Colloid & Polymer Science Colloid Polym Sci 272:1166–1173 (1994)

ESR study on the stability of W/O gel-emulsions

V. Rajagopalan[1]), C. Solans[2]), and H. Kunieda[1])

[1]) Department of Physical Chemistry, Division of Materials Science and Chemical Engineering, Yokohama National University, Hodogaya-ku, Yokohama, Japan
[2]) Departamento de Tensioactivos, CID, C.S.I.C., Barcelona, Spain

Abstract: W/O gel-emulsions (high-internal-phase-volume-ratio emulsions) form in water (or brine) /tetraethyleneglycol dodecyl ether/heptane system above the HLB (hydrophile-lipophile balance) temperature of the system. A salt, which largely decreases cloud temperature in a water-nonionic surfactant system, makes the surfactant film rigid and the gel-emulsions hence become very stable. The effect of added salt on the apparent order parameter "S," and the isotropic hyperfine splitting constant "a_N" in gel-emulsions was determined by the ESR spin probe method using 5-doxyl stearic acid as the spin probe. The apparent order parameter "S," and the isotropic hyperfine splitting constant "a_N" increase with increasing salinity in Na_2SO_4, $CaCl_2$, and NaCl systems. It is considered that the surfactant molecules are tightly packed in these systems and this tendency is highly related to the stability of gel-emulsions. The salt dehydrates the hydrophilic moiety of surfactant and hence the lateral interactions of surfactant molecular layer at the water-oil interface increases.

The observed difference in the apparent order parameter between the ordinary emulsions and the gel-emulsions suggests that most of the surfactant molecules are adsorbed at the oil-water interface (the surface of the water droplet) in gel-emulsions.

Key words: Gel-emulsions – ESR spin-probe method – order parameter – isotropic hyperfine splitting constant – correlation time – stability

Introduction

It is known that clear gels showing a predominant elastic rheological behavior form in very diluted regions of some nonionic surfactant systems [1–6]. These gels are of the utmost interest for practical purposes such as cosmetics, drug formulation, jet fuel, etc. [6–9]. Gels have been found in both the oil-rich and water-rich regions of ternary, water/nonionic surfactant/oil systems, and are high-internal-phase-ratio emulsions or highly concentrated emulsions [10]. Due to their characteristic features, they are also referred to as gel-emulsions [11–17].

The early investigations in the area of highly concentrated emulsions were mainly concerned with geometric packing constraints [1, 2, 5] and rheological properties [2, 5, 18, 19] of O/W type emulsions. Systematic studies on the corresponding W/O type emulsions were undertaken more recently [11–15]. Lately, a growing interest in this subject has developed, and the aspects such as formation [11–13, 20–22], stability [15, 23–25], macro- and microstructure [16, 26–30], and rheological properties [17, 31] of both highly concentrated O/W and W/O emulsions have been intensively investigated.

In order to form the W/O gel the nonionic surfactant should be lipophilic and it is formed above the HLB temperature of the system. Our studies on W/O gel emulsions showed that they consist of two isotropic phases. The dispersed phase which is a submicellar surfactant solution in water, and a continuous phase which is a swollen reverse micellar solution or W/O microemulsion [12]. These gel emulsions can be formulated with a large amount of water (i.e., higher than 99% w/w) and very low surfactant concentration (i.e., lower than 0.5% w/w) [12].

It is also seen that the viscosity and the stability of these gels change significantly on the addition of salt and also depend on the type of salt [15]. A salt which largely depresses the cloud temperature of nonionic surfactant aqueous solution, causes a significant stabilization of the gel-emulsions. In our previous paper [15], we had suggested the increase in packing of surfactant film at water-oil interface upon addition of salt to be the cause for the gel stability, but this has not been directly verified yet.

Spin-labeling technique has been extensively used in the past to study biological systems [32, 33] and, also in micellar chemistry, to study the structural [34, 35] and dynamic properties [36–41] of micelles. The ESR spectra of spin probes have provided valuable information about the dynamic nature of the association of monomers in micelles, the dynamics of solubilization of compounds by micelles, and the rate of motion of solubilizates within micelles. In biological systems the interest has been to study the correlation time, apparent order parameter, and the isotropic hyperfine splitting constant which is related to the rotational mobility of the spin label and therefore indicates the local fluidity of membranes such as lipids, etc. Thus, ESR has proved to be a very good tool for the study of micellar chemistry, biological systems and, in general, colloid science.

In this context, we have used the ESR spin probe method to study the packing of surfactant molecules in gel-emulsions by measuring the apparent order parameter and the isotropic hyperfine splitting constant, and by varying the water content and the salinity of the systems.

