

Reactive Extraction of Propionic Acid with Aliquat 336 Dissolved in 1-Decanol and n-Dodecane

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Abstract

This paper deals with propionic acid extraction by Aliquat 336, a quaternary amine dissolved in n-dodecane and 1-decanol. Chemical equilibrium experiments have been carried out to investigate the effect of modifier, 1-decanol on the extraction efficiency of Aliquat 336 in n-dodecane at fixed initial acid concentration of 0.27 gmol/l. Extraction efficiency is determined in terms of distribution coefficients and degree of extraction. The effect of extractant (Aliquat 336) concentration, effect of diluents (1-decanol and n-dodecane) composition have also been derived. It was found that distribution coefficients increased with increasing the 1-decanol concentration in the diluents. The maximum distribution coefficient obtained with Aliquat 336 dissolved in pure 1-decanol is 6.4. The extraction equilibrium constants have been determined. The number of extractant, Aliquat 336 molecules in the acid:amine complex has been estimated through mathematical model.

INTRODUCTION

The carboxylic acids are most widely used in the field of food and beverages as an acidulant and also in pharmaceutical and chemical industries. Fermentation technology for the production of organic acids in particular has been known for more than a century and acids have been produced in aqueous solutions. In the recent past, the interest towards propionic acid recovery from fermentation broths and waste streams increased. This interest is caused by growing demand of pure, naturally produced propionic acid used in chemical, pharmaceutical and food industries.

Among various available alternate processes for simultaneous removal of the product, extraction is often the most suitable one. Reactive extraction with a specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxyl-carboxylic acids [1]. Reactive Extraction is developed to intensify separation by solvent extraction and represents a connection between chemical (solute and extractant reaction) and physical phenomena (diffusion and solubilization of the system components). Some of the advantages of reactive extraction are increased reactor productivity, ease in reactor pH control without requiring base addition, and use of a high-concentration substrate as the process feed to reduce process wastes and production costs. This method may also allow the process to produce and recover the fermentation products in one continuous step and reduce the down stream processing load and the recovery costs [2].

Long-chain aliphatic amines are effective extractants for the separation of carboxylic acids from dilute aqueous solution [3-5]. The amines have been favored because of lower cost and generally higher distribution coefficient. Among different amines, extraction with primary amines is characterized by a large mutual solubility of the aqueous and organic phase; secondary amines have the highest reported distribution coefficient, but tend to form amides in the downstream regeneration by distillation; quaternary amines extract carboxylic acids at both acidic and basic pH via an anion exchange mechanism [4]. Consequently, quaternary and tertiary amines are the most attractive for extractive fermentation on the basis of their low aqueous solubility and intermediate basicity, the latter providing for reasonable extracting power along with the possibility of stripping. The specific chemical interactions between the amines and the acid molecules to form acid-amine complexes in the extractant phase allow more acid to be extracted from the aqueous phase [5]. Generally, the amine extractants are dissolved in a diluent such as a ketone, an alcohol, hydrocarbons, etc., that is, an organic solvent that dilutes the extractant to the desired concentration and controls the viscosity and density of the solvent phase. Many factors have been found to influence the equilibrium extraction characteristics of these systems. Three important variables are the nature of the acid extracted, the concentration of the extractant, and the type of diluent [6-8].

Zhong et al. [9] studied the reactive extraction of propionic acid using Alamine 304-1 in 2-octanol, 1-dodecanol, and Withohol 85 NF as diluents at various amine volume fractions from (0 to 100) %

and found extraction to be maximum at the amine volume fraction between (20 and 40) %. Studies on the propionic acid reactive extraction using trioctylamine in various diluents (hexanol, butyl acetate, and petroleum ether) show the positive effect of the different diluents on the extraction [10]. Uslu et al. [11] and Kumar et al. [12] studied reactive extraction of propionic acid using Aliquat 336 (quaternary amine) dissolved in five pure solvents (cyclohexane, hexane, toluene, methyl isobutyl ketone, 1-octanol and ethyl acetate) and binary solvents (hexane + MIBK, hexane + toluene, and MIBK + toluene) under various experimental conditions. In all cases, 1:1 acid-amine complexes were formed with no overloading. However a study on the same acid with the tertiary amine (Alamine 336) diluted in toluene at 298.15 K indicated more propionic acid to be transferred to the organic phase than would be expected from the 1:1 stoichiometry of the reaction, thus 2:1 and 3:1 acid-amine complexes were considered [13]. This indicates that complexation depends on the extractant-diluent system chosen.

