

Determination of Size Parameters of Water-Aerosol OT-Oil Reverse Micelles from Their Nuclear Magnetic Resonance Data

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The fraction of bound water in the water core, water core radius, thickness of the bound water layer, and effective head-group area of the surfactant of H₂O-Aerosol OT-isooctane and H₂O-Aerosol OT-cyclohexane reverse micellar droplets have been calculated from the aggregation parameters and chemical shifts of water proton resonance data. The calculated values agree quite well with those reported in the literature. It has been concluded that because of the flexibility of the surfactant molecule particularly due to internal rotation about the C-C bond of the ethane skeleton of the succinic acid part, the system can form very stable water/oil (w/o) microemulsions, particularly in isooctane media. The droplets have surfactant monolayer thickness of about 9-11 Å except in the micellar region and in the region where it forms large microemulsion droplets. In the former case the packing constraint does not permit all the surfactant molecules of the droplets to remain exactly at the interface. Hence, some of the surfactant molecules remain outside the interface and thereby increase the thickness of the AOT monolayer to a value of about 15 Å. In the latter case the system is stabilized by dissolving solvent molecules in the monolayer so that the effective length of the surfactant in the droplet is largely increased. Detailed calculation of the packing factor, $v/(f_{\text{AOT}}l_c)$, of the surfactant for various sizes of the droplets has been made and was found to be above one, the favorable condition for the formation of w/o microemulsions.

Introduction

The size, shape, and other aggregational parameters of H₂O-AOT-oil reverse micelles have been determined by various techniques.¹⁻¹⁰ In some of these methods like ultracentrifugation, fluorescence spectroscopy, etc. the equilibrium micellar systems are perturbed and the results obtained are sometimes incoherent. In order to study the unperturbed system, capillary viscometry, classical light scattering, photon correlation spectroscopy, etc. have been successfully used to determine the size and shape of the aggregates. These methods are macroscopic and ignore any microscopic events such as rotation of the surfactant molecules in the aggregated system. The heterogeneous water present in the aqueous core of the droplet is a subject of considerable interest from the point of view of their catalytic activities, particularly reactivities of enzymes dissolved in it,¹¹ which supports the importance of the determination of bound water and free water in w/o microemulsion droplets. Recent observations on rotational isomerism of the AOT molecule and its dependence on the amphiphilicity in various systems^{12,13} have shown that the water-binding capacity of the surfactant depends on the composition of the rotamers of AOT existing in a particular system. Accurate determinations of the mean average aggregation number \bar{n} , of the droplets have been reported in the literature,^{4,7,8} and recently Eicke et al.¹⁴ have shown that the theoretical estimates of the polar

head-group area of AOT compared favorably with those calculated from the experimentally determined mean average aggregation numbers. In this paper it has been shown that when the above aggregational parameters of the droplets are available, a detailed evaluation of size parameters of the water core of AOT reverse micelles is possible from the NMR data which are of direct consequence of the rotational isomerism of the surfactant molecule.

The w/o microemulsion droplets have been shown to consist of a water core with diameter depending on the amount of dissolved water, and the aqueous core is surrounded by the monolayer of interfacial surfactant film.¹⁵ Detailed NMR investigating for AOT reverse micelles have been reported by various authors,^{5,16-19} and recently Eicke²⁰ from water proton NMR studies of H₂O-AOT-isooctane demonstrated the existence of three distinct states of water—bound water, trapped water, and apparently free water—existing in the water core of the microemulsion droplet. Because of the rapid exchange, the observed chemical shifts of water proton resonances are the sum of the weighted average chemical shifts of protons in various states of water. Strongly bound water molecules exhibit proton chemical shifts in a relatively upfield direction whereas the chemical shifts of proton resonances of apparently free water appear toward downfield, approaching that of ordinary water. If one assumes monodispersity and spherical shape of the reverse micellar droplets with a structure similar to that shown in Figure 1, it can be said that the observed chemical shifts of water proton magnetic resonances are the sum of the weighted average shifts of the bound water protons and free water protons present inside the droplet, i.e.

$$\delta_{\text{obsd}} = P_B \delta_B + P_F \delta_F \quad (1)$$

where δ_{obsd} , δ_B , and δ_F are the observed chemical shifts and the chemical shifts of bound and free water protons, respectively. P_B and P_F are the mole fractions of bound and free water, respectively, inside the water core. The presence of water molecules, if any,

