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PHASE BEHAVIOR OF PSEUDOTERNARY BRINE/ALKANE/ ALCOHOL-SECONDARY ALKANESULFONATES SYSTEMS
Surfactant ratio effects of salinity and alcohol

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Dodecanesulfonates (isomer mixtures) have been synthesized by the process developed in our laboratory.

First, pseudoternary phase diagrams of water or (brine) decane/dodecanesulfonates-butan-1-ol systems were drawn and compared with those of a commercial sample (Hostapur 60). In the presence of NaCl, a three-phase region (Winsor III) appears for the two systems, and is larger with the home-made surfactants. This region is interesting in enhanced oil recovery because it leads to very low interfacial tensions.

Then, the behavior of the Winsor III region was investigated as a function of the alcohol/surfactant mass ratio (C/T). At a constant salinity (2.5 mass% NaCl) a value of 2 for C/T gives the best compromise for a larger W III region with both systems. For this ratio, optimal salinity values of 1.55 and 1.65 mass% for our sample and Hostapur 60, were found, respectively.

Keywords: *alcohol/surfactant ratio, microemulsion, optimal salinity, phase diagram, secondary alkanesulfonate, surfactant, Winsor regions*

Introduction

Since the identification of microemulsions by Schulman and coworkers in the early 1940's [1], their applications have been extended to numerous technological areas from tertiary (or enhanced) oil recovery (EOR) to nanoparticle synthesis [2–5].

Microemulsions are transparent, isotropic, thermodynamically stable dispersions of oil and water, stabilized by amphiphiles, more often surfactants [6–8]. Microemulsions form spontaneously when a surfactant, or more commonly a mixture of surfactants and cosurfactants (usually alcohols), lowers the oil/water interfacial tension to ultra-low values (often less than 10^{-3} mN m^{-1}), so that the free enthalpy of mixing ($\Delta G_m=\gamma_i\Delta A-T\Delta_{conf}S$) becomes negative due to the overcompensation of the low interfacial energy $\gamma_i\Delta A$ by the negative configuration entropy term, $T\Delta_{conf}S$ [9].

Projects on tertiary oil recovery by means of microemulsions have been mainly concerned, firstly, with the ability of a microemulsion to solubilize oil and water simultaneously and, secondly, with the attainment of very low interfacial tensions [10]. Consequently, the phase behavior of these systems (water, oil, surfactant and cosurfactant) is very important and has been the subject of intensive studies [2, 6, 10–12].

Winsor [13] was the first to classify the complex phase behavior exhibited by multicomponent microemulsion systems consisting of water, inorganic salt, oil, surfactant and cosurfactant. Type I (W I) is an aqueous microemulsion in equilibrium with an upper oil phase, type II (W II) an oil-rich microemulsion in equilibrium with a lower aqueous phase and type III (W III) a middle-phase microemulsion in equilibrium with a lower aqueous phase and an upper oil phase. The single-phase microemulsion region is called Winsor IV (W IV). Another notation system, especially employed by Kahlweit *et al*. [14], uses the symbols $\underline{2}$, $\overline{2}$, 3 and 1, respectively. The WIII domain is of considerable interest from a fundamental point of view, and for practical applications like surfactant flooding for oil recovery [15].

The main surfactants used in enhanced oil recovery have been aromatic sulfonates and petroleum sulfonates. However, other compounds have been investigated and have shown promising results, e.g. α-olefinsulfonates [16, 17] as well as primary and secondary alkanesulfonates (SAS) [18, 19].

As we are interested by the use of surfactants in EOR, we have established some pseudoternary phase diagrams of water (or brine)/decane/sodium dodecanesulfonates-butan-1-ol systems with isomeric dodecanesulfonates synthesized by a new process developed in our laboratory [20–22]. These diagrams

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(nature of the phases and sizes of the regions) were compared with those obtained in the same conditions with a commercial SAS sample (Hostapur 60) [23].

In this paper, the phase behavior of our sodium dodecanesulfonates and Hostapur are presented with an emphasis on the three-phase region (W III) at different alcohol/surfactant ratios and salinities. The optimal salinities have been determined for the synthesized and the commercial surfactant mixtures.

Experimental

Materials

As described elsewhere in more detail [20], sodium dodecanesulfonates were prepared by photosulfochlorination with sulfuryl chloride. *n*-dodecane (Sigma, 99%) was converted into the corresponding *n*-alkanesulfonyl chlorides, then reacted with sodium hydroxide to give an isomeric mixture of sodium dodecanesulfonates [21, 22, 24]. The most common commercial SAS (Hostapur 60, a mixture of C_{14}–C_{16} compounds) was a kind gift of Clariant (France) and was used as received. All other chemicals were of commercial origin (Aldrich, Sigma, Fluka, 99% purity) and were used without further purification. Synthetic brines were aqueous solutions of sodium chloride. Distilled water was used.

