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Liquid-liquid demixing of Tergitol solutions by sodium salts

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ABSTRACT

The salting out effect of different inorganic (Na_2CO_3, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4, Na_2HPO_4) and organic ($C_2H_3Na_2O_2$, $C_4H_4Na_2O_6$, $C_6H_5Na_3O_7$) sodium-based salts has been demonstrated in aqueous solutions of the non-ionic surfactant Tergitol NP10. To do that, the solubility curves of the systems (Tergitol NP10 + salt + H_2O) were determined by the cloud point method at $T = 298.15$ K and 0.1 MPa. Additionally, a polynomial and three different exponential equations, including the most frequently used Merchuk model, were employed to describe the binodal curves. These data, together with the tie-lines, the tie-line length and the slopes of the tie-lines, allowed full characterization of the phase behaviour of the systems. Finally, Bancroft, Othmer-Tobias, and Setschenow empirical equations were employed to shed light on the thermodynamic consistency of the experimental tie-line data.

1. Introduction

During the last decades, a growing interest in the development of more biocompatible separation methods has paralleled the great development of biotechnological processes. Thus, the need of implementing downstream strategies providing a mild environment, avoiding structural damages in the produced biomolecules, has led to a new bloom of aqueous biphasic systems. They have been defined as two incompatible aqueous phases generated by the mutual immiscibility of two hydrophilic chemicals above a certain concentration [1]. The main type of interactions governing the aqueous segregation is the hydrogen bonding, so the greater capacity to promote these interplays is pursued when this separation platform is designed. In this line, high charge density salts have been proposed as suitable salting out agents in aqueous solutions of polymers [2], ionic liquids [3] or surfactants [4]. The use of aqueous solutions of the latter entails both operational and economic advantages, especially when biotechnological products are targeted. The reason is that surfactants are amphiphilic compounds bearing a hydrophilic head and a hydrophobic tail. This characteristic confers on them the ability to form micelles and makes them useful for design strategies for the separation of hydrophobic chemicals. Among the existing type of surfactants, non-ionic ones are commonly used due to their higher hydrocarbon solubilizing power, stability against pH and ionic strength changes and low toxicity [5,6]. The hydrophilic head of these surface-active compounds is usually made by glucose units or polymerized glycol ether, and the hydrophobic tail is constituted by linear or nonylphenol alcohols or fatty acids. In this sense, 80% of the world market is covered by nonylphenol ethoxylates, followed by octylphenol ethoxylates [7]. These facts lay the foundation for their interest in both environmental and biotechnological processes [8,9], as they have already been applied for furthering the bioavailability of hydrophobic contaminants or to extract hydrophobic antioxidant molecules in microalgal cultures, respectively.

The analysis of literature data and our previous experience [10–13] in this field suggest the use of water-soluble surfactants bearing high hydrophobicity to obtain greater immiscibility windows in the presence of an array of salting out agents. A useful tool to classify surfactants on the basis of their hydrophobicity is the Hydrophilic-Lipophilic Balance (HLB), which is a parameter relating the apolar and polar moieties of the molecule. It usually varies between 1 (low solubility in water) and 30 (high solubility in water) and offer insight into the percent of ethoxylation of a given surface active compound. In addition due to its interesting physicochemical features, Tergitol NP10 was labelled by the Food Safety and Inspection Service of the U.S. Department of Agriculture as a readily biodegradable compound. It can be considered as a promising candidate in a portfolio of applications (*e.g.* cleaning, food packaging, *etc.*) [14]. On the basis of the above-mentioned properties and the absence of literature data on its application for extraction processes, we were to investigate this non-ionic surfactant.

In this work, the phase disengagement potential of five inorganic (Na_2CO_3, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4, Na_2HPO_4) and three organic ($C_2H_3Na_2O_2$, $C_4H_4Na_2O_6$, $C_6H_5Na_3O_7$) salts in aqueous

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solutions of Tergitol NP10 was analysed after experimentally characterizing the solubility curves and the tie lines at $T = 298$ K and 0.1 MPa. Different empirical equations were proposed to fit the experimental data and the conclusions were supported by the analysis of relevant thermodynamic functions like the Gibbs energy of hydration.

2. Materials and methods

2.1. Materials

The non-ionic surfactant Tergitol NP10 and the inorganic (Na_2CO_3, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4, Na_2HPO_4) and organic ($C_2H_3NaO_2$, $C_4H_4Na_2O_6$, $C_6H_5Na_3O_7$) salts were used as received without further purification. The main characteristics of the chemicals are compiled in Table 1. Milli-Q water was used in all the experiments. The reagents were used as received without further purification.

2.2. Experimental procedure

The cloud point titration method [1] was used to ascertain the solubility curves at $T = 298.15$ K and 0.1 MPa. The temperature (F200 ASL digital thermometer, ±0.01 K) was controlled by means of a circulating water bath and magnetic stirring was employed to ease components mixing. In brief, the selected salt was added to a glass vessel containing a Tergitol NP10 water solution with known concentration. Once turbidity was detected, the amount of salt was weighed (Sartorius Cubis MSA balance, 125P-100-DA, $\pm 2\cdot 10^{-4}$ g), thus indicating the entering in the biphasic region. Then, ultra-pure water was added drop wise up to reaching a transparent solution, defining a point from the solubility curve. This operation was repeated until the immiscibility region was completely mapped.

