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Estimation of the Aggregation Number and Core Radius of Microemulsions

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Summary. A simple working method for the estimation of the aggregation numbers and core radii from weight measurements of sodium bis-2-ethylhexylsulphosuccinate (aerosol-*OT* or *AOT*)/decane/water microemulsions of several compositions is proposed.

Starting out from the hypotheses that (i) the density of the water inside the droplets is the same as that of free water, (ii) all the surfactant is localized as interface, and (iii) the penetration of the organic phase into the interface is negligible, values for the aggregation number and core radii comparable to those determined using more sophisticated methods were obtained.

The results/methodological simplicity ratio may be of great advantage in kinetic work on reaction mechanisms in microemulsions.

Keywords. Microemulsions.

Abschätzung von Aggregationszahl und Radius von Mikroemulsionen

Zusammenfassung. Es wird eine einfache Methode zur Abschätzung von Aggregationszahl und Core-Radius von Mikroemulsionen aus Gewichtsmessungen von Natriumbis-2-ethylhexylsulphosuccinat (aerosol-*OT* oder *AOT*)/Decan/Wasser-Mikroemulsionen verschiedener Zusammensetzung vorgeschlagen. Unter den Annahmen, daß (i) die Dichte von Wasser innerhalb der Aggregationen die gleiche als bei freiem Wasser ist, (ii) das ganze Emulsionsmittel in der Grenzfläche vorliegt und (iii) das Eindringen der organischen Phase in die Grenzfläche vernachlässigbar ist, können Werte für Aggregationszahlen und Core-Radien erhalten werden, die durchaus mit entsprechenden Werten aus aufwendigeren Methoden vergleichbar sind. Das Leistungsverhältnis (Ergebnisse/geringer Aufwand) ist sehr vorteilhaft und macht die Methode für kinetische Arbeiten zur Bestimmung von Reaktionsmechanismen in Mikroemulsionen interessant.

Introduction

One of the most attractive aspects of studies on the structures and properties of microemulsions lies in the possibilities of these being used as a molecular scale reactor in the sense that the microemulsion droplet can be effectively considered as a "microreactor", such that a microemulsion can act as a template that regulates the steric characteristics of the products resulting from a chemical reaction [1, 2] and even the actual mechanism itself [3 – 5].

Research carried out involving the use of more or less sophisticated techniques (small angle neutron scattering, light scattering, etc.) has afforded valuable information concerning microemulsions: the size and shape of the droplets, distribution and interactions, etc. However, the use of such techniques, even though fully justified (in view of the precision of the results) for fundamentally structural objectives, may not be as appropriate, both for reasons of cost and necessary experience, in investigations where an exact knowledge of structural properties is not the final aim of the work; e.g. for kinetic studies of reactions in microemulsions.

The present work proposes a simple method that permits a good estimation of the aggregation number and the radii of the aqueous cores from weight measurements of microemulsions of bis-2-ethylhexylsulphosuccinate (aerosol-*OT* or *AOT*)/decane/water of different composition. Apart from its simplicity, the method has the additional advantage of not altering the microemulsion under study.

The *AOT*/decane/water system was chosen for several reasons: (i). The microemulsion phase is especially simple because it does not incorporate a fourth component as a cosurfactant [6], and at the same time it permits the solubilization of a considerable amount of water; (ii). In *AOT* systems, encounters among discrete droplets are essentially elastic [7], and (iii). This system has proved to be of particular use in the kinetic study of reactions [3].

Experimental Part

The surfactant *AOT* was from Fluka and was used without further purification; the decane used as organic phase was from Merck.

For preparing each microemulsion, an amount of *AOT* was weighed and then dissolved in sufficient decane to reach the desired concentration of surfactant. The necessary amount of water (also by direct weighing) was then added to this solution to obtain microemulsions with the desired values for the $w = [H_2O]/[AOT]$ ratio. The mixture was shaken until a completely stable and transparent fluid was obtained.

With each of the mixtures thus prepared, of known composition by weight, the mass of a given volume was measured at 294 K with a precision of ±0.0001 g. Measurements were always carried out five times, in all cases obtaining a relative standard deviation of less than 0.1%.

Results and Discussion

From the above-mentioned measurements (if penetration of the organic phase into the interface is assumed to be negligible) it is possible to know the volume fraction taken up by solute (water + *AOT*), θ, in the bulk of the organic phase, as follows:

$$\theta = \frac{V_T - V_D}{V_T} \tag{1}$$

where V_D is the decane volume and V_T the total volume of microemulsion. Table 1 shows the values thus obtained for θ for different [water]/[*AOT*] ratios.