2. Experimental section

2.1 Materials

Homogeneous tetraethyleneglycol dodecyl ether (abbreviated as $R_{12}EO_4$) was kindly supplied by Nihon Surfactant Co. Heptane was obtained from Tokyo Kasei Kogyo Co. Sodium chloride, calcium chloride (dihydrate), and sodium hydroxide were obtained from Junsei Chemical Co. Sodium sulfate (anhydrous) and potassium iodide were obtained from Wako Pure Chemical Industries Ltd. and the spin probe, 5-doxylstearic acid was obtained from Molecular Probes Inc. All the materials were used without further purifications and double-distilled water was always used for all experimentation purposes.

2.2 Methods

2.2.1 Preparation of gel-emulsions: The surfactant ($R_{12}EO_4$) and the spin probe were weighed in the ratio of 100:1, respectively, and then shaken in a vortex mixer for about 5 min until we obtained a clear homogeneous mixture of the surfactant and spin probe. It is this mixture of spin probe and surfactant that is used for the preparation of gels and for all further experimentations.

Gel-emulsions were prepared by shaking a test tube containing oil, water or aqueous solution, and surfactant with the spin probe. If necessary, the formation of gels was aided by the presence of glass beads to enhance the local agitation [12].

2.2.2 ESR measurements: The ESR measurements were recorded using JEOL-FE1XG and JEOL-ME-3X spectrometers with 100 KHz field modulation. Since the present systems contain a large amount of water, a capillary tube (ϕ = 1.54 mm) was used to avoid heating of the sample by microwave radiation.

In order to determine the free rotation time of this spin probe (5-doxylstearic acid) in water, we had prepared a solution of 0.001 M NaOH in which the spin probe concentration was kept fixed at 2×10^{-4} M and the free rotation time was determined. The addition of NaOH was necessary in order to dissolve the spin probe in water. The ESR spectra was recorded (Fig. 3(a)) and the correlation time was calculated according to the following formula [42]:

$$\tau_c = 6.6 \times 10^{-10} \Delta H_{(m=+1)} [(I_{m=+1}/I_{m=-1})^{1/2} - 1]s\,, \qquad [1]$$

where $\Delta H_{(m=+1)}$ is the width of the low field line, $I_{m=+1}$ and $I_{m=-1}$ are the peak heights of the low field and high field lines, respectively.

The correlation time was determined to be 1.85×10^{-10} s which is consistent with the results obtained by an earlier author [43].

In order to make sure that there does not exist any interaction between the individual spin probes, we had prepared two samples. One in which the surfactant to spin probe weight ratio was 100:1, and the other in which the surfactant to spin probe weight ratio was 1000:1; both the samples had heptane in the appropriate ratio ($R_{12}EO_4$/heptane = 0.415/0.585). The correlation times in the two cases were determined to be 2.27×10^{-10} s and 2.29×10^{-10} s, respectively, thus very clearly indicating the non existence of any interaction between the individual spin probes and, henceforth, the surfactant to spin probe ratio was maintained at 100:1 for all further experimentation.

The anisotropic spectras were characterized by using the apparent order parameter S given by the following equation [44]:

$$S = (a_0/a_N)\,(A_{\|}-A_{\perp})/(A_{zz}-1/2(A_{xx}+A_{yy})), \qquad [2]$$

where the principal values of the hyperfine splitting tensor [45] were taken as $A_{xx} = 6.3$ G, $A_{yy} = 5.8$ G, $A_{zz} = 33.6$ G. The polarity correction factor involves $a_0 = 1/3(A_{xx} + A_{yy} + A_{zz}) =$ 15.23 G and $a_N = 1/3(A_{\|} + 2A_{\perp})$. The isotropic hyperfine splitting constant a_N is a measure of the polarity of the spin label.

2.2.3 VEM (Video Enhanced Microscopy): A differential interference phase-contrast (Nomarski-type) microscope (Nikon, X2F-NTF-21) with a video-enhanced system (Hamamatsu Photonics Co., Argus 10) was used to observe gel- and ordinary emulsions.

3. Results and discussion

3.1 Phase behavior in a gel-emulsion system

A nonionic surfactant changes from water soluble (forming a micelle in water) to oil soluble (forming a reverse micelle in oil) with rise in temperature. This transition temperature of the solution behavior is called the hydrophile-lipophile balance (HLB) temperature. At this temperature the three phases consisting of surfactant, water, and oil phases appear and the type of emulsion changes from O/W type to the W/O type. Therefore, it is also called the phase inversion temperature (PIT). At temperatures above the PIT, the surfactant acts as a lipophilic one, i.e., a W/O emulsifier, whereas below the PIT it acts as a hydrophilic one, i.e., an O/W emulsifier. A highly concentrated W/O emulsion can be formed in the water-rich region of a ternary system above its HLB temperature. Since the HLB temperature for the $R_{12}EO_4$/heptane system is 14.0 °C, gel-emulsions can be formed at temperatures below the room temperature to about 50 °C.

