용매추출에 의한 **Propionic acid** 회수에 관한 연구

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A Study on the Recovery of Propionic acid by Solvent Extraction

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Introduction

With an increase in demand for environmentally friendly material, the recovery of organic acids from dilute solutions resulting from fermentation processes has become of interest. Economics of the process, however, depends on the development of an effective recovery method for the organic acids from the broth. 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. Propionic acid is being used as a cellulosic solvent in pharmaceutical industries and also can be used to provide propionates, which are used as fungicides. It is also used in the electroplating industry and to prepare perfume esters.

The purpose of this work is to determine LLE data of toluene + water + propionic acid + EAc and the LLE data for the quaternary system were measured at 25℃ under atmospheric pressure. The effect of the mixed solvents to separate propionic 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℃ have been reported for the type1 systems toluene + water + propionic acid and EAc + water + propionic acid, and type2 system toluene + EAc + water. LLE data have also been predicted with the UNIFAC method, and they are compared with the experimental data at 25℃.

Experimental section
  1. Quaternary Equilibrium Date Determination

The mutual solubility(binodal curve) in toluene + water + propionic acid + EAc was determined at 25℃ 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℃. 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℃). 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 SeriesⅡ gas chromatograph, equipped with a thermal conductivity detector(TCD). A 6ft×1/8in. column packed

with Porapack 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.

Results and Discussion

1. Liquid-Liquid Equilibrium Data

Quaternary solubility curves of each mixed solvent $R_1(75:25)$, $R_2(50:50)$, and $R_3(25:75)$ were shown in Figures 1 and 2. The mutual solubility data and the compositions for each of the ternary systems toluene + water + propionic acid, EAc + water + propionic acid, and toluene + EAc + water were shown in Figure 3.
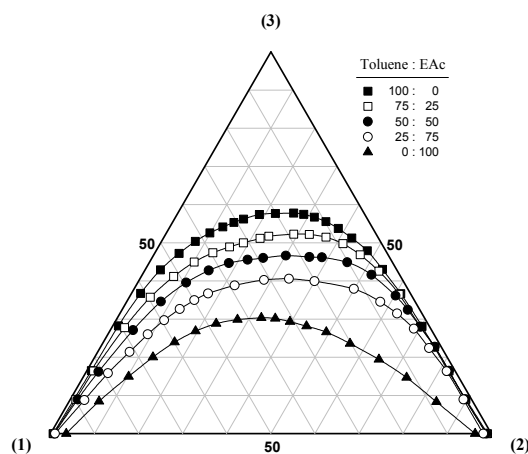

Fig. 1. The effect of mixing ratio on binodal curves for toluene+water+propionic acid+ EAc quaternary system at 25℃ (wt%).
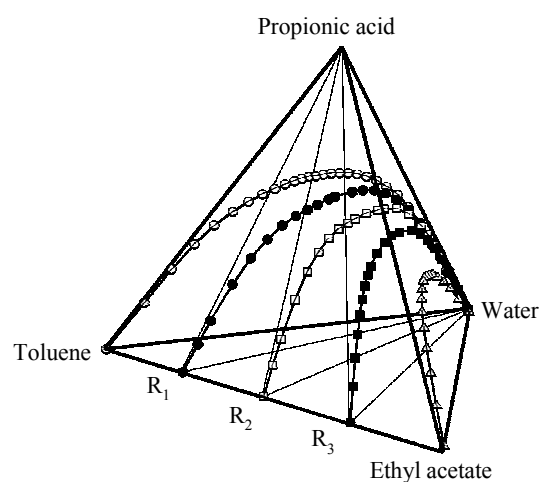

Fig. 2. Representation of binodal curves for toluene+ water+propionic acid+EAc quaternary system at 25℃ (wt%).
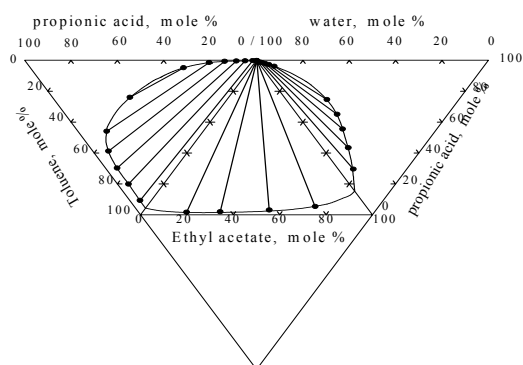

Fig. 3. Binodal curves and tie-lines for liquid-liquid equilibrium of toluene+water+ propionic acid, EAc+water+propionic acid, toluene+EAc+water (mol%).

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

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

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

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

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

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 and by equation (6) for the quaternary system.

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

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

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).

$$D = \frac{\text{propionic acid wt.\% in solvent layer}}{\text{propionic acid wt.\% in water layer}} = \frac{x_{31}}{x_{32}} \tag{7}$$

$$S = \frac{\text{propionic acid wt.\% in solvent-free solvent layer}}{\text{propionic acid wt.\% in solvent-free water layer}} = \frac{x_{31}/(x_{31}+x_{21})}{x_{32}/(x_{32}+x_{22})} \tag{8}$$
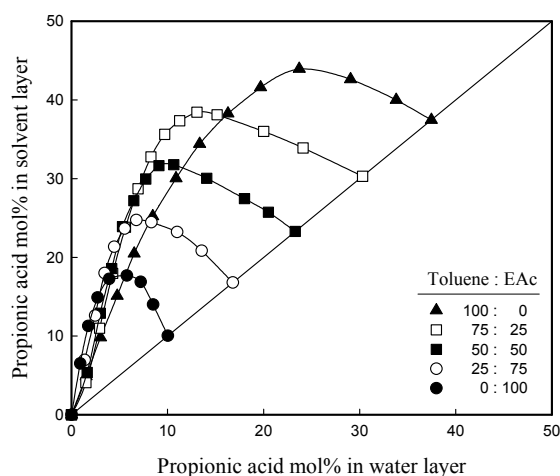
Fig. 4. Distribution of propionic acid between water layer and solvent layer at 25℃.
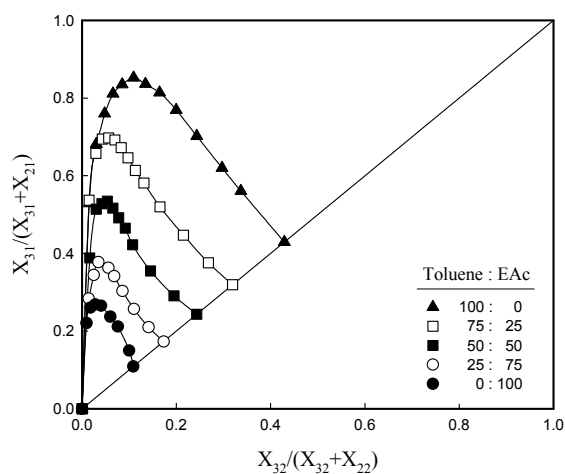

Fig. 5. Selectivity of propionic acid between water layer and solvent layer at 25℃.

Conclusion

Liquid-liquid equilibrium data were determined for the quaternary system toluene + water + propionic acid + ethyl acetate at 25℃ and atmospheric pressure. The variation of selectivity with mixtures of both solvents is of little significance, with toluene 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 propionic 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 toluene + water + propionic acid and ethyl acetate + water + propionic acid composed of type1 were shown within an average root mean square deviation of 3.39 mol%, and for toluene + ethyl acetate + water composed of type2 was shown within 1.09 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 3.21 mol%.

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