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Quaternary ‘*N*-alkylaldonamide–brine–decane–alcohol’ systems Part III. Microstructure of the monophasic microemulsion domain studied by fluorescence

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Abstract

The phase diagram of the ‘*N*-alkylaldonamide–brine–decane–alcohol’ system shows, in addition of the polyphasic Winsor I, III and II microemulsions, a large monophasic domain. Investigation of its structure by nuclear magnetic resonance (NMR) has determined three different zones: a bicontinuous microemulsion, a water-in-oil microemulsion and a solution of small surfactant aggregates solvated by water and butanol. The purpose of this paper is to confirm the existence of these three zones and their microstructure by introducing a fluorescent probe in the system. Pyrene has been chosen as a probe because its fluorescence is very sensitive to the polarity and viscosity of the medium and to local concentration. The well-known structure of the microemulsions in the polyphasic equilibrium has first been studied by the fluorescence method. The monophasic domain has then been investigated by the same method and the results correlated to the information obtained by fluorescence in the polyphasic systems and by NMR in the monophasic area. The evolution of pyrene fluorescence and the discontinuities in the measured fluorescence parameters observed at the boundaries of the three zones delimited by the NMR study support the previous conclusions concerning the microstructure of the monophasic area. © 2000 Elsevier Science S.A. All rights reserved.

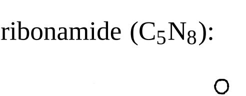
Keywords: *N*-alkylaldonamide; Microemulsions; Fluorescence phase diagram

1. Introduction

Several *N*-alkylaldonamides have been synthesised and studied a few years ago in our laboratory [1–4]. This family of compounds presents a set of interesting properties which result from their amphiphilic structure and their ability to form hydrogen bonds between neighbouring molecules. As a result, thermotropic and lyotropic behaviour have been observed. Smectic and lamellar phases have been identified, respectively, in the neat phase and in aqueous solution. As a complement to these studies, it was essential to study the behaviour of these compounds in binary hydrocarbon–water systems. Because of their remarkable properties and their large number of applications, microemulsions have received special attention in recent years. Particularly, the knowledge of their microstructure is of great importance and many attempts are made concerning the relationship between microemulsion structure and measurable physical properties.

In the first paper [5], it has been shown that two *N*-alkylaldonamides, *N*-decylisosaccharinamide and *N*-octylribonamide, form microemulsions in quaternary systems of ‘*N*-alkylaldonamide–brine–decane–alcohol’.

N-decylisosaccharinamide (IsoN_{10}):



$$\mathrm{CH_2OH{-}CHOH{-}CH_2{-}\underset{\displaystyle CH_2OH}{\overset{\displaystyle OH}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}(CH_2)_9{-}CH_3}$$

N-octylribonamide (C_5N_8):

$$\mathrm{CH_2OH{-}(CHOH)_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}(CH_2)_7{-}CH_3}$$

The phase diagram of this system corresponding to a vertical cut in the phase tetrahedron keeping the brine/decane ratio constant and equal to unity has a phase separation diagram with a characteristic ‘fish shape’ (Fig. 1). At low surfactant concentration, it presents different kinds of polyphasic equilibrium with microemulsions having a well-defined structure [6–11]:

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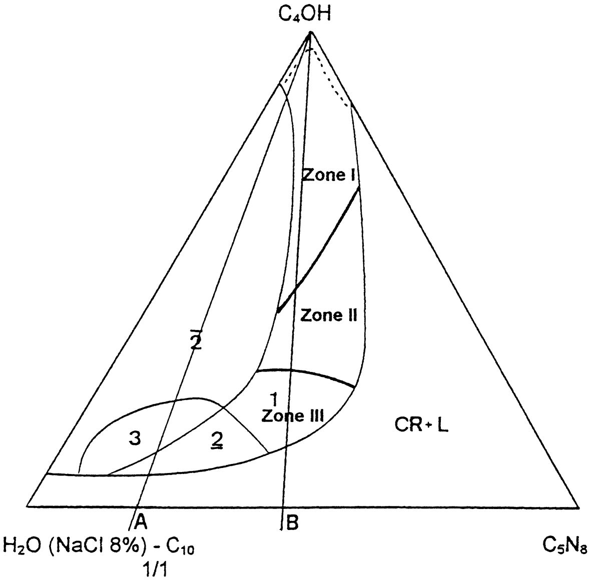

Fig. 1. ‘*N*-octylribonamide–brine–decane–butanol’ phase diagram keeping the H_2O (NaCl 8%)/decane ratio=1 (T=25°C). CR+L: crystal+liquid, A: 0.25 dilution line, B: 0.85 dilution line.

