

PROPERTIES OF AMPHIPHILIC ELECTROLYTES IN NONPOLAR SOLVENTS

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Abstract - This review reports on the properties of micelles in nonpolar media and on oil-continuous (W/O) microemulsions. Recent experimental and conceptual progress is considered.

INTRODUCTION

Since the classical investigation of Hartley (1) and McBain and Hutchinson (2) ionic surfactants or detergents, i.e. the "classical" soap molecules which are composed of two spatially separated hydrophilic and hydrophobic molecular moieties, are known to show considerable electrical conductivities in dilute aqueous solutions. These conductivities are quite comparable with those of strong electrolytes as is the case, for example, with cetylsulfonic acid. It has become customary to distinguish anionic and cationic surfactants, a notion which conventionally refers to the limiting case where a relative small counterion is attached to a large lipophilic anion or cation which is covalently bound to the hydrocarbon moiety of the soap molecules. A characteristic feature of these compounds is the observation of simultaneously large electrical conductivities and remarkably small osmotic pressures above a rather well-defined soap concentration (the so-called critical micelle conc. = cmc, see Figs. 1+2). The latter observation could be consistently interpreted as being due to homoassociation processes leading to micelle formation. Hence amphiphilic electrolytes are often called colloidal electrolytes.

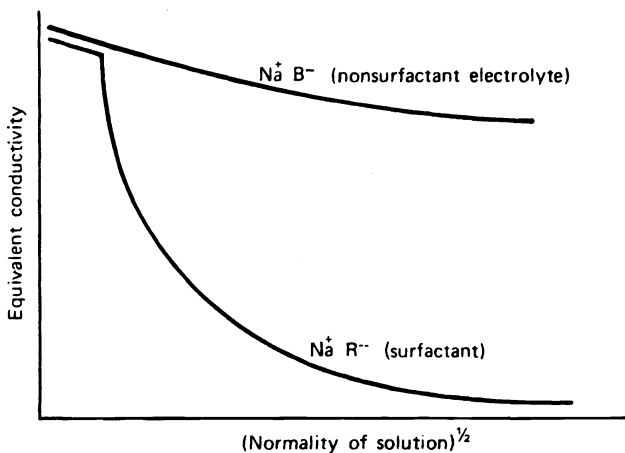


Fig. 1. Typical plot of the equivalent conductivity versus the square root of electrolyte concentration; upper curve: nonsurfactant electrolyte, lower curve: ionic surfactant. The break in the curve is attributed to the critical micelle concentration (cmc).

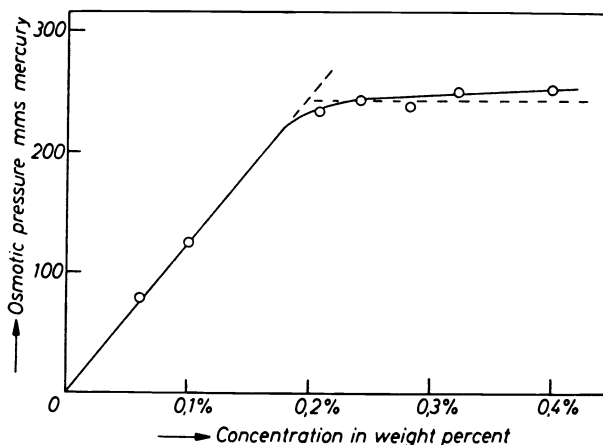


Fig. 2. Change of osmotic pressure with sodium dodecyl sulfate concentration (from L. Hess and L.A. Suranyi, *Z. phys. Chem.* **184**, 321 (1939)) break in plot  $\approx$  cmc.

