

## MOLECULAR PROBE TECHNIQUES IN THE STUDY OF COLLOIDAL SYSTEMS

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**abstract:** This review presents some examples obtained by molecular techniques in the study of non-ionic reverse micelles of poly(ethylene oxide) type surfactants: tetraethylene glycol mono-n-dodecyl ether (C<sub>12</sub>E<sub>4</sub>), Triton X-100, and triblok copolymers poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*- poly(ethylene oxide) (L62 and L64 Pluronics). By using specific spectral parameters of spin, fluorescence and UV-VIS probes the microenvironment characteristics: polarity, viscosity and order degree in reverse micelle were investigated. The polarity data were expressed in a common scale, to be able to compare the results obtained using different spectroscopic methods. The aggregation number of the micelles has been obtained from time-resolved fluorescence quenching method.

### Introduction

Professor Eugen Angelescu has started in Bucharest, as early as 1960, a systematic study of organic colloids, of changes in physico-chemical properties as a function of the dispersion degree in the transition from molecular to colloidal region. The way the amphiphilic molecules self-assemble and the structure of the interface was found to depend on the polarity of the solvent, concentration, temperature, polar or non-polar additives, counterions [1]. The colloidal domain, with its self-assembling systems has since been recognized to be one of the most fascinating and important research areas, revealing the basic mechanisms of Nature's ways to achieve highly organized systems.

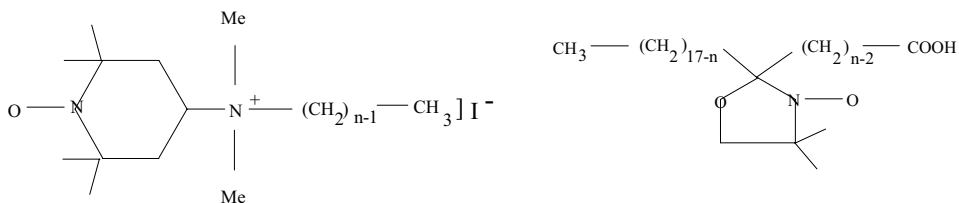
Among amphiphilic molecules, the nonionic surfactants are of significant industrial, biological and physicochemical interest. Solutions of the nonionic polyoxyethylene amphiphile have been the subject of many studies on their phase diagrams [2,3], and it is only in the last 10 years that the micellar structural and dynamical properties attracted a considerable attention. They show a wide variety of aggregation and phase behaviours in binary and ternary systems depending on concentration and temperature, such as micelles, hexagonal, lamellar and two different cubic type liquid crystals as well as reverse micelles. Whether they are alkyl ethers, alkyl-aryl-ethers or block-copolymers of the poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) type, the phase behaviour proved to be similar [4,5].

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## Results and Discussion

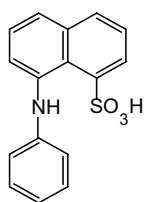
*The molecular probes* are well suited to report about the *local* values of structural parameters in these complex microheterogeneous systems. The electron paramagnetic resonance (EPR or ESR) spectroscopy of **spin probes** is a powerful technique for studying the aggregation behavior, microviscosities and local polarities, the effect of different solubilizates and the dynamics of the micellization process [6,7].



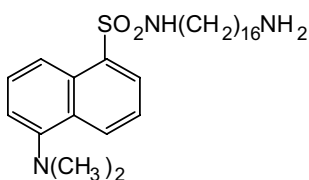
CAT *n n*-doxyl stearic acid

This possibility of using this technique for the study of different molecular structures arouses in connection with two important milestones: (i) the development of the theories describing the EPR line shapes of free radicals under different dynamic conditions [8,9] and (ii) the synthesis of stable nitroxide radicals [10÷14]. The potential for the success of the ESR method stems also from the fact that the motions associated with the aggregation of amphiphilic molecules are on a time scale that influences the ESR spectrum. Since the magnitude of the anisotropic magnetic interactions are larger in ESR than in NMR, the two techniques are sensitive to motions on different time scales. The successful use of nitroxides as spin probes has resulted from the unique possibility to vary their chemical structure without significant changes in their paramagnetic properties. Thus, the chemical structure can be adjusted according to the needs of the investigated system, while the experimental setting, the methodology used and the interpretation of the results remain basically the same. Nitroxide radicals are optimal as spin probes because their spectra, while very sensitive to the modifications of many parameters of the environment, are reasonably simple and allow a small number of parameters to be defined for the description of the radical behaviour.

