

AGGREGATION IN SURFACTANT SOLUTIONS: FORMATION AND PROPERTIES OF
MICELLES AND MICROEMULSIONS

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Abstract - The present view regarding the formation and properties of micelles in aqueous and hydrocarbon media as well as the corresponding microemulsions is discussed. Particular emphasis has been put on new results concerning W/O microemulsions.

INTRODUCTION

The opposing physical properties within typical amphiphilic molecules as, for example, surface active agents (= surfactants), which are to be considered exclusively in the following, lead to a competitive situation between adsorption and homoassociation processes. Phenomenologically, the adsorption concept necessarily introduces a second phase (eventually in a dispersed state), i.e. a phase boundary where the surfactant tends to accumulate, thereby reducing the interfacial free energy of the system. Homoassociation can proceed in strictly binary solutions where the molecular arrangement is such that the antagonistic group of the surfactant with respect to the solvent (= dispersion medium) is shielded from the latter. This process, of course, is also driven by a decrease of the free energy of the surfactant solvent system. Generally speaking, the formation of a stable emulsion (understood as an adsorption process at the oil/water interphase) has to be achieved by a surfactant concentration smaller than the critical micelle concentration (cmc) (1), (2) or by any critical concentration leading to higher organised structures (bilayers).

The situation discussed recently in the literature (2), namely that a particular surfactant prefers to form micelles instead of being adsorbed in the interface, neglects the fact that the interfacial free energy (γ) has not to decrease to zero in order to attain the equilibrium state of the whole system. The entropic contribution due to the dispersion tendency of the surfactant has to be considered. (A negative value of γ , as is occasionally believed to be prerequisite for a stable system, is incompatible with general principles of thermodynamic stability).

In the following two typical examples of considerable interest are to be discussed, representing the above mentioned two cases of adsorption and homoassociation, i.e. the formation and properties of micelles and microemulsions. In particular the difference between the two mutually antagonistic types (normal and inverted micelles as well as W/O and O/W microemulsions) of these two phenomena will be examined.

Micelles

a) Micelles in aqueous surfactant solutions.

Solutions of molecules with pronounced amphiphilic character exhibit unusual concentration dependent properties: dilute solutions behave like normal electrolytes (if ionic surfactants are considered), at higher, rather well defined concentrations, quasi-sudden changes of several physical properties are observed (see Fig. 1). This phenomenon has been successfully ascribed to the formation of organised aggregates, i.e. micelles. The concentration above which micelles exist in equilibrium with monomers (and eventually small subunits) is the so-called critical micelle concentration (cmc).

Micelles formed by amphiphiles are generally considered to be the result of at least two opposing forces: attractive forces which are favoring the aggregation of monomers and repulsive forces which prevent the (unlimited) growth to very large aggregates and eventually

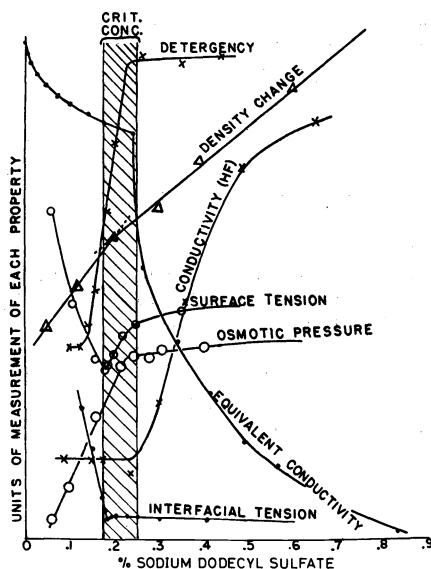


Fig. 1. Changes in some physical properties of an aqueous solution of SDS at the cmc. From W.C. Preston, *J. Phys. Colloid Chem.* **52**, 84 (1948)

to a continuous phase. As a third condition the cooperativity has to be taken into account. It expresses the fact that a few surfactant monomers are not sufficient to shield the antagonistic moieties with respect to the solvent. In other words a nucleation step is involved in the building up of micelles which is less favourable compared with the growing steps. The micelle formation in aqueous surfactant solutions compares very nicely with this scheme: the so-called hydrophobic effect favours the aggregation and hence an attraction between the paraffin chains of the amphiphiles which simultaneously leads to a relief of the strain on the hydrocarbon-separated water molecules. From this point of view the statement appears reasonable that micelle formation in aqueous media is entropy driven. The water retains the polar (ionic) head groups of the surfactants which are responsible for the repulsive interaction.

