306. On the Formation of Water/Oil-Microemulsions

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Summary. The formation of a so-called water/oil (W/O)-microemulsion (AOT/isooctane/water) was followed by light scattering and ultracentrifuge measurements. With increasing weighed-in water concentrations the microemulsion is stabilized by repeated aggregational processes of micelles containing water due to a decrease of the free interfacial enthalpy.

This process conforms very satisfactorily to a model describing an adsorption of surfactants at the water/hydrocarbon interface resulting from dipole-image dipole interactions.

While there exists already a large number of experimental results on so-called microemulsions formed by nonionic and ionic surfactants in aqueous and nonaqueous media (*e.g.* [1–4]) relatively little is known quantitatively with regard to the mode of origin of these microemulsions. In a preceding paper details of the solubilization process and micellar aggregation phenomena have been investigated with the help of dielectric increment measurements [5]. More recently the exchange of water and aqueous electrolyte solutions between micelles in apolar media was followed by fluorescence quenching experiments. Such an exchange was to be expected as a necessary prerequisite with respect to the experimentally observed considerable monodispersity of lipophilic micelles containing polar liquids [6]. Finally, the stabilizing effect of polar liquids on lipophilic micelles was predicted theoretically on the basis of dipole-image dipole interactions between the solubilized water 'pool' and the surfactant molecule [7].

In order to check the predictions of this theoretical approach and to investigate details of the micellar aggregation process and thus of the formation of a so-called W/O-microemulsion a micellar system with a particular high solubilization ratio (water/surfactant) was selected.

Finally, it is believed that the present investigation may contribute towards a clarification as to the thermodynamic stability of these systems.

Materials and Methods. – Aerosol OT (= AOT = Sodium di-2-ethylhexylsulfosuccinate, Mol.-Wt. = 444.56) was used as a suitable representative model of an anionic surfactant because of its pronounced solubilizing capacity in some nonpolar organic solvents. The compound, a commercial product (*Fluka AG*, Buchs/SG) of pharmaceutical quality, had been purified and dried additionally before use. The procedure is described elsewhere [8].

According to preliminary investigations isooctane was chosen as the most suitable solvent. The commercial product (*Fluka AG*, Buchs/SG) of high grade purity was distilled over 'Siccon' followed by a continous distillation over sodium/potassium alloy. The residual water content of the isooctane was determined by the *Karl-Fischer*-method to be 0.0052%. Bidistilled water was used as solubilizate.

The ternary solutions were prepared by dissolving the predetermined amount of surfactant in about 2/3 of the calculated solvent volume. The solubilizate was then added with a microsyringe. This solution was shaken and treated in an ultrasonic bath to ensure that the solubilizate was taken up by the micelles. Following this procedure the solution was adjusted to the exact concentration by adding further solvent. Dilutions with definite molar ratios of water and surfactant could be obtained by adding further solvent to the above prepared stock solution.

Apparent molecular-weight-determinations of the solubilizing lipophilic micelles were made with an analytical ultracentrifuge (model *E. Beckmann*) with *Schlieren* optics at 25 ± 0.01° and with the help of light scattering measurements applying a Photo-Gonio-Diffusometer (type 42000, *FICA*, Paris).

The sedimentation velocities were determined at $2-6 \cdot 10^4$ rpm the sedimentation equilibria at $2-3 \cdot 10^3$ up to $2.4 \cdot 10^4$ rpm depending on the water content of the investigated solutions. Diffusion coefficients were evaluated at about $5 \cdot 10^3$ rpm.

The average apparent molecular weights were calculated according to the *Svedberg* equation

$$\overline{M} = \frac{R\,T\,s}{(1-v_2^*\varrho)\,D} \tag{1}$$

or they could be derived from the sedimentation equilibria measurements, *i.e.*

$$\overline{M} = \frac{2\,R\,T}{(1-v_2^*\varrho)\,\omega^2}\;\frac{\Delta \ln c}{\Delta\, r^2} \tag{2}$$

where v_2^* is the partial specific volume of the dispersed phase (= lipophilic micelles and solubilizate) in ml/g, ϱ the density of the solvent (isooctane) in g/ml, s the sedimentation coefficient in cm^2/s, r the distance from the centre of rotation in cm, ω the angular velocity in s^{-1}, c the concentration in g/ml, T the absolute temperature in K, and R the gas constant.