Furthermore, taking into account the physical meaning of θ, one can also write:

$$\theta = \frac{N_A[AOT]V_d}{n} \tag{2}$$

where N_A is the Avogadro number, $[AOT]$ is the molar concentration in the final

Table 1. Values of volume fraction taken up by solute (water + *AOT*) in *AOT*/decane/water microemulsions of different composition at 294 K*

$w = [H_2O]/[AOT]$	$\theta/(\%)$		
	$[AOT] = 0.1\,m$	$[AOT] = 0.2\,m$	$[AOT] = 0.4\,m$
6	3.97	7.69	13.3
10	4.34	8.58	14.9
14	-	9.56	-
15	4.96	9.73	-
20	5.58	10.70	18.6
25	6.08	11.80	-
30	6.60	12.79	21.8
35	7.11	13.93	-
40	7.70	15.03	25.3

microemulsion, n the aggregation number (number of *AOT* molecules per droplet) and V_d the total volume of a droplet (water + surfactant).

Since the critical micellar concentration (c.m.c.) is much lower than the working concentration, as was the case in the present work (for the *AOT* the c.m.c. lies in the $10^{-3} - 10^{-4}$ mol/dm^3 range) [8], it can be presumed that all the surfactant is localized as interface. Thus, the microemulsion can be considered as a monodisperse population of spherical droplets (see Fig. 1), separated from the organic phase by a monolayer of *AOT*. On the other hand, for $w \geqslant 6$ the density of the water forming the core of the droplets is practically the same as that of the "free" water [9–11]. According to the foregoing, V_d represents the total volume of the water core (V_W) and the film of surfactant (V_S):

$$V_d = V_W + V_S \tag{3}$$

where V_W is:

$$V_W = S_W n w \tag{4}$$

S_W being the specific volume of a water molecule inside the droplet.

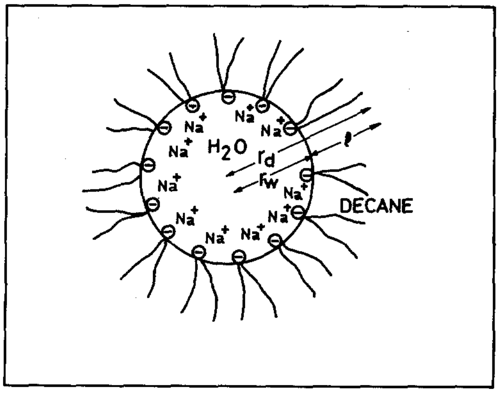

Fig. 1. Schematic illustration of the structure of a droplet in an *AOT*/decane/water microemulsion

If the total micellar radius is r_d, r_w the one corresponding to the aqueous core and "l" the thickness of the interface film formed by the tails of the surfactant (see Fig. 1), one obtains:

$$r_w = \left(\frac{3}{4\pi} V_W\right)^{1/3} \tag{5}$$

$$r_d = r_w + l \tag{6}$$

therefore

$$V_d = \frac{4\pi}{3} r_d^3 = \frac{4\pi}{3}\left[\left(\frac{3\,V_W}{4\pi}\right)^{1/3} + l\right]^3 \tag{7}$$

Considering equation (4), one has:

$$\theta = \frac{N_A[AOT]}{n}\frac{4\pi}{3}\left[\left(\frac{3}{4\pi} S_W n\, w\right)^{1/3} + l\right]^3 \tag{8}$$

which can be reorganized as:

$$n^{1/3} = \frac{l}{\left(\frac{3}{4\pi}\right)^{1/3}\left[\left(\frac{\theta}{N_A[AOT]}\right)^{1/3} - (S_W w)^{1/3}\right]} \tag{9}$$

It is thus apparent that S_W and "l" must be known to obtain the values for the aggregation number and the core radius.

Regarding S_W, since under the working conditions ($w \geq 6$) the behaviour inside the droplets does not differ substantially from that of the bulk, the density of the

