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Effects of salts and sucrose on the phase behavior of ternary mixtures of water, decane, and mono-ethylene glycol butyl ether

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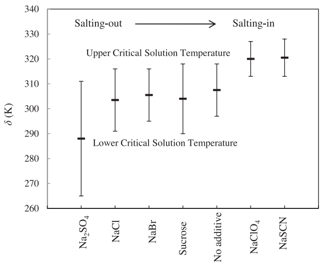
HIGHLIGHTS

- Effects of additives on the phase behavior of system water/decane/C_4E_1 were studied.
- Salt effect on four independent parameters has been determined and interpreted.
- Minimum surfactant concentration needed to form a Winsor III or IV was measured.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, liquid–liquid equilibriums are reported for different ternary systems of aqueous solutions with decane as oil and mono-ethylene glycol butyl ether (C_4E_1) as surfactant. The appearing Winsor phases and their evolution are shown by drawing temperature versus surfactant weight fraction for a given ratio of aqueous solution to oil. The obtained diagrams have the well-known fishlike shape. Four parameters are used to discuss the influence of the additives: the perpendicular and horizontal asymptotes to the realms-of-existence of the Winsor III phase. The two horizontal asymptotes, i.e., the LCST (lower critical solution temperature) and UCST (upper critical solution temperature) show no significant changes upon adding chloride salts, except for the triethylphenylammonium cation as counter-ion. By contrast, significant changes of the values of these two parameters are found when the nature of the anion of sodium salts changes. The two perpendicular parameters γ_0 (minimum concentration of surfactant needed to form a Winsor III) and $\tilde{\gamma}$ (minimum surfactant concentration needed to reach the Winsor IV phase from a Winsor III one) are only little affected by the nature of the additive. Two other parameters in relation with Winsor III area are also studied: δ reflects the vertical extent of the realms-of-existence of Winsor III versus temperature (δ = UCST – LCST), while $\xi = \tilde{\gamma} - \gamma_0$ reflects its horizontal extension. The value of δ is affected by the nature of the anion of sodium salts and strongly increases in presence of Na_2SO_4, but also with sucrose as additive. The effect of additives has in general a more pronounced influence on the values of the LCST and UCST than on ξ. The results are discussed in terms of Hofmeister effects, of salting-in and salting-out and of the resulting depletion and adsorption on the interfacial film of the Winsor III middle microemulsion.

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C_iE_j	$CH_3(CH_2)_{i-1}(CH_2CH_2O)_jOH$
LCST	lower critical solution temperature
UCST	upper critical solution temperature
DPnP	dipropylene glycol propyl ether
Greek letters	
α	oil content, $\alpha = \frac{W_{\text{oil}}}{(W_{\text{oil}}+W_{\text{water}})}$
γ	surfactant weight fraction, $\gamma = \frac{W_{\text{surfactant}}}{(W_{\text{surfactant}}+W_{\text{oil}}+W_{\text{water}})}$
δ	difference between LCST and UCST in the fish diagram (K)
ξ	difference between γ_0 and $\tilde{\gamma}$ in the fish diagram (weight fraction)

1. Introduction

One of the most important parameters influencing phase diagrams and thermodynamic properties of industrial surfactant systems is salinity. Franz Hofmeister, a pharmacologist, investigated the influence of salts on the solubility of egg-white protein in water [1]. He made a classification of salts according to their ability to enhance (salting-in) or decrease (salting-out) protein solubility. Salting-in anions are weakly hydrated and strongly polarizable with a low surface charge density. They are termed "soft" ions. On the contrary, salting-out anions are strongly hydrated and weakly polarizable and usually of high surface charge density ("hard" ions) [2,3]. The effect of cations is usually less pronounced and goes in the opposite way, i.e., soft cations salt proteins out and hard cations salt them in.

Microemulsions are multi-component monophasic mixtures [4] which are thermodynamically stable [5] and usually consist of water, hydrocarbon, and surfactant, sometimes with further components such as co-surfactant and co-solvent [6]. Microemulsions show optical clarity and high solubilization capacity, and are isotropic with ultralow interfacial tension [7–9]. Since microemulsions systems are used in several industrial applications, e.g. herbicides, pharmaceutical and production of drugs, detergents, food, petroleum and petrochemical industries, it is important to know their behavior and characteristics. Therefore, the study of microemulsion systems is still ongoing [6,10–12]. With the long-term increase of petrol price, they become also again interesting for petroleum industry.

