



Acetic acid extraction from aqueous solutions using fatty acids



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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.

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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 back-mixing 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

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Nomenclature

Symbols

E	extraction factor (-)
f_E	fraction extracted (-)
K_{comp}	complexation equilibrium coefficient (L/mol)
K_D	distribution coefficient (-)
K_p	partition coefficient (-)
Mwt	molar weight (g/mol)
N	number of equilibrium stages (-)
x	mass fraction in aqueous phase (-)
y	mass fraction in solvent phase (-)
z	fraction fatty acid that is dissociated (-)
$\beta_{i,j}$	selectivity ($=K_{D,i}/K_{D,j}$) (-)
S	solubility (wt%)
S/F	solvent to feed ratio on volume basis (-)

Abbreviations

aq	aqueous phase
CI	confidence interval
f	final
HAc	acetic acid
HPLC	high pressure liquid chromatography
i	initial
ICP-OES	inductively coupled plasma – optical emission spectroscopy
max	maximum
MCFA	medium chain fatty acid
min	minimum
NaOHex	sodium hexanoate
org	organic phase
w	water

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 tributylphosphate (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 Blahušák 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:

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

Table 1
Distribution coefficients for several extraction solvents.

Solvent	Type	K_D	Basis	Ref.
Methylisobutyl ketone	I	0.66–0.76	Mass	[14]
Octanol	I	0.56	Mass	[14]
25.9 wt% TOPO in n-heptane/n-hexanol (2:1 vol)	II	4.7	Volume	[15]
Tributylphosphate	II	2.2–2.7	Volume	[15]
0.5 M Tri-n-octylamine in ethyl acetate	III	3.6	Mass	[8]
18.6 wt% trioctyl amine in chloroform	III	9.9	Volume	[15]
Diisotridecylamine	III	33.4	Volume	[15]

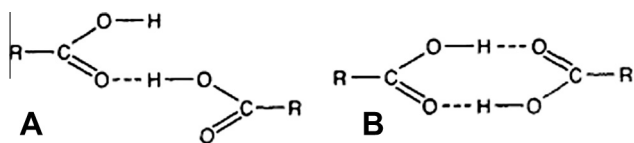


Fig. 1. Dimerization of carboxylic acid in linear (A) and cyclic (B) form, depending on type of solvent. Derived from Fujii et al. [22] with permission © 1988, American Chemical Society.

Table 2
Dimerization constants of acetic acid in organic solvents measured by IR – adapted from Fujii et al. [22], with permission © 1988, American Chemical Society.

Solvent	T (°C)	K_2 (dm ³ /mol)
n-Hexane	25	3200 ± 500
Carbon tetrachloride	25	1400 ± 200
Toluene	25	446 ± 70
Benzene	20	390 ± 70
Chlorobenzene	25	496 ± 80
Chloroform	25	300 ± 50
1,2-Dichloroethane	25	108 ± 20
Dichloromethane	25	126 ± 20

On the basis of these dimerization constants, it was expected that distribution coefficients of acetic acid are for MCFA much higher than for alcohols and ketones could possibly be obtained, while recovery may be easier than for the amines and the ionic liquids. The equilibrium extraction was investigated to prove the principle of carboxylic acid extraction with carboxylic acids and the extraction equilibrium was described with a mathematical model.

2. Theory

In the extraction system of acetic acid from dilute aqueous solutions using fatty acids several equilibria play a role. In Fig. 2 the equilibria are displayed for a system where sodium salts (phosphates) are applied to influence the pH. In such systems, acetic acid and fatty acid dissociate in the aqueous phase, the non-dissociated acids partition over the phases, and in the organic phase the complexation through hydrogen bonding takes place.

Acetic acid is so hydrophilic that distribution of its sodium salt over the phases is not likely, while for the fatty acids also distribution of their sodium salt over both phases was taken into account (*vide infra*).

The dissociation equilibria of aqueous acetic acid and aqueous fatty acid are described in Eqs. (2) and (3). To limit the complexity of the figure, dissociation equilibria of the phosphate salt (equilibria of phosphoric acid) are not displayed, but have been applied similarly in order to calculate the activities of the electrolytes. Temperature dependent correlations were used for the dissociation coefficients of water, acetic acid and the first two dissociation equilibria of phosphoric acid [23,24]. For the third dissociation equilibrium coefficient of phosphoric acid [25] and the dissociation equilibrium coefficient of hexanoic acid [26] literature values were used. Non-ideality for the electrolytes was accounted for by the extended Debye-Hückel approximation (Eq. (4)) in which I_c is the ionic strength, A and B are solvent-parameters [27] and d_i is the ion size parameter [28]; the ion size parameter of hexanoic acid was not known in literature and thus a value of 1 was assumed.

