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SOME ASPECTS ON THE HYDRATION OF SURFACTANT MICELLES

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Abstract - A review of the hydration properties of surfactant micelles
is presented. Water self-diffusion studies are found to give global
hydration numbers corresponding approximately to the hydration of the
counterions and the polar head-groups. The hydration numbers are in-
consistent with water penetration into micelles and other arguments
against such an effect are discussed as well. Furthermore, the hydra-
tion of counterions and the effect of solubilization on hydration are
discussed. Sodium cholate differs considerably in its self-association
behaviour from micelle-forming amphiphiles and this is found to apply
also for the hydration characteristics.

INTRODUCTION

The aggregation of amphiphilic compounds into micelles and other structures,
being associated with eliminating the unfavourable contact between the non-
polar groups and water, is an event specific to aqueous solutions. An impor-
tant question refers to exactly how much of the amphiphile - water contact
that is retained in the micelles. That the major part of the hydrocarbon
chain - water contact is eliminated on micelle formation is inherent in our
view of the driving forces of micelle formation but has also been directly
demonstrated by a large number of experimental studies. However, several
authors have presented strikingly opposing views of micelle hydration. These
are mainly based on spectroscopic probe studies which have been taken to in-
dicate that there is an extensive penetration of water far into micelles.
The present article, in reviewing previous results and presenting some novel
experimental information, examines in a broad way the matter of the hydration
of amphiphilic aggregates. Questions to be discussed include global hydration
numbers, location of water molecules, counterion hydration, hydration dyna-
mics and effect of solubilization on hydration. In particular we examine the
evidence taken to show that there is a deep water penetration into micelles.

In considering the exposure of the hydrocarbon chains to water, the dynamic
state of the micelle must be taken into account. The life-time of a monomer
in a micelle may be of the order of a microsecond and, in view of the well-
established dynamic state of a micelle, this implies that less extensive
motions occur on a shorter time-scale. The dynamic protrusion of methylene
groups from the hydrocarbon core of a micelle has recently been examined by
Aniansson (1) who came to the conclusion that there is a considerable pro-
trusion. Thus every third monomer would protrude more than one methylene
group and the average protrusion would be one methylene group. A considerable
roughness of the micellar surface has been inferred also by others and an
attempt to visualize the dynamic roughness of the micelle surface is given in
Fig. 1.

GLOBAL HYDRATION NUMBERS OF MICELLES

There is a large number of both thermodynamic, transport and spectroscopic
methods wich can be used for investigations of the hydration of amphiphilic
aggregates. The micelle-water interaction is highly dynamic and stoichio-
metrically not well defined and, therefore, the concept of a single hydration
number is a simplification; the meaning of a hydration number will be depen-
dent on the particular experimental approach considered. An initial suitable
definition for our present purpose is to take the micelle hydration number as
the number of water molecules moving with the micelle as a kinetic entity.
Such a global hydration number can be deduced from transport properties, e.g.
viscosity and diffusion. Mukerjee (2) has given a useful description of the
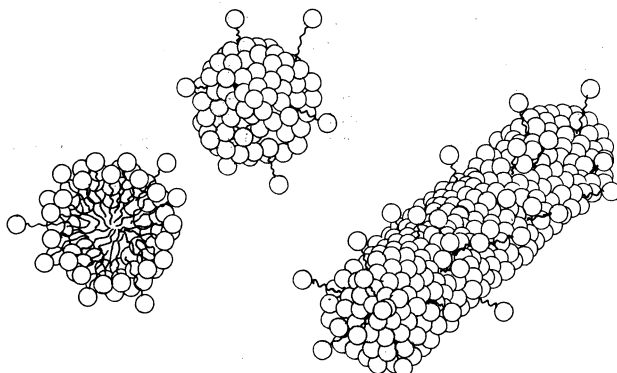evaluation of hydration numbers from viscosity data. The procedure involves

Fig. 1. A picture of spherical and cylindrical micelles showing
the protrusion of some amphiphile molecules. The interior shows
the disorded state of the hydrocarbon chains. (By the courtesy
of J. Ulmius.)

the determination of the intrinsic viscosity and comparing it with the par-
tial specific volume of the amphiphile. The precision of the method is re-
duced since certain corrections, mainly for electroviscous effects, may have
to be applied.

