테트로하이드로푸란 – 물 – 혼합용매의 다성분계 액-액평형에 관한 연구

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A study on the Multicomponent Liquid-Liquid Equilibria of THF - Water - Binary solvents

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Introduction

  Tetrahydrofuran (THF) is an organic solvent, an important organic raw material, and the precursor of polymers. THF is used by manufacture of solvents, surface coating, protection coating adhesives, film of various resin and is used to PVC command resin specially.

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.

Liquid-liquid equilibrium data are important in chemical-engineering applications such as separation equipment design, especially to separate organic compounds from their aqueous mixtures. These data also provide valuable information about the molecular interactions and macroscopic behavior of fluid mixtures and can be used to test and improve thermodynamic models for calculating and predicting fluid-phase equilibria.

The purpose of this work is to determine liquid-liquid equilibrium (LLE) data of 1-pentanol(1) + water(2) + THF(3) + propyl acetate(4) mixture and the LLE data for the quaternary system were measured at 298.15 K and atmospheric pressure. The effect of the mixed solvents to separate THF from aqueous solution was investigated. The system studied was a type C quaternary system and the ternary systems relevant to the quaternary mixtures at 298.15 K have been reported for the type 1 systems water + THF + 1-pentanol and water + THF + propyl acetate, and type 2 system water + 1-pentanol + propyl acetate. LLE data have also been predicted with the UNIFAC method, and they are compared with the experimental data at 298.15 K.

Quaternary Equilibrium Data Determination.

  The binodal (solubility) curves in water + THF + propyl acetate + 1-pentanol mixture was determined at 298.15 K and atmospheric pressure by the cloud-point method as described by Othmer et al. For the determination of the mutual solubility data, accurately known masses of the solvent mixture (propyl acetate + 1-pentanol) was placed in a thermostated glass-stoppered bottle and water was titrated into the bottle from a microburet with an uncertainty of ±0.01 cm3 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 298.15 K. To determine points on the water side, the same procedure is followed, starting with an initial measured quantity of water in the bottle. The solvent mixture (propyl acetate + 1-pentanol) was added in the bottle from the microburet until the solution become turbid.

The end point (the major central part of the solubility curves) had been confirmed by adding solvent (to determine solubility curve of solvent side) or water (to determine solubility curve of water side) until the turbidity disappears. The transition point between the homogeneous and heterogeneous zones was determined visually.

For the tie-line measurement, an equilibrium cell was immersed in a thermostat at the desired temperature (±0.1 ℃). Mixture of known masses of water, THF, and solvents lying within the heterogeneous gap were introduced into the equilibrium cell, 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 a syringe from aqueous layer and organic layer. The mixtures of aqueous and organic layer were analyzed on a HP 5890 SeriesⅡgas chromatograph, equipped with a thermal conductivity detector (TCD). A 1.8 m × 3.2 mm column packed with Porapack Q was used. The injector and detector temperatures were maintained at 200 ℃ and 230 ℃ respectively. The column temperature was programmed for an initial temperature of 150 ℃nd a final temperature of 200 ℃ The heating rate was 2 ℃min, and the flow rate of helium carrier gas was 30 ml/min.

Results and Discussion

 LLE for the quaternary system 1-pentanol (1) + water (2) + THF (3) + propyl acetate (4) mixture was measured at 298.15 K and atmospheric pressure. The compositions of mixtures are expressed as w_i' and w_i'' which denote the mass fraction of the ith component in the aqueous and organic layer, respectively. The quaternary experimental data exhibit type C quaternary LLE behavior as shown in Fig 1 and are composed of two ternary LLE mixtures of type 1 having a plait point, water + THF + 1-pentanol and water + THF + propyl acetate systems, and one ternary LLE mixture of type 2 having two immiscible binary pairs, water + 1-pentanol + propyl acetate system. The reliability of measured tie-line compositions was ascertained by making Othmer-Tobias[17] and Hand[18] plots for the quaternary system. The plots are presented in Fig 2 and 3. The linear correlation coefficients for the system in 75/25, 50/50, and 25/75 mass ratios as mixed solvents are 0.9980, 0.9924 and 0.9889 in Othmer-Tobias, and 0.9915, 0.9857 and 0.9882 in Hand, respectively. The linearity of the plots (a correlation factor close to 1) indicates the degree of consistency of the related data. The effect of mixing ratio on binodal curves for the quaternary system at 25 ℃is shown in Fig 4. As shown in Fig4, the heterogeneous zone of isoamyl alcohol was increased with addition of butyl acetate, but mixed solvents, butyl acetate / isoamyl alcohol in 75/25, 50/50, and 25/75 mass ratios were not better than the pure solvent, butyl acetate as an extractant solvent.