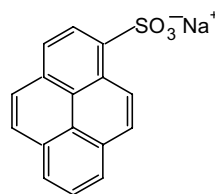
Fluorescence spectroscopy has been applied to the determination of critical micelle concentrations, micelle size and shape, micro polarity and micro viscosity, using **fluorescent probes**, whose fluorescent properties, intensities, intensity ratios, lifetimes, quenching and polarization, depend on physical parameters of the micelles [15-19]. The method is also applied for the study of the modification of these parameters with surfactant composition, concentration, temperature, interaction with different additives (salts, polymers, proteins, etc.). The fluorescent probes: 1-anilinonaphtalene-8-sulphonic acid (ANS), N-(5-dimethyl-amino-naphtalene-1-sulphonyl)hexadecyl amine (Dansyl) and pyrene sulphonic acid sodium salt (PSA), all of special purity, were used for reverse micelle characterization.



ANS

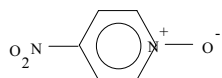


Dansyl

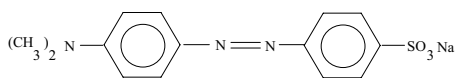


PSA

UV-Vis **absorption probes** are those molecules, which present a clear solvatochromic effect. The absorption probes, 4-nitropyridine-N-oxid (NP) and methyl orange (MO) were found suitable for studies in reverse micelles.



NP MO



### Reverse micellar (RM) systems

Systematic studies of RM systems of polyethylene oxide(PEO)-alkyl ethers, PEO-alkyl-arylethers and block-copolymers of PEO-poly(oxypropylene(PPO))-PEO series have been undertaken by using TRFQ of fluorescent probes for determination of aggregation numbers and the spin probe technique combined with other molecular probe techniques (UV-VIS, fluorescence) for structural characterization of the aggregates.

#### Determination of micellar sizes by the TRFQ method

The fluorescence quenching technique allows the determination of micellar size (see reviews [16,17,20÷22]. In order to have a good resolution of the intramicellar quenching process, the probe-quencher pair has to be selected so as to ensure that the quenching process in micelles is very rapid compared to the fluorescence lifetime of the probe. An efficient quencher should deactivate the excited probe on the first encounter. Infelta *et al.* [23] and Tachiya [24] suggested that, for small, monodisperse micelles, with a random distribution of the quencher and probe molecules among the micelles (a Poissonian distribution), and when the quencher moves between micelles during the lifetime of the excited probe, the fluorescence intensity decay according to the equations:

$$\ln [F(t)/F(0)] = -A_2 + A_3 \cdot \exp [(-A_4 t) - 1] \quad (1)$$

Where  $A_2 = k_0 + k_q \cdot k_- \cdot n / (k_q + k_-)$ ;  $A_3 = n \cdot k_q^2 / (k_q + k_-)^2$ ;  $A_4 = k_q + k_-$ ;  $k_q$  being the first-order rate constant for quenching in a micelle with one quencher,  $k_-$  the exit rate constant of a quencher leaving the micelle,  $k_0$  the unquenched decay rate of the probe fluorescence (the reciprocal of the lifetime) and  $n$  the average number of quenchers per micelle. If  $k_-$  is much less than  $k_q$  and  $k_0$ , eq. 1 reduces to [25]:

$$\ln [F(t)/F(0)] = -k_0 \cdot t + n \cdot \exp [(-k_q t) - 1] \quad (2)$$

The expressions for the parameters  $A_2$ ,  $A_3$ , and  $A_4$  are:

$$A_2 = k_0; \quad A_3 = n = [Q]/[M]; \quad A_4 = k_q$$

This is the ideal case for the determination of the aggregation numbers  $N$ .

$$N = n \cdot [S_{\text{mic}}] / [Q_{\text{mic}}] \quad (3)$$

The parameters  $k_q$  and  $n$  are estimated by fitting experimental data to eq. (2), while  $k_0$  is obtained from fluorescence decay curve without quencher. In this case the tails of the decay curves – with and without quencher – are parallel (in logarithmic representation). The "mic" subscript at S and Q indicates the surfactant and quencher concentrations in micelles.

