

APPLICATION OF THE CALORIMETRY TO STUDIES OF COLLOIDAL PHENOMENA

Enthalpies of micellization and enthalpies of adsorption of zwitterionic surfactants onto silica gel

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Abstract

The importance of calorimetric methods in studies of colloidal phenomena is illustrated by the analysis of the experimental enthalpies of dilution and adsorption for aqueous solutions of three zwitterionic surfactants: 1-12 betaine, 3-12 betaine, and 3-12 sulfobetaine. The batch microcalorimeter 'Montcal 3', used to obtain these data, is described. The molar enthalpies of micellization and the differential molar enthalpies of adsorption onto silica gel are shown to be functions of the headgroup hydrophilicity, fixed by the type of negatively charged center and the number of methylene groups separating the charged sites.

Keywords: adsorption, calorimetry, micellization, silica gel, zwitterionic surfactants

Introduction

The complexity of surfactant adsorption at the solid/water interface, the phenomenon of great technological and commercial importance, requires different experimental techniques to be applied so as to investigate the subsequent stages of the process. Comparison of data from all these measurements yields greater insight into the possible mechanism of adsorption and its evolution with the surface coverage. Moreover, systematic studies are needed to explore all variables of the system and to establish their influence on the degree of adsorption and the energetics involved. In the first place, the experimental results should be based on studies of surfactant adsorption onto model substrates, the advantages of which include their simple geometries and the fact that the hydrodynamics associated with these are well-characterized. The comparisons of the various solid collectors for their abilities to adsorb a given surfactant molecule are obscured by the different particle size distributions or specific surface areas available for surfactant molecules, the different chemical pretreatments employed, and the crystalline structures involved. However, within each experimental series on a

given substrate, significant conclusions can be drawn with respect to chemical structure of the surfactant (e.g., alkyl chain length, type of polar head group, intramolecular charge separation distance), surfactant concentration, and the properties of the liquid medium (e.g., *pH*, temperature, and salinity).

In measuring ionic surfactant adsorption on mineral oxides, certain powerful measurement tools have been utilized. They include adsorption isotherms, electrokinetic data, contact angle measurements, and calorimetric measurements of the enthalpy of micellization and the enthalpy of adsorption [1–6]. The use of microcalorimetry has the double interest of leading to a direct knowledge of the interactions involved and also of being suitable for systems containing heterogeneous surfaces, such as those of most inorganic powders. Investigations into the nature of forces between all the components of such systems have a primary role in colloid science [7].

The micelle formation of some carboxybetaine and sulfobetaine molecules in the bulk aqueous solution as well as their adsorption onto silica gel have been examined by means of the batch microcalorimeter 'Montcal 3'. In this paper, some basic data are presented.

Principle mechanisms relevant to adsorption of ionic surfactants

In aqueous solutions, mineral surfaces acquire an electric charge, which is caused by the dissociation of amphoteric surface hydroxyl groups and this is determined by the *pH*. This surface charge exerts an influence on the distribution of ions in the solution; as a result, an electric double layer will form. The principle intermolecular forces relevant to adsorption of ionic surfactants include long-ranged forces such as the London–van der Waals attraction and the coulombic attraction or repulsion, and short-range structural forces due to changes in the solvent structure in the vicinity of a surface or interface. In general, adsorption of surfactants involves simple ions rather than micelles.

The presence of an electrical charge, borne by the surfactant molecules and by the solid surface, can result in adsorption of the solute occurring successively by ion exchange and ion pairing mechanisms. Surfactant ions adsorb physically as individual ions onto oppositely charged sites unoccupied by other counterions or replace other counterions preadsorbed at the solid/water interface. In both cases, the adsorbing ions may displace water molecules. Effects arising from the displacement process, such as changes in the state of aqueous medium upon adsorption of one type of ion and desorption of the other, can modify the energetics of the process in a marked manner, in particular in the case of solid surfaces which exert a pronounced long-range effect on the arrangement and motion of the surface water molecules [5, 6].

The apolar portion of surfactant ions has an important role in promoting the adsorption process because it increases the affinity of these organic ions to the

interfacial region. The effect results from pushing out the hydrophobic moiety from the bulk phase, on the one hand, and from cohesive chain-chain interactions between the hydrophobic alkyl chains, on the other hand. These hydrophobic interactions are responsible for the formation of surface aggregates. Usually, different structures are discussed, such as hemimicelles, admicelles, or surface micelles. The shape of surface aggregates depends on different parameters of a given adsorption system (e.g., strength of solid-surfactant interaction, surface heterogeneity, density of surface charge, hydrophilicity of surface).