Ourselves, we have been interested in determining micelle hydration numbers
from the translational self-diffusion coefficient of water. Ideally, some of
the water molecules can be considered as associated with the micelles and
having the translational mobility of the micelles while the rest of the water
molecules are free having the translational mobility of pure water. In rea-
lity, certain corrections may have to be applied, notably for the hydration
of the non-associated amphiphile and of the free counterions and furthermore,
the mobility of free molecules may be retarded inter alia due to obstruction
effects. The observed diffusion coefficient can be written as an average
over all the different environments $\underline{i}$ that the water molecules sample, i.e.

$$D = \Sigma P_i D_i \qquad\qquad\qquad\qquad (1)$$

where P_i is the fraction of the water molecules in site $\underline{i}$ characterized by
the diffusion coefficient D_i. We used as an experimental approach the open-
ended capillary tube method[1] employing tritium labelling. Hereby it is
usually possible to determine diffusion coefficients with a precision of
1-2 %. However, the applicability of the technique depends on the consistency
etc. of the sample; for highly viscous cases, studies are thus precluded and
for anisotropic phases the interpretation is difficult.

It is a general observation in our studies of the water diffusion as a func-
tion of the surfactant concentration that the diffusion coefficient decreases
much more rapidly below than above the c.m.c. The mobility of a water mole-
cule bound to a micelle is much lower than that of a water molecule hydrating
the surfactant monomer but the reduction in surfactant-water contact is
evidently enough   to compensate for this effect. It is possible to
quantify the effect using eq. (1) which can schematically be written

$$D_w = P_w^{nm} D_w^{nm} + \frac{n_{mic} m_{mic}}{55.5} D_{mic} \qquad\qquad (2)$$

where D_{mic} is the diffusion coefficient of the micelles, m_{mic} is the molality
of surfactant in micellar form and n_{mic} the micelle hydration number (per
amphiphile ion). P_w^{nm} is the fraction of water molecules not associated with
the micelles and D_w^{nm} the corresponding effective diffusion coefficient.
In reality the first term of eq. (2) consists of three parts corresponding

in addition to the free water molecules to the water molecules hydrating the free amphiphile ions and the free counterions. The magnitude of this term can be established knowing the concentrations of free amphiphile ions and counterions, their self-diffusion coefficients and the effect of the non-associated surfactant on the water self-diffusion coefficient (from pre-c.m.c. studies). In the second term, D_{mic} can be determined separately (for example from the self-diffusion coefficient of a solubilizate (3)) but in most cases $D_{mic} \ll D_w^{nm}$ so that the second term may be neglected. The main effect of micelle hydration is then a reduction of P_w^{nm}, a reduction which is due to micelle hydration and gives information on n_{mic}. A further simplification is often possible for surfactants with low c.m.c:s in that the correction for a change in D_w due to an altered concentration of non-associated surfactant is negligibly small.
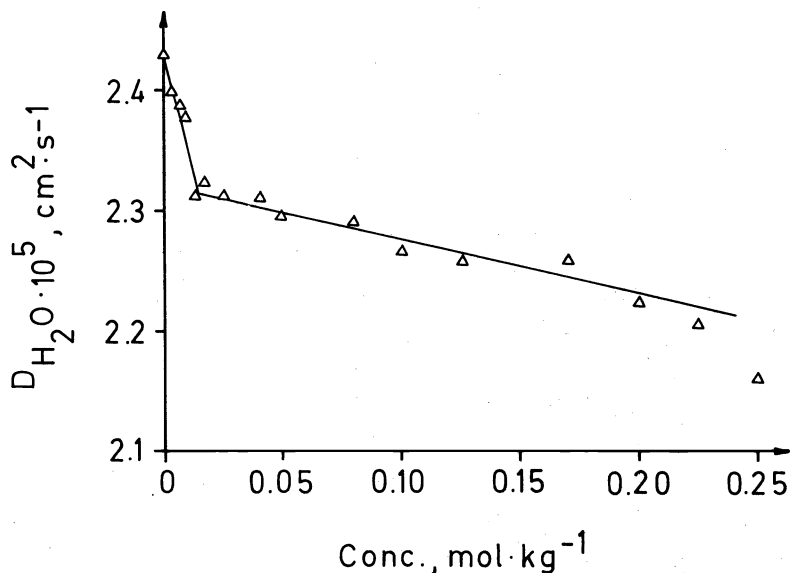

Fig. 2. Concentration dependence of the water self-diffusion coefficient for solutions of sodium octylbenzenesulfonate at 33 °C. (By the courtesy of M.-C. Puyal.)

