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Abstract Fluorescent probes incorporated in ternary surfactant systems have proved valuable in elucidating structure, dynamics and phase behaviour. The intriguing case of microemulsions using non-ionic surfactants, such as alkyloligoethylene oxides, can form phases simultaneously bicontinuous in oil and water. Fluorescence analysis provides both sensitivity and selectivity to monitor these systems. We have used pyrene and rhodamine 6G as probes to enrich our knowledge of the $C_{12}E_5$/alkane/water system, with particular relevance to the bicontinuous phase. Pyrene has been used as a dynamic probe, studying both excimer formation and quenching by molecular oxygen. This provides a useful tool to monitor transitions between microemulsion phases. Both steady state and time-resolved fluorescence measurements indicate a change in localisation on passing from one phase to another. Information was also obtained on microviscosities in these systems using fluorescence depolarisation making use of the well-known laser dye rhodamine 6G. Comparison of the fluorescence characteristics of these systems provides a means to monitor at the microscopic level changes in phase behaviour.

Keywords Anisotropy · $C_{12}E_5$ · Fluorescence · Pyrene · Rhodamine 6G

Introduction

The physical structures and phases created in microemulsions containing the non-ionic poly(oxyethylene) surfactant $C_{12}E_5$ [$C_{12}H_{25}(OCH_2CH_2)_5OH$] have generated considerable interest. The phase diagrams for $C_{12}E_5$/water/alkane systems have been extensively studied [1–3]. Particularly valuable information has come from ^{1}H-NMR self-diffusion measurements using pulsed-gradient spin echo techniques [1], where the observation of high diffusion coefficients for both water and oil indicates that neither can be in a confined environment, such as a droplet. An important feature of these systems is their ability, under certain conditions of composition and temperature, to form phases that are bicontinuous in oil and water [4, 5]. This is of both practical and theoretical importance and although experimental evidence exists for these phases [1, 2], ideas on their exact structures are still speculative. We have previously used solvatochromic fluorescence probes to investigate this region [6]. We report an extension of this study using other fluorescent probes.

Fluorescence techniques have proved useful in elucidating the shape of aggregates and the rate and dimensionality of diffusion in microheterogeneous systems [7, 8]. A molecule of particular note for use to probe this type of system is pyrene, as the ratio of the intensity of the first and third bands of its emission spectrum (I_1/I_3) provides a measure of the polarity of the local environment [9, 10]. Its ability to form excimers has also

been put to use to follow the transition through the bicontinuous region in a $C_{12}E_5$/water/tetradecane system [11]. The fact that its fluorescence lifetime and quantum yield are sensitive to the presence of oxygen also provides an interesting property for studying dynamic behaviour. We also consider the use of fluorescence depolarisation for studying fluidity in the three microemulsion regions of this system.

Experimental

Samples of the ternary surfactant systems of $C_{12}E_5$/water/tetradecane containing ca. 10^{-5} M pyrene or rhodamine 6G were prepared in the manner described previously [11] to provide samples that were (i) rich in water (*o/w*) present at 34 °C, (ii) bicontinuous in both oil and water (*bic*) present at 45 °C, and (iii) rich in oil (*w/o*), at 57 °C. These correspond to weight fractions $[C_{14}H_{30}/(H_2O + C_{14}H_{30})]$ of tetradecane of 0.1, 0.45, and 0.9, respectively.

Steady state fluorescence and absorption measurements were performed using Spex Fluorolog and Shimadzu UV-3101PC spectrometers, respectively. The time-resolved fluorescence measurements were performed using a single-photon counting spectrometer equipped with a nanosecond coaxial flashlamp filled with a nitrogen/hydrogen gas mixture for the pyrene measurements and hydrogen for the rhodamine 6G measurements. The detection of the fluorescence, monitored at a right angle to the excitation, was made using a Philips XP2020 photomultiplier. The decays and anisotropy were analysed using software provided by IBH Consultants Ltd. The pre-exponential factors (α_i) are shown normalised to 1 and the errors are taken as 3 standard deviations. The goodness of fit was judged both in terms of a chi-squared (χ^2) value and weighted residuals.

Results and discussion

Pyrene has proved to be a valuable probe molecule as the intensity ratio between the first and third emission peaks can be used to ascertain the polarity of the probes environment and confinement effects can be observed via its ability to form excimers. This coupled with the fact that the excited state lifetime is drastically affected by oxygen quenching makes pyrene a versatile probe molecule. Pyrene's excimer forming properties have been used to probe phase transitions in the ternary system of $C_{12}E_5$/water/tetradecane [11]. The transition through the bicontinuous phase (oil fraction 0.45) is clearly seen by a decrease in the excimer/monomer ratio (I_E/I_M).

