Hydration pressure of a homologous series of nonionic alkyl hydroxyoligo(ethylene oxide) surfactants

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The hydration pressure of a homologous series of nonionic surfactants of the type CH3(CH2)nh−1(OCH2CH2)mOH (CnEm) was determined by using sorption gravimetry. The hydration pressure shows a non-exponential decay on hydration and the curves are best fitted with a rational function. The non-exponential character is explained by contributions arising from the bending energy of non-lamellar liquid crystalline phases. The parameters obtained show that hydration of pure nonionic surfactants is correlated with the number of the oxyethylene groups in the headgroup. However, they are almost independent of the length of the alkyl chain. Exceptions are surfactants in the solid crystalline state that almost prevent hydration. Furthermore, the respective mesophase structures do not dominate the hydration behaviour. The Gibbs free energy (free enthalpy) of hydration is ~1.3 kJ mol−1 per oxyethylene group.

1 Introduction

Hydration pressure is correlated with important interactions in colloid systems and it was originally introduced by Langmuir. Later, it was extensively discussed for the disjoining pressure of phospholipid membranes because it is important for the approach of biological surfaces (e.g. cell fusion, stress on cartilage, osmotic dehydration, freezing induced dehydra-
tion1). Hydration pressure (also expressed by the hydration force) is a general phenomenon, i.e. it also plays a role for surfac-
tants, DNA, proteins, polyelectrolytes and polysaccharides.2–5 It represents a measure of the resistance to remove hydration water from a hydrophilic surface. A number of possible origins of this phenomenon have been discussed in various theoretical and experimental descriptions.4–8 We use the empirical definition: hydration pressure is the hydrostatic pres-
sure which maintains the chemical equilibrium of hydration water that is attached to a hydrophilic surface with a water phase existing under reference conditions (see also refs. 9 and 10).

Biomembranes are complex systems and therefore, model systems are required to study the basic properties of lipid membranes in detail. One of these model systems are phospholipid membranes modified by nonionic surfactants such as alkyl hydroxyoligo(ethylene oxide) surfactants, CH3(CH2)nh−1−
(OCH2CH2)m−OH (CnEm). Many studies were performed to investigate the structural and thermodynamical consequences of the incorporation of surfactants of this oxyethylene-type in model membranes.11–16 Moreover, CnEm are also useful tools for applications in biochemistry17,18 such as for the solubilisation of biomembrane components.19,20

This paper will present a systematic study on the hydration of pure CnEm surfactants as a function of the hydrophobic alkyl chain length, n, and of the number of the hydrophilic oxyethylene groups, m. The paper continues previous investigations from Klose et al.21 In this study, the hydration behaviour of the homologous series C12Em was examined for different headgroup sizes (n = 2–8) and two selected relative humidities (84.2 and 97.0%). Klose et al. found that the number of adsorbed water molecules grows linearly with the number of the oxyethylene groups and that the effective water binding energy increases by 7 kJ mol−1 by adding one oxyethylene group.

The present study reports sorption isotherms performed over the whole humidity range and it includes the investigation of surfactants with varied hydrophobic chain length (CnE8, CnE10, CnE12, CnE14, CnE16 and CnE18 with m = 2, 4, 6, 8). It should be expected that the variation of the hydrophobic chain length has little influence on the hydration parameters in contrast to a variation of the size of the hydrophilic head-
group. This study reports these differences for the given homologous series.

The hydration pressure was derived from the sorption isotherms according to the “osmotic stress method”22. Hydration pressure shows for phospholipids an exponential decay on hydration in the case of lamellar phases,6 and an exponential decay6 or a rational decay in the case of hexagonal phases.23,24 Another study performed on CnEm surfactants fitted the hydra-
tion pressure curves (hydration force curves) of lamellar phases and hexagonal phases by an exponential function.25 The CnEm surfactants show in fact a variety of liquid crystalline phases7,18 and we found an empirical description to fit all of these curves by a simple rational function. We try to give an explanation for the rational decay behaviour and we present the corresponding parameters. Furthermore, the sorption iso-
therms gave the Gibbs free energy (free enthalpy) of hydration.