Results obtained on poly(oxyethylene)[4]dodecylether,  $C_{12}E_4$ , in three different solvents: cyclohexane, decane, and dodecane, with various water additions are presented below [26]. The dependence of the aggregation number,  $N$ , on solvent, temperature, and water concentration, was investigated with ruthenium bipyridyl (the dichloride salt of  $Ru(bpy)_3^{2+}$ ) as probe and methylviologen ( $MV^{2+}$ ) as quencher. The radius of polar core,  $R_{pc}$ , and the surface area per polar head,  $A_{ph}$ , were calculated by the following equations:  $R_{pc}^3 = 3 N/4\pi(V_{H_2O} + V_{EO}) = N(262.8 + 30W)/4.19 (\text{\AA}^3)$ ;  $A_{ph} = (4 \pi R_{pc}^2)/N (\text{\AA}^2)$  assuming that all the water and the polyoxyethylene part of the surfactant lie within the polar core, which is spherical, monodisperse, and separated from the oil phase by a monolayer of alkyl chains of  $N$  surfactant molecules. At very low  $W = [H_2O]/[\text{surfactant}]$  molar ratio, the micelles are spherical with no water core. At higher  $W$ , a pool of free water is formed and the  $A_{ph}$  is smaller and remain independent of  $W$ . These data, supported by DLS measurements, point to a spherical shape for the micelles whose size varies between 30  $\text{\AA}$  (at  $W = 1.34$ ) and 60  $\text{\AA}$  (at  $W = 13.4$ ).

**Table 1. Calculated  $N$ ,  $R_{pc}$ , and  $A_{ph}$  Values for 15%  $C_{12}E_4$ /Oil/Water Systems at 8° C.**

H <sub>2</sub> O %	Cyclohexane			Decane			Dodecane		
	$R_{pc}$ ( $\text{\AA}$ )	$A_{ph}$ ( $\text{\AA}^2$ )	$N$	$R_{pc}$ ( $\text{\AA}$ )	$A_{ph}$ ( $\text{\AA}^2$ )	$N$	$R_{pc}$ ( $\text{\AA}$ )	$A_{ph}$ ( $\text{\AA}^2$ )	$N$
1	14.9	61.9	45	16.7	54.3	64	18.2	49.6	84
2	17.9	59.9	67	19.9	51.8	96	24.5	42.0	200
3	22.6	54.0	121	32.6	35.1	380	35.4	32.4	484
4	24.9	53.1	142	40.2	31.4	649	48.3	26.2	1121
5	29.5	51.3	213						
6	32.3	51.2	256						
7	35.5	50.5	313						
8	39.1	49.7	386						
9	41.6	50.2	433						

In conclusion, the micelle size depends on solvent nature, the aggregation being favoured in longer linear hydrocarbon. The aggregation numbers and  $R_{pc}$  increase with  $W$  and decrease with temperature.

*Polarity profiles in reverse micelles of Triton X-100*

The polarity and ordering profile in RM of Triton X-100 in cyclohexane and benzene/n-hexane have been studied with the aid of spin probe and absorption probe techniques.

*Spectral properties of NP.* The molecular absorption probe 4-nitropyridine-N-oxide (NP) is soluble in water and only scarcely soluble in non-polar solvents. Its distribution coefficient for water/cyclohexane, water/n-hexane and water/benzene are higher than 1500.

The  $\pi - \pi^*$  absorption band of NP is blue shifted with increasing polarity of the solvent [27] (for instance  $\lambda_{\max}$  is 315 nm in water, 330.2 nm in methanol and 348 nm in acetone. In protic solvents, the hydrogen bonding plays an important role in the solvatochromism of NP involving the N-oxide group. In non-hydrogen bonding solvents, dipol-dipol interaction causes a small blue-shift. In polar solvents, the ground state of the molecule is stabilized and the transition energy increases, i.g. leading to a negative solvatochromism. Spectral measurements of the NP absorption in different solvents have shown that its transition energy,  $E_{\text{NP}}$ , can be used as a polarity parameter, similar to Kosower's  $Z$  value [28]. The maxima were converted into transition energy by means of the relation (derived from  $E = h\nu$ ):  $E_{\text{NP}} (\text{kcal mol}^{-1}) = 28590 / \lambda_{\max}$ , where  $\lambda_{\max}$  is expressed in  $\text{nm}$ .