$$K_{HAc} = \frac{\gamma_{H^+} \gamma_{Ac^-} [H^+]_{aq} [Ac^-]_{aq}}{[HAc]_{aq}} \quad (2)$$

$$K_{HFA} = \frac{\gamma_{H^+} \gamma_{FA^-} [H^+]_{aq} [FA^-]_{aq}}{[HAc]_{aq}} \quad (3)$$

$$\log \gamma_i = - \frac{AZ_i^2 \sqrt{I_c}}{1 + Bd_i \sqrt{I_c}} \quad (4)$$

For the extraction of the undissociated acetic acid, the homogeneous extraction mechanism [29] was applied, in which partitioning of acetic acid to the organic phase (Eq. (5)) takes place and complexation of acetic acid with hexanoic acid occurs in the organic phase (Eq. (6)). The overall distribution coefficient of acetic acid between the two phases is defined as the ratio of the concentration acetic acid in both phases on mass base (Eq. (7)).

$$K_{p,HAc} = \frac{[HAc]_{org}}{[HAc]_{aq}} \frac{\rho_{HFA}}{\rho_w} \quad (5)$$

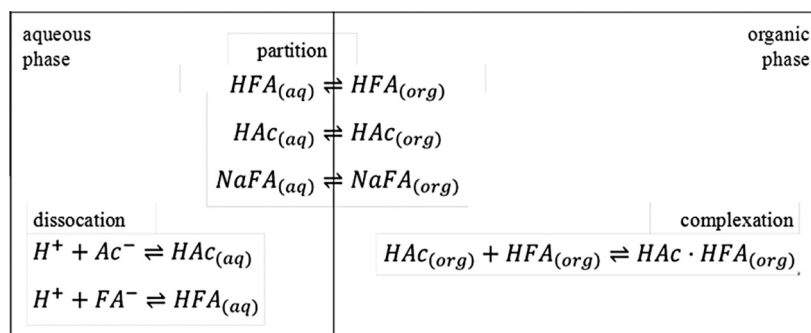


Fig. 2. Extraction scheme showing the main equilibria in extraction of acetic acid from dilute aqueous solution using fatty acids as extraction solvent.

$$K_{comp} = \frac{[\text{HAc} \cdot \text{HFA}]_{org}}{[\text{HAc}]_{org} [\text{HFA}]_{org}} \quad (6)$$

$$K_D = \frac{\frac{[\text{HAc}]_{org} + [\text{HAc} \cdot \text{HFA}]_{org}}{\rho_{\text{HFA}}}}{\frac{[\text{HAc}]_{aq} + [\text{Ac}^-]_{aq}}{\rho_w}} \quad (7)$$

It was found that the solubility of the dissociated fatty acid is higher than that of the undissociated fatty acid, and therefore, in the calculation of the overall partitioning of fatty acid, both dissociated and undissociated fatty acid in water were taken into account. The total solubility of fatty acid in the aqueous phase is described as the sum of the fraction fatty acid that is dissociated multiplied with its solubility and the fraction fatty acid that is undissociated multiplied with its solubility, as described in Eqs. (8) and (9). The ratio $[\text{FA}^-]/[\text{HFA}]$ can be calculated using the Henderson–Hasselbalch relation [29].

$$[\text{HFA}]_{aq,tot} = Z_{\text{FA}^-} \cdot S_{diss} + (1 - Z_{\text{FA}^-}) \cdot S_{undiss} \quad (8)$$

$$Z_{\text{FA}^-} = \frac{\frac{[\text{FA}^-]}{[\text{HFA}]}}{1 + \frac{[\text{FA}^-]}{[\text{HFA}]}} \quad (9)$$

The partitioning of the sodium salt of the fatty acid is defined in Eq. (10).

$$K_{p,\text{NaFA}} = \frac{\frac{[\text{NaFA}]_{org}}{\rho_{\text{HFA}}}}{\frac{[\text{NaFA}]_{aq}}{\rho_w}} \quad (10)$$

In case of extraction with non-dissociating and non-complexing extraction agents, Eqs. (6), (8), and (10) do not apply.

3. Materials and methods

3.1. Chemicals

The chemicals used were acetic acid (>99.7%), 1-octanol (>99%), hexanoic acid (>98%), heptanoic acid (>99%), octanoic acid (>98%) and sodium phosphate dibasic anhydrate (>99%), all supplied by Sigma–Aldrich, the Netherlands. And hexyl methyl ether (>98%) was supplied by TCI-Europe.

3.2. Experimental procedures

3.2.1. Liquid–liquid extraction experiments

Liquid–liquid extraction experiments were performed with medium chain fatty acids (MCFA's) hexanoic and heptanoic acid as solvents. Furthermore experiments with octanol and hexyl methyl ether as solvents were performed. For all equilibrium extractions, solutions were prepared of 1 wt% acetic acid in water and different concentrations Na_2HPO_4 from 0 to 0.20 M to manipulate the pH. In Erlenmeyer flasks, 25 mL aliquots of the acetic solutions were brought into contact with 15 mL of the solvent. The phases were magnetically stirred at 500 rpm at room temperature and extraction was carried out for at least 12 h, which was long enough to reach equilibrium (validated experimentally). Subsequently the phases were separated by settling for at least 4 h. Samples taken from the aqueous phase were analyzed by high pressure liquid chromatography (HPLC) to determine the concentrations of the acids, and samples taken from the organic phase were analyzed with Karl Fisher titration to determine the water content. Several samples of organic phases were also analyzed by HPLC on the contents of the acids to validate the use of the mass balance to determine the organic phase concentrations in all other experiments. In some cases for samples of the aqueous phase, the pH was determined. For some samples, both aqueous and organic,

of the extraction experiments with hexanoic acid, sodium concentrations were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES).

