



AGGREGATION OF PLURONIC F127 AND POLYDIMETHYLSILOXANE-GRAFT-POLYETHER BLOCK COPOLYMERS IN WATER AND MICROSTRUCTURE OF AGGREGATES AS EVALUATED BY MOLECULAR PROBE TECHNIQUES

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A comparative investigation of the aggregation in aqueous solution of a poly(ethylene oxide)-poly(propylene oxide)- poly(ethylene oxide) block copolymer (PEO-PPO-PPO) (Pluronic F127) with a polydimethylsiloxane-graft-polyether (PDMS-PEO) has been done. The spectroscopic parameters obtained from absorption spectra of the 4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide-2-undecyl (TEMIDO-undecyl) and fluorescence spectra of pyrene and 1,10-bis(1-pyrene)decane (PD) in aqueous solutions of block copolymers allowed the evaluation of the critical micellization concentration (CMC), its variation with temperature, as well as micropolarity and microviscosity sensed by the probe in its environment. The effect of different concentrations of *n*-hexanol, added in PDMS-PEO micelles, is evidenced by the variation of monomer and excimer parameters of the PD probe.

INTRODUCTION

Pluronic block copolymers are used in numerous applications such as cosmetics, detergency, textiles, emulsification and drug adjuvants, because of their ability to form various aggregates in water and their low toxicity.¹⁻¹⁰ The PEO-PPO-PEO block copolymers can be used to synthesize in a controlled way a wide range of nanometer-sized materials^{2,3} or as drug carriers.^{4,5} In the case of inorganic nanoparticles, the most efficient way to overcome the problem of their extreme instability is to use polymer-assisted synthesis nanoparticles.³

Siloxane surfactants are widely used in many technical applications, such as in textile manufacture, in cosmetics formulations, as agricultural adjuvants, and as paint additives.¹¹ One of the intriguing properties of siloxane surfactants, is their spontaneous spreading, so-called superspreading, on hydrophobic solid

surfaces.¹² The flexibility and the low cohesive energy of the dimethylsiloxane chain, are believed to be responsible for the unusual properties of siloxane surfactants.¹³ The aggregation and phase behavior of siloxane surfactants with various structures, for example, ABA-type or combtype molecules, is described in the literature.¹⁴⁻²⁰ The micelles formation of an amphiphilic polydimethylsiloxane-graft-polyether copolymer in aqueous solution was evidenced.²¹

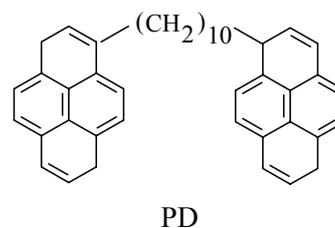
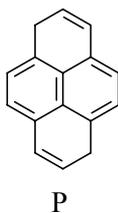
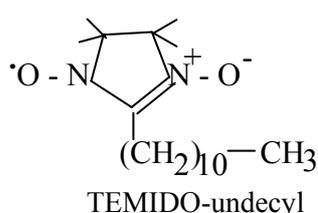
Given their multiple applications, the understanding of the block copolymers micellar microstructure is a necessity. In most of the systems studied, commercially available Pluronics and siloxane surfactants, with different structures and compositions, were compared with respect to their physicochemical properties in aqueous solutions. However, there is still a lack of systematic investigations on microstructure-property relationships of these co-polymer surfactants in aqueous solution. In the present

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work, a comparative investigation of the aggregation in aqueous solution of Pluronic F127 with a polydimethylsiloxane-graft-polyether (PDMS-PEO) has been done. For this purpose we used the methods of absorption and fluorescence (steady-state and time-resolved) spectrometry. The measured parameters of the absorption and fluorescence probe bring information on the parameters of aggregation process and on the micropolarity and microviscosity in the area of the probe solubilisation in micellar aggregate. Also, the effect of increasing amounts of *n*-hexanol added in solutions on the properties of aggregates will be highlighted.