In both equations the partial specific volume v_2^* is replaced by the apparent specific partial volume $\overline{v}_c$. Both magnitudes are connected by the relation

$$v_2^* = \overline{v}_c + \frac{m_1\,m_2}{m_1+m_2}\left(\frac{\partial \overline{v}}{\partial m_2}\right)_{m_1,\,T,\,P} \tag{3}$$

where m_1 and m_2 are the masses of the solvent and the dissolved substance. $\overline{v}$ is the specific volume of the solution. It can be shown [9] that the difference between v_2^* and $\overline{v}_c$ in a 1% solution is about 10^{-4} and, therefore, to be neglected.

Solutions to be investigated by light scattering were passed through a D-5 glass filter (porediameter 4–6 μ) applying N_2-pressure. By this means the solutions could be obtained essentially dustfree. The measurements were made with nonpolarized, horizontally, or vertically polarized light at 546 nm and 25 ± 0.05°. The average apparent molecular weights $(\overline{M})$ of the micelles were determined according to eq. (4)

$$\frac{1}{(\overline{M})} = \frac{2\,\pi^2\, n_B^2\,(dn/dc)^2}{\lambda^4\, N_L}\;\frac{i^B_{u,\,90^\circ}}{R^B_{u,\,90^\circ}}\;\lim_{c,\,\theta\to 0}\left(\frac{c}{i_{corr}}\right) f \tag{4}$$

where i_{corr} are the corrected scattered intensities which were obtained under different angles of observation (θ), c is the total concentration $(c = c_{AOT} + c_{H_2O})$ in g/ml, n_B the index of refraction of benzene ($n_D^{25} = 1.5025$ at $\lambda = 546$ nm), λ the wavelength of the light used, N_L *Avogadro*'s number, dn/dc the refractive index increment of the solution, $i^B_{u,90^\circ}$ the scattered intensities of benzene at 90° (angle of observation), $R^B_{u,90^\circ}$ the *Raleigh* ratio of benzene at 90° ($= 1.63 \cdot 10^{-3}$ m^{-1} [10]) and f the *Cabannes* correction factor [11]. The refraction index increment (dn/dc) was determined at 25° and $\lambda = 546$ nm using a *Brice-Phoenix* Differential refractometer (model BP-2000-K).

Results and Discussion. – The average apparent molecular weight of the AOT micelles in isooctane without solubilizate determined by vapor pressure osmometry, light scattering, and ultracentrifuge measurements are in reasonable agreement with each other and with data from the literature, *i.e.* $\bar{n}_n$ (vapour pressure osmometry): 7100, $\bar{n}_w$ (sedimentation/diffusion): 8290, $\bar{n}_w$ (sedimentation equilibrium): 7770, and $\bar{n}_w$ (light scattering): 6860.

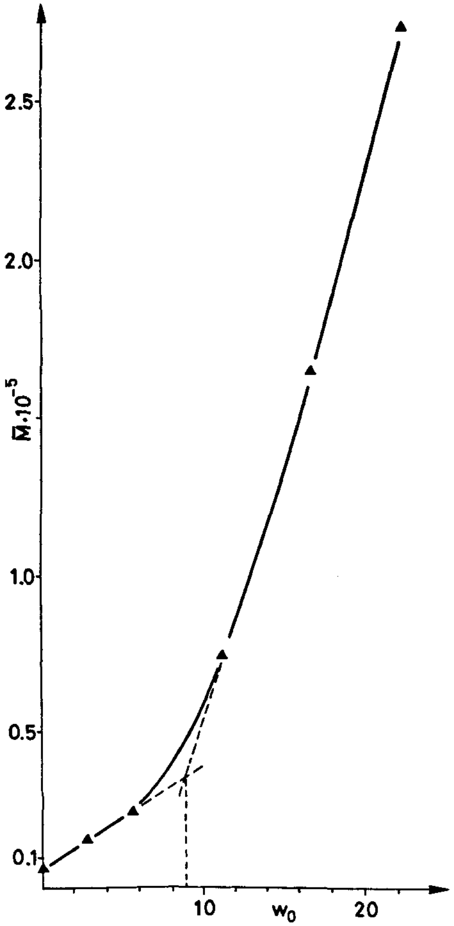

Fig. 1. *Variation of the average apparent molecular weights* ($\bar{M}$) *of the solubilizing AOT micelles in isooctane with increasing water content* $w_0 = [H_2O]/[AOT]$.

