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Partitioning equilibria in multicomponent surfactant systems for design of surfactant-based extraction processes

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A B S T R A C T

Aqueous biphasic systems based on nonionic surfactants have perspective applications in extraction processes, in particular, cloud point extraction of hazardous compounds or high valued products, especially biomolecules. Additives (e.g., ionic surfactants, salts) and variations in pH can significantly affect the surfactant-based separation processes, representing an additional degree of freedom for their optimization. However, there are few systematic studies of phase and partition behavior for these multicomponent surfactant systems.

In this study we examined the clouding, phase compositions and partitioning equilibria for aqueous mixed surfactant systems of a nonionic surfactant (Triton X-114), ionic surfactants (cetyltrimethylammonium bromide or sodium dodecyl sulfate) and NaCl, in order to improve the extraction efficiency. Vanillin was used as a model substance at three different pH values, specifically in (partly) dissociated or non-dissociated states. The partition coefficients obtained in the batch experiments were compared to the predictions by the thermodynamic model COSMO-RS. Based on this knowledge a continuous multistep extraction process was carried out.

To the best of our knowledge this is the first demonstration of using a mixed surfactant system for continuous countercurrent cloud point extraction.

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1. Introduction

Aqueous surfactant solutions (mainly non-ionic mixtures) split into two phases if the temperature is increased beyond the cloud point temperature (CP). One of the phases is a concentrated surfactant solution, the surfactant rich phase, and the other one is the surfactant lean phase (or aqueous phase), where surfactant concentration is close to its critical micelle concentration (cmc). This phenomenon has been used to perform the extraction (cloud point extraction, CPE) of hazardous compounds or high valued products from

aqueous solutions. CPE has significant advantages compared to many other separation processes due to the mild extraction conditions (low temperature and ionic strength), the low toxicity of surfactants as well as their biocompatibility. Based on the CPE, a number of extraction methods have been developed for the separation, preconcentration or purification of different substances such as metalorganic ions, hydrophobic biomolecules and organic compounds (e.g., [Quina and Hinze, 1999](#); [Mukherjee et al., 2011](#); [Yazdi, 2011](#); [Wang et al., 2003](#); [Wang, 2007](#)). Thereby, the efficiency is based on the capability of the micelles to solubilize different solutes mainly by

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hydrophobic interactions but also by hydrogen bonds formation and electrostatic interactions or by their combination (Mukherjee et al., 2011; Quina et al., 1995).

Up to now mainly batch extraction processes were employed, typically involving the following steps (Xie et al., 2010): first, the surfactant solution (at the concentration \gg cmc) is added to the aqueous solution containing the solute to be extracted. The solutes are solubilized into micelles. Next, the temperature is increased to obtain phase separation. Depending on the viscosity and the density difference between two phases, different time is needed to reach phase equilibrium, when there is no change in either the phase volumes or concentration of surfactant in the dilute phase. Thereby the solutes are preconcentrated in the surfactant rich phase (mainly smaller volume in comparison with aqueous phase). Finally, the concentrations of organic (or bioorganic) compounds in each phase are analyzed.

The use of mixtures of nonionic and ionic surfactants (also with salt additives) could enhance the extraction efficiency, since synergetic effects occur upon the addition of ionic surfactants to aqueous solutions of nonionic surfactants (e.g., Szymczyk et al., 2014 and Gharibi et al., 2000, for binary and ternary mixtures including alkyltrimethylammonium bromide, Triton X-100 or Triton X-114). Such effects are reflected in a reduction of the cmc, change of the viscosity, micellar size, specific features of phase boundaries, reduction of the surface tension, changing in solubilization capacity (Smirnova, 2005; De Oliveira and Gehlen, 2002). Furthermore, solubilization in mixed ionic–nonionic systems is enhanced significantly due to ion/ion surfactant–solute interactions (Mehling et al., 2013; Bhat et al., 2009).

It was shown before, that salts as well as ionic surfactants influence the aggregation numbers and the CPs of nonionic surfactants significantly (Panchal et al., 2006; McCarroll et al., 1998; Sadaghiana and Khan, 1991; Gu and Galera-Gómez, 1995; Komaromy-Hiller et al., 1996). For example, the addition of salt results in increased aggregation number of Triton X-114, while ionic surfactants (SDS or CTAB at concentrations of 0.12 mM) had no effect on the aggregation numbers of Triton X-114 (Komaromy-Hiller et al., 1996). With rising temperature micellar growth was observed, close to the cloud point temperature the aggregation numbers increased dramatically (Komaromy-Hiller et al., 1996). While the influence of salts can mainly be attributed to the salting in/salting out effect, strong electrostatic interactions need to be considered in case of the ionic surfactants.

