Diffuse Interface in Oil-in-Water Microemulsions at Low Surfactant Concentration of the Brine-Toluene–*n*-Butanol-Sodium Dodecyl Sulfate System.

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Abstract. – The system brine (65.74%, with NaCl salinity of 6.5%), toluene (31.9%), *n*-butanol (2.3%) and SDS (0.04%) displays at room temperature a new type of phase equilibrium between an upper oily transparent phase and a lower oil-in-water microemulsion domain; the latter exhibits two regions different in composition and structure. The oil-microemulsion interface is sharp, while the microemulsion-microemulsion interface is diffuse, the diffuse region being a few millimeters thick. Results on the composition and structural investigations are shown in terms of index of refraction, gaschromatography and diffusion coefficient (quasi-elastic light scattering analysis). To account for the observed results, an interpretation is proposed in terms of structural change of the o/w microemulsion (droplet coalescence).

1. Introduction.

A microemulsion, which is a fluid mixture of water (or brine) and hydrocarbon stabilized by amphiphilic substances (surfactant and often a cosurfactant), can exist as a single phase or coexist with an excess of oil or an excess of water or both (respectively, Winsor IV, I, II and III phases) [1]. The structure of the microemulsion changes from the Winsor I to the Winsor IV; more details and references are given in ref. [2]. A general review on the microemulsion field can be found in ref. [3]. The interest for Winsor's microemulsion lies in the very low values of the interfacial tension between the microemulsion phase and the phase(s) in excess ($\simeq 10^{-3}$ dyn/cm) and in their very large solubilization capability [4]. The origin of low interfacial tensions has been interpreted either in terms of critical phenom-

ena [5-8] or in terms of particular structures of the microemulsion phases [9, 10]. The transition from one Winsor equilibrium to another is driven by parameters like salinity of the brine, surfactant and/or alcohol concentration, temperature. A theoretical approach in line with the Talmon-Prager model [11] has been developed [12-14]. The Widom model includes the description of two- and three-phase equilibria, critical points and critical end points.

A system composed by water, toluene, sodium dodecyl sulfate (SDS) and n-butanol, for which the salt concentration in water is progressively increased, exhibits a phase transition Winsor I → III → II [2, 3, 15]. The proportions of the component as reported in ref. [15] are, by weight, brine 46.8%, toluene 47.25%, SDS 1.99%, n-butanol 3.96%. For a fixed NaCl salinity of 6.5% (by weight) (optimal salinity [1]), the sample is of Winsor III type. The two liquid-liquid interfaces, which appear flat by visual observation, have been intensively investigated by LANGEVIN et al.; at the optimal salinity, the two interfacial tensions between the microemulsion and oily phases and microemulsion and aqueous phases are identical, the identity occurring only in this case [7, 15].

Following a suggestion by Prof. B. WIDOM, we have investigated Winsor microemulsions at very low surfactant concentration, in order to test possible analogies between systems composed of water, salt, hydrocarbon and alcohol [16], and those composed of water, salt, hydrocarbon, alcohol plus surfactant. Maintaining the previous salinity (6.5%), while varying the ratio brine/toluene, we have observed a new and interesting behaviour for a sample (S) composed (by weight) of brine 65.74%, toluene 31.90%, n-butanol 2.30% and SDS 0.04%. For that particular composition, the sample appears separated into three domains as shown in fig. 1: an upper transparent oily phase for $0 \leqslant h < +1$ cm, an intermediate microemulsion turbid region for $-0.7 \leqslant h \leqslant 0$ cm and a lower transparent region for $-1.75 \leqslant h \leqslant -0.7$ cm. The oil-microemulsion interface (o-m) is sharp, while the interface between the intermediate and lower regions is diffuse.

In the present paper we report investigations on the composition (index of refraction and gaschromatography) and the structure (quasi-elastic light scattering) of the S-sample.

2. Materials and methods.

2˙1. *Sample preparation*. – Toluene was from SdS or Merck (uvasol), n-butanol from SdS (puran) or Merck, sodium dodecyl sulfate (SDS) from Serlabo or Merck, NaCl from Prolabo or Merck; the water was either tridistilled or taken from a Millipore Milli-Q System. Commercial products without further purification were used. No influence of the trade mark was observed.

For all the experiments, the cell filled with the sample was placed inside an oven; horizontal and vertical temperature differences, inside the cell, were smaller than 0.01 °C at the temperature investigated, $T = 20$ °C. The measurements were repeated for a month during the stabilization time of the sample (which resulted to be almost a week) and after the attained stabilization; the sample was considered stable because the measurements remained identical. The thermal stabilization for all the time was ± 0.025 °C.

