(Liquid + liquid) equilibria of the (water + propionic acid + Aliquat 336 + organic solvents) at $T = 298.15$ K

Hasan Uslu *, İsmail İnci

İstanbul University, Engineering Faculty, Chemical Engineering Department, 34320 Avcilar, İstanbul, Turkey

Abstract

In this work, trioctyl methyl ammonium chloride (Aliquat 336) was studied for its ability to extract propionic acid at various amine concentrations. The extraction of propionic acid with Aliquat 336 dissolved in five single solvents (cyclohexane, hexane, toluene, methyl isobutyl ketone, and ethyl acetate) and binary solvents (hexane + MIBK, hexane + toluene, and MIBK + toluene) was investigated under various experimental conditions. The loading factors Z, extraction efficiency E and overall particular distribution coefficients were determined. All measurements were carried out at $T = 298.15$ K. The obtained results and the observed phenomena were discussed by taking into consideration the mechanism of extraction and the concentration of the interaction product in the aqueous phase.
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Keywords: Extraction; Propionic acid; Trioctyl methyl ammonium chloride

1. Introduction

Tertiary amines and quaternary ammonium salts have been found to be efficient extractants for carboxylic acid recovery. Usually, they have been dissolved in inert diluents in order to improve the physical properties of the organic phase, and/or active diluents to prevent third phase formation and to improve the extraction. Extractive recovery of carboxylic acids from dilute aqueous solutions, such as fermentation broth and wastewater, which have acid concentrations lower than 10% (w/w) has received increasing attention. Solvent extraction with conventional solvents such as alcohols, ketones, ethers, and aliphatic hydrocarbons is not efficient when applied to dilute carboxylic acid solutions because of the low aqueous activity of carboxylic acids resulting in low distribution coefficients [1–3]. However, carboxylic acid extractions with aliphatic amines have large distribution coefficients. Several aliphatic amines have been used successfully to extract car-

boxylic acids. For propionic acid the classical approach for recovery from a fermentation broth has been to add calcium hydroxide to form the calcium salt of the carboxylic acid, to which an acid such as sulphuric acid is added to liberate the free carboxylic acid [4–6]. This approach consumes chemicals (*e.g.* lime and sulphuric acid) and produces a waste salt stream. Consequently, such methods are falling out of favour. The strong amine interaction with the acid allows formation of acid amine complexes and so this complexes provide for high distribution coefficients. In addition, the high affinity of organic base for the acid gives selectivity for the acid over non-acid components in the mixture [7]. However, primary amines are too soluble in water to be used with aqueous solutions. Secondary amines are subject to amide formation upon regeneration by distillation. Consequently, tertiary and quaternary amines have received most attention. Extraction of carboxylic acids with tertiary amines has been extensively studied [8].

Uslu and Inci [9] have studied the extraction of glycolic acid by Aliquat 336 in different diluting solvents. They have found low distribution coefficients for glycolic acids. Furthermore, Uslu [10] has examined the extraction of

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* Corresponding author. Tel.: +90 5356220740.
  E-mail address: hasanuslu@gmail.com (H. Uslu).

propionic acid with tertiary amine and has found high distribution coefficients. However, to date, the extraction of propionic acid with quaternary amines has not been documented in the literature. It is essential to understand the effects of different factors on the extraction of propionic acid with a quaternary amine before a production process could be optimally designed [11].

In this work, Aliquat 336 was studied for its ability to extract propionic acid at various amine concentrations. Prior to this work, quaternary amines have not been well studied for their abilities to extract organic acid. Also, five diluents, cyclohexane, hexane, toluene, methyl isobutyl ketone, and ethyl acetate were investigated for their abilities to increase the extract on the amine extractant. As a result of extraction experiments, distribution coefficients, extraction efficiencies and loading factors are also presented in this work.