2 Materials and methods

The nonionic surfactants of the type CH3(CH2)nh−1−
(OCH2CH2)m−OH CnEm were obtained from Fluka Chemie
AG and used without further purification. The sorption iso-
therms were determined by using the isopiestic method at a
temperature of 25 °C. The surfactants were dried over fresh
P₂O₅ which is a very efficient drying agent. The residual water
amount over P₂O₅ is smaller than 25 ng per litre of dry air.²⁷
The amount of water sorbed by the surfactants were deter-
bined by a microbalance system (Sartorius) and the humidity
was adjusted by a series of saturated salt solutions (RH = 11–
97%). The samples were thus equilibrated at the respective
humidity, and the achievement of the chemical equilibrium was
checked by time dependent measurements by using a computer-
aided data-processing. The water content, \( R_w \), is expressed by the molar ratio of water and surfactant:
\[ R_w = n_w/n_s. \]

The maximal absolute deviation of water content was
\( \Delta R_w < 0.5 \); the relative reproducibility, \( \Delta R_w < 0.05–0.1 \) (See also refs. 28 and 29).

3 Results and discussion

The sorption isotherms of the homologous series of \( \text{C}_n \text{E}_m \) (n = 8, 10, 12, 14, 16) are shown in a logarithmic plot in
Fig. 1. There is no systematic difference between the curves
in the range of \( n = 8–14 \). Only \( \text{C}_{16} \text{E}_4 \) shows a strong deviation
at low humidities. At these conditions, it sorbs almost no
water. However, at humidities higher than \( RH = 55\% \), the
hydration behaviour is very similar to that of the other surfac-
tants. The water/surfactant phase diagram¹⁸ of \( \text{C}_{16} \text{E}_4 \) does not
show a solid–liquid transition at this temperature. However,
upon increasing relative humidity, FTIR measurements per-
fomed in our laboratory (not shown) indicated that the sur-
factant shows a lyotropic chain melting transition between a
solid, nearly dehydrated phase and a fluid, well-hydrated
phase. Note that this behaviour is in contrast to phospholipids
which still sorb a substantial amount of water in the solid-like
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phase. Note that this behaviour is in contrast to phospholipids
which still sorb a substantial amount of water in the solid-like
gel-phase.³ The surfactants arrangements are obviously very
closely packed in the solid phase, so that water is almost not
sorbed. The molecular conformations of \( \text{C}_n \text{E}_m \) surfactants in the
dry and solid state are described by Matsuura et al.³⁰

The sorption isotherms for the series of the varied head-
group size \( \text{C}_1 \text{E}_m \) with \( m = 2, 4, 6, 8 \) show a different beha-
vour (Fig. 2) compared to the series of \( \text{C}_n \text{E}_m \) with \( n = 8, 10,
12, 14, 16 \). Such as expected,²¹ the amount of sorbed water
increases with the number of oxyethylene units of the head-
group. However, for lower water activities, there were no mea-
surable differences between \( \text{C}_{12} \text{E}_4 \) and \( \text{C}_{12} \text{E}_6 \). Furthermore,
there are remarkable differences in the case of \( \text{C}_{12} \text{E}_8 \). The
sorption isotherm of \( \text{C}_{12} \text{E}_4 \) reveals a possible lyotropic phase
transition at about \( RH = 50\% \). The water/surfactant phase
diagram¹⁵ indeed shows a transition between the lamellar
phase and the solid phase at about 9 wt% of water. This is also
confirmed by a recent study³¹ on the same system showing a
solid-to-mesophase transition.

Hydration pressure, \( P_h \), shows for phospholipids an exponen-
tial decay on hydration in the case of lamellar phases.⁹ This
derpendence is usually described by:
\[ P_h = P_{h,0} \exp \left( \frac{-R_w}{R_{w,0}} \right) \]

where \( P_{h,0} \) and \( R_{w,0} \) are the hydration pressure at zero hydra-
tion and the decay constant. The hydration can also be
described by the water layer distance, \( d_w \). In the case of
non-lamellar phases the curves of hydration pressure vs. hydra-
tion can be more complex. For instance, in the case of hexago-
nal phases, the curves can be described by a rational decay.

Figs. 3 and 4 present the hydration pressure of the nonionic
surfactants as a function of the water content, \( R_w \). The respec-
tive hydration pressure was determined by the osmotic stress
method:
\[ P_h = -(RT/V_w)\ln a \]

![Fig. 1](image1.png)  
**Fig. 1** The amount of water molecules per surfactant, \( R_w = n_w/n_s \), sorbed by the nonionic surfactants \( \text{C}_n \text{E}_m \) as a function of relative humidity, RH, at 25 °C and normal pressure.

![Fig. 2](image2.png)  
**Fig. 2** The amount of water molecules per surfactant, \( R_w = n_w/n_s \), sorbed by the nonionic surfactants \( \text{C}_{12} \text{E}_m \) as a function of relative humidity, RH, at 25 °C and normal pressure.

