Electrostatic interactions inside the aqueous core of spherical reversed micelles (L2 phase)

F. Akoum, O. Parodi

To cite this version:

F. Akoum, O. Parodi. Electrostatic interactions inside the aqueous core of spherical reversed micelles (L2 phase). Journal de Physique, 1985, 46 (10), pp.1675-1681. <10.1051/jphys:0198500460100167500>. <jpa-00210117>

HAL Id: jpa-00210117
https://hal.archives-ouvertes.fr/jpa-00210117

Submitted on 1 Jan 1985
Electrostatic interactions inside the aqueous core of spherical reversed micelles (L\textsubscript{2} phase)

F. Akoum
Groupe de Dynamique des Phases Condensées (*), Laboratoire de Minéralogie Cristallographie, U.S.T.L., place E. Bataillon, 34060 Montpellier Cedex, France

and O. Parodi
Département de Physique des Milieux Désordonnés, Université de Provence, Centre St Jérôme, rue H. Poincaré, 13397 Marseille Cedex 4, France

(Reçu le 6 mars 1984, révisé le 20 décembre 1984, accepté le 23 avril 1985)

Abstract. — We propose a model for describing electrostatic interactions in the aqueous core of a spherical reversed micelle. Some counterions are located at the surface of the aqueous core, the others are distributed inside the core following a Boltzmann law. The nonlinearized Poisson-Boltzmann equation is solved in spherical geometry; an asymptotic expansion of its solution is found near a logarithmic divergence. We give an evaluation of the enthalpy of association of a counterion to the surface of the aqueous core. Assuming that the area by polar head remains constant, we obtain the electrostatic energy of the micelle and we show that the electrostatic energy by monomer is a function of the aggregation number.

1. Introduction.
In nonpolar solvents, water can be dispersed by adjunction of suitable amphiphilic surfactants. Large amounts of water can be solubilized in a ternary system of oil-water-aerosol OT, giving a stable solution (L\textsubscript{2}) of monodisperse reversed micelles [1] : water is then confined in spherical pools limited by the hydrophilic ionized polar heads of the surfactant molecules while the lipophilic chains are directed towards the solvent.

Last years extensive studies have been carried out by different experimental techniques to determine the structural parameters of the so-called L\textsubscript{2} phase, especially the size and the shape of the micelles [2-5]. The nature of water contained in reversed micelles has been tested by fluorescence probing [6] or by N.M.R. studies [7]. It was found to be different from ordinary bulk water especially at low water content.

Theoretical investigations of the stability of microemulsions differ by their description of the different contributions to the free energy of the system [8-11]. In the case of ionic surfactants the electrostatic energy is one of these contributions. For direct charged micelles (oil in water microemulsions) the electrostatic interactions between micelles depend on the degree of binding of the counterions to the micellar surface. Assuming spherical micelles, the ionic distribution around each micelle is obtained by solving the Poisson-Boltzmann equation which can be linearized: the electrostatic potential decreases far from a micelle as \(\exp(-r/\lambda_d)\), where \(\lambda_d\) is the Debye length. Furthermore the growth of spherical direct micelles is limited by a geometrical constraint: the radius must be shorter than the length of the extended amphiphilic chain of the surfactant molecule. Upon

(*) Laboratoire associé au C.N.R.S.
further growing micelles are deformed into ellipsoids, cylinders or disks with inhomogeneous curvature.

The case of reversed micelles (water in oil microemulsion) is different. Since there is no electrostatic interactions between spherical and overall neutral micelles, the electrostatic energy comes from the distribution of the counterions inside the aqueous core of the micelles.

The aim of this paper is to give a detailed description of this distribution and of the electrostatic energy of a reversed micelle. After a presentation of the model (section 2), we derive in section 3 the potential distribution inside the micelle by solving the nonlinearized Poisson-Boltzmann equation. The expression of the electrostatic energy is then obtained in section 4.

