Fluid Phase Equilibria 427 (2016) 175–179

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Extraction equilibria of 2,4,6-Trinitrophenol by (amberlite LA2 + ester) solvents

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A R T I C L E I N F O

Article history:
Received 25 May 2016
Received in revised form
29 June 2016
Accepted 3 July 2016
Available online 6 July 2016

Keywords:
Reactive extraction
Picric acid
Amberlite LA-2
Ester

A B S T R A C T

Extraction equilibria of 2,4,6-Trinitrophenol (picric acid (PAH)) between aqueous and organic phases was investigated at 298.15 K. All experiments was reported on the extraction of picric acid by amberlite LA2 which is secondary amine dissolved in different seven (7) esters such as diethyl malonate, dimethyl phthalate, diethyl glutarate, propyl acetate, diethyl succinate, diethyl sebacate, ethyl propionate, as well as single diluents. Experimental results obtained from batch extraction were evaluated in respect to distribution coefficients (K_D), loading factors (T_T), stoichiometric loading factor (T_S), separation factor (S_f) and extraction efficiency (E). The dimethyl phthalate gave highest synergistic effect with LA2 as extraction efficiency value of 95%. The highest values of possible equilibrium complexation constants for (acid/amine) (1:1) K_{11} was determined as 10.969 for dimethyl phthalate at 1.762 mol kg^{-1} amine concentration.

1. Introduction

2,4,6-Trinitrophenol (PA) are extensively studied for the basis of pairing anions in solvent extraction [1–5], use to product selective sensors [6], consecutive injection examination with PA [7], its dispersal into ionic liquids [8], and so on [9]. The free acid is necessary for the assembly of supplies and specialty chemicals in industries. Hence, to be cost-effective, the separation process involves the removal of impurities, concentration of the salted part, change of the acid salt into the free acid, and refining of the free acid to its necessary clarity [10]. In isolation, the expenses related with product recovery, concentration, and purification have been great in the taking account for about 70% of the product cost [11–13].

Various methods for separating organic acids from its aqueous solutions can be seen in the literature. The ancient method of those is related with precipitation of the unsolvable different calcium salts of acids with $Ca(OH)_2$ or $CaCO_3$ after that re-acidification with H_2SO_4 solution [5]. one of the another methods is physical extraction (LLLE) in which a solute is removed from an aqueous to water-insoluble organic phase based on the physical interaction of the these phases. Electro dialysis, nano-filtration, adsorption, absorption and reverse-osmosis have been tried to separate organic acids from aqueous phase. One of the latest methods is reactive extraction which is based on forming chemical complexation along with extraction. The main consideration of reactive extraction based on reaction of between the extractant in the organic media and the acid in the aqueous media and then reaction complexes formed are solubilized in the organic phase by means of diluents. Generally, phosphorous-based and aliphatic amine extractants are used in the reactive extraction studies. As seen from literature there are very limited study on both physical and reactive extraction of picric acid. Ferreira and Lopes [14] studied separation of picric acid from aqueous solutions by means of physical extraction. Only pure diluents were used as solvents such as 4-Methyl-2-pentanone, 2-methylpropyl ethanoate, and diisopropyl ether. The maximum distribution coefficient values were found with 4-methyl-2-pentanone. They reported that the solvents efficiencies are extremely low. Sekine et al. [15] investigated extraction of picric acid from aqueous media by reactive extraction method. Tri-octylphosphine oxide (TOPO) and trioctyl amine (TOA) were used as extractant and cyclohexane was used to dilute them. The extraction efficiency was increased many times with using TOA and TOPO as well as cyclohexane. The removal of picric acid was investigated by Bhatt et al. [16] using N,N,N,N′,N′,N’-hexaethyl-ethane-1,2-diammonium dibromide ionic liquid (IL) in non-ionic surfactant Triton X-114 (TX-114). The effects of various working parameters for instance pH of solution, temperature, contact time, surfactant concentration, were examined and ideal conditions were found.