3.2.2. Analytical procedures

Aqueous phase concentrations of acetic acid, fatty acid or hexyl methyl ether were determined using HPLC by analysis of 1 mL samples in an Agilent Technologies 1200 series HPLC system, with a 300 mm × 7.7 mm Hi-plex H column equipped with pre-column and using RID detection. The injection volume was 10 μL, the temperature was 65 °C and 5 mM aqueous sulfuric acid was used as eluent with a flow rate of 0.6 mL/min. Standard samples of known composition in the range of interest were injected both before and after analysis to obtain calibration curves.

Concentrations acetic acid in the organic phase were obtained by mass balance calculations. For selected samples, these calculated results have been ascertained by HPLC measurements of the organic phase. For the HPLC of the organic phase the same procedure was used as for the aqueous phase, except that in this case the sample had to be diluted 1:250 in water prior to injection.

Karl Fischer titration was used to measure the water content in the samples of the organic phase, using a Metrohm 787 KF Titrino with hydranal as titrant and 1:3 methanol to dichloromethane as solvent. pH measurements were performed for some of the samples of the aqueous phases, using a Metrohm 785 DMP Titrino.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to measure sodium concentrations in samples of both organic and aqueous phases from extraction experiments with hexanoic acid. A Varian Liberty II sequential type ICP-OES system was used and detection was done for both wavelengths of sodium (330.2 and 589.6 nm).

3.3. Numerical procedures

To gain more insight in the extraction mechanism and to be able to do predictions of desired parameters, a numerical model of the extraction system was implemented in a MATLAB code. The solve tool was used to solve the system of non-linear equations that describe the extraction system. The partition and complexation coefficients were fitted to the system by a non-linear least square algorithm, lsqnonlin. The accuracy of these parameter estimates, based on 95% confidence intervals, was calculated using the nlparci tool.

4. Results and discussion

4.1. pH of the aqueous phase as function of amount of buffer salt

For the extraction experiments done in this study model solutions were used, representing a low concentrated acetic acid solution from a fermentation process with mild conditions. For 1 wt% acetic acid solution the pH was measured as function of the concentration Na_2HPO_4 to indicate the amount of phosphate salt required to make aqueous solutions with an initial pH of 6, which was considered as reasonable for mimicking fermentations.

The results of these measurements are shown in Fig. 3, indicating that for a model solution of 1% acetic acid and pH 6 a concentration of 0.20 M Na_2HPO_4 is needed.

The line represents the model simulation (Eq. (2) together with the dissociation equilibria for the phosphate salts, using the extended Debye–Hückel approximation for the activity coefficients of the electrolytes), which shows good correspondence with the measured results and can thus be applied to describe the aqueous phase equilibria in the extraction model.

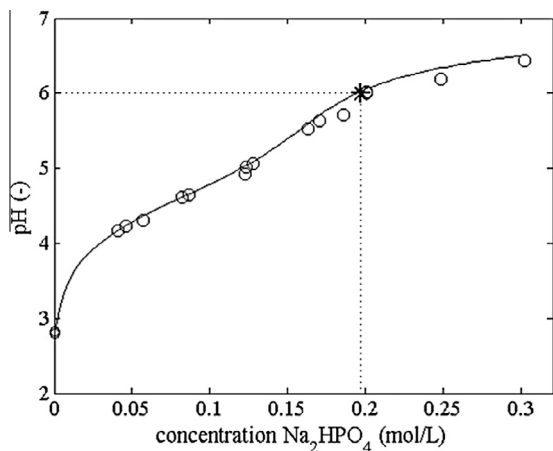


Fig. 3. Experimental and simulated pH values as function of the concentration Na_2PO_4 in a 1 wt% acetic acid solution. Symbols: Measured values (\circ), Calculated amount of buffer for pH 6 (*). Line shows the simulated trend. Dashed lines included for illustrative purposes only.

4.2. Validation of the experimental extraction method with octanol

Extractions using octanol instead of fatty acids were performed to validate the experimental procedure, as data for extraction with octanol is known from literature [14]. Besides that, with this experiment the numerical model of the extraction system could be verified for pH regulation by varying phosphate concentrations.

The obtained distribution coefficients for lab scale extractions with octanol are shown in Fig. 4. This data shows a significant pH-dependency of the distribution coefficient. The extraction runs best at low pH, when acetic acid is mostly present in its undissociated form. This is in accordance with literature [5].