EXPERIMENTAL

Materials. Pluronic F 127 (triblock copolymer) $(EO)_n(PO)_m(EO)_n$ (MW=12600) ($m=70$, $n=100$) from BASF Corp



Preparation of samples. The polymer solutions with various concentrations expressed as weight % or (mol/kg) were prepared by solving the copolymers in water, and were stored 24 hours before measurements. Stock solutions of the probes in ethanol or cyclohexane were prepared, of which adequate amounts were taken and thoroughly evaporated on the walls of a flask by means of a nitrogen stream. Afterwards the sample solutions were added and, after 5 minutes of stirring, were left overnight to ensure the solubilization of the probe. The final concentrations of the probes were: 7.5×10^{-5} M (TEMIDO-undecyl), 10^{-6} M (pyrene) and 1.3×10^{-6} M (PD).

UV-VIS measurements. The absorption spectra were recorded by means of a Shimadzu 2501 PC spectrophotometer at 23 °C with an accuracy of 0.2 nm, in 1 cm silica cells. The measurements have also been carried out at 20, 25, 30 and 35 °C. The absorption of TEMIDO-undecyl at λ_{\max} in surfactant solutions obeyed the Bouguer-Lambert-Beer rule over the concentration range investigated.

Fluorescence measurements. The steady-state fluorescence spectra were recorded with a SPEX Fluorolog 3 Spectrofluorimeter. The methodology followed in fluorescence lifetime measurements using time-correlated single-photon counting is the same as described before.²³ It is well known that the pyrene fluorescence spectrum is very sensitive to the polarity of the environment.²⁴ The ratio between the intensities of the first and the third vibrational peaks in the fluorescence spectrum of pyrene (I_1/I_3) is used as a measure of the polarity in the environment of the probe in

and the L7200 diblock copolymer $(Si(CH_3)_2-O)_n(EO/PO)_m$ (MW=19000), with 30% siloxane, and hydrophilic part 75%EO, 25%PO (PDMS-PEO) from Goldschmidt AG, Essen, Germany were used without purification. These two copolymers have the percentage of the hydrophilic part (70%) very close. The polymers employed for calibration of spectroscopic parameters were tetraethyleneglycol (TEG) (Loba Chemie), average molecular weight 200, and poly(propylene glycol) (PPO) (Aldrich), average molecular weight 2 000. Beside TEG and PPO, cyclic polydimethylsiloxane (PDS) (BASF), liquid paraffin/hexadecane and ethanol/water mixtures have also been utilized for calibration. Use has been made of deionized or double-distilled water.

The probes used were: 4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide-2-undecyl (TEMIDO-undecyl), (content > 97%), compound prepared by I. Drăguțan *et al.*,²² as UV-Vis absorption probe and pyrene (P) and 1,10 bis (1-pyrene) decane (PD) of special purity, as fluorescence probes, supplied by Molecular Probes, Inc.

micellar solution.^{25,26} For 1,10-bis(1-pyrene)decane, the fluorescence of the monomer is sensitive to polarity, while the intramolecular-excimer fluorescence is sensitive to the viscosity of the medium^{27,28} and can therefore be used as a viscosity sensor for synthetic polymers,²⁹⁻³¹ inner regions of membranes and micelles, etc.

Calibration procedures. To obtain information on micropolarity and microviscosity the spectral parameters in reference solutions were also measured. The values of the polarity-sensitive parameters in the absorption spectra of TEMIDO-undecyl (E , λ_{\max}) were "translated" into local hydration values by means of calibration curves representing the variation of the corresponding parameter in a set of TEG/water calibration mixtures with different w values, which represents the molar ratio $[H_2O]/[EO]$. Thus, local hydration values w_{eff} are obtained for the location of the probe in the micelles. The calibration solutions were used for all spectral measurements.

RESULTS AND DISCUSSION

In literature there are multiple CMC values, obtained by different methods and for different manufacturers and lot.³²⁻³⁷ This is why one of the aims of this work was to determine the aggregation properties of triblock copolymer Pluronic F127

and L7200, the last one being a representative of the less extensively studied poly(siloxane)-poly(ethylene oxide) diblock copolymers, PDMS-PEO. For this purpose a number of spectral parameters of the absorption and fluorescence probes were measured as a function of polymer concentration to obtain the CMC value. The temperature dependence of CMC value was also investigated. The results obtained with molecular probes in polymers solutions will be compared with the data obtained in calibration mixtures (ethanol/water and TEG/water mixtures) in order to bring information on the water distribution in the PEO part of the Pluronic F127 and L7200 micelles.