The tie lines were experimentally determined by adding the salting out agent to a binary mixture Tergitol NP10-water in a glass ampoule. After a stirring step, the mixture was left to settle for 48 h to guarantee that the equilibrium was reached. Afterwards, the phases were split and weighed.

3. Results and discussion

3.1. Study of the segregation capacity of inorganic and organic salts

First of all, five sodium-based inorganic salts (Na_2CO_3, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4, Na_2HPO_4) were used to elucidate the influence of different anions, keeping constant the cation at $T = 298.15$ K and 0.1 MPa. Sodium was selected on the basis of our previous experience [15] and its favourable Gibbs energy of hydration ($-365\ \mathrm{kJ\cdot mol^{-1}}$). In this line, the low values of these thermodynamic parameters for each anion have made us to investigate their ability to promote phase splitting in the presence of aqueous solutions of Tergitol NP10. This information will be key to attain a proper design of new surfactant-based aqueous biphasic system.

The equilibrium data presented in terms of $\mathrm{mol\cdot g^{-1}}$ in Fig. 1 (also listed in Table 2) reveal a great concordance between the phase segregation capacity and the values of the Gibbs energy of hydration [16]. Hence, HPO_4^{2-} ($-1789\ \mathrm{kJ\cdot mol^{-1}}$) is the anion leading to solubility curves closer to the water vertex, while SO_4^{2-} ($-1080\ \mathrm{kJ\cdot mol^{-1}}$) is the one with the lowest capacity to trigger phase disengagement. In between, CO_3^{2-} ($-1315\ \mathrm{kJ\cdot mol^{-1}}$), SO_3^{2-} ($-1295\ \mathrm{kJ\cdot mol^{-1}}$), and $S_2O_3^{2-}$ (no data available) display similar phase segregation behaviour, despite the differences detected in the values of the considered thermodynamic function. From these cases, it seems clear that there is not a straightforward relationship between the binodal curves position and the Gibbs energy of hydration of the salt so, so despite the informative nature of this function, going to the bench is still mandatory.

Although the studied inorganic salts entail a great salting out potential, the appeal of organic salts in terms of their ecotoxicity

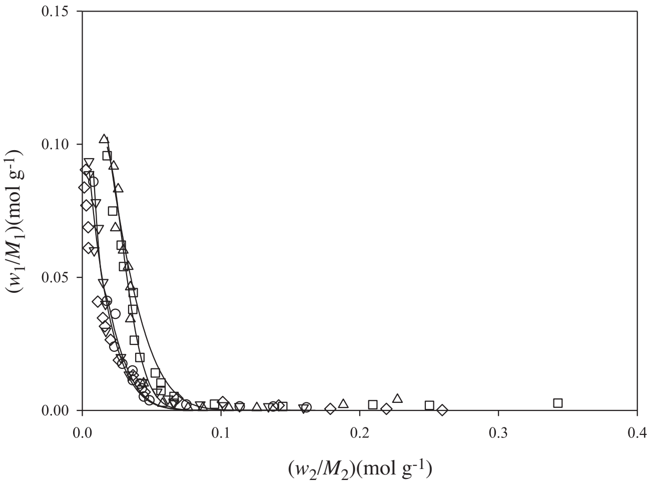
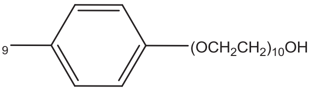


Fig. 1. Plot of solubility data for {Tergitol NP10 (1) + inorganic salt (2) + H_2O (3)} at $T = 298.15$ K and 0.1 MPa: (○), Na_2CO_3; (▽), Na_2SO_3; (△), $Na_2S_2O_3$; (□), Na_2SO_4; (◇), Na_2HPO_4. Solid lines represent the fittings to Eq. (3).

Table 1
Purities and suppliers of chemicals.

Chemical	Supplier	Mass fraction purity**	CAS-number
$C_2H_3NaO_2$ (Sodium acetate)	Panreac	0.98	127-09-3
$C_4H_4Na_2O_6$ (Sodium L-tartrate)		0.99	6106-24-7
$Na_2S_2O_3$ (Sodium thiosulfate)		0.99	10102-17-7
Na_2SO_3 (Sodium sulfite)	Scharlau	0.98	7757-83-7
Na_2SO_4 (Sodium sulfate)		0.99	7757-82-6
Na_2HPO_4 (Disodium hydrogen phosphate)		0.98	7558-79-4
$C_6H_5Na_3O_7$ (Sodium citrate)		0.99	6132-04-3
Na_2CO_3 (Sodium carbonate)	VWR	0.99	497-19-8
Tergitol NP10*** 	Sigma-Aldrich	*	127087-87-0

* 1% of water is determined by the supplier.

** Purity was indicated by the supplier.

*** Tergitol NP10 is a mixture of chemicals bearing this kind of chemical structure with 10 units of EO and an average molecular weight of 660.89 g/mol.