Solubility and tie-line data for ternary aqueous mixtures of cyclopentanol with organic solvents at T = 298.2 K: Experiments and NRTL model

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ABSTRACT

Liquid–liquid equilibrium (LLE) data are of great importance for the separation processes that are applied in the chemical industry. Cyclopentanol is a product used by many industries that may contaminate in wastewater. The purpose of this work is to obtain LLE data for cyclopentanol separation. Ternary LLE systems of water + cyclopentanol + organic solvents (MIBK, ethyl acetate, furfural or n-butanol) were investigated at T = 298.2 K as well as atmospheric pressure. The solubility and tie-line data of these ternary LLE systems were obtained by direct analysis method. The reliability of the LLE experimental results was validated by the uncertainty propagation calculation. Distribution coefficients (D) and separation factors (S) were calculated in order to evaluate the capability of organic solvents for the selective separation of cyclopentanol. Percentage separations (E) of cyclopentanol were also studied. Good correlations of the experimental LLE data with modeling results calculated by the non-random two liquid (NRTL) model were presented and confirmed by the *rmsd* values. The latter values were found to be less than 4%.

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1. Introduction

Cyclopentanol is a cyclic alcohol which is prepared by hydrogenation of cyclopentanone [1,2]. It is mainly used in the perfume industry and in the manufacture of nylon [3]. During the operation of these processes, cyclopentanol may contaminate in wastewater. In the purification of wastewater and prevention of environmental contamination, the separation of cyclopentanol from wastewater is highly important.

Liquid–liquid extraction is a major separation process in the chemical and petrochemical industries due to its less energy consumption and high efficiency over distillation processes [4]. The efficiency of this process is based on the physical and chemical properties of selective organic solvents used for separation of the target component present in water. There are practical concerns in selecting the organic solvent like viscosity, density, boiling point, interfacial tension and thermal stability [5]. In order to design and enhance the liquid–liquid extraction process, precise liquid–liquid

equilibrium (LLE) data of ternary systems are required. Ternary diagrams involving a solubility curve and tie-lines are of great importance for the ternary LLE systems [6–8]. These are obtained by direct analysis method or by cloud-point titration [9].

Thermodynamic models are also important for predicting thermodynamic properties of the ternary LLE systems, particularly the activity coefficient models. The non-random two liquid (NRTL) model is one of the activity coefficient models which is cited in numerous literature [10–14]. This model was reported by Bouneb et al [15] who showed its application to a wide variety of mixtures for vapor–liquid and liquid–liquid phase equilibria. The model is based on a semi-empirical physical model combined with a molecular local composition concept as described by Bart [16]. Moreover, the model involves binary interaction parameters which can be obtained by experimental equilibrium results.

The main purpose of this work is to provide a new series of LLE data. The liquid phase behavior for the ternary LLE systems consisting of water, cyclopentanol and efficient organic solvents was studied at a temperature of 298.2 K together with atmospheric pressure. The organic solvents such as, methyl isobutyl ketone (MIBK), ethyl acetate, furfural and n-butanol were selected for such study. MIBK is non-toxic, highly selective and relatively less miscible in aqueous solutions [17]. Ethyl acetate is a good solvent and benign for the environment [18]. Furfural and n-butanol are the

Nomenclature

a, b, c, e	NRTL coefficients for the binary interaction parameters
D	distribution coefficient
E	percentage separation (%)
G	NRTL parameter in Eqs. (7) and (10)
k	integer number
m	mass of components (g)
n	number of independent observations in Eqs. (1) and (2) or number of tie-lines in Eq. (11)
$rmsd$	root-mean square deviation (%)
S	separation factor
T	temperature (K)
$u(X_i)$	standard uncertainty
w	mass fraction
x	mole fraction
X	input quantity from the measurement in Eqs. (1) and (2)

Greek letters

α	non-random parameter
γ	activity coefficient
τ	NRTL parameters in Eqs. (7), (8) and (10)

Superscripts

cal.	modeling results
expt.	experimental results
I	aqueous-rich phase
II	organic-rich phase

Subscripts

i, j, k	indices for all components
1	water
2	cyclopentanol
3	organic solvents

preferable solvents which are used in the industry [19,20]. The solubility and tie-line data for each ternary system were obtained by the direct analysis method and their reliability was validated by the uncertainty propagation calculation. The separation capability of the selected organic solvents was expressed in terms of distribution coefficients (D) and separation factors (S) calculated by the tie-line data. The amount of cyclopentanol that was separated in the ternary systems was also studied and expressed by the percentage separation (E). Finally, the LLE data of the investigated systems were correlated with the modeling results obtained by the NRTL model. These correlations were evaluated by the $rmsd$ values.