- Winsor I: lower oil in water microemulsion phase in equilibrium with an upper excess oil phase also represented by $\underline{2}$.
- Winsor III: bicontinuous microemulsion phase coexisting with both water and oil excess phases also represented by 3.
- Winsor II: upper water in oil microemulsion phase in equilibrium with a lower excess water phase also represented by $\overline{2}$.

In addition, at higher surfactant concentration, when the microemulsion phase has absorbed the excess phase(s), the system becomes monophasic in a large domain. Its microstructure varies depending on the concentration range under consideration.

In the second paper [12], the microstructure of the monophasic equilibrium of the ‘*N*-octylribonamide–brine–decane–butanol’ system has been investigated by nuclear magnetic resonance (NMR). From measurements of chemical shifts, relaxation times and exchange rates, three different zones have been distinguished in the monophasic area of the phase diagram. The first one, zone I (when the surfactant concentration is lower than 25%) is characterised by small surfactant aggregates solvated by water and butanol. Zone II, when the surfactant concentration is larger than 25%, corresponds to an inverse microemulsion of water droplets in a continuous decane–butanol medium. In zone III, the microemulsion evolves to a bicontinuous structure.

The purpose of this paper is to confirm these three microstructures by introducing a probe in the system and studying its fluorescence. Peak position, fluorescence quantum yield, excimer formation or the intensity ratio of different vibronic bands of the fluorescent compound are sensitive to the changes in local polarity and/or viscosity. For these reasons, fluorescence probes are widely used for the structural studies of organised media. Fluorescence measurements can be applied not only to monophasic systems but also to polyphasic systems.

Fluorescence of pyrene and pyrene derivatives has been used since a very long time in the study of micellar systems [13]. This method has been extended more recently to gelation and gel media [14], monoparticle surfaces [15,16] and hydrophobically modified polymers [17]. In micellar systems, various degrees of sophistication of the method have been developed including steady-state fluorescence and lifetime measurements, sometimes involving quenching studies. The drawbacks of this probe when it is dissolved in organic micelles which are dispersed in a continuous aqueous phase have been discussed [18]. Most of the present results concern either aqueous micelles dispersed in a continuous organic phase containing the organic probe or bicontinuous microemulsions. The use of pyrene is then allowed.

It will be shown here that it is possible to explore a complex phase diagram by very simple steady-state techniques and a single pyrene concentration which gives both excimer to monomer intensities and the vibrational structures of the monomer fluorescence. The first step of this work is thus the study of fluorescence in the microemulsions of the two- or tri-phasic equilibria. In the second step, this information has been used to investigate the monophasic domain. Next, by correlating the data obtained by fluorescence and NMR measurements, it was possible to confirm the microstructure of the one-phase equilibrium of the ‘*N*-octylribonamide–brine–decane–butanol’ system.

2. Experimental part

2.1. Synthesis

N-octylribonamide (C_5N_8) was synthesised at room temperature by addition of stoichiometric amounts of *N*-octylamine to a methanol solution of D(+)-ribonic acid-γ-lactone. The crude product was recrystallised twice in methanol.

2.2. Composition of the phases

The composition of the phases was determined by gas chromatography (Perkin Elmer 8320 with a polydiphenyldimethyl siloxane 0.2μ column). Mixtures were prepared by weight in sealed tubes which were rapidly warmed to the isotropic phase. Then, they were vigorously shaken and allowed to cool in a thermostated bath. Each phase was taken and dissolved in pyridine. The composition was determined in two steps:

- a part of the solution was injected to give the decane, butanol and water contents;

- a part of the solution was evaporated and dissolved in a silylation reagent (Tri-Sil). After reaction (1 h at 80°C), the solution was injected to give the surfactant content.

2.3. Fluorescence measurements

Samples of microemulsions were prepared by weighing surfactant, brine, decane and butanol in 2 mm quartz cells. For the fluorescence measurements, the last two components were 5×10^{-3} mol/l in pyrene to allow the ratio of excimer to monomer fluorescence to be studied [19,20]. The mixtures were warmed to the isotropic phase, shaken and allowed to cool at room temperature until attainment of equilibrium. Samples were deoxygenated by bubbling with purified N_2. The fluorescence emission spectra were recorded by reflection using a Perkin Elmer MPF-2A spectrofluorometer at an excitation wavelength of 340 nm. In these conditions, the shape of the fluorescence curves indicates that reabsorption of the fluorescence is negligible. The excitation spectra of the monomer and excimer fluorescence being identical, the formation and fluorescence of ground-state dimers can be precluded. With only the evolution of the spectra being involved, they have not been corrected for the sensitivity of the photomultiplier. Pyrene concentration in the organic phase, whatever the excess or oil-in-water microemulsion, was confirmed to be 5×10^{-3} mol/l by UV absorption spectroscopy. Using the same method, the pyrene concentration was shown to be equal or lower than 10^{-5} mol/l in the excess aqueous phases.