The good linear relation between  $E_{\text{NP}}$  and  $Z$ , in various solvents and solvent mixtures can be expressed as:  $Z = 3.008 \times E_{\text{NP}} - 178.4$

Clearly, NP is well suited as a polarity probe. Its small dimensions further favour its use in the study of micropolarity in reverse micelles. The polarity range covered by this probe makes it interesting for the study of the polar core in RM of poly(oxyethylene) type surfactants. Using  $Z$  values one can compare results obtained with different probes in the same system. The transition energies measured for MO in the mixtures of water with TEG and TGME were plotted against  $E_{\text{NP}}$ . Straight line was obtained and the relationship can be expressed as:  $E_{\text{NP}} = -1.68 \times E_{\text{MO}} + 194.0$

*Micropolarity in reverse micelles of Triton X-100*, using NP as a UV-VIS probe.

The absorption spectra of NP in TX (0.66 M)/cyclohexane/H<sub>2</sub>O RM, as a function of water content ( $w = [\text{H}_2\text{O}]/\text{EO}$ , molar ratio) at 298 K, show an increasing blue-shift of the absorption maxima indicating a polarity increase of the probe environment. In order to interpret the corresponding  $E_{\text{NP}}$  (and  $Z$ ) values in terms of water-distribution in the polar core, measurements have been made on a series of homogeneous TEG/water and TGME/water mixtures, for which  $E_{\text{NP}}$  and  $Z$  values have also calculated [30].

The data (Table 2) show that for both RM systems, the polarity at NP site is lower than in TEG/water mixture with the same  $w$ .

*ESR measurements of polarity profile.* The simple classification of probes into hydrophilic/hydrophobic is too coarse to describe their location in micelles and reverse micelles. Quite on the contrary, owing to the non-uniform, continuously changing composition of the aggregates of nonionic, PEO type surfactants, each probe molecule will have a different location, as a result of the fine balance of its hydrophil/hydrophobe interactions. This is even more so with amphiphilic probes.

**Table 2. Dependence of the  $\lambda_{\max}$  (nm) of NP probe on the  $w$  values in TX-100 (0.66 M) / cyclohexane / H<sub>2</sub>O, TX-100 (0.28 M) / benzene - *n*-hexane (30:70 v/v) / H<sub>2</sub>O, TEG/ H<sub>2</sub>O and TGME/ H<sub>2</sub>O systems.**

		TX-100/cyclohexane/H <sub>2</sub> O								
$w$		0.01	0.13	0.23	0.33	0.43				
$\lambda_{\max}$ (nm)		352.0	348.2	346.1	343.0	341.				
		TX-100/benzene-hexane/H <sub>2</sub> O								
$w$		0.01	0.11	0.21	0.31	0.43	0.53	0.62	0.75	0.83
$\lambda_{\max}$ (nm)		352.0	349.7	347.6	345.3	343.8	343.4	342.5	341.3	340.7
		TEG/H <sub>2</sub> O								
$w$		0.03	0.25	0.50	0.78	1.00	1.28	1.50	1.80	
$\lambda_{\max}$ (nm)		344.0	341.0	337.4	335.0	333.0	331.0	329.0	326.4	
		TGME/H <sub>2</sub> O								
$w$		0	0.10	0.25	0.50	0.85				
$\lambda_{\max}$ (nm)		353.0	352.0	350.0	347.0	343.0				

Using a series of related cationic probes, CAT *n*, has checked these ideas. All probes have the same nitroxide head bound to the ammonia group, but differ by the length of a hydrocarbon chain substituent. Thus, the  $a_N$  values, describing the local polarity can be directly compared. The probes will have different radial positions, those with the shorter chain having the nitroxide group in the most polar region.