Phase diagram of a water/$R_{12}EO_4$/heptane system at 25 °C is shown in Fig. 1. Two-phase region consisting of oil phase and excess water is extended from a water-oil axis. Surfactant is mainly dissolved in oil and forms reverse micelles. Therefore, tie lines are focused to a water apex in the two-phase region. There is a region including liquid crystal (LC) in the vicinity of a water-surfactant axis, but the details are omitted.

W/O type emulsions can be formed in the main two-phase region by mere hand shaking. The W/O emulsion close to the water apex includes a large amount of water, and the system is very viscous and translucent; due to these properties it is called a gel-emulsion or highly concentrated emulsion. As the volume fraction of excess water (internal phase) exceeds that of closest packing of spheres, the water droplets are not spherical but polyhedral, as is shown in Fig. 2. The structure of

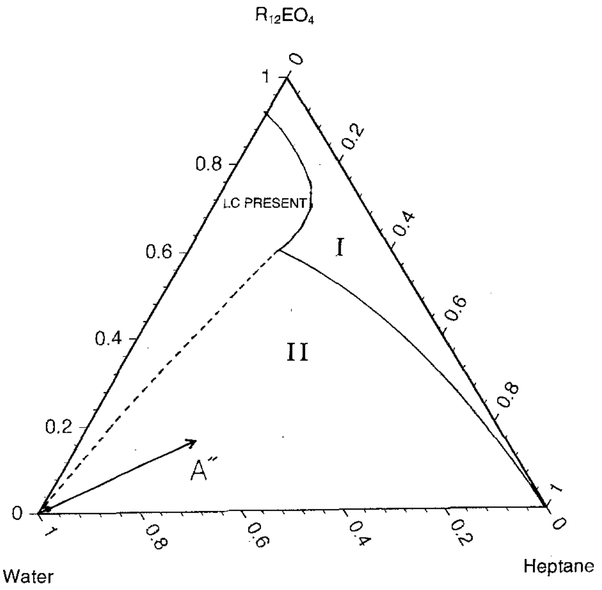

Fig. 1. Phase diagram of a water (or brine)/$R_{12}EO_4$/heptane at 25 °C. I and II represent isotropic one- and two-phase regions

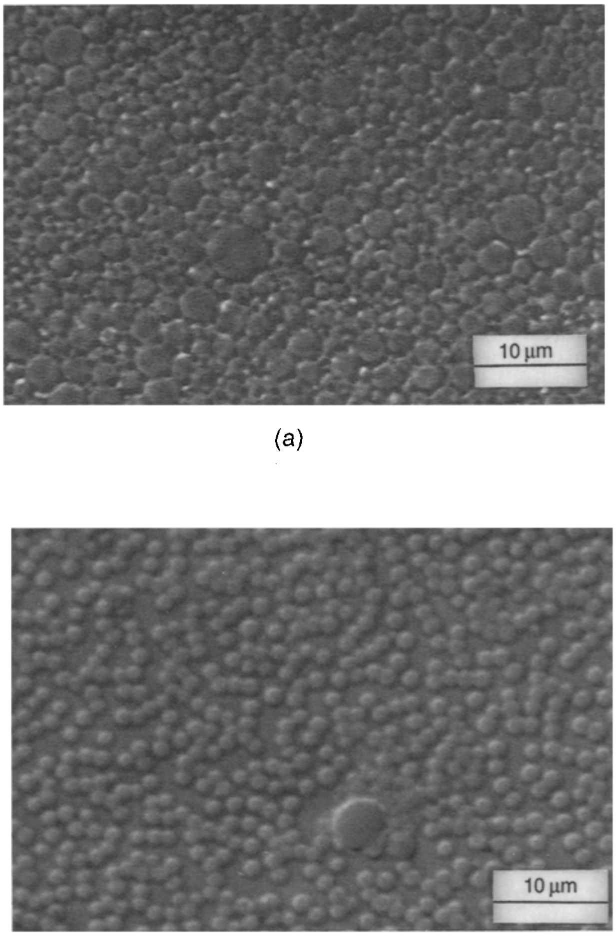

Fig. 2. VEM pictures of a) gel-emulsion at the filled circle in Fig. 1, composition: $R_{12}EO_4$ + heptane is 1.20 wt% and water is 98.80 wt%, and b) ordinary W/O emulsion, composition: the $R_{12}EO_4$/heptane ratio is 0.415/0.585 and 36.9 wt% water

gel-emulsions resembles that of aged foams and the water droplets are covered by a very thin continuous phase, an oil phase. Therefore, the interfacial area is very large, although the volume of the oil phase is very small.

