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2002 J. Phys.: Condens. Matter 14 4805

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# A survey of the phases and the metastable phases in the ternary systems of divalent metal [bis-2-ethylhexyl]-sulphosuccinate/iso-octane/water

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Received 19 October 2001

Published 2 May 2002

Online at [stacks.iop.org/JPhysCM/14/4805](http://stacks.iop.org/JPhysCM/14/4805)

## Abstract

This paper surveys the phases for three systems: Co(AOT)<sub>2</sub>/iso-octane/water, Ni(AOT)<sub>2</sub>/iso-octane/water, and Cu(AOT)<sub>2</sub>/iso-octane/water, over a wide region of the phase diagram prism ( $T = 5\text{--}80\text{ }^\circ\text{C}$ ;  $\alpha = 0.50, 0.75, \text{ and } 0.90$ ;  $\gamma = 0.02\text{--}0.22$ ). At low surfactant concentration, these systems present Winsor progressions ( $2\Phi\text{--}3\Phi\text{--}2\Phi$ ) without the addition of salt. We found a variety of phases at higher surfactant concentration: the one-phase microemulsion  $1\Phi$ , which is probably bicontinuous, and several examples of two coexisting phases: coloured transparent phases coexisting with a transparent or with an opaque birefringent phase, and transparent birefringent phases coexisting with excess oil. Three coexisting phases were also found, where an iso-octane-rich phase is coexisting with a coloured isotropic transparent phase, and an opaque birefringent phase.

## 1. Introduction

Ternary mixtures of water (W), hydrocarbon (O), and surfactant (S) present a rich variety of phases and spatial microstructures [1]. Although, they appear homogeneous, the direct contact between oil and water molecules is strongly disfavoured; they must have separated domains. Therefore, the system will structure itself in such a way that surfactant molecules are always located at the interfaces of those domains: non-polar tails are immersed in the oil and polar heads in water. This surfactant monolayer will be the main construction block of the isotropic or of the anisotropic phases. Water and oil merely fill the space on both sides of the monolayer. To fulfil energetic, entropic, and aggregate interaction requirements, the monolayer must acquire various topologies: spherical, cylindrical, planar, inverse spherical, inverse cylindrical, spongelike, bilayer, etc [2]. These structures can be ordered, in which

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case we have a liquid crystal [3], or they are disordered forming an isotropic liquid phase (microemulsions) [2]. The theoretical approach used to understand the phase behaviour in these ternary systems is quite difficult [4]. However, geometric models employing geometrical parameters [5] and the use of the Helfrich free energy [6], to take into account the local curvature of the surfactant/oil/water interface, have been of great help.

In the case of ionic surfactants, AOT (sodium [*bis*-2-ethylhexyl]-sulphosuccinate), which has been studied extensively, has played a key role in understanding the W/O/S phase behaviour. At low surfactant concentration and low temperature, the ionic surfactant forms a W/O microemulsion ( $\bar{2}\Phi$ ). As temperature increases, the surfactant forms the O/W microemulsion ( $\underline{2}\Phi$ ). This ternary system usually does not exhibit a three-phase region, where microemulsion coexists with water- and oil-rich phases, at intermediate temperatures. However, the addition of salt as a fourth component induces the formation of a three-phase body ( $3\Phi$ ), at intermediate temperatures [7]. The key to understanding this behaviour emerges from the realization that the temperature is the most fundamental of the field variables controlling the phase behaviour of the microemulsions [8]. This feature is manifested around the so-called hydrophile–lipophile balance temperature, at  $\bar{X}$  in the ‘fish diagram’, where the affinities of the surfactant toward water and oil are exactly equal. Here, the oil–water interface consisting of a monolayer of surfactant molecules has on average zero mean curvature. Thus, a bicontinuous structure is formed in the three-phase body and in the one-phase microemulsion ( $1\Phi$ ) [8–10]. On increasing the surfactant concentration, other phases appear: lamellar, reversed hexagonal, etc. Although, in many of the phases of this system, the roles of the oil chain and of the added salts are reasonably well understood, the reported phase diagrams of W/O/AOT, with AOT purified using a variety of methods, differ considerably as regards the extents and shapes of the phases. This is because small amounts of residual impurities have a large effect [11, 12]. Therefore, there is no generally accepted full picture to hand for the phase behaviour of this system [11]. In fact, impurities in the original AOT and hydrolysis of this diester [13] lead to the formation of more hydrophilic compounds, such as a monoester, a dicarboxylate ion, and a hydrophobic alcohol.