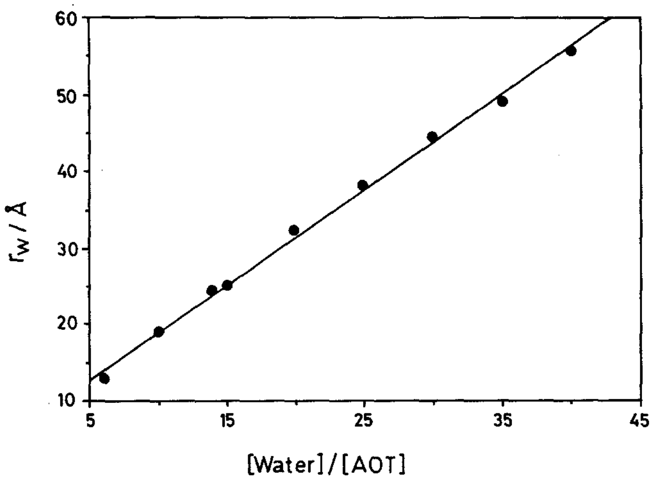

Fig. 2. Variation of the aqueous core radius with the $w = [H_2O]/[AOT]$ ratio for AOT/decane/water microemulsions ($[AOT] = 0.2\,m$), at 294 K. Similar results were found for microemulsions with initial concentrations of $0.1\,m$ and $0.4\,m$

Table 2. Values of the aggregation number and the radius of the aqueous core in *AOT*/organic phase/water microemulsions determined with different working techniques

Organic phase	w	Technique	n	r_w/Å	Ref.
n-Decane	20	Small angle neutron scattering	-	34.4	[12]
n-Hexane			-	33.1	
n-Heptane			-	35.8	
n-Octane			-	34.4	
Cyclohexane	8	Viscosity	114	18.6	[10]
Toluene			112	18.7	
Chlorobenzene			108	19.3	
Toluene	9.56	Light scattering	-	15.8	[10]
Isooctane	11.11	Sedimentation (ultracentrifuge)	-	21.35	[14]
	20	X-ray scattering	450	36	[15)
-	30		550	50	
	40		600	55	
	20	Radiolysis	250	35	[15]
-	30		350	42	
	40		800	62	
Decane	10	Weight measurements	116	19.6	this work
	15		175	26.0	
	20		267	33.0	
	25		349	39.0	
	30		494	46.7	
	35		592	52.1	
	40		738	59.0	

water in the aqueous core can be considered to be equal to unity. According to Day et al. [11], a value of 1.03 nm was estimated for "*l*".

The aggregation numbers and the radii of the aqueous cores obtained with the above considerations are shown in Table 2. This Table also shows the results obtained in the study of *AOT*/organic phase/water microemulsions using more sophisticated techniques. Figure 2 shows the variation of the core radius with w for microemulsions with an initial concentration of 0.2 m of *AOT* in decane. From these results and those offered in Table 3, good consistency among the results obtained with different techniques can be inferred, not only regarding the actual values of r_w and n, but also in the trends observed referring to: (i) an increase in the value of both parameters as the value of w increases, and (ii) the practical independence of the core radius and aggregation number values from the surfactant concentration.

It should also be noted that in view of previous research [6, 11, 12–15] the origin of these trends is easily foreseeable within the framework of the assumptions

Table 3. Aggregation number and aqueous core radius of micelles formed in *AOT*/decane/water microemulsions of different composition at 294 K

$w=[H_2O]/[AOT]$	$[AOT]$/molal					
	0.1		0.2		0.4	
	n	r_w/Å	n	r_w/Å	n	r_w/Å
6	63	13.3	63	13.0	76	14.2
10	114	19.5	105	19.0	129	20.3
14	-	-	146	24.4	-	-
15	188	26.7	162	25.3	-	-
20	258	32.7	244	32.1	295	34.2
25	376	40.0	322	38.0	-	-
30	515	47.4	424	44.4	542	48.2
35	691	55.1	492	49.1	-	-
40	876	62.4	608	55.9	729	58.6

made. Indeed, in this context the amount of water in the microemulsions would be given by:

$$\frac{4\pi}{3} r_w^3 \delta_w N \tag{10}$$

where N is the number of droplets and δ_w the density (mol/volume) of the core water. If, additionally, all the surfactant is localized on the surface, its total amount could be expressed as:

$$4\pi r_w^2 \alpha_s N \tag{11}$$

where α_s represents the surface density (mol/area) of surfactant in the interface; this would imply a linear dependence of the [water]/[*AOT*] ratio on the radius assuming that δ_w and as α_S are independent of the size of the droplet.

It should therefore be stressed that the dependence found between the values of w and certain structural parameters, such as r_w should not be extrapolated out of the context in which such dependence is found. This precaution is supported by results that have suggested the possibility that some of the hypotheses assumed might not be sufficiently suitable [16]. If this is the case, the simple relationship found would merely be the result of concurrent factors that would mask a greater underlying complexity.

However, we believe that the ease in obtaining such parameters and the consistency with those determined by much more complex techniques in many cases may justify the use of the proposed method.

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