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Measurement and correlation of phase equilibrium data of the mixtures consisting of butyric acid, water, cyclohexanone at different temperatures

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ABSTRACT

In this work, experimental solubility and tie-line data for the (water + butyric acid + cyclohexanone) system were obtained at $T = (298.2, 308.2, \text{and } 318.2)$ K and atmospheric pressure. The ternary system investigated exhibits type-1 behavior of LLE. The experimental tie-line data were compared with those correlated by the UNIQUAC and NRTL models. The consistency of the experimental tie-line data was determined through the Othmer Tobias and Hand correlation equations. Distribution coefficients and separation factors were evaluated over the immiscibility regions. A comparison of the extracting capability of the solvent at different temperatures was made with respect to separation factors. The Katritzky and Kamlet–Abboud–Taft multiparameter scales were applied to correlate distribution coefficients and separation factors in this ternary system. The LSER models values were interpreted in terms of intermolecular interactions.

1. Introduction

(Liquid + liquid) equilibrium (LLE) studies have been the subject of much interest in recent years [1–9]. In particular, LLE investigations for ternary aqueous mixtures of carboxylic acids with organic solvents are important in evaluation of industrial solvent extraction units. Precise LLE data are needed for efficient separation operations, which can be obtained from direct measurements.

Butyric acid (BA) is one of the important carboxylic acid, which has many scientific and industrial applications [10]. Due to its industrial importance, the extraction of this acid from aqueous mixtures is an important problem [11,12]. Some significant investigations have been carried out in recent years on the LLE measurements and the extraction of BA from aqueous solutions by Kırbaşlar and co-workers [13–15], Bilgin and co-workers [16,17], and Uslu and co-workers [18]. More recently, we reported the LLE data for the aqueous mixture of BA with cyclohexane [19].

In this research, cyclohexanone was tested as organic solvent for recovery of BA from water. Cehreli and co-workers [20] have used this solvent as an agent of extraction in the determination of LLE data for the ternary aqueous mixtures of propionic acid. The focus of this study is placed on the phase behavior of LLE for the aqueous mixtures of BA with cyclohexanone. For this system, three different temperatures were chosen in order to observe the change of equilibrium characteristics. At each temperature, the phase compositions were measured.

Distribution coefficients (*D*) and separation factors (*S*) were determined from the tie-line data to establish the possibility of the use of this solvent for the separation of BA from water. The experimental data were correlated using the UNIQUAC and NRTL models [21,22]. The values for the interaction parameters were obtained and the calculated compositions compared with the experimental ones. In general, according to these comparisons, both the correlation models are applicable for the LLE calculations of the system investigated.

2. Experimental

2.1. Materials

Butyric acid and cyclohexanone with stated mass fraction purity higher than 0.99, and 0.995, respectively, were obtained from Merck. Since cyclohexanone can be easily oxidized to adipic acid, it was used after double distillation. Deionised and redistilled water was used throughout all the experiments. All materials were used as received without any further purification.

2.2. Apparatus and procedure

The solubility curves for the ternary mixtures were determined by the cloud point method in an equilibrium glass cell [23]. The binary mixtures of known compositions were prepared by

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weighing and introduced into the glass cell. The temperature of the cell was controlled by a water jacket and maintained with an accuracy of within ±0.1 K that was checked with a digital thermometer (Lutron TM-917). At each temperature, the third component was progressively added using a microburet. The end-point was determined by observing the transition from an appearance to a disappearance of the heterogeneous mixture. All the measurements were repeated at least three times. The average of these readings was taken for the component compositions and reported in table 1.

A 250 cm^3 glass cell connected to a thermostat was made to measure the LLE data. The equilibrium data were determined by preparing the ternary mixtures of known compositions. The mixtures were prepared directly inside the extraction cell, and the components were weighed on an analytical balance. The overall mixtures were stirred for 4 h, and then left to settle for 4 h for phase separation. For this ternary mixture, this time is long enough to achieve equilibrium. When the equilibrium was achieved, the system separated into two liquid phases that become clear and transparent with a well-defined interface. Then, the organic liquid phase was almost completely collected with glass syringe into a container and weighted. The remaining aqueous phase was also collected and weighted. After separation, samples of both phases were transparent and were carefully analyzed to determine their compositions.

2.3. Analysis

The aqueous and organic phases were weighed and analyzed to define the composition of the components in order to determine the LLE tie lines. For the complete determination of the LLE data, the following method was used. The concentrations of the acid (BA) in both phases were determined by potentiometric NaOH titration in the presence of phenolphthalein as an indicator. The water content of the organic phase was measured by the Karl–Fisher method [24] using Metrohm-870 KF Titrino plus Karl–Fisher titrator. The titrator was calibrated with a standard solution of sodium tartrate.