In the last ten years, there has been increasing interest in divalent metal 2-*bis*[2-ethylhexyl] sulphosuccinate ( $M(\text{AOT})_2$ ) surfactants. This is because they can produce, on reduction, porous microstructured matter for templates and for catalytic purposes [14], quite important for the chemical engineering industry. W/O/ $M(\text{AOT})_2$  ternary systems form reverse spherical micelles, at low water content. On increasing the water content, spherical W/O droplets change into cylinders. This has been done for  $\text{Cu}(\text{AOT})_2$ ,  $\text{Co}(\text{AOT})_2$ , and  $\text{Cd}(\text{AOT})_2$  [15, 16]. This study has been extended to other surfactants of the type  $M(\text{AOT})_2$  with similar results [17]. Because the surfactants have to be synthesized by means of a relatively long procedure, most of the studies have focused mainly on the oil-rich and low-water-content region of the phase diagram. This is the case for the system W/iso-octane/ $\text{Cu}(\text{AOT})_2$ , which is by far the most extensively studied system [18–20]. Here, one finds a rich variety of phases and microstructures at 22 °C, such as: reverse spherical micelles, non-spherical micelles, lamellae; as well as, supra-molecular aggregates such as: interconnected cylinders, lamellar spherulites, and interdigitated micelles.

The aim of this paper is to present a preliminary survey of the phases that can be found in ternary systems of the kind W/iso-octane/ $M^{2+}(\text{AOT})_2$ , where  $M = \text{Co}$ ,  $\text{Ni}$ , and  $\text{Cu}$ , in a region of the concentration–temperature prism. Sometimes, the key to understanding the phase behaviour of ternary systems is first to study the two-component system (W + S). AOT is insoluble in water at room temperature; its solubility increases as temperature is increased, as for a typical ionic surfactant. However, there is evidence that AOT derivatives decompose in water [13]. Therefore, we tried first using the ternary system, because the presence of

the oil was expected to make the AOT more stable. Up to now, there have been no reports of a microemulsion three-phase body, nor of Winsor progressions in such systems. These progressions are expected to occur in these systems, without the addition of salt, due to the strong ionic strength of the media imposed by the divalent metal counter-ions. As we will show, this is the case. In addition, we will show that the systems involving cobalt and nickel surfactants have a variety of phases which are as rich as the system with the copper surfactant.

## 2. Experimental section

### 2.1. Reactants

AOT (98%) and iso-octane (>99%) were supplied by Aldrich Chemicals (Milwaukee, USA).  $NiCl_2$  (98%),  $CoCl_2 \cdot 6H_2O$  (99–102%), ethanol (99.8%), and the protonated strong cationic resin (Amberlyst 15) were supplied by Merck (Germany).  $Cu(SO_4)_2 \cdot 5H_2O$  (99%) was supplied by Baker (Mexico). The weakly acidic macroporous cation exchanger resin (Bio-Rex 70) was supplied by Bio-Rad Laboratory (California, USA). Deionized Water (Millipore Milli-Q) was used in all the processes. All chemicals were used without further purification.

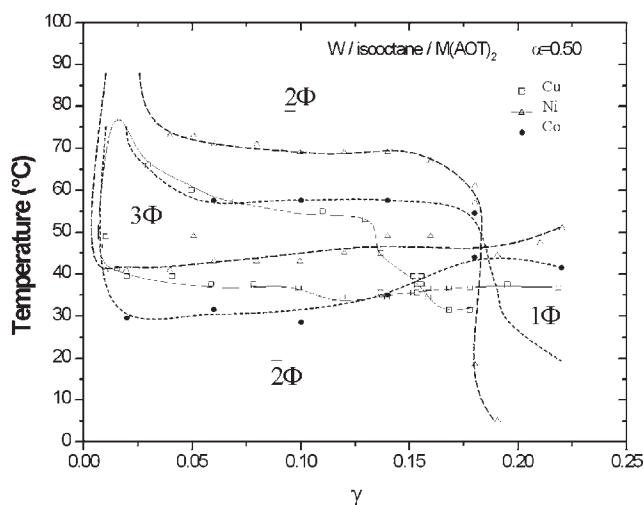
### 2.2. Procedure for preparing the surfactant

