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Back extraction of propionic acid from loaded organic phase

Amit Keshav[a], Kailas L. Wasewar[b,*]

[a] Department of Chemical Engineering, National Institute of Technology (NIT) Raipur, Chhattisgarh 492010, India
[b] Department of Chemical Engineering, Visvesvaraya National Institute of Technology (VNIT), Nagpur 440010, Maharashtra, India

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ABSTRACT

Study of back extraction and hence regeneration of the acid from the loaded organic phase is essential for the design of a complete reactive extraction process. In this paper, the backextraction of propionic acid from the loaded organic phase (tri-n-octylamine (TOA)+diluent) was studied using different techniques, like, temperature and diluent swing, using NaOH or trimethyl amine. It was found that temperature swing regeneration could result in recovery as high as 88% of acid in two stages from organic phase, TOA+MIBK. However, from TOA+alcohols, the recovery by this technique was average. Diluent swing is not successful in efficiently recovering acid from the organic phases employed. NaOH, in stoichiometric ratio, could completely recover the acid, but in the form of sodium propionate. The 100% acid recovery was accomplished using trimethylamine (TMA), when used in stoichiometric ratio slightly higher than (1:1). Along with the complete recovery acid can be easily separated from TMA as the base is volatile. Kinetics of backextraction of propionic acid using TMA was also studied and it was found to be fast.

1. Introduction

Propionic acid is widely used in processes, such as, in the production of cellulose plastics; in the manufacture of ester solvents, perfume bases; in food industries to suppress the growth of mould and rope in breads and cakes; for the manufacture of arthritic drugs, herbicides, plasticizers and as mould preventives in silage and hay (Playne, 1985). Isolation of propionic acid from dilute waste streams and fermentation broths is an economic problem. The high solubility in water, renders traditional solvents such as alcohols, ethers, esters and inert diluents (hexane, n-heptane) etc., to be successfully employed for acid extraction. The conventional method (calcium hydroxide precipitation), includes addition of calcium hydroxide to form calcium salt of propionic acid, to which sulphuric acid is added to liberate free propionic acid (King and Tamada, 1990). This method of recovery is expensive and unfriendly to environment, as it consumes a lot of lime and sulfuric acid, and also generates calcium sulphate sludge as solid waste.

Reactive extraction, using organophosphorous compounds, tertiary and quaternary amine etc., is a successful technique for the recovery of acid from dilute aqueous solutions. Out of the above extractants, tertiary amines have proved to be most successful in recovery of carboxylic acids from dilute solutions (Keshav et al., 2008a–f; Uslu and İnci, 2007; Wasewar and Pangarkar, 2006).

Various aspects of reactive extraction, such as, influence of type of extractant, acid concentrations, nature of the acid and diluent, effect of extraction temperature, water co-extraction and non idealities in both phases, were studied in literature. For the complete design of reactive extraction process, it is essential to study both the forward and backward steps. Extensive work on the extraction of propionic acid using reactive extraction technique was done by the authors; yet, very few literature and effort have been made on the backextraction of propionic acid from the loaded organic phases obtained in the first step.

Gu et al. (1998) studied reactive extraction of propionic acid using Alamine 304-1 in 2-octanol, 1-dodecanol and Witcohol 85 NF as diluents at various amine concentrations (0–100%) and found extraction to be maximum at the amine concentration between 20% and 40%. Regeneration of acid from loaded organic phase by distillation was also studied. For the understanding of equilibrium characteristics and to search an efficient recovery system for reactive extraction of propionic acid, tri-*n*-butyl phosphate (TBP) in eight different diluents (1-dodecanol, benzene, toluene, heptane, hexane, butyl acetate, petroleum ether, and paraffin liquid) (Keshav et al., 2008b), tri-n-octylphosphine oxide (TOPO) in hexane (Keshav et al., 2008c), tri-n-octyl amine (TOA) in different diluents (*n*-heptane, petroleum ether, ethyl acetate and oleyl alcohol) (Keshav et al., 2008d), TBP, TOA and Aliquat 336 in 1-octanol (Keshav et al., 2008a), TBP, TOA and Aliquat 336 and their mixed binary solutions in sunflower oil (Keshav et al., 2008e), Aliquat 336 in oleyl alcohol (Keshav et al., 2008f), were employed. Equilibrium parameters, such as, distribution coefficients, loading ratio, degree

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* Corresponding author. Tel.: +91 712 2801561.
E-mail addresses: amitkeshav2000@yahoo.co.in (A. Keshav), k_wasewar@rediffmail.com (K.L. Wasewar).

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of extraction and equilibrium complexation constants were obtained. All these studies confirm that TOA is a better extractant and in particular, with methyl-iso-butylketone (MIBK) and in alcohols as diluents, the efficiency of the TOA, as an extractant, has been markedly improved.

Results of authors work suggest that tri-n-octylamine is the best extractant in the forward step of reactive extraction, i.e., the recovery of acid from aqueous phase. Regeneration of acid from the loaded organic phase involves reversal of the reaction, to recover the acid as a product phase and the acid free extractant for recycle. The acid can be back extracted from loaded organic phase using various regeneration techniques. In present paper, techniques such as, using NaOH or trimethyl amine (TMA) and by temperature and diluent swing were used for the regeneration of acid from the loaded organic phase. Comparison among the various methods was made and it was found that TMA is the best backextractant for regeneration of the acid. In order to prove that the process is successful on the commercial scale, kinetics of the process was also studied and it was found that the kinetics is fast enough.