As the most important 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 important is distribution and selectivity. Distribution (D) and selectivity (S) were calculated as following Equation (1) and (2).

$$D = \frac{w_2''}{w_2'} \qquad (1)$$

$$S = \frac{w_2'' / (w_2'' + w_1'')}{w_2' / (w_2' + w_1')} \qquad (2)$$

Fig 5 and 6 illustrate the effect of the distribution and selectivity for the mixed solvents, 1-pentanol / propyl acetate in 75/25, 50/50, and 25/75 mass ratios. As forthe binodal curves, they were also not better than the pure solvent, propyl acetate as an extractant solvent. Perhaps this is because of higher mutual solubility of water and 1-pentanol when compared with those for water and propyl acetate. The results indicate that the solubility of THF is high enough in propyl acetate.
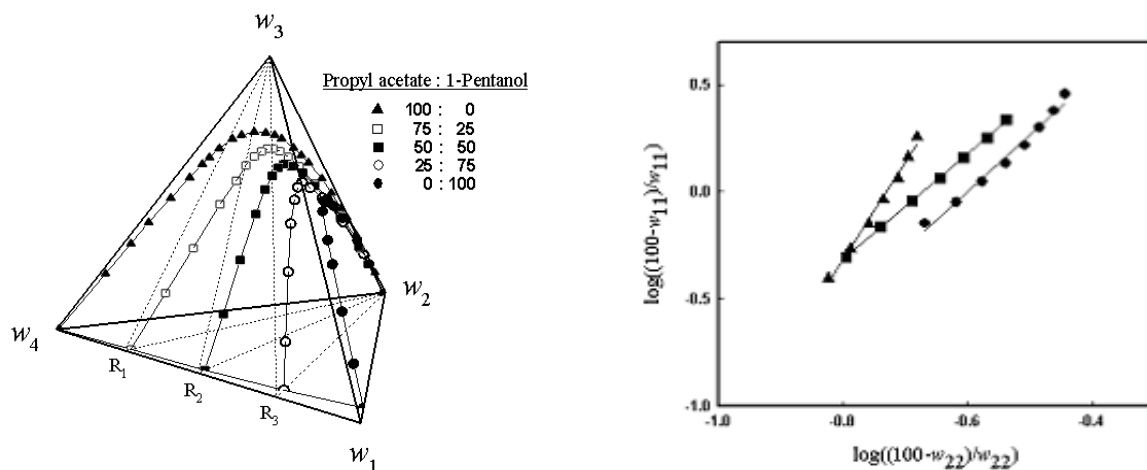

Fig 1. Phase equilibrium of 1-pentanol(1) + water(2) + THF(3) + propyl acetate(4) mixture at 298.15 K. R1, R2, and R3denote quaternary sectional planes.