2. The charged hollow sphere model

We assume a spherical symmetry for the whole micelle (Fig. 1). The aqueous core is surrounded by $N$ amphiphilic molecules. The polar heads limiting the water pool are ionized carrying the charge $-e$ (anionic monovalent surfactant).

As usual, the area by polar head $\sigma$ is defined by

$$N \sigma = 4 \pi R^2$$

where $R$ is the radius of the aqueous core of the micelle.

We model the amphiphilic interface of a reversed micelle by analogy with direct micelles and lamellar systems: for them it is well known that an important fraction of the counterions remains bounded to polar heads, on sites which appear to be very close or inside the polar region. In the same way, for a reversed micelle, we assume that $\beta N(0 \leq \beta \leq 1)$ counterions are localized on the micellar interface. This hypothesis is supported by geometrical considerations: a crude evaluation of the area of the AOT head group gives $25 \, \text{Å}^2$, which is about twice smaller than the $\sigma$ parameter introduced by (1) and commonly given by experimental techniques.

The effective charge of the micellar interface is therefore $-Ne(1 - \beta)$; the charge density is assumed to be continuous and uniformly distributed on a sphere. $N(1 - \beta)$ counterions are all solubilized in the water core and one gets for them a Boltzmann distribution; their local concentration varies with the electrostatic potential and with the temperature $T$. No ion is solved in the continuous aliphatic medium, and micelles are supposed to be electrically neutral.

3. The potential distribution.

3.1 The Poisson-Boltzmann equation for reversed micelles. — Inside the aqueous core, the electrostatic potential $V(r)$ is solution of Poisson's equation

$$\Delta V = -\frac{4 \pi e n(r)}{\varepsilon}$$

where $e$ is the ionic charge, $\varepsilon$ the dielectric permittivity, and $n(r)$ the local concentration of the $(1 - \beta)N$ free counterions at the distance $r$ from the centre of the micelle.

Since the micelle is spherical and electrically neutral, the potential vanishes outside the micelle. The boundary conditions for $V(r)$ are therefore

$$V(r = R) = 0$$

and from the Gauss theorem

$$-\left(\frac{dV}{dr}\right)_{r=R} = \frac{Ne(1 - \beta)}{\varepsilon R^2}.$$  

On the other hand, the electric field must be continuous inside the micelle. From symmetry considerations, it must be radial and therefore vanishes at the centre:

$$\left(\frac{dV}{dr}\right)_{r=0} = 0.$$  

For the ionic concentration we assume a Boltzmann law:

$$n(r) = n(R) \exp \left(-\frac{eV(r)}{kT}\right)$$

where $k$ is Boltzmann's constant, $T$ the temperature, and $n(R)$ is the value of $n(r)$ at the zero potential surface that is at the water core surface.

From equations (2) and (5), $V(r)$ is solution of the Poisson-Boltzmann equation:

$$\Delta V = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dV}{dr}\right) = -\frac{4 \pi e}{\varepsilon} n(R) \exp \left(-\frac{eV(r)}{kT}\right)$$

with boundary conditions (3) and (4).
In order to solve these equations, let us define new dimensionless variables:

\[ x = \kappa r, \quad \xi = \kappa R \quad (7) \]

and

\[ e^{\frac{V(r)}{kT}} = f(x) - f(\xi). \quad (8) \]

Equation (6) now writes:

\[ \frac{\kappa^2}{x^2} \frac{d}{dx} \left( x^2 \frac{df}{dx} \right) = -\frac{4\pi e^2}{\epsilon kT} n(\xi) \exp f(\xi) \exp -f(x) \quad (9) \]

and can be simplified by setting

\[ \kappa^2 = \frac{4\pi e^2}{\epsilon kT} n(\xi) \exp f(\xi) \quad (10) \]

or

\[ \kappa^2 = \frac{4\pi e^2}{\epsilon kT} n(0) \]

\( \kappa^{-1} \) is the Debye radius corresponding to the ionic concentration \( n(0) \) at the centre of the water core.