TEMIDO-undecyl is soluble in polar and nonpolar solvents and only slightly soluble in water. The spectrophotometric properties of the nitronyl nitroxide monoradicals in the UV-VIS region and their negative solvatochromism are known.³⁸

The electronic absorption spectrum is characterized by two bands. The long wavelength band, in the visible range (a $n \rightarrow \pi^*$ transition) is of low intensity and is shifted to shorter wavelengths in more polar solvents. The short wavelength band (a $\pi \rightarrow \pi^*$ transition) is more intense and also shows hypsochromic shifts with polarity of the solvent. In polar solvents, the ground state of the TEMIDO-undecyl molecule is

stabilized and the transition energy increases, which brings about the blue shift of the absorption maxima. In protic solvents, the hydrogen bonds which imply the probe N-O group play an important role in TEMIDO-undecyl solvatochromism. One can observe the shift of UV-band (I) from 357 nm in dodecane to 348 nm in 1,4-dioxane, to 323 nm in ethanol and to 313 nm in water; the visible band (II) shifts from 588 nm in dodecane to 543 nm in water. The spectral absorption measurements of TEMIDO-undecyl in various solvents have shown that the transition energies for UV band, E_T , can be used as polarity parameters.

Table 1 lists the transition energies for the absorption bands (in UV range) of TEMIDO-undecyl probe in Pluronic F127, in L7200, in various solvents and in reference solutions. To obtain transition energy values, the equation E (kcal mol^{-1}) = $28591.2 / \lambda_m$ (nm) was used.

Figure 1 shows the UV absorption spectra of TEMIDO-undecyl in aqueous solutions of Pluronic F127 (a) and L7200 (b) of various concentrations of surfactants. One can observe the bathochromic (red) shift of λ_m (maximum of the absorption band) with increasing surfactant concentration, caused by the decrease of the micropolarity in TEMIDO-undecyl environment as micelles are formed (Fig. 1 and Table 1).