According to various experimental information the hydrocarbon core of the "aqueous" micelle has a liquid-like structure (3), (4). This has been confirmed, in particular, by spectroscopic probing techniques (5), (6). Hence the micelle in aqueous surfactant solutions presents itself to the surfactant monomer as an equivalent with respect to the (macroscopical) oil/water interface. It might be not unreasonable, therefore, to consider this type of micelle formation an "auto-solubilization" to stress the close resemblance between adsorption and homoassociation processes. The hydrocarbon core of a micelle in aqueous surfactant solutions is characterized by its excellent solvent power for crystalline non-polar compounds (7). This latter feature appears remarkable and could serve as a more fundamental distinction between "normal" and inverted micelles than the generally cited apparently more obvious differences. The free energy of micellization is customarily (8) referred to the standard free energy of a monomer in a micelle, i.e. ΔG_n^0 represents the free energy of transfer of a monomer from the aqueous solution to a micelle of size n , (Note a)

$$-RT \ln K_n = n\Delta G_n^0$$

The left hand side of this equation is the standard free energy of forming a micelle of size n . ΔG_n^0 is made up of two contributions corresponding to the above discussed main factors which control formation and size of micelles in aqueous surfactant solutions. It has been pointed out repeatedly, e.g. (9), (10), (11) that the degree of association of aqueous micelles is much larger than can be accommodated by a micelle with a spherical core.

Note a. It has been pointed out by Stigter (27) that besides the integral process of micelle formation, also a differential process (describing the condition for reversible micelle growth) has to be considered. The free energy changes for both processes show a gap of about 1 kT/ion , probably due to deficiencies in the Gouy-Chapman model.

Tanford reasonably attributes this fact to the thermodynamical requirements of the hydrophobic effect which forces an increase in aggregation to prevent contact between the hydrocarbon core of the micelle and the aqueous environment. Thus disk-like shapes have been proposed (9), (11). Detailed considerations by Tanford (10) confirm these more intuitively reached conclusions.

b) Micelles in nonpolar surfactant solutions.

Apart from the lengthy dispute in the past concerning the existence of micelles in apolar media there was probably agreement as to the different interactions responsible for the stability of such entities. Since the apolar tails of the surfactants which belong to inverted (reversed) micelles stay in contact with the hydrocarbon solvent, there is only a small entropic effect which has to be considered regarding the stability of the micelles. This entropic contribution corresponds to the transition of a monomer from the solution to the micellar pseudo-phase (12). In addition there might be another slight entropic effect accompanying the topological transformation during micelle formation in hydrocarbon solvents (13).

The small effect of the solvent on the aggregational state of inverted micelles is best demonstrated by Fig. 2.

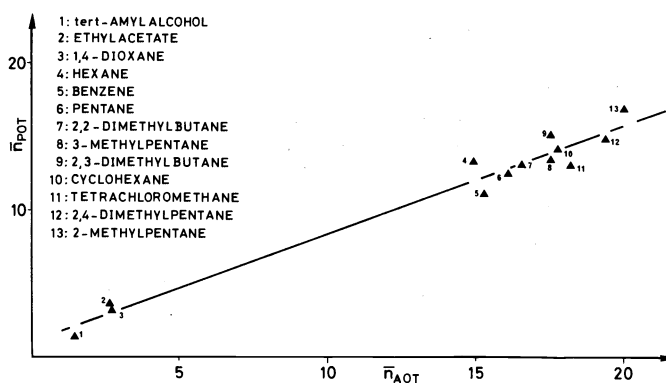


Fig. 2. Correlation diagram between mean aggregation numbers \bar{n}_{POT} and \bar{n}_{AOT} concerning the solvent dependent aggregate sizes of AOT and sodium di-2-ethylhexyl phosphate (= POT).