3. Results and discussion

3.1. Choice of the probe

NMR investigations have allowed us to identify surfactant aggregates, W/O and bicontinuous microemulsions in the monophasic domain of the ‘*N*-octylribonamide–brine–decane–butanol’ phase diagram [12]. For the study of microstructures in which the continuous phase is hydrophobic, an appropriate fluorescent probe should be soluble in the aqueous phase. However, from our different experiments, we could not find any fluorescent probe which is soluble enough in a water phase that always contains 8% NaCl. The ‘*N*-octylribonamide–brine–decane–butanol’ systems have thus been studied introducing pyrene as the fluorescent probe. Pyrene has been chosen because of its well-known photophysical characteristics. Particularly, the ratio of the intensities of the third and the first vibronic band, I_3/I_1, is very sensitive to the polarity of the solvent [21,22]. It decreases on going from aliphatic hydrocarbons to polar solvents and is a good indicator of the polarity of the probe microenvironment in the micellar structure. In addition, the efficient formation of pyrene excimer can be exploited to probe the microviscosity of the microemulsion medium. The photophysical processes of pyrene fluorescence have been detailed [23,24]. If thermal dissociation of the excimer (minimal at ambient temperature) [24,25] and radiationless transitions [26] are omitted, the ratio of excimer to monomer fluorescence intensity is

$$\frac{I_E}{I_M} = \frac{k_{DM}[^1M]}{k_{FM}} \tag{1}$$

where I_E and I_M stand for the fluorescence intensity, respectively, of the excimer and the monomer, k_{DM} is the rate constant for excimer formation, k_{FM} is the rate constant for monomer fluorescence and $[^1M]$ is the monomer concentration in the ground state. As excimer formation is a diffusion-controlled process [23], its rate is given by the Einstein–Schmoluchowski equation [27]:

$$k_{DM} = \frac{8RT}{3000\eta} \tag{2}$$

where R, T and η are, respectively, the gas constant, the temperature and the viscosity of the medium. The intensity ratio I_E/I_M can be related to the viscosity of the medium by

$$\frac{I_E}{I_M} \propto \frac{[^1M]T}{\eta} \tag{3}$$

The measurement of the ratio of the excimer fluorescence intensity at 466 nm to the monomer fluorescence intensity at 390 nm is related to the efficiency of pyrene to form excimer in the medium. From studies in micellar medium [28] and according to Eq. (3), three significant factors can influence the possibility of excimer formation. These are, first, the probability of an encounter between an excited and a ground-state pyrene molecule, which is proportional to the local concentration, second, the lifetime of excited pyrene, and third, or the diffusion rate of a ground-state pyrene molecule to an excited pyrene molecule which is dependent on the viscosity of the medium.

3.2. Calibration curve

As the fluorescence of pyrene depends on the polarity and the viscosity of the solvent, the I_3/I_1 and the I_E/I_M will vary with the decane–butanol composition in the ‘*N*-octylribonamide–brine–decane–butanol’ systems. To take into consideration variations due to a modification in the composition of the medium, two calibration curves have been established (Fig. 2A and B). These curves show the decrease of the I_3/I_1 and I_E/I_M ratios in the 5×10^{-3} mol/l pyrene solutions, when the butanol concentration increases in decane–butanol mixtures. The decrease in I_3/I_1 is due to the increase in solvent polarity. The decrease in I_E/I_M results from the increased viscosity of the solvent. We will further refer to the values represented on these curves as I_3/I_1cal and I_E/I_Mcal.