The sodium atom of the AOT surfactant was exchanged for the counter-ions  $Cu^{2+}$ ,  $Co^{2+}$  or  $Ni^{2+}$ . AOT dissolved in a 50% ethanol–water mixture was eluted in a column packed with a protonated strong cationic resin (Amberlyst), to make the acid form of AOT, which we call  $H^+AOT^-$ . We controlled the production of this acid form by following the pH, and the  $Na^+$  in the eluted liquid *in situ*, using atomic absorption spectrophotometry. To obtain the metal derivatives, the solution of  $H^+AOT^-$  was eluted again through two similar in-line columns packed with the weakly acidic macroporous cation exchanger resin (Bio-Rex 70), both columns having been previously charged with the appropriate metal to be exchanged (Cu, Ni, or Co). The final eluted liquid mixture was collected in a single-neck round-bottom flask placed on ice to prevent hydrolysis. The counter-ions were followed by atomic absorption spectrophotometry, as well as by following the pH. The mixture was distilled in an evaporator at low pressure to eliminate the ethanol in the alcohol–water mixture, until we obtained an opaque colourful jelly. The remnant ethanol and water in the jelly was extracted by means of seven or more successive distillations with iso-octane, until we got a clear colourful jelly. The chemical structure of the compounds was verified by means of  $^1H$ -NMR, and  $FAB^+$  mass spectrometry. The water remnant was in the region of 1.5%, as obtained by Karl Fisher titration.

### 2.3. Phase diagram

Ternary mixture samples were prepared by weighing in a  $N_2$  atmosphere in glass tubes. The tubes were vacuum sealed after freezing the sample with liquid nitrogen. This ensured that we would not have solvent loss when high temperatures were reached; however, the shape and size of the sample tubes prevented us from centrifuging the samples. The data points were determined in thermostated samples with the aid of a water bath to  $\pm 0.1^\circ C$ . Phase transition temperatures were determined by visual inspection of the transmitted and scattered light and between crossed polarizers, when necessary. The number and types of the phases were recorded. We followed the usual notation to determine the concentration in the phase prism:

$$\alpha = \frac{O}{W + O} \quad \text{and} \quad \gamma = \frac{S}{W + O + S}$$



**Figure 1.** Temperature versus  $\gamma$  for the ternary mixtures W/iso-octane/M(AOT)<sub>2</sub>, where M = Co, Ni and Cu.

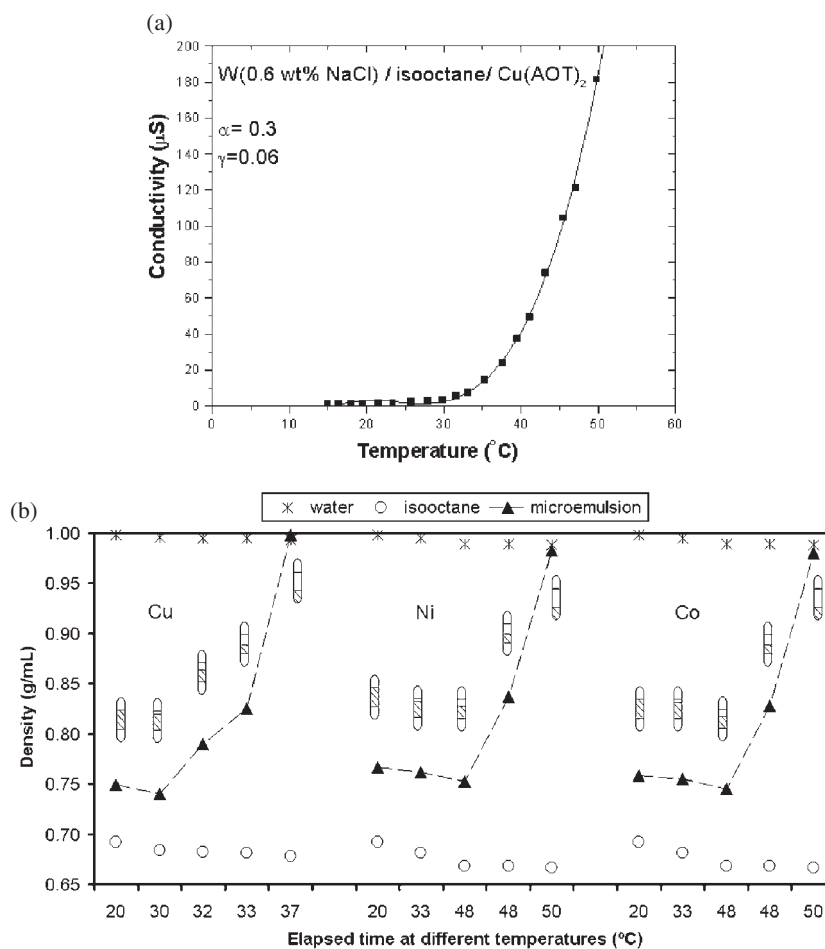
Here, the letters represent the weights of the different chemical species.

