Ternary phase diagrams for aqueous mixtures of butyric acid with several solvents: Experimental and correlated data

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A B S T R A C T

Octan-1-ol, acetophenone, ethyl butanoate (ethyl butyrate), ethyl pentanoate (ethyl valerate), and 1,3-diethyl propanedioate (diethyl malonate) were used as solvents for determining the ternary liquid phase diagrams of aqueous mixtures consisting butyric acid, with the intention of bringing more effective and environmental friendly solvents into use. The liquid–liquid equilibrium (LLE) data for water + butyric acid + solvent ternary systems were investigated at 298.15 K and atmospheric pressure. The ternary phase diagrams composed of solubility data and tie-lines were presented graphically. The reliability of the experimental tie-lines was tested by Othmer–Tobias correlation. The experimental tie-line data were compared with the results correlated by means of UNIQUAC model, and predicted by the UNIFAC method. It is concluded that the used solvents may be adequate extractants to extract butyric acid from its dilute aqueous solutions.

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1. Introduction

Although the chemical synthesis of butyric acid with starting materials derived from crude oil is currently more desirable due to its low production cost and large scale supply, the increasing consumer demand for organic natural products in food additives, preservatives, and pharmaceutical products leads to the natural butyric acid production by microbial fermentation. For industrial applications, the anaerobic microorganism *Clostridium butyricum* has been used intensively in the fermentation process, because of the capability to utilize of many carbon sources including hexose, pentose, glycerol, lignocellulose, molasses, potato starch, and cheese-whey permeate [1]. During the fermentation process, the pH of the culture medium decreases simultaneously with the product accumulation, which causes to different product distribution and/or acid inhibition, where relative high pH (e.g. >6) is beneficial for cell growth and biosynthesis [2,3]. This leads in turn either to the necessity of adding a neutralization agent or removing the acid in situ in order to maintain the optimal range of the fermentation. Furthermore, after any industrial process, butyric acid found in the waste water needs also to be removed because of theenvironmental

and economical aspects. At this point, solvent extraction methods in various types play a significant role for separating carboxylic acids from their aqueous solutions, allowing production and separation simultaneously [4–7].

Solvents used in extraction processes should be chosen carefully. On one hand, they should have low cost, low toxicity, great stability, and rather high boiling temperature properties, while their viscosity and densities should be close to those of water. On the other hand they should give proper liquid–liquid equilibrium (LLE) data for the excellent design and productive operation of the related extraction equipment.

Several studies have been carried out to obtain LLE data for the extraction of butyric acid from its dilute aqueous solutions using different solvents in various chemical structures which are summarized in Table 1 within related literatures [8–22]. As a continuation of the previous studies on the recovery of butyric acid from dilute aqueous solutions, the present work aims to produce new LLE data. We have alternatively focused on octan-1-ol, acetophenone, ethyl butanoate, ethyl pentanoate, and 1,3-diethyl propanedioate as new potential replacements of toxic solvents which are mainly the members of chlorocarbons or aromatic hydrocarbons for separation of butyric acid from its dilute aqueous solutions. In this paper, the experimental LLE results of the {water + butyric acid + solvent (Octan-1-ol, acetophenone, ethyl butanoate, ethyl pentanoate, 1,3-diethyl propanedioate)} ternary systems at $T = 298.15$ K were reported, for which no such data are available in the literature. The

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Nomenclature and units:

A, B	Othmer–Tobias correlation constants
a	UNIQUAC interaction parameter [K]
d	distribution coefficient
n_D	refractive index
N	number of tie-lines
q	molecular UNIQUAC surface parameter
r	molecular UNIQUAC volume parameter
R	general gas constant [J mol^{-1} K^{-1}]
R^2	Othmer–Tobias correlation coefficients
rmsd	root mean square deviation
S	separation factor
T	temperature [K]
Δu	UNIQUAC interaction parameter [J mol^{-1}]
x	concentration in mole fraction
ρ	density [kg m^{-3}]

Superscripts

cal	calculated
exp	experimental
I	aqueous phase
II	organic phase

Subscripts

b	boiling
i, m, n	component
j	phase
k	tie-line

experimental tie-line data were compared with the results correlated by means of UNIQUAC model [23], and predicted by the UNIFAC method [24].

2. Experimental

Butyric acid, octan-1-ol, acetophenone, ethyl butanoate, and 1,3-diethyl propanedioate were purchased from Merck and ethyl pentanoate was obtained from Aldrich. All chemicals were used as received (with mass fraction purities higher than 0.98) and without further purification. Deionised and bidistilled water was used throughout all experiments. The purity of the chemicals was checked on the basis of their densities and refractive indexes at (293 ± 0.10) K, and boiling temperatures at (101.325 ± 0.5) kPa. Refractive indexes and densities were measured with Anton Paar density meter (Model DMA 4500) integrated with a refractive index unit (Model RXA 170) both in $\pm 10^{-5}$ precision. Boiling temperature measurements were performed by using a Fischer boiling point apparatus. The sources, mass fraction purities, and measured

Table 1
LLE studies performed on (water + butyric acid + solvent) ternary systems.