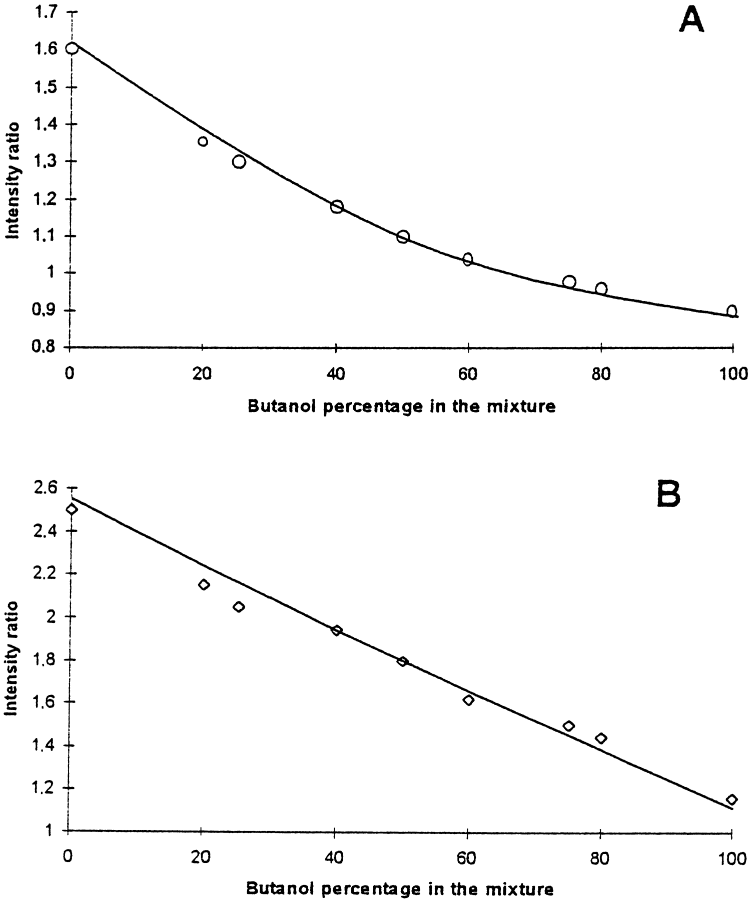

Fig. 2. Evolution of the experimental I_3/I_1 (curve A) and I_E/I_M (curve B) ratios in decane–butanol mixtures as a function of the butanol concentration (wt.%) in the decane–butanol mixture.

3.3. Fluorescence in the polyphasic systems

The phase diagram of the '*N*-octylribonamide–brine–decane–butanol' system is given in Fig. 1, the coordinates being expressed in weight fraction. This section of the paper describes the pyrene fluorescence in the well-known structure of the Winsor I, II or III microemulsion. The fluorescence of pyrene is followed as a function of butanol concentration on different dilution lines, keeping the *N*-octylribonamide/brine–decane ratio constant. We present here the results obtained for the dilution line corresponding to a ratio of 0.25 indicated in Fig. 1. They cover a butanol concentration between 6 and 35 wt.%. By increasing the butanol concentration, the Winsor I, III and II are successively encountered. For each phase, the I_3/I_1 and I_E/I_M ratios (denoted I_3/I_1exp and I_E/I_Mexp) are measured and the composition of decane and butanol is determined by gas chromatography. The ratio between decane and butanol in each phase is calculated and the corresponding I_3/I_1cal and I_E/I_Mcal values are measured on the calibration curves. The volume of the microemulsion phase and that of the excess organic and aqueous phases are given in Fig. 3 as a function of the global butanol concentration. The excess organic phases have been shown by GPC to contain 4% butanol and 96% decane. The excess aqueous phases contain 1% C_5N_8, 1% butanol and 98% water in Winsor I, II and III. The pyrene concentration is 5×10^{-3} mol/l in the excess organic phases, in the continuous phase of W/O microemulsions and in the organic part of the bicontinuous microemulsions. The experimental fluorescence ratios I_3/I_1exp and I_E/I_Mexp measured as a function of the global butanol concentration are given in Table 1. The lower intermediate and upper phases are, respectively, denoted L, I and U. The values corresponding to the microemulsion phases are shadowed. In the excess aqueous phases, I_3/I_1exp can be measured and has a low value, the medium being highly polar. The concentration is too low in these phases to allow excimer formation; I_E/I_Mexp can thus not be measured. In the excess organic phases, the pyrene concentration is 5×10^{-3} mol/l. The values of I_3/I_1exp and I_E/I_Mexp could be measured and they correspond to the decane/butanol content of the phases given in the calibration curves (Fig. 2). The results of the microemulsion phases will now be considered in detail.

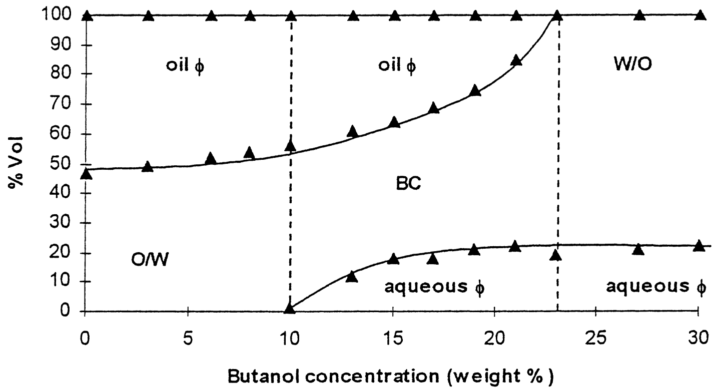

Fig. 3. Evolution of the phase volume of the ‘*N*-octylribonamide–brine–decane–butanol’ system as a function of the global butanol concentration on a dilution line, keeping the C_5N_8/H_2O (NaCl 8%) – C_{10}=0.25. O/W: oil-in-water microemulsion, BC: bicontinuous microemulsion, W/O: water-in-oil microemulsion.