#### 2.4. Measurements

Density was measured with a high-precision flow densimeter (model 03, Dpr Sodev Inc.) coupled to a high-stability water bath. Phases were extracted with a short Teflon capillary, which sends the fluid to the vibrating tube (the densimeter and samples were at the same temperature). Conductivity was measured in vigorously stirred samples kept in closed containers, to avoid solvent evaporation, with a conductivity meter (model 3200, YSI Inc.) and a platinum cell, at several temperatures. In all cases, the sample temperature was controlled by a thermostated water bath to  $\pm 0.1$  °C.

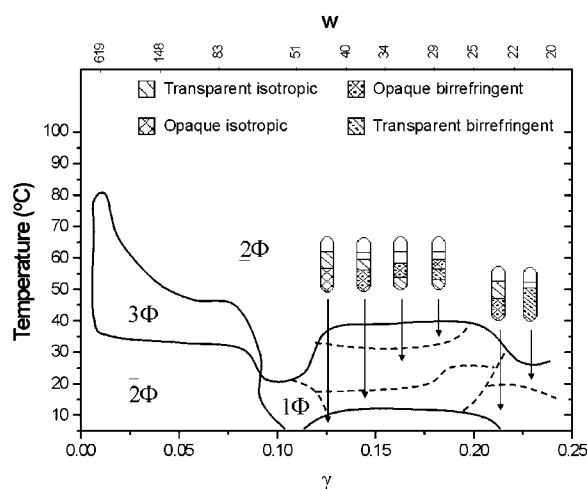
### 3. Results and discussion

The results of our survey for the water/iso-octane/M(AOT)<sub>2</sub> ternary mixtures are presented in figure 1, for  $\alpha = 0.5$  and for  $\gamma$  from 0.02 up to 0.22. For the three surfactants, we obtained a Winsor progression without the need for salt addition. This is a different behaviour from that well known to be exhibited by the AOT surfactant [7]. This progression has not been observed before, in systems with M(AOT)<sub>2</sub> surfactants. In our case, there is an oil-rich microemulsion ( $\bar{2}\Phi$ ) in equilibrium with excess water at low temperature, and a water-rich microemulsion ( $\underline{2}\Phi$ ) in equilibrium with excess oil phase, at high temperature. Three phases with an intermediate-phase microemulsion ( $3\Phi$ ), in simultaneous equilibrium with excess oil and excess water, are found at intermediate temperature. The shape of the phase body is elongated upwards at low surfactant concentration. At larger surfactant concentration, we found the one-phase microemulsion ( $1\Phi$ ). The hydrophile–lipophile balance temperature [8] is around 36 °C for Cu(AOT)<sub>2</sub>, 43 °C for Co(AOT)<sub>2</sub>, and 47 °C for Ni(AOT)<sub>2</sub>. These values are relatively close to the value of 41 °C given for the system D<sub>2</sub>O (0.6 wt% NaCl)/decane/AOT [8]. Since the surfactant concentration is low, we probably have spherical reverse micelles at low temperatures, and normal spherical micelles at high temperatures [9].



**Figure 2.** (a) Conductivity versus temperature for the 3 $\Phi$  microemulsion when the surfactant is Cu(AOT)<sub>2</sub>. (b) Density measurements made over several weeks for microemulsions in the three-phase body and the temperatures at which these measurements were made.