Analysis

The dodecanesulfonates obtained were purified by recrystallization from ethanol (95%) and their functionality checked by IR spectrometry. The anionic active matter content was determined by two-phase titration with Hyamine 1622 [25].

The surface activity of our surfactant mixture was determined by surface tension measurements and the critical micelle concentration [b] value was found to compare well with those of commercial SAS, given the chain length difference between the two samples [21, 22].

Phase diagrams

The triangular pseudoternary phase diagrams were tetrahedron cuts characterized by a fixed cosurfactant/surfactant (C/T) mass ratio, so that the apices were decane (oil), water or brine (a pseudocomponent) and the surfactant-cosurfactant mixture. Phase diagrams were constructed (in mass%) by a conventional titration technique. After each addition of a component to a weighed mixture of known composition maintained in a thermostated bath at 30°C, the sample was homogenized under stirring and centrifuged. NaCl being insoluble in decane and butan-1-ol, a constant NaCl/H_2O ratio was assumed in all water-containing phases.

The observation of macroscopic properties (phase number, physical state) of the samples to the naked eye allowed to determine the boundaries between microemulsion (homogeneous), two- and three-phase regions and then to draw the phase diagram.

In order to follow the behavior of the different phases with salinity and cosurfactant/surfactant ratio and to determine the optimal salinity, the brine/oil mass ratio was kept equal to 1.

Results and discussion

Pseudoternary phase diagrams

The phase diagrams of the water/*n*-decane/SAS (home-made sodium dodecanesulfonates or Hostapur 60)

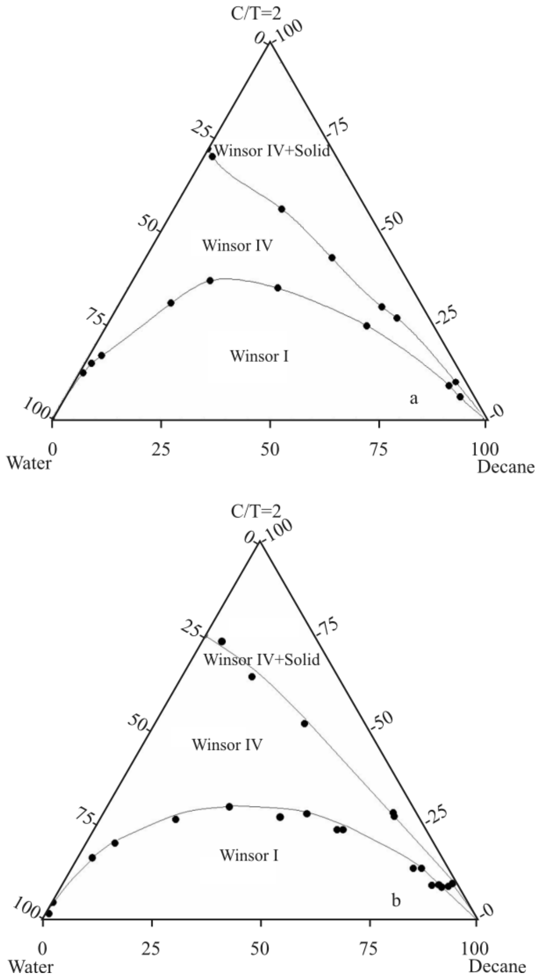

Fig. 1 Pseudoternary phase diagrams of water/decane/surfactant-cosurfactant systems at 30°C a – Water/decane/sodium dodecanesulfonates-butan-1-ol system and b – Water/decane/Hostapur 60-butan-1-ol system

– butan-1-ol systems have been drawn [22]. It can be seen from Fig. 1 that the diagram of our system (a) presents the same phase regions as those of the system [26]. A large microemulsion region is obtained for our SAS sample system (a), though a bit narrower than that obtained with the commercial sample system (b). As the single-phase region (W IV) observed is not split up, these diagrams (without salt) belong to the U type defined by Clausse *et al*. [27]. It is likely that, as with other systems, a transition occurs from an oil-in-water microemulsion near the water apex to a water-in-oil microemulsion near the decane apex through a bicontinuous structure where the amounts of oil and water are of the same order of magnitude [28]. A two-phase region (W I) is located at the bottom of the diagrams [23].

Salinity is one of the critical parameters in the EOR application of microemulsions. So, we have determined the phase diagrams for the previous systems with the same cosurfactant to surfactant ratio (C/T=2) at a constant salinity of 2.5 mass%.

