

용매 추출에 의한 Tetrahydrofuran의 회수

김영규, 옥동석, 박동원*
동아대학교 화학공학과
(dwpark@dau.ac.kr*)

The Recovery of Tetrahydrofuran by Solvent Extraction

Young-kyu Kim, Dong-seok Ok, Dong-won Park*
Department of Chemical Engineering, Dong-A University
(dwpark@dau.ac.kr*)

Introduction

Liquid-liquid extraction has grown in importance in recent years because of the growing demand for temperature-sensitive products, higher-purity requirements, more efficient equipment, and availability of solvents with higher selectivity.¹ Considerable data of a physical-chemical nature are necessary for the development of liquid-liquid extraction processes and the design of equipment for them.² And liquid-liquid extraction is often more acceptable than distillation as a technique for separating liquids because it does not involve a heating process.³

The efficient separation of ring-containing compounds (e. g., cyclic ethers and cyclic alcohols) from aqueous solutions is important in the chemical industry, where many solvents have been tested to improve such recovery.

Tetrahydrofuran (THF) is an organic solvent, an important organic raw material, and the precursor of polymers. Due to its proton-accepting nature, it is used as a solvent in many chemical industries. Many chemical and pharmaceutical industries encounter problem in separating THF from aqueous waste streams since their mixture form azeotropes at low compositions of water.⁴

The purpose of this work is to determine liquid-liquid equilibrium (LLE) data of water + THF + solvent (*n*-heptane, butyl acetate, isopropyl acetate, isoamyl alcohol) at 25 °C and atmospheric pressure. The selection of the optimum solvent to separation THF from aqueous solution was investigated. In addition, the LLE data have been predicted with the UNIFAC method,⁵⁻⁷ and they are compared with the experimental data at 25 °C.

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 °C 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) °C. The cell was filled with homogeneous water + THF mixtures prepared by weighing. The solvent was titrated into the cell from a microburet with an uncertainty of ±0.01 cm³. 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 + THF 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 °C). 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 \times 1/8 in. column packed with Porapak Q was used. The injector, column and detector temperatures were maintained at 200 °C, 200 °C, and 230 °C, respectively. 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 .

Results and Discussion

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 water + THF + *n*-heptane, butyl acetate (BAC), isopropyl acetate (iPac), and isoamyl alcohol (iAA) are presented in Fig. 1.

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.⁵⁻⁷

The experimental and predicted tie-lines and binodal curves for the system are plotted in fig. 2 to 5. The reliability of experimentally measured tie-line data can be ascertained by applying the Hand correlation. The correlation is shown in fig. 6.

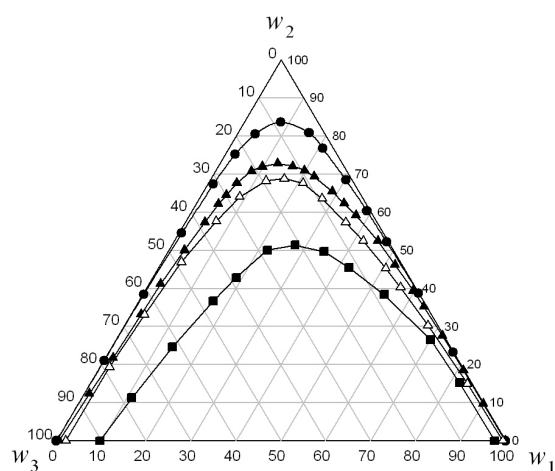


Fig. 1. Comparison of the binodal curves for the water (1) + THF (2) + solvent (3) systems; ●, *n*-heptane; ▲, BAC; △, iPac; ■, iAA.

