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Liquid–liquid equilibrium data for ternary systems of water + lactic acid + C4–C7 alcohols at 298.2 K and atmospheric pressure

Lucas Domingues[a], Phylipe Andrian Cussolin[a], Julio Lopes da Silva Jr.[b], Leonardo Hadlich de Oliveira[b,*], Martín Aznar[b]

[a] *Departament of Pharmacy, Centro Regional Universitário de Espírito Santo do Pinhal, Av. Hélio Vergueiro Leite, 13990-000 Espírito Santo do Pinhal, SP, Brazil*

[b] *School of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, 13083-852 Campinas, SP, Brazil*

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ABSTRACT

Liquid–liquid equilibrium data for water + lactic acid + {1-butanol or 2-butanol, 1-pentanol, 1-hexanol, 1-heptanol} systems at $T = 298.2$ K and atmospheric pressure (≈95 kPa) were determined by density and refractive index measurements. The systems present Treybal's type I binodal curves. Obtained tie line data were correlated with NRTL model. Cloud points, tie lines, partition coefficients, selectivities and percent of extraction indicate that 1-pentanol is better than the other solvents studied for lactic acid removal from water.

1. Introduction

Recovery of lactic acid from water is subject of research in biotechnology due to the environmental concern this acid represents when fermentation streams and waste vinasses with high acid content, are produced. The possibility to add value also causes interest in lactic acid removal from water [1,2]. Lactic acid can be used, industrially, as a preservative, an antioxidant, and as improver of taste and quality of foods [2,3]; as a raw material for the production of biodegradable polylactic acid, which can substitute conventional petroleum plastic materials in polymer industry [4]; and for controlled drug delivery in pharmaceutical industry [5].

Several techniques are proposed to separate lactic acid [6]; among them, methods based on liquid–liquid extraction. Leonard et al. [7] determined partition coefficients of lactic acid between water and 1-butanol, 1-pentanol, 1-hexanol, among several other solvents; Ratchford et al. [8] propose a method for recovery lactic acid from water using tertiary amines; Petritis and Geankoplis [9] measured cloud points and tie lines for water + lactic acid + 1-butanol (these data are compared with the ones determined in this work); Şahin et al. [10] reported liquid–liquid equilibrium data for water + lactic acid + 1-octanol, 1-nonanol, and 1-decanol; Achour et al. [11] published results for water + lactic acid + a solvent mixture; Kyuchoukov et al. [12] developed a new method for lactic acid extraction from water solutions, based on a quaternary ammonium salt as extractant; Planas et al. [13] performed lactic acid purification using aqueous biphasic systems, but small partition coefficients were obtained; Yankov et al. [14] also reported partition coefficients of lactic acid in aqueous biphasic systems and its influence on phase separation. Patents that report the use of this operation also can be found [15–20].

In this work, a continuation of studies involving the recovery of organic compounds from water using liquid extraction is presented [21–23]. Liquid–liquid equilibrium data for water + lactic acid + {1-butanol, or 2-butanol, 1-pentanol, 1-hexanol or 1-heptanol} at $T = 298.2$ K and atmospheric pressure (≈95 kPa) were determined using density and refractive index measurements. Data correlation was made with NTRL model.

2. Experimental

Chemicals used in this work and their selected properties are presented in Table 1. Purchased chemicals were used as received. Distilled water was obtained in a Quimis Q341 distiller.

The procedure employed to determine the liquid–liquid equilibrium data, basically consisted of binodal curves and tie lines

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* Corresponding author. Tel.: +55 44 99179871.
E-mail addresses: lucasdomingues25@uol.com.br (L. Domingues), leonardoh.deoliveira@gmail.com (L.H. de Oliveira), maznar@feq.unicamp.br (M. Aznar).

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Nomenclature

Arabic letters

A	NRTL interaction energy adjustable parameter
B	NRTL temperature dependent interaction energy adjustable parameter (K)
c	concentration in g/100 mL, used to compare with literature data
C_0	see Eq. (7)
E	percent of extraction percent
F	concentration-based objective function
G	a Boltzmann-type local composition energy interaction between i and j
h	distance between the tie line and its feed point
K	partition coefficient
M	molecular weight (kg kmol^{-1}); total number of tie lines in Eqs. (4) and (5)
n	refractive index
N	total number of components in Eqs. (4) and (5)
P_i	regression parameters in Eq. (6), $i = 0–5$
R	ideal gas constant (=8.314 J mol^{-1} K^{-1})
S	selectivity
T	temperature (K)
u	standard uncertainty
u_c	combined standard uncertainty
v	variable used for uncertainty calculation
w	mass fraction
W	weight associated with component n in tie line m at phase d and temperature t
x	molar fraction

