Determination of micellar system behavior in the presence of salt and water-soluble polymers using the phase diagram technique

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Abstract

The application of micellar systems has been growing during the last years because of their importance in various practical situations. Continued development of their application is necessary. If the principal economic interest of microemulsions is for some time enhanced oil recovery, the following also have significant applications such as pharmaceutical preparations, painting, and products for engine lubrication. The effect of variation in composition of anionic surfactants (α oleifin sulfonates) and the presence of a water-soluble charged polymer (Xanthan gum) and an uncharged polymer [poly (ethylene glycol)] on the phase behaviour of pseudo- ternary systems of water–oil surfactants was investigated. Several domains were observed when the composition of surfactants and cosurfactants (e.g., pentanol) in a mixture is varied. The appearance of these domains in the phase diagram has been attributed to the formation of different Winsor systems.

Keywords: Phase diagram; Anionic surfactant; Polymer; Phase behaviour; Microemulsion

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1. Introduction

The study of micellar solution behaviour has several uses in many fields such as chemistry, biochemistry, pharmaceuticals, and medicine as well as in industry. The field of existence of these micellar systems is related to the nature of additives and to their concentrations in the formula. Winsor [1] showed that these systems can present, on balance, four different states, bearing this name (WI, WII, WIII, and WIV). Recently, an interest in the incorporation of polymers in the formulation of microemulsions was developed in order to improve the rheological properties. The influence of solute and composition of the mixtures on the phase boundaries [2,3] and on the organization of surfactants in solution and at the solid–liquid interface [4–6] has been well studied. In this work, we have varied the composition of the surfactant and investigated the effect of salt, the nature and the concentration of Xanthan gum and the poly- (ethylene glycol) on pseudo-ternary system behaviours by using the technique of the layout of phase diagrams. To this end, we have fixed the essential objectives, the observation, the analysis and the interpretations of the various fields of existence of microemulsions and their modifications by adding salt and water-soluble polymers.

2. Experiment

2.1. Materials

The surfactants [α olefinesulfonates of sodium (AOS) with a general formula of R–$(CH_2)n$–$CH = CH_2$] are industrial products manufactured by Witco Chemical that have been the subject of several works in enhanced oil recovery [7–9]. Three types were considered: AOS in C12, C14 and C16 with a purity of 37%. A high-purity grade was purchased from Fluka and used as received. Poly(ethylene glycol) (PEG 1500) was supplied from Sigma with a molecular weight average of 1500. Xanthan gum was purchased from Rhodia (France); n-dodecane and n-pentanol (analytical grade) were purchased from Fluka. The salt, sodium chloride (99%), was purchased from Prolabo.

2.2. Preparation of mixtures

Investigations of systems containing three components were made by using a geometrical representation (technical squaring). With the introduction of a fourth component to the system (cosurfactant, CS), the study of phase diagrams should be done by using a geometrical representation in space. In general, it is more convenient to be brought back to plane representations such as the triangular ternary diagrams known as pseudo. One of the tops of the triangle then represents the active mixture (MA = S+CS). The second top represents the aqueous phase (W). The last top consists of oil (O). It was shown [7,9] that a report/ratio CS/S = 2.5 gives better results. This report/ratio was maintained constant in this study.

3. Results

3.1. C_{12}–dodecane–water system

Fig. 1 shows the phase diagram of a ternary system containing C_{12}–dodecane–water. It presents a biphasic area (WII) located at the bottom of the diagram. The studied system contains two phases: overcome aqueous phases of microemulsion. This figure also presents a monophasic field (WIV). This field indicates that there is total miscibility of the three compounds present in our system.

3.2. C_{14}–dodecane–water system

Fig. 2 gives the same interpretations as in the case of Fig.1, but with two differences. The monophasic area (WIV) presents a small reduc-

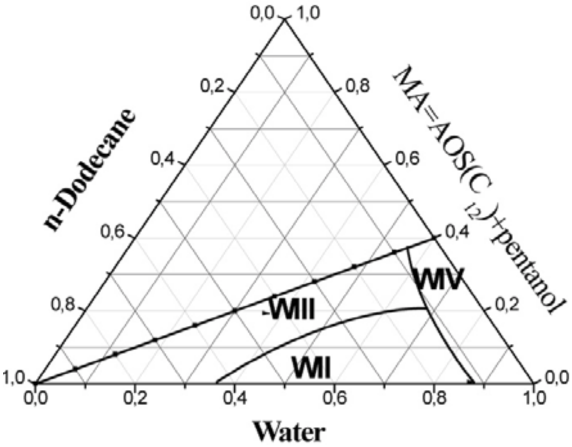

Fig. 1. Phase diagram of water/n-dodecane/MA system.