Judging from the experience with electrolytes in nonpolar solvents one should expect rather small electrical conductivities due to the considerably reduced dissociation of even the most typical strong electrolytes and the formation of all kinds of association structures, i.e. generally oligomers, as demonstrated by Fuoss and Kraus (3). Contrary to what one should expect from these early investigations of electrolytes in nonpolar solvents, the formation of large homoassociative structures i.e. micelles, of ionic surfactants in nonpolar media is generally less pronounced compared with colloidal electrolytes in aqueous solutions. This is probably the main reason that the micellization phenomenon of amphiphilic electrolytes in nonpolar solutions has been experimentally verified comparatively late. The small aggregation numbers of the micellar entities caused relatively small changes of the physical parameters used to detect these association processes. This fact caused many debates as to whether at all such well-defined aggregates exist in nonpolar media. However, in view of the large amount of experimentally available data, these discussions have now been settled and the formation of the so-called reversed or inverted micelles in non-aqueous media is considered to be beyond doubt (4). Many surfactants indeed show a rather broad transition region between the monomer (or oligomer) state to the micellar region due to a low cooperativity of the micellization process. It is certainly meaningful to question whether in such cases the micellar concept is justified (5). Such situations occur more frequently with the so-called cationic surfactants in nonpolar media.

A particular interesting group of anionic surfactants, i.e. alkyl- and arylsulfonates, form, on the other hand, remarkably stable and (according to a generally agreed terminology) monodisperse micellar aggregates; the sizes of which are temperature and weighed-in concentration independent within a large range of the respective variables (see Figs. 3 and 4). Micelles of di-2-ethylhexylsulfosuccinates will be considered in this context in some detail. The sodium salt of this compound forms micelles in isooctane which do not change their sizes between  $-80$  and about  $100^{\circ}\text{C}$ . This surprising stability puzzled workers for quite some time. Finally it became apparent that small traces of water which can hardly ever be excluded from the nonpolar surfactant solutions were responsible for the high stability and low polydispersity of some of these detergent aggregates (6). According to the investigations of Zundel (7), Oedberg et al. (8), Sunamoto et al. (9), and of other authors, Zundel suggested that a water molecule is attached to the counterion which links via two hydrogen bridges other sulfonate surfactant molecules, thus forming some kind of a network structure. This model obtained much support by extensive IR- and NMR- as well as by more indirect techniques (e.g. the decrease of the aggregation number of the homoassociates by increasing the hydrophobicity of the counterions (6)) that it may claim to be rather realistic. From this consideration the different behaviour of the cationic surfactants may be inferred: with increasing hydrophobicity of the counterion, the attachment of a water molecule becomes less and less probable.

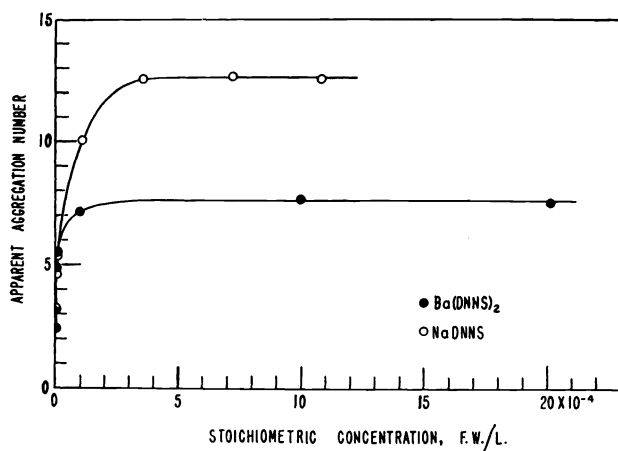


Fig. 3. Concentration dependence of sodium and barium dinonyl naphthalene sulfonate aggregates (micelles) in benzene at 25°C. (11)