Two surfactants, namely AOT (= sodium di-2-ethylhexyl sulfosuccinate) and the analogous POT (sodium-di-2-ethylhexyl phosphate) were correlated. Only the slightly polar ethylacetate or dioxane considerably reduced the aggregational tendency of both surfactants due to the interactions with the polar (hydrated) groups. The slope of the correlation diagram corresponds to the ratio of the smallest aggregate sizes of both surfactants detected. These were considered in the frame of the micellization model as nuclei (14). The enthalpic contributions consist of two parts, i.e. dispersion and electrostatic interactions where the latter include particularly hydrogen bond formation. According to the recent experimental results from photon correlation spectroscopy (15), positron annihilation technique (16), IR spectroscopic investigations (17) and vapor pressure osmometric measurements of increasingly hydrophobic (= tetra alkylammonium) ions of di-2-ethylhexyl sulfosuccinate (18) it was concluded that hydrogen bond formation (and generally hydration interactions) are decisive regarding the formation and stability of inverted micelles. These conclusions were strongly confirmed by careful IR spectroscopic OH-vibration analyses (17) which resulted in the following model (see Fig. 3). The figure illustrates the case for small amounts of water attached to the ionic groups. This is believed to be the experimental situation generally met with the formation of inverted micelles. The importance of the hydration interaction is seen in Fig. 4 where the average aggregation number \bar{n} is plotted versus the weighed-in concentration c_0 of various ionic derivatives of di-2-ethylhexyl sulfosuccinates with increasingly hydrophobic counterions. The effect is quite apparent and shows the expected trend. It appears, therefore, justified to assume that minute amounts of water are essential for the formation, and surprising stability (15), of many ionic micelles in hydrocarbon solvents. This applies in particular to those surfactants with strongly hydrophilic head groups and which are capable to form hydrogen bonds stabilized by polarization.

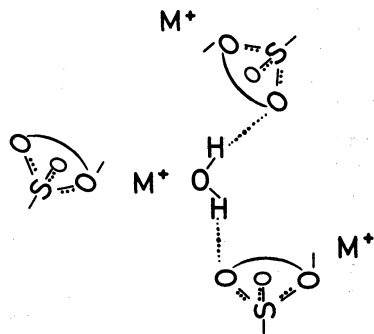


Fig. 3. Formation of trimers of AOT at low degree of hydration according to Zundel's model (17).

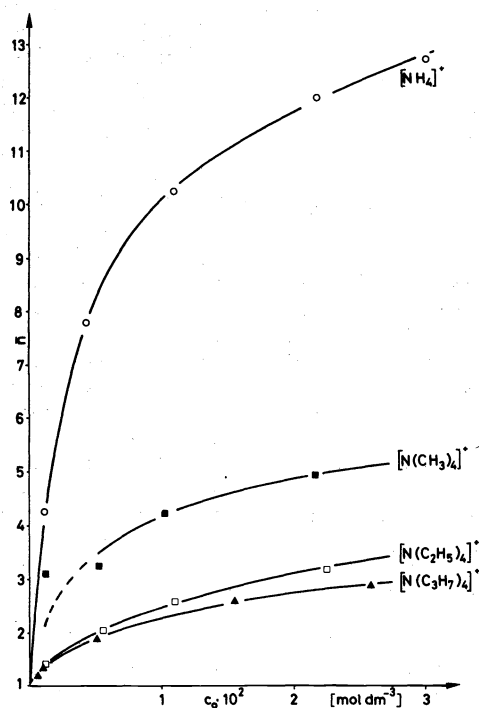


Fig. 4. Number average aggregation number (\bar{n}) of AOT with different tetraalkylammonium counterion vs. surfactant concentration in benzene at 25°C.

