 0.120   | 0.550   | 0.960         | 0.023      | 0.017      |
|              | 0.352         | 0.130   | 0.518   | 0.955         | 0.026      | 0.019      |
|              | 0.389         | 0.143   | 0.468   | 0.952         | 0.030      | 0.018      |
|              | 0.490         | 0.164   | 0.346   | 0.941         | 0.039      | 0.020      |
|              | 0.591         | 0.160   | 0.249   | 0.917         | 0.052      | 0.031      |
| 323.15       | 0.184         | 0.000   | 0.816   | 0.987         | 0.000      | 0.013      |
|              | 0.240         | 0.048   | 0.712   | 0.979         | 0.007      | 0.014      |
|              | 0.286         | 0.085   | 0.629   | 0.973         | 0.013      | 0.014      |
|              | 0.360         | 0.124   | 0.516   | 0.959         | 0.021      | 0.020      |
|              | 0.431         | 0.152   | 0.417   | 0.951         | 0.027      | 0.022      |
|              | 0.543         | 0.158   | 0.299   | 0.941         | 0.037      | 0.022      |
|              | 0.541         | 0.162   | 0.297   | 0.939         | 0.037      | 0.024      |
|              | 0.578         | 0.160   | 0.262   | 0.932         | 0.042      | 0.026      |
|              | 0.601         | 0.156   | 0.243   | 0.931         | 0.043      | 0.026      |

Table 3

LLE data for water (1) + 2-propanol (2) + isopropyl acetate (3) at atmospheric pressure

| <i>T</i> (K) | Organic phase |         |         | Aqueous phase |            |            |
|--------------|---------------|---------|---------|---------------|------------|------------|
|              | $x_1^I$       | $x_2^I$ | $x_3^I$ | $x_1^{II}$    | $x_2^{II}$ | $x_3^{II}$ |
| 283.15       | 0.074         | 0.000   | 0.926   | 0.993         | 0.000      | 0.007      |
|              | 0.090         | 0.035   | 0.875   | 0.979         | 0.014      | 0.007      |
|              | 0.114         | 0.071   | 0.815   | 0.970         | 0.023      | 0.007      |
|              | 0.163         | 0.128   | 0.709   | 0.956         | 0.038      | 0.006      |
|              | 0.192         | 0.155   | 0.653   | 0.951         | 0.042      | 0.007      |
|              | 0.259         | 0.202   | 0.539   | 0.941         | 0.052      | 0.007      |
|              | 0.359         | 0.241   | 0.400   | 0.927         | 0.065      | 0.008      |
|              | 0.404         | 0.250   | 0.346   | 0.925         | 0.066      | 0.009      |
|              | 0.496         | 0.252   | 0.252   | 0.917         | 0.075      | 0.008      |
| 308.15       | 0.613         | 0.230   | 0.157   | 0.892         | 0.092      | 0.016      |
|              | 0.111         | 0.000   | 0.889   | 0.995         | 0.000      | 0.005      |
|              | 0.150         | 0.056   | 0.794   | 0.971         | 0.023      | 0.006      |
|              | 0.186         | 0.106   | 0.708   | 0.966         | 0.028      | 0.006      |
|              | 0.222         | 0.144   | 0.634   | 0.908         | 0.95       | 0.042      |
|              | 0.317         | 0.202   | 0.481   | 0.942         | 0.050      | 0.008      |
|              | 0.415         | 0.237   | 0.348   | 0.931         | 0.060      | 0.009      |
|              | 0.484         | 0.250   | 0.266   | 0.920         | 0.069      | 0.011      |
|              | 0.536         | 0.243   | 0.221   | 0.916         | 0.072      | 0.012      |
| 323.15       | 0.139         | 0.000   | 0.861   | 0.996         | 0.000      | 0.004      |
|              | 0.182         | 0.063   | 0.755   | 0.985         | 0.009      | 0.006      |
|              | 0.244         | 0.150   | 0.606   | 0.972         | 0.022      | 0.006      |
|              | 0.292         | 0.185   | 0.523   | 0.965         | 0.027      | 0.008      |
|              | 0.378         | 0.233   | 0.389   | 0.954         | 0.037      | 0.009      |
|              | 0.435         | 0.243   | 0.322   | 0.946         | 0.043      | 0.011      |
|              | 0.435         | 0.244   | 0.321   | 0.945         | 0.044      | 0.011      |
|              | 0.505         | 0.244   | 0.251   | 0.941         | 0.049      | 0.010      |
|              | 0.617         | 0.229   | 0.154   | 0.917         | 0.066      | 0.017      |
|              | 0.698         | 0.208   | 0.094   | 0.881         | 0.095      | 0.024      |

the sequence of ethyl acetate > isopropyl acetate > ethyl caproate at the same conditions. The areas of the two-phase region, therefore, decrease with an increase of temperature for each ternary system and decrease in the order of the mixtures containing ethyl caproate > isopropyl acetate > ethyl acetate.