The increase of the average apparent molecular weight of the lipophilic micelles containing H_2O with increasing water content and constant amount of AOT is shown in Fig. 1. The steeping of the slope of the curve at about 9 mol H_2O/mol AOT corresponding to an additional increase of the average apparent molecular weight of the micellar aggregates indicates apparently an association of the micelles with solubilized water. It can be shown, actually, that starting from this amount of water the more favourable surface to volume ratio of the larger (spherical) aggregates is responsible for this micellar aggregation.

The average aggregation numbers $\bar{n}_{AOT}$ and $\bar{n}_{H_2O}$ in Table 1 were calculated from the average apparent molecular weights obtained by light scattering measurements with the theoretically reasonable assumption (see [7]) that the total amount of water is equally distributed between all micelles, *i.e.*

$$\bar{n}_{AOT} = \frac{\bar{M}}{M_{AOT} + w_0 M_{H_2O}} \qquad (5)$$

where $w_0 = [H_2O]/[AOT] = \bar{n}_{H_2O}/\bar{n}_{AOT}$ is the known molar ratio of water and Aerosol OT. $\bar{M}$, M_{AOT}, and M_{H_2O} are the average apparent molecular weight of the lipophilic micelles containing water, and the molecular weights of AOT and water, respectively.

Table 1. *Average aggregation numbers of AOT($\bar{n}_{AOT}$)- and H_2O($\bar{n}_{H_2O}$)-molecules according to equation (5)*

$\bar{M}\ 10^{-4}$	0.686	1.543	2.465	7.489	16.47	27.33	100.0	154.4
w_0	0	2.78	5.56	11.11	16.67	22.22	36.0	44.44
$\bar{n}_{AOT}\ 10^{-2}$	0.15	0.31	0.45	1.16	2.21	3.24	9.157	12.41
$\bar{n}_{H_2O}\ 10^{-3}$	0	0.087	0.252	1.29	3.69	7.19	32.967	51.15

$\bar{M}$ = average apparent molecular weight of micellar aggregates; w_0 = weight in conc. of H_2O: $[H_2O]/[AOT]$.

As long as a macroscopic treatment is justified the shape of the polar liquid solubilizate is assumed to be spherical (minimum surface [7]). In the same approximation the solubilizate is considered to represent a pseudo-phase covered with a monomolecular surfactant layer. According to this assumption the spherical surface fraction f_{AOT} covered by one surfactant molecule can be calculated as well as the radius of the corresponding water sphere, *i.e.*

$$F_{sphere} = f_{AOT}\,\bar{n}_{AOT} = (4\pi)^{1/3}\,(3\,V_{H_2O})^{2/3} \qquad (6)$$

where $V_{H_2O} = v_{H_2O}\,\bar{n}_{H_2O}$ is the volume of the solubilized water per micelle, v_{H_2O} is the average volume of one water molecule at 25° corrected with respect to the apparent specific partial volume at the actual water concentration.

Fig. 2 shows a plot of $\bar{f}_{AOT}$ as a function of the molar ratio of water and AOT. The considerable initial increase of $\bar{f}_{AOT}$ with small added amounts of water slows down with higher weighed-in water concentrations approximating, apparently, a limiting value of about 54 $Å^2$. This value corresponds very satisfactorily to data quoted by *Sonntag et al.* [12] with respect to alkylsulfonates. These surfactants form coalescence stable films at a surface area per surfactant molecule between 52 and 57 $Å^2$. The minimum value of this ratio with regard to these compounds is, approximately, 42 $Å^2$. Thus, it may be concluded that the initial steep increase of $\bar{f}_{AOT}$ with small amounts of water starting from $\bar{f}_{AOT}$-values as low as 29.7 $Å^2$ is due to the decomposition of 'interstitial' positions of surfactants within the 'micellar' membrane.