Polar diluents that enhance the extracting power of amines are more favorable than nonpolar diluents as shown in the extraction of citric, lactic, and succinic acid [14]. The aim of this study is to show the influence of inert and active (modifier) diluent concentrations on the extraction efficiency and determination of the equilibrium extraction constant and the number of extractant reacting molecules. The maximum distribution coefficient obtained with Aliquat 336 dissolved in pure 1-decanol is 6.4, but 1-decanol is also showing the toxicity towards the bacterium used for propionic acid fermentation. So combination of non toxic (n-dodecane) and toxic (1-decanol) have been used with Aliquat 336.

THEORY

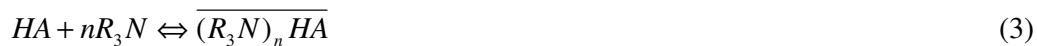
For simplicity, we used apparent equilibrium constants, expressed in terms of species concentrations. The physical extraction of propionic acid is neglected, as well as the acid dimerization and the water co-extraction. The interaction between acid and amine is realised through hydrogen bonding of non-dissociated acid molecule:



or by ion-pair formation:



If more than one amine molecule takes part in the complex formation, the process description is as follows:



$$K_E = \frac{\overline{[HA(R_3N)_n]}}{[HA][N_3R]^n} \quad (4)$$

The undissociated molecules concentration in the aqueous phase $[HA]$ can be calculated from the total concentration C_{HA} and the dissociation constant (pK_a).



$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (6)$$

$$C_{HA} = [HA] + [A^-] \quad (7)$$

$$[HA] = \frac{C_{HA}}{(1 + K_a/[H^+])} \quad (8)$$

The distribution coefficient K_D is defined as a ratio of the total (analytical) acid concentrations in the organic ($\overline{C_{HA}}$) and the aqueous (C_{HA}) phases given in eq. (9):

$$K_D = \frac{\overline{C_{HA}}}{C_{HA}} = \frac{\overline{[HL(R_3N)_n]}}{C_{HA}} \quad (9)$$

From Eq (4), (8) and (9)

$$K_D = K_E \frac{[R_3N]^n}{1 + K_a/[H^+]} \quad (10)$$

Above equation, represented in logarithmic form, gives a straight line.

$$\log K_D + \log(1 + K_a/[H^+]) = \log K_E + n \log([R_3N]) \quad (11)$$

If $[\overline{R_3N}]_{in} > n \overline{[HL(R_3N)_n]}$, initial extractant concentration, $[\overline{R_3N}]_{in}$ can be used to determine n and K_E .

EXPERIMENTAL

Reagents and Solutions

Aliquat 336 (quaternary alkylammonium salt) with purity of 98% is supplied by SpectroChem, India. It is used as extractant without further purification. Dodecane with 99% purity is utilized as an inactive and nontoxic diluent and 1-decanol with 99% purity, as modifier (active diluent) supplied by Sd Fine Chemicals. Propionic acid (99%) is delivered by Merck as analytical grade reagents. Organic phases are prepared by diluting the extractant - Aliquat 336 in dodecane with 1-decanol. Modifier (1-decanol) is varied from 10 to 85% in organic phase. The aqueous solution is prepared by diluting the propionic acid in de-ionized water without pH adjustment. All chemicals were used without any pretreatment.

Experimental Procedure

The extraction equilibrium experiments were carried out at room temperature with equal volumes (15 ml) of the aqueous and organic solutions shaken at 100 rpm for 12 hours in the glass flasks of 100 ml. on a temperature controlled reciprocal shaking machine (HS 250 basic REMI labs). Our preliminary studies had shown that 12 h of mixing time is sufficient to reach equilibrium. After attaining equilibrium, the phases were brought into contact with each other for separation. The initial concentration of propionic acid, 0.27 kmol/m^3 in aqueous solution is fixed. The effect of modifier in the organic phase is studied at a fixed acid concentration of 0.27 kmol/m^3 . Aliquat 336 is diluted in the range of 15-60% (v/v) with dodecane and 1-decanol (2:1 v/v). The initial and equilibrium pH values of propionic acid solution are determined using a digital pH-meter of ArmField Instruments (PCT 40, Basic Process Module). After settling, organic and aqueous phases separated. The concentration of acid in the aqueous phase is determined by taking a sample of 2 ml and using potentiometric titration with sodium hydroxide solutions of 0.015 N, and using phenolphthalein as indicator. The acid concentrations in the organic phase are calculated by mass balance. The reproducibility is checked by carrying out duplicate experiments in some selected cases.