3.2 *Change in apparent order parameter and the isotropic hyperfine splitting constant in the presence of salt*

The addition of salt to various experimental systems has been an area of interest for researchers because the addition of salts has invariably brought about significant changes in the structural parameters of the systems. Gel-emulsions are not in equilibrium state and with time they break into two isotropic phases. The gel-emulsion region indicated by a filled circle near the water apex in Fig. 1 is unstable and the separation of excess water (internal phase) is observed within 1 h. It is known that the addition of some inorganic salts stabilize the W/O type gel emulsion [15]. Not only do the salts stabilize the gels, but in addition they also shift or change the solubilization curve because the HLB temperature decreases on the addition of salts like NaCl [28].

The effect of added salt on the stability of highly concentrated W/O emulsions was found to be dependent on the type of added salt [15]. Salts which have large salting-out effect decrease the cloud point in water-nonionic surfactant system, and are more effective in stabilizing gel-emulsions. Thus, it is seen, as expected, that Na_2SO_4 $CaCl_2$ and NaCl stabilize the gel-emulsion, whereas KI destabilizes the gel-emulsions (Fig. 5 of ref. [15]). The change in properties of polymers due to the addition of salts has been experimentally verified [46, 47]. The lateral interactions of surfactant molecules increase due to the dehydration of the hydrophilic portion of the surfactant in the presence of salt; as a consequence, the droplet film becomes more rigid. These deductions have been confirmed by interfacial tension measurements and rheological determinations [17, 29]. Addition of NaCl was found to produce an increase in interfacial tension between aqueous (internal) phase and microemulsion (continuous) phase in emulsion. In fact, it was also found that the parameters that lead to an increase of the interfacial tension (temperature, salinity, oil-to-surfactant ratio) produced analogous effects on storage (elastic) modulus, G′ [17, 29]. This means that the interfacial film becomes more rigid, thus enhancing the stability of gel-emulsions.

Although the salting-out of the surfactant is observed upon addition of salt, the surfactant is still in a liquid state, even at very high salinity. In fact, in a psuedo-binary brine-surfactant system, the cloud temperature is below 0 °C at 20 wt% Na_2SO_4 and the surfactant is not dissolved in water, but, instead of solid, a liquid surfactant phase is separated from water at room temperature.

The gel-emulsions were prepared for a composition inside the filled circle in Fig. 1 and all the ESR spectra recorded at the same composition except for the salinity. The ESR spectra in 10 wt% NaCl, 20 wt% NaCl systems are shown in Figs. 3(b) and (c). The anisotropic ESR spectra suggest a change in the apparent order parameter S and the isotropic hyperfine splitting constant a_N, suggesting an increase in the packing of the hydrocarbon chains.

We also see that the high field line of the anisotropic spectra broadens significantly. The degree of restriction of the spin label is reflected in the high field line, which has appreciably broadened. The broadening of the anisotropic spectra leads to a noticeable reduction in the peak-to-peak amplitude. The high field line has the shortest relaxation time and hence is most sensitive to the changes in the mobility of the spin label. The distance between the low field and high field lines does not significantly change by a very large value for all our spectra, thus suggesting that although the packing of surfactant molecules increases, the fluidity of the surfactant films at the water-oil interface does not change significantly. This fact also suggests that there is negligible interaction between the doxyl moiety and the hydrophilic part of the surfactant [48]. In other words, the surfactant films do not resemble liquid crystalline-like or solid-like structure, but are in a liquid state as far as the rigidness is concerned. Thus, the above observation confirms the packing of the hydrocarbon chains to be the cause for the stability observed in these systems.

The data was analyzed according to Eq. (2) and the results are as shown in Fig. 4. Figure 4 very clearly shows that in the case of Na_2SO_4 there is a sizeable change in the apparent order parameter S as compared to the $CaCl_2$ and NaCl added