With respect to size and shape of inverted micelles the former is, as a rule, considerably smaller than aqueous micellar aggregates. Since no thermodynamically determining factor, like the hydrophobic effect, exists in the case of inverted micelles it appears to be accepted that steric restrictions are important, i.e. the ratio of the cross-sectional areas of the hydrocarbon to the polar moieties essentially determines size and shape of the aggregates (19).

Quite frequently prolate ellipsoids have been suggested according to experimental results (19), (20), for example in the case of AOT. For other surfactants, like dinonylnaphthalene sulfonates (21), spherically shaped aggregates seem more probable. Thus, contrary to a general driving force as with association phenomena in aqueous surfactant solutions where the hydrophobic effect forces the micelle to adopt a shape which guarantees the most favourable shielding from water, specific sterical effects seem to dominate the shape of inverted micellar aggregates.

Microemulsions

A phenomenon closely related to the formation of micelles is the building up of thermodynamically stable emulsions, so-called microemulsions. The process giving rise to the final formation of a microemulsion is the so-called solubilization, i.e. the encaging of the respective antagonistic component in the binary oil/water system by the surfactant. It might appear reasonable to consider this solubilization as the leading phenomenon compared to the micelle formation.

Extrapolation to zero solubilize amount would lead automatically to the micellar aggregate which appears according to this point of view as an auto-solubilization phenomenon. Such a leading role attributed to the microemulsion formation is confirmed by the fact (2) that a thermodynamically stable emulsion can be obtained only if the necessary concentration of surfactant required to build up the microemulsion is smaller than the corresponding cmc. Thus solubilization and micellization are competitive processes. This is nicely demonstrated by Fig. 1 where the onset of the solubilization process (= "detergency" curve) clearly precedes that of the micellization. Which emulsion type, i.e. W/O-, or O/W- is formed, depends largely on the nature of the surfactant. It is, moreover, possible that a phase inversion occurs depending on the water to oil ratio and the temperature of the system. The latter is generally called the phase-inversion temperature (PIT, Shinoda). Whether such an inversion leads to a

thermodynamically stable microemulsion can be inferred from considerations based on classical thermodynamics (22) (Note b). The properties of both these emulsions, however, are different in many respects according to the respective continuous phases. Comparing both emulsion types it appears that a more natural transition exists between normal micelles and the corresponding microemulsion. These micelles already contain a hydrocarbon core with liquid-like structure. The microemulsion is thus formed by adding up increasing amounts of oil (within the stability region of the microemulsion) which are soluble in the hydrocarbon core. It is interesting to note that also solid material is easily solubilized without the addition of a dissolving agent as is the case with solubilizate taken up by inverted micelles. Hence O/W-microemulsions represent in their simplest form a ternary system while W/O-emulsions are generally to be considered quaternary systems.

With regard to the stability against coalescence there is a noteworthy difference between W/O- and O/W-emulsions. The O/W type is certainly better stabilized by the electrostatic repulsion of the electrical double layer than the W/O microemulsion. The latter is stabilized by sterical repulsion between the micellar "membranes".

In the last few years the interest appears to have strikingly shifted towards W/O-microemulsions. The main reason for this is probably the opportunity to investigate the structure of water in the hydrocarbon environment in the presence of surfactant: in particular its dependence on the water concentration, influence on the micellar membrane by the hydrophobic hydration (23) and the sensitivity of the water structure on additives (salt and hydrocarbon). Moreover, the discovery of a remarkable catalytic activity has considerably fostered the research on this type of emulsion.

