UNIFAC 모델을 이용한 삼성분계(용매+물+부탄산) 액-액 평형

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Liquid-liquid equilibrium of the ternary system (solvents + water + butyric acid) with UNIFAC model at 25 ℃ and atmospheric pressure

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Introduction

The extraction of organic acids from aqueous media and other broth has been investigated in connection with the development of the biotechnology in the last decade. The efficient separation of organic acids from aqueous solutions is of economic importance in the chemical industry, for example in the fermentation industry. Solvent extraction processes as a promising recovery technique have been proposed as an alternative to the conventional precipitation process, and many solvents have been tried to improve such recovery [1].

Butyric acid is employed in the diary or food industries to increase the fragrance of beverages or foodstuffs, in the pharmaceutical industry, and as a raw material for the production of biodegradable polymers based on β-hydroxy-butyrate. This makes biotechnological production of butyric acid interesting [2].

The purpose of this work is to determine liquid-liquid equilibrium (LLE) data of *o*-xylene + water + butyric acid, ethyl ether + water + butyric acid, isopropyl acetate + water + butyric acid, ethyl acetate + water + butyric acid, and the LLE data for the ternary systems were measured at 25 ℃ and atmospheric pressure. The selection of the optimum solvent to separate butyric acid from aqueous solution was investigated. In addition, The LLE data for these ternary systems were correlated by UNIFAC.

Experimental section

According to Treybal's classification, the all ternary systems in this study were formed type 1 having a plait point. The mutual solubility (binodal curve) data were determined at 25 ℃ and atmospheric pressure by the cloud-point method as described by Othmer et al. The mutual solubility data were determined in an equilibrium cell equipped with magnetic stirrer and isothermal fluid jacket. The cell was kept in a constant-temperature bath maintained at (25±0.1) ℃. The cell was filled with homogeneous water + butyric acid mixtures prepared by weighing. The solvent was titrated into the cell from a microburet with an uncertainty of ±0.01 cm^3. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. This pattern was convenient to provide the aqueous-rich side of the curves. The data for organic-rich side of the curves were therefore obtained by titrating homogeneous solvent + butyric acid binaries with water until the turbidity had appeared. For the tie-line measurement, an equilibrium cell was immersed in a thermostat controlled at the desired temperature (±0.1 ℃). The pure components were added, and the mixture was stirred for at least 1 h with a magnetic stirrer. The two-phase mixture was allowed to settle for at least 24 h. Samples were taken by syringe from the upper and lower mixtures. The mixtures of aqueous and

organic phase were analyzed on an HP 5890 Series II gas chromatograph, equipped with a thermal conductivity detector (TCD). A 6 ft×1/8 in. column packed with Porapak Q was used. The injector and detector temperatures were maintained at 200 ℃. The column temperature was programmed for an initial temperature of 130 ℃ and a final temperature of 250 ℃. The heating rate was 50 ℃/min, and the flow rate of helium carrier gas was 30ml/min. The uncertainty of the mass fraction measurements for the overall composition determination was ±0.002 [3].
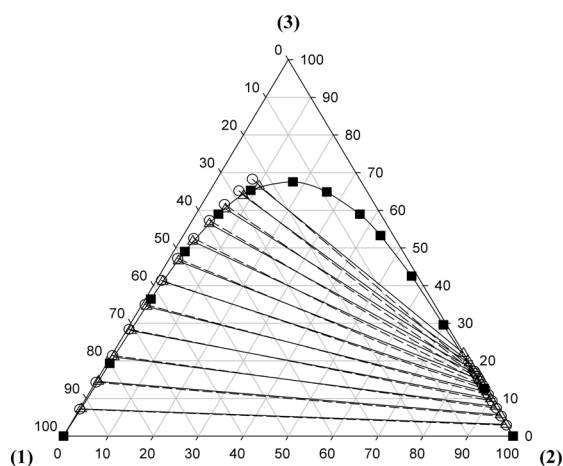
Results and Discussion