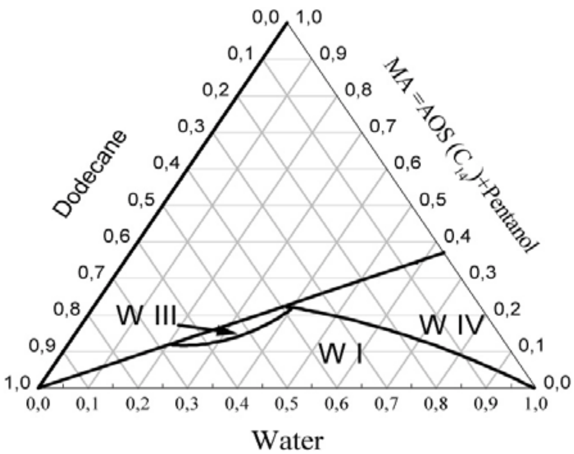

Fig. 2. Phase diagram of AOS (C_{14})–water–MA system.

tion; on the other hand, the diphasic area (WII) does not present a significant modification.

3.3. C_{16}–dodecane–water system

The study of the areas presented in Fig. 3 show that the monophasic field is wider than that obtained in the case of the first two surfactants (C_{12} and C_{14}). This figure also reveals the existence of a small gelatinous field broader (WIV). The field gives a solubilization of the system compounds.

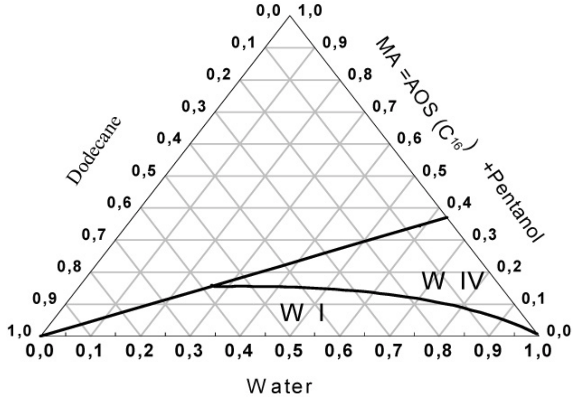

Fig. 3. Phase diagram of AOS(C_{16})–water–MA system.

4. Discussion

By examining the three studied systems, we can conclude that the diagrams take the same forms and the same presentations with small modifications. However, the AOS in C_{12} presents the desired broader monophasic field (WIV). This field gives a solubilization of the compounds of the system.

4.1. Influence of salinity

The influence of salinity on the modification of different field in the phase diagrams was made in the presence of AOS in C_{12} for a ratio of CTA/TA = 2.5. Fig. 4 shows the diagram with content of NaCl to 0.5%. In this case, monophasic, biphasic, and triphasic zones appear and are divided along the phase diagram. The reduction in the field representing the biphasic system (WI) was noticed. Fig. 5 shows the diagram with a content of 2% NaCl. The triphasic zone localized in Fig. 4 disappears and a broad monophasic field was observed which supposes that the triphasic system passed to only one phase (solubilization of the compounds present).

The addition of a salt to the ternary pseudo system modifies the behaviour of this last in the direction of the formation and of the widening of

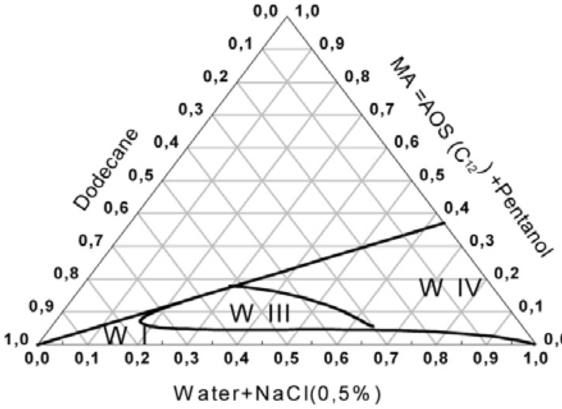

Fig. 4. Effect of NaCl (0.5%) on phase behavior.