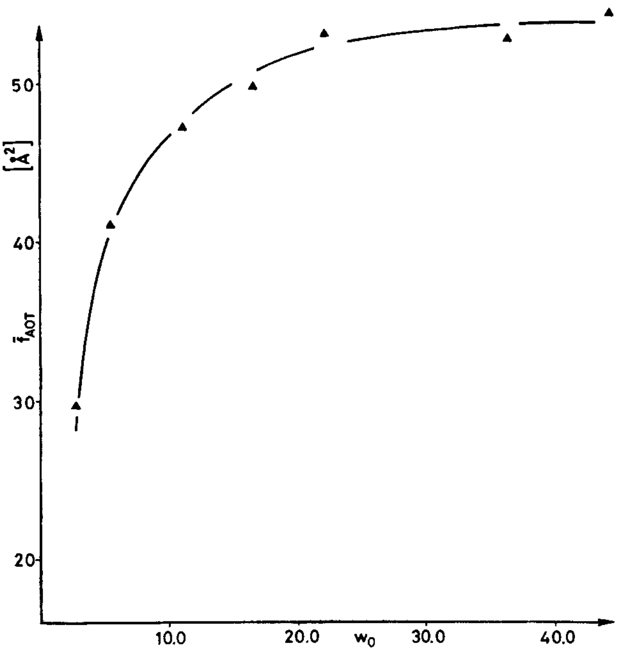

Fig. 2. *Average surface fraction* ($\bar{f}_{AOT}$) *of the water/hydrocarbon interface covered by one surfactant molecule versus weighed-in amount of water* $w_0 = [H_2O]/[AOT]$

At increasing weighed-in water-concentrations the formation of these microemulsions proceeds *via* repeated aggregational processes of micellar aggregates containing water. This process is characterized by a decrease of the surfaces of the new aggregates, which are assumed to be spheroids due to the non-linear relation between surface and volume. The continuation of this process makes it possible for the microemulsion to take up increasing amounts of water. The actual driving force for this aggregation is a decrease of the free interfacial enthalpy. It has been shown [7] that the free interfacial enthalpy change $\Delta\sigma$ for the process: unsolubilized polar liquid → solubilized polar liquid can be expressed approximately by

$$\Delta\sigma = -\left(\frac{2\,k\,\theta}{F} - \frac{2\,k\,T}{F}\ln\frac{\theta}{T}\right) n_a \qquad (7)$$

where it has been assumed that $\Delta\sigma$ is independent of the curvature of the interface. F denotes the area of the spherical interface, k the *Boltzmann* constant, n_a the number of surfactant molecules adsorbed at the interface and θ a 'characteristic' temperature (defined by the apparent dipole moment and the immersion of the polar molecular portion in the solubilizate) describing the effect of the particular surfactant on the decrease of the interfacial free enthalpy.

Investigations with the help of the analytical ultracentrifuge offer a direct proof of the micellar aggregation. Due to the very slow adjustment of the equilibrium between two aggregational states of the micelles both entities can be observed. Thus the following data were derived under the assumption of a constant $\bar{n}_{H_2O}/\bar{n}_{AOT}$-ratio corresponding to the satisfactory monodispersity observed with these microemulsions at constant w_0 – considering equation (5) – (see Table 2):

Table 2. *Average apparent molecular weights* ($\bar{M}$) *of two micellar aggregates derived from sedimentation/diffusion-ultracentrifuge measurements at* $w_0 = [H_2O]/[AOT] = 11.11$

w_0	$\bar{M}$	$\bar{n}_{AOT}$	$\bar{n}_{H_2O}$	$\bar{f}_{AOT}$[Å^2]	r[Å]
11,11	78440	122	1352	46.9	21.35
	51320	80	885	53.2	18.40

$\bar{n}_{AOT}$, $\bar{n}_{H_2O}$: average aggregation numbers of AOT- and H_2O-molecules; $\bar{f}_{AOT}$: average spherical surface fraction covered by one surfactant molecule; r: radius of spherical aqueous pseudo-phase.

The results derived from the ultracentrifuge measurements show that the peak appearing first is due to a micellar aggregate with an apparent average molecular weight $\bar{M} = 51320$. According to Table 2 the value of $\bar{f}_{AOT} = 53.2$ Å^2 corresponds to the maximum spherical surface fraction per surfactant monomer observed (see Fig. 2). At the same water-to-AOT ratio the larger micellar aggregate ($\bar{M} = 78440$) which appears to be the sole entity after about 30 minutes run and is considered to be the result of an aggregational process of the smaller micellar units exhibits a $\bar{f}_{AOT}$-value of 46.9 Å^2 thus, indicating that more water per surfactant monomer may be taken up by larger aggregates.

With increasing amounts of solubilized water the tendency towards an aggregation of micelles is more emphasized corresponding to the thermodynamically stable equilibrium state with $\sigma \rightarrow 0$. At a ratio of 44.4 mol H_2O per mol AOT, only one sedimentation maximum is detectable refering to the same time interval of observation.

