Emulsification solvent extraction of phosphoric acid by tri-*n*-butyl phosphate using a high-speed shearing machine

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A B S T R A C T

The emulsification solvent extraction of phosphoric acid by tri-*n*-butyl phosphate was investigated using a high-speed shearing machine. The effects of phase ratio, rotor speed, extraction time, extractant and phosphoric acid concentration on extraction yield and drop size were studied. The emulsification solvent extraction achieved the same extraction yield as the conventional solvent extraction ranging from 3000 to 5000 rpm and the extraction rate increased by 120 times. The extraction rate increased by increasing the oil to aqueous phase ratio. The same extraction yield could be reached at 1000 and 2000 rpm as the conventional extraction by adding kerosene. Emulsification became easier with higher phase ratio or more kerosene. Higher rotor speed, extractant concentration and lower phosphoric acid concentration contributed to smaller drop size. The phase ratio of tri-*n*-butyl phosphate to phosphoric acid hardly affected drop size. A model was proposed to predict average drop size to provide information for demulsification.

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1. Introduction

Phosphoric acid is widely used in food, fertilizer, pharmaceutical, electronic and other industries [1]. The most frequently used way to produce phosphoric acid is the wet process method. However, the wet process phosphoric acid must be purified because it contains a lot of undesired impurities [2]. Solvent extraction is an ideal and efficient technique with low consumption to remove the impurities from the phosphoric acid [3]. Tri-*n*-butyl phosphate (TBP) can serve as an effective extractant because of its immiscibility with the aqueous solutions and good selectivity to phosphoric acid [4–6]. The vibration sieve-plate tower, packed tower and mixer-settler are usually applied for the extraction process. As these conventional extraction processes take a long time to reach the liquid-liquid equilibrium, the extraction always requires a long residence time which leads to large extraction equipments and also large amount of solvent circulation.

Recently, some extraction techniques have been developed, such as microfluidic extraction [7], membrane extraction [8], microemulsion extraction [9] and emulsification solvent extraction [10−12]. Microfluidic extraction and membrane-based extraction are unfit for the extraction of phosphoric acid from the wet process phosphoric acid. Sludge with a complicated composition appears constantly in the extraction process, which would plug the

micropore of microchannel or membrane. It is equally unhelpful to use the microemulsion extraction method. The phosphoric acid is a product with low additional value, while the surfactants used in the microemulsion extraction causes high costs. Emulsification solvent extraction is an approach which can enhance the extraction rate by high-speed shearing, ultrasound-assisted or adding surfactants. It is a suitable method for the phosphoric acid extraction from the wet process phosphoric acid without sludge blocking problems. It is also an efficient and economically acceptable method when a high speed shearing machine is utilized.

Works have been carried out to study the emulsification solvent. Ugwoke and Kinget [10] investigated the influence of process parameters on the particle size and microencapsulation efficiency of the gelatin microspheres prepared by the emulsification solvent extraction technique. Luo et al. [11] studied on the removal of Fe^{3+} from the sodium dihydrogen phosphate by emulsification solvent extraction using a high speed shearing machine. María et al. [12] used the ultrasound-assisted emulsification extraction for orange peer metabolites by methanol–water mixture. As for the phosphoric acid extraction system, our prior research indicates that phosphoric acid and TBP can form water-in-oil emulsion by high-speed shearing without surfactant. Phosphoric acid, as the dispersed phase, forms micron scale drops dispersing in the continuous phase TBP. The emulsification increases the contact interfacial area between the oil and aqueous by reducing the drop size, which can promote the mass transfer rate and shorten the equilibrium time. Then the extraction finished by follow-up demulsification

Nomenclature

a	constant
C, C_1, C_2, - C_6	constants
Di	drop diameter in size interval i (m)
d_{max}	maximum stable drop diameter (m)
d_{32}	Sauter mean drop diameter (m)
d_{43}	mass mean drop diameter (m)
L	rotor diameter (m)
m_i	weight of the initial phosphoric acid solution (g)
m_r	weight of the raffinate aqueous phase (g)
N	rotor speed (s^{-1})
N_i	number of drops in size interval i
Po	power number
Q_3	function of volume cumulative distribution
t	extraction time (s)
Va	volume of aqueous phase (m^3)
V_T	volume of tri-n-butyl phosphate (m^3)
V_k	volume of kerosene (m^3)
V_{swept}	impeller swept volume (m^3)
w_i	the initial phosphoric acid solution phosphoric acid concentration (%)

w_r	phosphoric acid concentration of the raffinate aqueous phase (%)
x_i	upper size of a particle size interval (m)
x_{i-1}	lower size of a particle size interval (m)

