(Liquid + liquid) equilibria of the (water + butyric acid + dodecanol) ternary system

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Abstract

(Liquid + liquid) equilibrium (LLE) data for the (water + butyric acid + dodecanol) ternary system have been determined experimentally at $T = (298.2, 308.2$ and $318.2)$ K. Complete phase diagrams were obtained by determining binodal curves and tie lines. The reliability of the experimental tie lines was confirmed by using the Othmer–Tobias correlation. The UNIFAC method was used to predict the phase equilibrium in the ternary system using the interaction parameters determined from experimental data of CH_3, CH_2, COOH, OH and H_2O functional groups. Distribution coefficients and separation factors were evaluated for the immiscibility region.

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1. Introduction

The efficient separation of organic acids from aqueous solutions is an important problem in the chemical fermentation industry where many solvents have been tested to improve such recovery [1–3]. The LLE data of the related systems are needed for the design of an efficient and effective extraction system and numerous studies have been carried out to improve such techniques [4–8].

A detailed evaluation of solvents for the extraction of butyric acid is not available in the literature. Nevertheless, Zigová *et al.* carried out screening of 14 solvents for the extraction of butyric acid and a tertiary amine in different diluents, C_8 to C_{18} alcohols, dibutyl ether, toluene, and vegetable oils, have been tested [9–11]. Recently, Kırbaşlar *et al.* [12–14] examined LLE data of three different ternary systems.

This study is part of a research programme on the recovery of butyric acid from dilute aqueous solutions using high-boiling solvents. In this paper, LLE results were presented for the (water + butyric acid + dodecanol) systems. The phase equilibrium data were predicted using the UNIFAC model of Fredenslund *et al.* [15], using UNIFAC-LLE prediction parameters published by Magnussen et al. [16].

2. Experimental

Butyric acid and dodecanol were purchased from Merck and were of >0.99 and >0.98 mass fraction purity, respectively. Butyric acid and dodecanol were used without further purification. The GC analysis did not detect any appreciable peaks of impurities. Deionised water was further distilled before use. Refractive indices were measured with an Abbé-Hilger refractometer; its stated accuracy is $\pm 5 \cdot 10^{-4}$. Densities were measured with an Anton Paar (Model 4500) density meter. Boiling point measurements were

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TABLE 1
Densities ($\rho/kg \cdot m^{-3}$) and refractive indices (n_D) at $T = 298.2$ K and boiling temperatures (T_b/K) at $p = 101.325$ kPa of the pure components [17]

Compound	$\rho/kg \cdot m^{-3}$		n_D		T_b/K	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Water	997.08 ± 0.01	997.0	1.3322 ± 0.0005	1.3325	373.2 ± 0.1	373.2
Butyric acid	952.80 ± 0.01	952.8	1.3975 ± 0.0005	1.3980	436.7 ± 0.1	436.9
1-Dodecanol	830.80 ± 0.01^a	830.9^a	1.3964 ± 0.0005	–	532.5 ± 0.1	533.2

[a] Superscript of density indicates the temperature at 297.2 K.

obtained by using a Fischer boiling point apparatus. The estimated uncertainties in the density and boiling point measurements were $\pm 1 \cdot 10^{-2}$ kg $\cdot$ m^{-3} and 0.1 K, respectively. The measured physical properties are listed in table 1 along with literature values [17].

Three different temperatures (298.2, 308.2 and 318.2) K were selected to study the ternary equilibrium system in order to observe the evaluation of the binodal curves and tie lines. At each temperature, individual solubility curves were determined by the cloud-point method in a magnetically stirred equilibrium cell [18]. The end point was determined by observing the transition from a homogenous to a heterogeneous mixture. The mutual solubility of the (water + dodecanol) system was determined by using cloud-point method, too. A weighed amount of one component was placed in the cell; then the other component added until a permanent heterogeneity was observed.

Tie-line data were obtained by preparing ternary mixtures (water + butyric acid + dodecanol) of known overall compositions lying within the two-phase region. After being stirred vigorously, the mixture was allowed to reach equilibrium in an electronically controlled shaker (4 h) at a constant temperature. After the complete separation of the phases (5 h), a suitable amount of each layer was removed for detailed analysis in GC. All mixtures were prepared by weighing with a Sartorius (CP 224 S Model) scales with an accuracy of $\pm 1 \cdot 10^{-7}$ kg. The solvent was added by an automated microburet with an accuracy of $\pm 3 \cdot 10^{-9}$ m^3.

The liquid samples were analysed by a gas chromatograph (Hewlett–Packard GC, Model 6890 Series) equipped with thermal conductivity detector (TCD) for the quantitative determination of water, butyric acid and dodecanol. A 15-m long HP-Plot Q column (320 μm i.d., 20 μm film thickness) was used with a temperature-programmed analysis. Column temperature was held at 383 K (5 min) and rose to 450 K at 10 K $\cdot$ min^{-1}; and to 523 K (2 min) by 25 K $\cdot$ min^{-1} ramp rate and injection mode, split ratio 100/1; detector, TCD; injector temperature of 523 K and detector temperature of 473 K; carrier gas being nitrogen 6 cm$^3 \cdot$ min^{-1} and with injected volume of 0.001 cm^3 (1 μL) of liquid sample.

3. Results and discussion

The experimental tie lines of the (water + butyric acid + dodecanol) ternary system at each temperature are given in table 2. The experimental and predicted equilibrium data of the ternary system at $T = 298.2$ K are plotted in figure 1. As can be seen from figure 1, it was found that dodecanol was insoluble in water but miscible with butyric acid. Also, similar results were observed at $T = 308.2$ K and $T = 318.2$ K.

To measure the selectivity and extraction strength of the solvent to extract butyric acid, the distribution coefficient, D, for butyric acid and separation factors, S, were calculated as follows:

$$D = w_{23}/w_{21}, \tag{1}$$

$$S = \frac{\text{distribution coefficient of butyric acid}}{\text{distribution coefficient of water}}$$
$$= (w_{23}/w_{21})/(w_{13}/w_{11}), \tag{2}$$

where w_{23} and w_{21} are the butyric acid mass fraction in solvent-rich and water-rich phases, respectively. The w_{13} and w_{11} are the water mass fraction in solvent-rich and water-rich phases, respectively.

The distribution coefficients (D) and separation factors (S) for each temperature are given in table 3. The effectiveness of extraction of butyric acid by dodecanol is given by its separation factor, which is a measure of the ability of dodecanol to separate butyric acid from water. This quantity is found to be greater than 1 (separation factors varying between 33 and 150) for the ternary system reported here, meaning that extraction of butyric acid by dodecanol is possible. The separation factor is not constant over the whole two-phase region. The extracting power of the solvent at each temperature, plots of D against w_{21} and S against w_{21} are shown in figures 2 and 3, respectively.

The reliability of experimentally measured tie lines can be ascertained by applying the Othmer–Tobias correlation [19] at each temperature as follows:

$$\ln\{(1 - w_{33})/w_{33}\} = a + b \cdot \ln\{(1 - w_{11})/w_{11}\}, \tag{3}$$

where w_{11} being mass fraction of water in the water-rich phase; w_{33} is mass fraction of dodecanol in the solvent-rich phase; a and b are the constants of equation 3. The Othmer–Tobias plot is shown in figure 4 at only