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http://dx.doi.org/10.1016/j.fluid.2016.07.002
0378-3812/

In this study, the extraction of picric acid from its aqueous solutions by secondary amine (Amberlite LA-2) in quite a few solvents (seven esters) such as diethyl malonate, dimethyl phthalate, diethyl glutarate, propyl acetate, diethyl succinate, diethyl sebacate, ethyl propionate were used as for diluting Amberlite LA-2. Experiments were done also with the single pure solvents. The survey of the literature shows that the reactive extraction of picric acid has not been stated for presented ternary systems (picric acid + Amberlite LA-2 + Esters).

1.1. Theoretical

According to Young and co-workers [17] some assumption such as negligible of solubility of LA-2 and esters in water, and accepting only reaction of between LA2 and molecular PAH, must be considerate for definition of reactive extraction mechanism.

In this study, reactive extraction of PAH can be defined by Eq. (1),

$$\mathrm{PAH}(1) + \overline{\mathrm{R_2N}}(2) \leftrightarrow \overline{\mathrm{PAH} - \mathrm{R_2N}}(3), \quad \mathrm{K}_{11} = \frac{\mathrm{a}_3^1}{\mathrm{a}_1^1 \cdot \mathrm{a}_2^1} \tag{1}$$

In Eq. (1), a_1 is the activity of not formed of dissociate portion of PAH in aqueous media, a_2 is the activity of LA-2 in organic media, a_3 activity of complex between PAH and LA-2 in organic media.

Eq. (1) can be presented in respect to dissociated types, hydrogen ions and acid radical anions, since it has been applied in the literature on reactive extraction [17]. Considering the dissociation equilibrium, one can express that both ideas are same, the only modification being in the values of equilibrium constants. Switching the activities by the yields of molalities and molal activity coefficients.

So Eq. (1) represents

$$\mathrm{K} = \left(\mathrm{m}_{(\mathrm{PAH})\cdot(\mathrm{R_2N})}\gamma_{(\mathrm{PAH})\cdot(\mathrm{R_2N})}\right) \Big/ \times \left(\mathrm{m}_{(\mathrm{PAH})}\cdot\gamma_{(\mathrm{PAH})}\right)\cdot\left(\mathrm{m}_{(\mathrm{R_2N})}\cdot\gamma_{(\mathrm{R_2N})}\right) \tag{2}$$

In Eq. (2) $\mathrm{m}_{(\mathrm{HA}).(\mathrm{R3N})}$ and $\gamma_{(\mathrm{HA}).(\mathrm{R3N})}$ are molality and molal activity coefficient of complex, respectively.

The concentration of undissociated PAH can be found by,

$$\mathrm{C}_{\mathrm{PAH}} = \frac{\mathrm{C}_{\mathrm{PAH,total}}}{1 + 10^{\mathrm{pH} - \mathrm{pK_A}}} \tag{3}$$

The total equilibrium concentration of PAH in the organic phase is calculated with Eq. (4)

$$\overline{\mathrm{C}}_{\mathrm{PAH}} = \overline{\mathrm{C}}_{\mathrm{PAH-R_2N}} = \mathrm{K}_{11}\cdot\mathrm{C}_{\mathrm{PAH}}\cdot\overline{\mathrm{C}}_{\mathrm{R_2N}} \tag{4}$$

Free LA-2 concentration in the organic phase can be obtained by,

$$\overline{\mathrm{C}}_{\mathrm{R_2N}} = \mathrm{C}^0_{\mathrm{R_2N}} - \overline{\mathrm{C}}_{\mathrm{HA-R_2N}} = \mathrm{C}^0_{\mathrm{R_2N}} - \mathrm{K}_{11}\cdot\mathrm{C}_{\mathrm{PAH}}\cdot\overline{\mathrm{C}}_{\mathrm{R_2N}} \tag{5}$$