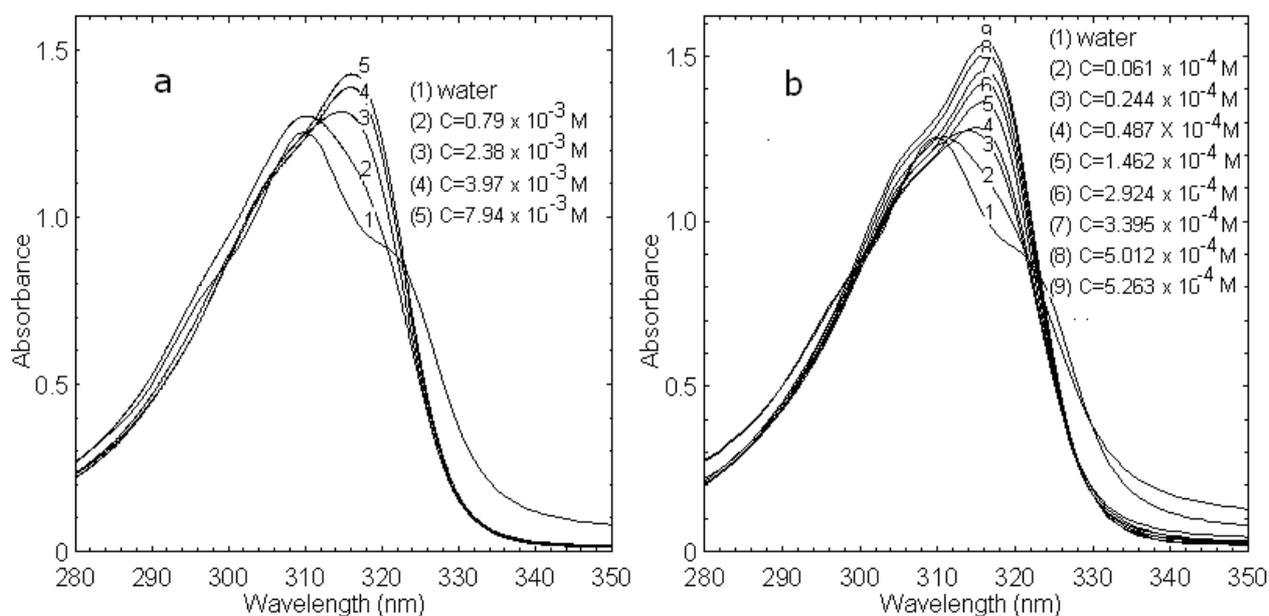


Fig. 1 – UV absorption band of TEMIDO-undecyl in aqueous solutions of Pluronic F127 (a) and L7200 (b) of various concentrations of surfactants (mol/Kg).

Table 1

Transition energies for the main UV absorption bands of TEMIDO-undecyl probe in Pluronic F127 and L7200 and reference solutions at 23 °C

System, surf. conc (10 ⁻⁴ mol/kg)	E _{UV} (kcal/mol)	Solvents and reference solutions	E _{UV} (kcal/mol)	
F 127/water 0.034	0.102	Water	92.23	
	0.325	DMF	89.29	
	0.79	n-hexanol	90.13	
	1.16	o-xylene	88.68	
	1.70	PPO	88.95	
	2.38	Ethanol	90.47	
	3.968	Ethanol/H ₂ O 90%	90.74	
	7.938	Ethanol/H ₂ O 80%	90.91	
	L7200/water 0.015	0.031	Ethanol/H ₂ O 70%	91.05
		0.061	Ethanol/H ₂ O 60%	91.20
0.122		Ethanol/H ₂ O 50%	91.34	
0.244		TEG	89.60	
0.487		TEG/H ₂ O w=0.25	89.90	
1.462		TEG/H ₂ O w=0.50	90.22	
2.924		TEG/H ₂ O w=0.75	90.47	
3.395		TEG/H ₂ O w=1.00	90.62	
3.629		TEG/H ₂ O w=1.25	90.73	
4.049		TEG/H ₂ O w=1.50	90.85	
4.386		TEG/H ₂ O w=1.75	90.96	
4.785		TEG/H ₂ O w=2.00	91.05	
5.012				
5.263				

Spectral absorption measurements of TEMIDO-undecyl in various solvents have shown that its transition energies, E_T, can be utilized as a polarity parameter similar to Kosower's Z values (transition energies corresponding to the charge transfer bands of 1-ethyl-4-carbomethoxypyridine iodide).³⁹

Thus, a good linear relationship between E_T and Z has been observed for TEMIDO-undecyl, as

described by the equations: $Z = 11.2 E_T - 936$, where E_T and Z are expressed in kcal/mol. The equation was established by measurements in ethanol/water mixtures (Fig. 2a). Using these dependences, Z values for TEG/water mixtures were obtained. Z values were plotted as a function of w (Fig. 2b).