![Fig. 3](image3.png)  
**Fig. 3** Hydration pressure, \( P_h \), of nonionic surfactants \( \text{C}_n \text{E}_4 \) and its fitting function according to eqn. (3) at 25 °C as a function of the water amount, \( R_w = n_w/n_s \). The lyotropic phases are indicated by the nomenclature of Luzatti and co-workers.⁵¹
where $R$ is the gas constant (8.3145 kJ mol\(^{-1}\) K\(^{-1}\)), $T$ the absolute temperature (298.15 K), $V_w$ the molar volume of water (18.05 × 10\(^{-6}\) m\(^3\) mol\(^{-1}\)) and $A_w$ is the water activity.\(^{10}\) A possible question may arise because of the use of the bulk value for the molar volume of water for the whole hydration range. The water volume deviates more and more from the bulk property\(^{32,33}\) at low hydration. However, this fact is mostly not considered in the corresponding literature and we also avoid a further discussion and use the molar volume as a fixed parameter. But one should keep in mind possible deviations, especially at very low hydration. The water activity, $a_w$, is related to the relative humidity, RH, by $a_w = RH/100$.

The shape of the hydration pressure curves resemble the respective curves, which are known from phospholipids\(^{37}\) (eqn. (1)). However, it is difficult to fit them by an exponential function (Fig. 5). We found that the following function (eqn. (3)) gives a much better description of the measured values.

$$P_h = P_0/(1 + R_0/R_0)$$

(3)

In their nomenclature, $P$ is the contribution of the bending energy to the osmotic pressure, $K_0$ the bending modulus, $R_0$ the minimum energy radius, $R_{pp}$ a curvature radius and $A_{pp}$ the cross sectional area. The curvature radius, $R_{pp}$, is correlated with the hydration, $R_a$, given by $n_w/n$. This can be explained by a geometrical consideration. The volume of a water slice in the inverse hexagonal phase is given by $n_w V_w = 2\pi R^2 d$, where $n_w$ is the number of water molecules, $V_w$ the molar volume of water, $d$ the thickness of the water slice and $R$ the radius of the water slice. In the case of the inverse hexagonal phase, the water content is proportional to the square of the slice radius which is linearly related to the curvature radius. Therefore, it is reasonable to compare eqns. (3) and (4) and it is plausible that the hydration dependence of the bending energy gives an important contribution to the non-exponential behaviour described by eqn. (3). Rand et al. report that dehydration of polar groups also contributes to the osmotic pressure at lower hydration. Because we cover the whole hydration range, it is reasonable to suggest that the rational decay function at zero water content, $P_0$, and a decay parameter, $R_0$. Why is there a difference between the decay functions given by eqns. (1) and (3)? The figures suggest that the hydration pressure curves which show a rational decay behaviour belong to surfactant dispersions which mostly exist in a non-lamellar state. This indicates that the non-lamellar character of the surfactant aggregates is also responsible for the non-exponential decay. The non-lamellar phase structures are composed of arrangements of curved layers. This suggests that the curvature contributes to the non-exponential behaviour. In fact, for some phospholipid systems it is known that the hydration dependence for non-lamellar phases is strongly influenced by the curvature energy of the layers. This dependence is determined by the bending modulus, especially at higher hydration. A theoretical approach for the inverse hexagonal phase of phospholipids which shows a rational decay function of hydration pressure is reported by Rand et al.\(^ {24}\)

$$P = K_0(1/R_{pp} - 1/R_0)(-1/R_0^2)/(A_{pp}/2)$$

(4)

where $R_{w,\infty}$ is the hydration if the water activity approaches $a_w \to 1$. We determined the Gibbs free energy of hydration by integration using the results obtained from the sorption isotherm, covering all humidities and hydration states measured ($a_w = 0.11–0.97$). This creates some deviations with the integral energy because the integration do not cover the whole

The parameters represent the extrapolated hydration pressure at zero water content, $P_0$, and a decay parameter, $R_0$. Some of the lyotropic phases of the surfactants are known from the literature.\(^ {7,18}\) Such liquid crystalline phases are indicated in Figs. 3 and 4. One can thus find lamellar (L\(_a\)), micellar and inverse micellar (L\(_1\), L\(_2\)), bicontinuous (V\(_1\)) and hexagonal phases (H\(_1\)) (nomenclature according to Luzatti and co-workers\(^ {34,35}\). Figs. 3 and 4 show that there is no obvious correlation between the hydration pressure and the type of the liquid crystalline phase structure.
integration range, given by the integration limits, \( R_w = 0 \) and \( R_w = \infty \). However, the differences will not be dominant. The results of the fitting procedure show that the variation of the alkyl chain length has little effect on the decay parameter. The extrapolated hydration pressure and the Gibbs free energy of hydration. This means that the hydration is dominated by the number of the oxyethylene units, i.e. the number of water-accessible hydrophilic segments. A similar result was found for the solution enthalpy of a series of \( C_{12}E_m \) surfactants, because the contribution of the alkyl chains is close to zero at room temperature.\(^{37} \) However, one could assume that a change of the alkyl chain length also leads to a moderate change of effective chain diameter due to a variation of the chain order. A variation of the chain diameter could change the accessibility of water (effective surface area), but these effects are obviously not dominant. The only exception in this series is \( C_{16}E_4 \) which shows the lyotropic phase transition mentioned above.