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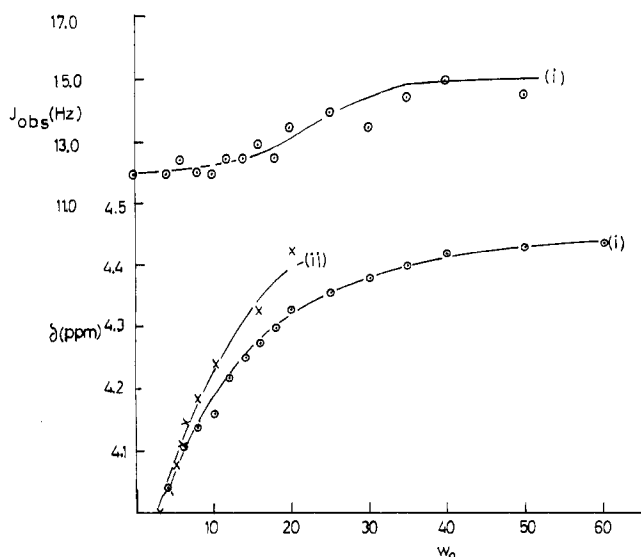


Figure 1. Variation of water proton chemical shifts and observed coupling constant values, J_{obs} , with w_0 in H_2O -AOT-oil reverse micelles: (i) H_2O -AOT-isooctane and (ii) H_2O -AOT-cyclohexane.

outside the micelles is, however, neglected. Substituting $P_F = 1 - P_B$, one obtains from eq 1

$$P_B = \delta_{\text{obsd}} - \delta_F / (\delta_B - \delta_F) \quad (2)$$

The fraction of interfacially bound water, P_B , can also be represented as a function of water core size from purely geometrical consideration as

$$P_B = 1 - (1 - d/r_w)^3 \quad (3)$$

where d is the thickness of the bound water and r_w is the radius of the water core inside the micelles. Equation 3 can be rearranged as

$$d/r_w = 1 - (1 - P_B)^{1/3} \quad (4)$$

From the hard-sphere model concept of a reverse micelles,²¹ the relation between P_B and various size parameters can be made as follows.

If \bar{n} is the mean average aggregation number of the surfactant per droplet and n_B and n_F are the number of bound and free water molecules, respectively, present in the water core of each droplet, then one can write

$$\bar{n}w_0 = n_B + n_F$$

where w_0 is the molar ratio of water and AOT in the system. But $P_F = n_F/(\bar{n}w_0)$ and hence

$$\bar{n} = n_F / (P_F w_0) \quad (5)$$

If r_F is the radius of the free water core within the water pool, then

$$n_F = \frac{4}{3}\pi r_F^3 / 30$$

since 30 \AA^3 is the volume of a water molecule in bulk water. Substituting the value of n_F in eq 5, one obtains

$$\bar{n} = \frac{\frac{4}{3}\pi r_F^3}{30P_F w_0} = \frac{\frac{4}{3}\pi (r_w - d)^3}{30(1 - P_B)w_0} \quad (6)$$

If f_{AOT} is the effective head-group area of the AOT molecule at w/o interface in the droplet at a particular w_0 , then it can be represented as

$$f_{\text{AOT}} = 4\pi r_w^2 / \bar{n} \quad (7)$$

Substitution of \bar{n} in eq 7 gives

$$f_{\text{AOT}} = 90r_w^2 w_0 (1 - P_B) / (r_w - d)^3$$

which on rearranging gives

$$r_w (1 - d/r_w)^3 = 90w_0 (1 - P_B) / f_{\text{AOT}}$$

If one substitutes the value of d/r_w from eq 4, the value of r_w comes out to be

$$r_w = 90w_0 / f_{\text{AOT}} \quad (8)$$

Replacing f_{AOT} from eq 7 in eq 8 by \bar{n} , one gets

$$r_w = \left(\frac{90w_0 \bar{n}}{4\pi} \right)^{1/3} \quad (9)$$

Once the values of P_B and r_w are known, a straightforward calculation of bound water thickness, d , can be made from eq 4.

Experimental Section

Materials and Purifications. Sodium bis(2-ethylhexyl)sulfosuccinate, i.e. AOT (Fluka AG), of pharmaceutical grade purity was additionally purified by the method described elsewhere.¹² Solvents were of AR grade, and they were dried before use. Double-distilled water was used for preparing microemulsions.

NMR Spectra. All spectra were recorded on a 60-MHz Varian EM360 high-resolution spectrometer. Tetramethylsilane was added as an internal reference for chemical shift measurements. The instrument was locked at Me_4Si frequency for field/frequency stabilization. AOT solutions (0.1 mol/L) were used for taking spectra. The partial spectra of AOT were retraced on an expanded scale. The separation of the doublets was measured from the spectra on an expanded scale. J_{obsd} , the observed coupling constant, values were calculated as described earlier¹² and were reported in hertz. Chemical shifts were, however, reported in ppm. The calculated values of chemical shifts (in ppm) were corrected up to the third place of the decimal.