In order to compare the capability of the auxiliary agents for separation of 2-propanol from aqueous solutions with liquid–liquid extraction, the separation factors (*S*) were calculated for each system. The separation factor is defined as

$$S = \frac{X_{\text{IPA}}^I (1 - X_{\text{IPA}}^{II})}{X_{\text{IPA}}^{II} (1 - X_{\text{IPA}}^I)} \quad (1)$$

with

$$X_{\text{IPA}}^I = \frac{x_{\text{IPA}}^I}{x_{\text{IPA}}^I + x_{\text{W}}^I} \quad (\text{in organic phase}) \quad (2)$$

Table 4

LLE data for water (1) + 2-propanol (2) + ethyl caproate (3) at atmospheric pressure

| <i>T</i> (K) | Organic phase |         |         | Aqueous phase |            |            |
|--------------|---------------|---------|---------|---------------|------------|------------|
|              | $x_1^I$       | $x_2^I$ | $x_3^I$ | $x_1^{II}$    | $x_2^{II}$ | $x_3^{II}$ |
| 283.15       | 0.031         | 0.000   | 0.969   | 0.9996        | 0.0000     | 0.0004     |
|              | 0.037         | 0.054   | 0.909   | 0.9844        | 0.0147     | 0.0009     |
|              | 0.056         | 0.116   | 0.828   | 0.9731        | 0.0262     | 0.0007     |
|              | 0.086         | 0.205   | 0.709   | 0.9582        | 0.0390     | 0.0028     |
|              | 0.122         | 0.282   | 0.596   | 0.9534        | 0.0442     | 0.0024     |
|              | 0.169         | 0.353   | 0.478   | 0.9493        | 0.0485     | 0.0022     |
|              | 0.213         | 0.386   | 0.401   | 0.9467        | 0.0521     | 0.0012     |
|              | 0.268         | 0.417   | 0.315   | 0.9398        | 0.0579     | 0.0023     |
|              | 0.322         | 0.427   | 0.251   | 0.9364        | 0.0609     | 0.0027     |
|              | 0.445         | 0.400   | 0.155   | 0.9306        | 0.0676     | 0.0018     |
|              | 0.587         | 0.330   | 0.083   | 0.9013        | 0.0936     | 0.0051     |
| 308.15       | 0.040         | 0.000   | 0.960   | 0.9997        | 0.0000     | 0.0003     |
|              | 0.070         | 0.091   | 0.839   | 0.9860        | 0.0126     | 0.0014     |
|              | 0.112         | 0.188   | 0.700   | 0.9740        | 0.0231     | 0.0029     |
|              | 0.150         | 0.282   | 0.568   | 0.9668        | 0.0309     | 0.0023     |
|              | 0.187         | 0.332   | 0.481   | 0.9644        | 0.0340     | 0.0016     |
|              | 0.239         | 0.381   | 0.380   | 0.9585        | 0.0395     | 0.0020     |
|              | 0.288         | 0.400   | 0.312   | 0.9485        | 0.0481     | 0.0034     |
|              | 0.347         | 0.403   | 0.250   | 0.9472        | 0.0491     | 0.0037     |
|              | 0.399         | 0.403   | 0.198   | 0.9434        | 0.0531     | 0.0035     |
|              | 0.523         | 0.358   | 0.119   | 0.9343        | 0.0629     | 0.0028     |
|              | 0.669         | 0.277   | 0.054   | 0.8979        | 0.0956     | 0.0065     |
| 323.15       | 0.045         | 0.000   | 0.955   | 0.9999        | 0.0000     | 0.0001     |
|              | 0.083         | 0.114   | 0.803   | 0.9893        | 0.0098     | 0.0009     |
|              | 0.124         | 0.213   | 0.663   | 0.9797        | 0.0192     | 0.0011     |
|              | 0.170         | 0.296   | 0.534   | 0.9705        | 0.0274     | 0.0021     |
|              | 0.201         | 0.348   | 0.452   | 0.9652        | 0.0315     | 0.0033     |
|              | 0.242         | 0.389   | 0.369   | 0.9617        | 0.0355     | 0.0028     |
|              | 0.297         | 0.400   | 0.303   | 0.9553        | 0.0427     | 0.0020     |
|              | 0.363         | 0.400   | 0.237   | 0.9559        | 0.0415     | 0.0026     |
|              | 0.428         | 0.391   | 0.181   | 0.9509        | 0.0473     | 0.0018     |
|              | 0.557         | 0.341   | 0.102   | 0.9423        | 0.0558     | 0.0019     |
|              | 0.700         | 0.250   | 0.050   | 0.9020        | 0.0908     | 0.0072     |

$$X'_{\text{IPA}} = \frac{x_{\text{IPA}}^{\text{II}}}{x_{\text{IPA}}^{\text{II}} + x_{\text{W}}^{\text{II}}} \quad (\text{in aqueous phase}) \quad (3)$$

where  $X'_{\text{IPA}}$  represents the mole fraction of 2-propanol on the solvent-free basis. Fig. 5 presents the variations of both  $X'_{\text{IPA}}$  and the separation factor with  $X'_{\text{IPA}}$  for water + 2-propanol + ethyl acetate, water + 2-propanol + isopropyl acetate, and water + 2-propanol + ethyl caproate at 308.15 K. Ethyl caproate gives higher separation factors, comparing with other two entrainers.

