J. Chem. Thermodynamics 57 (2013) 152–159

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

(Liquid + liquid) equilibria of aqueous solutions of butyric acid with *n*-heptane and toluene at $T = (298.2, 308.2, \text{and } 318.2)$ K

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ARTICLE INFO

Article history:
Received 13 June 2012
Received in revised form 31 July 2012
Accepted 25 August 2012
Available online 10 September 2012

Keywords:
(Liquid + liquid) equilibrium
Ternary mixture
Butyric acid
NRTL model
UNIQUAC model

ABSTRACT

Solubility and tie line data for the (water + butyric acid + *n*-heptane) and (water + butyric acid + toluene) ternary systems were determined at $T = (298.2, 308.2, \text{and } 318.2)$ K and atmospheric pressure. Solubility data were obtained by the cloud-point titration method. The concentration of each phase was determined by acidimetric titration, the Karl-Fischer technique, and refractive index measurements. The experimental tie-line data were correlated using the UNIQUAC and NRTL thermodynamic models. The reliability of the experimental data was determined through the Othmer–Tobias and Hand plots. Distribution coefficients and separation factors were evaluated for each system over the immiscibility regions.

1. Introduction

(Liquid + liquid) equilibrium (LLE) investigations for ternary aqueous mixtures of carboxylic acids with organic solvents are important both from a scientific and technological point of view. Precise LLE data of the mixtures consisting of water, carboxylic acid and solvents are always needed for efficient separation operations. Due to their industrial importance, significant studies have been carried out on the solubility and LLE behavior of carboxylic acids in various ternary systems by many researchers [1–12].

Butyric acid (BA) is one of the most widely used carboxylic acids, which has many important applications in chemical, beverage, food, cosmetic and pharmaceutical industries [13]. Due to its industrial importance, the extraction of BA from aqueous solutions is an important problem in the various industries. Up to now, important LLE data have been reported on the LLE measurements and the extraction of BA from aqueous solutions [12–18]. As far as the authors are aware, hydrocarbons [14–16], heavy alcohols [17–19], esters [20–25] aliphatic amines [26,27] and ketones [28] have been mainly used in the recovery of the acid from water. In the past, tie-line data for the ternary system consisting of water, BA, and an aromatic hydrocarbon (toluene) have been reported by Leung and Badakhshan [14] at various temperatures. The LLE data for non-aqueous mixtures of (acetonitrile + BA + *n*-heptane) at $T = 298.15$ K have been reported by Letcher and Redhi [29].

In this research, *n*-heptane and toluene were investigated as organic solvents for recovery of BA from water. To the best of our knowledge, the LLE data of the (water + BA + *n*-heptane) ternary system have not been reported in the available literature. In addition, this work presents the LLE results for the (water + BA + toluene) ternary system at various temperatures for comparison. However, the most obvious differences between this work and the published work [14] are due to use of the different temperatures ranging, different thermodynamic models, and different measuring methods. On the other hand, for a comparison of the extracting capabilities of the solvents for the separation of (water + BA) mixtures, the distribution coefficients and separation factors were determined for the system including toluene as well. In this work, three different temperatures were chosen in order to observe the change of equilibrium characteristics. At each temperature $T = (298.2, 308.2, \text{and } 318.2)$ K, the phase compositions were measured.

The tie-line data were correlated using the universal quasi chemical (UNIQUAC) method of Abrams and Prausnitz [30] and the non-random two-liquid (NRTL) model of Renon and Prausnitz [31,32]. The values for the interaction parameters were obtained and the calculated compositions compared with the experimental ones. Distribution coefficients and separation factors were determined from the tie-line data to establish the possibility of the use of these solvents for the separation of BA from water.

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http://dx.doi.org/10.1016/j.jct.2012.08.029

2. Experimental

2.1. Materials

Butyric acid, *n*-heptane and toluene with stated mass fraction purity higher than 0.99 were obtained from Merck. The stated purity of the materials was checked on the basis of their refractive indices and densities. Deionised and redistilled water with an electrical conductivity less than 5 $\mu S \cdot cm^{-1}$ at $T = 298.2$ K was used throughout all experiments. All materials were used as received without any further purification. The measured refractive index and density data of the chemicals used in this study along with the literature values are listed in table 1.

2.2. Apparatus and procedure

The sample weighing was carried out with an AND electronic analytical balance (model HR-200) with an accuracy of ±0.0001 g. Refractive indices and densities of the pure liquids were measured at $T = 298.2$ K using an Abbe Refractometer (Model CETI) and a DA210 (Kyoto electronic) density meter, respectively. The uncertainties in the refractive index and density measurements were ±0.0002 and ±0.01 $kg \cdot m^{-3}$, respectively.

