Fluid Phase Equilibria 463 (2018) 34–47

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Liquid-liquid equilibrium data for ternary systems of water + acetic acid+ acetate esters at 293.2 K and 303.2 K and ≈ 95 kPa

Laerti Reis Roque [a], Rafaela Rocha Pinto [b], Leonardo Hadlich de Oliveira [c, *], Sarita Cândida Rabelo [a]

[a] Brazilian Bioethanol Science and Technology Laboratory (CTBE), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas - SP, Brazil
[b] School of Chemical Engineering (FEQ), State University of Campinas (Unicamp), Campinas - SP, Brazil
[c] Laboratory of Adsorption and Ion Exchange (LATI), Chemical Engineering Department (DEQ), State University of Maringá (UEM), Maringá - PR, Brazil

ARTICLE INFO

Article history:
Received 21 September 2017
Received in revised form
1 February 2018
Accepted 5 February 2018
Available online 8 February 2018

Keywords:
Acetic acid
Density
Refractive index
Liquid-liquid equilibrium
NRTL

ABSTRACT

Liquid-liquid equilibrium data for water + acetic acid + {ethyl or butyl or isobutyl of isoamyl or heptyl acetate} systems at $T = \{293.2$ and $313.2\}$ K and atmospheric pressure ($P \approx 95$ kPa) were determined by density and refractive index measurements. Binodal curves were constructed utilizing cloud point method and tie lines were determined using equations obtained through cloud point data fit. Partition coefficients, ester selectivities and percent of extraction were calculated in order to compare the solvents employed. It was verified that immiscibility region increases in the order: ethyl < butyl ≈ isobutyl < isoamyl < heptyl. Partition coefficients were higher for systems with ethyl acetate. Selectivity values achieved were all above 1, and heptyl acetate presented greater values among all solvents studied. Percent of extraction for acetic acid feed molar between 0.05 and 0.12 is greater for ethyl acetate; from 0.12 to 0.20, it is greater for butyl acetate; and, from 0.24 to 0.30, only data for heptyl could be determined. Different temperatures utilized did not presented significant variation in the results obtained. Experimental data were correlated with NRTL model, presenting root mean square deviation equal to 1.074 for 55 tie lines. NRTL was also used to estimate plait points for all systems.

1. Introduction

One of the major problems in the commercial production of the second generation ethanol (2G ethanol) are the toxic compounds generated during the fractionation process of the lignocellulosic material [1]. Through this step, known as pretreatment, it is possible to obtain sugars, such as D-xylose and D-glucose as the major reaction products, but one problem associated with this hydrolytic process is the toxic compounds generation (furanic aldehydes, aliphatic acids and phenolic compounds), regarded as a great limiting factor in fermentation processes of hydrolysates [2].

Acetic acid is released from the hemicellulosic chain during the pretreatment step, being the major aliphatic compound present in the hydrolysates lignocellulosic. When this acid (in the undissociated form) enters in the cell, it becomes dissociated in the protoplasm because its pH. This fact leads to a decrease in the intracellular pH and can generate the cellular death, thus decreasing the productivity and yield of ethanol production [3]. Detoxification treatments with solvents have been revealed interesting combined the best inhibitor removal and lower alteration of sugar yields could be achieved. The solvents must have proper characteristics in terms of solubility with the acid and in terms of facilities of separation from the acid for recycling. The liquid-liquid equilibrium (LLE) data will provide better understanding of the system behavior and will enable evaluation of a liquid–liquid extraction process to detoxification step of the hemicellulosic hydrolysate.

Separation of acetic acid is a state-of-art example of organic acids removal from aqueous solutions. Azeotropic and extraction distillations were often used to separate acetic acid from such mixtures, utilizing mainly esters as entrainers [4]. Recovery of acetic acid utilizing liquid extraction has been subject of study since many years ago [5].

In literature water + acetic acid + esters ternary systems were studied using the following solvents: ethyl acetate at 283, 288.15, 298, 298.2, 303.15, and 313 K [6–9]; propyl acetate at 298.15, 313.15 and 363.65 K [10]; butyl acetate at 298.15, 303.15, 304.15, 308.15,

* Corresponding author.
E-mail address: leonardoh.deoliveira@gmail.com (L.H. de Oliveira).

https://doi.org/10.1016/j.fluid.2018.02.003
0378-3812/

332.15 and 366.15 K [11,12]; 2-methyl propyl acetate at 304.15, 332.15 and 366.15 K [11]; cyclohexyl acetate at 298.16, 308.16, and 318.16 K [13]; dimethyl glutarate at 298.2, 308.2, and 318.2 K [14]; dimethyl phthalate at 293.16 K [15]; and diethyl phthalate at 293.16 K [15].

This work is part of a research project on second generation ethanol production where the detoxification of sugarcane bagasse hemicellulosic hydrolysate has been studied by liquid-liquid extraction. LLE data for water + acetic acid + {ethyl acetate or butyl acetate or isobutyl acetate or isoamyl acetate or heptyl acetate} systems at T = (293.2 or 313.2) K and atmospheric pressure ≈ 95 kPa were determined utilizing cloud point method, and density and refractive index measurements. Partition coefficients, ester selectivities and percents of extraction were determined using tie line data. NRTL model was utilized to correlate equilibrium data, providing calculated binodal curve and plait point for each system. Data determined here, excluding using ethyl acetate at T = 293.2 K and propyl acetate at T = 313.2 K, were not found in literature.

2. Experimental

2.1. Chemical products

Chemical products utilized here and their molar mass, purity, supplier, and properties, *i.e.*, density and refractive index at 293.2 K and 313.2 K are presented in Table 1. Purchased chemicals were used as received and their purities were taken into account in all experiments. Distilled water was obtained in an ELGA DV35 distiller (Lane End, UK), and its purity was considered be equal to 1.