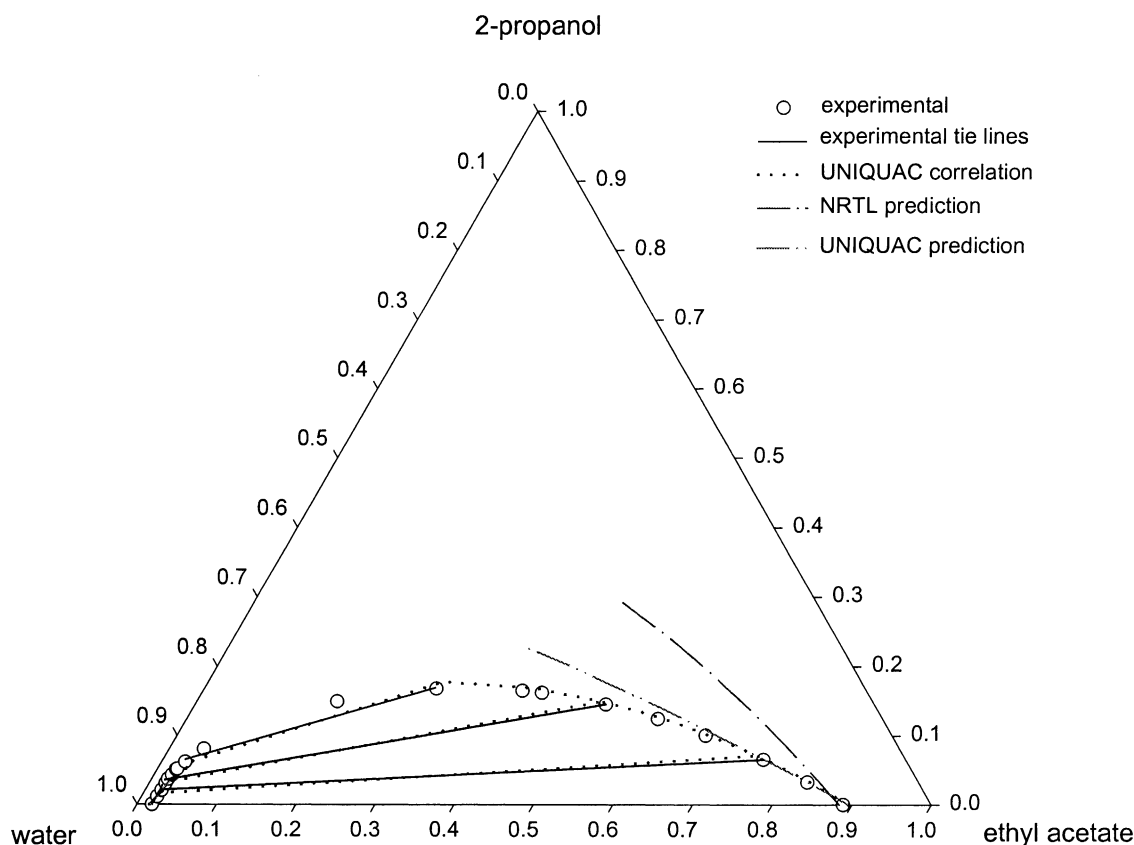


Fig. 1. LLE phase diagram for water + 2-propanol + ethyl acetate at 283.15 K.

#### 4. LLE calculation

At liquid–liquid equilibrium, the compositions of two coexistent liquid-phases can be calculated from the criteria of LLE (equality of the constituent fugacities between the coexistent phases) together with the material balance equation. The calculation procedure was detailed in Walas [6]. Based on 1 mol of feed with total composition  $z_i$ , the compositions of the coexistent liquid-phases are solved simultaneously from the following equations:

$$1 - \sum_{i=1}^{n_c} \frac{z_i}{\beta + K_i(1 - \beta)} = 0 \quad (4)$$

with

$$K_i = \frac{x_i^{\text{II}}}{x_i^{\text{I}}} = \frac{\gamma_i^{\text{I}}}{\gamma_i^{\text{II}}} \quad (5)$$