Greek letters

α	non-randomness parameter
γ	activity coefficient
δe	mutual solubility relative error between experimental and literature values
δx	percent root-mean-square-deviation
Δg	binary interaction characteristic energy (J mol^{-1})
ρ	density (kg m^{-3})
τ	binary interaction characteristic energy parameter
θ	physical property (ρ or n) in Eq. (6)

Subscript

i,j,k	components
n	component
m	tie line
d	phase
t	temperature (K)
1,2,3	represent water, furfural and solvent

Superscripts

feed	respect to the feed point
aq	aqueous phase
org	organic phase
exp	experimental
calc	calculated

determination, was similar to that previously reported [23]. Aqueous phase cloud point compositions were determined by the addition, drop-by-drop, of known amounts of alcohol into a previously weighed mixture of water + lactic acid. The organic phase cloud point compositions were achieved in the inverse way, adding water into a mixture of alcohol + lactic acid. After the "cloud" was reached, which is characterized by a slightly turbid mixture, its density and refractive index were measured. Density was measured in an Anton Paar DMA 5000 U-tube densimeter, $\pm 5 \times 10^{-3}$ kg m^{-3} precision, using 1 mL of liquid sample. Refractive index was measured in a Metler Toledo RE40D refractometer, $\pm 1 \times 10^{-4}$ precision, using 0.2 mL of liquid sample. This procedure provides the physical property versus concentration (mass fraction) behavior, which was fitted with surface equations of the type $z = a + bx + cx^2 + dy + ey^2 + fxy$, for systems without 2-butanol, and with plane equations, $z = a + bx + cy$, for the system with 2-butanol. Here, z is the physical property; a, b, c, d, e, and f are constants; x and y are concentrations. These equations are detailed in Section 4.

Tie lines were obtained by adding known quantities of water, lactic acid and alcohol inside of jacketed equilibrium glass vessels of ≈23 mL, designed for circulation of water from a thermostatic bath. The alcohol to water feed mass ratio was approximately 0.6 for all tie lines. The mixture was vigorously agitated for 3 h of and left settle for at least 12 h. After this, it was observed two transparent separated liquid phases with a well-defined interface. Approximately 1.5 mL of each equilibrium phase was collected with a HSW 5 mL syringe and the properties, ρ and n, were measured. This syringe is not equipped with rubber piston; this avoids a possible damage of the sample due to an observed swelling of rubber pistons in the presence of alcohols. Water and lactic acid concentrations in each phase were calculated from the measured values of ρ and n and equations obtained from binodal data. The alcohol concentration was determined by difference.

3. Thermodynamic modeling

Liquid–liquid equilibrium data for water + lactic acid + alcohol systems determined here – a total of 32 tie lines – were correlated with the well-known non-random two-liquid model (NRTL) [29]. NRTL equations are given by:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left[\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{ki}}{\sum_k G_{kj} x_k} \right] \tag{1}$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} = A_{ij} + \frac{B_{ij}}{T} \quad (\tau_{ij} \neq \tau_{ji}) \tag{2}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (\alpha_{ij} = \alpha_{ji}) \tag{3}$$

A_{ij}, B_{ij} and α_{ij} parameters were estimated with the Fortran code tool TML-LLE 2.0 [30]. The procedure, based on the modified Simplex method [31], consists in the minimization of a concentration-based objective function, F [32].

$$F = \sum_t^T \sum_d^D \sum_m^M \sum_n^{N-1} \left\{ W_{nmdt} \left(x_{nmdt}^{\exp} - x_{nmdt}^{calc} \right)^2 \right\} \tag{4}$$

Calculated compositions were compared with the experimental ones through the percent root-mean-square deviation (*rmsd*), given by:

$$\delta x = 100 \sqrt{\frac{\sum_d^D \sum_m^M \sum_n^N (x_{nmd}^{\exp} - x_{nmd}^{calc})^2}{2MN}} \tag{5}$$

4. Results and discussion

The solubility data determined for water + lactic acid + {1-butanol or 2-butanol, 1-pentanol, 1-hexanol, and 1-heptanol}, at $T = 298.2$ K and ≈95 kPa, shown in Table 2. In order to validate the method used, mutual solubility between water and alcohol determined in this work was compared to the ones proved to be reliable and already published in literature [33–36]. This comparison is presented in Table 3 and indicates that the applied method is suitable. The binodal curves obtained are presented in Figs. 1 and 2.