Equation (9) now writes:

\[ \frac{1}{x^2} \frac{d}{dx} \left( x^2 \frac{df}{dx} \right) = -f(x). \quad (11) \]

From equation (8), condition (3) is always satisfied. Let us now point out that \( f(x) \) is defined by equation (8) up to a constant. We can adjust this constant and set:

\[ f(0) = 0 \quad (12) \]

\( f(x) \) is now completely defined as

\[ f(x) = \frac{e}{kT} [V(r) - V(0)]. \]

Using equations (4), (1) and (7), one easily finds:

\[ \left( \frac{df}{dx} \right)_{x=0} = -\frac{(1 - \beta) L_B R}{\sigma \xi} \quad (13a) \]

\[ \left( \frac{df}{dx} \right)_{x=0} = 0 \quad (13b) \]

where \( L_B = \frac{4\pi e^2}{\epsilon kT} = 4\pi n_b \) (\( n_b \) is the Bjerrum length, 7.15 Å at 298 K for water with \( \varepsilon = 78.3 \)).

Equation (11), with the boundary conditions given by equations (12) and (13b), completely determines a universal function \( f(x) \). The actual scale for this function is obtained by the knowledge of \( \kappa \) or of \( \xi = R/\kappa \). \( \xi \) is deduced from equation (13). Finally the actual potential is obtained from \( f(x) \) by means of equation (8).

The solution of equations (11)-(13) cannot be expressed with the help of well-known mathematical functions. An approximate expression is easily found for small values of \( f \), i.e. in the neighbourhood of \( x = 0 \), using the « Debye approximation » : \( \exp -f \approx 1 - f \). Equation (11) is thus linearized and the solution is

\[ f^0(x) = 1 - \frac{\sinh x}{x}. \quad (14) \]

This approximation is valid as far as \( f^0 \) remains much smaller than one, i.e. in the range \( 0 \leq x \leq 2 \).

From equations (11) and (13) it results that \( df/dx \) is a decreasing function of \( x \) and, using equation (12), that \( f \) is negative for \( x > 0 \) and has no minimum.

A computer solution of equation (11), using a finite difference method, suggests a discontinuity for a finite value of \( x \), \( x = A \). A hyperbolic behaviour \( f \approx C(A - x)^{-n} \) (\( C \) and \( n > 0 \)) is incompatible with equation (11). On the other hand, the \( \exp - f \) term suggests a logarithmic divergence

\[ f(x) \approx a \ln \left( \frac{A - x}{b} \right). \]

This expression allows for the cancellation of higher order terms in equation (11) for \( a = 2 \) and \( b = \sqrt{2} \). Using an iterative procedure, one finally obtains the following asymptotic expansion

\[ f^A(x) = 2 \ln \frac{A - x}{\sqrt{2}} - 2 \frac{A - x}{A} - \frac{4}{3} \frac{(A - x)^2}{A^2} \ln(A - x). \quad (15) \]

The constant \( A \) has been fitted by a method of least squares. One finds

\[ A = 3.2740 \pm 0.00005. \]

Are plotted \( f^0(x), f^A(x) \), in figure 2 and the numerical solution \( f(x) \) of equation (11). \( f^A(x) \) appears as a good approximation for \( f(x) \) if \( x > 2.5 \).

Fig. 2. — Solution of the Poisson-Boltzmann equation; \( f^0 \) is the linearized solution near the origin, \( f^A \) the asymptotic expansion of the numerical solution \( f \).
In order to determine the potential distribution inside the micelle, one must calculate $\xi$ from equation (13). For given values of $R$ and $\sigma$, $\xi$ depends only on the association coefficient for counterions, $\beta$.

3.2 Counterion binding. — Counterion binding to the micellar surface can be experimentally characterized from quadrupolar relaxation data; NMR spectroscopy has been successfully applied to study the degree of association of the counterions in direct micellar solutions [12-13] as well as in the $L_2$ phase of ternary systems (see [14] for CTAB-$n$ hexanol-water). On the $L_2$ phase of AOT-water-heptane, taking advantage of the difference in the relaxation rate of sodium ions in two states, bounded to the micellar surface and free in the bulk water, Wong and coworkers [6] give an estimate of the degree of association of the counterions. 72% appears to be a lower limit.

