



Solubility and tie line data for the aqueous solutions of butyric acid with 1-octanol and 2-ethyl-1-hexanol at various temperatures

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ABSTRACT

This study demonstrates the experimental and correlated tie line data for the aqueous solutions of butyric acid with two octanol isomers ($C_{18}H_{38}O$) at $T=(298.2, 308.2, \text{ and } 318.2)\text{ K}$ and $p=101.3 \pm 0.4\text{ kPa}$, for the first time. The chosen isomers were 1-octanol and 2-ethyl-1-hexanol. The obvious difference between these two isomers is that the first isomer is a straight and later is a branched primary alcohol. Experimental solubility data were obtained using the cloud point method. The tie line data were determined by acidimetric titration, the Karl–Fischer technique, and refractive index measurements. Both the ternary systems exhibit type-1 behavior of LLE. The tie-line data were correlated using the UNIQUAC and NRTL models. For each system, the Othmer–Tobias and Hand correlations equations were used to establish the quality of the tie-line data. Distribution coefficients and separation factors were calculated over the biphasic area.

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1. Introduction

Butyric acid (BA) is a colorless organic acid with an unpleasant smell. It is an important carboxylic acid that has a large range of industrial applications [1]. This acid is mainly produced by chemical and fermentation processes [2–4]. It can also be produced from petrochemical resources [5]. In bio-production, various fermentation methods have been employed from biomass [6,7]. However, future purification is required and the extraction of this acid from water is an important problem.

In the past, various investigations have been carried out on the extraction and liquid–liquid equilibrium (LLE) measurements of carboxylic acid such as BA from water [8–14]. Many organic solvents with various chemical properties have been used as extractants in the LLE measurements [15–23]. More LLE data for the aqueous solutions of BA with various organic solvents, mainly hydrocarbons, at various temperatures have been reported in our previous publications [24–28]. In this study, we present the solubility and tie-line data for [water + BA + 1-octanol (1OCT)] and [water + BA + 2-ethyl-1-hexanol (2EH)] ternary systems at $T=(298.2, 308.2, \text{ and } 318.2)\text{ K}$. 1OCT is a straight chain alcohol and is almost insoluble in water. 2EH is a branched and chiral

eight-carbon alcohol (Fig. 1), which is slightly soluble in water (1.1 gL^{-1}).

To the best of our knowledge, the LLE data of the (water + BA + 1OCT or 2EH) ternary systems have not been reported in the available literature. For a comparison of the extracting capabilities of the solvents for the separation of the acid from water, the distribution coefficients and separation factors were determined. The quality of the experimental tie-line data was determined by the Othmer–Tobias [29] and the Hands [30] correlation equations for the studied systems. Experimental tie-line data were correlated using the UNIQUAC [31] and the NRTL models [32]. The values for the UNIQUAC and NRTL interaction parameters were obtained.

2. Experimental

2.1. Materials

1-Octanol, 2-ethyl-1-hexanol, and butyric acid with stated mass fraction purities higher than 0.99 were purchased from Merck. The stated purity of the materials was checked on the basis of their refractive indices. Deionized and redistilled water with an electrical conductivity less than $5\ \mu\text{S/cm}$ at $T=298.2\text{ K}$ was used throughout all experiments. All materials were used as received without any further purification. The refractive index and density data of the chemicals used in this study along with the literature values are listed in Table 1.

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Table 1The measured and literature values for the refractive index (n) and density (ρ) of the pure components at $T=298.2$ K and $p=101.3$ kPa.^a

Component	Source	Mass fraction purity	n_D		ρ (g cm ⁻³)	
			Exp.	Lit.	Exp.	Lit.
Butyric acid	Merck	>0.99	1.3977	1.3975 [15]	0.95268	0.95280 [15]
1-Octanol	Merck	>0.99	1.4276	1.4275 [37]	0.82169	0.82157 [37]
2-Ethyl-1-hexanol	Merck	>0.99	1.4293	1.4290 [42]	0.83022	0.82910 [42]
Water	–	Deionized and redistilled	1.3324	1.3322 [15]	0.99705	0.99708 [15]

^a Uncertainties u are $u(n_D)=0.0002$, and $u(\rho)=0.00003$ g cm⁻³.

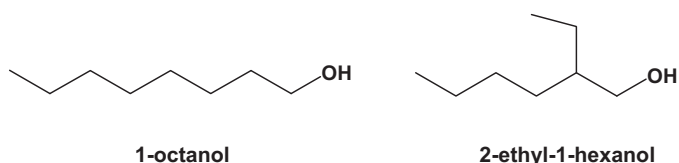
2.2. Apparatus and procedure

The refractive indices and density of the solutions were determined at $T=298.2$ K and $p=101.3 \pm 0.4$ kPa using an Abbe Refractometer (Model CETI) and DA-210 (Kyoto electronic) density meter. The instruments were initially calibrated before being used. The uncertainty in refractive index and density measurements were ± 0.0002 and ± 0.00003 g cm⁻³, respectively. The temperature of the instruments was controlled by circulation of water and was measured with a copper–constantan thermocouple located near the sample and was measured to an accuracy of ± 0.1 K. The temperature of the samples was measured with a precision digital thermometer (Lutron TM-917). The sample weighing was carried out with an AND electronic analytical balance (model HR-200) with an accuracy of ± 0.0001 g.