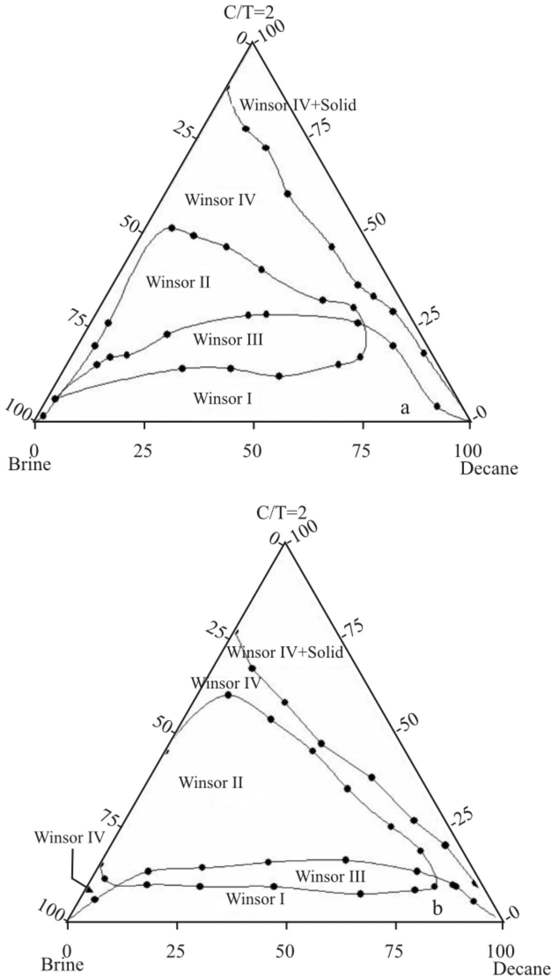

Fig. 2 Pseudoternary phase diagrams of brine/decane/surfactant-cosurfactant/systems at 30°C
a – Brine/decane/sodium dodecanesulfonates butan-1-ol system; b – Brine/decane/Hostapur 60-butan-1-ol system

As shown in Fig. 2, the addition of salt (sodium chloride) to the pseudoternary mixtures of surfactant-cosurfactant, decane and water strongly changes the phase diagrams.

Salt greatly reduces the extent of the microemulsion (W IV) areas, particularly for the Hostapur 60 system (Fig. 2b). In the corresponding diagram, the single-phase region is split into two parts: a smaller one in the brine-rich region and the other extending from the pseudobinary brine-active mixture (C/T) axis to the decane-rich region, whereas, for our sulfonates the W IV region is less reduced and remains continuous (Fig. 2a). For the two systems, a two-phase realm (W II) appears in the brine-rich region. This two-phase region is very large for the Hostapur 60 system and starts from the pseudobinary brine-active mixture axis. In the case of our sulfonate system, the W II region is less important and is entirely located inside the diagram, as observed by Bellocq *et al*. for the brine/toluene/SDS-butan-1-ol system [29].

As expected, the merging of the two-phase regions, W I and W II, for the two systems (a and b), generates a three-phase domain. Indeed, for anionic surfactants, this three-phase equilibrium is only obtained in the presence of salt [30]. However, the W III region is larger and more shifted towards the brine corner for our sulfonate system. On the other hand, it requires a little more surfactant than with Hostapur 60.

Owing to the importance of the W III domain in EOR, the effects of cosurfactant:surfactant ratio and salinity on the behavior of this particular region have been studied.

Effect of the butan-1-ol: surfactant ratio

The properties of microemulsions depend upon numerous parameters, such as temperature, water salinity, nature of other components particularly that of the alcohol used as a cosurfactant [13]. Many authors have studied the influence of the amount of salt or cosurfactant on the modification of the macroscopic state of the system (Winsor types I, II, III, IV) [31, 32].

The results obtained for an alcohol/surfactant ratio ranging between 1 and 4 at a constant salinity of 2.5 mass% NaCl are reported in Fig. 3. The W III region is more important when the C/T ratio is lower than 2 for Hostapur 60 and ranges between 2 and 4 for our sulfonates. So we kept this ratio equal to 2 for both sytems in order to study the behavior of this region as a function of salinity.