A microemulsion can be in equilibrium with other phases or constitute the middle phase of a three-phase system. The corresponding equilibrium conditions are interesting whenever extraction processes are involved. The related phase diagrams are typically of the well-known fish type, when temperature is drawn as a function of surfactant concentration for a given water-to-oil ratio. In particular for the extraction of petroleum from the rock, these diagrams are of interest [12–14] as well as for extractions out of reactive microemulsions [15] or for some cleaning processes.

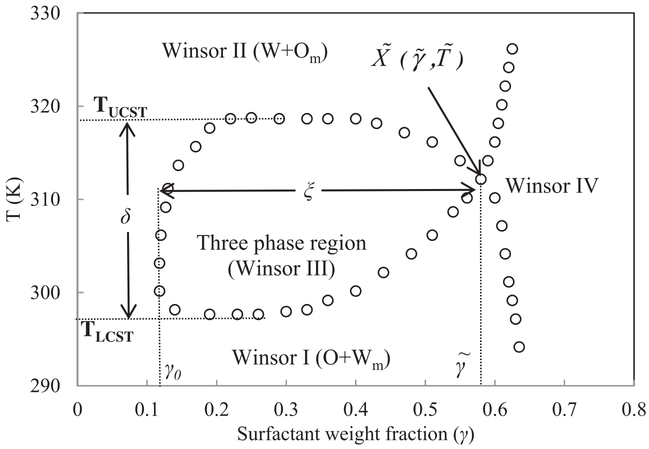

Fig. 1. Fishlike phase diagram at $\alpha = 0.5$ for the ternary (water/decane/C_4E_1) system. The different types of Winsor (I, II, III and IV) are represented. γ_0 is the minimum surfactant concentration necessary to form the Winsor III, $\tilde{\gamma}$ is the minimum surfactant concentration to reach the Winsor IV from the Winsor III. This means that $\tilde{\gamma}$ is the abscissa of the "fish tail" point, $\tilde{X}(\tilde{\gamma}, T)$.

Winsor type phases (Winsor I, II, III and IV) were originally introduced by Winsor [16,17] to study the liquid–liquid equilibrium of surfactant systems. Depending on temperature, surfactant concentration, oil nature and the presence of salt, Winsor I, Winsor III (which represents the three-phase region) or Winsor II phase equilibrium occurs. At high surfactant weight fractions, usually a single-phase region (Winsor IV) is formed [14,18,19]. An important characteristic is the occurrence of the middle phase in the Winsor III. The volume and the realms-of-existence of this middle phase and of cause the realms-of-existence of the entire Winsor III are very sensible to the composition, to the nature of the used compounds and to the temperature. Four important parameters can be used to characterize the surface of existence of the Winsor III on a diagram. They are the lower critical solution temperature (LCST) of existence of the Winsor III, the upper critical solution temperature (UCST) of the Winsor III, the concentration γ_0, which is the minimum concentration of surfactant needed to form the Winsor III and the concentration $\tilde{\gamma}$, which is the minimum concentration of surfactant needed to reach the Winsor IV from the Winsor III. These four parameters linked to the associated abscissa and ordinate can be used to draw four asymptotes to the surface of existence of the Winsor III domain in a fishlike diagram, temperature versus surfactant concentration (see Fig. 1). Apart from these four asymptotes, there are two other important parameters in relation with Winsor III area; the first one, δ, reflects the maximum extent of the realms-of-existence of Winsor III as a function of temperature, δ = UCST – LCST; the second parameter is the maximum extension in surfactant concentration, $\xi = \tilde{\gamma} - \gamma_0$, see Fig. 1.

The effects of salts on such liquid–liquid equilibria of water, nonionic surfactant and oil mixtures were extensively described [20–22]. We particularly appreciate the contribution of Kabalnov et al. [22], in which the authors link the measured phase extensions to the depletion and adsorption behavior of respectively salting-out and salting-in salts at the interfacial film of the Winsor III middle phase microemulsion. As discussed in [2], a salting-in salt would help hydrating the interfacial film and thus stabilize the microemulsion by adsorption. A salting-out salt would dehydrate the interfacial film by depletion, making it more hydrophobic and consequently break the microemulsion.

The present study is motivated by two points:

- i) some of us [2] had already studied the effect of Hofmeister salt and other additives on the realms-of-existence of a Winsor IV microemulsion (without other phases in equilibrium).
- ii) No systematic study of salt effects on the phase behavior as a function of surfactant concentration versus temperature has been published until now using nonionic short chain "surfactants" of the C_iE_j type. We are aware that short-chain C_iE_j are in fact hydrotropes or co-solvents rather than real surfactants. However, we keep the name in agreement with engineers' habits in this field.

In particular, in the present study, the fishlike diagram of ternary system water, decane and mono-ethylene glycol butyl ether (C_4E_1)