2. Theory

There are various methods available for the regeneration of the carboxylic acid from the loaded organic phase.

(a) *Using NaOH*: In this method of backextraction, the loaded organic phase was contacted with sodium hydroxide solution. This method was suggested by Yabannavar and Wang (1991a) who employed it for the back extraction of lactic acid from a loaded organic phase (lactic acid+Alamine 336+oleyl alcohol).

(b) *Using HCl*: This method was also suggested by Yabannavar and Wang (1991b). Concentrated HCl was used to essentially displace the lactic acid from the loaded organic phase (lactic acid+Alamine 336+oleyl alcohol). It was possible to regenerate the solvent by distilling diluent in the dispersed organic phase.

(c) *Temperature-swing regeneration*: In this scheme, the extraction has been carried out at relatively low temperature, producing an acid-loaded organic extract and an aqueous raffinate waste stream containing the unwanted feed components (Tamada and King, 1990). During regeneration, the extract was contacted with a fresh aqueous stream at a higher temperature to produce an acid-laden aqueous product stream and an acid-free organic phase. The concentration of the acid achievable in this stream depends on the amount of change in the extraction equilibrium between temperatures and can be higher than that in the original aqueous feed stream (Tamada and King, 1990).

(d) *Using trimethyl amine* (*TMA*): Poole and King (1991) investigated the regeneration of lactic acid extracted in the organic phase using a stronger volatile amine in aqueous phase. The most obvious water-soluble, volatile base is ammonia. However, ammonia and both primary and secondary amines form amides when they are heated in mixtures with carboxylic acids (Mitchell and Reid, 1931; Poole and King, 1991; Streitwieser and Heathcock, 1976). The amides are sufficiently stable so it is difficult to reverse the process and recover the amine.

(e) *Diluent swing regeneration*: This is based on a shift of the equilibrium distribution of acid from the aqueous phase to the organic phase between forward and back extraction, caused by a change in composition of the diluent with which the extractant is mixed. This diluent composition swing facilitates back extraction of acid into an aqueous product phase. The composition of the acid-laden organic phase leaving the extractor is altered, by either removal of the diluent or addition of another diluent, to produce a solvent system that promotes distribution of the acid to the aqueous phase. The altered organic phase is contacted with a fresh aqueous stream in the regenerator to produce the acid-laden aqueous product and the acid-free solvent for recycle to the extractor (Tamada and King, 1989). Adjustment of the diluent composition can also occur before this solvent reenters the extractor.

3. Materials and methods

3.1. Materials

TOA ($C_{24}H_{51}N$) (98%, ACROS, India), a tertiary amine was used as extractant. Propionic acid (CH_3CH_2COOH; 99% purity; molar mass 74.08; density 992 kg/m^3; Himedia, India) and diluents: MIBK, 1-decanol, and 2-octanol were employed for the study. Double distilled water was used to prepare the solutions of various concentrations of propionic acid. Sodium hydroxide (Ranbaxy India Ltd.), trimethyl amine (TMA; C_3H_9N, molar mass 59.11, assay 30% in water) and diluents hexane, petroleum ether and toluene were used as back-extraction reagents. Mobile phase for HPLC was composed of ammonium dihydrogen phosphate (RFCL India Ltd.) solution in millipore water (RFCL India Ltd.). Orthophosphoric acid (Ranbaxy India Ltd.) was used for pH adjustment of mobile phase of HPLC.

3.2. Methods

Back extraction by temperature swing involved shaking of equal volumes (20 ml) of loaded organic phase and water phases for 12 h at 363 K in a water bath, followed by settling of the mixture for at least 2 h at a same temperature. In diluent swing, the loaded organic phase was first contacted with another diluent and then with water for 12 h at 305 K. The aqueous phases, after the settling period of 2 h, were titrated with NaOH solution to determine the acid transferred. Backextraction by NaOH and TMA were carried out by equilibrating known volumes (50 ml each) of aqueous phase (different concentrations of TMA) and propionic acid loaded organic phase of known concentration in a temperature-controlled shaker bath (305 K) for 24 h. The two phases were allowed to settle for 24 h in a separating vessel for complete phase separation. Aqueous phase acid concentration was determined by a high-pressure liquid chromatography (HPLC) system (Waters 1523) consisting of a binary pump, refractive index detector (Waters 2414) and dual λ absorbance detector (Waters 2487). The sample was eluted by 0.1 kmol/m^3 aqueous ammonium dihydrogen phosphate solution adjusted to pH 2.2 by an aqueous phosphoric acid solution endowing at a rate of 0.002 l/min in a reverse phase C-18 column (4 mm i.d. $\times$ 150 mm in length). Propionic acid was detected at 236 nm. The acid content in the organic phase was determined by a mass balance. Few experiments were carried out in duplicate and consistency was found within $\pm 2\%$.

Kinetics experiments were carried out in 0.06516 m internal diameter glass stirred cell with an effective interfacial area of 0.003333 m^2. The vessel was equipped with a stainless steel dual four flat blade stirrer (diameter=0.048 m). Known volumes of loaded organic solvent and TMA (aqueous phase) (100 ml each) were taken and regeneration was carried out for a definite period at T=305 K. Samples of aqueous phase were taken out at different time intervals for analysis till it reaches equilibrium. It was found that the equilibrium is established within 30 min. Aqueous phase acid concentration was determined by HPLC. The acid content in the organic phase was determined by mass balance. Few experiments were repeated to check the consistency in the results. The variation was found within $\pm 2\%$.