Results and Discussion

The observed chemical shifts of water proton resonances are shown in Figure 1. The fraction of bound water layer, P_B , water core radius, r_w , thickness of the bound water layer, d , and head-group area of surfactant molecule, f_{AOT} , have been calculated from eq 2, 9, 4, and 7, respectively, and the results of the systems H_2O -AOT-isooctane and H_2O -AOT-cyclohexane are shown in Tables I and II, respectively. The hydrodynamic radii of the droplets in these systems as reported by Eicke et al.⁶ and Day et al.⁷ are also incorporated in these tables, and they have been used for calculations of the packing parameters of the surfactant molecules in the droplets. The difference, $r_h - r_w$, calculated for H_2O -AOT-isooctane system with $w_0 < 10$ comes out to be about 15 Å, the thickness of the surfactant monolayer, l_c , in the droplet. The value agrees quite well with that reported by Eicke et al.⁶ l_c , however, decreases with increasing w_0 to a minimum value of 9 Å. With further increase of the droplet size the calculated values of l_c increase once again and are found to be considerably larger than the formal length of the AOT molecule.³ The thickness of the surfactant monolayer in the H_2O -AOT-cyclohexane system was found to be about 11 Å with a little variation in the higher w_0 ranges. Day et al.⁷ estimated the l_c values for H_2O -AOT-cyclohexane systems by the viscometric method and found about 9 Å, although an earlier reported value for the formal length of the AOT molecule was about 11 Å.³ This shows that the effective surfactant length in the microemulsion droplet is dependent on the water content as well as on the nature of the bulk solvent. The variation is probably due to various stereospecific orientations of the surfactant molecule at the w/o interface. Calculated values of the polar head-group area, f_{AOT} , in both the systems agree quite well with those reported in the literature.^{4,8,9} The thickness of the bound water layer, d , is also influenced by the water/surfactant ratio. In the entire microemulsion region, this thickness lies between 3 and 5 Å with the minimum at the maximum droplet size. It can reasonably be assumed that the bound water is composed of water molecules hydrogen bonded to the negatively charged surfactant membrane layer as well as coordinated to

TABLE I: NMR Data and Size Parameters of the H₂O-AOT-Isooctane System

w_0	δ , ppm	P_B	\bar{n}^a	r_h , ^b Å	r_w , Å	l_c , Å	d , Å	f_{AOT} , Å ²	$v/(f_{AOT}l_c)$
4	4.030	0.78	35	25	10	15	3.96	35.9	3.25
6	4.090	0.68	50	28	14	14	4.42	42.5	2.70
8	4.140	0.60	72	32	16	16	4.21	44.7	2.30
10	4.180	0.53	98	34	19	15	4.22	46.3	2.00
12	4.220	0.47	129	37	22	15	4.19	47.1	1.84
14	4.250	0.42	176	40	26	14	4.32	48.4	1.63
16	4.275	0.37	215	42	29	13	4.14	49.3	1.51
18	4.300	0.33	257	43	32	11	4.00	50.0	1.38
20	4.320	0.30	302	44	35	9	3.92	51.0	1.28
25	4.360	0.23	447	52	43	9	3.59	52.0	1.22
30	4.380	0.20	613	62	51	11	3.66	53.3	1.23
35	4.400	0.17	778	76	58	18	3.49	54.2	1.34
40	4.415	0.14	965	98	65	33	3.18	56.8	1.57
50	4.430	0.11	1380	118	79	39	3.00	56.8	1.57

^a Data taken from ref 4. ^b Data taken from ref 6.TABLE II: NMR Data and Size Parameters of the H₂O-AOT-Cyclohexane System

w_0	δ , ppm	P_B	\bar{n}^a	r_h , ^a Å	r_w , Å	l_c , Å	d , Å	f_{AOT} , Å ²	$v/(f_{AOT}l_c)$
1	3.910	0.98	27	17	6	11	4.37	16.7	3.97
2	3.950	0.92	36	19	8	11	4.60	22.3	3.01
3	3.995	0.84	47	20	10	10	4.60	26.7	2.34
4	4.035	0.77	59	22	12	10	4.60	30.7	2.06
5	4.075	0.71	72	23	14	9	4.73	34.2	1.78
6	4.110	0.65	86	25	15	10	4.40	32.9	1.81
7	4.145	0.59	101	26	17	9	4.37	36.0	1.62
8	4.180	0.53	114	28	19	9	4.23	39.8	1.55
10	4.240	0.43	136	31	21	10	3.59	40.7	1.55
15	4.320	0.30	178	38	27	11	3.03	51.5	1.46
20	4.380	0.205	257	46	33	13	2.44	53.2	1.45

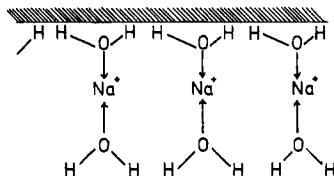
^a Data taken from ref 7.