Most of the available information stems from thermodynamical investigations. Comparatively little work was directed towards structural details. Only more recently a systematic photon correlation spectroscopic study has been performed (15) on ternary W/O-microemulsions, i.e. H₂O/AOT/isooctane, which revealed generalizable results regarding ternary W/O-microemulsions formed by ionic surfactants. It appears that for the first time experimental evidence has been presented that there actually exists a physically reasonable difference between inverted micelles and W/O microemulsions. This could have been inferred already from the well-known phase diagrams (T-(amount of H₂O solubilized)) of a W/O-microemulsion (Fig. 5).

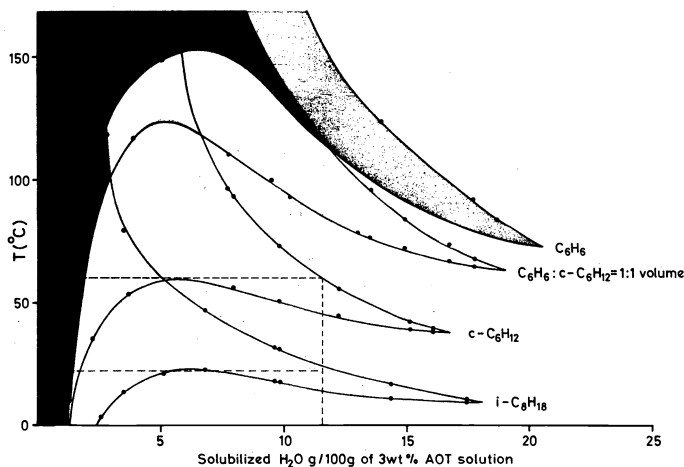


Fig. 5. Phase diagrams of AOT in different solvents and solvent mixtures. Temperature plotted vs. amount of solubilized water. From (24).

This is illustrated in more detail by Fig. 6 and Fig. 7 which show plots of the hydrodynamical radii (r_h) and the incremental surface area covered by one AOT molecule (\bar{f}_{AOT}) of the oil/water interface versus the temperature and the amount of added water (w_o), respectively. Both figures mutually support each other, indicating a splitting into two groups of essentially similar curves (Fig. 6) within a narrow w_o -range and a clear change in the slope of \bar{f}_{AOT} versus w_o in Fig. 7 at about the same w_o -values. The lower group of curves in Fig. 6 is attributed to the micellar domain, characterized by the very weak temperature dependence. In contrast with this group is the upper ensemble of curves which strongly depends on tem-

Note b. Naturally, one would expect cosurfactants to be considered in order to produce stable microemulsions with high contents of solubilized material. However, the present discussion is concerned with the proper microemulsion phenomena which can be produced without the addition of cosurfactants.