Table 1
Evolution of the I_3/I_1exp and $I_EI_M$exp ratios in the lower, inner and upper phases of the polyphasic systems as a function of the global butanol concentration (wt.%) on the dilution line, keeping C_5N_8/H_2O (NaCl 8%) – C_{10}=0.25[a]

% C_4OH (global)	Number of phases	I_3/I_1exp			I_E/I_Mexp		
		L	I	U	L	I	U
6	$\underline{2}$	**1.12**		1.53	**0.55**		2.38
10	$\underline{2}$	**0.99**		1.54	**0.65**		2.34
12	3	0.63	**1.01**	1.52	–	**0.88**	2.33
16	3	0.67	**0.97**	1.51	–	**0.84**	2.36
20	3	0.70	**0.94**	1.53	–	**0.81**	2.33
24	$\overline{2}$	0.65		**1.08**	–		**1.02**
27	$\overline{2}$	0.63		**1.06**	–		**1.07**
35	$\overline{2}$	0.62		**1.02**	–		**1.17**

[a] $\underline{2}$ or $\overline{2}$ indicate that the microemulsion phases are, respectively, the lower and the upper ones.

3.3.1. *Intensity ratios of pyrene vibronic bands I_3/I_1 in the microemulsions*

Let us first remember that, in the experimental conditions used in the present work, reabsorption of the monomer fluorescence does not occur (Section 2.3). Table 2 and Fig. 4 show the evolution of the I_3/I_1cal and I_3/I_1exp ratios on the dilution line in the microemulsion phases as a function of the global butanol concentration. Table 2 also gives the decane/butanol ratio in the microemulsion phase. The limits of the different equilibrium as a function of butanol concentration are indicated. Most variations arise from change in decane and butanol contents in the microemulsion phase. Change of one microstructure to another corresponds to discontinuities in I_3/I_1exp. The comparison between I_3/I_1exp and I_3/I_1cal shows that the ratio measured in the microemulsion phase are always lower than those

Table 2
Evolution of the decane/butanol, the I_3/I_1exp, the I_3/I_1cal, the I_E/I_Mexp and the I_E/I_Mcal ratios in the microemulsion (ME) phase of the polyphasic systems as a function of the global butanol concentration (wt.%) on the dilution line keeping C_5N_8/H_2O (NaCl 8%) – C_{10}=0.25[a]

% C_4OH (global)	Number of phases	Ratio in the ME phase		I_3/I_1exp	I_3/I_1ca1	I_E/I_Mexp	I_E/I_Mcal
		% Butanol	% Decane				
6	$\underline{2}$	70	30	1.12	1.26	0.55	2.04
10	$\underline{2}$	54	46	0.99	1.13	0.65	1.83
12	3	50	50	1.01	1 10	0.88	1.78
16	3	43	57	0.97	1.06	0.84	1.69
20	3	38	62	0.94	1.04	0.81	1.63
24	$\overline{2}$	56	44	1.08	1.15	1.02	1.86
27	$\overline{2}$	52	48	1.06	1.12	1.07	1.81
35	$\overline{2}$	43	57	1.02	1.06	1.17	1.69

[a] $\underline{2}$ or $\overline{2}$ indicate that the microemulsion phases are, respectively, the lower and the upper ones.

given in Fig. 2A which were measured for the corresponding decane–butanol mixtures. As the lifetime of the excited pyrene is long, in solution, each excited molecule senses an average environment. The literature gives information about I_3/I_1 in micelles and microemulsions. In micellar solutions, the low I_3/I_1 values indicates that pyrene is not located in the hydrocarbon medium formed by the hydrophobic part of the surfactant, but can be influenced by the more polar environment of the interface [29–31]. In O/W microemulsions, the I_3/I_1 ratio is larger than in micelles but stays below the ratio measured in the corresponding solvent. This increase is attributed simultaneously to the removal of water molecules from the interface and its replacement by less polar alcohol molecules [32] and to the solubilisation of the probe in the hydrophobic core formed by the organic phase [33]. *In all 'N-octylribonamide–brine–decane–butanol' microemulsions*, I_3/I_1exp is always lower than I_3/I_1cal. The difference between the ratios is constant in the oil-in-water and the bicontinuous microemulsion, but it decreases in the water-in-oil microemulsion when the butanol concentration increases. *In the oil-in-water and the bicontinuous microemulsion*, the pyrene environment stays unchanged and the fluorescence of the probe varies as a function of the composition of the medium. *In the water-in-oil microemulsion*, the probe moves freely in the organic continuous phase. Although the medium becomes more polar (due to butanol addition on the dilution line), the average environment of pyrene is less polar because the probability of spending time near the interface decreases when the volume of the continuous phase increases. Thus, water-in-oil microemulsion can be differentiated from oil-in-water or bicontinuous microemulsion by the difference between I_3/I_1exp and I_3/I_1cal as a function of butanol concentration.