Type	Solvent	*T* (K)	Literature
Alcohol	Nonanol	298.15, 308.15, 318.15	8
	Isoamyl alcohol	298.15, 308.15, 318.15	9
	Oleyl alcohol	298.15, 308.15, 318.15	10
	Dodecanol	298.20, 308.20, 318.20	11
	1-Undecanol	298.15	12
	n-Hexanol	298.20, 308.20, 318.20	13
Ester	Cyclohexyl acetate	298.15, 308.15, 318.15	14
	Ethly propionate	298.15	15
	Dimethyl phthalate	298.15	15
	Dibutyl phthalate	298.15	15
	Dimethyl succinate	298.15	16
	Dimethyl glutarate	298.15	16
	Dimethyl adipate	298.15	16
	Diethyl maleate	298.15	17
	Isobutyl acetate	298.20, 303.20, 308.20, 313.20	18
Alkane	*n*-Heptane	298.20, 308.20, 318.20	19
	n-Hexane	298.20, 308.20, 318.20	13
	Cyclohexane	298.20, 303.20, 308.20, 313.20	20
	Methylcyclohexane	298.20, 308.20, 318.20, 328.20	21
Ketone	Cyclohexanone	298.20, 308.20, 318.20	22
Aromatic	Toluene	298.20, 308.20, 318.20	19

physical properties of the chemicals are listed in Table 2, along with literature values [25].

The tie-line end compositions of liquid phases at equilibrium were established by analysing the conjugate phases independently. Mixtures of known masses of water, acid and solvent lying within the heterogeneous gap were introduced into the equilibrium cell and were stirred vigorously for at least 4 h, and then left for 4 h to settle down into raffinate (aqueous) and extract (solvent) layers. The liquid samples withdrawn from both phases were analysed by a gas chromatograph (Hewlett Packard GC, Model 6890 Series), equipped with a thermal conductivity detector (TCD) and a flame ionisation detector (FID) for the quantitative determination of water, butyric acid, octan-1-ol, acetophenone, ethyl butanoate, ethyl pentanoate, and 1,3-diethyl propanedioate. A 50 m long SGE B1 column (320 μm diameter with a 0.5 μm film thickness) was used with a temperature-programmed analysis. Column temperature, from (343.15 ± 2) K to (503.15 ± 3) K at 20 K min^{-1}, at 503.15 K (3 min) injection mode, split ratio 100:1; injector and detector temperature, (523.15 ± 2) K; carrier gas, nitrogen 1 cm^3 min^{-1}; injected volume of 0.3 μL of liquid sample. The uncertainty of the mole fraction measurements for the overall composition determination was ± 0.002.

3. Results and discussion

The measured equilibrium tie-line data were given in Table 3, for which x_i^I and x_i^{II} refer to the molar fractions of the *i*th component in the aqueous and solvent phases, respectively. Table 3 shows

Table 2
Densities (ρ) and refractive indexes (n_D) at 293.15 K and boiling temperatures (T_b) at 101.325 kPa of the pure components along with their provenances and mass fraction purities[a].

Compound	Supplier	Purity (mass fraction)	ρ (kg m^{-3})		n_D		T_b (K)	
			Expt.	Lit. [25]	Expt.	Lit. [25]	Expt.	Lit. [25]
Water		Deionised and bidistilled	999.70	998.23	1.3325	1.3330	373.25	373.15
Butyric acid	Merck	0.99	952.60[b]	952.80[b]	1.3982	1.3980	436.80	436.90
Octan-1-ol	Merck	≥0.99	825.95[b]	826.20[b]	1.4280	1.4295	468.20	468.31
Acetophenone	Merck	≥0.98	1027.90	1028.10	1.5361	1.5372	475.10	475.15
Ethyl butanoate	Merck	≥0.98	873.25[b]	873.50[b]	1.3891[b]	1.3898[b]	394.55	394.45
Ethyl pentanoate	Aldrich	0.99	877.15	877.00	1.4125	1.4120	419.30	419.25
1,3-diethyl propanedioate	Merck	≥0.98	1055.25	1055.10	1.4135	1.4139	473.05	473.15

[a] Standard uncertainties *u* are $u(\rho) = 0.01$ kg m^{-3}, $u(n_D) = 0.0001$, $u(T_b) = 0.1$ K, $u(p) = 0.5$ kPa.
[b] At 298.15 K.