2˙2. *Methods*. – Index-of-refraction profiles as a function of the height h, $n(h)$, were carried out with a He-Ne laser by the minimum deviation method [17] and the laser beam deflection technique [18] at given constant temperatures. A two-mirror beam steeering

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[1] «The middle phase microemulsion contains equal volumes of oil and brine and practically all of the surfactant at a specific salinity defined as the optimal salinity of the given system» (p. 8 of ref. [4]).

system allowed us to scan the sample vertically with a spatial resolution of 100 μm. The vertical deflections, due to vertical index of refraction gradients inside the sample, were detected by a Schottky barrier photodiode (United Detector Technology Inc.), the vertical displacement resolution being 1/100 mm. To calibrate the apparatus, measurements were made on a SO-sample, composed as described in subsect. 2`1, but without surfactant. The SO-sample was a two-transparent-phase sample, oily and aqueous, separated by a concave meniscus placed almost at the o-m interface height of the S-sample. Absolute n values are obtained with a 0.04% relative accuracy; the relative indetermination along a single profile results of the order of 0.002%.

Quasi-elastic light scattering analysis [19] was performed with a krypton ion laser (coherent CR500K, $\lambda = 530.9$ nm). The sample thickness was 0.3 cm to avoid multiple scattering. The time-dependent correlation function of the scattered intensity was measured by a digital correlator with 100 channels; the time resolution of the whole apparatus was 1 μs, the resolution on the scattering angle was better than $\pm 0.1°$. Details on data analysis are reported in ref. [20, 21]. The relaxation time of the correlation function (τ) was worked out with a relative accuracy better than 3%. Micrometric beam steering provided vertical scanning across the sample; the detector system was correspondingly displaced. To test the optical alignments, the constancy of τ on a dilute suspension of polystyrene spheres was checked for different heights. On the S-sample the presence of small n gradients gave vertical deflections and focusing of the beam which did not affect the results.

Gaschromatographic analysis was performed on a Perkin Elmer Sigma 1 System, using 2 m columns packed with Carbowax 20M, on Chromasorb W.

3. Results and discussion.

The upper phase of S-sample results homogeneous in composition (constant n) and no autocorrelation function of the scattered intensity is detectable, in the limit of resolution of the apparatus, confirming the visual observation from which it was defined transparent in the introduction (see fig. 1). The index of refraction value describes it as an oily phase rich in toluene; $n_u = 1.4930$ at $T = 20.10$ °C (toluene $n = 1.4968$; n-butanol $n = 1.3991$ and brine $n = 1.3444$ at $T = 20$ °C [22, 23]).

For the part of the sample placed below the o-m interface, which looks nonhomogeneous, the $n(h)$ profile is reported in fig. 2 at $T = 20.10$ °C, for h varying from 0 cm (just below the meniscus of the o-m interface) to the bottom of the cell. Contrary to the upper phase, a correlation function of the scattered intensity is detectable in all this region. For all the h values investigated, the correlation function relaxes exponentially with time with a characteristic time $\tau(h, q)$; q is the scattering wave vector, $q = (4\pi n/\lambda) \sin(\theta/2)$. τ^{-1}/q^2 has been observed to be constant at fixed h, in the angular range $30° \leq \theta \leq 90°$, ensuring homodyne detection at all h for $\theta = 90°$. The q-independence of τ^{-1}/q^2 also means that, at the investigated temperature, no near-to-critical phenomenon has been detected. The mutual diffusion coefficient of the dispersion, $D = 1/(2\tau(q) q^2)$ (homodyne detection) is reported as a function of h in fig. 3, from the o-m interface to the bottom of the cell, at $T = 20.34$ °C.