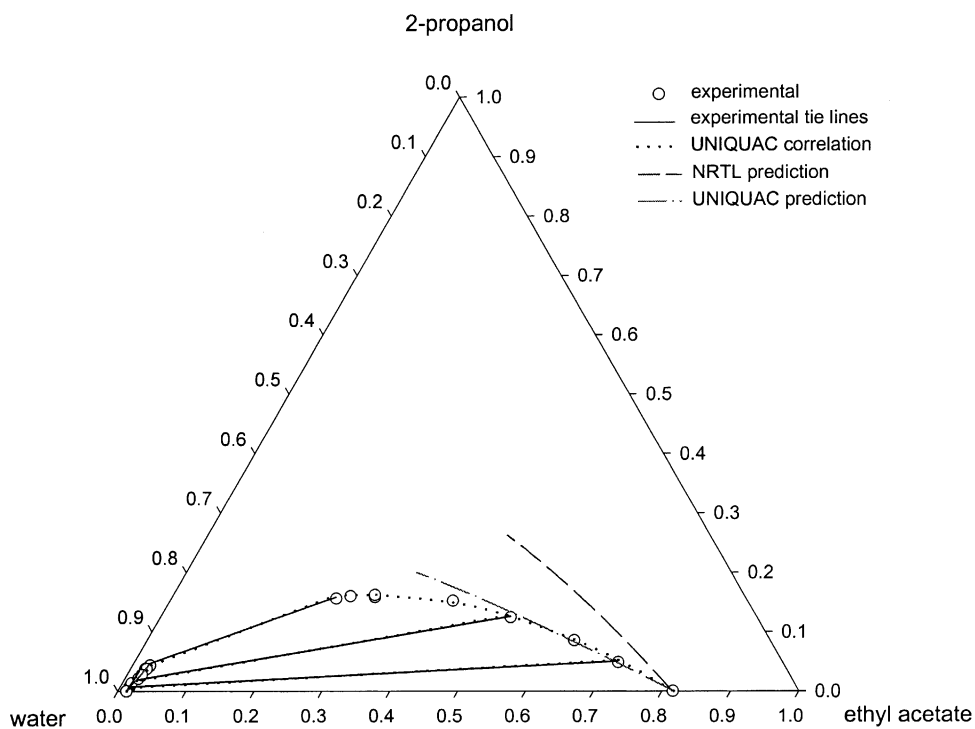


Fig. 2. LLE phase diagram for water + 2-propanol + ethyl acetate at 323.15 K.

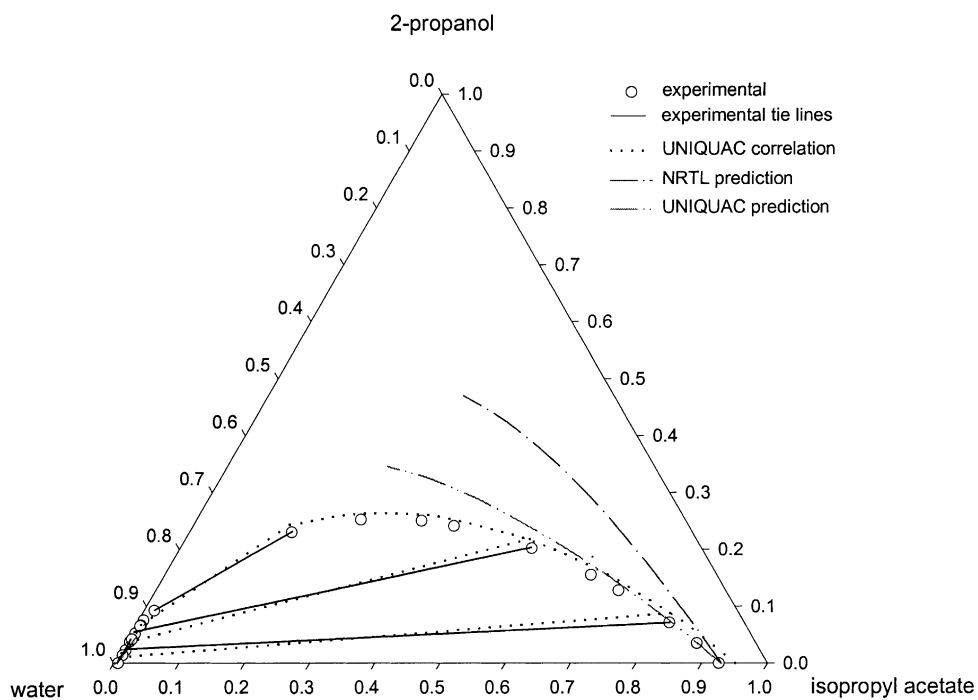


Fig. 3. LLE phase diagram for water + 2-propanol + isopropyl acetate at 283.15 K.