In order to take advantage of the other properties (I_1/I_3 ratio and sensitivity to oxygen) preliminary measurements were performed using (ca. 10^{-5} M) pyrene in pure constituent solvents. The outcome is summarised in Table 1. This table shows that the fluorescence decay time for pyrene in pure tetradecane is significantly shorter than that obtained using $C_{12}E_5$ and that the effect of degassing is more pronounced when using tetradecane as the solvent. This can relate to high oxygen solubility in tetradecane [12]. The values obtained for the I_1/I_3 ratio confirm the less polar environment of the oil and a more polar one in $C_{12}E_5$, although this is still much lower than the value of 1.87 found for water [10].

Table 1 Fluorescence decay times for pyrene in pure $C_{12}E_5$ and tetradecane. The excitation wavelength was 340 nm and the emission was 393 nm. The effect of degassing (DG) the sample is also shown along with the I_1/I_3 ratio (range for all temperatures) from the steady state spectrum

Temp [°C]	$C_{12}E_5$			Tetradecane		
	τ/ [ns]	χ^2	I_1/I_3	τ [ns]	χ^2	I_1/I_3
34 (DG)	306.0 ± 3.0	1.06		194.9 ± 0.9	1.06	
34	134.6 ± 0.6	1.07	1.2–1.3	27.5 ± 0.12	1.19	0.4–0.6
45	115.0 ± 0.6	1.07		22.4 ± 0.13	1.26	
57	102.4 ± 0.6	1.13		18.6 ± 0.12	1.18	

Table 2 Fluorescence decay times for pyrene in $C_{12}E_5$/water/tetradecane. The effect of degassing the sample (DG) is also shown along with the I_1/I_3 ratio from the steady state spectrum

| Region	Temp [°C]	τ_1 [ns]	α_1	τ_2 [ns]	α_2	χ^2	I_1/I_3
o/w	34	10.6 ± 0.12	0.10	92.0 ± 0.45	0.90	1.18	0.96
DG	34	264.2 ± 0.8	1			1.08	
bic	49	8.6 ± 6.0	0.08	37.0 ± 0.39	0.92	1.12	0.80
DG	49	302.4 ± 1.8	1			1.03	
w/o	57	27.4 ± 21.0	0.72	37.7 ± 4.2	0.28	1.11	0.71
DG	57	231.2 ± 1.2	1			1.09	

A comparative study using the ternary system is presented in Table 2. This shows that the effect of degassing is not only limited to increasing the decay time, but also affects the number of fluorescence components required to give an adequate fit to the decay. In all cases the degassed lifetimes could be fitted to a monoexponential decay model. The recovered decay times are generally less than those obtained for pyrene in pure $C_{12}E_5$, but greater than in pure tetradecane. Given the hydrophobic nature of pyrene, this can relate to its location in the tail region of the surfactant close to the oil phase. Also the values obtained for the I_1/I_3 ratio tend to confirm this fact, although in the bicontinuous region the decay time is about the same as that obtained for pure $C_{12}E_5$.

Further information can be ascertained from the results from the corresponding aerated samples. In all three cases a sum of two exponential components was required to fit the data. A possible explanation involves the pyrene occupying environments with different oxygen concentrations (solubility) and/or quenching dimensionalities [8]. From the overall trends of the lifetimes obtained coupled with the I_1/I_3 ratio it is apparent that the pyrene has a preference for the surfactant tail region.

To see if any other trends were present in the time-resolved data the decays of the aerated samples were analysed globally by linking the decay times. The outcome of this analysis is shown schematically in Fig. 1. In order to fit the data the sum of three exponentials was required. This clearly shows that the decay time of the major fluorescent component changes depending on which region of the phase diagram is observed. The longer-lived decay associated with the o/w

region relates to pyrene situated closer to the polyoxyethylene head in the swollen micellar structures found in this region. This component becomes negligible (or non-existent) in the other regions. The shorter-lived fluorescence (major component in the w/o region) most likely relates to pyrene in bulk tetradecane. The small quantity found in the water rich region can be ascribed to pyrene deep in the micelle interior. In the bicontinuous region the major component expresses a different decay time, which can relate to movement away from the surfactant head, but because of the confinement of the surfactant the less polar environment of pure tetradecane is not achievable, except for approximately 20% of the emission ascribed to pyrene in the oil channels.

Small angle neutron scattering measurements on the water rich region show that this consists of spherical $C_{12}E_5$ micelles swollen with oil [13]. It is reasonable to assume that normal three-dimensional quenching behaviour is observed in this system, such that the decay of excited pyrene can be represented by