In mixed solutions, containing salt as well as ionic surfactant, the contrary effects can compensate each other (e.g., Gu and Galera-Gómez, 1995; Panchal et al., 2006). Despite an increased CP at the presence of ionic surfactant, it was observed that the CPs of the mixed systems could be lower than those of the Triton X-114/water system at sufficient concentration of added electrolyte (Gu and Galera-Gómez, 1995; Marszall, 1990) due to salting-out effect of the electrolytes (Gu and Galera-Gómez, 1995). Thus, the change in CPs of nonionic surfactant can be controlled by adjusting the content of the additives (ionic surfactant and salt).

Different thermodynamic models may be applied to describe phase behavior of surfactant systems. Predictive models allow to adjust the composition of the multicomponent system (aqueous surfactant mixture + additives) for a given separation process. The thermodynamic a priori model COSMO-RS was successfully used for the prediction of solute partitioning between water and non-ionic, ionic and

zwitterionic micelles as well as the influence of additives (Mokrushina et al., 2007; Mehling et al., 2012, 2013). Such predictions are an adjuvant tool for the effective design of the CPE. To make the CPE attractive for engineering applications the efficient treatment of large volume streams is essential, that is why a scale up to continuous multistage extraction units is required (Trakultamupatam et al., 2005; Taechangam et al., 2008; Ingram et al., 2012, 2013).

To the best of our knowledge, only single surfactant solutions were used for CPE so far. In this work the possibility to increase the efficiency of the continuous cloud point extraction by using a multicomponent surfactant mixture is investigated. The choice of the multicomponent surfactant solution is based on the experimental study of phase and partition behavior and predictions with COSMO-RS.

For this purpose we examined the clouding (CPs), phase compositions (liquid–liquid equilibria) and partitioning equilibria (partition coefficients) for aqueous solutions of non-ionic surfactant (Triton X-114) in presence of ionic surfactants (cetyltrimethylammonium bromide or sodium dodecyl sulfate) and/or NaCl in order to increase the extraction efficiency of the model solute vanillin at both “natural” pH (without addition of any acid or base) and at pH = 11, where it dissociates. The partition coefficients obtained in the batch experiments were compared with predictions of COSMO-RS. Using these data the continuous countercurrent cloud point extraction of vanillin was performed in the extraction column.

2. Material and methods

2.1. Chemicals

The nonionic surfactant (1,1,3,3-tetramethylbutyl)phenylpolyethylene glycol, $n=8$, Triton X-114 BioChemica (99+%, AppliChem) and ionic surfactants (cetyltrimethylammonium bromide, CTAB (>99%, Serva Elektrophoresis GmbH), sodium dodecyl sulphate, SDS (98.5+%, Sigma–Aldrich)) were used without further purification. The water content in Triton X-114 (0.3 wt.%) was evaluated by Karl-Fisher titration method. Some surfactant characteristics are given in Table 1. Vanillin (3-methoxy-4-hydroxybenzaldehyde, pure >99% with $pK_a = 7.39$) was supplied from Carl Roth, Germany. Sodium chloride (>95%) was received from Carl Roth, Germany. Deionized water was used to prepare solutions. For adjusting the pH value NaOH ($\geq 99\%$) and HCl (37%) from Sigma–Aldrich were used. For analysis by HPLC acetonitrile $\geq 99\%$ (Carl Roth, Germany) was employed.

2.2. Experimental methods

2.2.1. Cloud point temperature determination

Cloud points (CP) were observed visually for aqueous solutions with Triton X-114 concentration of 4 wt.% both at natural pH (without addition of acid or base) and at pH = 11. The samples in glass tubes (10 mL) were immersed in a water bath (Lauda D20 KP) and equilibrated under periodic agitation. We noted the temperature at which changing in transparency occurs on heating (at a rate of 0.5 °C/min) and on cooling (at a rate of 0.1 °C/min). The experiments were performed in triplicate; the maximum relative error was ± 0.3 °C.¹

¹ We are aware that the CP value depends on method of detection (Gu and Galera-Gómez, 1995). Since we are mainly interested in changes in the CPs of surfactant solutions under study, this does not affect our discussion.

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