Mathews & Hirschhorn [13] already observed in the system AOT/dodecane/H_2O two types of micellar aggregates of different average apparent molecular weight containing water. They did not, however, offer an explanation of the phenomenon.

It is now possible to describe the growing of these lipophilic micelles with increasing water content on the basis of dipole-image dipole interactions occurring between the surfactant molecules and the spherically assumed aqueous pseudo-phase. Thus, physically, an adsorption process of the surfactant molecules at the water/hydrocarbon interface is considered.

The interaction energy (W) of the dipole (μ) of the ionic surfactant molecule with its image within a spherically assumed polar liquid phase (radius a) with dielectric constant (ε_2) is given by [7]

$$W = -\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1(\varepsilon_1 + \varepsilon_2)}\left(\frac{a}{r_0 + a}\right)^3 \frac{\mu^2}{\left(r - \frac{a^2}{r_0 + a}\right)^3}(1 + \cos^2\vartheta) \qquad (8)$$

where ε_1 is the dielectric constant of the dispersion medium, r_0 the shortest distance between the centre of the dipole and the spherical interface, r the distance between the centre of the liquid sphere and the reference point (P) with respect to which the potential is to be determined, and ϑ the angle between the dipole and the line connecting its centre with that of the spherical liquid phase.

The average concentration of dipolar surfactant molecules (pointing in all directions) at the point P is

$$c_r = \frac{c_\infty}{2} \int_0^\pi e^{-\frac{W}{kT}} \sin\vartheta \, d\vartheta \qquad (9)$$

and c_∞ is the concentration of monomeric surfactant molecules in equilibrium with the pure micellar state. From equation (9) the number of surfactant molecules n_a adsorbed at the interface (r = a), *i.e.* $n_a = F \int_a^\infty (c_r - c_\infty) dr$, is obtained thus

$$n_a = \frac{c_\infty}{12} F \frac{a}{r_0 + a} \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 (\varepsilon_1 + \varepsilon_2)} \frac{\mu_{app}^2}{kT} \right)^{1/3} \frac{e^{2 z_a}}{z_a^{7/3}} \qquad (10)$$

where

$$z_a = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 (\varepsilon_1 + \varepsilon_2)} \frac{\mu_{app}^2}{r_0^3 kT} .$$

An apparent dipole moment has been introduced if the surfactant molecule is built into the solubilizing micelle. This variation of μ (usually a decrease) is experimentally confirmed (see [8] [14]). Equation 10 can be transformed by inserting the relation $z = z_a r_0^3$, *i.e.*

$$n_a = \frac{c_\infty}{12} F \frac{a}{r_0 + a} r_0^7 z^{-2} e^{2 \frac{z}{r_0^3}} \qquad (11)$$

which, after taking the natural logarithm, yields

$$\ln n_a = \ln \left(F \frac{a}{r_0 + a} \right) + \ln K \qquad (12)$$

where $\ln K$ is given by

$$\ln K = \ln \frac{c_\infty}{12} - 2 \ln z + 7 \ln r_0 + \frac{2z}{r_0^3} . \qquad (13)$$

Equation (12) represents a straight line with a slope of 1 and an ordinate intercept equal to $\ln K$ if $\ln n_a$ is plotted versus $\ln \left(F \frac{a}{r_0 + a} \right)$.

This plot is shown in Fig. 3 using the following data: $c_\infty = 2.2 \cdot 10^{-4}$ g ml^{-1}, $\mu_{app} = 1.32$ D, $r_0 = 1.32$ Å, $\varepsilon_1 = 2$, $\varepsilon_2 = 80$, $k = 1.38 \cdot 10^{-16}$ erg K^{-1}, $T = 298$ K. The agreement between experiment and model is very satisfactory. The diagram indicates, furthermore, the limitations of the macroscopic phase model at very small weighed-in concentrations of water.

