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Phase diagrams for the aqueous solutions of butyric acid with cyclohexane at different temperatures: Experimental and correlated data

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ABSTRACT

In this work, experimental tie-line data for the (water + butyric acid + cyclohexane) system were obtained at $T = 298.2$, 303.2, 308.2, and 313.2 K and atmospheric pressure. The investigated ternary system 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. The influence of temperature on the equilibrium characteristics and separation factor was found to be considerable at the temperatures studied. A comparison of the extracting capability of the solvent at different temperatures was made with respect to separation factors. The Katritzky LSER model was applied to correlate distribution coefficients and separation factors in this ternary system. The LSER model values showed good regression fits to the experimental results.

1. Introduction

Liquid–liquid equilibria (LLE) investigations for ternary aqueous mixtures of carboxylic acids with organic solvents are important in the evaluation of industrial units for solvent extraction processes [1–9]. The accurate interpretation of phase equilibria for the different ternary mixtures is a fundamental and important key to improving solvent extraction techniques.

The carboxylic acid used in the current study was butyric acid (BA). It has many scientific and industrial applications [10]. As a detailed evaluation of solvents for the extraction of BA using the liquid–liquid extraction technique is not available in the literature, the extraction of this acid from aqueous mixtures is still an important problem. Some important investigations have been carried out in recent years on the LLE measurements and the extraction of BA from aqueous solutions by Kırbaşlar and coworkers [11–13], and Bilgin and coworkers [14,15]. Lately, more LLE data for the ternary aqueous mixture of BA with organic solvents at 298.2 K have been reported by Uslu and coworkers [16]. Heavy alcohols, aliphatic amines, and esters have mainly been used for extraction of the acid from aqueous solutions [17–19].

In this research, cyclohexane was tested as organic solvent for recovery of BA from water. In our previous work, this solvent has been used as an extractant in the determination of LLE data for the ternary aqueous mixtures of propionic acid with organic solvent [20]. The focus of this study is placed on the phase behavior of LLE for the aqueous mixtures of BA with cyclohexane. For this system, four different temperatures were chosen to study the ternary equilibrium system 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 equations [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 investigated system.

2. Experimental

2.1. Materials

Butyric acid and cyclohexane with stated mass fraction purity higher than 0.99, and 0.995, respectively, were obtained from Merck. Deionized and redistilled water was used throughout all the experiments. All materials were used as received without any further purification.

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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 prepared binary mixtures of known compositions were introduced to the glass cell. The temperature of the cell was controlled by a water jacket and maintained with an accuracy of within ±0.1 K. 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.

A 250 ml 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 prepared mixtures were introduced into the extraction cell and were stirred for 4 h, and then left to settle for 4 h for phase separation. When the equilibrium was achieved, 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 find 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.

Knowing 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 moles of BA in the aqueous and in the organic phases) one can evaluate the other unknown variables (mass of water in the aqueous phase and moles of cyclohexane in the aqueous and in the organic phases).

Due to extremely low solubility of cyclohexane in aqueous phase, application of this method is practical, as it has been reported by Gomez-Siurana et al. [25]. The water content in the aqueous phase and the amount of the organic solvent in both phases were determined by using mass balance equations. Moreover, the experimental information on the binodal curves along the calculation procedure was used for the examination of the calculated LLE data. In this way, refractive indices of the samples lying on binodal curves were measured and used for building standard curves. Then the calculated composition of several samples were checked and corrected according to these calibration curves. All weighting was carried out with an analytical balance that was accurate to within ±0.0001 g. The estimated uncertainties in the mole 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 + cyclohexane) were determined at $T = 298.2$, 303.2, 308.2 and 313.2 K and atmospheric pressure. The experimental values for the ternary system at each temperature are listed in Table 1.

Table 1
Experimental tie-line data in mole fraction for (water + BA + cyclohexane) at different temperatures.

Aqueous phase mole fraction			Organic phase mole fraction		
x_1 (water)	x_2 (BA)	x_3 (cyclohexane)	x_1 (water)	x_2 (BA)	x_3 (cyclohexane)
$T = 298.2$ K					
0.975	0.017	0.007	0.017	0.287	0.696
0.966	0.028	0.006	0.025	0.366	0.610
0.954	0.034	0.012	0.037	0.432	0.531
0.948	0.044	0.009	0.066	0.498	0.436
0.930	0.056	0.014	0.113	0.531	0.356
$T = 303.2$ K					
0.980	0.019	0.001	0.018	0.287	0.695
0.970	0.030	0.001	0.036	0.374	0.590
0.959	0.040	0.001	0.062	0.429	0.509
0.950	0.049	0.001	0.097	0.473	0.430
0.939	0.059	0.002	0.147	0.496	0.358
$T = 308.2$ K					
0.979	0.020	0.001	0.019	0.286	0.695
0.968	0.031	0.002	0.038	0.365	0.597
0.957	0.042	0.002	0.065	0.424	0.511
0.946	0.052	0.002	0.105	0.466	0.428
0.935	0.063	0.002	0.151	0.480	0.370
$T = 313.2$ K					
0.977	0.021	0.002	0.022	0.284	0.694
0.967	0.031	0.002	0.041	0.360	0.599
0.956	0.042	0.002	0.080	0.414	0.506
0.944	0.053	0.003	0.127	0.452	0.421
0.933	0.064	0.003	0.159	0.467	0.375

The LLE diagrams as a function of temperature for the ternary system are plotted in Figs. 1–4.

Because (BA + water) and (BA + organic solvent) are two liquid pairs that are completely miscible and the only liquid pair (water + organic solvent) is partially miscible, this ternary system behave as type-1 LLE. The area of the two-phase region obviously depends on the mutual solubilities of water and the organic solvent. In general, temperature and the type of organic solvent are the most important factors, which influence the equilibrium characteristics and the immiscibility region of the ternary system.

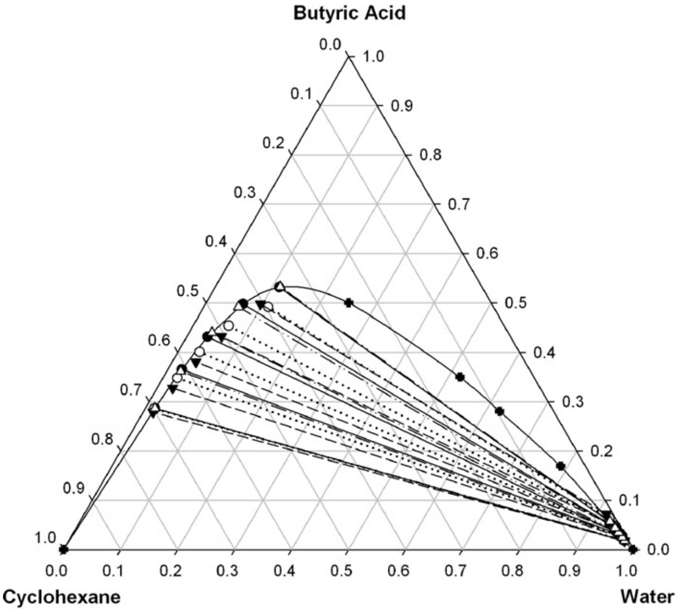

Fig. 1. Ternary phase diagram for LLE of [water (1) + BA (2) + cyclohexane (3)] at $T = 298.2$ K; (•) experimental points, (o) UNIQUAC calculated points, (♦) NRTL calculated points ($\alpha = 0.3$), (△) NRTL calculated points (regressed α).