The adsorption of surfactants from aqueous solution has an important influence on the surface properties of the solid adsorbent. Individual surfactant ions adsorbed on oppositely charged surface sites act to screen the surface charge and diminish the tendency of the surface to repeal other, similarly charged surfaces. Thus solid adsorbents in the form of finely divided particles, dispersed in the aqueous phase in part because of their mutual electric repulsion, usually flocculate at some point as their charge is neutralized by the adsorption of surfactant ions. Furthermore, since surfactant ions adsorbed via an ion exchange or ion pairing mechanism are oriented with their hydrophobic group towards the aqueous phase and since they cause the dewetting of a mineral surface, the solid surface becomes increasingly more hydrophobic. This is shown by an increase in the contact angle at the solid/water/air interface [1-3]. If adsorption of surfactant ions is continued beyond the isoelectrical point, then the charge of the Stern layer is reversed and the substrate acquires a charge whose sign is that of the adsorbate ion. Orientation of the adsorbed surfactant ion during this process is with the hydrophilic head towards the aqueous phase, imparting increasing hydrophilic character to the substrate as adsorption continues. The contact angle decreases again and the tendency to disperse in water increases.

Description of the 'Montcal' microcalorimeter

The calorimeter 'Montcal' is designed to measure the enthalpies of mixing of liquids, the enthalpies of micellization, and the enthalpies of adsorption from solutions. Our main contribution to the development of the apparatus consists in preparing the designs for the calorimetric cell, the interior agitation system, and the system of injection which allows the reagents to be introduced into the cell at a given time and in given quantities. The homogeneity of the solution or suspension is ensured by a horizontal agitator with a variable speed of rotation which can be adjusted to the nature of the liquid-solid system studied. The thermistors, calibration coil, and the injection part are immersed in the solution or suspension.

The mode of stirring as well as the heat exchangers for the injecting solution are shown in Fig. 1. A pyrex glass stirrer is placed inside the calorimetric device and inside the cell; it is connected indirectly to the external part of the calo-

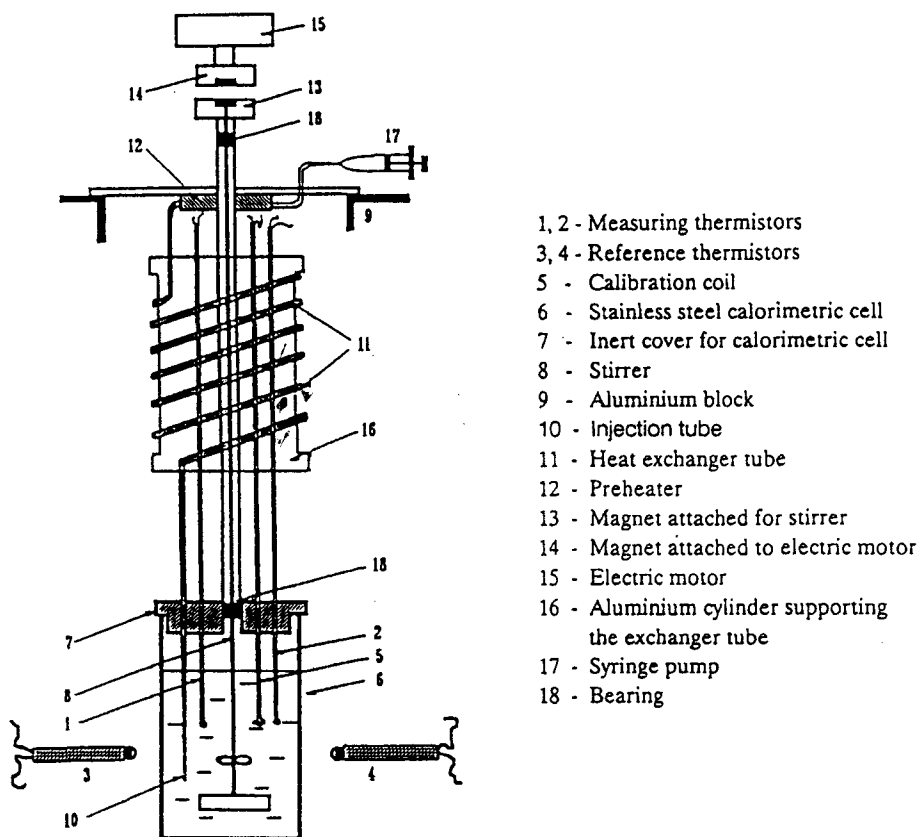


Fig. 1 Schematic representation of the calorimetric cell and the liquid injection and agitation systems of the 'Montcal' microcalorimeter