Greek letters

ε	local energy dissipation rate per mass of fluid (W/kg)
σ	interfacial tension (N/m)
τ_c	turbulent stress (force per area) acting on surface of drop (N/m^2)
τ_d	internal viscous stress (force per area) resisting drop deformation (N/m^2)
τ_s	stress (force per area) due to interfacial tension resisting drop deformation (N/m^2)
μ_d	viscosity of dispersed phase (Pa·s)
ρ_c	density of continuous phase (kg/m^3)
ρ_d	density of dispersed phase (kg/m^3)
φ	volume fraction of dispersed phase

process to make a complete phase separation. The systematic study of emulsification solvent extraction is very less currently, and the emulsification solvent extraction of phosphoric acid by tri-n-butyl phosphate has never been studied before. It is of significance to study the factors that affect the emulsification solvent extraction yield and rate. The drop size of dispersion phase has an important influence on the contact area between the two phases, which results in further influence on the extraction rate. Besides, the drop size also affects the complete separation of two phases in the demulsification operation. So it is also required to study and predict the drop size distributions and average drop size of emulsion.

In this paper, the emulsification solvent extraction of phosphoric acid by tri-n-butyl phosphate using a high-speed shearing machine was studied. We conducted a series of experiments to examine the effects of phase ratio, rotor speed, extraction time, extractant and phosphoric acid concentration on the extraction yield and drop size. The relationship between d_{43} and d_{max} for the W/O emulsion was discussed. A mathematical model was proposed to predict the drop mean size. The density and viscosity of the emulsion and the interfacial tension between the two equilibrated phases were also measured.

2. Experimental section

2.1. Materials

Tri-n-butyl phosphate (purity ⩾ 98.5 wt%) was produced by Luoyang Zhongda Chemical Co. Ltd., Henan, China. Kerosene (Zhongcui Chemical Co. Ltd., Sichuan, China) was washed with concentrated sulfuric acid, then neutralized with 5% Na$_2$CO$_3$ solution, and finally washed with water until the pH was neutral and distilled at 458–528 K. The oil phase was saturated with water before use. Phosphoric acid (analytical pure, 85 wt%) was supplied by Kelong Chemical Co. Ltd., Sichuan, China. Deionized water was used throughout the experiments.

2.2. Conventional solvent extraction

Experiments were carried out at a constant temperature of 323 K controlled by a water bath. Appropriate volumes of initial

phosphoric acid solution and oil with a total volume of 360 ml were mixed in a tall beaker. The mixtures were stirred for a certain time at a rotor speed of 400 rpm (the rotor linear velocity: 1.55 m/s) using an agitator (S312, Meiyingpu Instrument and Meter Manufacturing Co. Ltd., Shanghai, China). When the stirring was stopped, the mixtures were quickly separated into two phases by centrifugation. The phosphoric acid concentration of the aqueous phase was measured.

2.3. Emulsification solvent extraction

Emulsification solvent extraction experiments were carried out with the materials prepared as same as the conventional solvent extraction. The mixtures were emulsified by a high-speed shearing machine and its structure was shown in Fig. 1. (JRJ-300-I, Fluko Equipment Co. Ltd., Shanghai, China). The diameter and height of rotor were 28 mm and 15 mm respectively and the diameter of inner stator was 28.4 mm. A shield covering on the rotor was used to avoid entraining air bubbles into the mixtures that resulted in a poor mixing condition. The rotor was set at the same place in each experiment and started at a desired rotor speed. Then the stirring was stopped and a homogeneous and milk white emulsion was obtained. A 150 ml sample of the emulsion was immediately taken for the drop size distribution (DSD) and the average drop size analysis and another 80 ml for the viscosity measurement. Meanwhile, the left emulsion was centrifuged for the complete separation of the two phases. The phosphoric acid concentration of aqueous phase was determined. The interfacial tension between the equilibrated oil and aqueous phase was measured.

2.4. Analysis

Measurements of the DSDs and the average drop size of the emulsion were performed in a particle size analyzer (OPUS, Sympatec GmbH Co. Ltd., Clausthal-Zellerfeld Germany). The measuring field was washed with the corresponding equilibrium oil phase before each use. Drop size distribution can be expressed as the density distribution ($q_3$ln(x)), which is calculated from the Eq. (1):

$$q_3 \ln(x) = \frac{dQ_{3,i} \times 2.3}{\ln(x_i/x_{i-1})} \tag{1}$$