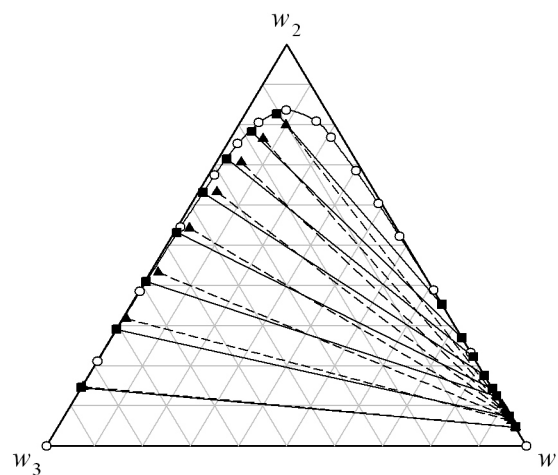


Fig. 2. Ternary diagram for experimental LLE of water (1) + THF (2) + *n*-heptane (3); ○, experimental solubility curve; ■, experimental tie-line data; ▲, calculated (UNIFAC) tie-line data (dashed line).

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 eq (1) and (2). The extracting power of the solvent is shown in fig. 7 and 8.

$$D = \frac{\text{THF mass fraction in organic layer}}{\text{THF mass fraction in aqueous layer}} = \frac{x_{23}}{x_{21}} \quad (1)$$

$$S = \frac{\text{THF mass fraction in solvent-free organic layer}}{\text{THF mass fraction in solvent-free aqueous layer}} = \frac{x_{23} / (x_{23} + x_{13})}{x_{21} / (x_{21} + x_{11})} \quad (2)$$

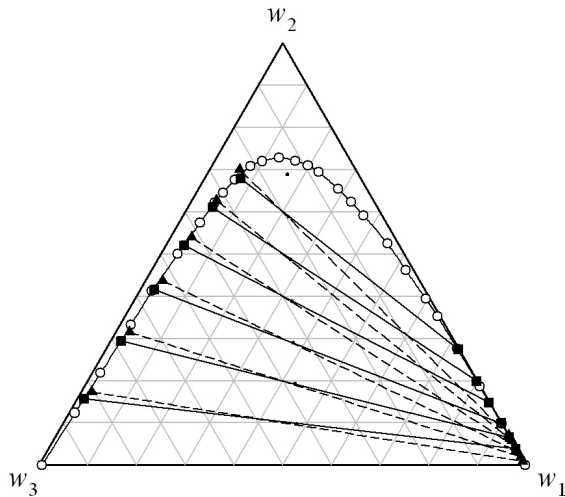


Fig. 3. Ternary diagram for experimental LLE of water (1) + THF (2) + BAc (3); ○, experimental solubility curve; ■, experimental tie-line data; ▲, calculated (UNIFAC) tie-line data (dashed line).

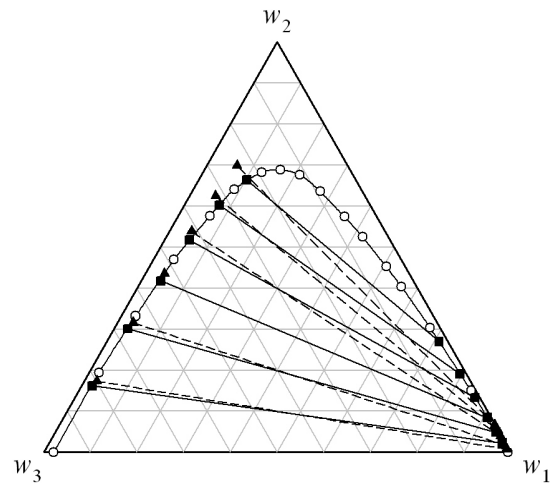


Fig. 4. Ternary diagram for experimental LLE of water (1) + THF (2) + iPac (3); ○, experimental solubility curve; ■, experimental tie-line data; ▲, calculated (UNIFAC) tie-line data (dashed line).

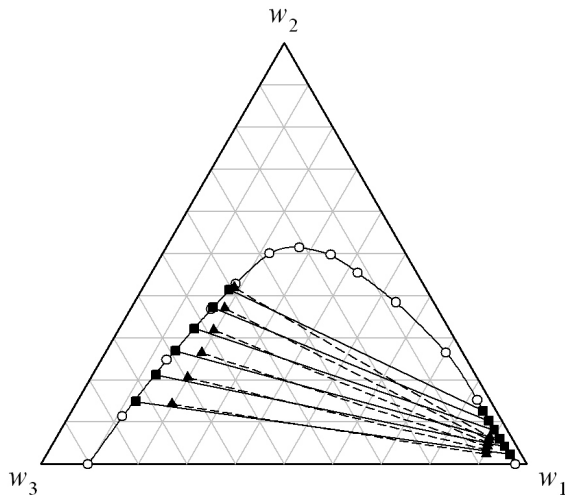


Fig. 5. Ternary diagram for experimental LLE of water (1) + THF (2) + iAA (3); ○, experimental solubility curve; ■, experimental tie-line data; ▲, calculated (UNIFAC) tie-line data (dashed line).