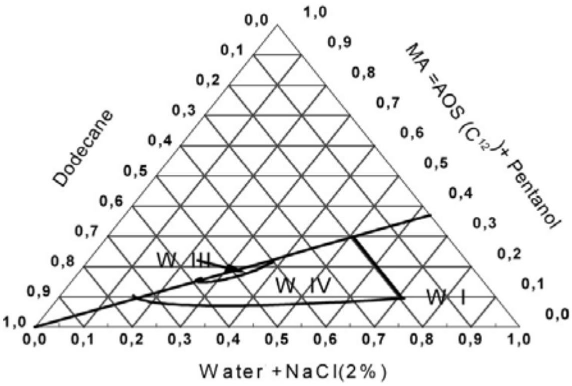

Fig. 5. Effect of NaCl (2%) on phase behavior.

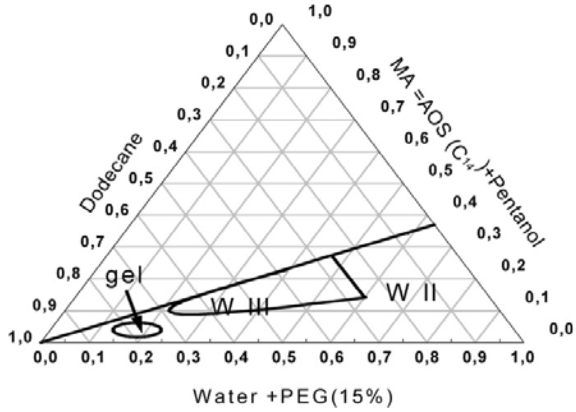

Fig. 6. Effect of poly(ethylene)glycol on phase behaviour.

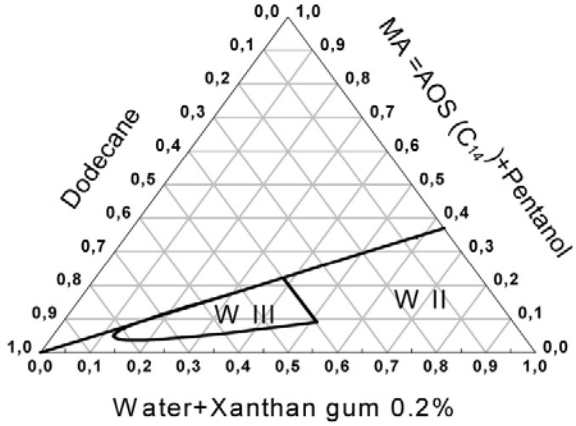

Fig. 7. Effect of Xanthan gum on phase behavior.

the monophasic field (WIV), i.e., the addition of salt allows a solubilization of the components. In addition, the formation of a gelatinous zone is considered.

4.2. Influence of polymers

In the literature, two illustrations of the interaction between polymers and surfactants are allowed. The first describes the interaction in terms of association of surfactant with polymer in aqueous solution (that is favoured for polymers of the hydrophobic groups). The second describes the introduction in terms of micellization of the molecules of surfactants on the chain of polymer.

The addition of a quantity of the PEG polymer to water modifies the behaviour of phases of the microemulsion as shown in Fig. 6, which indicates a triphasic zone (WIII) in the vicinity of the field at high values of concentrations of oil and for very weak concentrations of active mixture (MA).

It seems that the areas determined previously are influenced by the addition of polymers and that the direction of this modification is not easy to determine. Also, we note the appearance of a disphasic area (WII) which comes to replace the previously given monophasic zone. In the case of the addition of Xanthan gum, we can observe in

Fig. 7 a triphasic zone that appears and a very broad diphasic field (WII). The results obtained with Xanthan gum reveal triphasic and monophasic zones similar to the preceding diagrams; however, the direction of the modification of phase diagrams is not specified.

5. Conclusions

Investigations of the effect of the hydrocarbon length chain of surfactant showed that the AOS in C_{12} gives the best results. The layout of the pseudo-ternany diagrams with constant ratio and variable salinities shows that these last influence the behaviour of the phases. The introduction of NaCl into the system gives a broad field of existence of microemulsions (WIII and WIV). Thus, the succession of the systems of WINSOR I → IV → II or WI → III → II is made possible under the effect of a variation of salinity. These variations are visible by plotting the phase diagrams. The introduction of polymers into the system shows a modification of the obtained diagrams.

The layout of the diagrams of the ternary and pseudo-ternary systems gives a good approach of balances between phases and a later forecast of such balances.

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