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COLLOIDS AND SURFACES A

Micellization and adsorption of a zwitterionic surfactant: *N*-dodecyl betaine—effect of salt

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Abstract

Time-resolved fluorescence quenching, self-diffusion measurements and calorimetric investigations have been used in order to investigate the effect of salt on aggregation in aqueous solutions and the adsorption onto silica gel of the zwitterionic surfactant *N*-dodecyl betaine (NDB).

The micelle aggregation number of NDB stays constant when the NDB or salt concentration increases but decreases with an increase of temperature. Evidence is presented for the binding of cations and anions to micellar aggregates. The degree of binding has been obtained for Na^+, Ca^{2+} and Cl^- ions; it is always larger for the anion.

Enthalpies of micellization were obtained directly from calorimetric curves of NDB in dilution experiments. The observed decrease of the endothermic enthalpies of micellization with increasing temperature or salinity is attributed to a structural change in the water molecules around the alkyl chain of the free monomers.

The adsorption isotherms of NDB onto silica gel depend very little on temperature, and a plateau is reached near the CMC. At saturation, the adsorbed amount of NDB depends on the salt and follows the sequence NDB < (NDB + NaCl) < (NDB + $CaCl_2$).

The exothermic differential molar enthalpies of adsorption demonstrate the same behaviour as the enthalpies of micellization with varying temperature or salinity. Adsorption onto silica gel depends on the NDB concentration, the salt concentration and temperature.

Keywords: Adsorption; Micellization; *N*-dodecyl betaine; Salt effect; Silica gel; Zwitterionic surfactant

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1. Introduction

In spite of the wide applicability of zwitterionic surfactants [1] and their increased commercial use, theoretical work, as revealed by a survey of the literature, is less comprehensive than investigations on ionic and non-ionic surfactants. Of particular importance is the synergistic effect that this class of surfactants displays when they are used in conjunction with other types of surfactant [2].

Studies of amphoteric surfactants have concerned phase diagrams and microemulsions systems, the features of which are markedly different from those of many ionic and non-ionic surfactants. It is noteworthy that salt hardly affects the evolu-

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tion of the different phase regions and that there is considerable temperature stability [3–5]. Micellization in aqueous solution has been studied recently [6] for a series of zwitterionic surfactants of increasing intercharge distance [7–9], with particular emphasis on aggregate structure. To our knowledge, few studies [10] have dealt with the effect of salts on the micellization of zwitterionic compounds, and particularly the interaction between small ions and zwitterionic micelles carrying a net charge equal to zero.

In the present work we have analyzed the solution behaviour and interfacial properties of the *N*-dodecyl betaine, $C_{12}H_{25}N^+(CH_3)_2$–CH_2–CO_2^- (NDB). Micellization in the presence and absence of salt is investigated by tracer self-diffusion, and enthalpies of demicellization are obtained directly from calorimetric measurements as previously carried out for ionic systems [11]. The behaviour of NDB at a solid–liquid interface is also investigated by plotting the adsorption isotherms onto silica gel, and the corresponding differential molar enthalpies of adsorption are obtained.

2. Materials and methods

NDB was prepared using the method of Tori and Nakagawa [12]. Treatment of the NDB aqueous solutions with ion exchange resin was carried out in order to eliminate sodium chloride, a byproduct of the reaction. The radioactive labels used in tracer self-diffusion experiments were ^{14}C-enriched decane (specific activity, 7.5 mCi mmol^{-1}) and ^{14}C-enriched decanol (specific activity, 10 mCi mmol^{-1}) from Paris Labo. Sodium-22 chloride and calcium-45 chloride were Amersham International products, Radiochemical Centre, Buckinghamshire, UK.

Micelle aggregation numbers, *N*, were obtained using time-resolved fluorescence quenching [13]. Fluorescence decay curves were recorded using the single photon counting technique. Pyrene and tetradecyl pyridinium chloride were used as the fluorescence probe P and the quencher Q, respectively. Two measurements were performed on each surfactant solution: one with micelle-solubilized pyrene only, at very low $[P]\cong 10^{-6}$ M, which yielded the probe fluorescence lifetime in the micellar environment, and the second with the same low [P] and a quencher concentration [Q] comparable to the micelle concentration [M]. Eqs. (1) and (2) were fitted to the decay curves in the absence of quencher and in the presence of quencher at $[Q]/[M]\cong 1$, respectively.

$$I = I_0 \exp\left(\frac{-t}{\tau}\right) \qquad (1)$$

$$I = I_0 \exp\{-A_2t - A_3[1-\exp(-A_4t)]\} \qquad (2)$$

The fitting yields τ, the pyrene fluorescence lifetime, and the constants A_2, A_3, and A_4. In the present study, it was found consistently that $A_2{}^{-1}\cong\tau$ (no probe and/or quencher intermicellar migration on the fluorescence time-scale). In this case, the micelle aggregation number is given by $N=(C-\text{CMC})A_3/[Q]$, where C is the surfactant concentration and $A_4 = k_Q$, the rate constant for intramicellar quenching. The overall error on *N* is estimated to be ±10%.

The silica gel adsorbent is a specimen Spherosil XOB 015 manufactured by Rhône Poulenc, France. The surface area determined by the BET and Harkins and Jura methods are equal to 24.6 m^2 g^{-1} and 25 m^2 g^{-1}, respectively [14]. This latter value has been used in our calculations. The adsorption isotherm is drawn by measuring the surfactant concentrations before and after adsorption, with use of a differential refractometer (Waters R403).