The dependence of the number of monomers ($\bar{n}_a$) adsorbed in the water/hydrocarbon interface on the number of water molecules ($\bar{n}_{H_2O}$) is plotted in Fig. 4. The

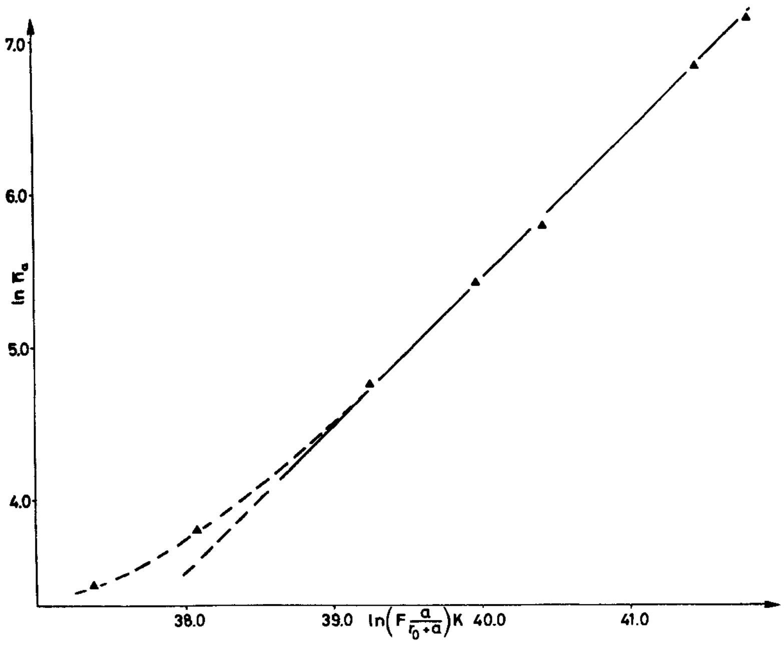

Fig. 3. *Check of the validity range of the theoretical model* (eq. (12)): $\ln \bar{n}_a = \ln\left(F\frac{a}{r_0 + a}\right) + \ln K$. Experimental data (▲). Parameters are given in the text.

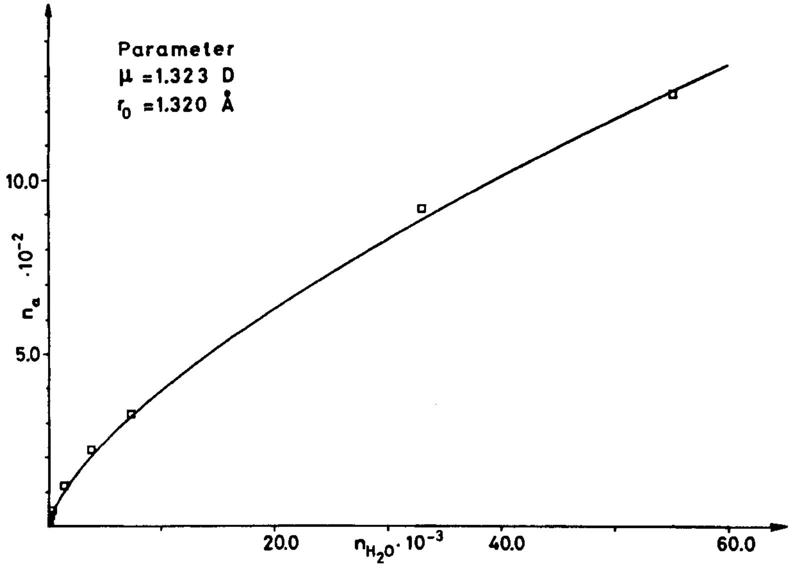

Fig. 4. *Average number of monomers* ($\bar{n}_a$) *adsorbed in the water/hydrocarbon interface as a function of water molecules* ($\bar{n}_{H_2O}$) *contained in the spherical aqueous pseudo-phase*

continuous curve through the experimental points corresponds to the theoretical model. For this calculation equation (10) was used in the following form

$$n_a = \frac{c_\infty}{12} F \frac{a\, r_0}{r_0 + a} \frac{e^{2\left(\frac{\theta}{T}\right)}}{\left(\frac{\theta}{T}\right)^2} \tag{14}$$

where $\theta = z_a \cdot T$ is the 'characteristic' temperature determined essentially by μ^2/r_0^3 already mentioned above. The value of a may be expressed by

$$a = \left(\frac{3\, v_{H_2O}\, \bar{n}_{H_2O}}{4\pi}\right)^{1/3}. \tag{15}$$

v_{H_2O} is the volume of one water molecule, *i.e.* 29.9 Å^3 at 25°.

The coincidence between experiment and theory confirms evidently the underlying model for considering the surfactant molecules adsorbed at the macroscopic spherical water/hydrocarbon interface.

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