



Separation of propionic acid by diethyl carbonate or diethyl malonate or diethyl fumarate and the synergistic effect of phosphorus compounds and amines

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ABSTRACT

The recovery of propionic acid from aqueous solutions such as fermentation broth and wastewater is an important problem where liquid extraction is the favorite process. Liquid–liquid equilibrium (LLE) data were investigated for mixtures of water + propionic acid + diethyl carbonate or diethyl malonate or diethyl fumarate at 298.15 K. The solubility curves and the tie-line end compositions of liquid phases at equilibrium were determined experimentally, and the tie-line results compared with the data correlated by means of UNIQUAC model. The phase diagrams for the ternary mixtures including both the experimental and correlated tie-lines are presented. The reliability of the experimental tie-lines was confirmed by using Othmer–Tobias correlation. The distribution coefficients and the separation factors for the immiscibility region are calculated. In order to boost the distribution of propionic acid between aqueous and organic phases, the distribution was investigated by using organic solutions composed of amine {tributylamine (TBA)} and phosphorus containing compounds {triethylphosphine oxide (TOPO) or tributyl phosphate (TBP)} dissolved in diethyl carbonate, diethyl malonate and diethyl fumarate, in the concentration range of about 0.06–1.00 mol/l. It was observed that the used solvents may serve individually as adequate agents to extract propionic acid from its dilute aqueous solution; however, the extraction performance can be improved by using phosphorus containing compounds or amines, mostly by using tributylamine dissolved in diethylmalonate.

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1. Introduction

Liquid extraction process of obtaining propionic acid from aqueous solutions is an important approach in the chemical industry where various organic solvents have been investigated and reported to improve such recovery [1–5]. Especially, the recovery of propionic acid from aqueous solutions such as fermentation broth and wastewater including lower than 10% (w/w) acid concentrations has received increasing interest.

The use of propionic acid as additives, particularly in the food, pharmaceutical or cosmetic industries, makes its origin important since consumers have preferences for natural products. Recently, there has been growing interest in producing propionic acid from whey lactose using *Propionibacterium* [6,7]. Fermented whey has been shown to be a natural ‘fungistatic’ agent when incorporated in bread or other bakery products. It can replace chemical preservatives and is of substantial commercial importance in the sale of ‘natural’ bakery products. The Na⁺, Ca⁺⁺ and K⁺ salts of propionic acid have also been listed as preservatives which are of the cate-

gory known as generally recognized as safe (GRAS) food additives [8].

With the goal of investigating new solvents as potential replacements for chlorocarbons or aromatic hydrocarbons for separations, we have focused on the dibasic esters, which have excellent properties for industrial applications. They are environmentally friendly and have low cost, low toxicity, great stability, and rather high-boiling temperatures, while their viscosity and densities are close to those of water. The dibasic esters are used as novel solvents in separation techniques [9–12]. On the other hand, because of their hydrophilic characters carboxylic acids are not easily extracted by apolar solvents. Therefore reactive extraction with aliphatic secondary and tertiary amines (having large polarity because of nitrogen–oxygen bond) or with some phosphorus compounds (having also large polarity because of phosphorus–oxygen bond) has been considered as suitable separation methods [13–17]. Such extractants are called generally as ‘complexing agents’ and are dissolved in a diluent that dilutes the extractant to the desired concentration and controls the viscosity and density of the organic phase.

The aim of this study is to investigate recovering propionic acid from dilute aqueous solution by using environmental friendly solvents, namely dibasic ester, with high-boiling point. For this purpose, liquid–liquid equilibrium (LLE) results were reported for the

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Table 1
Densities (ρ) and refractive indexes (n_D) at 293.15 K and boiling temperatures (T_b) at 101.325 kPa of the pure components [18].

Compound	ρ (kg/m ³)		n_D		T_b (K)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Water	999.90	998.23	1.3324	1.3330	373.20	373.25
Propionic acid	988.10 ^a	988.20 ^a	1.3808	1.3809	414.20	414.30
Diethyl carbonate	969.10 ^a	969.20 ^a	1.3845	1.3845	399.13	399.15
Diethyl malonate	1055.08	1055.10	1.4138	1.4139	473.15	473.15
Diethyl fumarate	1045.21	1045.20	1.4411	1.4412	487.10	487.15
Tributyl phosphate	972.67 ^a	972.70 ^a	1.4225 ^a	1.4224 ^a	562.05	562.15
Tributylamine	776.98	777.00	1.4297	1.4299	489.60	489.65

^a At 298.15 K.

three ternary systems: (water + propionic acid + diethyl carbonate), (water + propionic acid + diethyl malonate), and (water + propionic acid + diethyl fumarate) at $T = 298.15$ K, for which no such data have previously been presented. Furthermore, tributylamine (TBA), trioctylphosphine oxide (TOPO) and tributyl phosphate (TBP) were selected as reactive extractants to improve the extraction performance, by taking into consideration that phosphorus compounds are more environmental friendly than amines.