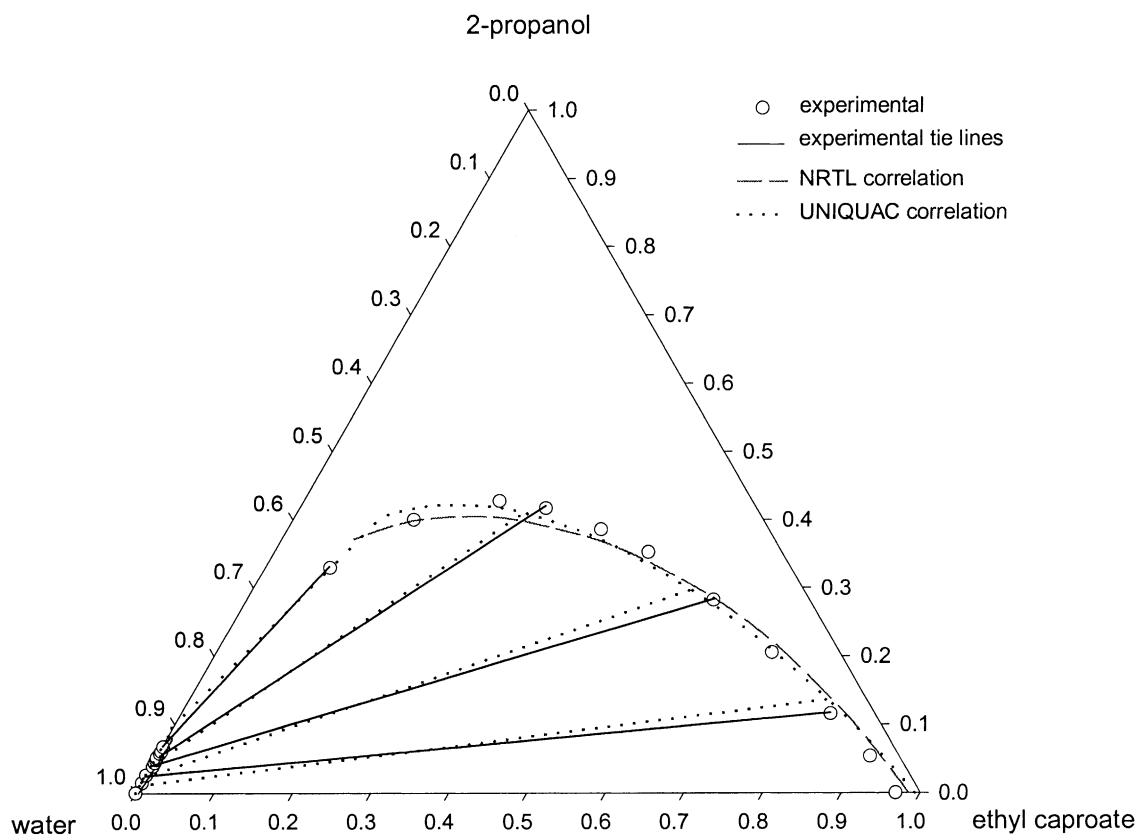


Fig. 4. LLE phase diagram for water + 2-propanol + ethyl caproate at 283.15 K.

where  $\beta$  is the fraction of the total material presented in the first liquid phase (the organic-rich phase),  $n_c$  the number of components, and  $K_i$  the distribution ratio for component  $i$ . The activity coefficient  $\gamma_i$  is calculated from a solution model. Among several others, the NRTL or the UNIQUAC model is commonly to be chosen to implement LLE calculation. Theoretically, the LLE behavior of a ternary system can be estimated from a solution model with the model parameters determined from phase-equilibrium data of the constituent binaries. Tables 5 and 6 list the binary parameters of the NRTL and the UNIQUAC models, respectively, for the constituent 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 vapor–liquid equilibrium (VLE) binary data. Since the VLE data of 2-propanol + ethyl caproate are currently unavailable, the LLE prediction did not include the ternary system of water + 2-propanol + ethyl caproate. The predicted results from these two solution models are also reported in Tables 5 and 6. Figs. 1–3 show that the NRTL model appears to overestimate the two-phase region. The UNIQUAC model reproduces well a portion of the binodal locus, but the deviations from the experimental values become substantially large in the region near the plait point.

In order to improve representation of the binodal locus, the isothermal ternary LLE data were correlated with the NRTL and the UNIQUAC models by adjusting six model-parameters simultaneously.



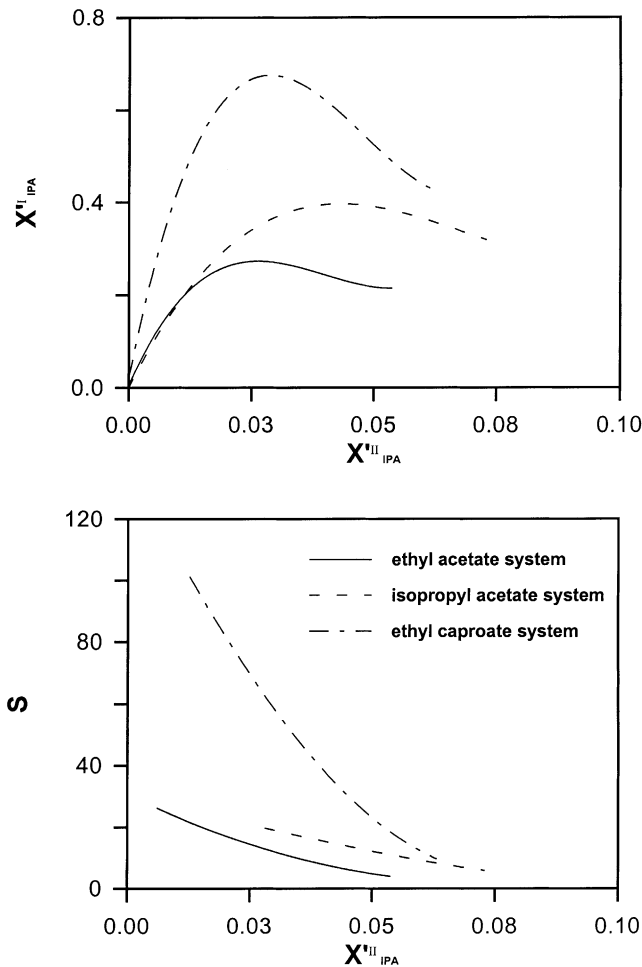


Fig. 5. Separation factors and distributions of 2-propanol in two liquid-phases at 308.15 K.

The objective function of the parameter determination is defined as

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

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  $n$  the number of tie-lines. Tables 7 and 8 present the correlated results from the NRTL and the UNIQUAC, respectively. In general, the average deviations from the NRTL model are slightly smaller than those from the UNIQUAC model, except for the system containing ethyl acetate. In Figs. 1–4, the correlated binodal locus and tie-lines obtained from the UNIQUAC model are compared with the experimental results. As expected, the results of data correlation are much better than those of the prediction with the model parameters determined from the constituent binaries.

