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On the influence of some strong electrolytes on the partitioning of acetic acid to aqueous/organic two-phase systems in the presence of tri-*n*-octylamine Part II: Toluene as organic solvent

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ABSTRACT

Water-insoluble amines (dissolved in an organic solvent/organic solvent mixture) are often used for the extractive recovery of carboxylic acids from aqueous phases. The basic design of the extraction process requires a thermodynamic framework that should be able to describe the liquid–liquid phase equilibrium not only in the phase forming systems (water + carboxylic acid + organic solvent + reactive extractant), but also when the aqueous feed phase contains additionally small amounts of strong electrolytes. Even small amounts of strong electrolytes might considerably reduce the recovery rate. In part I of this series such a model was presented and discussed for methyl isobutyl ketone as organic solvent and tri-*n*-octylamine (TnOA) as the chemical extractant. The present part II is to demonstrate that the procedures/methods described for methyl isobutyl ketone as organic solvent can be applied also for other organic solvents. By way of example, here toluene is that organic solvent. New experimental results are reported for the influence of sodium chloride, sodium nitrate, sodium sulfate, sodium acetate and hydrochloric acid on the partitioning of acetic acid to coexisting aqueous/organic liquid phases of the system (water + toluene + tri-*n*-octylamine) at 25 °C. An extension/adaptation of the previously published thermodynamic framework is successfully applied to describe/predict the new experimental liquid–liquid phase equilibrium data.

1. Introduction

Bioengineering processes are commonly used for the production of carboxylic acids. In such processes carboxylic acids have to be recovered from diluted aqueous solutions. The downstream process consists of several steps. Reactive extraction is a commonly applied technology for the first step. Water-insoluble organic amines (e.g., tri-*n*-octylamine, TnOA) dissolved in an organic solvent are often used as reactive extractants for carboxylic acids. The amines form complexes with carboxylic acids (and their hydrates) which are insoluble in water but soluble in certain organic solvents and solvent mixtures. The carboxylic acids are so extracted into the organic phase. In the next step, they are reextracted into an aqueous phase by changing the pH and/or the temperature. The computer-assisted design of such processes requires a reliable thermodynamic model for the Gibbs energy of the liquid phases. Such a model was developed in previous work based on experimental data for the partitioning of some single carboxylic acids [1–6]. Later, the model was extended to the competitive extraction of two carboxylic acids [2,7–9]. Industrial applications revealed that the recovery rate of a carboxylic acid is reduced by the presence of strong electrolytes such as, for example, an inorganic salt. This is particularly important at rather high dilution of the carboxylic acids. Therefore, recently we studied the partitioning of inorganic acids [10,11] and the influence of some single sodium salts and of hydrochloric acid on the distribution of citric acid to aqueous/organic two-phase systems with either methyl isobutyl ketone (MIBK) [12] or toluene [13] as organic solvent and on the partitioning of acetic acid in liquid two-phase systems of water and MIBK [14]. All these investigations dealt with tri-*n*-octylamine as a model substance for a reactive extractant. Organic solvents are always required for several reasons, for example, to avoid the precipitation of the acid/amine complexes. In the present contribution the previous investigations are extended to the influence of some single sodium salts (chloride, nitrate, sulfate and acetate, respectively) and of hydrochloric acid on the partitioning of acetic acid to aqueous/organic two-phase systems with toluene (instead of MIBK [14]) as organic solvent at 298 K. The experimental results for the liquid–liquid equilibrium are presented, discussed and compared

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to correlation results (for the partitioning of the single electrolytes sodium acetate and hydrochloric acid, respectively) and prediction results (for the influence of sodium acetate and hydrochloric acid on the partitioning of acetic acid).

2. Materials

Acetic acid (minimum 99.8% GC) was purchased from JT Baker BV, Deventer, The Netherlands. Sodium nitrate, sodium chloride, sodium sulfate (minimum 99.5%) and toluene (minimum 99.7% GC) were purchased from Riedel de Haën, Seelze, Germany. Hydrochloric acid (Fixanal 1.0 mol) was purchased from Merck AG, Darmstadt, Germany. These chemicals were used as delivered, i.e., without further purification. Tri-*n*-octylamine (minimum 99%) was from BASF AG, Ludwigshafen a. Rh., Germany. Before use TnOA was washed with deionized water to remove eventually present traces of water-soluble amines. Deionized water was used in all experiments.

3. Liquid–liquid phase equilibrium experiments

In the experiments equal volumes (about 25 cm^3) of an aqueous feed (containing acetic acid and the strong electrolyte) and a toluene solution (containing about 10 or 20 mass percent of the amine) were equilibrated at (298.15 ± 0.1) K. After equilibration and phase separation (by centrifugation) samples of both phases were analyzed. The experimental procedures were described in detail before (Schunk et al. [12]) and are not repeated here.

3.1. *Organic phase analysis*

The organic phase was analyzed for

- The stoichiometric concentration of the protons from the extracted acids: all acids dissolved in the organic phase were reextracted into an aqueous phase that contained a known amount of NaOH. Afterwards, the surplus (i.e., the non-reacted) NaOH was neutralized by aqueous HCl in a titration step. From the known amounts of NaOH and HCl (determined by titration) the total amount of protons bound in acids and dissolved in the organic phase was determined with an uncertainty of – in most cases – better than 4%. That relative uncertainty can increase to about 10% when the molality of the acid is below about 0.01 mol/kg solvent.
- The concentration of chloride and sulfate: the concentrations of these ions were determined by ion chromatography applying the "internal standard" procedure. For that analysis the anions were reextracted from the organic phase into an aqueous phase (see Ziegenfuß [1]). The experimental uncertainty is about 7% (chloride) and about 9% (sulfate), respectively.
- The organic phase concentration of nitrate: that concentration was not determined experimentally.
- The amount of dissolved/coextracted water: it was determined by Karl-Fischer titration with an estimated uncertainty of approximately 4%.

The "total" (here also called "stoichiometric") concentration of acetic acid in the organic phase was calculated from these results as described previously, cf. Appendix A [14].

3.2. *Aqueous phase analysis*

The aqueous phase was analyzed for

- The proton concentration by acid-base titration (see Ziegenfuß [1]). This method yields the "total" concentration of protons in

Table 1
Organic and aqueous feed solutions

Organic phase	Aqueous phase				
$\tilde{\xi}_{\mathrm{TnOA}}^{(\mathrm{org}),0}$(mass%)($\tilde{m}_{\mathrm{TnOA}}^{(\mathrm{org}),0}$(mol/kg))()	With NaCl $\tilde{m}_{\mathrm{NaCl}}^{(\mathrm{aq}),0}$(mol/kg)	With NaNO$_3$ $\tilde{m}_{\mathrm{NaNO_3}}^{(\mathrm{aq}),0}$(mol/kg)	With Na$_2$SO$_4$$\tilde{m}_{\mathrm{Na_2SO_4}}^{(\mathrm{aq}),0}$(mol/kg)	With HCl $\tilde{m}_{\mathrm{HCl}}^{(\mathrm{aq}),0}$(mol/kg)	With NaAc $\tilde{m}_{\mathrm{NaAc}}^{(\mathrm{aq}),0}$(mol/kg)
10	0.05			0.02	0.05
(0.32)	0.10			0.10	0.50
	1.00			1.50	1.00
20	0.05	0.05	0.10		
(0.71)	0.10	0.10	0.50		
	0.50	0.20	1.00		