2. Experimental

The chemicals, propionic acid (Merck, >99%), diethyl carbonate (Merck, >99%), diethyl malonate (Aldrich, 99%), diethyl fumarate (Merck, $\geq 97\%$), tributyl phosphate (Fluka, $\geq 99\%$), trioctylphosphine oxide (Sigma–Aldrich, 99%), and tributylamine (Merck, $\geq 98\%$) were used without further purification. The purity of the chemicals was checked on the basis of their densities and refractive indexes at 293 ± 0.20 K. Deionised and redistilled water was used throughout all experiments. Refractive indexes and densities were measured with Anton Paar densimeter (Model DMA 4500) integrated with a refractive index unit (Model RXA 170) both in $\pm 10^{-5}$ precision. Boiling point measurements were performed by using a Fischer boiling point apparatus. The estimated uncertainties in the boiling point measurements were 0.1 K. The measured physical properties of the chemicals except TOPO are listed in Table 1, along with literature values [18].

The individual solubility curves for the systems (water + propionic acid + diethyl carbonate), (water + propionic acid + diethyl malonate) and (water + propionic acid + diethyl fumarate) were determined by the cloud-point method in a magnetically stirred equilibrium cell. The experiments were carried out at 298.15 K and the temperature was controlled using an electronic controller with an accuracy of 0.1 K. The cloud point was determined by observing the transition from a homogeneous to a heterogeneous mixture. All mixtures were prepared by weight accurate to ± 0.0001 g. The transition point between the homogeneous and heterogeneous zones was determined visually. The reliability of the method depends on the precision of the Metrohm micro-burette with an accuracy of ± 0.005 cm³, and is limited by the visual inspection of the transition across the apparatus. The accuracy of the visual inspection of the transition is achieved by waiting approximately 5 min in the transition point and observing the heterogeneity. All visual experiments were repeated at least three times in order to acquire high accuracy. The detailed experimental procedure and the schema of the equilibrium cell are given in the previous work [19]. Mutual solubility values of the water + diethyl carbonate or diethyl malonate or diethyl fumarate binaries were measured also by using cloud-point method.

End-point determinations of the tie-lines of the related systems were based upon the independent analysis of the conjugate phases that were regarded as being in equilibrium. For this purpose, mixtures of known masses of water, acid and solvent lying within the

heterogeneous gap were introduced into the equilibrium cell and were stirred vigorously for at least 4 h, and then left for 4 h to settle down into raffinate (aqueous) and extract (solvent) layers. The liquid samples withdrawn from both phases were analysed by a gas chromatograph (Hewlett Packard GC, Model 6890 Series), equipped with a thermal conductivity detector (TCD) and a flame ionisation detector (FID) for the quantitative determination of water, propionic acid, diethyl carbonate, diethyl malonate and diethyl fumarate. A 15 m HP-Plot Q column (320 μ m diameter with a 20 μ m film thickness) was used with a temperature-programmed analysis. Column temperature, from 343.15 K to 503.15 K at 20 K/min, at 503.15 K (3 min) injection mode, split ratio 100:1; detector, TCD; injector and detector temperature, 523.15 K; carrier gas, nitrogen 1 cm³/min; injected volume of 0.3 μ l of liquid sample.

In the second phase of the experiments, the extraction equilibria of propionic acid have been determined in liquid–liquid systems composed of water and diethyl carbonate or diethyl malonate or diethyl fumarate containing certain amount of TBP or TOPO or TBA. Aqueous propionic acid solution was prepared with an initial concentration of about 1 mol/l. Organic phases are prepared either by pure solvents or by mixing the solvents with TBP or TOPO or TBA to produce solutions in different concentrations, in the range of 0.06–1.00 mol/l. Experiments were performed by shaking equal volumes (10 ml) of initial aqueous and organic phases in glass flasks, placed in a thermostated shaker bath at 298.15 K for 5 h, which preliminary tests have shown to be a sufficient time for equilibrium. Thereafter the phases were separated after 5–8 h settling. Temperature was controlled using an electronic controller with a precision of 0.1 K. Propionic acid analysis was performed only in aqueous solutions. Acid concentrations in organic phase were found via material balance. The mutual solubilities of organic and aqueous phases were minimized by the preliminary saturation of diluent in water, and so the mutual solubilities are taken as negligible in the range of variables investigated.

3. Results and discussion

3.1. Phase equilibria

The experimental tie-line compositions of the equilibrium phases at 298.15 K, were given in Table 2, for which x_{i1} and x_{i3} refer to the mole fractions of the i th component in the aqueous and solvent phases, respectively. It was found that the used solvents are very little soluble in water. However, water shows a large solubility in diethyl malonate, which is a disadvantage in the extraction processes. The experimental tie-lines together with UNIQUAC correlated results, and the experimental binodal curves plotted for the mentioned ternary systems at 298.15 K are shown in Figs. 1–3. The plait point values of the systems are reported in Table 3.

The effectiveness of propionic acid extraction with the used solvents is given by its separation factor. To show the selectivity and extraction strength of the solvents to extract propionic acid, the

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