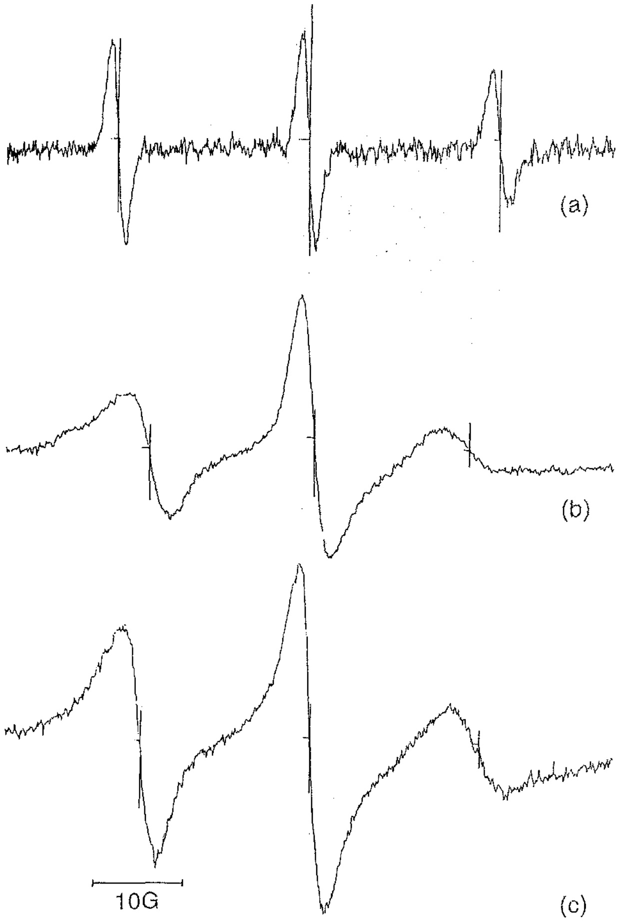

Fig. 3. The ESR spectra of a) 5-doxylstearic acid in NaOH isotropic solution, b) 10 wt% NACl, and c) 20 wt% NaCl in gel-emulsions. The compositions of gel-emulsions are the same as that in Fig. 2(b) except for the salinity

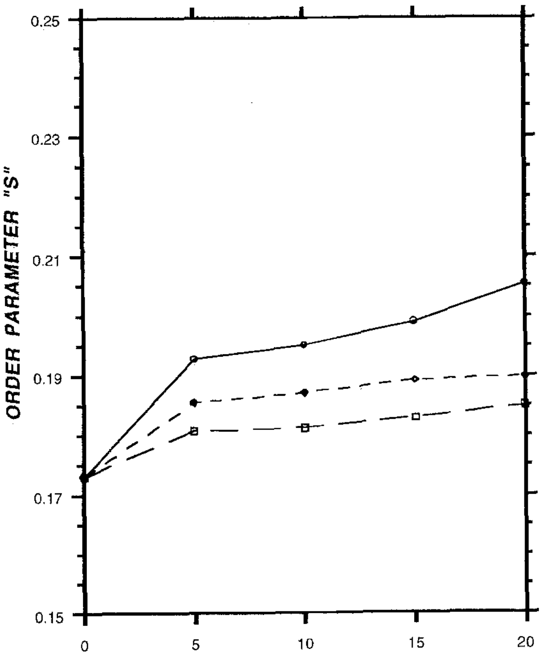

Fig. 4. Apparent order parameter S in gel-emulsions as a function of added salt concentration in water, (□) NaCl, (◇) $CaCl_2$ and (o) Na_2SO_4. Composition : $R_{12}EO_4$ + heptane 1.2 wt% and water or aqueous solution 98.8 wt%

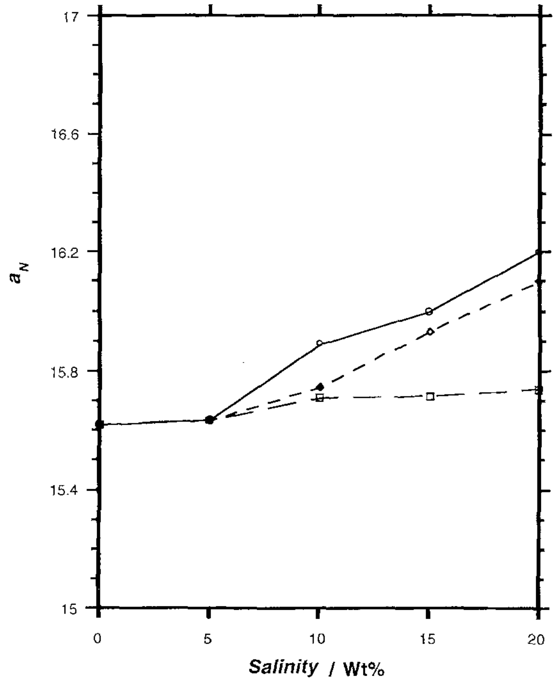

Fig. 5. Isotropic hyperfine splitting constant a_N in gel-emulsions as a function of added salt concentration in water. (□) NaCl, (◇) $CaCl_2$, and (○) Na_2SO_4. Composition: $R_{12}EO_4$ + heptane 1.2 wt% and water or aqueous solution 98.8 wt%

systems. The apparent order parameter S in the case of KI could not be determined because the spectrum does not seem to be well defined and, hence, the calculation was not possible due to the fact that the spectra of the high field line is very broad and it looks as if there is a superposition of the spectra from the interface and the reverse micellar state. Namely, gel-emulsion in the KI system is too unstable for measurement of the ESR spectra. The change in the isotropic hyperfine splitting constant a_N, as shown in Fig. 5, is also consistent with the above conclusion.