The partition coefficient for this system was fitted to the measured acetic acid concentrations in the aqueous phase by the model, in which it was assumed that only physical partitioning takes place for extraction with octanol. A value of $K_{p,\text{HAc}} = 0.66 \pm 0.023$ (95% CI) was found as defined by Eq. (5) for a feed solution of 1% acetic acid. Literature values for the distribution coefficient were available only for higher feed concentrations, which makes comparison difficult. However, the determined value of the partition

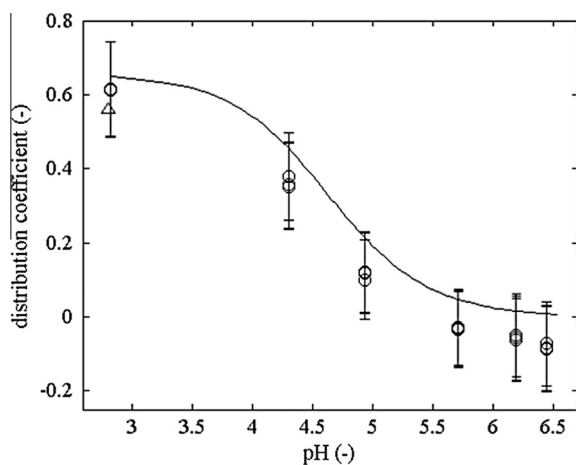


Fig. 4. Distribution coefficients on weight basis for extraction with octanol as function of the pH that is varied using different concentrations of Na_2HPO_4 . Symbols: Measured values (\circ) with error bars showing the possible error, Literature value [5] for unbuffered extraction with octanol (Δ). Line shows the model calculation using the fitted $K_{p,\text{HAc}} = 0.66$.

coefficient (for feed of 1%) follows the trend of the literature values of 0.56 (feed of 5%) and 0.50 (feed of 10%) [30], which validates the experimental procedure.

Error bars indicate the error, mainly caused by the error in the HPLC (1%) having a relatively large influence at low concentrations. This is also the cause of the negative values for the calculated distribution coefficients: acetic acid concentrations a little bit higher than initial were detected leading to negative values in the organic phase by solving the mass balances.

4.3. Extraction with fatty acids

4.3.1. Determination of the physical partitioning using hexyl methyl ether

To verify the homogeneous extraction mechanism comprising of physical partitioning of acetic acid over the phases, and a homogeneous organic phase complexation (Fig. 2), the physical partitioning was studied independently from the complexation, and to study the physical partition in absence of complexation through hydrogen bonding, extraction experiments were carried out with hexyl methyl ether as solvent. Hexyl methyl ether is a solvent comparable in chain length and polarity, in which no complexation is expected, so the partition coefficient could be determined by fitting the partition coefficient to the measured concentration acetic acid in the aqueous phase (Fig. 5) at varying pH. For the partitioning coefficient, as defined in Eq. (5), $K_{p,\text{HAc}} = 0.19 \pm 0.024$ was found. This value is lower than the values of 0.66 for octanol, and that for methylisobutylketone of 0.66–0.76 [14], and this might be expected, because the ether functionality is much less accessible than the ketone functionality and the alcohol functionality of octanol.

4.3.2. Preliminary distribution coefficient estimation

Based on the dimerization constants presented in Table 2, and assuming the partition coefficient using hexyl methyl ether is a good assumption for the physical partitioning into hexanoic acid, an estimation was made on the distribution coefficients that might be expected. From Table 2 it follows, that the more apolar the solvent is, the higher the dimerization constant of acetic acid. As the complexation mechanism of acetic acid with fatty acids is comparable to its dimerization, the trend in the complexation constant is expected to be similar and also the values for the complexation coefficient are expected to be in the same order of magnitude. For the complexation of acetic acid with hexanoic acid, the hexa-

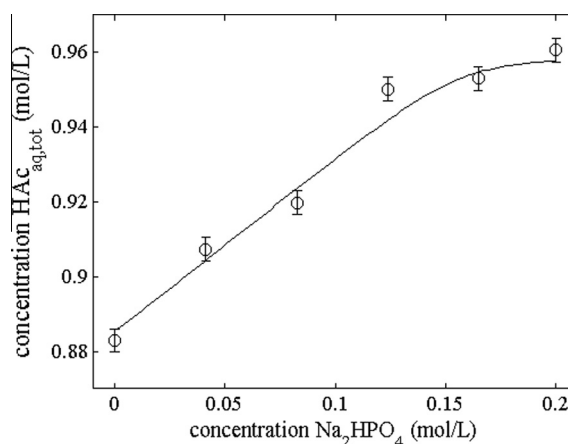


Fig. 5. Concentration acetic acid in the aqueous phase after extraction with hexyl methyl ether as a function of the concentration of Na_2HPO_4 . Symbols: Measured values (\circ) with error bars showing the error. The line shows the model calculation using the fitted parameter $K_{p,\text{HAc}} = 0.19$.