Fig. 1. Ternary diagram for experimental LLE of *o*-xylene (1) + water (2) + butyric acid (3); ■, experimental solubility curve; △, experimental tie-line data; ○, calculated (UNIFAC) tie-line data.
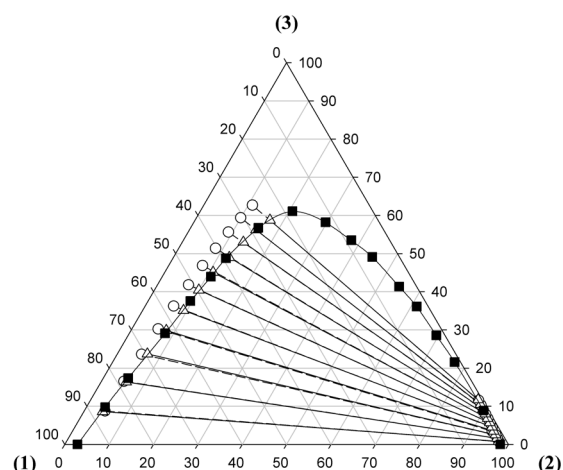

Fig. 2. Ternary diagram for experimental LLE of ethyl ether (1) + water (2) + butyric acid (3); ■, experimental solubility curve; △, experimental tie-line data; ○, calculated (UNIFAC) tie-line data.
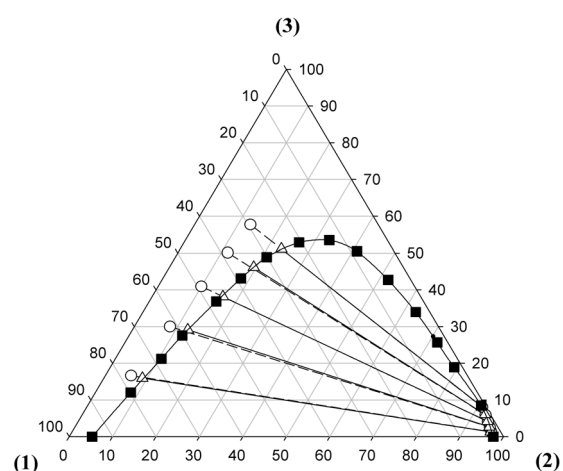

Fig. 3. Ternary diagram for experimental LLE of isopropyl acetate (1) + water (2) + butyric acid (3); ■, experimental solubility curve; △, experimental tie-line data; ○, calculated (UNIFAC) tie-line data.
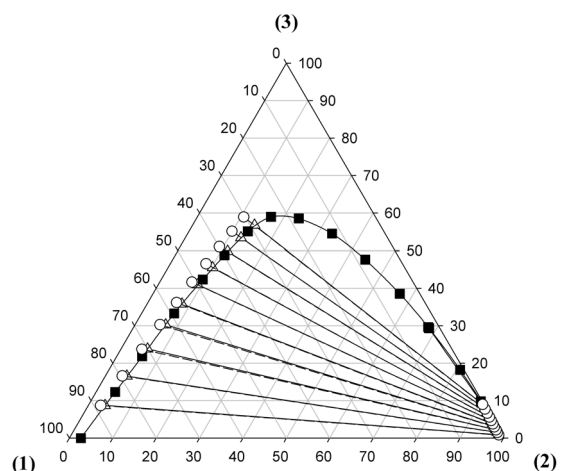

Fig. 4. Ternary diagram for experimental LLE of ethyl acetate (1) + water (2) + butyric acid (3); ■, experimental solubility curve; △, experimental tie-line data; ○, calculated (UNIFAC) tie-line data.

1. Liquid-Liquid Equilibrium Data

The mutual solubility data, the experimental tie-line data, and calculated (UNIFAC) tie-line data for

each of the ternary systems *o*-xylene + water + butyric acid, ethyl ether + water + butyric acid, isopropyl acetate + water + butyric acid, and ethyl acetate + water + butyric acid are presented in Figs. 1 - 4.

2. UNIFAC predicted LLE Data

Since experimental data are often missing or of poor quality, group contribution methods have become increasingly valuable. The great advantage of the group contribution concept is that it is possible to predict a large number of systems using only a relatively small number of group interaction parameters. The most common group contribution method for the prediction of phase equilibrium is UNIFAC.

In this model, the activity coefficient is expressed as the sum of two parts, namely combinatorial and residual. For any component *i*, the activity coefficient is expressed as

$$(x_i \gamma_i)^{\mathrm{I}} = (x_i \gamma_i)^{\mathrm{II}} \qquad (i=1, 2, \cdots, N) \tag{1}$$

$$\ln \gamma_i = \ln \gamma_i^{C}(combinatorial) + \ln \gamma_i^{R}(residual) \tag{2}$$

$$\ln \gamma_i^{C} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi}{x_i} \sum_j x_j l_j \tag{3}$$

$$\ln \gamma_i^{R} = \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \tag{4}$$