The curves $n(h)$ and $D(h)$ inflect at the same height (~ -0.7 cm). A smaller sub interface region (range $(0 \div -0.2)$ cm of fig. 2) with linear n gradient, where the scattering is stronger than in the rest of the sample, does not appear in terms of diffusion coefficient variation. The quasi-elastic measurements clearly establish that the whole region of the S-sample placed below the o-m interface scatters light, despite the apparent visual transparency of the lower part (see fig. 1). The corresponding $D(h)$ profile displays two constant D zones, for $0 \geq h \geq -0.5$ cm and $-1.2 \geq h \geq -1.6$ cm, respectively, in which the
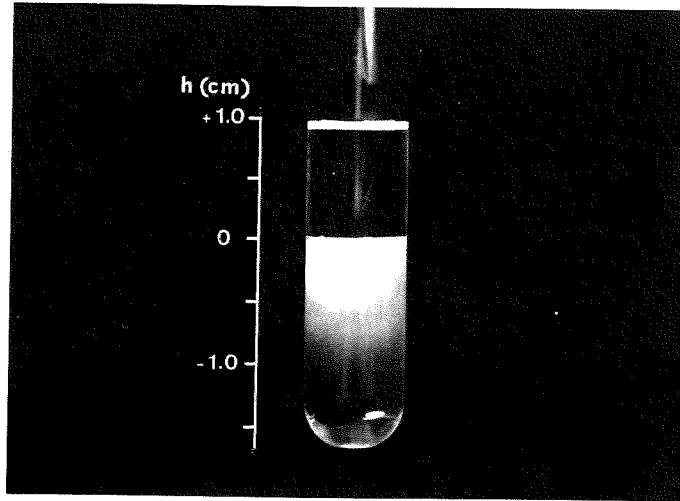
Fig. 1. – Picture of the S-sample composed by 65.74% brine (6.5% NaCl salinity), 31.90% toluene, 2.30% n-butanol and 0.04% SDS. The cell is cylindrical, 1 cm in diameter. The height scale is shown aside; at $h = 0$ cm there is the oil-microemulsion (o-m) interface. The scattering region appears blue in reflection and orange in transmission if a white-light source is used; in the picture the sample is illuminated with a white-light source placed in front of it. Due to the cell diameter, multiple scattering surely increases the scattered light intensity of the intermediate region.
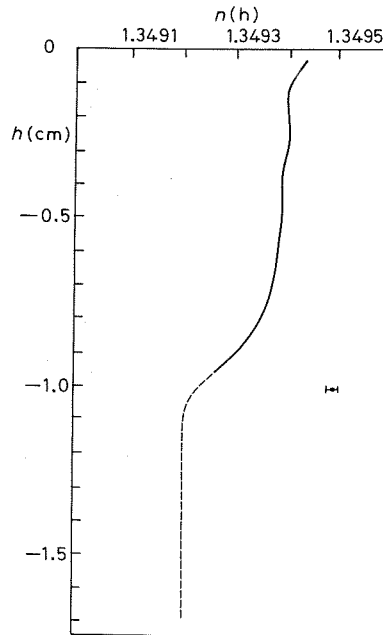

Fig. 2. – Index of refraction $vs.$ height for the intermediate and lower regions of the S-sample at $T = 20.10$ °C. The height scale is the same of fig. 1; $h = 0$ cm and $h = -1.75$ cm correspond to the o-m interface and to the bottom of the sample, respectively. The solid line corresponds to measurements done by the laser beam deflection technique (the investigation was not possible for $h < -1$ cm for the presence of the oven wall); the error bar shown aside represents the relative indetermination along the profile. The dashed line is a guide for the eyes to connect the $n(h)$ profile to two values of the lower region of the sample, measured by an Abbe refractometer (absolute indetermination ± 0.0001).
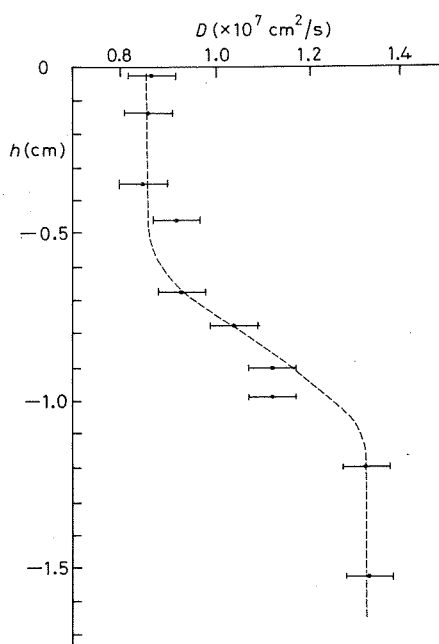
Fig. 3. – Diffusion coefficient *vs.* height in homodyne detection ($\theta = 90°$) at $T = 20.34$ °C for the intermediate and lower regions of the S-sample. The o-m interface is located at $h = 0$ cm and the bottom at -1.75 cm. The dotted line is a guide for the eyes.

D values differ by a factor 1.5, separated by a zone of progressive D variation. In all cases, the order of magnitude of D is typical of microemulsion [24]. Moreover, the *n*-butanol/toluene ratio of the upper oily phase as deduced from the gaschromatographic analysis is 2.44% (volume by volume) for the S-sample, while it is only 1.46% for the SO-sample, indicating that a larger quantity of toluene is transferred under the o-m interface due to the presence of surfactant. The same result can be inferred by calculations on n values for S-sample and SO-sample, as will be deduced later on. All these results suggest the existence of oil in water microemulsion structures with toluene cores throughout the sample below the o-m interface, the new fact being the inhomogeneity of the region.