Knowing the mass of the three components in the initial mixtures, mass of separated phases, and the three known variables (mass of water in the organic phase and mass of BA in the aqueous and in the organic phases) one can evaluate the other unknown variables. Thus, the water content in the aqueous phase and the amount of the organic solvent in both phases were determined by using mass balance equations.

TABLE 1
Experimental solubility data in mass fraction for (water + BA + cyclohexanone) at different temperatures.[a]

T = 298.2 K		T = 308.2 K		T = 318.2 K	
w_1 (water)	w_2 (BA)	w_1 (water)	w_2 (BA)	w_1 (water)	w_2 (BA)
0.051	0.000	0.056	0.000	0.068	0.000
0.068	0.090	0.069	0.069	0.082	0.063
0.093	0.170	0.082	0.129	0.101	0.127
0.096	0.191	0.101	0.191	0.120	0.187
0.122	0.277	0.120	0.251	0.140	0.245
0.157	0.358	0.140	0.309	0.159	0.302
0.180	0.412	0.162	0.365	0.182	0.356
0.230	0.497	0.182	0.418	0.204	0.408
0.295	0.536	0.216	0.463	0.238	0.450
0.390	0.511	0.253	0.501	0.285	0.479
0.504	0.435	0.317	0.512	0.361	0.480
0.610	0.333	0.422	0.481	0.530	0.390
0.689	0.247	0.555	0.371	0.638	0.289
0.804	0.128	0.651	0.279	0.723	0.206
0.896	0.034	0.794	0.138	0.825	0.103
0.921	0.000	0.921	0.000	0.926	0.000

[a] Standard uncertainties u are $u(T)$ = 0.1 K, and $u(w)$ = 0.001.

Moreover, the experimental information on the binodal curves along the calculation procedure was used for the check of the calculated LLE data. In this way, refractive indices of the prepared standard samples were measured and used for building standard curves. It was found that such standard curves can be made for analysis of organic phase, since the composition of data-points in aqueous phase is close. Therefore, this method was mainly used for characterization of solvent rich phase composition (figure 1). Then the calculated composition of tie-line samples were checked and corrected according to these calibration curves and the data consistency.

All weighting was carried out with an analytical balance accurate to within ±0.0001 g. The estimated uncertainties in the mass fractions were about 0.001. The temperature was estimated to be accurate to within ±0.1 K.

3. Results and discussion

3.1. Experimental LLE data

The experimental tie-line data for the ternary system (water + BA + cyclohexanone) were determined at T = (298.2, 308.2, and 318.2) K and atmospheric pressure. The experimental values for the ternary system at each temperature are listed in table 2. The LLE diagrams at various temperatures for the ternary system are plotted in figures 2 to 4. Because (BA + water) and (BA + cyclohexanone) are two liquid pairs that are completely miscible and the only liquid pair (water + cyclohexanone) is partially miscible, this ternary system behave as type-1 LLE. The area of the two-phase region depends on the mutual solubility of water and the organic solvent.

The efficient separation of the acid from aqueous solution is an important concept in the chemical industries. To indicate the ability of the solvent in the recovery of the acid, separation factors (S) were calculated from the experimental data. The separation factor is defined as,

$$S = \frac{\text{distribution coefficient of the acid } (D_2)}{\text{distribution coefficient of water } (D_1)} = \frac{w_{23}/w_{21}}{w_{13}/w_{11}}, \tag{1}$$

w_{13} and w_{23} are the mass fractions of water and BA in the organic-rich phase, respectively; w_{11} and w_{21} are the mass fractions of water and BA in the aqueous phase, respectively.

The distribution coefficients and separation factors for the ternary system are given in table 3. The separation factors are not

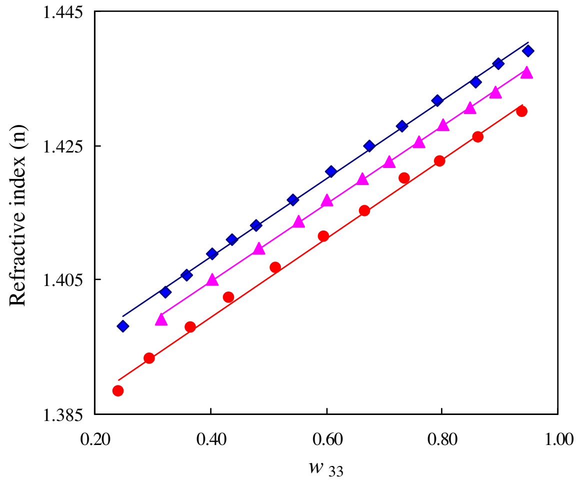

FIGURE 1. Refractive index standard curves for cyclohexanone in organic phase (w_{33}) at different temperatures; (◆) 298.2 K, (▲) 308.2 K, and (●) 318.2 K.