Figure 2. Schematic illustration of bound water layer within aqueous core of reverse micelles.

sodium ions which are in the vicinity of the double layer of the interface. The water molecules of hexahydrated sodium ions which are hydrogen bonded with the polar groups of the surfactant molecules construct the bound water region⁵ and may in a two-dimensional diagram be represented as shown in Figure 2. The thickness of the water monolayer is approximately 1.2 Å,²² and the O-Na⁺ bond distance is also about 1.2 Å.²³ This gives the thickness of the bound water layer at maximum interfacial sodium ion concentration as (1.2 + 1.2 + 1.2 + 1.2) Å, i.e. 4.8 Å. This agrees quite well with the calculated values. With increasing size of the droplet the dissociated sodium ions are distributed more to the bulk water core^{5,14} and the thickness of bound water layer is proportionally reduced.

From the above results it appears that micellization and solubilization by AOT in nonpolar solvents are mainly governed by the amphiphilicity in that solvent. In the isooctane system the entire range of solubilization can be divided into three distinct regions: (i) $0 < w_0 < 10$, (ii) $10 < w_0 < 30$, and (iii) $w_0 > 30$. A considerable amount of water solubilization by nonpolar solvents like isooctane without adding any cosurfactant is a unique characteristic of the AOT w/o microemulsion system, and this is perhaps possible, as appears from Tables I and II, because of the flexibility of AOT molecular structure, particularly due to restricted rotation about C-C bond of the ethane skeleton of the succinic acid part of the molecule. The mean average size parameters of the surfactant molecule are dependent, besides other

factors, on the composition of the rotamers in the equilibrium mixture, and in some nonpolar solvents they change in such a highly favorable direction such that large water solubilization and stable microemulsion with this surfactant are possible. This has been confirmed from the calculations of the packing factor ($v/f_{AOT}l_c$) of the AOT molecule in microemulsion system, which were always found to be above one (Tables I and II), the condition for formation of stable reverse micellar droplets.²⁴ In the micellar region $w_0 < 10$, the equilibrium composition of rotamers of AOT is mainly populated by gauche conformers having all the polar groups oriented along the same stereospecific direction at the interface and rotation is highly restricted because of the so-called "hard interface". With the increased water content in the droplet the interface becomes more and more "soft", causing an increase in the population of the trans conformer in the equilibrium rotamer composition. The system finally becomes saturated by trans population at and beyond $w_0 = 30$ (Figure 1).

At a certain rotamer composition, the apparent head-group area, f_{AOT} , of AOT molecules is the sum of the weighted average head-group areas of three rotamers (ref 12), i.e.

$$f_{AOT} = P_1f_1 + P_2f_2 + P_3f_3 \quad (10)$$

where P 's are the mole fractions of three rotamers in the equilibrium mixture having corresponding head-group areas f 's, respectively. In the gauche conformer the polar groups—two esters and one sulfonic group—are directed along the polar side from the interface, making the effective head-group area very large. In the small micellar region ($w_0 < 10$) where the surfactant molecules are mainly dominated by the gauche conformer, the small interfacial area of the droplet cannot accommodate all the AOT molecules to be located exactly at the interface. Eventually, some of the molecules are to remain out of the interface. Relatively low f_{AOT} values (Figure 3) in these droplets are the inevitable corollary of the packing constraint experienced by the surfactant molecules. A slight increase in droplet size (r_w) increases the interfacial area ($4\pi r_w^2$) enormously such that the packing con-

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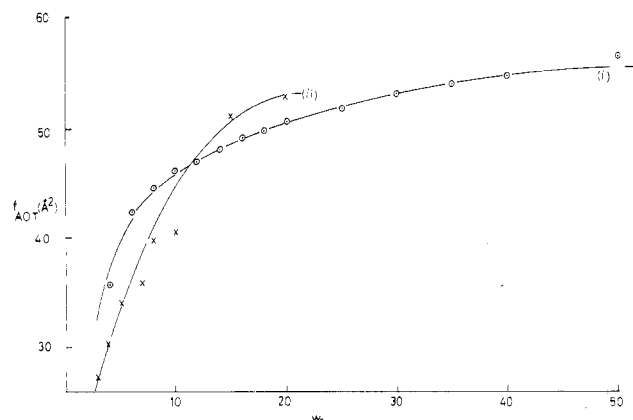