3.3.2. Excimer formation in the microemulsions

Table 2 and Fig. 5 show the I_E/I_Mexp and the corresponding I_E/I_Mcal ratios in the microemulsions following the 0.25 dilution line. On passing from one microstructure to the next one, discontinuities of I_E/I_M are observed as reported for I_3/I_1 in Fig. 4. In the three microemulsions, I_E/I_Mexp is lower than I_E/I_Mcal. In each type of microemulsion, I_E/I_Mcal decreases when the butanol concentration increases. In the bicontinuous microemulsion, I_E/I_Mexp varies

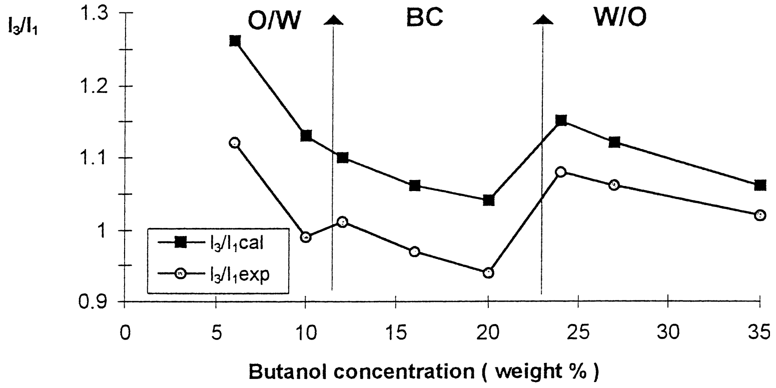

Fig. 4. I_3/I_1cal (■) and I_3/I_1exp (○) ratios as a function of the global butanol concentration on the dilution line, keeping C_5N_8/H_2O (NaCl 8%) – C_{10}=0.25. O/W: oil-in-water microemulsion, BC: bicontinuous microemulsion, W/O: water-in-oil microemulsion.

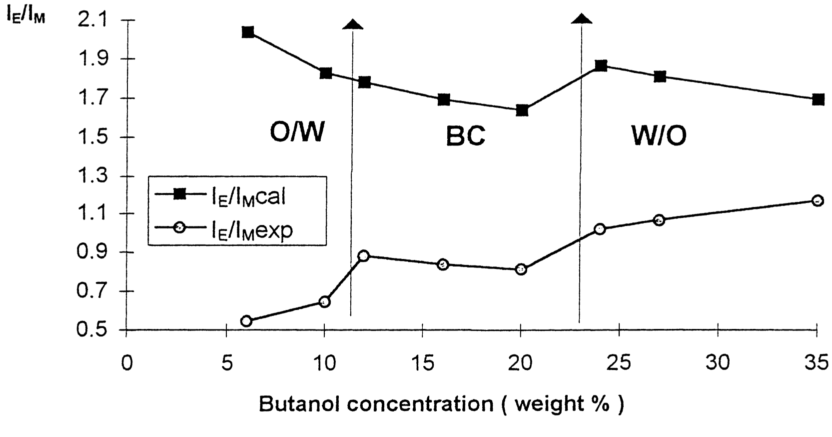

Fig. 5. I_E/I_Mcal (■) and I_E/I_Mexp (○) ratios as a function of the global butanol concentration on the dilution line, keeping C_5N_8/H_2O (NaCl 8%) – C_{10}=0.25. O/W: oil-in-water microemulsion, BC: bicontinuous microemulsion, W/O: water-in-oil microemulsion.