In our model, the counterions are either located at the surface of the water core of the micelle or free inside the water bulk. We introduce the enthalpy $\Delta h^+$ of association of a counterion to the micellar surface and write the equilibrium condition which does exist between the two states of the counterions.

The electrochemical potential $\chi(R)$ of a bound counterion writes:

$$\chi(R) = -\frac{\partial(Ts)}{\partial\beta} - \Delta h^+ + \chi_\infty$$  \hspace{1cm} (16)

where $\chi_\infty$ is the standard electrochemical potential of a counterion, and $s$ the entropy per bound counterion.

The value of $s$ depends on the number of possible sites for counterions on the micellar interface. Since the area by anionic polar head ($\approx 58 \text{Å}^2$) is much higher than the area actually occupied by one polar head ($\approx 25 \text{Å}^2$) and since both anions and cations are monovalent, the simplest assumption is that there is one possible site for cationic counterions per anionic polar head on the micellar interface. In this case, a fraction $\beta$ of these sites is occupied and the resulting entropy is classically given by

$$s = k(\beta \ln \beta + (1 - \beta) \ln (1 - \beta)).$$ \hspace{1cm} (17)

In this case, there is no contribution of the electrostatic energy to $\chi(R)$ since $V(R) = 0$.

Since we assume that the water core of the micelle is a solution of free ions in water, the electrochemical potential for counterions at $r = 0$ writes

$$\chi(0) = kT \ln \frac{n(0)}{n_w} + eV(0) + \chi_\infty$$ \hspace{1cm} (18)

where $n_w$ is the concentration of the water molecules, $n(0)$ and $V(0)$ are the ionic concentration and the electrostatic potential at the origin.

In equation (18), we have made an implicit assumption of ideal solutions. This means that we take account of the electrostatic interactions between ions via a mean field approximation and that we neglect any other kind of interaction. This is the basic assumption for the Poisson-Boltzmann distribution.

The equilibrium condition writes

$$\chi(R) = \chi(0)$$

i.e. by equations (16)-(18)

$$n(0) = n_w \frac{\beta}{1 - \beta} \exp \left(\frac{\Delta h^+}{kT} - \frac{eV(0)}{kT}\right).$$ \hspace{1cm} (19)

By equations (5), (7) and (10), the value of $\xi$ is related to $n(0)$:

$$n(0) = \frac{\xi^2}{R^2 L_w}. $$ \hspace{1cm} (20)

Equating (19) and (20) and using equations (16) and (13), one gets:

$$\exp \left(\frac{\Delta h^+}{kT} = \frac{\beta}{1 - \beta} \frac{R^2 L_w}{\xi} \exp f(\xi)\right).$$ \hspace{1cm} (21)

We have numerically solved equations (13a) and (21) for values of $\beta > 0.72$ using the experimental data of $R$ and $\sigma$ obtained by Cabos and Delord [2] in the case of dilute micellar solutions of the AOT-water-heptane system. They measured $R$ and $N$ with an accuracy of $10\%$ for different values of the hydration number $\omega$, ratio of the molar concentrations of water and AOT; $\sigma$ is obtained by (1).

Taking $\beta$ as a parameter, equation (13a) is first solved using the asymptotic expansion (15) of $f$; one gets a value of $\xi$ useful to determine $\Delta h^+$ from (21).