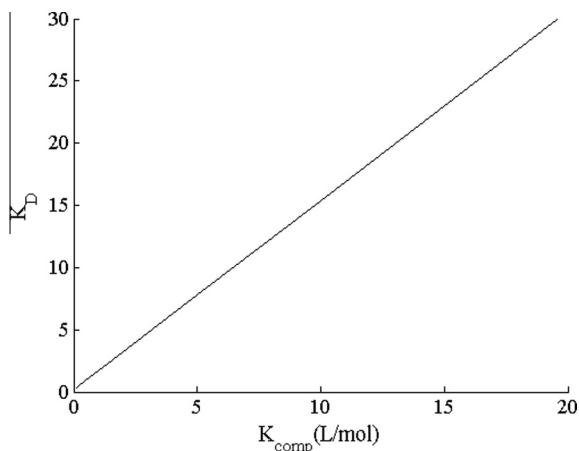


Fig. 6. Distribution coefficient estimation for acetic acid in pseudo-constant organic phase hexanoic acid concentration as function of the complexation constant between hexanoic acid and acetic acid.

noic acid itself acts as solvent. Considering that hexanoic acid has a polar carboxylic group, but the rest of the molecule being rather apolar, the solvent will have a medium polarity. Therefore, the distribution coefficient was calculated for complexation constants ranging from 0.1 to 20, assuming a pseudo-constant hexanoic acid concentration of 8 mol/L. The estimated distribution coefficient as function of the complexation constant between hexanoic acid and acetic acid is displayed in Fig. 6.

From Fig. 6 it may be concluded that, even when the complexation constant for acetic acid with hexanoic acid is 5–10 times as small as the lowest value for the dimerization constant in Table 2, still distribution coefficients close to those observed for tertiary amines may be expected. Hence, further research on the extraction of acetic acid using the fatty acids hexanoic acid and heptanoic acid was performed.

4.3.3. Extraction with hexanoic acid

The obtained distribution coefficients and pH values for extractions with hexanoic acid are displayed in Fig. 7. The distribution coefficients show the proof of principle for the extraction of acetic acid from dilute aqueous solutions using fatty acids. The distribution coefficients, however, are not higher than those of other carbon-bonded oxygen bearing extractants (Table 1). A possible explanation is that hexanoic acid also is able to dimerize itself,

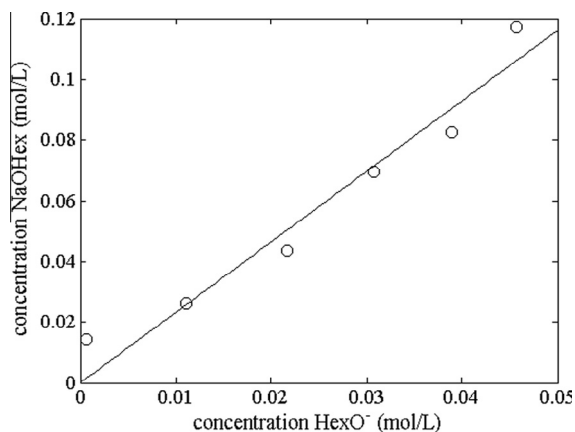


Fig. 8. Concentration sodium hexanoate in the organic phase as function of concentration hexanoate in the aqueous phase. Symbols: Measured values (\circ). Line shows fit with least square method – fitting parameter $K_{p,NaOHex} = 2.50$.

which competes with double hydrogen bond formation between hexanoic acid and acetic acid and therefore the effect of enhanced extraction by complexation will be smaller. Another issue might be the co-extraction of water. However, as displayed in Fig. 9, the selectivity at low pH is about 12, meaning hardly any water is present in the hexanoic acid phase.

When comparing the distribution using hexanoic acid with octanol (Fig. 4), it can be observed that although the maximum distribution at low Na_2HPO_4 concentration is comparable, in the case of hexanoic acid at increasing Na_2HPO_4 concentration up to 0.2 M, the distribution coefficient is not approaching zero, although in both cases the initial pH is 6 and initially the acetic acid is mostly dissociated. This difference can be explained by leaching of hexanoic acid to the aqueous phase and dissociating there, yielding extra acidity (Eq. (8)). This effect is further enhanced by partition of sodium hexanoate from the aqueous to the organic phase, which in effect is an exchange of H^+ for Na^+ in the organic phase, resulting in an increasing concentration of H^+ in the aqueous phase (Eq. (10)). This increased acidity leads to a shift in the dissociation equilibrium of acetic acid in the aqueous phase towards the undissociated form, which promotes extraction.

To verify this hypothesis, these equilibria have been investigated in more detail. To be able to describe the solubility of hexanoic acid in the aqueous solution, the solubilities in water of both

