



Distribution of cyclohexanol and cyclohexanone between water and cyclohexane



Yinchuan Pei^a, Qinbo Wang^{a,*}, Xing Gong^a, Fuqiong Lei^a, Binwei Shen^b

^a Department of Chemical Engineering, Hunan University, Changsha, 410082 Hunan, PR China

^b Quzhou Bozhi Chemical Technology Co., Ltd., Quzhou, 324002 Zhejiang, PR China

ARTICLE INFO

Article history:

Received 20 December 2014

Received in revised form 26 January 2015

Accepted 18 February 2015

Available online 5 March 2015

Keywords:

Liquid–liquid equilibrium

Determination and correlation

Water

Cyclohexane

Cyclohexanol and Cyclohexanone

ABSTRACT

Liquid–liquid equilibrium (LLE) data for ternary systems water + cyclohexane + cyclohexanol and water + cyclohexane + cyclohexanone were measured at (303.2–333.2)K and under atmospheric pressure. The reliability of the experimental tie-line data was checked by the empirical Othmer–Tobias correlation. The distribution coefficient and separation factor were used to investigate the distribution of cyclohexanol and cyclohexanone between water and cyclohexane. The results show that the distribution coefficient of cyclohexanol or cyclohexanone between organic and aqueous phases increases with the increasing content of cyclohexanol or cyclohexanone in water, and so does it with the increasing of temperature. By using the NRTL and UNIQUAC activity coefficient models, the experimentally determined LLE data, along with the LLE data for another ternary system water + cyclohexanol + cyclohexanone [G. Xing, W. Qinbo, L. Fuqiong, S. Binwei, J. Chem. Eng. Data 59 (2013) 1651–1655], were correlated simultaneously. Good agreements were obtained between the correlated and experimentally determined tie-line data. The binary NRTL and UNIQUAC interaction parameters were obtained. Furthermore, four sets of quaternary LLE data for water + cyclohexane + cyclohexanol + cyclohexanone were experimentally determined at 318.2 K. The experimentally determined quaternary LLE data were compared with the NRTL model predicted LLE data, and generally agreements were obtained. It further verifies the reliability of the obtained binary model parameters, and indicates the obtained parameters could be used for prediction, as well as design and optimization of the related separation process.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

KA oil, the abbreviation for the mixture of cyclohexanone and cyclohexanol, is one of the key intermediate of nylon industry. The most important use of KA oil is to manufacture adipic acid and caprolactam, which are intermediates of nylon-66 and nylon-6 polymers [1,2]. Meanwhile, cyclohexanone could also be used as a good solvent for paint, and synthetic material of printing ink, plastic, epoxy resin, adhesive of PVC resin, photosensitive recording material and other organic compounds. Cyclohexanol can be the industrial solvent, raw material of plasticizer (like dicyclohexyl phthalate) and flattening agent in the textile industry. It also has a wide application in the fields of disinfectant, spice, pesticide, disinfectant, wood preservative and leather softener.

Generally KA oil is produced by the liquid-phase oxidation of cyclohexane at around 433 K and (1.0–2.0) MPa. In order to avoid the further oxidation of KA oil to dibasic acids, the molar conversion per pass of cyclohexane is generally controlled to be lower than 0.04, and the selectivity of KA oil could be optimized to be (0.70–0.85) [1,3].

In the oxidation process, besides the desired products KA oil, several by-products are also produced simultaneously, such as mono- and dicarboxylic acids, esters, and other oxygenated materials [4,5]. Generally, saponification is used to remove these by-products, where large amount of exhausted lye would be generated. It's a kind of black viscous liquid and the value of COD is about $(5–7) \times 10^4$ mg/l. Nowadays, burning and chemical methods are used to treat with exhausted lye, which leads to serious environmental pollution. Furthermore, the beneficial dicarboxylic acids and esters would be converted into organic salts and difficult to be recovered after saponification, which would lead to great wasting.

* Corresponding author. Tel.: +86018057026077; fax: +86073188664151.

E-mail address: qinbowang@126.com (Q. Wang).