The solubility data of the ternary systems were determined by the cloud point titration method [33,34]. Feed binary mixtures were prepared by mass. The prepared binary mixtures of known compositions were introduced to a glass cell with a volume of about 20 ml. At each temperature, the third component was gradually added into the cell using a Brand Transferpette micropipette with an accuracy of ± 0.001 ml, which is agitated continuously with a magnetic stirrer. The titration endpoint was determined visually by observing the transition from a homogeneous to a heterogeneous mixture. The precision of the visual determination of the endpoint was attained by waiting about 5 min in the endpoint and observing the turbidity. In order to obtain the solubility data of the aqueous-rich and organic-rich sides of the curves, the feed homogeneous mixtures of either (water + BA) or (solvent + BA) were titrated against the third component (solvent or water). All the visual measurements were repeated at least three times in order to acquire high accuracy. The average of these readings was taken for the component compositions. The uncertainty in the mass fraction of the solubility data was estimated to be better than ± 0.0007 .

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 a jacketed 250 ml equilibrium glass cell. The prepared mixtures were introduced into the extraction cell and were agitated vigorously. The temperature was estimated to be accurate to within ± 0.1 K. For the studied systems, both the stirring and settle times were at least 4 h for complete phase separation. The resting time for system containing 1OCT was at least 5 h and it was at least 6 h for the other system.

The concentrations of BA in both phases were measured by potentiometric NaOH titration. The water contains of the aqueous

**Fig. 1.** The molecular structures of the solvents used in this study.

layer (w_{11}) and the amount of the organic solvent in the organic layer (w_{33}) were measured by the refractive index method. The refractive indices of the prepared samples at equilibrium (lying on the binodal curves) with known composition were measured used for building standard curves [35]. Such standard curves were made for analysis of both the aqueous and organic layers, in order to obtain the composition of data-points. The calculated composition of tie-line samples were then checked and corrected according to these calibration curves and the data consistency. Equations for refractive index (n_D) as a function of w_{11} and w_{33} at various temperatures are given in Table 2.

Moreover, the Karl–Fischer titration (Metrohm-870 KF Titrimo plus Karl–Fischer titrator) and the calculation procedure were used for the check of the LLE data. The estimated uncertainty of all measured compositions is better than ± 0.001 .

3. Results and discussion

3.1. Experimental LLE data

Solubility data for the ternary systems of (water + BA + 1OCT or 2EH) were measured at $T=(298.2, 308.2, \text{ and } 318.2)$ K. The experimental data for the studied systems at various temperatures are given in Table 3. The experimental tie-line compositions of the equilibrium phases for these systems at each temperature are also listed in Table 4. The same data are plotted as triangular phase diagrams and shown in Figs. 2–4.

Because (BA + solvents) and (BA + water) are two liquid pairs that are completely miscible and the only liquid pair (solvents + water) is partially miscible, these ternary systems behave as type-1 LLE [36]. As can be seen from the triangular phase diagrams, the temperature effect on the immiscibility regions of the studied systems is very small. In addition, the biphasic region for the ternary system consisting of 2EH is fairly larger than the other system. However,

Table 2Equations for refractive index (n_D) as a function of water mass fractions (w_{11}) in the aqueous-rich phase and the solvent mass fractions in the organic-rich phase (w_{33}) at $T=(298.2, 308.2, \text{ and } 318.2)$ K and $p=101.3$ kPa.^a

System	T/K	Equation	R ²
Water + BA + 1-octanol	298.2	$n = -0.1134 w_{11} + 1.4412$	0.998
		$n = 0.0250 w_{33} + 1.3961$	0.998
	308.2	$n = -0.1090 w_{11} + 1.4358$	0.997
		$n = 0.0330 w_{33} + 1.3899$	0.997
	318.2	$n = -0.0846 w_{11} + 1.4122$	0.996
		$n = 0.0332 w_{33} + 1.3861$	0.995
Water + BA + 2-ethyl-1-hexanol	298.2	$n = -0.0830 w_{11} + 1.4127$	0.998
		$n = 0.0371 w_{33} + 1.3894$	0.998
	308.2	$n = -0.0881 w_{11} + 1.4155$	0.997
		$n = 0.0319 w_{33} + 1.3912$	0.997
	318.2	$n = -0.0816 w_{11} + 1.4081$	0.998
		$n = 0.0319 w_{33} + 1.3897$	0.997

^a Standard uncertainties u are $u(T)=0.1$ K, $u(p)=0.4$ kPa, $u(n)=0.0002$, and $u(w)=0.001$.

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