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Liquid – liquid equilibria of quaternary system phosphoric acid/sulfuric acid/water/tri-*n*-butyl phosphate and the formation of extraction complex at 303.2 K

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ABSTRACT

Nowadays, with the increasing scarcity of phosphate ore, many researchers are focused on the purification of wet – process phosphoric acid, which is leaching with strong acids. It produces mixtures of phosphoric acid and sulfuric acid (or nitric acid, or hydrochloric acid), which requires a separation process of mixed acids. This paper conducts an experiment about liquid – liquid equilibrium data of quaternary system $H_3PO_4 - H_2SO_4 - H_2O$ – TBP (tri – *n* – butyl phosphate). It determines mass percents of phosphoric acid in the two equilibria phases, and analyzes density, viscosity of two equilibrium phases. Equilibria data obtained are correlated by the Hand equation, Othmer – Tobias equation and Bachman equation, which all show good linear fitting. In addition, the formations of extraction complexes are analyzed with Pitzer's model and Sergievskii-Dannus's model, which calculates the thermodynamic equilibrium constant of extraction process.

1. Introduction

For a long time, industries such as dissolution of nonferrous metals with acids, treatment of metal surface with pickling and leaching phosphate ores with inorganic acids will produce inorganic acid containing metal ions or mixed abandoned inorganic acids (hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid and so on). Because of the high level of strong acids and metal ions, how to handle the spent liquor has always troubled industries.

The problem could be solved by acid – base neutralization, abandon or recycle. To all appearances, if there is an effectual way to dispose the effluent, recycle and reuse, it is more appropriate.

As is well-known, solvent extraction is one of the effective methods on mass transfer and separation process [1,2]. Solvent extraction process is adopted for its user-friendly control, safety production, environmental conservation, and economy. The method has obvious advantages of its application and it is extensively used [3]. The core of extraction lies in the selection of extraction agent. TBP is a neutral extraction agent. TBP can, for example, complex with acids in a ratio of 1:1 or 1:3, or complex with water in a 1:1 ratio in an inorganic complex reaction.

Nowadays, with the increasing scarcity of phosphate ore, many researchers are concentrated on the purification of wet – process phosphoric acid which is leaching with strong acids. It produces mixtures of phosphoric acid and hydrochloric acid, nitric acid or sulfuric acid, which is required a separation process of mixed acids.

In the purification of wet – process phosphoric acid, mostly used extraction agent is TBP, methyl isobutyl ketone (MIBK), trioctylamine (TOA) and so on [4–6]. This paper is focused on determining liquid–liquid equilibrium data of quaternary system $H_3PO_4 - H_2SO_4 - H_2O$ – TBP and using the Hand equation, Othmer – Tobias equation and Bachman equation to correlate the experimental data. Also, it calculates the activity coefficients of solutes in aqueous phase and activity of water with Pitzer's model, and then computing the thermodynamic equilibrium constant with Sergievskii-Dannus's model.

2. Experimental section

2.1. Materials

In this experiment, used compounds are shown in Table 1. Phosphoric acid (provided by Kelong, 85%) and Sulfuric acid

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Table 1
The basic parameters of materials in the experiment at 303.2 K, 88.4 kPa.

Material	Grade	Mass content	Density (g cm^{-3})	Viscosity (10^{-3} Pa s)
TBP	Analytical reagent	0.997	0.9748	1.0092
Phosphoric acid (85%)	Analytical reagent	0.884	1.6808	29.4588
Sulfuric acid (98%)	Analytical reagent	0.983	1.8273	14.0701
Water	Double distilled	–	–	–

Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.1$ kPa, u_r(mass content) $= 0.05$, u_r(density) $= 0.005$, u_r(viscosity) $= 0.05$.

(provided by Jinshan, 98%) are used as received. TBP (provided by Aoda Chemical Company, China) is used without any further purification. All of the reagents are analytical grade. Double distilled water is used in the experiment.

2.2. Procedure

Taking phosphoric acid and sulfuric acid into a dilute mixture with water, which is settled as aqueous phase and mixing with organic extraction agent in a 250 mL conical flask. The phase mass ratio is 1. After an hour constant temperature shaking, make it stewing for 2 h in a 250 mL separating funnel. The two phases will be hierarchical and could be separated. Analyzing the composition of every phase and neatening the data in a constitution table which is described as mass percent.