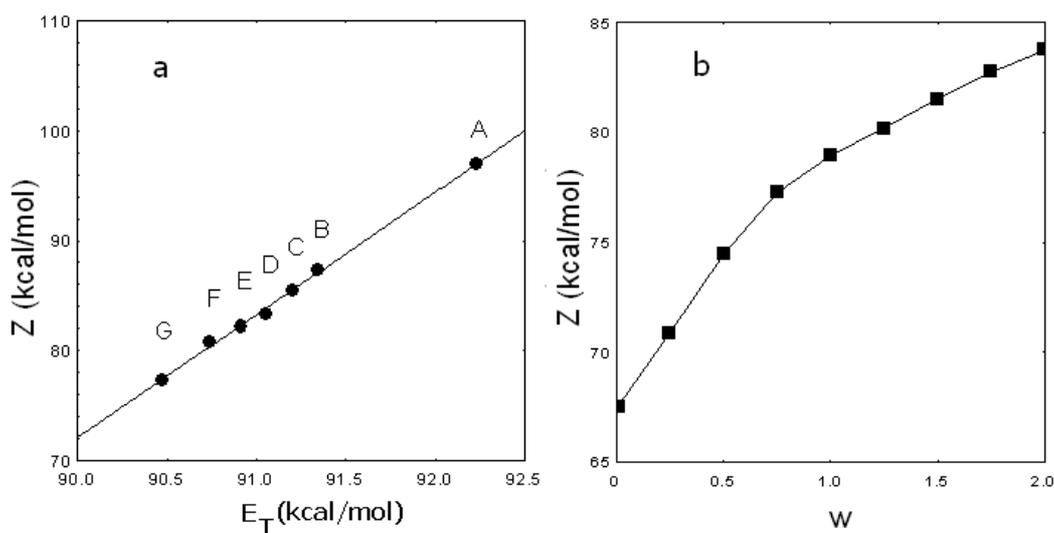


Fig. 2 – Kosower's Z values in (a) water (A); ethanol (B); 50 % v/v aq. ethanol (C); 60 % v/v aq. ethanol (D); 70 % v/v aq. ethanol (E); 80 % v/v aq. ethanol (F); 90 % v/v aq. ethanol (G) and (b) TEG/water reference system, as a function of water content, w, as determined by TEMIDO-undecyl absorption probe.

We have successfully used this relationship for measuring the micropolarity in F127 and L7200 micelles, by determination of effective water content, w_{eff} , of PEO chains.

The Kosower's Z values dependences on concentration of surfactant at 20 °C (Fig. 3a) evidence micellization by clear jumps of Z values. The micellization at 7.64×10^{-5} mol/Kg [0.1 % (wt/wt)] for Pluronic F 127/water and at 10^{-5} mol/kg [0.019 % (wt/wt)] for L 7200/water can be observed. The CMC value for Pluronic F 127 is greater than the value for L 7200 at 20°C, which is assigned to their structural differences in the hydrophobic part. To evidence the temperature dependence of CMC values, the absorption spectrophotometric measurements at 20, 25, 30 and 35 °C for F127 and L7200 have been done. The plot of Kosower's Z values corresponding to the absorption band maximum versus Pluronic F127 concentration (Fig. 3b) at different temperatures allows the CMC determination as a function of temperature.

It was shown that for L7200 there is no variation of the CMC function of temperature, due to presence of the siloxane tight coil in the surfactant structure. On the other hand, CMC was found to be temperature-dependent for the F127 surfactant. The obtained CMC values were: 7.64×10^{-5} mol/kg (20 °C), 3.22×10^{-5} mol/Kg (25 °C), 2.23×10^{-5} mol/kg (30 °C) and 1.03×10^{-5} mol/kg (35 °C) (Fig. 3b).

For polymer concentrations greater than CMC, the Kosower's Z values measured in the micellar solutions were compared to the values measured in the reference mixtures. Thus, the assignment of the probe localization in the hydrophilic micellar part, more precisely in the region of oxyethylene

chains, since the polarity is equivalent to that of TEG/water mixtures with different water contents, has been afforded.

The values of the polarity-sensitive parameter were "translated" into local hydration values by means of calibration curves, representing the variation of the corresponding parameter in a set of TEG/water mixtures with different water content, w , values (Fig. 2b). Thus, local hydration values w_{eff} are obtained for the location of the probe in the micelles.

For Pluronic F127/water micelles, the polarity indicated by TEMIDO-undecyl is greater than in L7200/water at the same polymer concentration, due to PPO chain presence in the corona of L7200 micelles.

Pyrene. The I_1/I_3 ratio of the corresponding vibrational components in the pyrene fluorescence spectrum, very sensitive to the polarity, decreases abruptly when aggregation begins and pyrene changes from water into the more hydrophobic, micellar environment. Thus this is a sensitive method to determine the CMC values. The fluorescence lifetime, τ , of pyrene increases when pyrene is solubilized in micelles and this fact can also be used to determine CMC. Figure 5 shows the dependence of I_1/I_3 and τ vs Pluronic F127 concentrations. The two curves clearly show the same CMC. The difference between the CMC values for these two surfactants also appears from pyrene fluorescence measurements: 2×10^{-5} mol/kg for L7200/water and 8×10^{-5} mol/kg for Pluronic F127/water. It is to emphasize that the CMC values for L7200 and for Pluronic F127 are of comparable orders of magnitude to the values obtained with the absorption probe TEMIDO-undecyl.

