Acetic acid extraction from aqueous solutions using fatty acids

H.M. IJmker, M. Gramblička, S.R.A. Kersten, A.G.J. van der Ham, B. Schuur *

University of Twente, Faculty of Science and Technology, Green Energy Initiative, Sustainable Process Technology Group, PO Box 217, 7500 AE Enschede, The Netherlands

ARTICLE INFO

ABSTRACT

A major challenge for production of acetic acid via bio-based routes is cost-effective concentration and purification of the acetic acid from the aqueous solutions, for which liquid–liquid extraction is a possible method. A main challenge in extraction of acetic acid from dilute aqueous solutions is to develop a solvent that allows for high distribution and selectivity in the extraction, and an effective and preferably simple recovery method to regenerate the solvent and recover the product. In this study fatty acids were proposed as extracting agents for acetic acid because of their ability to form double hydrogen bonded complexes that, compared to e.g. acid–base complexes were expected to be easier to regenerate. Experimental extraction studies with hexanoic acid and heptanoic acid showed that although the distributions were lower than were expected, these fatty acids are applicable for the extraction of acetic acid from dilute aqueous solutions, and an extraction model with homogeneous organic phase complexation was developed and found to describe the experimental equilibria for hexanoic acid accurately. The partition and complexation coefficients were determined for the extraction of acetic acid with hexanoic acid: $K_{p,HAc} = 0.145 \pm 0.019$ (–) and $K_{comp} = 0.338 \pm 0.039$ (L/mol). With a selectivity of the fatty acids for acetic acid over water of up to 12 for hexanoic acid, and up to 24 for heptanoic acid, significant concentration through extraction is possible, and further purification through fractionation during thermal recovery is considered.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Acetic acid is one of the world's most important chemicals with a broad spectrum of applications. The largest portion of the global acetic acid consumption is used for the production of polymers derived from vinyl acetate. Another major use of acetic acid is for the production of purified terephthalic acid, which is used to produce polyethylene terephthalate (PET). Furthermore, it is a key raw material for acetic anhydride and acetate esters, which are, like acetic acid itself, widely used as solvents [1,2].

Acetic acid is mainly produced via synthetic routes of which methanol carbonylation is nowadays the most important. Other routes proceed through liquid-phase oxidation of saturated hydrocarbons or, less frequently, via oxidation of ethylene or ethane. The oldest route is via fermentation of ethanol, sugar or biomass, which is nowadays less used, mainly because realization of cost-effective concentration and purification of the acetic acid from the fermentation broth is a major challenge [1,3]. However, due to rising oil prices and the increasing orientation towards more sustainable processes in industry, the interest in production of acetic acid – and other organic acids – via bio-based routes has increased. As a result, also the recovery of these organic acids from both fermentation broths [4–6] and from aqueous phases originating from pyrolysis of biomass [7,8] has received considerable attention recently.

Several methods have been proposed for the recovery of acetic acids from aqueous solutions. A well developed route is via salt precipitation. Major drawback is the stoichiometric coproduction of gypsum or (in newer routes) other salts [3,5]. Another proposed route is via the recovery of acetic acid esters after reaction with an alcohol. This method, however, takes extra process steps if acetic acid is the desired product [4,9]. Besides that, various membrane techniques have been proposed, including electrodialysis, ultrafiltration, pervaporation, reverse osmosis and pertraction [4,10]. Membrane extraction processes are mentioned as promising alternative for conventional liquid–liquid extraction, because backmixing is avoided and microbes are not directly exposed to the extraction liquid, which might be beneficial in some cases [10].

Furthermore, recently a lot of research has been done on affinity based separation methods for the recovery of carboxylic acids. For all of these methods there is a tradeoff between the separation capacity of the affinity based separation step and the effort needed

---

* Corresponding author. Tel.: +31 614178235.
 E-mail address: b.schuur@utwente.nl (B. Schuur).

in the regeneration step. Among the methods proposed are several adsorption methods, e.g. making use of basic/anion ion-exchange resins, in which the acetate ions are exchanged by ions in the resin [10,11], or using activated carbon [10]. Adsorption is considered as a reliable technology, suitable for recovery of substances of dilute and complex solutions as fermentation broth. A second affinity-based method is liquid–liquid extraction, in which the carboxylic acid is recovered by transfer to an organic solvent. Such a process comprises of two parts, i.e. extraction of the acid into the solvent and subsequently regeneration of the solvent to recover the product [12]. Extraction is considered to be an efficient, economical and environmentally friendly method [6]. Compared with adsorption it has a relatively high capacity and milder regeneration conditions, and therefore liquid–liquid extraction was focused on in this study.