Nomenclature

List of symbols

| | |
|------------------|---|
| T | Temperature, K |
| w_i | Liquid phase mass fraction of component i |
| u | Standard uncertainty |
| A, B | Othmer–Tobias equation constants |
| R^2 | Othmer–Tobias correlation coefficient |
| W_{ij} | Liquid phase mass fraction of component i in phase j |
| D | Distribution coefficient |
| S | Separation factor |
| x_i | Liquid phase mole fractions of components of component i |
| a_{ij}, b_{ij} | Binary parameters of component i and j for NRTL and UNIQUAC equations |
| q | van der Waals area parameter |
| r | van der Waals volume parameter |
| N | Number of all systems tie-lines |
| RSMD | Root mean square deviation |
| RD | Relative deviation |
| OF | The objective function of the optimized models |

Greek letters

| | |
|------------|---|
| η | Non-random parameter for NRTL |
| ψ_i | Volume fraction of component i for UNIQUAC equation |
| θ_i | Area fraction of component i for UNIQUAC equation |
| γ_i | The activity coefficient of component i |

Subscripts

| | |
|--------------|-----------------------|
| i, j, m, n | Components |
| s | Number of phase |
| k | Number of tie-line |
| t | Number of temperature |

Superscripts

| | |
|-----|-------------------|
| cal | calculated |
| exp | experimental |
| I | the aqueous phase |
| II | the organic phase |

dicarboxylic acids in the water were much greater than that in cyclohexane [7]. Finally, the density of water differs from that of cyclohexane apparently and the price of water is low. During the extraction process, the main oxidation products, i.e., cyclohexanone and cyclohexanol, are expected to be remained in the organic phase as much as possible. Thus, it is very essential to get a complete set of LLE data and the corresponding thermodynamic correlations that is important for simulation, design and optimize of separation operations.

Unfortunately, from the literature survey, there is no complete literature data for the system of water+cyclohexane+cyclohexanol+cyclohexanone, only part of ternary and binary data could be referenced. For the binary water+cyclohexane system, the temperature ranges at (287.15–523.11)K [8–22], and for the binary system of water+cyclohexanol, the temperature ranges at (273–457.87)K [23–32], and for the binary system water+cyclohexanone, the temperature ranges at (292.99–368.34)K [33–42]. For the ternary system, the work of Steyer and Sundmacher [43] reported the LLE data of ternary system water+cyclohexane+cyclohexanol at 295 K, however, the LLE data at other temperatures were unavailable.

In our previous work, the LLE data for ternary system water+cyclohexanol+cyclohexanone at (303.2–333.2)K had been reported [44]. As a continuation, in this work, LLE data for ternary systems water+cyclohexane+cyclohexanol and water+cyclohexane+cyclohexanone were also measured at (303.2–333.2)K. The reliability of the experimental tie-line data was checked by the empirical Othmer–Tobias correlation [45]. The distribution coefficient and separation factor were used to investigate the distribution of cyclohexanol and cyclohexanone between water and cyclohexane. By using the NRTL [46] and UNIQUAC [47] activity coefficient models, the experimentally determined LLE data, along with our previously reported LLE data for ternary system water+cyclohexanol+cyclohexanone [44], were correlated simultaneously. The binary NRTL and UNIQUAC interaction parameters were obtained. Furthermore, four sets of quaternary LLE data for water+cyclohexane+cyclohexanol+cyclohexanone were experimentally determined at 318.2 K to verify the predictability of the obtained thermodynamic model parameters. It further verifies the reliability of the obtained binary model parameters, and indicates the obtained parameters could be used for prediction, as well as design and optimization of the related separation process.

2. Experimental

2.1. Materials

N,N-dimethylformamide, cyclohexane, cyclohexanol, cyclohexanone and chlorobenzene were all obtained from Aladdin Chemistry Co., with a declared mass purity of 0.99. Gas chromatography was used to check the purities of these chemicals. Purified water was obtained from Hangzhou Wahaha Group Co.,

It is of great scientific and engineering interests to find a method that could not only recover the useful by-products, especially the dicarboxylic acids, but also separate them from the oxidized liquid mixtures, so as to reduce the use of alkali. Extraction might be alternative, and the choice of extractant becomes truly important. From our point of view, water is a better choice. First of all, it could be regarded as insoluble with cyclohexane [6], and it might not react with any component in the oxidized liquid mixtures. Secondly, solubilities of the

Table 1
Suppliers and mass fractions of the chemical reagent.

| Component | Suppliers | Mass fractions | Analysis method |
|-------------------------------|-----------------------|----------------|-----------------|
| Cyclohexane | Aladdin Chemistry Co. | >0.990 | GC ^a |
| Cyclohexanol | Aladdin Chemistry Co. | >0.990 | GC ^a |
| Cyclohexanone | Aladdin Chemistry Co. | >0.990 | GC ^a |
| Chlorobenzene | Aladdin Chemistry Co. | >0.990 | GC ^a |
| <i>N,N</i> -dimethylformamide | Aladdin Chemistry Co. | >0.990 | GC ^a |

^a Gas chromatograph.

Download English Version:

<https://daneshyari.com/en/article/6619712>

Download Persian Version:

<https://daneshyari.com/article/6619712>

[Daneshyari.com](https://daneshyari.com)