The results in Table 3 show, indeed a polarity profile, decreasing from CAT 1 to CAT 16. The polarity values for the same water content are almost equal in the two solvent systems, but, as with CAT 4, the  $\tau_c$  values for each probe are much lower in benzene-hexane as compared to cyclohexane as a solvent.

**Table 3. ESR parameters of a series of CAT *n* spin probes in the RM systems TX-100 (0.27 M)/cyclohexane/H<sub>2</sub>O and TX-100(0.27 M)/benzene-*n*-hexane 30:70 v/v/ H<sub>2</sub>O with  $w = 0.4$ , at 295 K.**

Probe	TX/cyclohexane		TX/benzene-hexane	
	$a_N$ (G)	$\tau_c(10^{10})s$	$a_N$ (G)	$\tau_c(10^{10})s$
CAT 1	16.05	5.8	16.00	4.4
CAT 4	15.95	10.9	15.95	6.3
CAT 8	15.60	15.2	15.70	12.5
CAT 11	15.60	20.0	15.70	13.6
CAT 16	15.40	24.8	15.60	15.3

The spectral parameters of CAT *n* spin probes and of 4-nitro-pyridine-N-oxide (NP) absorption probe were related to local hydration by means of a series of PEO/water calibration mixtures and have been expressed in terms of Kosover's *Z* values. This way the relative radial positioning of all probes was established and could be compared with those of 1-methyl-8-oxyquinolinium betaine (QB) and methyl orange (MO), previously used by Schelly *et al.* [29] in the same systems. A continuous variation of the polarity in RM was evidenced, from the most polar region in the center, with the polarity of ethanol/water mixtures (CAT 1, CAT 4 and QB) to a region corresponding to tetraethylene glycol

(TEG)/water mixtures and triethylene glycol monoethyl ether/water mixtures (NP and CAT 8), to a region at the limits of the core, with the polarities of the triethylene glycol dimethyl ether/water mixtures (MO) and to still lower values, found with the 16-doxyl probe, in the corona. The different hydration dynamics at various depths in the micelles showed earlier saturation in the outer regions of the core as compared to the central regions. The 16-DSA probe evidenced the compacting and ordering effects of the water on the surfactant chains in the polar core and corona. The RM in benzene/hexane appear to have a much lower viscosity in the polar core (over the whole range of  $W$ ) as compared to those in cyclohexane. The order degree of the chains is lower too and corona appears to be penetrable by  $\text{CuX}_2$ , at variance with the cyclohexane system. All the data are consistently explained by the loosening effect of benzene, solvating the surfactant chains in the corona.

#### *Reverse micelles of Pluronic L62 and L64*

The approach described above was extended in the study of RM of Pluronic L62 ((EO)<sub>6</sub>(PO)<sub>30</sub>(EO)<sub>6</sub>) and L64 ((EO)<sub>13</sub>(PO)<sub>30</sub>(EO)<sub>13</sub>) both in ternary system (surfactant/*o*-xylene/water)[31,32]. A whole series of cationic probes, CAT  $n$  ( $n = 1, 4, 8, 11$  and  $16$ ) and  $x$ -DSA ( $x = 5, 7, 10, 12$ , and  $16$ ) were used, leading to the determination of a polarity profile of the polar core and an ordering profile of the surfactant chains. The idea of using this homologous series of probes consists in the fact that the identical nitroxide moiety ensures that  $a_N$  values vary only as a result of different surroundings [30]. The probes positioning is a result of the fine balance of the interactions of the cationic head, which is always the same, and of the hydrocarbon chain "tail", which increases in a regular fashion with  $n$ . Therefore, as the hydrocarbon chain increases, the average position of the probes will shift from the polar part, further and further from towards the hydrophobic region.

Fluorescence and UV-VIS probes were also used to check the inner consistency of the results obtained from different spectral regions. The specific spectral parameters of all probes, measured in samples with various water quantities added ( $W$ ), were referred to a common polarity scale, the one proposed by Kosower. For this purpose calibration curves were determined from measurements of the spectra of all probes in the *same* TEG/water mixtures to which  $Z$  values have been previously assigned.