Surface tensions were measured by the Wilhelmy method with a Prolabo tensiometer (Tensimat 2000), dynamic viscosities were measured with use of the capillary method (Viscomatic MS), and density measurements were performed with a DMA 600 A. Paar instrument.

Calorimetric curves of the differential molar enthalpy of dilution were obtained with a calorimeter modified in our laboratory using the method described elsewhere [15–17]. The enthalpy of micellization at different temperatures was calculated from the experimental calorimetric curves of surfactant dilution by extrapolation to the CMC. For measurements of differential molar heats of adsorption, silica gel particles were introduced into the calorimeter cell. Known amounts of surfactant solution of known concentration were then added to a suspension in water of the particles, according to the procedure previously described [16]. All experiments have been performed at a non-fixed pH (about 6).

The self-diffusion coefficients were obtained by using the open-ended capillary tube method with radioactive labelling [18]. Since the macroscopic translational mobility of an ion or a molecule differs by 1–2 orders of magnitude depending on whether the species diffuses with a micelle as a kinetic entity or moves freely in the bulk solution, it is possible to quantify the populations of these two sites from an observed self-diffusion coefficient. Within this two-sites approximation, the observed self-diffusion coefficient of a species x is given by

$$D^{x} = p_{f}^{x} D_{f}^{x} + p_{m}^{x} D_{m}^{x} \tag{3}$$

where p_{f}^{x} and p_{m}^{x} are the fractions of non-micellized and micellized x, D_{f}^{x} is the self-diffusion coefficient of free x in the presence of micelles, and D_{m}^{x} is the self-diffusion coefficient of the micelles. Measurements on micelle-free systems yield D_{f}^{x}, the diffusion coefficient in such systems, which is then obtained from [19]

$$D_{f}^{x} = D_{f,0}^{x} \left(1 + \frac{\Phi}{2}\right)^{-1} \tag{4}$$

where Φ is the volume fraction of obstructing spherical micelles hindering the diffusion of x. The micelle self-diffusion coefficients D_{m} are obtained from measurements obtained when a very small amount of micelle-soluble and bulk insoluble compound (decane or decanol) is introduced to label the aggregates.

Our previous studies have concerned ionic surfactants [20]. The most important results were that the free surfactant concentration decreases above the CMC, that counterion binding is independent of the surfactant concentration, and that micelle hydration is small. We have applied the same method in order to describe quantitatively the aggregation of NDB, and in this paper we have especially studied this amphoteric surfactant in the presence of salt. As the behaviour of NDB at interfaces is studied with and without salt, we have also reported our previous results together with the results obtained when NaCl and $CaCl_2$ are added to NDB aqueous solutions. In this work, emphasis will be on three parameters, the micelle size and shape and the degree of counterion binding.

3. Properties in solution

The solubility of NDB in water is high, i.e. about 50%, and the CMC determined by density and refractivity measurements is equal to 1.9×10^{-3} mol kg^{-1} at 25°C, in agreement with literature data [21]. This value is much larger than the values reported for non-ionic surfactants of identical chain length (10^{-4} mol kg^{-1}), due to the presence of intermicellar repulsion, but is lower than for ionic surfactants of identical chain length (10 mM), showing that this repulsion is smaller than that between head groups carrying net charges. Furthermore, the betaine solutions are insensitive to increases in temperature or salinity and no turbidity is observed at high temperature or high concentration of added salts. Therefore the repulsive forces between NDB micelles do not seem to be changed to a great extent. In order to confirm this point, we have studied, by tracer self-diffusion, the aggregation of NDB in aqueous solutions with and without salt. We have added sodium and calcium chlorides to NDB, keeping constant and equal to 1 the ratio of salt to surfactant.

3.1. Micellar shape and size

One may assume that the observed decane and decanol self-diffusion coefficients are the same as that for NDB micelles. Indeed the two organic

Table 1
Diffusion coefficient, hydrodynamic radius and shape factor of NDB micelles in water and in the presence of salt

System[a]	D_{m0} (10^{-10} m^2 s^{-1})	R_0 (nm)	Shape factor
NDB without salt	1.00	2.4	2.2
NDB + NaCl	0.99	2.4	2.1
NDB + $CaCl_2$	0.95	2.6	2.2

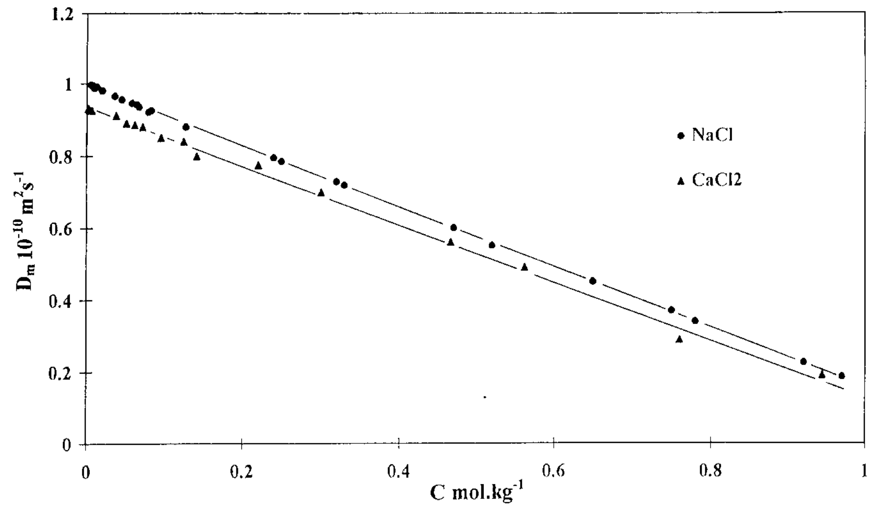

Fig. 1. Surfactant concentration dependence of the self-diffusion coefficients of decanol (or decane) for aqueous solutions of NDB in the presence of NaCl and $CaCl_2$ at 25°C.