in the same way as I_E/I_Mcal, but in the oil-in-water and in the water-in-oil emulsion, it increases when the butanol concentration increases, whereas I_E/I_Mcal decreases. As the pyrene concentration is kept constant, these variations can be attributed to the structure of the medium. Following Eq. (3), the factors that can influence the formation of excimer are the lifetime of excited pyrene, the local concentration and the viscosity of the medium. It has been shown that the lifetime of excited pyrene in the three kinds of microemulsions remains unaltered if the samples are deoxygenated [20]. Since the ‘*N*-octylribonamide–brine–decane–butanol’ mixtures have always been deoxygenated in this work, only the local concentration of pyrene and the viscosity of the medium have to be considered. *In the oil-in-water microemulsion*, pyrene is located in the micellar core. The microviscosity of this medium will influence the formation of excimer. After measurements of I_E/I_M in solvents with different viscosities, we could determine that the I_E/I_Mexp values should correspond to a viscosity of 12–16 cP. Compared to data from the literature [34], these values are too high for O/W microemulsions. Because I_E/I_Mexp increases with increasing butanol content in the O/W microemulsion, it can be said that this low I_E/I_Mexp can not be attributed to a viscosity factor. Indeed, in this kind of aggregates, intramicellar formation of excimer is only possible if two pyrene molecules are present in the micelle; therefore, the local concentration has to be considered. Knowing the volume of the organic phase and considering an aggregation number of 85 [35], the mean number of pyrene in each micelle can be calculated. It varies from 0.10 to 0.16 on the dilution line. The local concentration of pyrene is thus too low for the formation of intramicellar excimer and as the diffusion of pyrene in water is limited, the contribution to I_E/I_M can only arise from the formation of excimer during inter-droplet collisions [20]. The probability of such collisions increases on dilution with butanol which is solubilised in the microemulsion dispersed phase and increases its volume fraction. *In the bicontinuous microemulsion*, the I_E/I_Mexp ratio becomes larger. In this structure, the connectivity of the hydrocarbon phase is larger, but the diffusion of pyrene is still limited (I_E/I_Mexp is lower than I_E/I_Mcal) [19]. I_E/I_Mexp decreases as I_E/I_Mcal in relation with the butanol content and the viscosity of the organic phase. *In the water-in-oil microemulsion*, the I_E/I_Mexp ratio increases with increasing butanol concentration. In the continuous phase of the microemulsion, the formation of excimer is nevertheless limited as I_E/I_Mexp stays smaller than I_E/I_Mcal. It has been shown that the presence of water droplets in the W/O microemulsion prevents the free diffusion of pyrene molecules in the hydrocarbon phase and decreases the possibility of excimer formation [19]. When the butanol concentration increases, the volume of the continuous phase increases and the volume fraction of dispersed water decreases. The volume accessible for the free diffusion of pyrene is larger and the formation of excimer increases, as observed in this work, in spite of the increasing viscosity of the hydrocarbon phase. Similar results were obtained for two other dilution lines.

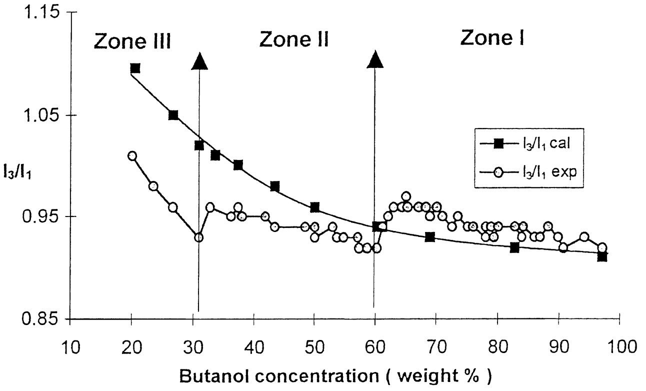

Fig. 6. I_3/I_1cal (■) and I_3/I_1exp (○) ratios as a function of the global butanol concentration on the dilution line, keeping C_5N_8/H_2O (NaCl 8%) – C_{10}=0.85.

3.4. Fluorescence in the monophasic system

The fluorescence of pyrene in the monophasic area of the phase diagram has been measured on a dilution line, keeping the *N*-octylribonamide/brine–decane constant and equal to 0.85 (Fig. 1). By increasing the butanol concentration, the three kinds of structure identified by NMR are evidenced by the presence of discontinuities in the I_3/I_1exp and I_E/I_Mexp curves (Figs. 6 and 7). They are, respectively, bicontinuous microemulsion, W/O microemulsion, and surfactant aggregates in zones III, II and I. Figs. 6 and 7 show, respectively, the I_3/I_1exp and I_E/I_Mexp ratios in the different structures. The corresponding I_3/I_1cal and I_E/I_Mcal obtained from the calibration curves and the limits of the three zones are also indicated.

In zone III of the monophasic domain, I_3/I_1exp is lower than I_3/I_1cal and the variations of the two ratios with the butanol concentration are identical. The same observations are made for the I_E/I_Mexp and I_E/I_Mcal ratios. From NMR results and from concentration area in the phase diagram, this zone has been suggested to be bicontinuous [12]. In this

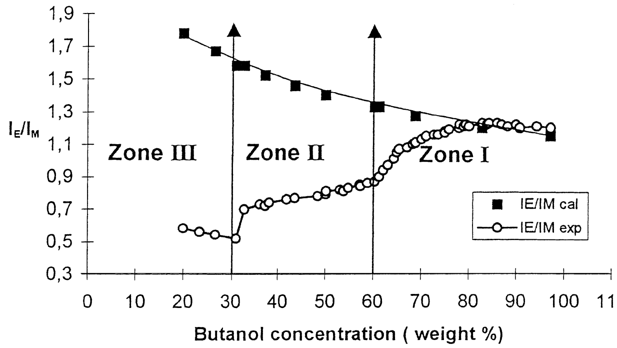

Fig. 7. I_E/I_Mcal (■) and I_E/I_Mexp (○) ratios as a function of the global butanol concentration on the dilution line, keeping C_5N_8/H_2O (NaCl 8%) – C_{10} 0.85.