2.2. Density and refractive index measurements

Density (ρ) and refractive index (n) were measured for all cloud points and equilibrium phases in an Anton Paar DSA 5000 M-tube densimeter (Graz, Austria), precise to $\pm 1 \times 10^{-3}$ kg m^{-3}, using 1.5×10^{-6} m^3 of liquid sample, and Anton Paar Abbemat 500 refractometer (Graz, Austria), precise to $\pm 1 \times 10^{-6}$, using 2×10^{-7} m^3 of liquid sample, respectively.

2.3. Binodal curves

Binodal curves and tie lines determined for ternary systems studied here were determined based on the procedure previously reported [25]. Cloud point method was utilized to determine the immiscibility region between water and acetic acid and esters. Water-reach phase cloud points were determined inserting drop-by-drop using Braun Injekt syringes known amounts of ester in a previously weighed water + acetic acid mixture until constant slightly turbidity was detected. Ester-reach phase cloud points were obtained by the same procedure, inserting water instead. A Sartorius TE214S (Goettingen, Germany) analytical balance, precise to ± 0.0001 g, was used to weight each component's mass inserted in the system. This procedure was taken inside a pyrex glass equilibrium cells of 25×10^{-6} m^3 and 27×10^{-6} m^3 internal volume. The cloud points determination was carried out at constant temperature, T = 293.2 or 313.2 K, controlled by the recirculation of water prevenient from a Tecnal TE-184 (São Paulo, Brazil) thermostatic bath, precise to ± 0.1 K, through the cell external jacket. After each cloud point was attained, samples of turbid ternary mixture were collected for density and refractive index measurements.

Experimental cloud points mole fractions, density and/or refractive index measurements were used to obtain, through data fit with software Statistica® 8.0, calibration expressions for calculation of tie lines unknown mole fractions in LLE data experiments. The general expressions obtained are shown in Equations (1)–(6).

$$x_1 = A_1 + B_1\rho n + C_1\rho^2 + D_1 n^2 \quad (1)$$

$$x_1 = A_2 + B_2\rho^2 + C_2 n^2 + D_2\rho^3 + E_2 n^3 \quad (2)$$

$$x_1 = A_3 + B_3\rho^2 + C_3 n^2 \quad (3)$$

$$x_2 = A_4 + B_4 x_1 + C_4 x_1^2 \quad (4)$$

$$x_2 = A_5 + B_5 x_1 + C_5 x_1^2 + D_5 x_1^3 \quad (5)$$

$$x_2 = A_6 + B_6 x_1 + C_6 x_1^2 + D_6 x_1^4 \quad (6)$$

Where x_1 is the water mole fraction, x_2 is the acetic acid mole fraction; A_1, B_1 (m^3 kg^{-1}), C_1 (m^6 kg^{-2}) and D_1 are fitting parameters for Equation (1); A_2, B_2 (m^6 kg^{-2}), C_2, D_2 (m^9 kg^{-3}) and E_2 are fitting parameters for Equation (2); A_3, B_3 (m^6 kg^{-2}) and C_3 are fitting parameters for Equation (3); A_4, B_4 and C_4 are fitting parameters for Equation (4); A_5, B_5,C_5 and D_5 are fitting parameters for Equation (5); A_6, B_6, C_6 and D_6 are fitting parameters for Equation (6).

Two kinds of calibration expressions were determined in this work. The first set, Equations (1)–(3), was obtained utilizing water mole fraction against density and refractive index; the second, Equations (4)–(6), using acetic acid mole fraction against water mole fraction. Using combinations of Equations (1) and (2) or 3 with Equations (4) and (5) or 6, it was possible to determine, simultaneously, the values for the mole fractions x_1 and x_2 in an unknown composition mixture for the systems studied in this work. Hence, solubility data for systems with ethyl acetate were

Table 1
Properties of chemicals at T = 293.2 and 313.2 K and P ≈ 95 kPa.[a]

Chemical	M/(kg kmol^{-1})	ρ/(kg m^{-3})				n				Mass fraction purity	Supplier
		T = 293.2 K		T = 313.2 K		T = 293.2 K		T = 313.2 K			
		Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit		
Water	18.015	998.397	998.768[b]	992.201	992.744[b]	1.3330	1.3330[b]	1.3306	1.3307[b]		
Acetic acid	60.052	1049.799	1048.9[c]	1028.134	1030.3[c]	1.3724	1.3730[c]	1.3644	1.3644[c]	0.997	Sigma-Aldrich
Ethyl acetate	88.107	900.569	900.92[d]	876.101	875.1[e]	1.3724	1.3724[d]	1.3619	1.3637[e]	0.995	Sigma-Aldrich
Butyl acetate	116.16	881.380	881.45[f]	860.059	860.67[f]	1.3943	1.3947[f]	1.3845	1.3858[f]	0.995	Sigma-Aldrich
Isobutyl acetate	116.16	871.303	873.4[g]	849.391	849.8[h]	1.3901	1.3902[g]	1.3802		0.98	Merck
Isoamyl acetate	130.187	872.492	873.2[i]	852.645	852.8[j]	1.4006	1.4008[i]	1.3912	1.3845[j]	0.99	Sigma-Aldrich
Heptyl acetate	158.24	870.582		852.589		1.4146		1.4054		0.98	Sigma-Aldrich

[a] Maximum standard uncertainties, u, are: $u(T)$ = 0.1 K, $u(\rho)$ = 0.450 kg m^{-3}, $u(n)$ = 0.0005. [b] Ref. [16]. [c] Ref. [17]. [d] Ref. [18]. [e] Ref. [19]. [f] Ref. [20]. [g] Ref. [21]. [h] Ref. [22]. [i] Ref. [23]. [j] Ref. [24].