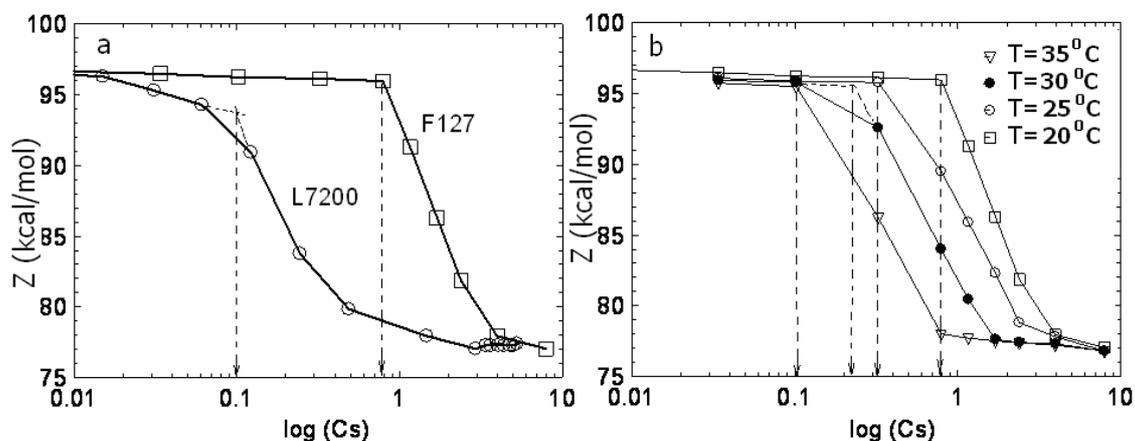


Fig. 3 – Kosower's Z values as a function of surfactant content (mol/Kg) as determined by TEMIDO-undecyl absorption probe in: (a) F127/water and L7200/water systems and (b) in F127/water system at various temperature.

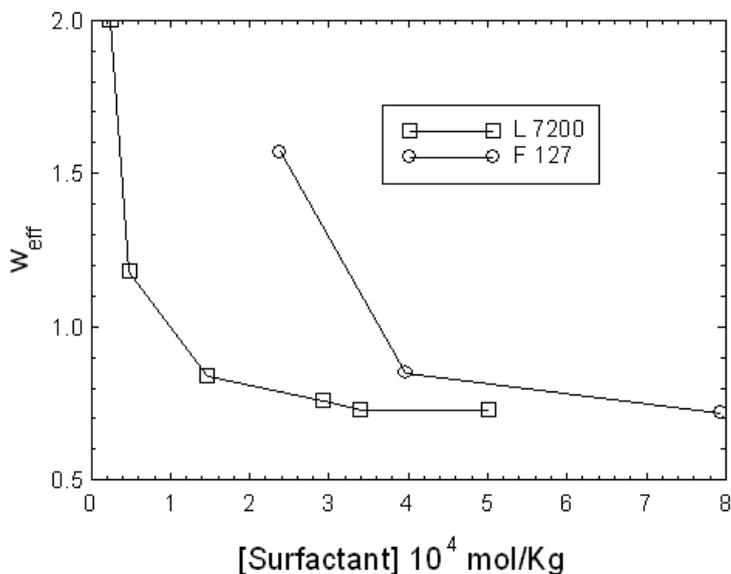


Fig. 4 – Dependence of the w_{eff} values on polymer concentration, obtained for TEMIDO-undecyl in Pluronic F127/water and L7200/water systems.