The extraction process was analyzed by means of the degree of extraction and distribution coefficient. The degree of extraction is defined as the ratio of nicotinic acid concentration in the extract phase to the initial nicotinic acid concentration in aqueous solution by assuming no change in volume at equilibrium. The distribution coefficient, K_D , is calculated with the relation as given by Eq. 9.

RESULTS AND DISCUSSION

In this work, equilibrium reactive extraction experiments are carried out to separate propionic acid from aqueous solution with Aliquat 336 dissolved in dodecane and 1-decanol at room temperature. The extraction efficiency is presented in terms of extraction degree and distribution coefficient as given in Figures 1 and 2. The degree of extraction increases markedly with increasing concentration of active diluent, 1-decanol at Aliquat 336 concentration of 15% (v/v) and slightly with Aliquat 336 concentration of 25% (v/v). Thus, the extraction efficiency with Aliquat 336 concentration of 25% (v/v) is less affected by the combination of diluents. The extraction degree varies between 81-84% with 15% Aliquat 336 and 85-86% with 25% Aliquat 336. When Aliquat 336 is used as extractant in a mixture with an inert diluent, dodecane and an active diluent (modifier), decanol in a reactive extraction of propionic acid, the solubility of extracted species increases in the organic phase. The influence of diluents on the values of K_E and n depends on the concentration of the modifier in the presence of inert diluent.

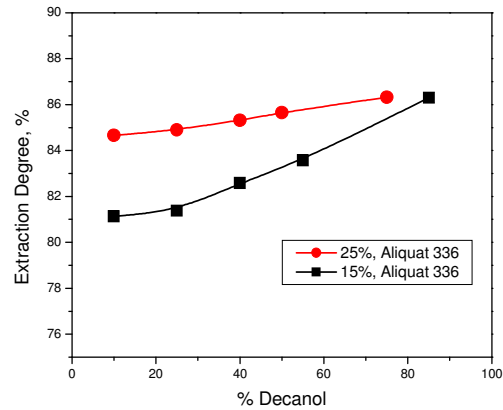


Figure 1. Influence of modifier (1-decanol) and Aliquat 336 concentration on the degree of extraction.

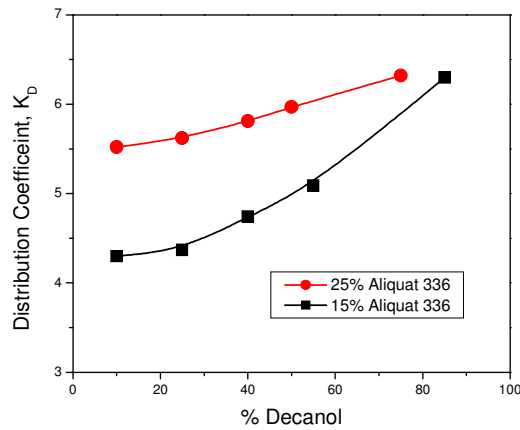


Figure 2. Influence of modifier (1-decanol) and Aliquat 336 concentration on the distribution coefficient.

The extraction studies is also done with various proportions of extractant, Aliquat 336 (15 – 60% v/v) dissolved in the dodecane +1-decanol (2:1 v/v). This study is used to get the influence of Aliquat 336 concentration and to determine the number of molecules of amine reacting with a molecule of acid. It can be seen from Figures 3 and 4, the extraction efficiency increases with increasing the concentration of the extractant. Initial range of concentration of amine, the effect is

predominant with a tendency to reach plateau at high concentration. The extraction degree and distribution coefficient are found 87.5% and 6.93 respectively at highest extractant concentration of 60% (v/v).