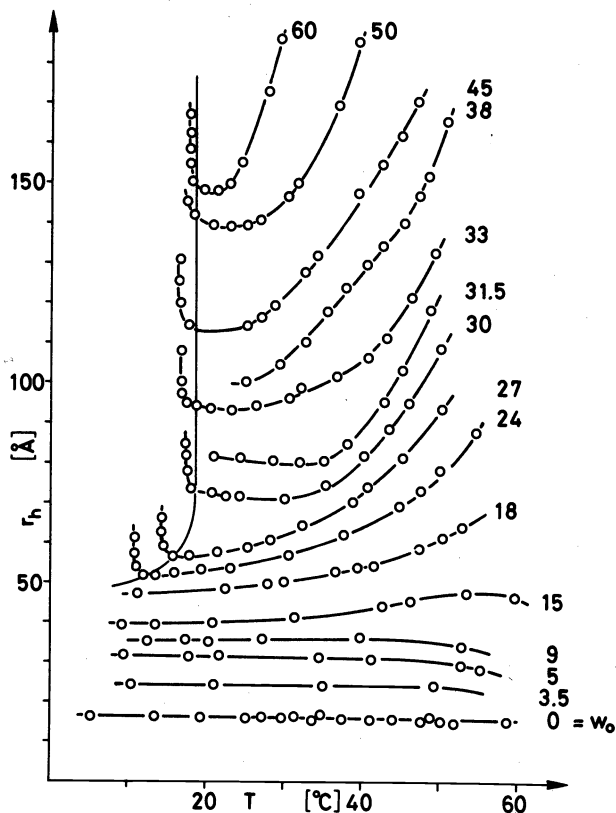


Fig. 6. Stokes radii (r_s) of microemulsion ($H_2O/AOT/isooctane$) droplets vs. temperature. Parameter: $w_0 = [H_2O]/[AOT]$. The vertical line indicates a stability boundary to the left of which spontaneous growth of the aggregates occurs which will ultimately lead to phase separation. From (15).

perature, pressure, mutual solubility of the microemulsion components etc. since now the interfacial free energy of the system is the relevant thermodynamical magnitude which determines the stability of the system. This is, accordingly, the microemulsion region. Fig. 7 expresses the same fact, as at low w_0 -values a steep increase of $\bar{f}_{AOT}(w_0)$ is displayed, whereas above $w_0 = 15-20$ the incremental coverage per AOT molecule of the oil/water interface stays approximately constant. Thus the curve reflects the transition from a micellar aggregate with a more or less ordered surfactant network to a more defined interfacial monolayer.

An interesting detail was the detection of an optical matching phenomenon which depended on the water content (Fig. 8). A recent analysis of this fact revealed a number of molecular details of the microemulsion. The minimum of the scattering intensity versus w_0 , i.e. the proper optical matching, could be excellently described by the adsorption model developed earlier on the basis of dipole - image dipole interactions between the water core and the adsorbed surfactant dipoles (25). Its validity is restricted to the microemulsion region which is clearly reflected in Fig. 8. The first part of the scattering plot $I_{90}(w_0)$ is best fitted using the initial part of the experimentally obtained $\bar{f}_{AOT}(w_0)$ plot (Fig. 7), thus identifying the maximum region of the scattered intensity with the micellar domain. The surprising coincidence of the applied equi-partition model with the experimental plot seems to point to a relatively small polydispersity. The physical parameters used to fit the scattering curve indicate that the surface conduction of the microemulsion droplets are negligible, i.e. they appear to the light like dielectric spheres (26).

The increasing residual scattering at higher temperatures (see Fig. 9) is straight-forwardly explained by the temperature dependent fluctuations of the interfacial surfactant layer covering the dispersed droplets (26). The fluctuations can be observed since the optical matching phenomenon is due to a compensation of the static contributions to the refractive

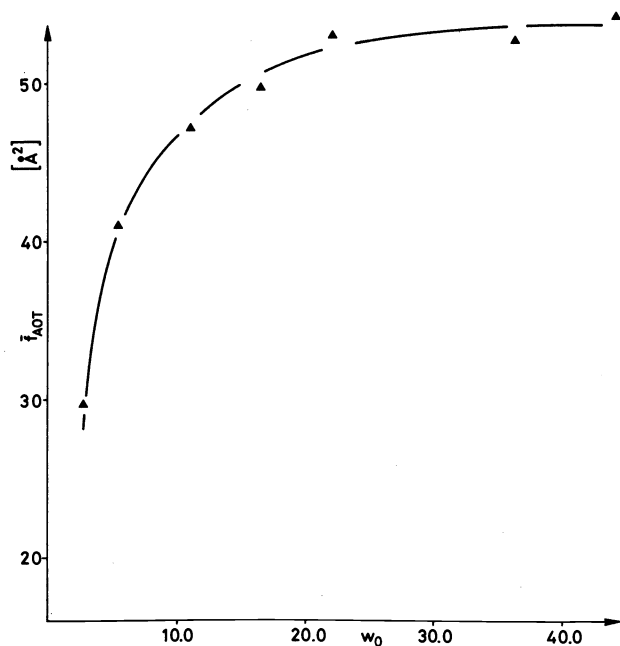


Fig. 7. Average surface fraction (\bar{f}_{AOT}) of the H₂O/oil interface covered by one surfactant (AOT) vs. weighed-in amount of water w_0 . From H.F. Eicke and J. Rehak, *Helv. Chim. Acta* 59, 2883 (1976).