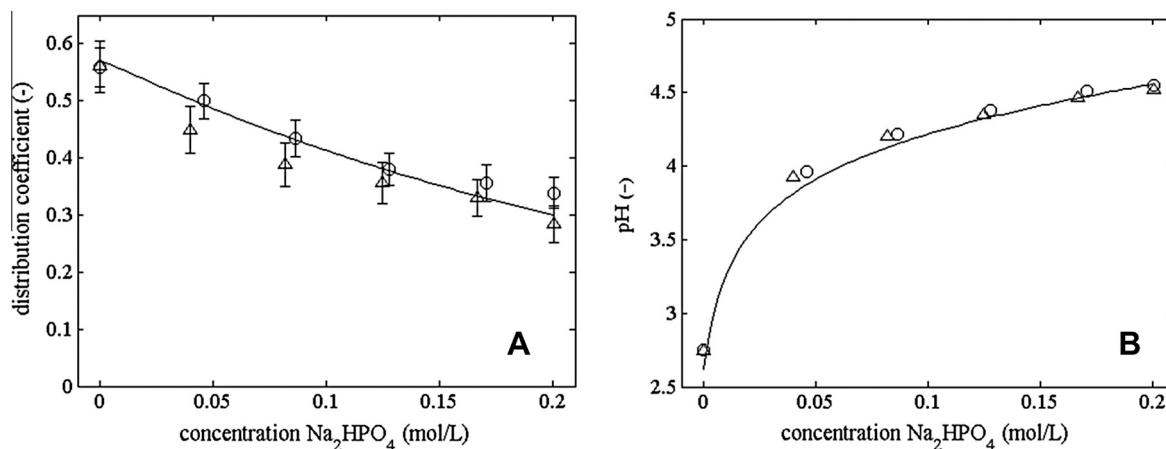


Fig. 7. Distribution coefficients on weight basis (A) and pH values after extraction (B) for extraction with hexanoic acid as function of the initial concentration Na_2HPO_4 in the 1% acetic acid solution. Symbols: Measured values for two different series (\circ and Δ). Lines show model calculations for these conditions.

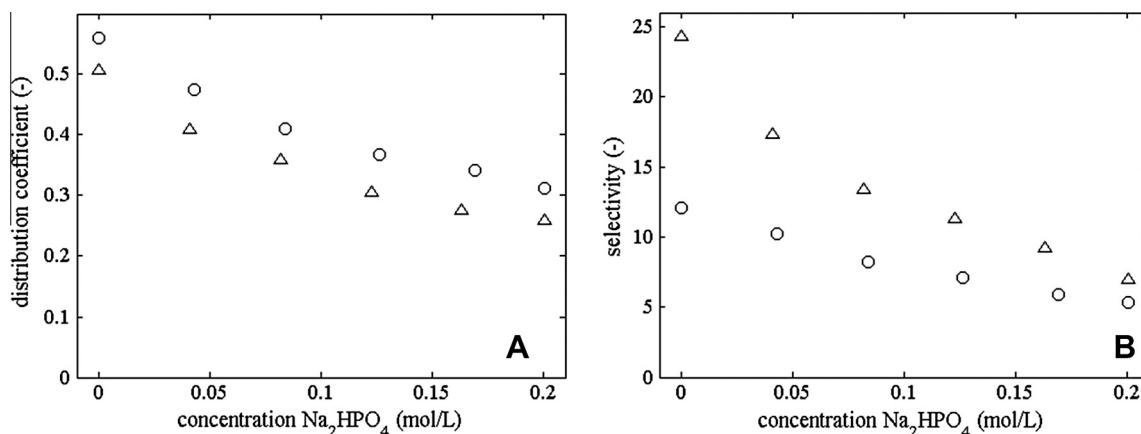


Fig. 9. Distribution coefficients on weight basis (A) and selectivities (B) for extraction with hexanoic and heptanoic acid as function of the initial concentration Na₂HPO₄ in the 1% acetic acid solution. Symbols: Average of measured values of two series with the same conditions for extraction with hexanoic acid (○). Measured values for heptanoic acid (△).

the undissociated form (in an acidic environment, pH ~ 2.7) and dissociated form of the hexanoic acid (in an alkaline environment, pH ~ 13) have been determined by HPLC. The solubility of undissociated hexanoic acid in water is 0.97 wt%, and the solubility of dissociated hexanoic acid is 2.33 wt%. The overall solubility of hexanoic acid in water was calculated according to Eqs. (8) and (9), taking into account the fraction of the hexanoic acid being dissociated. This means that the amount of reverse extracted hexanoic acid is larger than the amount of acetic acid extracted. However, if this aqueous stream can be recycled to the fermentation step, this will not result in losses of hexanoic acid. The effects of recycling hexanoic acid to the fermentation step requires careful investigation, such as the ability of the fermentation organisms to cope with the more acidic circumstances.

The total amount of acetic acid and hexanoic acid in the aqueous phase at equilibrium are not high enough to explain the low pH that was observed (Fig. 7B), and to explain the observed pH, the option of partitioning of sodium hexanoate from the aqueous to the organic phase was investigated by determining the concentration of sodium in both phases by ICP-OES. The partition coefficient was determined by fitting the concentration sodium hexanoate in the organic phase to the concentration hexanoate in the aqueous phase by the least square fit method (Fig. 8), assuming that the concentration sodium hexanoate is directly related to the concentration hexanoate in the aqueous phase. A partition coefficient of $K_{p,NaOHex} = 2.50 \pm 0.35$ (95% CI) was found, as defined by Eq. (10). It was thus found that indeed, the partitioning of sodium hexanoate takes place, and accounting for this in the calculations on the pH, it was possible to obtain a good accordance between the experimental observations and the model calculations (Fig. 7B).