compounds employed to label the micelles have a very low bulk solubility and are thus almost completely confined within the aggregates. Furthermore, the same D-values were obtained with the two labels. Close to the CMC (infinite micelle dilution) we obtained the interaction-free micellar diffusion coefficient $D_{m,0}$ in the presence of sodium and calcium chlorides (Fig. 1), which is related to the hydrodynamic micellar radius R_0 by the Stokes–Einstein law

$$D_{m,0}=\frac{kT}{6\Pi\eta R_0} \tag{5}$$

where η is the viscosity of the intermicellar medium, which is taken to be the viscosity of the solution at the CMC.

All self-diffusion coefficients decrease as the surfactant concentration is increased over a large concentration range. Repulsive interactions between micelles are responsible for this behaviour. We note that the variations in the self-diffusion coefficients are always linear in all the cases. The slopes of the curves $D=f([\text{NDB}]+[\text{salt}])$ are larger than the slope obtained in salt-free aqueous solutions [6]. The intermicellar interactions in the presence of salt are enhanced due to electrostatic repulsion, as the aggregates may bind anions and cations and consequently are charged. In the absence of salt we have shown [4] that they have a net charge equal to zero. In this case linear and relatively small variations in self-diffusion coefficients support the assumption that the size of the betaine aggregates stays constant, and that the aggregates are globular. The shape factors obtained from the dependence of the solution viscosity on concentration are found to be 2.2, 2.1 and 2.2 without salt and with NaCl and $CaCl_2$, respectively, close to the value 2.5 expected for spherical particles (see Table 1).

In the case of a solution of hard spheres without hydrodynamic interactions, the self-diffusion coefficient varies with the volume fraction of particles according to

$$D_m=D_{m,0}(1-2\Phi) \tag{6}$$

where D_m is the measured diffusion coefficient, $D_{m,0}$ is the diffusion coefficient in the absence of interaction, and Φ is the volume fraction of the particles.

We have calculated Φ from the formula given by Hayter and co-workers [22]. In the case of betaine solutions without salt, the micelle diffusion coefficient obeys Eq. (6). In the presence of salt we obtained

$$D_m=0.99(1-2.9\Phi)\times 10^{-10}\ \text{m}^2\ \text{s}^{-1}$$

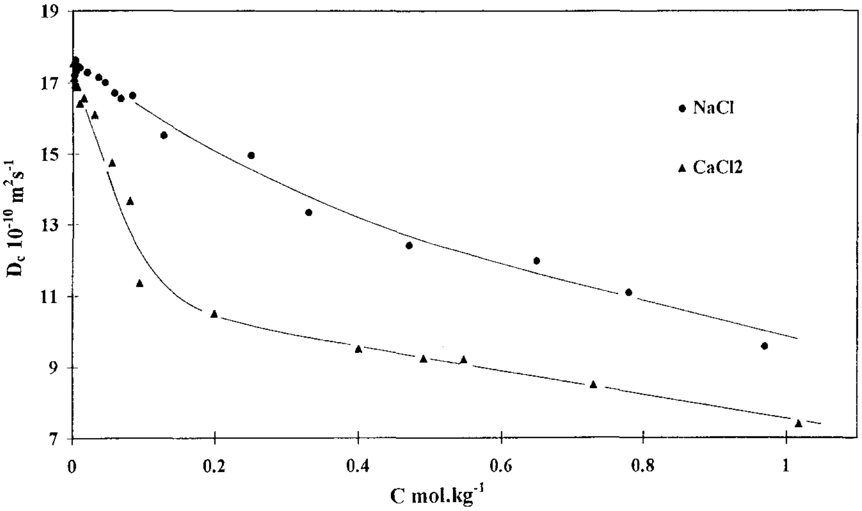

Fig. 2. Chloride self- diffusion coefficients in NDB + NaCl and NDB + $CaCl_2$ aqueous solutions as a function of surfactant concentration at 25 °C.

and

$$D_m = 0.95(1 - 2.8\Phi) \times 10^{-10}\ m^2\ s^{-1} \quad (7)$$

for the NDB + NaCl and NDB + $CaCl_2$ systems, respectively. The larger decrease of D_m upon increasing Φ in the presence of salts is due to electrostatic repulsion between the betaine micelles which have become electrically charged by binding ions, as shown below.

3.2. Counterion binding

The concentration m_m^c of counterions diffusing with the micelles is obtained from the equation

$$m_m^c = m_t^c - m_f^c = \frac{D_f^c - D_c}{D_f^c - D_m} m_t^c \quad (8)$$

where m_t^c is the total concentration of counterions, D_f^c is the self-diffusion coefficient of free counterions and D_c is the observed self-diffusion coefficient. In estimating D_f^c, we made an empirical correction for the intermicellar concentrations and took into account the obstruction effect of the micelles as described in a previous paper concerning ionic surfactants [18].

The binding of counterions to micelles in micellar systems has usually been described in terms of the degree of counterion binding β. In order to compare the interaction between ions and zwitterionic micelles with the binding of counterions to ionic micelles, we have calculated β, which is defined as $\beta = m_m^c/m_m^a$ for a monovalent ion and $\beta = m_m^c/2m_m^a$ for a divalent ion; m_m^a being the concentration of micellized surfactant ions. The error in β is very large at concentrations close to the CMC because of large errors in D_f^c and D_c. For the two systems studied (NDB + NaCl and NDB + $CaCl_2$), general observations may be deduced from Fig. 2. The self-diffusion coefficient D_{Cl} changes very little for concentrations from slightly above the CMC up to 5×10^{-2} mol kg^{-1}.