Figure 2(a) presents an example of an electrical conductivity measurement for a vigorously agitated microemulsion with a small quantity of added salt (0.06 wt% NaCl) as a function of the temperature. As we can see, there is a steep increase in the conductivity. Although, to prevent decomposition of the sample, we did not increase the temperature sufficiently to reach the conductivity plateau of the bulk salty water. Figure 2(b) presents density measurements made over several weeks for microemulsions in the three-phase body, and the temperatures at which these measurements were made. Each point corresponds to a sample from a set of samples prepared identically and under the same equilibration conditions; its container was opened to make the density measurement and then it was discarded. These measurements were taken, every two or three weeks. Here, we are observing how the densities and the relative amounts of the microemulsions are changing, slowly. In particular, for the cases of cobalt and nickel surfactants, we have two samples at 48  $^{\circ}\text{C}$ . The measurements on the first one were made after it had been at that temperature for a few days and those on the second one were made two weeks later. The change in conductivity and density probably corresponds to the structural

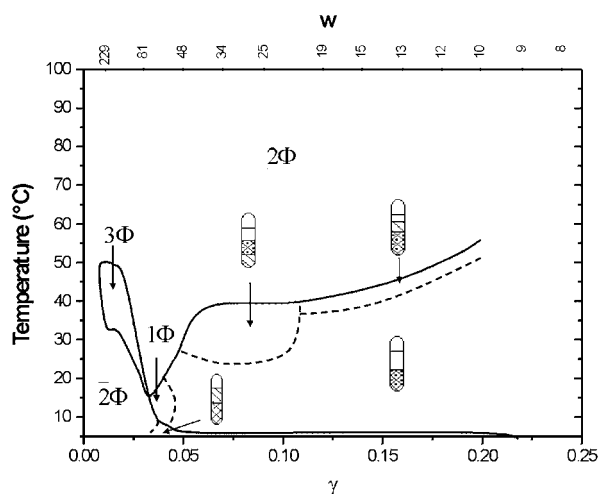


**Figure 3.** Temperature versus  $\gamma$  for the ternary mixture W/iso-octane/Cu(AOT)<sub>2</sub> for  $\alpha = 0.75$ , and the key to the observed phases. At the very top of each test-tube inset, there is always a vapour phase. White indicates low-density excess oil or high-density excess water, depending on the position.

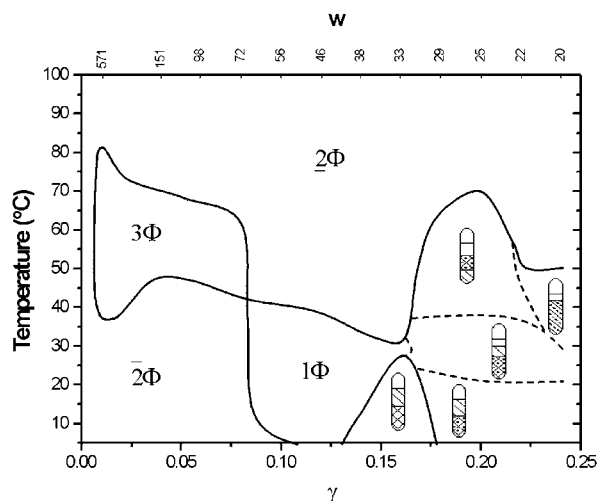
inversion from the W/O microemulsion to the O/W microemulsion. Usually this change takes place through an intermediate bicontinuous structure, for which the conductivity is high due to the interconnectivity of the system. This bicontinuous structure must also be present in the  $1\Phi$  microemulsion, just like in other systems [21]. In particular, this bicontinuous structure has been well characterized for a closely related system: the W/O/AOT system, by Chen and collaborators [8–10], using conductivity and neutron scattering measurements.

There are several comments to be made regarding this low-surfactant-concentration region of the phase diagram. Different stock surfactant preparations gave phase diagrams of the same kind, although there were important variations as regards at which temperature the phase changes occurred. However, the sequence of events is exactly the same. When the samples have just left the three-phase body, the system can return on lowering the temperature. After a few hours, the samples lose this reversibility property. In addition, for  $2\Phi$  microemulsion, the higher the temperature, the larger the degree of segregation of iso-octane. Although the initial compounds are pure, decomposition of the AOT is probably occurring, due to the presence of water and the increase in temperature. On leaving the three-phase body, the surfactant is more exposed to the water, and the temperature increase will probably cause the surfactant decomposition to proceed more rapidly. One possible explanation for the head of the ‘fish diagram’ being so elongated and deformed at low concentrations could be the alcohol liberated by the surfactant decomposition [11]. Similar effects have recently been reported for other microemulsions [12]. Figures 3–7 show how the head of the ‘fish diagram’ changes at different values of  $\alpha$ . The reason that other groups never saw the Winsor progression in the systems that we study here is that they never worked on that part of the phase diagram.