2. Experimental

2.1. Chemicals

Chemicals consisting of cyclopentanol ($C_5H_{10}O$, MW 86.13 g/mol), furfural ($C_5H_4O_2$, MW 96.08 g/mol), n-butanol (C_4H_9OH, MW 74.12 g/mol), methyl isobutyl ketone ($C_6H_{12}O$, MW 100.16 g/mol) and ethyl acetate ($C_4H_8O_2$, MW 88.11 g/mol) were used without further purification. The source of all chemicals and their important physical properties as publicized by the wikipedia website [21] is listed in Table 1. Distilled water was used in all experiments.

2.2. Apparatus and procedure

The equilibrium solubility data in the organic-rich and aqueous-rich phases of the ternary systems were obtained by direct analysis method. The weights of all components were obtained by a digital analytical balance-Mettler Toledo AE200 (with an accuracy of ±0.0001 g). A water jacket, that was checked using a digital thermometer (with an accuracy of ±0.1 K), was used to control the temperature of the systems. The binary mixtures of the known compositions of cyclopentanol and organic solvents were prepared in closed glass vessels. The binary mixtures were continually titrated with water until they became turbid. The end point of titration was achieved when the mixtures remained turbid for 15 min. During this time, the glass vessels were agitated periodically to observe the turbidity. These procedures were used to obtain the solubility curve of the organic-rich phase. In order to repeat all measurements at least three times, a known quantity of cyclopentanol was added into the mixtures for back transparency. The mixtures were again titrated with water until they became turbid, and the same end point of titration was taken. To obtain the solubility curve of the aqueous-rich phase, the binary mixtures with the predetermined compositions of cyclopentanol and water were prepared in the closed glass vessels. The organic solvents were continually added into the binary mixtures till turbidity. Thereafter, the glass vessels were agitated periodically to observe the turbidity for 15 min. The end point of titration was achieved when the mixtures remained turbid.

The tie-line data of the ternary systems were obtained from the ternary mixtures after reaching equilibrium composition. More water was successively added until the transition from homogeneous to heterogeneous state appeared in the mixtures. Thereafter, the mixtures were weighed and agitated vigorously at 200 rpm for 2 h. Then they were centrifugated and left for 14 h to complete separation. These periods were long enough for samples reaching two equilibrium liquid layers. The organic-rich phase was carefully withdrawn from the top layer of the glass vessel by syringe and then weighed. The remaining aqueous-rich sample was also weighed and analyzed by gas chromatography to determine the compositions of cyclopentanol and organic solvents. The composition of water was calculated by the mass balance equation. These results were used to be the tie-line data in the aqueous-rich phase. To obtain the tie-line data in the organic-rich phase, the composition of each component was calculated based on its composition difference in the mixtures and the aqueous-rich phase. Triangular phase diagrams for all ternary LLE data were plotted by the ProSim program.

2.3. Analyses

The aqueous-rich phases were analyzed by gas chromatography (Hewlett Packard 5890 Series II, with FID detector) using a

Table 1
Source and important physical properties of chemicals.

Chemical name	Source	Purity/% mass	Analysis method	Solubility in water [21] (g/100 mL H_2O; 298 K)	Normal boiling point (K) [21]
Cyclopentanol	Sigma–Aldrich	99.0	GC	Soluble	412–413
Furfural	Sigma–Aldrich	99.0	GC	8.3	435.0
n-Butanol	Erba Lachema	99.5	GC	10.0	390.8
Methyl isobutyl ketone	MicroChem	99.5	GC	1.9	390–391
Ethyl acetate	MicroChem	99.8	HPLC	8.3	350.2