In this range of concentrations, it is not possible to deduce any counterion binding from calculations because a small error in D_c results in a large error in β. One can only state that β_{Cl}, β_{Na} and β_{Ca} are very small, in contrast to what was found for ionic surfactants for which β is quite constant and large (between 0.5 and 0.7) over a wide concentration range. Moreover, we have also observed a reduction of β with increasing surfactant concentration at low micelle concentrations.

When the NDB concentration increases, D_{Cl}, D_{Ca} and D_{Na} decrease. Fig. 3 shows the variations of β_{Cl}, β_{Ca} and β_{Na}. For the NDB + NaCl and NDB + $CaCl_2$ systems, β_{Cl} is greater than β_{Na} and β_{Ca}. This result is in agreement with the effect of

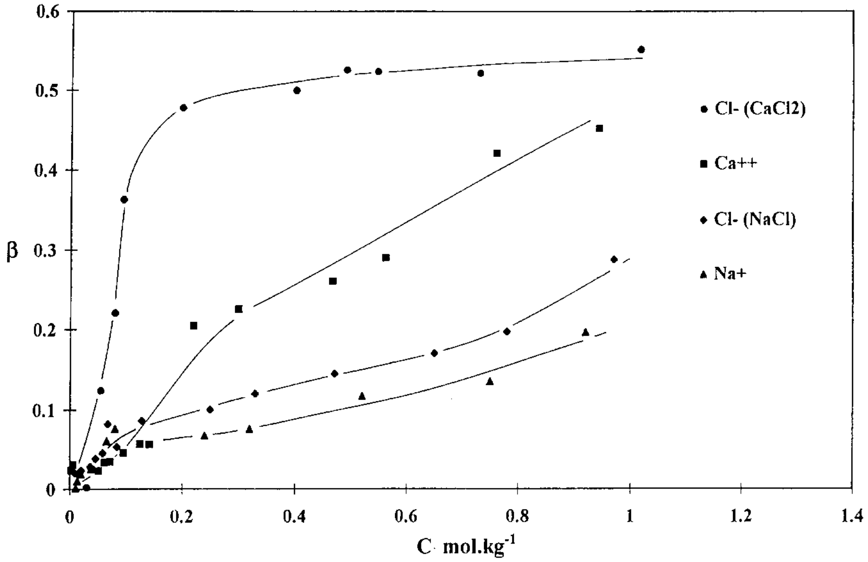

Fig. 3. Degrees of Cl^- and Ca^{2+} ion binding in NDB + $CaCl_2$ and degrees of Cl^- and Na^+ ion binding in NDB + NaCl versus the total surfactant concentration at 25°C.

anionic and cationic surfactants on the surface properties of betaines [23,24], which has been attributed to the displacement of the equilibrium between the betaine and its conjugated acid BH^+ caused by the interaction between BH^+ and anionic species [25]. We have noticed for the NDB + salt system that an increase in salt concentration leads to increased binding of the anion. When one compares the NDB + NaCl and NDB + $CaCl_2$ systems, because the ratio [NDB]/[salt] is approximately constant and close to unity, the concentration of chloride ions in the second system is twice that in the first system and β_{Cl} in the first system is about 2.5 times greater than β_{Cl} in the second system. There is an effect of the anion concentration on the binding to NDB micelles which may be related to the displacement of the equilibrium $NDB \leftrightarrow NDBH^+$ in the forward direction by the presence of the halide ion.

Table 2 gives the values of the micelle aggregation number N of NDB in water and water + NaCl under various conditions. The micelle aggregation number N decreases slightly on increasing temperature as expected. The most important result is the constant value of N when the salinity and/or the NDB concentration are increased, at each temperature studied.

Table 2
Aggregation number of NDB

NDB concentration (mol kg^{-1})	NaCl concentration (mol kg^{-1})	N		
		10°C	25°C	40°C
0.197	0	87	80	75
0.194	0.194	89	85	80
0.467	0.467	86	82	77

This implies that the decrease of the micelle self-diffusion coefficient in NDB + salt systems on increasing concentration is related to repulsive interactions between charged aggregates. Although the binding of Na^+ or Ca^{2+} ions is smaller than the binding of Cl^- ions, the values of β_{Na} and β_{Ca} are significant. Notice that β_{Cl}, β_{Na} and β_{Ca} keep increasing with the concentration.

The counterion binding to betaine micelles is different from that observed in ionic surfactant solutions. The first betaine micelles formed bind a very small fraction of anions and cations, and it seems that it is necessary to have a relatively large concentration of free counterions in the solution to obtain significant binding of anions and cations to NDB micelles.