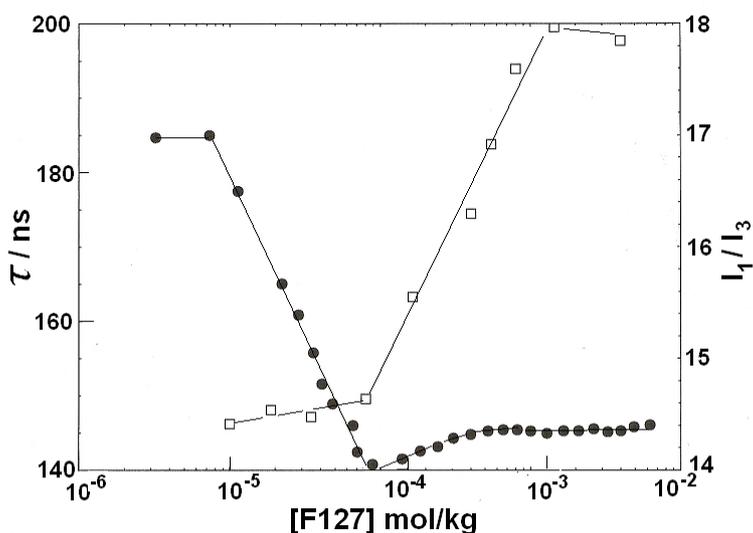


Fig. 5 – The dependence of I_1/I_3 (circles) and τ (squares) vs Pluronic F127 concentrations.

The I_1/I_3 values at concentrations greater than CMC, are similar in the two polymer aggregates: e.g. 1.46 for 10% L7200 and 1.47 for 5% F127. This means that the micropolarity sensed by pyrene in these two cases is practically the same. Values in this range are typical for polar solvents, alcohols⁴⁰. Comparing this value with the $I_1/I_3=1.15$, in the range of aromatic solvents²³, obtained for 2% $C_{12}E_8$ (octaoxyethylene glycol n-dodecylether), the conclusion is that the hydration in the interface with very long PEO chains of L7200 and F127 is higher, as compared to $C_{12}E_8$.

1,10 bis (1-pyrene) decane (PD) is more hydrophobic than pyrene, due to its molecular

structure. Therefore, it is expected to give information about a more hydrophobic micellar zone, generally for micellar core. Table 2 lists the intensity ratios for the two vibrational bands (at 377 nm and 397 nm) of the monomer fluorescence (polarity parameter) as well as the intensity ratios for the intramolecular excimer fluorescence band (at $\lambda_{\text{max}}=482$ nm) and the monomer fluorescence (at 377 nm) (microviscosity parameter). One can note from Table 2 that the I_{377}/I_{397} ratio is smaller at higher polarity, and the I_{482}/I_{377} ratio is smaller at higher viscosity. The micropolarity in the solubilization zone of the probe in 10% L7200 micellar solutions is higher than in PDS,

representing approximately the micellar “core”, and much lower than in neat TEG; it is thus very probable that the probe is solubilized in the interface region, which has an intermediate polarity between TEG and polysiloxane, the hydrophobic moiety. In the case of 20% and 35% solutions PD indicates a lower polarity than in PPO or in PDS and TEG, the probe being solubilized in micellar core.

The micropolarity measured with the same probe in the micelles of 30% L64 lies between those of TEG and PPO. According to the value of the polarity parameter, the interface is more polar

in L64 as compared to L7200. From the values listed in Table 2 some information about the microviscosity can be obtained. The microviscosity in L7200 micellar aggregates is lower than in 30% L64 micelles. It is interesting that the local viscosity in the interface region is even smaller than that of pure, short chain PEO. Also to be noted is the viscosity reduction effect of *n*-hexanol which is known to be a co-surfactant, solubilized at the interface (Table 2, Fig. 6). In the same time, one can observe a decrease of micropolarity, which can be explained by changing of the polymers packing.

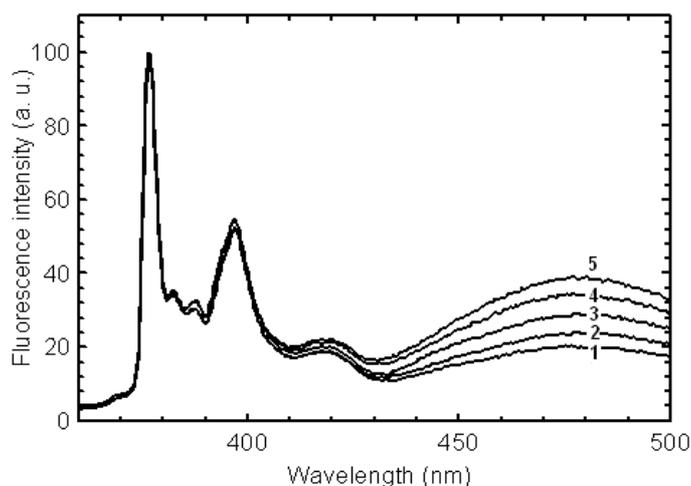


Fig. 6 – The normalized fluorescence spectra of PD in 20% L7200/water/*n*-hexanol; 0% (1); 0.7% (2); 1% (3); 1.5% (4) and 2.2% (5) *n*-hexanol.