The experimental LLE data and tie-lines were compared with predictions obtained by the UNIFAC. The RMSD(Root Mean Square Deviation), deviation of estimate by experimental compositions and the UNIFAC predictions was obtained by equation (5) for the ternary system [4-6].

$$\mathrm{RMSD}_3 = 100 \left[\sum_{i=1}^{N} \sum_{j=1}^{3} \sum_{p=1}^{2} (X_{jk}^{\exp}(i) - X_{jk}^{cal}(i))^2 / 6N \right]^{1/2} \tag{5}$$

In this study, the interaction parameters between CH, CH_2, CH_3, CH_2O, COOH, CH_3COO, ACH, $ACCH_3$, and H_2O groups were used to estimate the activity coefficients by the UNIFAC method.

3. Selectivity & Distribution

As the most importance in liquid-liquid extraction is the selectivity of solvent, the solvents having higher distribution and selectivity for solute should be selected after consideration for recovery, chemical stability, boiling and freezing point, corrosion and density, and so on. In this property, the most importance is distribution and selectivity. They are shown in equations (6) and (7).

$$D = \frac{\text{butyric acid wt.\% in solvent layer}}{\text{butyric acid wt.\% in water layer}} = \frac{x_{31}}{x_{32}} \tag{6}$$

$$S = \frac{\text{butyric acid wt.\% in solvent-free solvent layer}}{\text{butyric acid wt.\% in solvent-free water layer}} = \frac{x_{31}/(x_{31}+x_{21})}{x_{32}/(x_{32}+x_{22})} \tag{7}$$
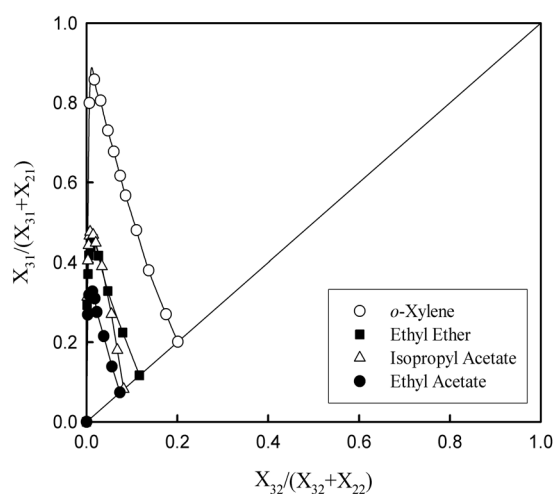
Fig. 5. Distribution of butyric acid between water layer and solvent layer at 25℃.
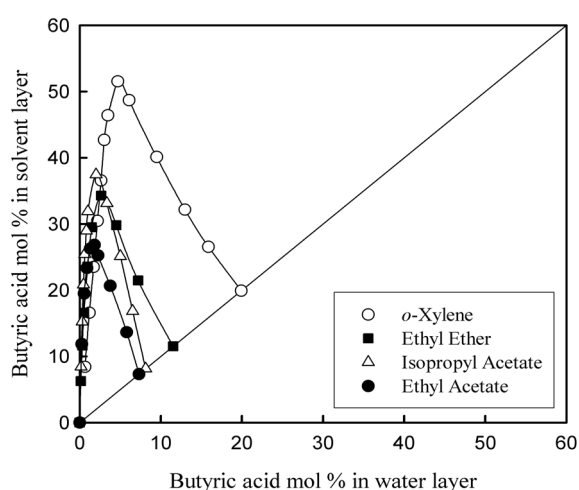

Fig. 6. Selectivity of butyric acid between water layer and solvent layer at 25℃.

Conclusion

LLE data were determined for the ternary systems of *o*-xylene + water + butyric acid, ethyl ether + water + butyric acid, isopropyl acetate + water + butyric acid, and ethyl acetate + water + butyric acid at 25 ℃ and atmospheric pressure. Complete phase diagrams were obtained by determining solubility and the tie-line data. Tie-line compositions were correlated by the Hand, and Othmer‐Tobias method. Analyzing the distribution and selectivity, we concluded that *o*-xylene appeared to be a better solvent for extraction purposes than the other when butyric acid needs to be extracted from its aqueous solution. The UNIFAC method was used to predict the phase equilibrium in the system using the interaction parameters determined from experimental data between CH, CH_2, CH_3, CH_2O, COOH, CH_3COO, ACH, $ACCH_3$, and H_2O groups. It is found that UNIFAC group interaction parameters used for LLE could not provide a good prediction. Distribution and selectivity were evaluated for the immiscibility region.

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