The solubility data for each ternary system were determined by the cloud point method in an equilibrium glass cell. The binary mixtures of known compositions were prepared gravimetrically 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 Brand Transferpette micropipette (with an accuracy of ±0.001 cm^3). The end-point was determined by observing the transition from an appearance to a disappearance of the heterogeneous mixture.

In order to obtain the bimodal curves of the aqueous-rich and organic rich sides, the feed homogeneous mixtures of either (water + acid) or (solvent + acid) were titrated against the third component (solvent or water). All the measurements were repeated at least three times. The average of these readings was taken for the component compositions. The average uncertainty in the mass fraction of the solubility data was estimated to be better than ±0.0008.

The LLE measurements for the ternary systems were made at $T = (298.2, 308.2, \text{and } 318.2)$ K. The experiments were carried out in equilibrium glass cell with a volume of approximately 250 cm^3. The temperature was estimated to be accurate to within ±0.1 K. The mixtures were prepared gravimetrically. They were placed in the extraction cell and were vigorously agitated by a magnetic stirrer for 4 h, and then left to settle for 4 h for phase separation. For these mixtures, these times (stirring and resting times) are long enough to achieve equilibrium. In order to determine the equilibrium time, preliminary experiments were carried out using Karl-Fischer titration and refractive index measurements. In this work, no variation of composition with stirring time was established more than 4 h.

TABLE 1a
The provenance and purity of the materials.

Chemical name	Provenance	Minimum initial mole fraction purity
Butyric acid	Merck	0.99
n-Heptane	Merck	0.99
Toluene	Merck	0.99

TABLE 1b
The measured and literature values for the refractive index (n) and density (ρ) of the pure components at $T = 298.2$ K.[a]

Component	n_D		$\rho/(kg \cdot m^{-3})$	
	Exp.	Lit.	Exp.	Lit.
Butyric acid	1.3976	1.3975 [17]	952.68	952.80 [17]
n-Heptane	1.3851	1.38512 [35]	679.49	679.58 [36]
Toluene	1.4940	1.4941 [37]	861.40	862.25 [37]
Water	1.3325	1.3322 [17]	997.07	997.08 [17]

[a] Uncertainties u are $u(n) = 0.0002$, and $u(\rho) = 0.001$ $kg \cdot m^{-3}$.

At equilibrium, each system separated into two liquid phases that become clear and transparent with a well-defined interface. The samples of organic rich phase were taken by a glass syringe from the upper layer and that of water-rich phase from a sampling tap at the bottom of the cell. After separation, samples of both phases were transparent and were carefully weighed and analyzed to determine their compositions in order to determine the LLE tie lines.

2.3. Analysis

The concentrations of the acid in both the phases were obtained by potentiometric NaOH titration. The water content of the organic phase was measured by the Karl–Fisher method using Metrohm-870 KF Titrino plus Karl–Fisher titrator. The titrator was calibrated with a standard solution of sodium tartrate.

2.3.1. Organic phase

Concentration analyses of water and BA were carried out for the organic phase using Karl–Fisher and potentiometric titrations, respectively. The mass of the third component can be evaluated by knowing mass of water, mass of the acid in the organic phase and using following equation.

$$\sum_i w_i = 1. \tag{1}$$

2.3.2. Aqueous phase

Concentration analyses of water and the acid were carried out for the aqueous phase using refractive index measurements and potentiometric titrations, respectively. The refractive indices of the aqueous phase at equilibrium were measured and used for building standard curves. Equations for refractive index (n) as a function of water and BA mass fractions in the aqueous phase, and correlation coefficients (R^2) for each system at $T = (298.2, 308.2, \text{and } 318.2)$ K were given in table 2. Therefore, mass of each solvent in the aqueous phase was calculated by knowing mass of water and mass of the acid in this phase. The calculated composition of tie-line samples were checked for the data consistency using mass balance equations. For both the system, the estimated uncertainty of all measured compositions is better than ±0.001.

Table 2
Equations for refractive index (n) as a function of water mass fractions (w_{11}) in the aqueous phase at $T = (298.2, 308.2, \text{and } 318.2)$ K.[a]

System	T/K	Equation	R^2
Water + BA + *n*-heptane	298.2	$n = -0.0744w_{11} + 1.4085$	0.992
	308.2	$n = -0.0750w_{11} + 1.4075$	0.992
	318.2	$n = -0.0748w_{11} + 1.4061$	0.991
Water + BA + toluene	298.2	$n = -0.0856w_{11} + 1.4139$	0.994
	308.2	$n = -0.0848w_{11} + 1.4105$	0.998
	318.2	$n = -0.0870w_{11} + 1.4088$	0.991

[a] Standard uncertainties u are $u(T) = 0.1$ K, $u(n) = 0.0002$, and $u(w) = 0.001$.