$$^1Py^* - k_{fl} \rightarrow Py + h\nu$$

$$^1Py^* + O_2 - k_q \rightarrow Py + O_2$$
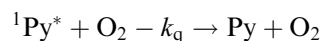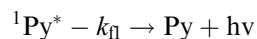
where k_{fl} contains both radiative and non-radiative components. Using the observed value for the fluorescence decay for the degassed system, the lifetime of the dominant component in the aerated o/w microemulsion (92.0 ns) and the quenching rate constant, taken as the rate of pyrene excimer formation in this phase [11], an oxygen concentration of 2.0 mM is estimated for the region where the pyrene is localised. This value is physically realistic, and lies between the oxygen solubility in aerated solutions of the ether tetrahydrofuran (2.1 mM) and the alkane dodecane (1.7 mM [12]). In contrast, using a similar treatment to calculate the oxygen concentrations in the other two microemulsion phases gives values 10.3 mM (*bic*) and 12.4 mM (*w/o*), which seem unrealistically high. A likely explanation is that there are differences in the kinetics of quenching of excited pyrene by oxygen and excimer formation. Studies on quenching of pyrene fluorescence by 3,4-dimethylbenzophenone in the L_3 phase of the $C_{12}E_5$ water binary system, which should have a very similar structure of the w/o microemulsions in the three component system, suggest the presence of regions where the probe and quencher are gathered together [8]. A similar situation may exist with pyrene excimer formation, whereas, with oxygen quenching three dimensional quenching behaviour may occur.

To provide data concerning the microviscosity of the different regions the well-known laser dye rhodamine 6G was used and the time-resolved anisotropy of this probe was measured in the three regions at different temperatures. Fig. 2 shows the outcome with the
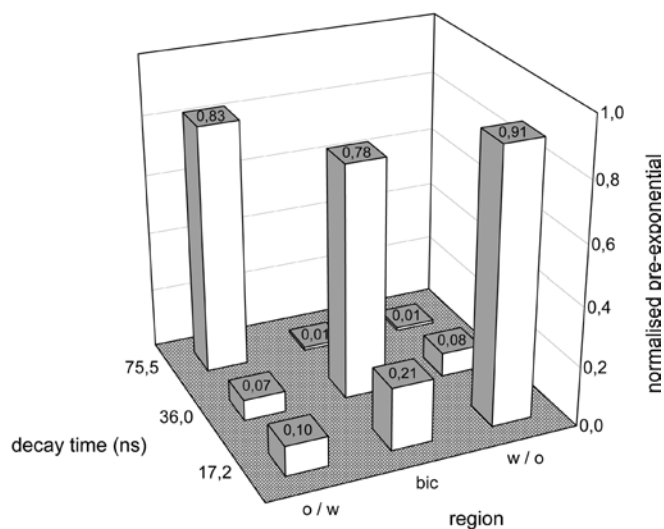

Fig. 1 Schematic representation of the global analysis of pyrene in $C_{12}E_5$/water/tetradecane showing the decay parameters. The global χ^2 is 1.13
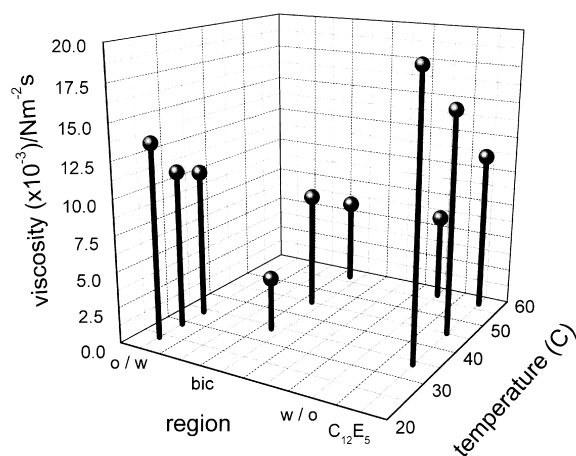
Fig. 2 The viscosity for the different ternary systems, along with that of pure $C_{12}E_5$ at different temperatures, obtained by the fluorescence depolarisation of rhodamine 6G

rotational correlation times (τ_R) converted to viscosities (η), ($\eta = \tau_R kT/V$, k is Boltzmann's constant, T absolute temperature and V is the effective volume [14]). The value obtained is probably an average microviscosity as the environment in practice is likely to be anisotropic. Generally there appears to be a decrease in viscosity with increasing the amount of tetradecane in the system. Interestingly for the bicontinuous region there

is a change in viscosity with temperature passing from the L + O to the L + W phase via the L phase where the viscosity experienced by the dye increases. Also the viscosities experienced by the rhodamine 6G are never as high as those in pure $C_{12}E_5$. As rhodamine 6G was found to only be sparingly soluble in tetradecane it is most likely situated close to the surfactant head, as the rotational correlation times recovered were longer than could be expected in bulk water. Although not as informative as the pyrene probe, rhodamine 6G is also seen to provide useful information on the dynamics of these systems.

Conclusion

In this work we have shown that by using fluorescence it is possible to monitor the different phases present in $C_{12}E_5$/tetradecane/water systems. From both the steady state fluorescence of concentrated pyrene solutions observing excimer formation and from the global analysis of aerated dilute solutions it is possible to monitor the transition from a phase rich in water to one rich in oil via a phase both continuous in oil and water.

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