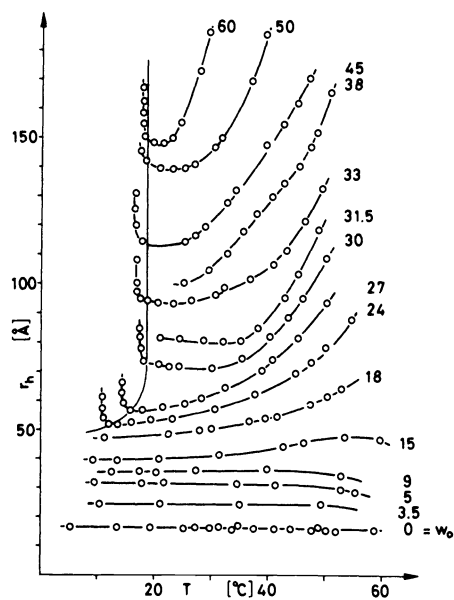


Fig. 4. Temperature dependence of the hydrodynamic radius ( $\bar{r}_h$ ) obtained from photon correlation spectroscopic measurements with sodium di-2-ethylhexyl sulfosuccinate (AOT) in isooctane. Parameter:  $w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$ .  $[\text{AOT}] = 7 \cdot 10^{-2} \text{ mol dm}^{-3}$ . (17)

It appears worthwhile to emphasize that the frequently encountered nonstoichiometric association pattern of dipolar molecules in nonpolar solutions is not concerned in this context. The latter processes may certainly occur without the presence of water. However, in the above particular case of micelles these species are probably more related to stoichiometric complexes than to the less well defined molecular aggregates. That this is probably the case is borne out by very recent small angle x-ray scattering measurements with di-iso-hexadecylzinculfonate in isododecane (10). The authors concluded from their measurements that mate-

rial with a comparatively low electron density exists in the so-called polar core of the inverted micelles. This material corresponds to apolar tails and eventually to some solvated solvent molecules. In view of Zundel's model this could be interpreted to indicate that a network structure is a realistic description of an inverted micelle.

#### PROPERTIES OF INVERTED MICELLES IN NONPOLAR MEDIA

Apart from their considerable concentration and temperature independent aggregation number of monomers, these inverted micelles exhibit also a relatively weak dependence on the non-polar solvent (4). Only the slightly polar ethylacetate or pseudo-apolar dioxane reduced the aggregational tendency of sodium di-2-ethylhexyl sulfosuccinate (AOT) or of the corresponding phosphate (POT) compound. (Fig. 5)

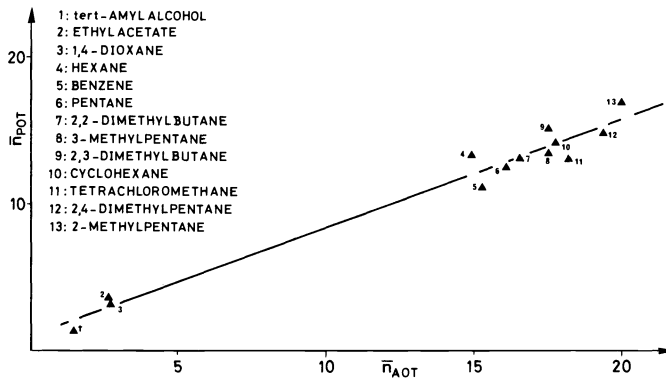


Fig. 5. Correlation of average association numbers of sodium di-2-ethylhexyl sulfosuccinate ( $\bar{n}_{AOT}$ ) and sodium di-2-ethylhexyl phosphate ( $\bar{n}_{POT}$ ) in different organic solvents, 25°C. (6)

This tendency is typical for a large number of anionic surfactants. Hence characteristic aggregation numbers of the above mentioned anionic surfactants were found in the range of 15-20 monomers for AOT and 10-15 for POT. The same behaviour has been reported in the case of dinonylnaphthalene sulfonates by Little and Singleterry (11).

An interesting question might arise as to whether these reversed micelles cause an enhanced electrical conductivity. Such a conductivity analysis has been carried out by Eicke and Arnold (12) in order to determine structural changes of the nonpolar surfactant solutions and to elucidate the micelle formation (Fig. 6). The electrical conductivity is indeed increasing in the range of the so-called critical concentration indicating an increased probability for dissociation within the micellar network structure and some kind of exchange mechanism within the micellar "phase" or between the micellar and the solution pseudo-phases. The latter concept stems from the frequently applied thermodynamic "phase-separation" model applied to describe the formation of micelles (13). These considerations are based on an electrical conductivity model in the case when the micelles have taken up some water, i.e. that so-called "swollen" micelles, have formed (14), see Fig. 7.