An example of a determination of micelle hydration by the self-diffusion method is given in Fig. 2 for the case of sodium p-octylbenzenesulfonate at 33 °C. Evidently, the concentration dependence of D_w can be described by two linear segments intersecting at the c.m.c. The hydration number obtained is ca. 9 and as can be seen in Table 1, rather similar results are obtained for some other surfactants. Mukerjee (2, 4) some time ago concluded from this type of data for a few cases that the micellar hydration numbers can be accounted for in terms of hydration of the polar head-groups and the counterions. As can be seen, the more recent self-diffusion results support this view and as will be demonstrated below it appears that many simple counterions retain their primary hydration sheaths on binding to micelles.

WATER PENETRATION INTO MICELLES

According to the classical picture of surfactant micelles, as it was first clearly presented by Hartley in the 1930's, there is in the micelle a mini-mization of the contact between the alkyl chains and the water. It is now well established that the main driving force for micellization is the hydro-phobic interaction (Refs. 5 and 6 are recent reviews of the subject). This picture of micelles has been questioned at several occasions mainly in connection with spectroscopic studies. Thus it has been suggested that there is an important penetration of water deep into micelles. Earlier results of this type (7 - 9) were strongly refuted by Mukerjee (4, 10) and Stigter (11) but as the matter has again been advanced by Menger (12 - 14) in some recent papers it deserves discussion.

TABLE 1. Micelle hydration numbers expressed as the number of
water molecules per amphiphile ion.

Amphiphile[a]	Hydration number
$C_{12}OSO_3Na$	9[b]
$C_{12}OSO_3Na$	8[c]
$C_{12}OSO_3Na$	12[d]
$C_{12}N(CH_3)_3Cl$	5[b]
$C_{14}N(CH_3)_3Cl$	5[b]
C_7CO_2Na	8.5-8.9[e]
C_7CO_2Na	8.7[f]
$C_8(C_6H_4)SO_3Na$	9[g]
$C_{12}NO(CH_3)_2$	10[d]
$C_8NO(CH_3)_2$	10[d]

a. C_n is a n-alkyl chain with n carbon atoms.
b. Ref. 2.
c. F. Tokiwa and K. Ohki, J. Phys. Chem. **71**, 1343-1348 (1967).
d. W. L. Courchene, J. Phys. Chem. **68**, 1870-1874 (1964).
e. P. Ekwall and P. Holmberg, Acta Chem. Scand. **19**, 455-468 (1965).
f. Ref. 25.
g. M.-C. Puyal, D.E.A., USTL, Montpellier, 1978.

In a typical spectroscopic experiment concerning the amphiphile-water contact, one monitors a parameter of a probe, intrinsic or added, and correlates the value with that found in a pure solvent of a given polarity. Such an approach is connected with two problems, the seriousness of which is often overlooked. Firstly, to be able to deduce information about the molecular environment in the micelle one must have independent information on the distribution of the probe in the micelle. Secondly, the relation between the spectroscopic parameter in question and the nature of the molecular environment of the probe should either have a sound theoretical basis or it should be experimentally tested in detail.

Several studies giving a water penetration into micelles may be criticized on the basis of one or both of these points. A typical example is provided by the careful ^{19}F NMR chemical shift studies by Muller and co-workers (7, 8). These authors inter alia investigated ω-CF_3 substituted amphiphiles. Hereby it was found that the ^{19}F chemical shift is approximately midway of that of water and hydrocarbon solutions. This could be taken to imply that the -CF_3 group has an environment consisting of about equal amounts of water and hydrocarbon (7, 8) but as shown recently by Mukerjee (4, 10) and by Muller (15) such an interpretation can be criticized on the basis of the two points mentioned above. Mukerjee (4, 10, 16) gave strong arguments for an important sampling of the -CF_3 groups of the micelle surface. Thus there is a marked non-ideality of the interactions between fluorocarbons and hydrocarbons which is manifested for micelles in terms of anomalously high c.m.c:s for partially fluorinated surfactants and a partial demixing of the micelles for solutions containing both fluorocarbon and hydrocarbon surfactants. Muller (15) has recently shown in a detailed study of the factors influencing ^{19}F chemical shifts that the underlying mechanism is too complex to permit conclusions about environment polarity.