Fig 2. Othmer-Tobias plots of 1-pentanol(1) + water(2) + THF(3) + propyl acetate(4) mixture at 298.15 ;▲(75/25),■(50/50),●(25/75)
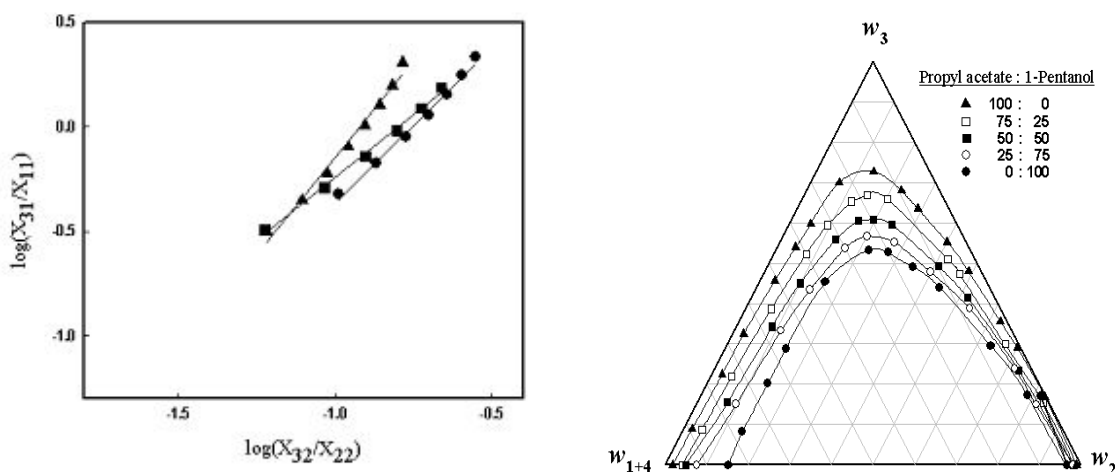
Fig 3. Hand plots of 1-pentanol(1) + water(2) + THF(3) + propyl acetate(4) mixture at 298.15 ;▲(75/25),■(50/50),●(25/75)

Fig 4. The effect of mixing ratio on binodal curves of 1-pentanol(1) + water(2) + THF(3) + propyl acetate(4) quaternary system at 298.15K   (wt%).
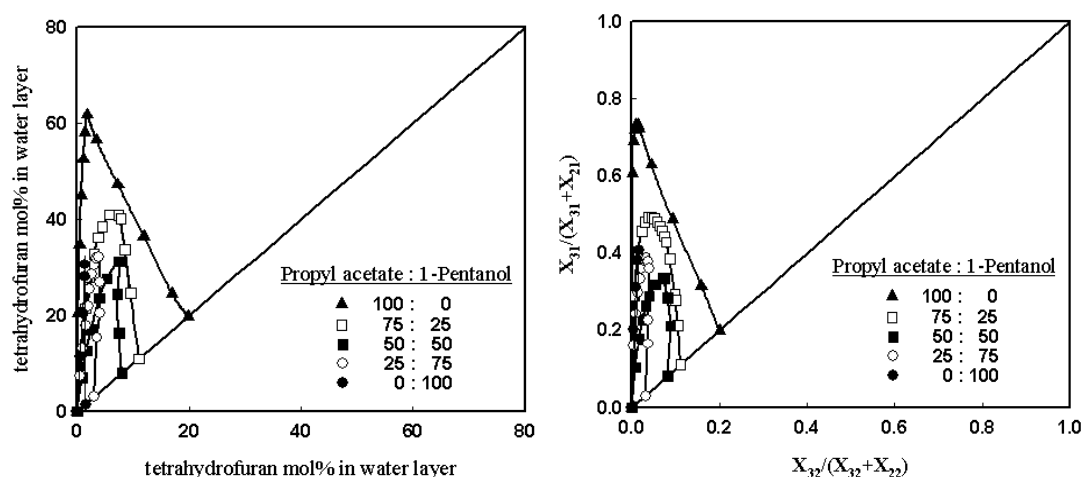
Fig 5 and 6. Distribution & Selectivity of THF between water and solvent layer at 298.15 K (mol%).

Conclusion

LLE data were determined for the quaternary system 1-pentanol(1) + water(2) + THF(3) + propyl acetate(4) mixture at 298.15 K and atmospheric pressure. The variation of selectivity with mixtures of both solvents is of little significance, with Propyl acetate appearing as the better extractant solvent on account of the wide heterogeneous zone in the solubility diagram, and distribution and selectivity. The usage of mixed solvents in 75/25, 50/50, and 25/75 mass ratios to improve the extraction of THF will only be advisable when both solvents show some favorable properties, such as distribution and/or selectivity, in order to take advantage of the synergistic effect of the mixture.

Finally, the calculations based on both UNIQUAC and NRTL models gave a good representation of the tie-line data for the systems 1-pentanol(1) + water(2) + THF(3), water(2) + THF(3) + propyl acetate(4) and 1-pentanol(1) + water(2) + THF(3) + propyl acetate(4). However, NRTL model, fitted to the experimental data, was more accurate than UNIQUAC model, as can be seen from the RMSD.

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