At high surfactant concentration (the ‘fish tail’), we found a rich variety of phases, some of them probably metastable. Figures 3 and 4 present diagrams showing some of the phases found for the water/iso-octane/Cu(AOT)<sub>2</sub> system, at  $\alpha = 0.75$  and 0.90, for different  $\gamma$ -values. Figures 5 and 6 present the same for the Ni(AOT)<sub>2</sub> surfactant, at  $\alpha = 0.75$  and 0.90. Finally, in figure 7, we present the phases for the case of Co(AOT)<sub>2</sub> surfactant at  $\alpha = 0.75$ . Dotted curves show approximately where the boundaries of the phases are located. The



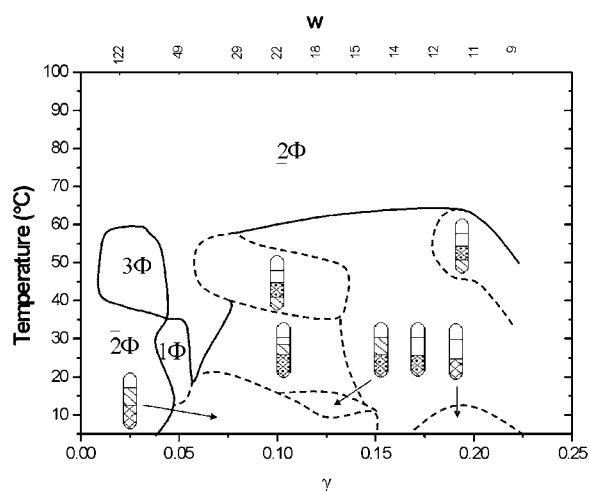
**Figure 4.** Temperature versus  $\gamma$  for the ternary mixture W/iso-octane/Cu(AOT)<sub>2</sub> for  $\alpha = 0.90$ . The other details are the same as for figure 3.



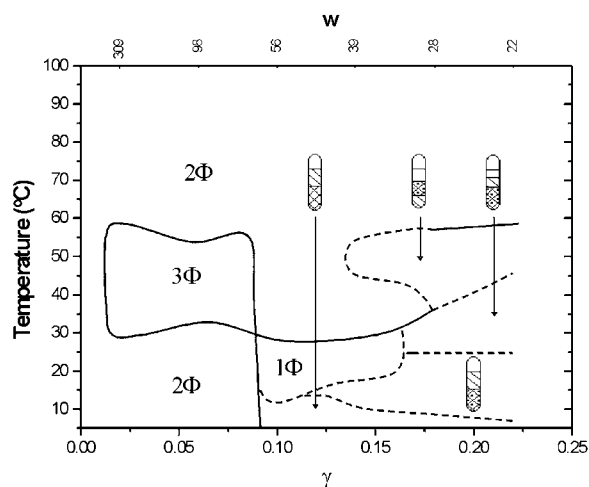
**Figure 5.** Temperature versus  $\gamma$  for the ternary mixture W/iso-octane/Ni(AOT)<sub>2</sub> for  $\alpha = 0.75$ . The other details are the same as for figure 3.

diagrams for the different metal surfactants share many similarities when a particular  $\alpha$ -value is considered. It is very difficult to know whether the phases which are presented in the diagrams correspond to equilibrium phases—because there is clear evidence of metastability, and the prolonged exposure to water makes it difficult to ensure that the changes do not correspond to partial decomposition of the samples. We prepared different groups of samples at specific concentrations, starting from 5 °C, and the temperature was increased by two degrees each time, using different equilibration waiting times. The equilibration waiting times were one day, two days, three days, and several weeks. In every run, we observed much the same sequence of phases until the  $\underline{2}\Phi$  microemulsion was reached. However, phase changes did not occur at the same temperatures. More than 10 °C difference was not uncommon. Also,





**Figure 6.** Temperature versus  $\gamma$  for the ternary mixture W/iso-octane/Ni(AOT)<sub>2</sub> for  $\alpha = 0.90$ . The other details are the same as for figure 3.