Menger et al. (12) studied water penetration using the amphiphile
$CH_3(CH_2)_7\overset{O}{\underset{||}{C}}(CH_2)_7N^+(CH_3)_3Br^-$ correlating the ^{13}C NMR chemical shift of the

carbonyl carbon with the shifts obtained in a range of solvents. Again one does not have a sufficiently good theoretical basis of the molecular cause of the shifts nor does one have independent information on the distribution of the carbonyl group in the micelle. The use of a polar probe like $-\overset{O}{\underset{||}{C}}-$ can certainly not be expected to report reliably on the environment

of the alkyl chains in a micelle. Rodgers and da Silva E Wheeler (17) in-
vestigated the quenching of pyrene fluorescence by inorganic ions and inter-
preted the effective quenching in terms of an extensive water penetration
deep into micelles. An assumption inherent in this work was though that
pyrene is solubilized remote from the micellar surface. However, it seems
that there is very good evidence for the solubilization of aromatic com-
pounds close the head-group region (4, 18 - 20) and there is, therefore, no
need to invoke any water penetration to explain these data. As regards a
Raman spectroscopic study (21) taken to support a less extensive water
penetration it can be said that the mode of interpretation has no theoretical
basis but is based on analogy. This refers also to a study of the vibronic
fine structure in pyrene fluorescence (22), but here pyrene solubilization
was, furthermore, taken to be in the interior of the micelles rather than in
the surface region, as in more recent studies (23, 24). Svens and Rosenholm
(9) from x-ray scattering data inferred partial water penetration into mi-
celles but it is clear that the model used in the analysis is oversimplified.
Menger (12 - 14) cites this work in favour of a much deeper water penetra-
tion than implied in the original paper (9).

It seems thus clear that the results taken as support of water penetration
have alternative reasonable interpretations and that there, therefore, is
no reason to abandon the classical picture of a micelle as an aggregate with
an apolar interior and a polar surface in contact with the surrounding
aqueous medium (4, 11). A most significant argument against a deep water
penetration seems to be given by the global hydration numbers of micelles
(2, 11, 25). The marked slope reduction at the c.m.c. in Fig. 2 is a very
direct demonstration that a strongly dominating part of the amphiphile-water
contact is eliminated on micellization. Several other pertinent observations
also exist. Brun et al. (26) obtained large positive isentropic apparent
compressibilities of several surfactants in micelles which indicates that the
interior of micelles resembles liquid hydrocarbons. Furthermore, the partial
molar volumes and compressibilities of solubilized alkanes are close to the
values of liquid alkanes but considerably higher than those in water (27).
The H/D isotope effect on ^{19}F NMR relaxation for partially fluorinated
and fluorocarbon surfactants disappears on micelle formation (28). Podo et
al. (29) observed no H/D isotope effect on ^{1}H NMR relaxation of the alkyl
protons, but a noticeable one for the ethoxy ones, for nonionic surfactant
micelles.

The low solubility of water in alkanes is of course in support of the ab-
sence of water penetration and more direct evidence on this point can be
obtained making use of the established similarity between different sur-
factant-water phases. Thus there is a low rate of water diffusion between
reversed micelles (30) as well as over lipid bilayers (31). Furthermore,
the stability ranges of different phases (32) are inconsistent with any
marked water penetration. Neturon diffraction studies using the D_2O/H_2O
exchange method show that water penetrates to the glycerol-fatty acid ester
group for phospholipid bilayers (33 - 35).

Menger (13) has recently from the building of space-filling molecular models
argued that it is impossible to pack the surfactant molecules into micelles
without leaving sizeable voids filled with water. However, this does not
agree with work by Gustavsson (cited in Ref. 5) which demonstrates the feasi-
bility of packing surfactant monomers into micelles without any water contact
except at the micellar surface.