The micellar phenomenon cannot be considered without mentioning a surfactant property which is intrinsically related to the existence of micelles. This is the so-called detergency, i.e. the tendency of soap molecules to take up (= solubilize) polar material, in particular water and hydrophilic molecules which may form hydrogen bridges to the respective hydrophilic groups of the surfactant molecules. Solubilization and micellization are actually competitive processes (15). Unpublished results regarding the solubilization of gases (16) have clearly demonstrated that the just mentioned hydrogen bridge formation appears to be essential in considering solubilization phenomena in nonpolar media. This observation would again stress the above discussed importance of hydrogen bridges with respect to the stability of these aggregates. Very recent results from small angle x-ray scattering in nonpolar AOT solutions with up to about 15 mol water per mol AOT indicate that water is solubilized

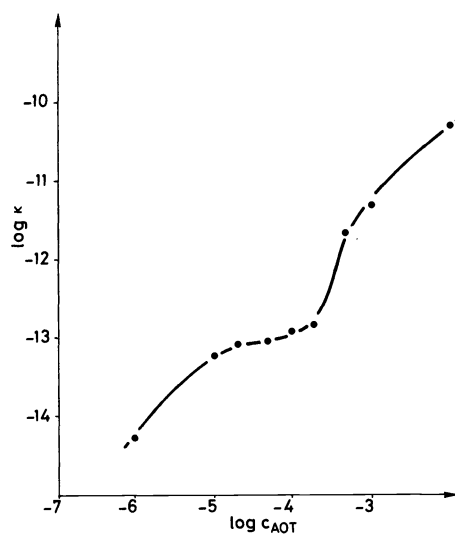


Fig. 6. Specific conductivity ( $\kappa$ ) versus concentration of sodium di-2-ethylhexyl sulfosuccinate in benzene at 20°C. (cmc at about  $2\text{--}3 \cdot 10^{-4} \text{ mol dm}^{-3}$ ). (12)

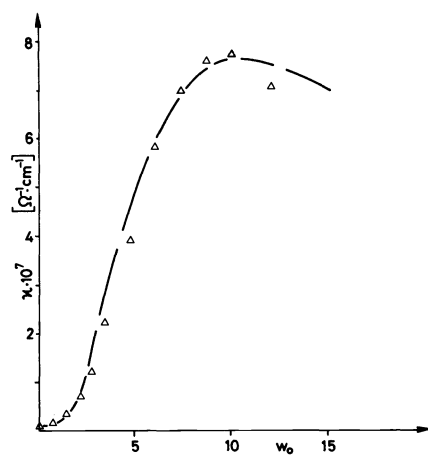


Fig. 7. Specific conductivity ( $\kappa$ ) of  $0.83 \text{ mol dm}^{-3}$  sodium di-2-ethylhexyl sulfosuccinate (AOT) in benzene at  $25.00 \pm 0.05^\circ\text{C}$  versus amount of solubilized water,  $w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$ . Experimental points ( $\Delta$ ), solid line calculated according to model, see (14).

by swelling the aggregates. The same observation has been made by quasi-elastic light scattering (see Fig. 4) and ultracentrifuge measurements (17). These investigations together with microcalorimetric, IR- and NMR-studies have shown consistently that up to about 15 water molecules in the case of the AOT/isooctane system are bound by hydration or trapped, i.e. the structure of this initially added water is considerably disturbed. From these investigations another conclusion as to a possible network structure could be obtained (18): the average surface fraction per surfactant monomer at the water/oil "interface" is steeply increasing with the initially added amount of water up to about  $[H_2O]/[AOT] = 15$ . Above this amount the value of the apparent surface fraction per AOT-molecule stays constant.