Table 5

Predicted results from the NRTL model with parameters determined from phase equilibrium data of the constituent binaries

| Mixture <sup>a</sup> | <i>T</i> (K) | <i>i</i> – <i>j</i> | $\alpha_{ij}$ | $a_{ij}$ (K) <sup>b</sup> | $a_{ji}$ (K) <sup>b</sup> | Data source <sup>c</sup> | $\Delta^d$ |
|----------------------|--------------|---------------------|---------------|---------------------------|---------------------------|--------------------------|------------|
| M1                   | 283.15       | 1–2                 | 0.2875        | 927.63                    | –55.35                    | [7]                      | 0.0592     |
|                      |              | 1–3                 | 0.2           | 977.74                    | 231.71                    | [8]                      |            |
|                      |              | 2–3                 | 0.37          | 26.56                     | 200.28                    | [9]                      |            |
|                      | 308.15       | 1–2                 | 0.2875        | 927.63                    | –55.35                    | [7]                      | 0.0457     |
|                      |              | 1–3                 | 0.2           | 1208.21                   | 141.33                    | [8]                      |            |
|                      |              | 2–3                 | 0.37          | 26.56                     | 200.28                    | [9]                      |            |
|                      | 323.15       | 1–2                 | 0.2875        | 927.63                    | –55.35                    | [7]                      | 0.0593     |
|                      |              | 1–3                 | 0.2           | 1346.90                   | 87.12                     | [8]                      |            |
|                      |              | 2–3                 | 0.37          | 26.56                     | 200.28                    | [9]                      |            |
| M2                   | 283.15       | 1–2                 | 0.2875        | 927.63                    | –55.35                    | [7]                      | 0.0557     |
|                      |              | 1–3                 | 0.2           | 1254.34                   | 316.89                    | [8]                      |            |
|                      |              | 2–3                 | 0.801         | 113.46                    | 209.92                    | [10]                     |            |
|                      | 308.15       | 1–2                 | 0.2875        | 927.63                    | –55.35                    | [7]                      | 0.0623     |
|                      |              | 1–3                 | 0.2           | 1500.04                   | 234.66                    | [8]                      |            |
|                      |              | 2–3                 | 0.801         | 113.46                    | 209.92                    | [10]                     |            |
|                      | 323.15       | 1–2                 | 0.2875        | 927.63                    | –55.35                    | [7]                      | 0.0714     |
|                      |              | 1–3                 | 0.2           | 1647.45                   | 185.33                    | [8]                      |            |
|                      |              | 2–3                 | 0.801         | 113.46                    | 209.92                    | [10]                     |            |

<sup>a</sup> M1: water (1) + 2-propanol (2) + ethyl acetate (3); M2: water (1) + 2-propanol (2) + isopropyl acetate (3).<sup>b</sup>  $a_{ij} = (g_{ij} - g_{ji})/R$ .<sup>c</sup> References [7], [9], and [10] provide binary VLE data; reference [8] provides binary LLE data.<sup>d</sup>  $\Delta = (\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 |(\hat{x}_{ijk} - x_{ijk})|)/6n$ , where *n* is the number of tie-lines.

Table 6

Predicted results from the UNIQUAC model with parameters determined from phase equilibrium data of the constituent binaries

| Mixture <sup>a</sup> | <i>T</i> (K) | <i>i</i> – <i>j</i> | $b_{ij}$ (K) <sup>b</sup> | $b_{ji}$ (K) <sup>b</sup> | Data source <sup>c</sup> | $\Delta^d$ |
|----------------------|--------------|---------------------|---------------------------|---------------------------|--------------------------|------------|
| M1                   | 283.15       | 1–2                 | –9.69                     | 206.14                    | [7]                      | 0.0175     |
|                      |              | 1–3                 | 65.15                     | 446.44                    | [8]                      |            |
|                      |              | 2–3                 | –227.14                   | 580.08                    | [9]                      |            |
|                      | 308.15       | 1–2                 | –9.69                     | 206.14                    | [7]                      | 0.0137     |
|                      |              | 1–3                 | 131.58                    | 335.55                    | [8]                      |            |
|                      |              | 2–3                 | –227.14                   | 580.08                    | [9]                      |            |
|                      | 323.15       | 1–2                 | –9.69                     | 206.14                    | [7]                      | 0.0216     |
|                      |              | 1–3                 | 129.73                    | 337.95                    | [8]                      |            |
|                      |              | 2–3                 | –227.14                   | 580.08                    | [9]                      |            |
| M2                   | 283.15       | 1–2                 | –9.69                     | 206.14                    | [7]                      | 0.0229     |
|                      |              | 1–3                 | 64.92                     | 521.51                    | [8]                      |            |
|                      |              | 2–3                 | –195.13                   | 470.79                    | [10]                     |            |
|                      | 308.15       | 1–2                 | –9.69                     | 206.14                    | [7]                      | 0.0276     |
|                      |              | 1–3                 | 8.69                      | 562.27                    | [8]                      |            |
|                      |              | 2–3                 | –195.13                   | 470.79                    | [10]                     |            |