Phosphoric acid concentration in the aqueous phase is measured by quinoline phosphomolybdate gravimetric method. The phosphorus pentoxide concentration would be determined firstly, and then it is converted to the concentration of phosphoric acid with coefficient 1.3808 [7]. Water concentration in the organic phase could be measured with Karl Fischer apparatus, the model is KF-01 [8]. Sulfate ion concentration is measured by ultraviolet and visible spectrophotometer. The other concentrations are calculated by mass balance. In addition, the densities and viscosities of the two phases are also measured in this paper. Density is determined with a pycnometer [9] and viscosity is determined by an Ubbelohde viscometer [10]. The precision for mass, density and viscosity is ±0.0001 g, ±0.0001 (g cm^{-3}), ±0.0001 (10^{-3} Pa s), respectively.

The articles [11,12] studied effects of temperature, concentration of acid on the solubility of TBP in aqueous phase. The solubility of pure TBP in water is about 0.4 g/L at 298.15 K and 0.4 g/L – 1.1 g/L in nitric acid (0–14 M) at temperature range 298.15 K–333.15 K. It showed that with increasing of acid concentration, solubility of TBP decreased gradually, passed through a minimum at about 8 M and subsequently increased with increasing of acid concentration. In the present system, the acid concentration is lower than 6 M. It estimates the TBP concentrations in the equilibrium aqueous phases refer to the papers [11,12].

3. Results and discussion

3.1. Equilibirum data of the quaternary system $H_3PO_4 - H_2SO_4 - H_2O - TBP$

In Table 2, the mass percent of components in the initial mixture, the aqueous phase and the organic phase are given. ω_1 refers to mass percent of H_3PO_4, ω_2 stands for mass percent of H_2SO_4, ω_3 and ω_4 are for H_2O and TBP, respectively.

In Table 3, ρ^A stands for the density of the aqueous phase and ρ^O stands for the density of the organic phase. It is the same situation for η^A and η^O, which stands for the viscosity of the aqueous phase and the organic phase, respectively.

Table 3 refers to the concentration of phosphoric acid in the initial mixtures versus the densities of the two phases or the viscosities of the two phases. It shows that the minimal D-value between the two phases is 0.05 ≥ 0.05 g cm^{-3} [13]. The bigger the difference in density between the two phases, the much more beneficial to the phase separation. The data also shows that the organic phase is superior and the aqueous phase is inferior.

Viscosity is an important physical property parameter for extraction process. There currently employ device of not fixed interface to process the procedure, which is of greater volumetric mass transfer coefficient and higher extraction efficiency in practical industrial equipment. One of the phase would be dispersed into tiny droplets (dispersion phase), which is distributed in the other liquid phase as far as possible (continuous phase). During the movement of liquid droplet, viscosity would impact on Reynolds number. While there is a complicated relationship between Reynolds number and drag force. It not only refers to internal loop in the liquid droplet, but also involves crush and deformation of droplet. To a certain extent, with increasing the liquid viscosity, the residence time of two – fluids increases sequentially; meanwhile, the contact and mixing between the two fluids become more uniform. In Table 3, difference of the viscosities between the two phases is enormous. The viscosity in the organic phase is greater than that in the aqueous phase. The values increase with the concentration of phosphoric acid and the sulfuric acid increasing. On the one hand, the viscosity changes with solution concentration; on the other hand, the increasing viscosity would influence the extraction process.

3.2. The reliability of the liquid–liquid equilibrium data

There are several equations to test the correlation of the liquid–liquid equilibrium data, such as Hand equation [14], Othmer – Tobias equation [15–17] and Bachman equation [18]. The former equation Eq. (1) (Hand equation) requires three experimentally determined points and the other two equations Eq. (2) (Othmer – Tobias equation), Eq. (3) (Bachman equation) require only two experimental points. They all result a straight line and show a great linear fitting which refers to a good correlation of the liquid–liquid equilibrium data.

$$\ln\left(\frac{\omega_1^A}{\omega_3^A}\right) = A + B\ln\left(\frac{\omega_1^O}{\omega_4^O}\right) \tag{1}$$

$$\ln\left(\frac{1-\omega_4^O}{\omega_4^O}\right) = a + b\ln\left(\frac{1-\omega_3^A}{\omega_3^A}\right) \tag{2}$$

$$\omega_4^O = m + n\left(\frac{\omega_4^O}{\omega_3^A}\right) \tag{3}$$

In the equations, ω_1^A, ω_1^O stand for the mass concentration of phosphoric acid in the equilibrium aqueous phase and organic phase, respectively. ω_3^A, ω_3^O and ω_4^A, ω_4^O represent the mass concentrations of water, TBP in the equilibrium aqueous phase and organic phase, respectively. The coefficients A, B, a, b, m, n are constants in the Hand equation, Othmer – Tobias equation and Bachman equation, respectively.