Table 2

Fluorescence parameters for 1,10 bis (1-pyrene) decane probe in various solvents and micellar solutions

Solvents	I_{377}/I_{397}	I_{482}/I_{377}	Micellar solutions	I_{377}/I_{397}	I_{482}/I_{377}
Ethanol	1.359	1.149	10% L7200	1.676	0.265
Ethanol /Glycerine (1:1 v/v)	1.169	1.033	10% L7200 +0.7 % <i>n</i> -hexanol	1.553	0.276
Glycerine	1.123	0.305	10% L7200 +1.0 % <i>n</i> -hexanol	1.468	0.323
TEG/water w=0.0	1.174	0.075	10% L7200 +1.5% <i>n</i> -hexanol	1.444	0.353
TEG/water w=0.2	1.074	0.09	20% L7200	1.927	0.202
TEG/water w=0.5	1.074	0.197	20% L7200 +0.7% <i>n</i> -hexanol	1.907	0.250
TEG/water w=0.7	1.061	0.284	20% L7200 +1.0% <i>n</i> -hexanol	1.867	0.298
TEG/water w=1.0	1.064	0.325	20% L7200 +1.5% <i>n</i> -hexanol	1.823	0.343
TEG/water w=1.5	0.765	0.856	20% L7200 +2.2% <i>n</i> -hexanol	1.817	0.392
TEG/ethanol (1:1 v/v)	1.150	0.823	35% L7200	1.862	0.172
[Si(CH ₃) ₂ -O] ₄ (PDS)	1.665	1.419	35% L7200 +0.8 % <i>n</i> -hexanol	1.826	0.228
PPO	1.683	0.103	35% L7200 +1.5 % <i>n</i> -hexanol	1.819	0.303
Hexadecane (deoxygened)	1.722	0.916	35% L7200 +2.0 % <i>n</i> -hexanol	1.820	0.311
Hexadecane/50% liquid paraffin (deoxygened)	1.718	0.526	30% L64	1.350	.1140

CONCLUSIONS

TEMIDO-undecyl absorbance parameters clearly show at 20 °C micellization at 7.64×10^{-5} mol/kg [0.1% (wt/wt)] for Pluronic F127/water and 10^{-5} mol/kg [0.19% (wt/wt)] for L7200/water. The

fluorescence parameters (lifetime and I_1/I_3 ratio) of pyrene indicate CMC values: 8×10^{-5} mol/kg for Pluronic F127/water and 2×10^{-5} mol/kg for L7200/water.

Study of CMC's variation with temperature showed that, while for the F127 micellization

process depends on temperature, for L7200 a single CMC value was obtained for all four temperatures at which measurements were made. This can be explained by the presence of siloxane tight coil in the structure of L7200 surfactant. The CMC values determined with TEMIDO-undecyl probe in the case of Pluronic F127 are: 7.64×10^{-5} mol/kg at 20 °C, 3.22×10^{-5} mol/kg at 25 °C, 2.23×10^{-5} mol/kg at 30 °C and 1.03×10^{-5} mol/kg at 35 °C.

The Kosower's Z values measured in Pluronic F 127 and L7200 solutions above CMC, compared to those obtained in the reference TEG/water mixtures, afford the assignment of the absorption probe localization in the hydrophilic intramicellar part of the micelle, more precisely in the PEO region.

The fluorescence probe PD reveals the micropolarity and microviscosity variation with L7200 concentration and with *n*-hexanol addition, in PD' solubilisation zone, interface for 10% L7200 and micellar core for 20 and 35% L7200.

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