Table 6 (Continued)

| Mixture <sup>a</sup> | <i>T</i> (K)               | <i>i</i> – <i>j</i> | <i>b</i> <sub><i>ij</i></sub> (K) <sup>b</sup> | <i>b</i> <sub><i>ji</i></sub> (K) <sup>b</sup> | Data source <sup>c</sup> | $\Delta$ <sup>d</sup> |
|----------------------|----------------------------|---------------------|--|--|--------------------------|-----------------------|
|                      | 323.15                     | 1–2                 | −9.69  | 206.14   | [7]                      | 0.0172                |
|                      |                            | 1–3                 | 87.57  | 403.57   | [8]                      |                       |
|                      |                            | 2–3                 | −195.13  | 470.79   | [10]                     |                       |
| Component            | Structural parameters [11] |                     |  |  |                          |                       |
|                      | <i>r</i>                   | <i>q</i>            |  |  |                          |                       |
| Water                | 0.9200                     | 1.4000              |  |  |                          |                       |
| 2-Propanol           | 2.7791                     | 2.5080              |  |  |                          |                       |
| Ethyl acetate        | 3.4786                     | 3.1160              |  |  |                          |                       |
| Isopropyl acetate    | 4.1522                     | 3.6520              |  |  |                          |                       |
| Ethyl caproate       | 6.1762                     | 5.2760              |  |  |                          |                       |

<sup>a</sup> M1: water (1) + 2-propanol (2) + ethyl acetate (3); M2: water (1) + 2-propanol (2) + isopropyl acetate (3).

<sup>b</sup>  $b_{ij} = (u_{ij} - u_{ji})/R$ .

<sup>c</sup> References [7], [9], and [10] provide binary VLE data; reference [8] provides binary LLE data.

<sup>d</sup>  $\Delta = (\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 |(\hat{x}_{ijk} - x_{ijk})|)/6n$ , where *n* is the number of tie-lines.

Table 7

Correlated results from the NRTL model

| Mixture <sup>a</sup> | <i>T</i> (K) | $\alpha_{ij}$ | <i>I</i> – <i>j</i> | <i>a</i> <sub><i>ij</i></sub> (K) <sup>b</sup> | <i>a</i> <sub><i>ji</i></sub> (K) <sup>b</sup> | $\Delta$ <sup>c</sup> |
|----------------------|--------------|---------------|---------------------|--|--|-----------------------|
| M1                   | 283.15       | 0.2           | 1–2                 | 169.52   | 18.17  | 0.0100                |
|                      |              |               | 1–3                 | 1067.58  | 236.67   |                       |
|                      |              |               | 2–3                 | –681.13  | 1382.45  |                       |
|                      | 308.15       | 0.2           | 1–2                 | 435.13   | 18.52  | 0.0163                |
|                      |              |               | 1–3                 | 997.40   | 187.78   |                       |
|                      |              |               | 2–3                 | –725.08  | 1447.41  |                       |
|                      | 323.15       | 0.2           | 1–2                 | 467.20   | –165.86  | 0.0140                |
|                      |              |               | 1–3                 | 1441.71  | 60.09  |                       |
|                      |              |               | 2–3                 | –796.73  | 1625.96  |                       |
| M2                   | 283.15       | 0.2           | 1–2                 | 1179.52  | –506.54  | 0.0062                |
|                      |              |               | 1–3                 | 1258.71  | 334.04   |                       |
|                      |              |               | 2–3                 | –523.93  | 1140.55  |                       |
|                      | 308.15       | 0.2           | 1–2                 | 1455.67  | –466.48  | 0.0178                |
|                      |              |               | 1–3                 | 981.74   | 353.77   |                       |
|                      |              |               | 2–3                 | 152.20   | 268.66   |                       |
|                      | 323.15       | 0.2           | 1–2                 | 1397.22  | –562.53  | 0.0074                |
|                      |              |               | 1–3                 | 1306.77  | 199.51   |                       |
|                      |              |               | 2–3                 | –233.61  | 187.16   |                       |
| M3                   | 283.15       | 0.2           | 1–2                 | 1085.98  | –315.31  | 0.0095                |
|                      |              |               | 1–3                 | 1133.76  | 723.66   |                       |
|                      |              |               | 2–3                 | –205.29  | 453.46   |                       |
|                      | 308.15       | 0.2           | 1–2                 | 1117.68  | –298.34  | 0.0146                |
|                      |              |               | 1–3                 | 1081.53  | 581.64   |                       |
|                      |              |               | 2–3                 | –258.90  | 443.76   |                       |

Table 7 (Continued)

| Mixture <sup>a</sup> | <i>T</i> (K) | $\alpha_{ij}$ | <i>I</i> – <i>j</i> | <i>a</i> <sub><i>ij</i></sub> (K) <sup>b</sup> | <i>a</i> <sub><i>ji</i></sub> (K) <sup>b</sup> | $\Delta^c$ |
|----------------------|--------------|---------------|---------------------|--|--|------------|
|                      | 323.15       | 0.2           | 1–2                 | 1287.92  | –415.31  | 0.0158     |
|                      |              |               | 1–3                 | 1226.11  | 637.26   |            |
|                      |              |               | 2–3                 | –401.74  | 262.10   |            |

<sup>a</sup> M1: water (1) + 2-propanol (2) + ethyl acetate (3); M2: water (1) + 2-propanol (2) + isopropyl acetate (3); M3: water (1) + 2-propanol (2) + ethyl caproate (3).

<sup>b</sup>  $a_{ij} = (g_{ij} - g_{ji})/R$ .

<sup>c</sup>  $\Delta = (\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 |(\hat{x}_{ijk} - x_{ijk})|)/6n$ , where *n* is the number of tie-lines.