**Figure 7.** Temperature versus  $\gamma$  for the ternary mixture W/iso-octane/Co(AOT)<sub>2</sub> for  $\alpha = 0.75$ . The other details are the same as for figure 3.

we have specific examples where samples that reached room temperature were left for five months at that temperature. They passed through the whole sequence of phases until the  $\underline{2}\Phi$  microemulsion was reached. The last transition to the  $\underline{2}\Phi$  microemulsion is reversible only for a very short period of time, as in the low-surfactant-concentration range, probably because of surfactant decomposition. For  $\underline{2}\Phi$  microemulsion, samples at  $0.16 < \gamma < 0.20$  and at  $\alpha = 0.75$  showed shear thickening, i.e., on vigorous agitation the viscosity increased up to a point where the mixture seemed like a gel. Curiously, after a period of time in the range 10–20 min, they returned to exhibiting the  $\underline{2}\Phi$  microemulsion appearance.

In all the figures presenting diagrams for  $\alpha = 0.75$  and  $0.90$ , we can find the one-phase bicontinuous microemulsion  $1\Phi$ , which is coloured by the metal counter-ion of the surfactant. At larger surfactant concentrations, we found several cases of two phases in apparent

equilibrium. One of them is a coloured isotropic transparent phase, another phase is an opaque coloured one in one case and, in another case, it is a birefringent opaque phase. We also found other apparent equilibria involving two phases, where one is an iso-octane-rich phase, which coexists with a coloured transparent birefringent phase in one case and, in another case, with a coloured opaque birefringent phase.

There are parts of the diagrams with an apparent equilibrium among three phases, as in the case where an iso-octane-rich phase is coexisting with a coloured isotropic transparent phase, and also with an opaque birefringent phase. Here, we have two cases: where the birefringent phase is denser than the coloured isotropic transparent phase and where it is heavier. All these cases are found at temperatures above those where the biphasic equilibria appear. Here, there is also a case which is probably metastable for the copper surfactant. An iso-octane-rich phase is apparently coexisting with a coloured isotropic transparent phase, and also with a birefringent phase, which has a transparent part and an opaque part. A common characteristic of all birefringent phases is that the domains of birefringence become smaller and less opaque as temperature is increased.

A comparison of our results for the case of the copper surfactant with those of Pileni's group [19,20] was made, and they agree in general (at the top of figures 4–7, we give the values of  $w$ , which was the symbol used by Pileni's group for the water/AOT ratio), although some differences were found. In particular, we found the same phases as were described by them for the area  $\text{II}_b$  at high gamma values. Accordingly,  $2\Phi$  microemulsion must be made up of interconnected cylinders. The phases in the area  $\text{III}_b$  are probably the same as those observed by us, because our phase had very low birefringence and they did not observe it. We found the same phases as them for areas  $\text{IV}_b$ ,  $\text{V}_t$ , and  $\text{V}_b$  with the birefringent phases. The birefringent phase in area  $\text{IV}_b$  corresponds to distorted lamellar structures and spherulites, and in area  $\text{V}_t$  there are spherulites with interconnected cylinders inside. However, we did not find the phases described as present in the thin area VI. Instead of these, we found a three-phase system with an iso-octane-rich phase, an isotropic coloured transparent phase, and a less strongly coloured opaque birefringent phase. The isotropic single phase found in area VII was also found, but at larger values of  $w$ .

In this preliminary survey, we have shown the phases, some of them metastable phases, presented by three systems which have an ionic surfactant. They presented a phase behaviour not observed before: Winsor progressions without the addition of salt. In the case of nickel and cobalt surfactants, we learned that they present a behaviour that is similar to that of the better known system with the copper surfactant. This work will enable us to make a systematic study using more suitable techniques for dealing with the microstructure of the phases—SAXS, light scattering, viscosimetry, freeze fracture electron microscopy, etc. This work is under way.

## Acknowledgments

We acknowledge the support of DGAPA and CONACYT grants, as well as the help of M Martinez in the chemical characterization and that of C Marquez in the chromatography.

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