When using Eqs. (4) and (5) the loading factor $\mathrm{T_T}$ can be presented form,

$$\mathrm{T_T} = \frac{\overline{\mathrm{C}}_{\mathrm{PAH}}}{\mathrm{C}^0_{\mathrm{R_2N}}} = \frac{\mathrm{K}_{11}\cdot\mathrm{C}_{\mathrm{PAH}}}{1 + \mathrm{K}_{11}\cdot\mathrm{C}_{\mathrm{PAH}}} \tag{6}$$

The stoichiometric loading factor, T_s, is the ratio of the PAH-LA-2 complex in the organic phase. This factor contains an adjustment term, $(\nu\cdot C^{*s}_{PAH})$ (C^{*s}_{PAH} is the concentration of PAH in aqueous media then extraction by means of single pure solvents).

$$T_s = \frac{\left(C^*_{PAH} - \nu\cdot C^{*s}_{PAH}\right)}{C^0_{R_2N}} \tag{7}$$

In Eq. (7), v is the volume fraction of diluent in organic phase, and C^{*s}_{PAH} is the extracted PAH concentration by physical extraction.

Distribution coefficients ($\mathrm{K_D}$) which is defined as ratio of PAH concentration between two phases after extraction are calculated as,

$$\mathrm{K_D} = \frac{\overline{\mathrm{C}}_{\mathrm{PAH}}}{\mathrm{C}_{\mathrm{PAH}}} \tag{8}$$

Degree of extraction is found according to Eq. (9)

$$E = \left(1 - \frac{C_{PAH}}{C_{PAH,total}}\right)\cdot 100 \tag{9}$$

The comparative ratio between physical relations and chemical reaction was assessed with respect to a revised separation factor which is stated the fraction of the PAH-LA2 to total extracted PAH

$$s_f = \frac{C^*_{PAH}}{C^*_{PAH} + C^*_{PA^-}} \tag{10}$$

2. Materials and methods

2.1. Materials

Picric acid (2,4,6-Trinitrophenol) (purity > 98% in mass) and Esters (purity > 98% in mass) were purchased from Sigma-Aldrich. Amberlite LA-2, which is also called Nlauryltrialkyl-methyl amine that has 24 to 28 carbon atoms (Sigma-Aldrich) > 99%, is an anion exchange extractant and is a yellow liquid with the molecular weight of 353.67 and its density of 0.83 g $\mathrm{mL^{-1}}$ at 298.2 K. Properties of chemicals used in this study were presented in Table 1.

2.2. Equilibrium experiments

0.061 mol $\mathrm{kg^{-1}}$ Initial concentrations of PAH which is the highest solubility in water were prepared dissolving in distilled water. For the organic phase, five different concentrations of LA-2 in esters were set (0.352 mol $\mathrm{kg^{-1}}$, 0.705 mol $\mathrm{kg^{-1}}$, 1.057 mol $\mathrm{kg^{-1}}$, 1.410 mol $\mathrm{kg^{-1}}$, 1.762 mol $\mathrm{kg^{-1}}$). These concentration were determined for the best extraction efficiency by doing preliminary tests. Esters were selected as diluents for preparing the organic phase. Equal volumes (20 mL) of the organic and aqueous phases were mixed in an Erlenmeyer flask by shaking for 2 h at 50 rpm and constant temperatures in a temperature controlled shaker. After equilibrium, the phases were permitted to become for 2 h to succeed a perfect separation of the phases. Once phase separation, the PAH concentration in the aqueous phase was found by base titration 0.01 N NaOH with using phenolphthalein indicator. The organic phase concentration of PAH after extraction was calculated by a mass balance. Equilibrium experiments and chemical analyses were achieved in duplicate, and the average measurements were used for calculations. Each experiment was studied for temperature of 298.2 K. In utmost circumstances the deviance between the amount of acid analyzed and the amount of acid identified by making the solutions by mass did not go above 3+/− %.

2.3. Discussion of results

The reactive extraction of PAH with LA-2 diluted in 7 various esters (diethyl malonate, dimethyl phthalate, diethyl glutarate, propyl acetate, diethyl succinate, diethyl sebacate, ethyl propionate) was investigated. The equilibrium results on the reactive