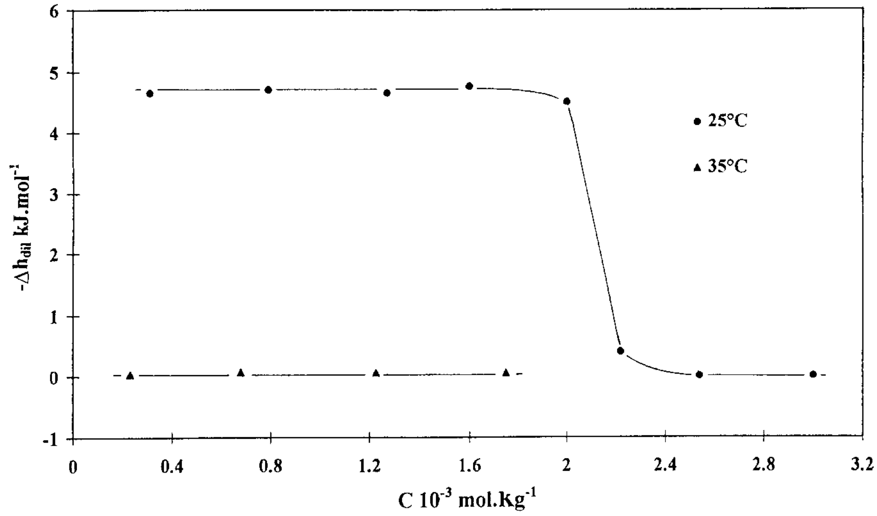

Fig. 4. Enthalpies of dilution of NDB at 25 and 35°C as a function of the equilibrium concentration.

3.3. Enthalpy of micellization

The enthalpy of micellization is composed of two main contributions:

(1) transfer of the aliphatic part of the NDB ($C_{12}H_{25}$ chain) from the bulk solution to the hydrophobic core of the micelle;

(2) transfer of the polar group from the bulk solution to the micellar coat layer.

The sum of the enthalpies of these processes is obtained from direct calorimetric measurements of dilution of the NDB stock solution, the initial concentration of which is several times higher than the CMC.

3.3.1. Effect of temperature

The temperature plays an important role in the enthalpy of micelle formation because of the interactions between water molecules and polar and aliphatic parts of the surfactant [18].

Fig. 4 shows the experimental enthalpy curves corresponding to NDB dilutions at 25 and 35°C. The analysis of exothermic curves of dilution allows one to distinguish three enthalpy regions, depending on the value of the concentration after dilution.

(1) At concentrations below the CMC (2.2×10^{-3} mol kg^{-1} at 25°C), the enthalpy of dilution (ΔH_1) is due to the total dissociation of micelles introduced into the water, and to dilution of the non-associated monomers; this last energy contribution is very small and in this case is negligible.

(2) In the region of the CMC, the enthalpy due to dilution (ΔH_2) decreases sharply. In this region, dissociation and dilution of micelles take place simultaneously.

(3) Above the CMC, the dilution exclusively concerns the micelles, and the energy contribution (ΔH_3) is close to zero.

Further injections of stock solution into the calorimeter cell, (where the introduced micelles have been already formed) provide a very weak energy contribution which results from interactions between micelles. The molar enthalpy of micellization Δh_m is defined by $\Delta h_m = +(\Delta H_3 - \Delta H_1)$.

The increase of ΔH_1 with temperature can be explained in terms of a variation in the water structure around the alkyl chains of the free surfactant monomers. During micellization, the structure is disrupted and the flexibility of the alkyl chains is increased. With a rise in temperature, the entropy of micellization is reduced probably as a result of a partial breakdown of the water structure, while the free enthalpy is approximately constant, following the constancy of the CMC.

The measured Δh_m value for NDB at 25°C, 4.65 kJ mol^{-1}, is about 25% smaller than the

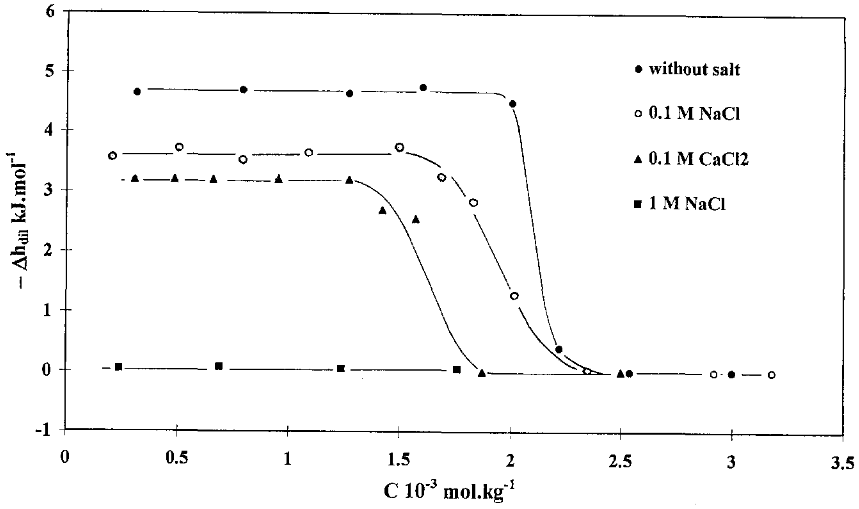

Fig. 5. Enthalpies of dilution of NDB at 25°C. Influence of NaCl and $CaCl_2$ on the enthalpy of micellization at 25°C.

reported value of 5.85 kJ mol^{-1}, obtained by an indirect method [13].

The interpretation of the enthalpy of micellization requires the separation of partial energy contributions from the polar and aliphatic parts of the molecules. Unfortunately, these data are not yet available for zwitterionic surfactants. For a further understanding of the separate energy contributions of alkyl and polar groups, respectively, to the enthalpy of micelle formation, it is necessary to study the thermodynamics of several series of homologous zwitterionic surfactants.

3.3.2. Effect of salt

Usually, the presence of salt in an aqueous solution brings about, for zwitterionic surfactants, micelle formation at the lowest equilibrium concentration. Fig. 5 shows that an increase in NaCl concentration brings about a decrease of the enthalpy of micellization. The water structure is organized by ions in such a way that micelle formation requires lower energy. The ions (Na^+, Ca^{2+} and Cl^-) are linked to the aggregates; moreover, they screen electrostatic repulsion between micelles and consequently promote their formation. At concentrations around the CMC, this phenomenon is negligible.