Results are given in tables I and II for $T = 298 K$, $\epsilon = 78.3$; they deserve a few remarks:

a) all values of $\xi$ have been found to be greater than 2.7 which justifies a posteriori the use of the asymptotic expansion (15) of $f$.

b) the last column gives the enthalpy of association of a counterion to the micellar surface. Due to the accuracy of the experimental data, the values of $\Delta h^+$ are given within an accuracy of $\pm 0.05 \text{kcal/mole}$.

c) we may compare the values of $\Delta h^+$ found here with the activation energy of the $^{23}$Na relaxation process evaluated by Wong et al. [6]. From the temperature variation of the linewidth of $^{23}$Na, these authors find, for reversed micelles of AOT with radii of 24.4 Å ($\omega = 16.4$), an activation energy $E_a$ of 5.4 kcal/mole, higher than that obtained in bulk water (2.5 kcal/mole). The comparison between these results and the value we have found for $\Delta h^+$ is not very simple. The broadening of the NMR line is a complex process which cannot be explained only by the presence of an energy barrier $\Delta h^+$. We therefore expect $\Delta h^+$ to be of the same order as, but smaller than $E_a$, which is effectively the case. Note finally that the value of $\beta$ is in our model a parameter which may be different for different values of $\omega$. 


Table I. — Radii $R$ and aggregation numbers $N$ are experimental data [2] obtained in the case of dilute solutions of AOT-water heptane micelles for different values of the hydration number $w$, $\xi$ is solution of equation (13a). $\Delta h^+$ is the enthalpy of association of a counterion. Results are given for $\beta = 0.8$.

<table>
<thead>
<tr>
<th>$w$</th>
<th>$N$</th>
<th>$R_1$</th>
<th>$R$</th>
<th>$A h^+$</th>
<th>kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1250</td>
<td>76</td>
<td>58</td>
<td>3.03</td>
<td>3.1</td>
</tr>
<tr>
<td>40</td>
<td>920</td>
<td>64</td>
<td>56</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>30</td>
<td>570</td>
<td>49.5</td>
<td>54</td>
<td>2.95</td>
<td>3</td>
</tr>
<tr>
<td>20</td>
<td>225</td>
<td>31</td>
<td>54</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>15</td>
<td>160</td>
<td>25.7</td>
<td>52</td>
<td>2.75</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table II. — The enthalpy of association $\Delta h^+$ is calculated from (21) for different values of $\beta$ and of the hydration number $w$.

<table>
<thead>
<tr>
<th>$w$</th>
<th>$\beta$</th>
<th>$\Delta h^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.8</td>
<td>3.1</td>
</tr>
<tr>
<td>40</td>
<td>0.85</td>
<td>3.6</td>
</tr>
<tr>
<td>30</td>
<td>0.90</td>
<td>4.2</td>
</tr>
</tbody>
</table>

4. Calculation of the electrostatic energy.

The ionic distribution function is shown in figure 3. Most of the counterions are found on the interface or very close to it. It is therefore obvious that, to a large extent, the electrostatic energy appears as a surface energy. As far as we can consider the area per anionic polar head as a constant, a surface energy will be proportional to the total number of surfactant molecules and will not depend on the micellar size.

This is not an exact picture. Beside a huge « surface energy term », the actual electrostatic energy will include non-trivial terms which will depend on the micellar size, and play a role in the determination of the micellar radius.

We shall now evaluate these non-trivial terms. The electrostatic energy of the ionic distribution is given in a mean field approximation by

$$ G_e = \frac{1}{2} \int e\rho(r) \, d^3r. $$

With the help of (5), (7) and (8) one gets:

$$ G_e = \frac{2 kT}{L_n \xi} \int_0^\xi x \frac{df(x)}{dx} \, dx. \quad (22) $$

The integral of (22) has been calculated using the tabulated values of $f(x)$ for $0 \leq x \leq 2.5$ and with the asymptotic expansion (15) for $2.5 < x \leq \xi$.