SOME FURTHER POINTS ON THE HYDRATION OF AMPHIPHILIC AGGREGATES

Although the general features of micelle hydration, with a limited number of
water molecules located mainly at the micellar surface, thus seem well sup-
ported, it is of interest also to consider some additional aspects. For
example it is important to know to what extent bound counterions retain their
hydration sheath. For alkali counterions, there is significant evidence to
suggest that the primary hydration sheath is retained. This has been demon-
strated from volumetric studies (36, 37) and NMR studies which monitor di-
rectly the counterion give good support for this. Thus ^{23}Na$^+$ relaxation in
surfactant systems remains slow down to quite low water contents (38) and
^{23}Na$^+$ and ^{133}Cs$^+$ chemical shift changes on micelle formation are quite
small in comparison with what would be expected for direct counterion-head-
group approaches (39). An illustrative observation, reproduced in Figure 3,
is that the H/D water isotope effect in ^{133}Cs$^+$ chemical shift does not
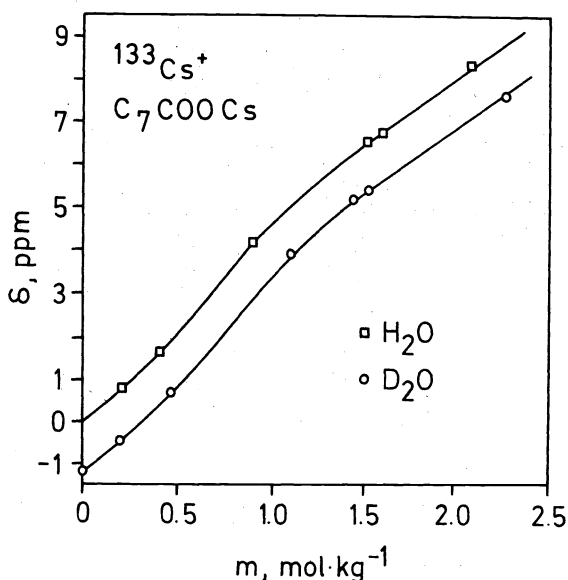
change even at very high concentrations (39).

Fig. 3. [133]Cs chemical shifts (ppm) of H_2O and D_2O solutions of cesium octanoate as a function of amphiphile molality. (After Ref. 39.)

Concerning the halide ions, we have yet incomplete information. The observation of charge-transfer interactions for I^- (40) and of rather large changes in Cl^- and Br^- quadrupole relaxation rates (41) on binding to micelles may be taken to suggest that there are significant direct counterion-head-group approaches. The marked counterion specificity noted in some cases for c.m.c., micellar size etc. points in the same direction.

Deuteron NMR quadrupole splittings of D_2O have been found useful to monitor the water orientation at amphiphilic surfaces in anisotropic surfactant-water phases, like lamellar and hexagonal mesophases. Since for a number of systems only ca. 5 water molecules per amphiphile are appreciably oriented and the water orientation is markedly alkali counterion dependent (42), these studies support the view of a limited hydration number and of hydrated counterions.

How solubilization influences micelle hydration is rather difficult to study since changes in physico-chemical parameters are small. For approximately spherical micelles of hexadecyltrimethylammonium bromide, self-diffusion studies indicate some release of hydration water on solubilization of octanol and hexanol but not on solubilization of cyclohexane (43); for higher concentrations there were interpretation difficulties. For anisotropic phases, the ^2H quadrupole splitting method can be useful. A study of hexagonal phases of water and sodium octanoate or sodium octylsulfate gave pronounced changes in the ^2H quadrupole splitting of D_2O (44). Roughly, a more polar solubilizate decreases water binding while a non-polar one gives a small effect or an increased water binding. This is according to expectation since a compound solubilized close to the micelle surface may displace some water whereas a compound solubilized in the micellar interior may increase the surface per polar group and thus increase hydration to some extent.