Figure 3. Variation of f_{AOT} with w_0 in (i) H_2O -AOT-isooctane and (ii) H_2O -AOT-cyclohexane systems.

straint is considerably reduced. This makes it possible for the AOT molecules, residing out of the interface, to come to the interface. Thus, the rate of increase of f_{AOT} with w_0 in this region is very large. Surfactant monolayer thickness, l_c , in the micellar droplets is found to be about 15 Å, about 4 Å more than the formal length of AOT molecule. This is quite reasonable when one considers the unequal arrangement of the surfactant molecules in the droplets as shown in Figure 4 and compares the size of the polar head group as determined by Kotlarchyk et al.⁹ Another interesting feature could be observed if one calculates the number of bound water molecules per surfactant molecule, i.e. $w_0 P_B$. The value was found to be about six for the droplets with $w_0 > 10$, and for the smaller ones it is considerably less. When hexahydrated sodium ions are considered being hydrogen bonded to the negatively charged interface constructing the bound water layer, it can be presumed that number of bound water molecules should be a minimum of six per AOT molecule. For the smaller droplets ($w_0 < 10$), because of the high packing constraint, the anhydrous AOT molecules existing at the apolar side of the interface could not reach the free water present in the aqueous core of the micellar droplet. A very long correlation time for sodium ions observed for these micelles^{5,14} also confirms the existence of strongly bound ion pairs, of anhydrous surfactant molecules which are rigidly bound in the aggregated system of the droplet. In the microemulsion domain ($w_0 > 10$) the packing constraint may be thought to be eliminated and the surfactant molecules in the droplets are all lying at the interface. This is based on the fact that the surfactant monolayer thickness (l_c) in these droplets is about the same as the formal length of the AOT molecule. The rate of increase of f_{AOT} with w_0 in this region is also much less because of the contribution of more trans rotamers in the equilibrium mixture of AOT ($f_{\text{AOT}}^{\text{trans}} < f_{\text{AOT}}^{\text{gauche}}$). Moreover, the number of bound water molecules per surfactant molecule for droplets in this range is about six, the hydration number of AOT. In the large microemulsion droplets ($w_0 > 30$) the surfactant molecules are mainly populated by trans rotamers and the droplets are further stabilized by dissolving solvent molecules in the surfactant monolayer, making an unusual increase of l_c values but main-

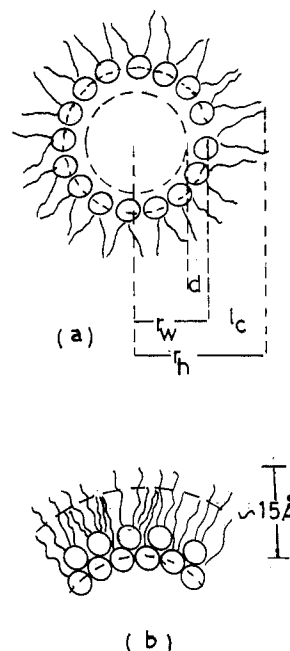


Figure 4. (a) AOT reverse micelle with an aqueous core. (b) Unequal association of AOT molecules at the interface.

taining a favorable packing factor to a value greater than one. This is confirmed from the fact that in presence of additive these droplets have much less water-solubilizing capacity if the additive is more soluble in the droplets than the solvent molecules.²⁵

Conclusions

It may thus be concluded that if the aggregational parameters like the mean average aggregation number and hydrodynamic radius of H_2O -AOT-oil droplet are determined by other experimental methods, the important size parameters of the droplets could, then, be calculated from the chemical shifts of water proton resonance. It is seen that the stability of the reverse micellar system is largely governed by the internal rotation of the surfactant molecule, leading to favorable packing factors which are always greater than one. The nature of the bulk solvent plays an important role in determining the rotamer composition in the equilibrium mixture. Water-AOT-isooctane is a unique reverse micellar system in which the internal rotation of the surfactant molecule leads to a favorable packing factor so that large amount of water solubilization is possible. The bound water layer thickness in the microemulsion droplets lies in a narrow range between 3 and 5 Å although the number of water molecules bound to a surfactant molecule remains a constant value of six.

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Registry No. AOT, 577-11-7; isooctane, 26635-64-3; cyclohexane, 110-82-7.

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