4. Properties at interfaces

4.1. Air–solution interface

Fig. 6 shows the surface tension γ plotted as a function of the logarithm of the concentration of NDB in aqueous solutions at 25 and 35°C, and in the presence of NaCl at 25°C. This method is widely used for determining CMCs as it can be applied to ionic or non-ionic surfactants, in contrast to conductivity measurements, which are restricted to ionic surfactants.

All the curves, including the calorimetric curves of dilution, show a sharp break at the CMC, indicating that our NDB sample is pure. A small difference in the CMC values is observed for the surface tension and the calorimetric measurements (approximately 5%).

In NDB solutions, in the absence of salt, the aggregates have a net charge equal to 0; the CMC was obtained from the superficial tension. The values of 1.9×10^{-3} mol kg^{-1} at 25°C and 1.8×10^{-3} mol kg^{-1} at 35°C agree with previous density and refractive index data [5]. In the presence of NaCl or $CaCl_2$, the CMC values are, respectively, 1.8×10^{-3} mol kg^{-1} (0.1 M NaCl), 1.0×10^{-3} mol kg^{-1} (1 M NaCl), 1.5×10^{-3} mol kg^{-1} (0.1 M $CaCl_2$), 0.9×10^{-3} mol kg^{-1} (1 M $CaCl_2$).

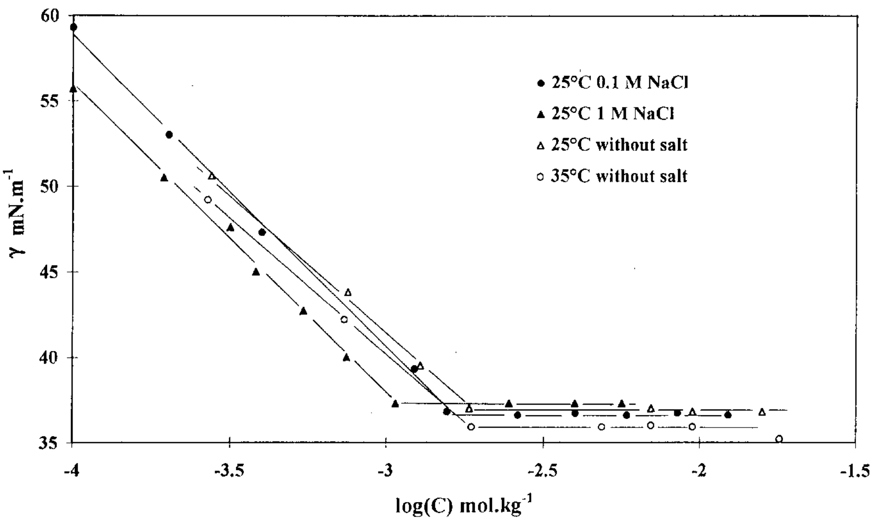

Fig. 6. Surface tension γ versus concentration of NDB in aqueous solutions at 25 and 35°C and in the presence of NaCl at 25°C.

From conductivity measurements, as further proof that the aggregates are charged, we obtained the same value for both salted systems, ([NDB]/[SALT] = 1), i.e. 2.2×10^{-3} mol kg^{-1}, which correlates with those obtained from density measurements, i.e. 2×10^{-3} mol kg^{-1} and 2.3×10^{-3} mol kg^{-1}, respectively, for NaCl and $CaCl_2$.

From the slope of the surface tension curves below the CMC one can calculate the surface excess concentration and the area σ per surfactant molecule at the air–solution interface. At 25°C and 35°C, σ is equal to 0.57 nm^2 and 0.59 nm^2 for the NDB solutions without salt. When one compares these values to that obtained from the molecular model [6], we can conclude that the polar head of the NDB is lying flat at the air–solution interface.

4.2. Solid–solution interface

To understand and compare the behaviour of NDB at the air–solution and solid–solution interfaces, we have carried out an extensive isotherm and calorimetric investigation.

4.2.1. Adsorption and temperature

Fig. 7 shows the adsorption isotherms of NDB onto silica at 25, 35 and 45°C. The first significant information gained is that the change in temperature causes no qualitative or quantitative change in the isotherm. At a low degree of coverage, θ (where θ is defined as $\Gamma/\Gamma_{\max}$, and $\Gamma_{\max}$ as the adsorption quantity corresponding to the saturation plateau), of the silica gel surface, below 0.05 the adsorption is very weak. The inset corresponding to dilute solutions (Fig. 7) shows more precisely that partition between adsorbed and free surfactant is largely favourable to the latter. When the equilibrium concentration is raised, the adsorption increases a little. In the vicinity of the CMC region, we observe a drastic adsorption increase (vertical part of the isotherm) and then the isotherm forms the saturation plateau.