As mentioned above, it is well established that the micelle is in a highly dynamic state. A recent ^{13}C NMR study showed that there is no marked change in the alkyl chain mobility on micellization (45) and likewise the water molecules of micelle hydration are very mobile. Although quantitative information is lacking it may be suggested that the motion has a time-scale of the order of $10^{-11} - 10^{-12}$ sec.; the local motion at the amphiphile aggregate surface is not far from being isotropic as can be inferred from the

low value of the order parameter (ca. 0.01) of the bound water molecules
(42). As regards water exchange kinetics, we know from the NMR studies that
there is a rapid water exchange but quantitative information has not been
available. However, Tiddy et al. (46) recently observed an ultrasonic re-
laxation in the frequency range around 10 MHz for concentrated surfactant
solutions and mesophases which they attributed to water exchange; further
studies along these lines will be followed with great interest.

This discussion has concerned the hydration of aggregates of typical micelle-
forming amphiphiles but it may be of interest for comparison to consider
results for an amphiphile of another type, sodium cholate. It has been demon-
strated that sodium cholate is not characterized by the strongly cooperative
association into large aggregates which occurs for surfactants (47 - 50).
Our self-diffusion studies further illustrate the marked difference in se-
veral respects between sodium cholate and micelle forming surfactants (51,
52). Thus the fraction of cholate aggregated changes only slowly with con-
centration and the aggregates remain fairly small over a wide concentration
range. The degree of counterion binding is highly variable being quite low
for the first-formed aggregates but increasing progressively to values ty-
pical of surfactants at high concentrations. For micelle-forming amphiphiles,
the degree of counterion binding generally has a closely constant value over
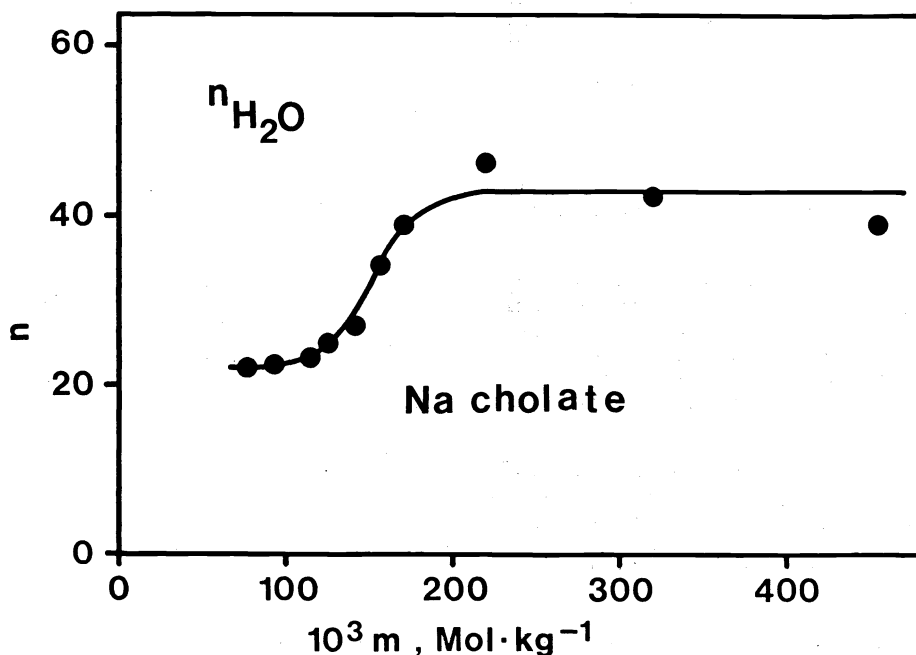a wide concentration range. As can be inferred from Fig. 4, hydration of

Fig. 4. Hydration number of cholate aggregates as a function of the
sodium cholate molality according to self-diffusion studies. (After
Ref. 52.)

cholate aggregates also shows some pecularities. Firstly, the hydration num-
ber is high and, secondly, it increases with increasing concentration.
(Certain difficulties in the evaluation necessitate some reservation as
regards the exact magnitude of the effects.) For surfactant micelles, al-
though not documented in detail, it seems that the hydration number stays
essentially constant or shows some decrease at higher concentrations. Al-
though far-reaching conclusions may not be drawn from these data they seem
to provide good support for a model involving a primary association in-
volving mainly hydrophobic interactions and a secondary association in-
volving non-hydrophobic (hydrogen bond) interactions (cf. Refs. 50, 53 and
54).

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