The above results also show that the type and the concentration of the added salt do significantly change the packing of the hydrocarbon chains of surfactants in the gels and it is this packing that gives rise to stability in these systems. In addition, the above results are in good consistency with the stability versus added salt concentration graph that has been published earlier [15]. Consequently, salt which decreases a cloud temperature stabilizes the gel-emulsions because the surfactant layers at the water-oil interface (water droplet film) are tightly packed.

It is well known that some inorganic salts stabilize even ordinary W/O emulsions [49]. The present conclusion may also be applicable to the ordinary emulsions.

3.3 Difference in structures of continuous medium in gel-emulsion and oil phase

If we fix the surfactant to oil ratio and draw the tie line to the water apex (line A″ of Fig. 1) we gradually proceed from the one-phase to the two-phase and then the gel emulsion region with increasing water concentration. We have performed a series of experiments along this line in order to follow the change in structure. The phase boundary was determined for the water, 10% Na_2SO_4, 10% NaCl, and 10% $CaCl_2$ systems, and the ESR spectra were recorded for all the systems well into their emulsion phase. The reason for performing this experiment was: It is believed that only a small percentage of reverse micelles exists in the continuous media (oil phase) of gel-emulsions because the interfacial area is extremely large when compared to the volume of the oil phase, and most of surfactant molecules are adsorbed at the oil-water interface (water droplet film). Although this result is well supported by the small-angle x-ray scattering data [29, 50], we still wanted to make sure that the resonance observed is from the interface and not from the reverse micelle in the continuous media. To achieve this end, the ratio of oil to surfactant was held fixed and the ESR spectra recorded for various concentrations of water, 10% NaCl, 10% $CaCl_2$, and 10% Na_2SO_4 aqueous solutions. The variations in the apparent order parameter and the isotropic hyperfine splitting constant with concentration are shown in Figs. 6 and 7 respectively.

As there is no self-organizing structure at an oil-surfactant axis in the absence of water [51], the ESR spectra is fairly isotropic; however, the degree of anisotropy increases as the water content increases. The reason for the increase in spectral anisotropy is mainly due to the two types of processes prevalent; namely, the Brownian tumbling of the reversed micelles and the lateral diffusion of surfactant molecules along the interface. These two processes modulate the hyperfine coupling tensor, A, and the g tensor. When the frequency of the two averaging processes falls

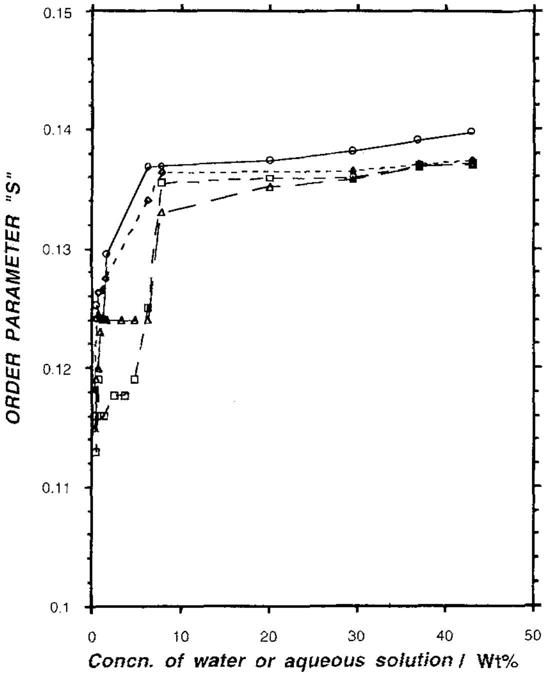

Fig. 6. The effect of added water (or salt solution) on the apparent order parameter S in oil phase (the line A″ in Fig. 1). (□) NaCl, (◇) $CaCl_2$, (o) Na_2SO_4, and (△) water. The $R_{12}EO_4$/heptane ratio is fixed at 0.415/0.585.