In the design of an extraction process three main aspects play a role. First of all the pH should be regulated in order to have the acid in undissociated form, as only undissociated acid is extracted to the solvent phase [5]. Secondly, the extraction solvent should be chosen such that it has a high partition coefficient of the carboxylic acid, meaning it has a high preference for the organic phase over the aqueous phase, and a high selectivity for extraction of carboxylic acid over water, in order to limit the co-extraction of water [12]. And thirdly, the extraction system should be reversible, so the solvent should be well recoverable [4].

The aim of this study was to investigate on a mild extraction method for the extraction of acetic acid from aqueous solutions, preferably without the generation of salt waste.

The three main groups of extraction solvents considered by Kertes and King [5] are ((I) the carbon-bonded oxygen bearing extractants such as alcohols and ethers, (II) organophosphorous extractants such as trioctylphosphine oxide (TOPO) and tributyl-phosphate (TBP), and (III) aliphatic amine extractants such as tri-n-octylamine (TOA). The types of extractants ((II) and (III)) show strong complexation and are usually used in one or more diluents, which mainly act as solvent for the complexes that these extractants form with the carboxylic acid and to adjust the viscosity and density of the organic phase. For the first group the distributions are relatively low [13] for the recovery of acids from the dilute aqueous acid solutions found in most fermentation streams. Distribution coefficients of some of these solvents are displayed in Table 1.

Recent research focuses on new solvents with higher distribution coefficients, facilitating extraction and thus making bio-based production of carboxylic acids more attractive. A new type of solvents proposed recently concerns ionic liquids, which are seen as potential green solvents. Attractive properties of ionic liquids are their temperature stability and practically zero vapor pressure. Marták and Schlosser [16] and Oliveira and co-workers [17] recently applied phosphonium-based ionic liquids for the extraction of low concentrated lactic acid solutions (e.g. waste water, fermentation broths) and achieved higher distribution coefficients than with most traditional extractants. Also butyric acid extraction with ionic liquids has been investigated [18] and Blahušiak and co-workers proposed a hybrid process for the recovery of butyric acid with ionic liquids and the regeneration of the solvents by short-path distillation [19]. Recovery of the lactic acid from the ionic liquid phase was studied experimentally as well, but proved to be rather difficult [17].

Next to the ionic liquids, also new types of amine extractants containing multiple nitrogen atoms that outperform the traditional TOA with regard to lactic acid distribution coefficients were proposed recently by de Haan and co-workers [20].

Notwithstanding the ongoing developments of new types of solvents for the extraction of carboxylic acids, not much is published about product and solvent recovery methods. An overview of proposed methods for recovery of lactic acid is given by Wasewar et al. [13], of which most is also applicable on carboxylic acids in general. This overview indicates that for solvents with good extraction properties, rather complex or energy demanding recovery methods are required, comprising back-extraction and several extra product recovery and purification steps. An effective recovery method is, however, of great importance to improve acetic acid extraction from solutions originating from bio-based processes [4].

As alternative extraction solvents, the use of solvents which supply both hydrogen bonding donor and acceptor pairs might be beneficial to address the acid functionality in acetic acid. One class of solvents that contains both a hydrogen bond donor and acceptor is the carboxylic acid class, from carboxylic acids it is known that in hydrophobic environments they tend to dimerize (Fig. 1) [5,21].

In this study medium chain fatty acids (MCFA) were investigated as new extraction solvent for diluted acetic acid solutions. By applying MCFA's pure, the solvent is rather apolar which is beneficial for the dimerization (Table 2) [22]. Fujii et al. [22] have reported dimerization constants of acetic acid in various organic solvents as listed in Table 2. The dimerization constant is defined as:

$$K_2 = \frac{[(HA)_2]}{[HA]^2} \tag{1}$$