It is tempting to interpret the observed variation of D in terms of a size variation of the microemulsion droplets, R_H. However, as the volume fraction of the dispersed phase φ may be relatively large and as it is obviously not possible to use a dilution procedure due to the particular nature of the S-sample, D and R_H may not be related through a simple Stokes-Einstein formula [19], $D_0 = kT/6\pi\eta R_H$ (with k the Boltzmann constant, T the absolute temperature and η the continuous phase viscosity). One rather expects a volume fraction variation and thus a $D = D_0(1 + \alpha\varphi + \ldots)$ with a virial term α [3, 24] which may be important for droplets with attractive interactions. In order to correctly relate mutual diffusion and size, we have to infer the local composition of the system, using the $n(h)$ measurements and reasonable hypotheses. We assume that on a SO-sample the salt is present only in the lower phase; a *n*-butanol partition occurs between the upper and the lower phases; there is no water in the upper phase (really the water content is negligible [25]) but there is toluene in the lower phase due to the *n*-butanol presence [26]. Moreover, because the addition of SDS does not justify the observed n value on the S-sample o/w microemulsion domain (see table I), an increase in toluene is there assumed. The composition of the phases as evaluated after the above hypotheses is reported in table I. The *n*-butanol partition coefficient in the

TABLE I. – *Phase composition of* S *and* SO *samples as evaluated by the measured index of refraction values, at* $T = 20°$ C.

	n value of the components	Total composition of the samples (ml)		Volume of the components for each phase (ml)			
				SO-sample		S-sample	
		SO	S	upper phase	lower phase	o/w domain	upper phase
n value of the phase				1.4933	1.3480	1.3490 [a]	1.4930
toluene	1.4968	0.58	0.58	0.563 [b]	0.0167	0.0234	0.5566 [b]
n-butanol	1.3991	0.045	0.045	0.0202 [b]	0.0248	0.0248	0.0202 [b]
brine (6.5% salinity)	1.3444	1.00	1.00	—	1.00	1.00	—
SDS	1.46	—	5.81(−4)	—	—	5.81(−4)	—

(a) Order of magnitude.

(b) The n-butanol/toluene ratio of SO and S samples upper phase, evaluated by the index of refraction, results to be 3.6%, identical in the two cases. The gaschromatographic analysis gives smaller ratios and different values in the two cases because the organic impurities mixed to toluene and n-butanol (always present in products which are not of gaschromatographic quality) are removed in the calculations.

presence of SDS can be estimated from titration curves [27]. The required average volume fraction results to be $\varphi = 0.028$.

The $n(h)$ gradient (fig. 2) reflects a composition gradient below the o-m interface. With $n = 1.3494$ and $n = 1.3492$ in the intermediate and lower regions, respectively, the $\varphi(h)$ values are 0.0274 and 0.026, respectively. The φ variation is then quite small, $\Delta\varphi = 1.4 \cdot 10^{-3}$, and is insufficient to account for the observed $D(h)$ variation even if one assumes a virial coefficient α of order -20, one of the smaller value found in the literature [24].

The two branches of the $D(h)$ profile at constant D values, suggest the existence of two neighbouring regions with scattering objects of different size, which can be evaluated from the D_0 formula assuming as viscosity that of the water, leading to $R_H = 230$ Å and 160 Å in the intermediate and lower regions, respectively. We want to emphasize that these values are surely over-estimated, as we have neglected the second virial coefficient contribution, but the ratio (~ 1.5) is presumably correctly estimated, owing to the small $\varphi(h)$ variation between the two regions. We could interpret the aspect of the S-sample in terms of two neighbouring microemulsion phases of different droplet sizes and same continuous phase.

The $D(h)$ reduction of a factor 1.5 could suggest a structural change in a unique microemulsion phase, related to the presence of aggregates, probably of dimeric type, formed for droplet coalescence. We have not been able to detect any important polydispersity either in the intermediate or in the lower regions, from a careful analysis of the quasi-elastic light scattering data, but a small per cent of dimeric aggregates superimposed to the larger quantity of droplets of given size (or *viceversa*) is quite difficult to detect in terms of departure of the autocorrelation function from a single exponential, expecially when the sizes are only slightly different. Recall that the existence of doublets of spheres with mean distances $2r_c$ between the centres has been observed in other microemulsion systems with attractive interaction [10]. In that case the microemulsion was of water-in-oil type in the concentrated region.

Moreover, we cannot exclude that the diffuseness of the S-sample is due to an incipient separation of a third phase in the intermediate region, attainment of the true equilibrium phase separation being extremely slow.

To better understand the new phenomenon presented in this paper, the role of the temperature as well as that of the alcohol will be discussed in a paper which is in preparation.

As a conclusion, we point out that the structural modification proposed to interpret the new type of phenomenon could be a sort of first-step aggregation of more complex structures, probably the forerunner of the bicontinuous structure of the Winsor middle phase.

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