Let us observe the same adsorption phenomenon by means of calorimetry. It is now well demonstrated that calorimetric studies of adsorption are much more sensitive to the nature of the solid compared with the adsorption isotherm study [26]. Thus, enthalpy curves of adsorption of the NDB on silica gel are shown in Fig. 8. The differential molar enthalpy of displacement $\Delta_{1,2}h_2$ curves are obtained also (as isotherms) at 25, 35 and 45°C and they are composed of two different ranges. The first corresponds to the part of the isotherm where adsorption is very weak. The differential molar enthalpy of displacement is exothermic and relatively high (in spite of the very small quantity adsorbed). At a degree of coverage

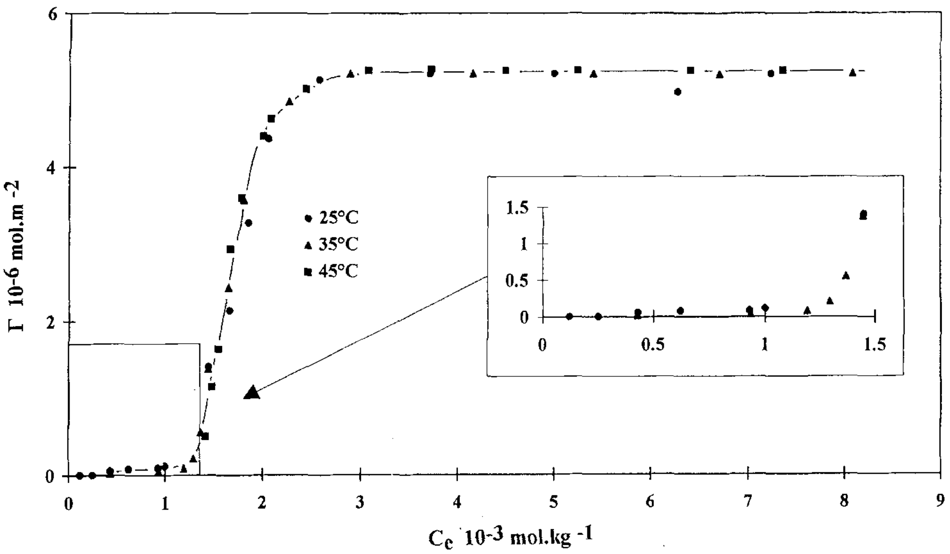

Fig. 7. Experimental adsorption isotherms of NDB onto silica at 25, 35 and 45°C.

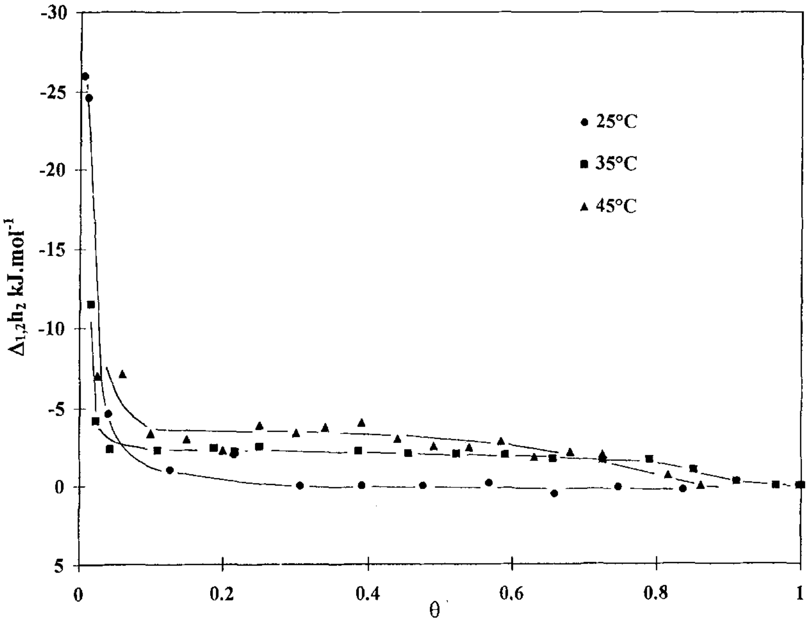

Fig. 8. Differential molar enthalpies of displacement versus degree of coverage, θ, at 25, 35 and 45°C.

of about 0.05, $\Delta_{1,2}h_2$ becomes constant, then, close to $\theta = 1$, the heat of adsorption tends towards a zero enthalpy value.

One interesting feature of our adsorption systems is that in the very weak adsorption region, the $\Delta_{1,2}h_2$ values are relatively high. The drastic decrease of $\Delta_{1,2}h_2$ which follows reflects a certain energy heterogeneity of the silica surface sites, which are available to direct interactions between amphoteric molecules and sites. At this stage of the adsorption, we can remark that a similar non-ionic surfactant adsorption behaviour on the same silica gel has been already observed [27]. This direct "individual" or "gaseous" adsorption constitutes the seeds around which one absorbs the remaining quantity of surfactant [28]. The $\Delta_{1,2}h_2$ then becomes constant. After reaching the CMC in the bulk solution, the isotherm plateau is formed. Consequently, it is normal that the differential molar enthalpy of displacement is close to zero. The description of the behaviour of zwitterionic systems is consistent with the analysis of both the calorimetric and the adsorption data.

A qualitative similarity is observed between the molar enthalpy of micelle formation in the bulk and results provided from calorimetric adsorption data onto silica. The variation in molar enthalpies of micellization in the bulk between 25 and 35°C is about -4.6 kJ mol^{-1}, while this quantity for the aggregation process onto the silica surface (degree of coverage, $\theta=0.5$) is equal to -2.3 kJ.mol^{-1}, this last value being taken from the horizontal slope of the differential molar enthalpies of displacement. Proceeding in this way, we hoped to confirm that after the first adsorption step, which is qualitatively finished at a degree of coverage of 0.05, the second step is due to hydrophobic driving forces, as in the process of micelle formation in the bulk solution.

After this first glance at the enthalpy of micelle formation curves and the calorimetric adsorption data, we are convinced that the adsorption process from a degree of coverage of 0.05 is due to a hydrophobic interaction between adsorbed molecules and simultaneously to direct interactions of the surfactant molecules with the solid surface.