The spectral measurements carried out with a wide range of molecular probes with various locations resulted in complementary and concordant conclusions regarding micellization, hydration (polarity) and microviscosity in various micellar zones at water addition, as follows: (i) water is a prerequisite for micellization: in the L64/*o*-xylene system: with no added water RM were not identified. The spin probes associate with surfactant chains, probably as unimers; starting from  $W =$  the spin probes positively detect 0.25 surfactant aggregates. The fluorescent probes yield the same minimal water quantity required for micellization:  $W = 0.4$  for L62/*o*-xylene and  $W = 0.2$  for L64/*o*-xylene systems as the spin probes; (ii) with increasing water content the polarity in the core increases, much more so in the center of the core than near the polar/apolar interface (PPO/PEO). Two regions can be distinguished in the polar core: one in which polarity is above average and increases with the quantity of dissolved water and a second region, where the polarity is below average, and at a certain water concentration saturation appears, so that polarity does not change at subsequent water dissolution; (iii) microviscosity data confirm the hydration profile, since increase of the water content brings about a decrease of the microviscosity in the middle of the core, and an increase at the polar/nonpolar interface; (iv) the values of the

polarity sensitive parameters of most probes in the reverse micelles have been “translated” into values of Kosower’s  $Z$  polarity factor. This way an ordering of all probes used was achieved, according to their hydrophobic character: Dansyl > NP > CAT16 > CAT 11 ~ ANS > CAT 8 > PSA > CAT 4 > CAT 1 (Fig. 1); (v) in the binary L62/water and L64/water systems in the  $L_2$  phase, formation of RM was proven by the polarity gradient indicated by the probes. Segregation of water is more advanced in the ternary systems than in the corresponding binary ones, the range of  $W$  values being double in the first case as compared to the second one, which points to the influence of the non-polar solvent on water distribution and is an indirect indications of the considerable solvation in the PPO region of ternary systems; (vi) the microviscosity is much lower in the ternary than in the binary systems at the same water content, owing to the considerable solvation of the PPO region, which determines a looser packing of surfactant chains, even in the PEO core; (vii) water contributes to the micellar ordering. For  $W \geq 1$  a considerable order at the polar/apolar interface and tighter packing in the corona were noted in both L62 and L64 ternary systems. In the corresponding binary systems the rather peculiar “freezing” of the surfactant chain rotation, encountered with longer PEO chains, was found at room temperature (295 K), which is not released even at higher temperature (320 K).

Fig. 1:  $Z$  values in (a) L62/*o*-xylene/water and (b) L62/water as a function of  $W$ ; the continuous line represents the calibration curve obtained with NP and PSA probes (UV-vis determinations) in TEG/water mixtures.



## Conclusion

The molecular probe technique, using specific spectral parameters of spin, fluorescence and UV-VIS probes, provide important information in reverse micelle regarding microenvironment characteristics: polarity, viscosity and order degree.

The "location" of the probe has been established using reference solutions, and the polarity data were referred in a common scale (Kosower's polarity factor), to be able to compare the results obtained using different spectroscopic methods, and the results were concordant.

The aggregation number of the micelles has been obtained from time-resolved fluorescence quenching method. For the reverse micelles investigated, the aggregation numbers and  $R_{pc}$  increase with  $W$  and decrease with temperature. The solvent has an important role on the size of the micelle.