#### PROPERTIES OF OIL-CONTINUOUS MICROEMULSIONS STABILIZED BY COLLOIDAL ELECTROLYTES

According to recent views the notion "microemulsion" can now be given a more precise physical meaning: the physical parameters mentioned above which have been used to follow the uptake of initial small amounts of water by micelles are also suitable to follow the transition from the micellar to the microemulsion region, i.e. to the solubilization of large quantities of water or aqueous solutions of substrates. In the case of AOT in isooctane up to about 130 mol water/mol AOT (at  $C_{AOT} = 0.2 \text{ mol dm}^{-3}$ ) can be solubilized. Similar figures are found for other anionic surfactant systems in nonpolar solvents. This corresponds to volume fractions of water,  $\Phi(H_2O)$ , of about 0.45, thus giving an idea of the large quantities of water which may be contained in a totally nonpolar solvent. The physical picture of these microemulsion particles is different from the above mentioned "swollen" micelles; referring to the same surfactant system one has to assume a transition (probably a more continuous one) from the micellar network structure to a more well-defined entity which can be visualized as consisting of an aqueous core and a surfactant monolayer. According to photon correlation spectroscopic (17) and recent NMR (19) measurements this transition extends up to a water/surfactant ratio of about 15 in the AOT/isooctane system.

The microemulsion region is characterized (in contrast to the micellar domain) by a sensitive temperature, pressure and additive (= cosurfactant) dependence. This situation is nicely demonstrated in Fig. 8 where  $D_2O$  has been solubilized by AOT in isooctane.

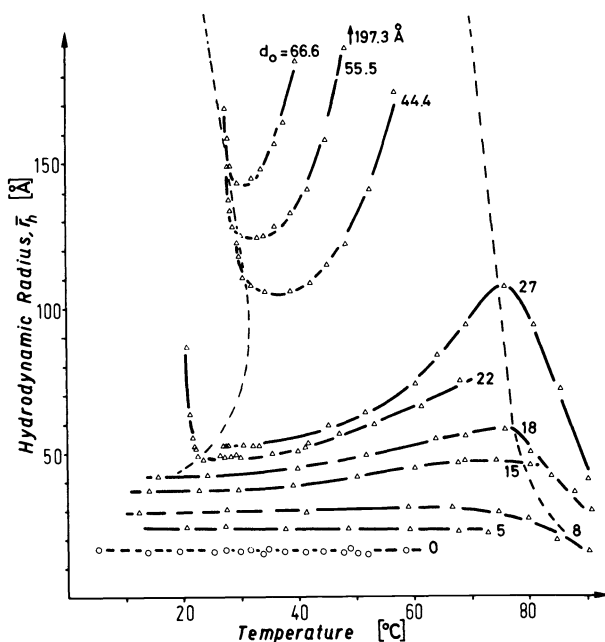


Fig. 8. Temperature dependence of hydrodynamic radius ( $\bar{R}_h$ ) derived from photon correlation spectroscopic measurements with sodium di-2-ethylhexyl sulfosuccinate in isooctane,  $d_0 = [D_2O]/[AOT]$ ,  $[AOT] = 5 \cdot 10^{-2} \text{ mol dm}^{-3}$ .

The diagram contains two coexistence curves enclosing the W/O-microemulsion region. On the left hand side, the low temperature region, the data points on the vertical branch of the

plot were determined every 30 sec. This boundary line is the so-called cloud point curve separating the stability region of the pseudo-one-phase microemulsion region from a pseudo-two phase domain. The experimentally observed particle growth may be interpreted by a coagulation process, leading to an increasing clustering of the microemulsion droplets and eventually to a macroscopic phase separation. The boundary line at higher temperatures, defined by the maxima of the temperature dependent hydrodynamic radii of the microemulsion droplets,  $\bar{r}_h$ , is the so-called solubilization curve. It could be shown quite recently (20) that these maxima correspond to phase transitions from closed aggregates (= microemulsion droplets) to open water/surfactant structures (probably lamellar lyotropic liquid crystalline structures). Hence, between these two boundary lines a structural homogeneous microemulsion region exists of closed aggregates, i.e. micelles and microemulsion droplets. The latter investigations were done with the help of electrooptical Kerr-effect measurements. They are in perfect agreement with the above mentioned quasi-elastic light scattering experiments. The phase transition between closed and open water/surfactant structures could also be confirmed by conductivity studies. The specific conductivity increased by about four orders of magnitude indicating a considerably increased coherence of the water structure.

