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Liquid-liquid equilibrium measurement and thermodynamics modeling for the systems water + thioglycolic acid + isopropyl ether/methyl tert-butyl ether at 298.15 and 308.15 K

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ABSTRACT

To separate thioglycolic acid (TGA) from its aqueous mixture, isopropyl ether and methyl tert-butyl ether were adopted as extractants, and the liquid-liquid equilibrium data for the ternary systems water + TGA + isopropyl ether/methyl tert-butyl ether were determined at 298.15 K and 308.15 K under pressure of 101.3 kPa. The influence of the different extractants and temperatures on the phase behavior was explored. In addition, the measured experimental data were correlated by the nonrandom two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) activity coefficient models, and the binary interaction parameters of the two models were also optimized.

1. Introduction

Thioglycolic acid (TGA) is a fine chemical raw material, which has a wide range of applications in the productions of functional cosmetics, polyvinyl chloride heat stabilizers, chlormezanone medicine and organic synthesis intermediates [1,2]. In general, TGA can be prepared by the sodium thiosulfate method, sulfur sodium hydride method, and sodium polysulfide method [3]. After preparation, an aqueous mixture contained TGA is finally obtained. In addition, when TGA is applied in the production of isooctyl thioglycolate, an aqueous solution contained TGA is also obtained [4]. Therefore, it is necessary to separate TGA from its aqueous mixture. Usually, distillation is applied to separate such an aqueous solution in chemical industry [5–10]. However, this separation technology suffers from high capital investment and requires high energy consuming to obtain the products. Comparatively, liquid-liquid extraction is an effective alternative method than distillation due to its high separation efficiency and energy savings [11–15].

Until now, few literature reported the liquid-liquid equilibrium (LLE) data for the system contained water and TGA. Xu et al. [16] measured the ternary systems of water + TGA + (butyl acetate, isobutyl acetate or isopropyl acetate). Zhou et al. [17] screened the suitable ionic liquids (ILs) using the COSMO-SAC model and presented the LLE data for the systems water + TGA + ILs. In this work, isopropyl ether and methyl tert-butyl ether were adopted as extractants to extract TGA from its aqueous solution. Retrieving from the NIST database, there have no liquid-liquid equilibrium data reported for the ternary systems water + TGA + isopropyl ether and water + TGA + methyl tert-butyl ether.

In the present work, the LLE data for ternary systems water + TGA + (isopropyl ether/methyl tert-butyl ether) were measured at 298.15 K and 308.15 K. The distribution coefficient (D) and selectivity (S) were calculated and analyzed to evaluate the extraction performance of the selected extractants. Moreover, the measured LLE data were correlated by the activity coefficient models of nonrandom two-liquid (NRTL) [18] and universal quasi-chemical (UNIQUAC) activity coefficient models [19], which are the most applied chemical thermodynamic models in phase equilibria calculations and correlation [20–23]. The commercial simulator Aspen Plus offers the tool to correlate the experimental data using

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the thermodynamic models. However, this tool cannot ensure the consistency of the obtained solutions and may lead to the incoherent parameters. For this limitation, another tool Graphical User Interface (GUI-MATLAB) developed by Reyes-Labarta [24–27]. for the analysis of Gibbs Energy surfaces was adopted in this work to check the coherent consistency of NRTL and UNIQUAC parameters obtained using Apsen Plus.

2. Experimental

2.1. Chemicals

The chemicals thioglycolic acid, isopropyl ether and methyl tert-butyl ether used in this work were analytical reagents and obtained commercially. The mass fractions of all the chemicals were greater than 0.99, which were checked and confirmed by gas chromatography (GC). The deionized water (conductivity < 1.0 μS cm^{-1}) was made in our lab by the ultra-pure water machine from Chengdu Down's Corning Technology Development Co., Ltd. The information about the chemical reagents used in this work is listed in Table 1.

2.2. Apparatus and procedure

The LLE experiment was performed by adding a specific mass ratio of water, TGA and isopropyl ether/methyl tert-butyl ether into a 50 mL round-bottomed flask, which can be found in our previous work [28,29]. According to the literature [30–32], the mixture of water, TGA and isopropyl ether or methyl tert-butyl ether was stirred vigorously for 4 h in a water bath with a temperature fluctuation of ±0.1 °C (SYC-15 B, Nanjing Huchuan electronic equipment Co., Ltd.) to ensure that the sample was mixed completely, and then the sample was settled and kept at constant temperature for about 14 h until it reached the equilibrium state.