2. Theoretical

The extraction of propionic acid HA with Aliquat 336 R_4NCl can be described by the reaction
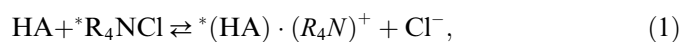
$$HA + {}^*R_4NCl \rightleftarrows {}^*(HA) \cdot (R_4N)^+ + Cl^-, \tag{1}$$

where HA represents the acid present in the aqueous phase and organic phase species are marked with (*). Reaction (1) can be characterised by the overall equilibrium constant, K:

$$K = (a^+_{HA\,R_4N}) \cdot (a^-_{Cl}) / (a_{HA}) \cdot (a_{R_4NCl}), \tag{2}$$

where a denotes activities [10]. Replacing the activities by the products of molalities $(mol \cdot kg^{-1})$ and molal activity coefficients, γ, equation (2) takes the form

$$K = (m^+_{HA\,R_4N} \cdot \gamma^+_{HA\,R_4N}) \cdot (m^-_{Cl} \cdot \gamma^-_{Cl}) / (m_{HA} \cdot \gamma_{HA}) \cdot$$
$$(m_{R_4NCl} \cdot \gamma_{R_4NCl}), \tag{3}$$

where m_{HA}, molality of acid in the aqueous phase, m_{R_4NCl}, molality of amine in the aqueous phase, γ_{HA}, molal activity coefficient of acid, γ_{R_4NCl}, molal activity coefficient of amine $\gamma^+_{HAR_4N}$, molal activity coefficient of complex.

The loading of the extractant, Z is defined as the total concentration of acid in the organic phase, divided by the total concentration of amine in the organic phase. The expression for the loading, Z, can be written in the form:

$$Z = C_{a,org} / C_{e,org}. \tag{4}$$

Distribution coefficients, D for propionic acid extracted from water into organic phase were determined as

$$D = C_{a,org} / C_a. \tag{5}$$

The efficiency of extraction, E is expressed as

$$E = (1 - (C_a / C_{ao})) \cdot 100, \tag{6}$$

where C_a is the concentration of acid in the aqueous phase after extraction and C_{ao} is the initial concentration of acid in the aqueous phase, $mol \cdot dm^{-3}$. An E value of 100% means that all of the acid in the aqueous phase has been removed and is present in the organic phase [12].

Extraction of carboxylic acids with tertiary amines – solvent systems can be explained by the formation of acid:amine complexes, which are effected by the diluents in different ways. Solvation of the complex by the diluent is a critical factor in the extraction of acid. The interactions between the complex and diluent can be divided into general solvation and specific interactions of the diluent with the complex [13–15]. Polar diluents have been shown to be more convenient diluents than inert ones (non-polar), due to their higher distribution. But in the extraction of propionic acid by the quaternary amine used in this study such an effect has not been found. It has been found that the polarity of the diluent is not important in extraction of propionic acid extraction by quaternary amine [16].

3. Experimental

Aliquat 336 (Fluka, 91042, mass fraction purity >0.99), propionic acid (Merck, 814186, mass fraction purity >0.99), cyclohexane (Merck, 2817, mass fraction purity >0.997), toluene (Merck, 8325, mass fraction purity >0.995), methyl isobutyl ketone (Merck, 820820, mass fraction purity >0.99), hexane (Merck, 822280, mass fraction purity >0.96) and ethyl acetate (Merck, 822277, mass fraction purity >0.99) were used without purification.

Propionic acid was dissolved in water to prepare the solutions with initial concentrations of acid (8% $(1.17 mol \cdot dm^{-3})$). Equal volumes of an aqueous propionic acid solution and an organic solution of Aliquat 336 were stirred for 2 h, which preliminary tests demonstrated to be a sufficient time for equilibration. The stirring were carried out in glass flasks immersed in a water bath at $T = 298.15$ K. After equilibration, both phases were separated and the aqueous phase was analysed.

The concentration of the acid in the aqueous phase was determined by titration with aqueous 0.1 N sodium hydroxide (relative uncertainty: 1%) [17]. Acid analysis was checked against a material balance. In most cases the deviation between the amount of acid analyzed and the amount of acid known from preparing the solutions by mass did not exceed 3%. The solubilities of amine salts and diluents in the aqueous phase were negligible in the range of variables investigated.

4. Results and discussion

Table 1 demonstrates the influence of organic solvent and the organic phase concentration of Aliquat 336 on the distribution coefficients of propionic acid. The propionic acid concentration in the initial aqueous phase was $1.17 mol \cdot dm^{-3}$ (=8% w/w). In the experiments, the concentration of Aliquat 336 in the organic phase varied between about 0.22 and 1.55. The distribution coefficient of propionic acid in that range is between about 2.44 and 0.15 in MIBK whereas it changes similarly between about 2.65 and 0.12 in ethyl acetate. It will be seen from table 1 that a considerable amount of propionic acid is removed