

용매추출에 의한 Butyric acid의 회수

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The Recovery of Butyric acid by Solvent Extraction

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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.

Butyric acid is employed in the dairy 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.

The purpose of this work is to determine liquid-liquid equilibrium (LLE) data of o-xylene + water + butyric acid + 1-butanol and the LLE data for the quaternary system were measured at 25°C under atmospheric pressure. The effect of the mixed solvents to separate butyric acid from aqueous solution was investigated. The system studied was a type2 quaternary system and the ternary systems relevant to the quaternary mixtures at 25°C have been reported for the type1 systems o-xylene + water + butyric acid and 1-butanol + water + butyric acid, and type2 system o-xylene + 1-butanol + water. LLE data have also been predicted with the UNIFAC method, and they are compared with the experimental data at 25°C.

Experimental section

1. Quaternary Equilibrium Date Determination

The mutual solubility(binodal curve) in o-xylene + water + butyric acid + 1-butanol was determined at 25°C and atmospheric pressure by the cloud-point method as described by othmer et al. For the determination of the mutual solubility data, an accurately weighted amount of a homogeneous mixture of two compounds was placed in a thermostated glass-stoppered bottle and one of the nonconsolute compounds was titrated into the bottle from a microburet until the solution became turbid, and the amount titrated was recorded. The bottle was kept in a constant- temperature bath. The temperature of the bath was maintained at 25±0.1°C. The end point has been confirmed by adding the consolute component until the turbidity disappears. The procedure was repeated to get the phase boundary curve.

2. Tie line Data Determination

For the tie-line measurement, an equilibrium cell was immersed in a thermostat controlled at the desired temperature(±0.1°C). The pure components were added, and the mixture was stirred for at least 1h with a magnetic stirrer. The two-phase mixture was allowed to settle for at least 24h. Samples

were taken by a syringe from the upper and lower mixtures.

The mixtures of aqueous and organic phase were analyzed on a HP 5890 Series II gas chromatograph, equipped with a thermal conductivity detector(TCD). A 6ft×1/8in. column packed with Porapak Q was used. The injector and detector temperatures were maintained at 140°C and 230°C, respectively. The column temperature was programmed for an initial temperature of 140°C and a final temperature of 200°C. The heating rate was 20°C/min, and the flow rate of helium carrier gas was 30ml/min.

Results and Discussion

1. Liquid-Liquid Equilibrium Data

Quaternary solubility curves of each mixed solvent R₁(75:25), R₂(50:50), and R₃(25:75) were shown in Figures 1 and 2. The mutual solubility data and the compositions for each of the ternary systems o-xylene + water + butyric acid, 1-butanol + water + butyric acid, and o-xylene + 1-butanol + water were shown in Figure 3.

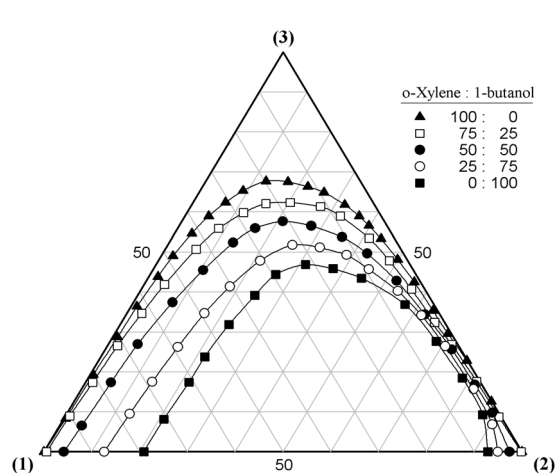


Fig. 1. The effect of mixing ratio on binodal curves for o-xylene(1) + water(2) + butyric acid(3) + 1-butanol(1) quaternary system at 25°C (wt%).

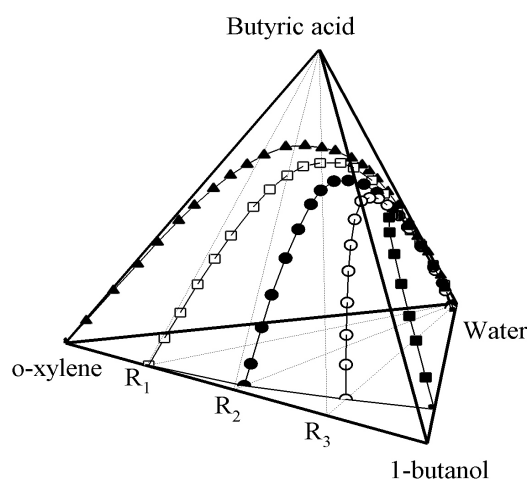


Fig. 2. Representation of binodal curves for o-xylene + water + butyric acid + 1-butanol quaternary system at 25°C (wt%).