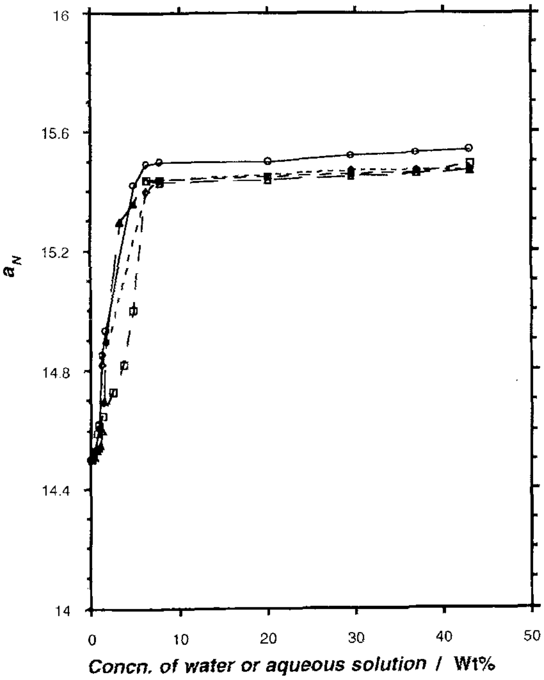

Fig. 7. The effect of added water (or salt solution) on the isotropic hyperfine splitting constant a_N in oil phase (the line A″ in Fig. 1). (□) NaCl, (◇) $CaCl_2$, (o) Na_2SO_4, and (△) water. The $R_{12}EO_4$/heptane ratio is fixed at 0.415/0.585.

below 10^8 s^{-1}, the resulting spectra is isotropic. As the size of the reversed micelles increases with increasing water content, Brownian tumbling decreases and the frequency of the averaging processes falls below 10^8 s^{-1}, which is not rapid enough to average out the anisotropies. This results in highly anisotropic spectra for the high water content systems. Such spectra are normally discussed in terms of the apparent order parameter. Order parameters provide information regarding the degree of organization of the surfactant molecules and the hyperfine splitting constant a_N, is used as a measure of the polarity of the spin label environment. Figure 7 illustrates the variation of a_N with water content. With increasing water content a_N increases, indicating that the environment of the spin label changes from an apolar one to a more polar one. The change, as expected, is more pronounced in our case because the doxyl group in the spin probe used 5-doxyl stearic acid, which is closer to the COO– group. This could be due to the molecular and segmental motion and the penetration of water into the surfactant layer, both of which will contribute to the increase in a_N with increasing water content. This behavior is not unexpected if one considers the model of the reverse micelle to be like the one proposed by Haering et al. [48].

At water contents higher than the solubilization limit for each of the systems phase separation occurs and the excess water phase is separated. Judging from Fig. 1, the composition of oil phase at the phase separation is practically the same as that of continuous media in the gel-emulsion because the dilution path is along the tie line. We have measured the ESR spectra in the emulsion state. If the spin probe is in the same state in a single reverse micellar phase or in a gel-emulsion, the order parameter should then be equal. However, we see that the maximum value of the order parameter in Fig. 6 is smaller than the minimum value for the order parameter of Fig. 4.

The spin probe is incorporated in reverse micelles at the maximum solubilization point in Fig. 6. On the other hand, in the gel-emulsion system, most surfactant molecules are at the water-oil interface (water droplet film) because surfactant concentration is very small (0.5 wt%)

and large interfacial area exists as is shown in Fig. 2(a). Therefore, it is considered that a very small number of reverse micelles is present in the continuous media in gel-emulsions and the spin probe mainly exists at the water-oil interface (water droplet film). In fact, the above-mentioned arguments suggest that in the case of gel-emulsions the spin probe molecules exist only in one state, and that is at the interface.

Consequently, we have separately observed the difference in order parameters at the water droplet film in gel-emulsions and the inside of the reverse micelles in the single isotropic phase. The surfactant molecules at the water droplet film can be considered to be more tightly packed when compared to those in reverse micelles.

Acknowledgements

The authors would like to gratefully acknowledge the help rendered by Prof. M. Yagi, Mr. Wada, and Mr. Senoue in recording the various ESR spectra, and Dr. Teruo Horiuchi of LION Corporation for his very useful suggestions and guidance. We also thank Mr. M. Akimaru (Nihon Surfactant Co.) for supplying pure tetraethyleneglycol dodecyl ether.