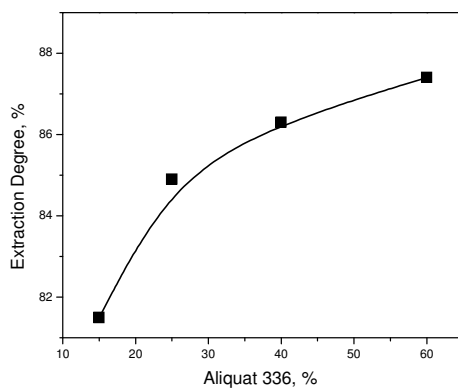


Figure 3. Effect of Aliquat 336 dissolved in dodecane and 1-decanol (2:1 v/v) on the extraction degree at initial propionic acid concentration 20 g/l.

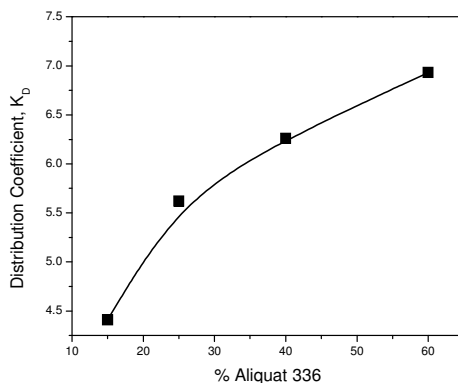


Figure 4. Effect of Aliquat 336 dissolved in dodecane and 1-decanol (2:1 v/v) on the distribution coefficient at initial propionic acid concentration 20 g/l.

A plot of equation (11) by taking, $\log K_D + \log\left(1 + \frac{K_H}{[H^+]}\right)$ on y-axis and $\log[\overline{R_3N}]_{in}$, on x-axis yields the straight line with slope n and intercepts $\log K_E$ as shown in Figure 5. The equilibrium pH

values have been used to calculate $[H^+]$ concentration. As discussed above, the solvent polarity is an important parameter that controls the extraction degree of ionizable solutes. The value of slope n and intercept $\log K_E$ are 0.34 and 0.85 respectively from Figure 5. The low value of n is showing more than one molecule of acid reacted with each molecule of extractant, Aliquat 336. Another important reason is significant physical extraction by an active diluent, 1-decanol. Therefore, the solvent polarity controls the extraction constant through its influence on separation efficiency and mechanism. The values of R^2 near about 0.99 are showing minimal deviation in the results.

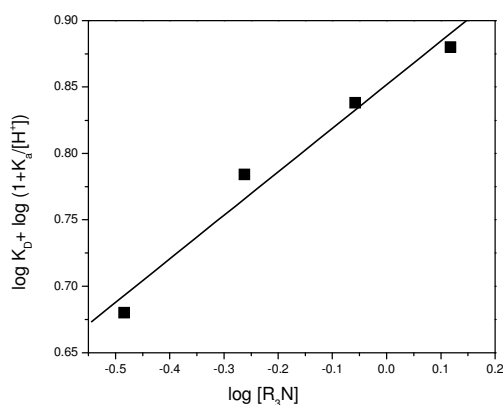


Figure 5. Graphical representation of equation (11) for the reactive extraction with Aliquat 335 in dodecane and 1-decanol (2:1 v/v)

CONCLUSIONS

The studies on reactive extraction of propionic acid with Aliquat 336 in the inert (dodecane) and active (decanol) diluents are used to provide data in the design of extractive fermentation for production of propionic acid. The extraction efficiency increases with increasing concentration of active solvent, but It also imposed toxicity towards bacterium used in fermentation of propionic acid. Distribution coefficient varies between 4.3-5.1 with varying concentration of 1-decanol from 10 to 55% at fixed 15% Aliquat 336 and 5.5-6.0 with varying concentration of 1-decanol from 10 to 50% at fixed 25% Aliquat 336. The extraction efficiency increases with increasing the concentration of the extractant, Aliquat 336 (15 – 60% v/v) dissolved in the dodecane +1-decanol (2:1 v/v). The highest value of the extraction constant has been obtained for reactive extraction with 60% of Aliquat 336 dissolved in the dodecane +1-decanol (2:1 v/v). The number of molecules of amine reacted with each molecule of acid, n and equilibrium constant, K_E are found to be 0.34 and 7.1 respectively. The solvent polarity found to be an important parameter that controls the extraction degree of ionizable solutes.

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