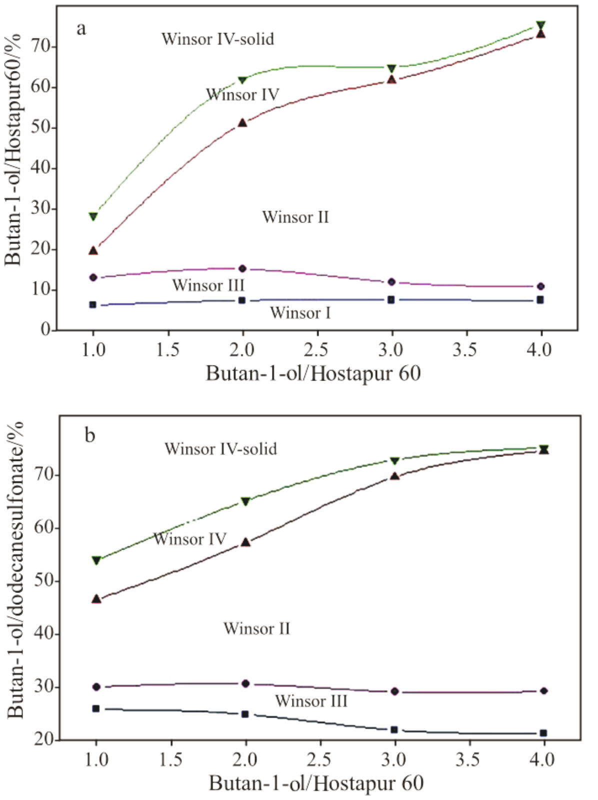

Fig. 3 Effect of the butan-1-ol/surfactant ratio on phase behavior (t=30°C, brine: 2.5 mass% NaCl, brine/oil=1) a – Sodium dodecanesulfonates and b – Hostapur 60

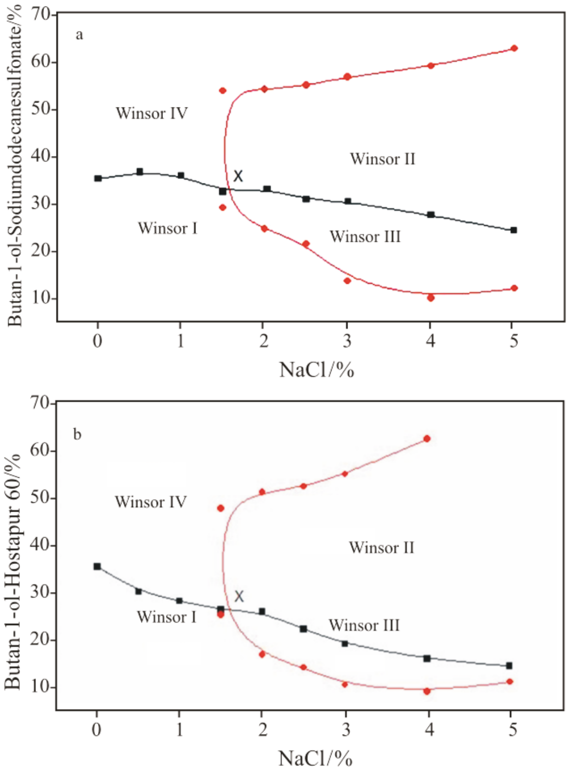

Fig. 4 Effect of salinity (t=30°C, butan-1-ol/surfactant=2, brine/oil=1) a – Sodium dodecanesulfonate and b – Hostapur 60

Optimal salinity

Several definitions of optimal salinity (NaCl*) have been considered, related to the minima of interfacial tensions in the three-phase regime (W III) or the equal solubilization of oil and water in the middle-phase microemulsion [15].

By optimal salinity we mean the salinity of the initial brine at which equal masses of oil and water are solubilized in a middle-phase microemulsion. The corresponding point X is common to the four Winsor regions (Fig. 4).

From Fig. 4a and b the optimal salinities are equal to 1.55 and 1.65 mass% for our sulfonate and Hostapur 60, respectively.

In all cases, for our sulfonate, the W III region is wider than that of the commercial sample.

Conclusions

We have established the pseudoternary phase diagrams of multicomponent systems containing sodium dodecanesulfonates synthesized by a new process. Because of their particular mode of preparation, the properties of these sulfonates are slightly different from those of commercial SAS. So, we have compared the behavior of our products with that of Hostapur 60 obtained by sulfoxidation. The phase diagrams of the two products present the same areas, however the microemulsion (W IV) and three-phase (W III) domains are larger for our sulfonates.

Phase behavior was studied as a function of butan-1-ol:surfactant ratio (C/T): the best results were obtained for a ratio of about 2 for Hostapur 60 and between 2 and 4 for our sulfonates, where the three-phase (W III) region is slightly wider in this whole range. For a C/T ratio of 2, the optimal salinity values are 1.55 and 1.65 mass% for our sample and Hostapur 60, respectively. In all cases, the area of the Winsor III region is more extended for our sulfonates. For EOR applications, interfacial tensions have to be measured and compared with ultra-low values obtained with other systems. Possible variations of the behavior of the samples prepared in the laboratory according to operation parameters must also be checked.

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