References

1. Lissant KJ (1966) J Coll Interf Sci 22:462
2. Lissant KJ, Mayhan KG (1973) J Coll Interf Sci 42:201
3. Groves MJ, Mustafa RMA and Carless JE (1974) J Pharm Pharmacol 26:616
4. Ali AA, Mulley BA (1978) J Pharm Pharmacol 30:205
5. Princen HM (1979) J Coll Interf Sci 71:55
6. Sagitani H, Hattori T, Nabeta K, Nagai M (1983) Nippon Kagaku Kaishi 1399
7. Attwood D, Florence AT (1983) in "Surfactant Systems" Chapman and Hall, New York
8. Ishida H, Iwama A (1984) Combust Sci Tech 37:79
9. Bampfield A, Cooper J (1988) in Encyclopedia of Emulsion Technology" Becher, (Ed), Marcel Dekker, New York Vol 3, 381
10. Princen HM (1988) Langmuir 4:486
11. Solans C, Azemar N, Comelles F, Sanchez Leal J, Parra JL (1986) Proc XVII Jorn CED/AID, 109
12. Kunieda H, Solans C, Shida N, Parra JL (1987) Coll and Surf 24:225
13. Solans C, Azemar N, Parra JL (1988) Prog Colloid Polym Sci 76:224
14. Solans C, Dominguez JG, Parra JL, Heuser J, Friberg SE (1988) Colloid and Polym Sci 266:570
15. Kunieda H, Yano N, Solans C (1989) Coll and Surf 36:313
16. Kunieda H, Evans DF, Solans C, Yoshida M (1990) Coll and Surf 47:35
17. Pons R, Solans C, Stebe MJ, Erra P, Ravey JC (1992) Prog Colloid Polym Sci 89:110
18. Princen HM (1983) J Coll Interf Sci 91:160
19. Princen HM, Kiss AD (1986) J Coll Interf Sci 112:427
20. Sebba F (1987) In: Foams and Biliquid Foams-Aphrons. John Willey and Sons Ltd
21. Rehage H, Platz G, Ebert G (1988) Bunsenges Phy Chem 92:1152
22. Mukesh D, Das AK, Ghosh PK (1992) Langmuir 8:807
23. Ruckenstein E, Ebert G, Platz G (1989) J Coll Interf Sci 133:432
24. Williams JM (1991) Langmuir 7:1370
25. Kizling J, Kronberg B (1990) Coll & Surf 50:131
26. Ravey JC, Stebe MJ (1989) Physica B 394:156
27. Ravey JC, Stebe MJ (1990) Prog Colloid Polym Sci 82:218
28. Solans C, Pons R, Zhu X, Davis HT, Evans P, Nakamura K, Kunieda H (1993) Langmuir 9:1479
29. Pons R, Ravey JC, Suvage S, Stebe MJ, Erra P, Solans C, Coll & Surf (in press).
30. Södderman O, Lonnqvist I, Balinov B (1992) in "Emulsions – A Fundamental and Practical Approach" Sjoblom (Ed), Kluwer Academic Publishers, Netherlands pp-239
31. Princen HM, Kiss AD (1989), J Coll Interf Sci 128:176
32. McConnel HM, McFarland BG (1970) Quart Rev Biophys 3:91
33. Smith ICP (1972) in "Biological Applications of Electron Spin Resonance" Swartz HM, Bolton JR, Borg DC, (Ed), Wiley-Interscience, New York pp. 483–539
34. Waggoner AS, Griffith OH, Christensen CR (1969) Proc Nat Acad Sci U.S. 57:1198
35. Waggoner AS, Keith AD, Griffith OH (1968) J Phys Chem 72:4129
36. Artherton NM, Strach S (1972) J Chem Soc Faraday Trans II 68:374
37. Brotherus J, Tormala P (1973) Kolloid ZZ Polym 251:774
38. Fox KK (1971) Trans Faraday Soc 67:2802
39. Nakagawa T, Jizonoto H (1972) Kolloid ZZ Polym 250:594
40. Oakes J (1971) Nature 231:38
41. Ohnishi S, Cyr TJR, Fukushima H (1970) Bull Chem Soc Japan 43:673
42. Martinie J, Michon J, Rassat A (1975) J Am Chem Soc 97:1818
43. Yoshioka H (1978) J Coll Interf Sci 66:352
44. Graffney BJ (1976) in "Spin Labelling" Berliner LJ, (Ed), Academic Press, New York pp.567
45. Graffney BJ, McConnel HM (1974) J Magn Reson 16:1
46. Lundberg RD (1966) J Polymer Sci. 4:1563
47. Hermes GG, Swann JC (1967) Biochemistry 6:1591
48. Haering G, Luisi P, Hauser H (1988) J Phys Chem 92:3574
49. Suzuki Y, Tsutsumi H (1989) Nikka No 10:1693
50. Pons R, PhD Thesis, (1992) University of Barcelona.
51. Olsson U, Jonströmer M, Nagai K, Söderrman O, Wennerström H, Klose G (1988) Progr Colloid Polym 76:75

Received August 5, 1993;
accepted January 20, 1994

Authors' address:

Hironobu KUNIEDA
DR. Eng., Associate Professor
Department of Physical Chemistry
Division of Materials Science and
Chemical Engineering
Yokohama National University, Tokiwadai 156
Hodogaya-ku, Yokohama 240, Japan