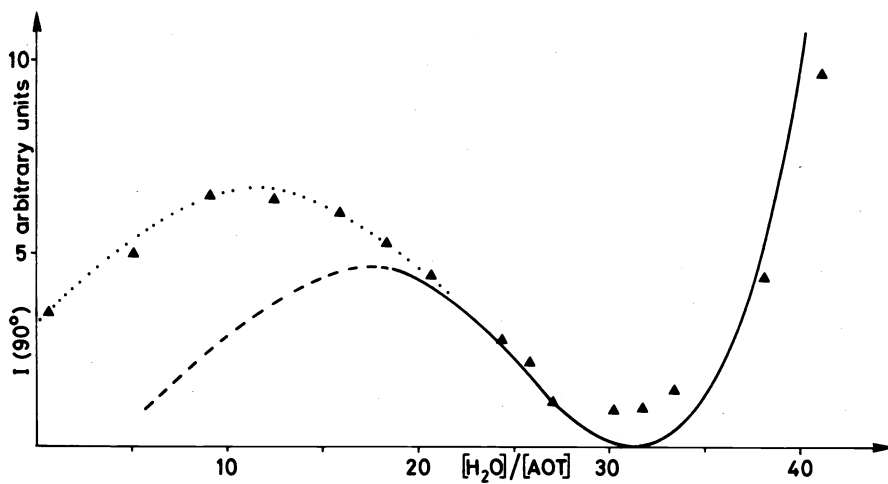


Fig. 8. Scattered intensity I_{90° vs. $w_0 = [H_2O]/[AOT]$ (Δ) at 25°C. System: H₂O/5,510⁻²m AOT/Isooctane. Solid line: Rayleigh scattering calculated according to monodisperse microemulsion model. Dotted line corresponds to initial part of $\bar{f}_{AOT}(w_0)$ curve (Fig. 7).

indices of the dispersed particles and the solvent (= oil), respectively. Hence, except for these fluctuation increments, the microemulsions discussed in the present paper are remarkably monodisperse.

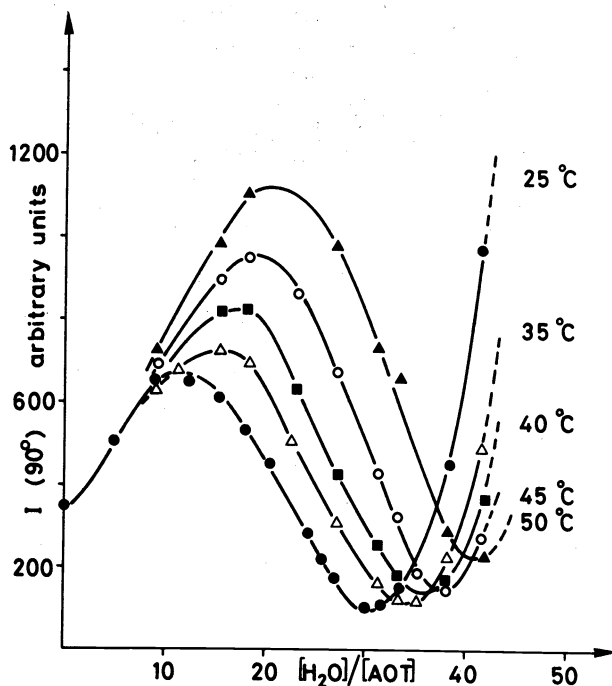


Fig. 9. Extrapolated intensities (I_{90°) vs. $w_o = [H_2O]/[AOT]$ for five temperatures. From (15).

It is believed that our present view of the microemulsion phenomena is already rather detailed on a microscopic (colloidal) level. The next step will certainly acquire deeper insights into the molecular interactions responsible for the observed phenomena.

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