Table 8

Correlated results from the UNIQUAC model

| Mixture <sup>a</sup> | <i>T</i> (K) | <i>i</i> – <i>j</i> | <i>b</i> <sub><i>ij</i></sub> (K) <sup>b</sup> | <i>b</i> <sub><i>ji</i></sub> (K) <sup>b</sup> | $\Delta^c$ |
|----------------------|--------------|---------------------|--|--|------------|
| M1                   | 283.15       | 1–2                 | 287.43   | –122.53  | 0.0050     |
|                      |              | 1–3                 | 65.15  | 446.44   |            |
|                      |              | 2–3                 | 218.00   | –36.78   |            |
|                      | 308.15       | 1–2                 | 294.18   | –139.07  | 0.0021     |
|                      |              | 1–3                 | 131.58   | 335.55   |            |
|                      |              | 2–3                 | 797.05   | –244.10  |            |
|                      | 323.15       | 1–2                 | 311.09   | –132.25  | 0.0022     |
|                      |              | 1–3                 | 129.73   | 337.95   |            |
|                      |              | 2–3                 | 783.35   | –248.26  |            |
| M2                   | 283.15       | 1–2                 | 319.23   | –152.07  | 0.0117     |
|                      |              | 1–3                 | 144.92   | 521.51   |            |
|                      |              | 2–3                 | 402.35   | –180.59  |            |
|                      | 308.15       | 1–2                 | 375.84   | –138.68  | 0.0179     |
|                      |              | 1–3                 | 98.69  | 562.27   |            |
|                      |              | 2–3                 | 386.90   | –78.55   |            |
|                      | 323.15       | 1–2                 | 276.68   | –155.50  | 0.0095     |
|                      |              | 1–3                 | 139.57   | 403.57   |            |
|                      |              | 2–3                 | 193.36   | –198.66  |            |
| M3                   | 283.15       | 1–2                 | 424.28   | –185.72  | 0.0173     |
|                      |              | 1–3                 | 250.80   | 870.59   |            |
|                      |              | 2–3                 | 18.88  | –69.56   |            |
|                      | 308.15       | 1–2                 | 448.45   | –198.20  | 0.0168     |
|                      |              | 1–3                 | 196.08   | 924.28   |            |
|                      |              | 2–3                 | 19.00  | –89.64   |            |
|                      | 323.15       | 1–2                 | 436.33   | –251.06  | 0.0162     |
|                      |              | 1–3                 | 363.97   | 657.28   |            |
|                      |              | 2–3                 | 211.53   | –367.89  |            |

<sup>a</sup> M1: water (1) + 2-propanol (2) + ethyl acetate (3); M2: water (1) + 2-propanol (2) + isopropyl acetate (3); M3: water (1) + 2-propanol (2) + ethyl caproate (3).

<sup>b</sup>  $b_{ij} = (u_{ij} - u_{ji})/R$ .

<sup>c</sup>  $\Delta = (\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 |(\hat{x}_{ijk} - x_{ijk})|)/6n$ , where *n* is the number of tie-lines.

## 5. Conclusions

LLE data are reported for the ternary mixtures of water + 2-propanol + ethyl acetate, water + 2-propanol + isopropyl acetate, and water + 2-propanol + ethyl caproate at temperatures from 283.15 to 323.15 K. Each ternary system exhibits a type-1 behavior of LLE. Over the experimental conditions, the two-phase region decreases with increasing temperature. Ethyl caproate is found to be a preferable entrainer for separation of 2-propanol from aqueous solutions. The binodal locus can be predicted qualitatively from the UNIQUAC model with the parameters determined from the phase equilibrium data of the constituent binaries. In general, the LLE data can be correlated well with the NRTL or the UNIQUAC model, when the six model-parameters were adjusted simultaneously.

### List of symbols

|                 |   |
|-----------------|---|
| $a$             | parameters of the NRTL model (K)  |
| $b$             | parameters of the UNIQUAC model (K)                                     |
| $K_i$           | distribution ratio for component $i$                                    |
| $n$             | number of tie-lines   |
| $n_c$           | number of components  |
| $n_p$           | number of calibration points  |
| $S$             | separation factor   |
| $T$             | temperature (K)   |
| $x$             | mole fraction   |
| $x_{ijk}$       | observed mole fractions of component $i$ in phase $j$ on tie-line $k$   |
| $\hat{x}_{ijk}$ | calculated mole fractions of component $i$ in phase $j$ on tie-line $k$ |
| $X'$            | solvent-free mole fraction  |
| $z_i$           | total composition of component $i$ in feed                              |

### Greek letters

|          |  |
|----------|--|
| $\alpha$ | non-randomness parameter in the NRTL model                         |
| $\beta$  | fraction of the total material presented in the first liquid phase |
| $\gamma$ | activity coefficient   |
| $\Delta$ | objective function   |

### Subscripts

|      |                                   |
|------|-----------------------------------|
| $i$  | component $i$                     |
| $ij$ | interactions of $i$ – $j$ pair    |
| IPA  | 2-propanol (or isopropyl alcohol) |
| $ji$ | interaction of $j$ – $i$ pair     |
| W    | water                             |

### Superscripts

|      |                  |
|------|------------------|
| act  | actual value     |
| aze  | azeotropic       |
| calb | calibrated value |
| I    | organic phase    |
| II   | aqueous phase    |

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