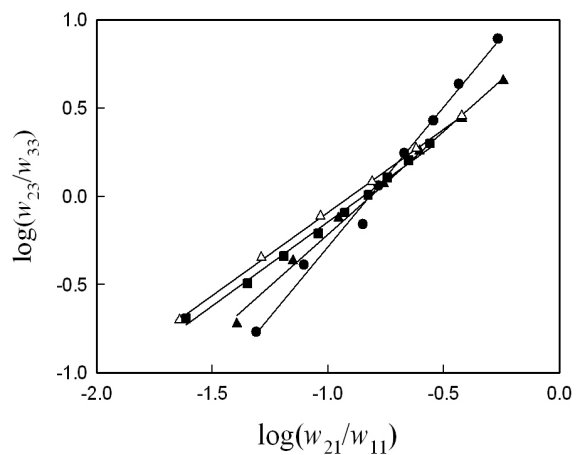


Fig. 6. Hand correlation for water (1) + THF (2) + solvent (3) systems; ●, *n*-heptane; ▲, BAc; △, iPac; ■, iAA.

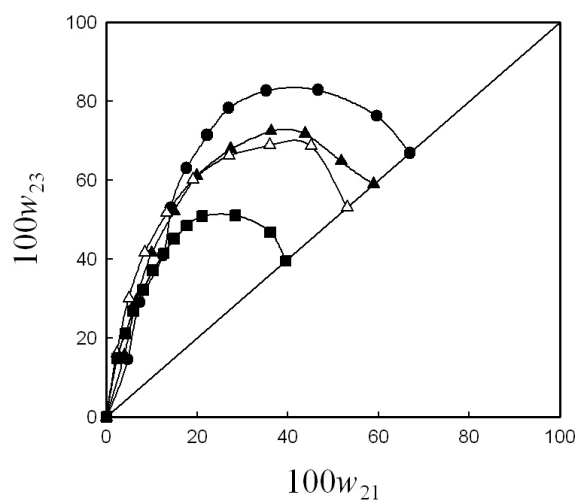


Fig. 7. Distribution of THF between aqueous layer and organic layer at 25 °C.

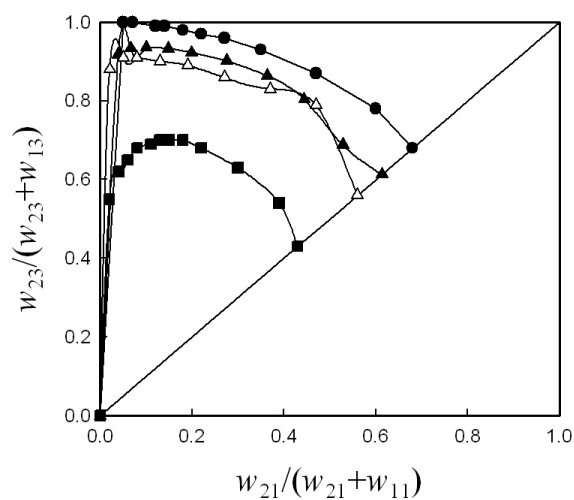


Fig. 8. Selectivity of THF between aqueous layer and organic layer at 25 °C.

Conclusion

LLE data were determined for the ternary systems of water + THF + solvent (*n*-heptane, butyl acetate, isopropyl acetate, isoamyl alcohol) at 25 °C and atmospheric pressure. Complete phase diagrams were obtained by determining solubility and the tie-line data. Tie-line compositions were correlated by the Hand method. Analyzing the distribution and selectivity, we concluded that *n*-heptane appeared to be a better solvent for extraction purposes than the other when THF 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. 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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