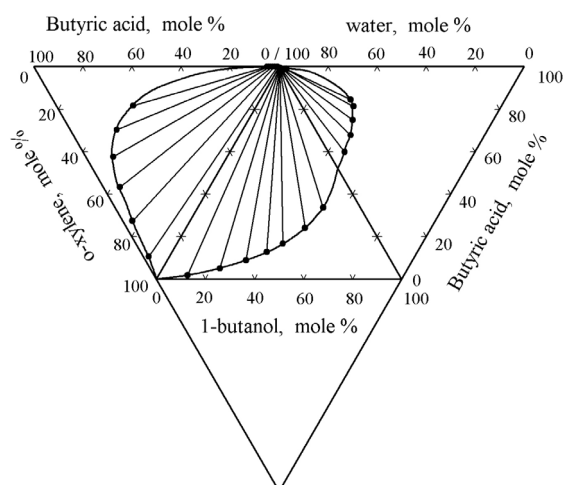


Fig. 3. Binodal curves and tie-lines for liquid-liquid equilibrium of o-xylene + water + butyric acid, 1-butanol + water + butyric acid, o-xylene + 1-butanol + water (mol%).

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 (Fredenslund et al., 1975, 1977; Hansen et al., 1991).

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

$$(x_i \gamma_i)^I = (x_i \gamma_i)^{II} \quad (i=1, 2, \dots, N) \quad (1)$$

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

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

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

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 and by equation (6) for the quaternary system.

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

$$\text{RMSD}_4 = 100 \left[\sum_{i=1}^N \sum_{j=1}^4 \sum_{\beta=1}^2 (X_{jk}^{\text{exp}}(i) - X_{jk}^{\text{cal}}(i))^2 / 8N \right]^{1/2} \quad (6)$$

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 (7) and (8).

$$D = \frac{\text{butyric acid wt.\% in solvent layer}}{\text{butyric acid wt.\% in water layer}} = \frac{x_{31}}{x_{32}} \quad (7)$$

$$S = \frac{\text{butyric acid wt.\% in solvent-free solvent layer}}{\text{butyric acid wt.\% in solvent-free water layer}} = \frac{x_{31}/(x_{31} + x_{21})}{x_{32}/(x_{32} + x_{22})} \quad (8)$$

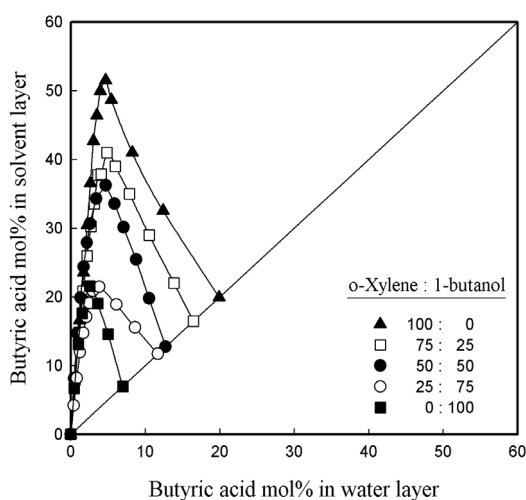


Fig. 4. Distribution of butyric acid between water layer and solvent layer at 25°C.

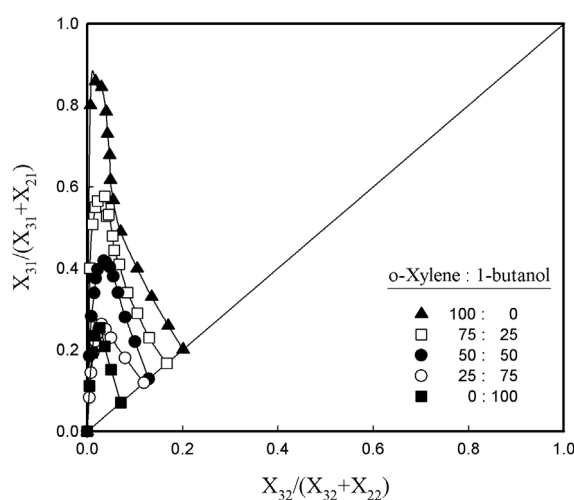


Fig. 5. Selectivity of butyric acid between water layer and solvent layer at 25°C.

Conclusion

Liquid-liquid equilibrium data were determined for the quaternary system o-xylene + water + butyric acid + 1-butanol at 25°C and atmospheric pressure. The variation of selectivity with mixtures of both solvents is of little significance, with o-xylene appearing as the better extractant solvent on account of the wide heterogeneous zone in the solubility diagram, and distribution and selectivity curve. The use of mixed solvents to improve the extraction of butyric acid will only be advisable when both solvents show some favorable properties, such as distribution coefficient and/or selectivity, in order to take advantage of the synergistic effect of the mixture.

Finally, the experimental data were also compared with the values predicted by UNIFAC model. In ternary system, the predictions for o-xylene + water + butyric acid and 1-butanol + water + butyric acid composed of type1 were shown within an average root mean square deviation of 4.75 mol%, and for o-xylene + 1-butanol + water composed of type2 was shown within 2.26 mol%. For the quaternary system, it was shown that UNIFAC model was capable of predicting the compositions within an average root mean square deviation of 5.08 mol%.

Literature cited

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