For the partition coefficient of acetic acid to hexanoic acid in the extraction model that was developed, the value was assumed to be the same as that for the extraction with hexyl methyl ether. This partition coefficient was subsequently used in the model calculations for hexanoic acid to fit the complexation coefficient. A value of $K_{comp} = 0.34 \pm 0.039$ (95% CI) L/mol was found, as defined by Eq. (6). As already discussed upon the unexpected low distribution, this complexation constant is significantly lower than dimerization constants for acetic acid in several solvents (Table 2), most likely due to the dimerization of hexanoic acid itself, impeding complexation of acetic acid with hexanoic acid. In addition, although not much, the presence of some water in the organic phase might further reduce the complexation constant by interfering in the hydrogen bonding.

4.3.4. Extraction with heptanoic acid

Extraction experiments similar to those described in the previous section where also carried out using heptanoic acid as extraction solvent. The distribution coefficients and selectivities obtained for both fatty acids are compared in Fig. 9. Comparing the data from both experiments shows that extraction with heptanoic acid yields only a slightly lower distribution coefficient and a significantly higher selectivity (defined as ratio of distribution coefficients of acetic acid and water). This can be explained by the fact that heptanoic acid has a longer apolar tail than hexanoic acid. Therefore the amount of acid groups per gram fatty acid is lower for heptanoic acid, resulting in a lower distribution coefficient. On the other hand also the hydrophobicity of heptanoic acid is higher, resulting in a lower co-extraction of water to the organic phase and thus a higher selectivity. This trend is expected for the whole range of medium chain fatty acids as extraction solvent, i.e. a longer chain length will result in a lower distribution coefficient and a higher selectivity. Because the distribution coefficient is not reduced much, but the selectivity is approximately doubled, reducing the energy costs during (thermal) recovery significantly, heptanoic acid appears to be the better solvent of the two fatty acids. With selectivities of up to 24, significant concentration of acetic acid can be achieved through extraction with fatty acids.

5. Conclusions

Extraction of acetic acid from aqueous solution using fatty acids as extraction solvent was proven to be possible. The principle of this extraction is the partition of acetic acid from the aqueous solution to the fatty acid phase, which is enhanced by double hydrogen bond formation between the acetic acid and the fatty acid molecules. Distribution coefficients were not as high as expected, which might be caused by dimerization of the fatty acid itself, and by co-extracted water.

The extraction system using hexanoic acid was successfully described with a mathematical model programmed in Matlab, including all dissociation, dissolution, partition and complexation equilibria and molar and charge balances. The model was validated on basis of experimental data. Experiments with hexyl methyl ether were used to determine the partition coefficient, and extractions with hexanoic acid for determining the complexation coefficient, the determined constants are $K_{p,HAc} = 0.19 \pm 0.024$ (-) and $K_{comp} = 0.34 \pm 0.039$ L/mol.

Comparison of extraction with hexanoic acid and heptanoic acid showed that the longer hydrocarbon tail resulting in higher

hydrophobicity contributes to a higher selectivity while the distribution coefficient was only slightly lower. Because of the higher selectivity heptanoic acid is considered as the better solvent of the two fatty acids, and with selectivities up to 24 minor amounts of water are co-extracted and significant concentration of aqueous acetic acid may be achieved through extraction with fatty acids.