Interesting information results from an examination of the cross-sectional area σ of one molecule at the solid–liquid and liquid–gas interfaces. The calculated σ value for NDB from the interface air–water is 0.58 nm^2 and from the isotherm plateau, is 0.30 nm^2. The cross-sectional area on the silica–solution interface, which is two times smaller than those measured at the air–solution interface, suggests a bilayer-like aggregate structure formation. This seems to be confirmed qualitatively by a similar evolution of surface and bulk aggregation with temperature.

4.2.2. *Adsorption in the presence of salt*

As has been previously described, the presence of salt in the solution provokes a displacement of the CMC towards lower concentrations. The same behaviour is observed during the adsorption process of NDB onto the silica– solution interface.

Fig. 9 shows adsorption isotherms without salt and with NaCl and $CaCl_2$.

The increase in NaCl and $CaCl_2$ concentrations

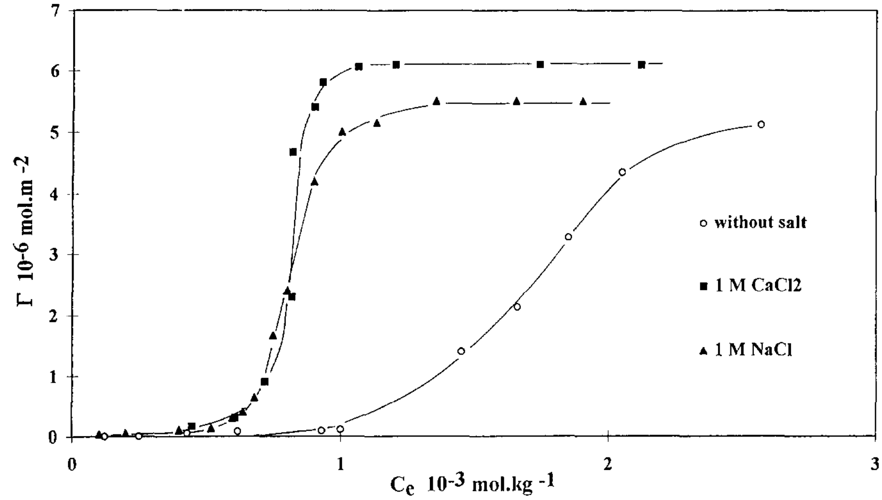

Fig. 9. Experimental adsorption isotherms of NDB onto silica at 25°C in the absence of salt, and in the presence of 1 M NaCl and 1 M $CaCl_2$.

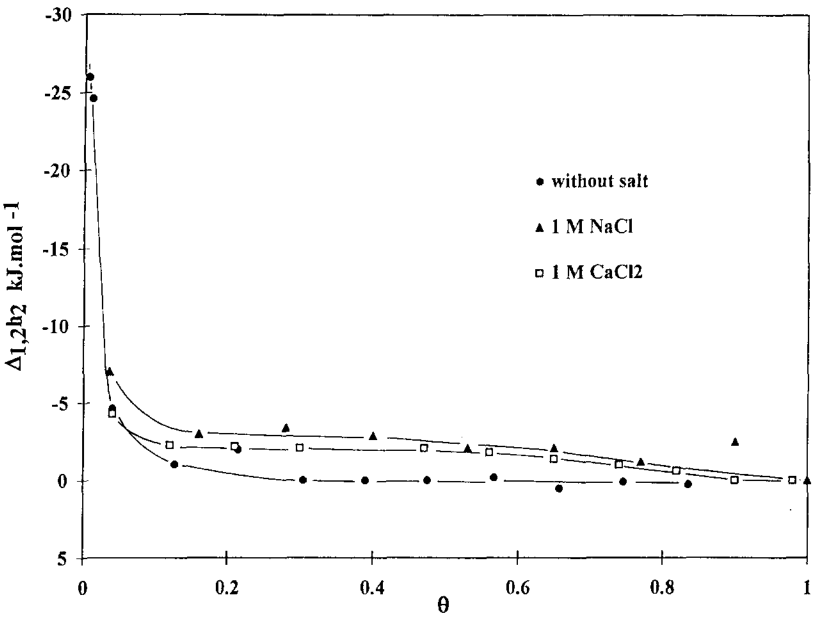

Fig. 10. Differential molar enthalpies of displacement versus θ at 25°C, in the absence of salt, and in the presence of 1M NaCl and 1 M $CaCl_2$.

in the surfactant solution from 0 to 1 M shifts isotherm plateau formation from about 2.5 to 1 mmol kg^{-1}. In parallel, the quantity adsorbed at plateau saturation increases by about 10%. The presence of salt in the solution brings about a screening of the electrostatic repulsion between dipolar heads, which leads to a slightly greater compactness on the surface. Differential molar enthalpies of adsorption performed under the same physicochemical conditions as the isotherms are presented in Fig. 10.

From the calorimetric diagrams, one sees that the increase in salt concentration raises the exothermicity of the adsorption. The same trend has been observed previously following an increase in temperature or salinity in the solution on the micelle-formation enthalpy.

5. Conclusions

The self-diffusion results have provided evidence for the binding of cations and anions to zwitterionic micellar aggregates, with a degree of binding of anions larger than that of cations.

Concerning the adsorption investigation, it is not easy to make precise statements about the structure of the adsorbed layer on the silica and to decide about a micellar or bilayer structure for the adsorbed surfactant. The more important conclusion of this report is that we can distinguish the existence of two mechanisms of adsorption: the first is the direct interaction of individual monomers with surface sites, and the second is interfacial aggregate formation.

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