Using NMR measurements the effective water binding energy of \( C_{12}E_m \) was determined.\(^{21} \) Therefore, it is interesting to compare the results for the Gibbs free energy of hydration obtained by sorption isotherms with those obtained by deuterium NMR relaxation.\(^{21,26} \) The NMR approach is based on a two-state model describing the mean spin-lattice relaxation time of \(^2\)H\(_2\)O at the amphiphile/water interfaces. The dependence of the relaxation times on the degree of hydration is fitted and one obtains the corresponding energy parameters. There is an excellent agreement concerning the linear behaviour of the energies vs. the number of oxyethylene units. The Gibbs free energy of hydration (eqn. (5)) determined by the sorption isotherms is \(-1.1 \pm 0.1 \) kJ mol\(^{-1}\) per oxyethylene group and the effective water binding energy is \(-0.7 \) kJ mol\(^{-1}\) in the case of the relaxation time method.\(^{21} \) This shows that the effective water binding energy obtained by NMR measurements is correlated, but not identical to the Gibbs free energy of hydration.

4. Conclusions

The present study shows that the hydration of the nonionic \( C_{12}E_m \) surfactants is little affected by the length of the hydrophobic chain (for \( C_{2\text{E}_4}; n = 8, 10, 12, 14, 16 \). However, the sorption of water is almost prevented at lower humidities if the surfactants are in the solid crystalline state (\( C_{12}E_4, C_{12}E_8 \)). The hydration is directly correlated with the number of the hydrophilic oxyethylene groups (for \( C_{12}E_m; m = 2, 4, 6, 8 \). The hydration pressure curves which were determined by the osmotic stress method can be empirically fitted by a rational function (eqn. (3)). This empirical function is presumably composed of contributions arising from the bending energy of curved layers and the energy arising from the dehydration of the polar headgroups. Furthermore, the Gibbs free energy of hydration (eqn. (5)) is \(-1.1 \pm 0.1 \) kJ mol\(^{-1}\) per oxyethylene group. It is correlated, but not identical to the effective water binding energy obtained by deuterium NMR relaxation.

Acknowledgements

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References


Table 1 The Gibbs free energy of hydration, \( \Delta G_0 \), hydration pressure at zero hydration, \( P_0 \), and the non-exponential decay constant, \( R_0 \), of the nonionic surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>( \Delta G_0 )/kJ mol(^{-1})</th>
<th>( \ln P_0/\text{MPa} )</th>
<th>( R_0 ) (mol/mol)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{12}E_4 )</td>
<td>(-4.4 \pm 0.7 )</td>
<td>(-0.2 \pm 0.1 )</td>
<td>(-0.3 \pm 0.1 )</td>
<td>Chain melting</td>
</tr>
<tr>
<td>( C_{12}E_6 )</td>
<td>(-4.2 \pm 0.6 )</td>
<td>(-0.2 \pm 0.1 )</td>
<td>(-0.3 \pm 0.1 )</td>
<td>Chain melting</td>
</tr>
<tr>
<td>( C_{12}E_8 )</td>
<td>(-3.9 \pm 0.6 )</td>
<td>(-0.2 \pm 0.1 )</td>
<td>(-0.3 \pm 0.1 )</td>
<td>Chain melting</td>
</tr>
<tr>
<td>( C_{12}E_4 )</td>
<td>(-5.6 \pm 0.6 )</td>
<td>(-0.2 \pm 0.1 )</td>
<td>(-0.3 \pm 0.1 )</td>
<td>Chain melting</td>
</tr>
<tr>
<td>( C_{12}E_8 )</td>
<td>(-7.8 \pm 0.8 )</td>
<td>(-0.2 \pm 0.1 )</td>
<td>(-0.3 \pm 0.1 )</td>
<td>Chain melting</td>
</tr>
</tbody>
</table>