One finds then

$$ G_e = \frac{2 \pi kT}{L_n \xi} \xi I(\xi) $$

where:

$$ I(\xi) = 16 A \ln (A - \xi) - 24(A - \xi) + \frac{4 A^2}{A - \xi} + \frac{8(A - \xi)^2}{A} \left[ 1 - 2 \ln (A - \xi) \right] $$

$$ - \frac{4(A - \xi)^3}{3 A^2} + \frac{32}{3} (A - \xi) \left[ \ln (A - \xi) - \frac{1}{2} \right] + \frac{128 (A - \xi)^3}{225 A^4} \left[ \ln (A - \xi) + \frac{3}{10} \right] $$

$$ - \frac{40}{9} \frac{(A - \xi)^4}{A^3} \left[ \ln (A - \xi) + \frac{1}{4} \right] + \frac{992}{81 A^2} (A - \xi)^3 \left[ \ln (A - \xi) + \frac{1}{6} \right] $$

$$ - \frac{8}{135} \frac{(A - \xi)^5}{A^4} \left[ \ln^2 (A - \xi) \right] - \frac{10 A^2 (A - \xi)^3}{A^2} - \frac{15 A(A - \xi)^4}{A} + \frac{6(A - \xi)^5}{A^3} - 20.68. $$
Plotted in $kT$ units in figure 4, for $\beta = 0.8$ and $\beta = 0.9$ and $\sigma = 58$ Å², the variation of $G_e$ versus the aggregation number $N$ exhibits, as expected, a preponderant term proportional to $N$ (« surface energy term »).

We can obtain a rough estimate of the variation of $G_e$ with $R$ and $\sigma$ (or $N$ from Eq. (1)), keeping only the first term in the expression of $f^A(x)$:

$$f^A(x) \simeq 2 \ln \frac{A - x}{\sqrt{2}}.$$  

In this case, equation (13) is easily solved and one gets:

$$\xi = \frac{\eta RA}{1 + \eta R}$$

where

$$\eta = \frac{(1 - \beta) L_0}{2 \sigma}$$

which leads to:

$$G_e \simeq \frac{2 \pi kT}{L_0 \eta} \left[ 3.9 \eta^2 R^2 + 5.95 \eta R - 2.05 - 8(1 + \eta R) \ln(1 + \eta R) \right]. \quad (23)$$

The first term in the bracket of the r.h.s. of equation (23) corresponds to the « surface energy term ».

It will give no contribution in the minimization of the free energy per monomer.

From figure 4, the « surface terms » appear to be much more important than the non-trivial part $G_e$ of the electrostatic energy. One therefore has

$$\frac{\langle \tilde{G}_e/N \rangle}{\langle G_e/N \rangle} \ll 1$$

and

$$\tilde{G}_e/N \simeq G_e/N - \langle G_e/N \rangle$$

$\tilde{G}_e/N$ is plotted versus $N$ in figure 5. It will contribute to the minimization of the free energy.

5. Conclusion.

The model developed here to describe the electrostatic interaction in the aqueous core of a reversed micelle is essentially based on a solution of the non-linearized Poisson-Boltzmann equation. Its solution obtained in terms of dimensionless variables is quite general and can be used for any ionic surfactant aggregated in water-in-oil microemulsion.

The electrostatic energy calculated for a micelle is not strictly a linear function of the aggregation number. The deviation to the linearity must give an important contribution in the stability of a solution of reversed micelles.

This model is in some aspects rather crude. The most questionable points are the following:

a) we have used the Poisson-Boltzmann theory which is not free from contradictions. The mean electrostatic field introduced here is certainly an...
approximation. Anyway the logarithmic divergence of the solution seems to be well described by an asymptotic expansion of the reduced electrostatic potential which can be used easily;

b) the localization of all the polar heads and most of the counterions on a sphere without thickness is probably an oversimplification. The actual situation is certainly more complex. A part of water molecules are bound to the polar heads and to counterions so that the polar head region has a finite thickness;

c) the existence of « holes » (sites for counterions) between polar heads can be assumed only if the area per polar head is greater than 25 Å²; our model cannot then be used to describe micelles with a low hydration number (ω < 10). Smaller hydration numbers seem to correspond to a different kind of aggregates with no free ions inside the core;

d) the surface per anionic polar head, σ, has been taken as a constant. Experiments show that σ does not depend on ω, as long as ω > 10.

In a further step, the other terms in the free energy (surface tension, entropic terms, etc...) should be taken into account. Variation of σ should be allowed and a minimization of the total free energy should lead to the stability condition of a solution of reversed micelles.

References