## REFERENCES

1. Angelescu, E. and Popescu, G. (1960) *Studii si Cercetari de Chimie* **VIII**, 565-78; (1961) **IX**, 447-57; (1961) **IX**, 593-601; Angelescu, E. (1962) *Revue de Chimie* **VII**, 655-63.
2. Sjoblom, J., Stenius, P. and Danielsson, I. (1987) **Nonionic Surfactants, Physical Chemistry**, Vol. 23, Schick M.J. (Ed), Marcel Dekker, New York, 369.
3. Degiorgio V. (1985) **Physics of Amphiphilies, Micelles, Vesicles and Microemulsions**, Degiorgio V. and Corti M. (Eds), North-Holland, Amsterdam; Magid J. (1987) **Nonionic Surfactants: Physical Chemistry**, Vol. 23, Schick M.J. (Ed), Marcel Dekker, New York.
4. Almgren, M., Brown, W. and Hvidt, S. (1995) *Colloid Polym. Sci* **273**, 2.
5. Alexandridis, P. and Hatton, T.A. (1995) *Colloid and Surfaces A* **96**, 1.
6. Caldararu, H. (1998) *Spectrochimica Acta Part A* **54**, 2309.
7. Wasserman, A.M. (1994) *Russ. Chem. Rev.* **63**, 373.
8. Kivelson, D. (1960) *J. Chem. Phys.* **33**, 1094.
9. Freed, J.H. and Fraenkel, G.K. (1963) *J. Chem. Phys.* **39**, 326.
10. Hoffmann, A.K. and Henderson, A.T. (1961) *J. Am. Chem. Soc.* **83**, 4671.
11. Lebedev, O.L., Khidekel, M.L. and Razuvaev, G.A. (1961) *Dokl.Akad.Nauk SSSR* **140**, 1961.
12. Neiman, M.B., Rozantsev, E.G. and Memedova, Yu.G. (1962) *Nature* **196**, 472.
13. Rozantsev, E.G. (1970) *Svobodnie Iminoxylnie Radicali*, Khimia, Moskva.
14. Briere, R., Lemaire, H. and Rassat, A. (1964) *Tetrahedron Lett.* **27**, 1775.
15. Caldararu, H., Carageorghopol, A., Vasilescu, M., Dragutan, I., Vasilescu, M. and Lemmetynen, H. (1994) *J. Phys. Chem.* **98**, 5320.
16. Almgren, M. (1992) *Advanced in Colloid and Interface Science* **41**, 9.
17. Almgren, M. (1991) **Kinetics and Catalysis in Microheterogeneous Systems, Surfactant Science Series**, Vol. 38, Grätzel M. and Kalyanasundaram K. (Eds), Marcel Dekker, New York, 63.
18. Winnik, F.M. (1993) **Interaction of Surfactants with Polymers and Proteins**, Goddard E.D. and Ananthapadmanbhan K.P (Eds), CRC Press, Boca Raton, FL, Chapter 9.
19. Winnik, F. M. and Regismond, S.T.A. (1996) *Colloids Surfaces A: Physicochem. Eng. Aspects* **118**, 1.

20. Lang, J. (1990) **The Structure, Dynamics and Equilibrium Properties of Colloidal Systems**, Bloor D.M. and Jones W. E. (Eds), Kluwer Academic Publishers, Dordrecht, 1-38.
21. Van der Auweraer, M. and De Schryver, F.C. (1990) **Inverse Micelles Studies in Physical and Theoretical Chemistry**, Vol. 65, Pileni M. (Ed), Elsevier, Amsterdam, 70-102.
22. Gehlen, M.H. and De Schryver, F.C. (1993) *Chem. Rev.* **41**, 9.
23. Infelta, P.P., Grätzel, F. and Thomas, J.K. (1974) *J. Phys. Chem.* **78**, 190.
24. Tachiya, M. (1975) *Chem. Phys. Lett.* **33**, 289.
25. Infelta, P.P. (1979) *Chem. Phys. Lett.* **61**, 88.
26. Vasilescu, M., Caragheorgheopol, A., Almgren, M., Brown, W., Alsins, J. and Johannsson, R. (1995) *Langmuir* **11**, 2893.
27. Gafney, B.J. (1976) **Spin Labeling I**, Berliner, L.J. (Ed.), Academic Press: New York, San Francisco, London, 567.
28. Knauer, B.R. and Naples, J.J. (1976) *J.Am.Chem.Soc.* **98**, 4395.
29. Seelig, J. (1976) **Spin Labeling I**, Berliner, L.J. Ed., Academic Press: New York, San Francisco, London, 373.
30. Caragheorgheopol, A., Bandula, R., Caldararu, H. and Joela, H. (1997) *J. Mol. Liquids* **72**, 105.
31. Vasilescu, M., Caragheorgheopol, A., Caldararu, H., Bandula, R., Lemmetyinen, H. and Joela, H. (1998) *J. Phys. Chem.* **102**, 7740.
32. Vasilescu, M., Caragheorgheopol, A. and Caldararu, H. (2001) *Adv. Colloid and Interface Science* **89-90**, 169.