structure, the pyrene is still influenced by the interface. The low I_3/I_1exp ratio is related to a higher mean polarity of the pyrene environment compared to the corresponding mixture of solvents. As shown by Rushforth et al. [36], the formation of excimer in a bicontinuous microemulsion depends neither on the viscosity nor on the lifetime of the excited pyrene but rather on the volume accessible for the free diffusion of the pyrene molecules. As in the bicontinuous microemulsion of the polyphasic system, the connectivity of the hydrocarbon phase prevents the free diffusion of pyrene, leading to low I_E/I_Mexp values.

In zone II, the I_3/I_1exp ratio decreases when the butanol concentration increases and stays lower than I_3/I_1cal; but the difference between the two ratios decreases. This evolution is the same as those observed in the water-in-oil microemulsion of the biphasic system. Pyrene molecules located in the continuous phase are still influenced by the proximity of the interface of the water droplets. However, the probability of their spending time near the polar interface decreases when the volume of the continuous phase increases with increasing butanol content. The presence of water droplets also limits the formation of excimer in this structure. Indeed, the fluorescence of excimer in the microemulsion is lower than those measured in the mixture of the corresponding solvents. However, when the butanol concentration increases, the volume fraction of water decreases and the freedom of pyrene to diffuse in the hydrocarbon phase increases. As in the Winsor II microemulsion, I_E/I_Mexp increases despite the increase in the viscosity of the medium.

Above 60% in butanol, *in zone I* of the monophasic area, I_3/I_1exp increases and becomes larger than I_3/I_1cal. Then, the two ratios evolve in the same way. Zone I has been assigned to surfactant aggregates solvated by water and butanol in a decane–butanol mixture [12]. In this structure, the fluorescence of pyrene does not depend any more on the presence of a polar interface. The aggregates do not influence the polarity of the hydrocarbon phase and the fluorescence of pyrene is the same as in the solvent mixtures. However, when aggregates are formed, butanol molecules that constitute the hydrocarbon phase are involved in their solvation, the continuous phase contains less butanol and I_3/I_1exp becomes larger than I_3/I_1cal. The same argument explains the jump in the increase in excimer formation at 60% butanol. In addition, surfactant aggregates are smaller than water droplets so that the free diffusion of pyrene is less limited. As a consequence, when the butanol concentration increases, the aggregates are diluted in the continuous phase and the I_E/I_Mexp curve reaches the I_E/I_Mcal curve. The pyrene fluorescence becomes identical to those in the mixtures of different solvents.

4. Conclusions

The study of the ‘*N*-alkylaldonamide–brine–decane–alcohol’ systems has shown that fluorescence and NMR are complementary in determining the dynamical and structural properties of the present quaternary mixtures. Indeed, NMR gives information on the molecular microenvironment and the mobility of the molecules in a given structure. By introducing a probe molecule in this structure and by measuring its fluorescence, modifications in the polarity, microviscosity and local concentration of the medium can be determined. Fluorescence has also the major advantage of being easily applicable to monophasic and to polyphasic systems.

In the present work, comparison of the pyrene fluorescence in the monophasic domain with its fluorescence in the microemulsion structures of the polyphasic areas confirms the presence of three different microstructures proposed by NMR for the monophasic region. This comparison involves the presence of discontinuities in the fluorescence functions, the variation of I_3/I_1exp and I_E/I_Mexp with butanol concentration and the difference between the experimental and calculated values of these parameters.

Because its fluorescence is very sensitive to factors such as polarity, viscosity or local concentration, pyrene has been demonstrated to be a good probe for the different microemulsion structures. In the polyphasic systems, these structures are well known and the pyrene fluorescence is easily understood after comparison of the experimental values with the values measured in mixtures of solvents. In the three microemulsions, pyrene is influenced by the proximity of the polar interface. This influence decreases in the water-in-oil microemulsion when the volume fraction of water droplets decreases. The formation of excimer in the inverse O/W microemulsion is very low because the local concentration of pyrene in the micelle is too small. In the bicontinuous microemulsion, the diffusion of pyrene is limited by the connectivity of the hydrocarbon domains, while in the water-in-oil microemulsion, the limitation is due to the presence of water droplets. When these are diluted in the continuous phase, the formation of excimer increases. In the solution of aggregates, the fluorescence tends to that measured in the solvent mixtures because the presence of the aggregates does not influence the behaviour of pyrene.

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