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References

- [1] H. Cheung, R.S. Tanke, G.P. Torrence, *Acetic Acid*, in: *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- [2] *Acetic acid: Market overview*, ICIS 2012. <<http://www.icis.com/chemicals/acetic-acid/?tab=tbc-tab2>> (January 2013).
- [3] T. Eggeman, D. Verser, Recovery of organic acids from fermentation broths, in: B. Davison, B. Evans, M. Finkelstein, J. McMillan (Eds.), *Twenty-Sixth Symposium on Biotechnology for Fuels and Chemicals*, Humana Press, 2005, pp. 605–618.
- [4] I. Jipa, T. Dobre, M. Stroescu, A. Stoica, Acetic acid extraction from fermentation broth: experimental and modelling studies, *Rev. Chim.* 60 (2009) 1084–1089.
- [5] A.S. Kertes, C.J. King, Extraction chemistry of fermentation product carboxylic acids, *Biotechnol. Bioeng.* 28 (1986) 269–282.
- [6] E. Alkaya, S. Kaptan, L. Ozkan, S. Uludag-Demirer, G.N. Demirer, Recovery of acids from anaerobic acidification broth by liquid-liquid extraction, *Chemosphere* 77 (2009) 1137–1142.
- [7] F.H. Mahfud, F.P. van Geel, R.H. Venderbosch, H.J. Heeres, Acetic acid recovery from fast pyrolysis oil. An exploratory study on liquid-liquid reactive extraction using aliphatic tertiary amines, *Sep. Sci. Technol.* 43 (2008) 3056–3074.
- [8] C.B. Rasrendra, B. Girisuta, H.H. van de Bovenkamp, J.G.M. Winkelman, E.J. Leijenhorst, R.H. Venderbosch, M. Windt, D. Meier, H.J. Heeres, Recovery of acetic acid from an aqueous pyrolysis oil phase by reactive extraction using tri-n-octylamine, *Chem. Eng. J.* 176–177 (2011) 244–252.
- [9] V. Ragaini, C.L. Bianchi, C. Pirola, G. Carvoli, Increasing the value of dilute acetic acid streams through esterification: Part I. Experimental analysis of the reaction zone, *Appl. Catal. B: Environ.* 64 (2006) 66–71.
- [10] H.G. Joglekar, I. Rahman, S. Babu, B.D. Kulkarni, A. Joshi, Comparative assessment of downstream processing options for lactic acid, *Sep. Purif. Technol.* 52 (2006) 1–17.
- [11] R. Evangelista, Z. Nikolov, Recovery and purification of lactic acid from fermentation broth by adsorption, *Appl. Biochem. Biotechnol.* 57–58 (1996) 471–480.
- [12] C.J. King, Acetic acid extraction, in: T.C. Lo, M.H.I. Baird, C. Hanson (Eds.), *Handbook of Solvent Extraction*, Wiley-Interscience, New York, 1983, pp. 567–573.
- [13] K.L. Wasewar, A.A. Yawalkar, J.A. Moulijn, V.G. Pangarkar, Fermentation of glucose to lactic acid coupled with reactive extraction: a review, *Ind. Eng. Chem. Res.* 43 (2004) 5969–5982.
- [14] T.C. Frank, L. Dahuron, B.S. Holden, W.D. Prince, A.F. Seibert, L.C. Wilson, Liquid-liquid extraction and other liquid-liquid operations and equipment, in: D.W. Green, R.H. Perry (Eds.), *Perry's Chemical Engineers' Handbook*, The McGraw-Hill companies Inc., 2008, pp. 15–29.
- [15] J. Kim, E. Iannotti, R. Bajpai, Extractive recovery of products from fermentation broths, *Biotechnol. Bioprocess Eng.* 4 (1999) 1–11.
- [16] J. Marták, Š. Schlosser, Extraction of lactic acid by phosphonium ionic liquids, *Sep. Purif. Technol.* 57 (2007) 483–494.
- [17] F.S. Oliveira, J.M.M. Araújo, R. Ferreira, L.P.N. Rebelo, I.M. Marrucho, Extraction of l-lactic, l-malic, and succinic acids using phosphonium-based ionic liquids, *Sep. Purif. Technol.* 85 (2012) 137–146.
- [18] M. Blahušiak, Š. Schlosser, J. Marták, Extraction of butyric acid by a solvent impregnated resin containing ionic liquid, *React. Funct. Polym.* 71 (2011) 736–744.
- [19] M. Blahušiak, Š. Schlosser, J. Cvengroš, Simulation of a new regeneration process of solvents with ionic liquid by short-path distillation, *Sep. Purif. Technol.* 97 (2012) 186–194.
- [20] A. Krzyżaniak, M. Leeman, F. Vossebeld, T.J. Visser, B. Schuur, A.B. de Haan, Novel extractants for the recovery of fermentation derived lactic acid, *Sep. Purif. Technol.* 111 (2013) 82–89.
- [21] H. Ziegenfuß, G. Maurer, Distribution of acetic acid between water and organic solutions of tri-n-octylamine, *Fluid Phase Equilib.* 102 (1994) 211–255.
- [22] Y. Fujii, H. Yamada, M. Mizuta, Self-association of acetic acid in some organic solvents, *J. Phys. Chem.* 92 (1988) 6768–6772.
- [23] W.G. Mook, Chemistry of carbonic acid in water, in: W.G. Mook (Ed.) *Environmental Isotopes in the Hydrological Cycle – Principles and Applications*, IAEA/UNESCO, 2000.
- [24] K.A. Hunter, *Acid–base Chemistry of Aquatic Systems – An Introduction to the Chemistry of Acid–Base Equilibria with Emphasis on the Carbon Dioxide system in Natural Waters*, University of Otago, Dugedun, 1998.
- [25] *CRC Handbook of Chemistry and Physics*, 94th ed. CRC Press, Internet Version 2014; 2014.
- [26] Hexanoic acid, TOXNET – Hazardous Substances Data Bank. <<http://toxnet.nlm.nih.gov/>> (July 2013).
- [27] B.M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria*, John Wiley & Sons, Inc., 2013.
- [28] D.C. Harris, *Quantitative Chemical Analysis*, fourth ed., W.H. Freeman & Co., 1995.
- [29] B. Schuur, J.G.M. Winkelman, H.J. Heeres, Equilibrium studies on enantioselective liquid–liquid amino acid extraction using a cinchona alkaloid extractant, *Ind. Eng. Chem. Res.* 47 (2008) 10027–10033.
- [30] F. Ratkovics, B. Palágyi-Fényes, É. Hajós-Szikszay, A. Dallos, (Liquid + liquid) equilibria of (ethanoic acid + an alcohol or a ketone or an ester or an aromatic hydrocarbon + water) at the temperature 293.15 K, *J. Chem. Thermodyn.* 23 (1991) 859–865.