After reaching phase equilibrium, the compositions of the upper layer (organic-rich phase) and the lower layer (water-rich phase) were analyzed by GC (Lunan SP-7820), which was equipped with a SE-54 (30 m × 0.32 mm × 1 μm) capillary column, and a thermal conductivity detector (TCD). Hydrogen was used as carrier gas with the purity of 99.999%, the injection temperature was fixed at 498.15 K, the oven initial temperature was maintained at 363.15 K for 3 min then increased at 40 K min^{-1} to reach 498.15 K, and the detector temperature were set at 498.15 K. All the measurements were repeated at least three times and the mean values were adopted.

3. Results and discussion

3.1. LLE experimental data

The LLE experimental data for the ternary systems water (1) + TGA (2) + isopropyl ether/methyl tert-butyl ether (3) were measured at 298.15 K and 308.15 K under pressure of 101.3 kPa. The determined experimental data for the ternary systems are all expressed in mole fraction and listed in Tables 2 and 3. The subscript 1, 2 and 3 represent water, TGA and isopropyl ether/methyl tert-butyl ether, the superscripts I and II refer to the organic-rich phase (upper phase) and the water-rich phase (lower phase), respectively. In order to explore the effects of temperature and the different extractants on separation of TGA from its aqueous solution, the corresponding triangular diagrams with the measured tie-lines for the systems are presented in Figs. 1–2.

As shown in Figs. 1 and 2, the phase behaviors of water (1) + TGA (2) + isopropyl ether/methyl tert-butyl ether (3) are classified as Treybal's type I [33], which have one partially miscible system. Meanwhile, the solubility of TGA in isopropyl ether and methyl tert-butyl ether is greater than in water. Also, it can be found that the immiscible region is slightly influenced by the temperature, which decreases when the temperature increases.

Table 2
Experimental LLE data (mole fraction), distribution coefficient (*D*) and selectivity (*S*) for the ternary system water (1) + TGA (2) + isopropyl ether (3) at T = (298.15 K and 308.15 K) under 101.3 KPa[a].

T/K	Organic phase		Aqueous phase		*D*	*S*
	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}		
298.15	water (1) + TGA (2) + isopropyl ether (3)					
	0.0758	0.0321	0.9869	0.0084	3.832	49.91
	0.1152	0.0607	0.9749	0.0169	3.584	30.34
	0.1475	0.0865	0.9636	0.0250	3.468	22.66
	0.1699	0.1178	0.9499	0.0351	3.353	18.75
	0.2054	0.1343	0.9357	0.0419	3.207	14.60
	0.2153	0.1585	0.9201	0.0526	3.013	12.87
	0.2545	0.1762	0.9049	0.0615	2.863	10.18
	0.2748	0.1849	0.8877	0.0740	2.497	8.068
	0.3138	0.1935	0.8698	0.0853	2.268	6.286
	0.3362	0.1967	0.8561	0.0944	2.083	5.303
	0.3899	0.1961	0.8393	0.1047	1.873	4.031
308.15	water (1) + TGA (2) + isopropyl ether (3)					
	0.1344	0.0432	0.9847	0.0084	5.112	37.46
	0.1411	0.0751	0.9766	0.0150	5.007	34.66
	0.2086	0.1015	0.9676	0.0246	4.128	19.15
	0.2420	0.1225	0.9553	0.0318	3.848	15.19
	0.2767	0.1323	0.9428	0.0412	3.209	10.93
	0.3257	0.1554	0.9280	0.0513	3.027	8.626
	0.3574	0.1686	0.9130	0.0626	2.692	6.879
	0.3826	0.1812	0.8957	0.0774	2.341	5.480
	0.4015	0.1891	0.8808	0.0890	2.124	4.660
	0.4199	0.1954	0.8621	0.1070	1.826	3.749

[a] Standard uncertainties: $u(T) = 0.06$ K, $u(p) = 0.1$ kPa, $u(x) = 0.0083$.

3.2. Distribution coefficient and selectivity

To evaluate the extraction performance of the extractants, two important parameters distribution coefficient (*D*) and selectivity (*S*) were calculated and are presented in Tables 2 and 3 The distribution coefficient and selectivity are defined by the following equations [34,35]:

Table 1
Details of the chemical reagents used in this work.

Component	CAS number	Mass fraction	Analysis method	Supplier
Thioglycolic acid	68-11-1	≥0.99	GC[a]	Shandong Xiya Chemical Co., Ltd.
Water	7732-18-5	–	GC[a]	Lab made
Isopropyl ether	108-20-3	≥0.99	GC[a]	Shanghai RichJoint Chemical Reagents Co., Ltd.
Methy tert-butyl ether	1634-04-4	≥0.99	GC[a]	Tianjin Guangfu Fine Chemical Co., Ltd.

[a] Gas chromatography.

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