The quasi-elastic light scattering experiments revealed another interesting property of the microemulsion particles (= droplets). An optical matching phenomenon was observed where the indices of refraction of water and the surfactants matched that of the isooctane at a particular water/surfactant ratio. The condition to observe such a matching phenomenon is defined by  $n(i-C_8) > n(H_2O)$  [where  $n$  = index of refraction] (21). From Fig. 9 it is seen that a residual scattering is observed apparently due to density fluctuations of the surfactants in the surfactant monolayer covering the microemulsion droplets.

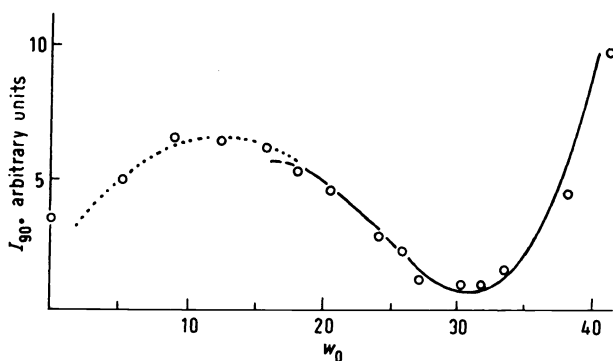


Fig. 9. Scattered intensity ( $I_{90}$ ) at right angle to the incident beam versus the amount of solubilized water,  $w_0 = [H_2O]/[AOT]$ ,  $25^\circ C$ ,  $[AOT] = 8.17 \cdot 10^{-2} \text{ mol dm}^{-3}$ ; open circles experimental points, solid line calculated according to theoretical model (21).

The main contribution to the observed light scattering below and above the matching condition is caused by density fluctuations of the droplets. Since the latter became "invisible" to the light, fluctuation processes within the surfactant layer become observable. The density fluctuations of the surfactants within the monolayer can be utilized to obtain information regarding the temperature dependent compressibility of the surfactant monolayer. Thus the compressibility of the oil/water interface (including the surfactant) as a function of the temperature passes (parabola-like) through a maximum and decreases again at higher temperatures. Considering the temperature dependent compressibility of an aqueous electrolyte solution ( $\approx$  ionic part of the surfactant) the compressibility of the predominantly apolar part of the surfactant layer can be determined qualitatively if the compressibilities of the apolar and ionic parts of the surfactant are considered to be approximately additive. The solubilization capacity can be considerably increased by the addition of so-called co-surfactants. These additives possess also an amphiphilic character as, for example, alcohols; however they are not sufficiently surface active to stabilize a microemulsion. Even additives which are apparently not surface-active like benzene or cyclohexane may considerably influence in minute amounts the solubilization capacity. A thermodynamical analysis of the cosur-

factant concept which elucidates some of the relevant aspects has been published some years ago (22). Cosurfactants are of particular importance if predominantly water or oil soluble surfactants are used to form oil in water or water in oil microemulsions, respectively. A particular interesting property of microemulsion droplets is their ability to catalyze reactions of solubilized substrates (20). An example is the rate of the aquation reaction of tris(oxalato)chromate (III) anion. In this case the rate in the reversed micelle is enhanced by a factor up to  $5 \cdot 10^6$  with respect to that in bulk water. In this reaction water is one of the reactants. The surfactant used was ammonium carboxylate in benzene (24). It appears characteristic that the so-called micellar catalysis is conducted in general in nonpolar cationic surfactant solutions. Whether it is justified, however, to introduce a new notion for these catalytical influenced reactions in the micellar pseudo-phase has been critically considered some time ago (25). In addition, photochemical reactions in microemulsions (26) and possibilities towards energy conversion have more recently been discussed. The numerous potentialities of microemulsions in applied science and technology cannot be estimated. Due to the rapidly increasing theoretical understanding and the almost explosive development of new experimental techniques new scientific and technological applications are to be expected.

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