rimeter, a stepper motor fitted with magnetic transmission. In spite of a relatively high speed of agitation (250–350 rpm), the calorimeter keeps the high sensitivity. A syringe pump injects a solution discontinuously so that both the integral and the differential molar enthalpies can be measured. The return of thermal signal to the initial baseline is very rapid (10–17 min). The calibration of the calorimetric system is performed by the Joule effect. The detailed thermodynamic formalism has been published previously [4]. We recall here some basic equations.

Let us consider the calorimetric experiment of adsorption of a given surfactant. n_T moles of surfactant diluted in n_W moles of water are injected into the suspension in the calorimetric cell. This suspension contains n_W^0 moles of water and m_s grams of solid particles with a surface area S . The enthalpy of adsorption ΔH is related to the change from the initial mixture:

$$(n_T + n_W) + (S + n_W^a) = (n_T + n_W) + [(S + n_W^a) + (n_W^a - n_W^a)]$$

initial concentration = C_0

(where n_W^a is the number of water molecules adsorbed onto the surface S)
to the final mixture:

$$(S + n_T^a + n_W^a) + (n_T^a + n_W + n_W^a - n_W^a)$$

final concentration = C_e

where n_T^a is the number of surfactant molecules remaining in solution, n_T^a the one adsorbed onto the surface S ; n_W^a corresponds to the number of water molecules adsorbed in pure water and n_W^a has the same significance but after adsorption of n_T^a moles of surfactant. For this process, we can consider that n_T moles are diluted from C_0 to C_e concentration. Only n_T^a moles arising from this diluted state are adsorbed onto solid substrate. In these conditions, the coverage ratio of the adsorbent takes the value of Θ .

Therefore

$$\Delta H = n_T[\Delta h(C_e) - \Delta h(C_0)] + n_T^a[\Delta h(\Theta) - \Delta h(C_e)] + (n_W^a - n_W^a)\Delta h_w$$

$\Delta h(C)$ is the molar enthalpy of dilution from a reference solution, $\Delta h(\Theta)$ is the molar enthalpy of adsorption from the same reference solution, and Δh_w a molar enthalpy of water displacement depending on the Θ value. The adsorption isotherm allows the n_T^a and n_T^a values to be calculated, whereas the calorimetric measurements permit the determination of ΔH and of the difference $\Delta h(C_e) - \Delta h(C_0)$. Therefore, it is possible to reach the term $\Delta H - n_T[\Delta h(C_e) - \Delta h(C_0)]$. It will be considered as the apparent adsorption term compared to the true one $n_T^a[\Delta h(\Theta) - \Delta h(C_e)]$. Indeed, it is impossible to estimate the term $(n_W^a - n_W^a)\Delta h_w$, related to the displacement of a part of adsorbed water molecules by the surfactant molecules.

To obtain the apparent differential molar enthalpy of adsorption, it is necessary to derive in function of n_T^a . A good approximation is obtained by calculating the term $\Delta\{\Delta H - n_T[\Delta h(C_e) - \Delta h(C_0)]\} / \Delta n_T^a$ for small Δn_T^a values.

Enthalpies of micellization and adsorption of betaines and sulfobetaines

A great interest is taken in zwitterionic surfactants on account of their good solubility in water and of little sensitivity of their solution properties to salts and

temperature. Zwitterions, which are compatible with all other types of surfactant, have certain advantages over the others, being, for example, less irritating to skin and eyes [8].

Very popular zwitterionic surfactants, the most frequently studied by many authors [8–11], are n - m carboxybetaines, $C_mH_{2m+1}N^+(CH_3)_2(CH_2)_nCOO^-$, and n - m sulfobetaines, $C_mH_{2m+1}N^+(CH_3)_2(CH_2)_nSO_3^-$; the letters m and n signify the number of carbon atoms in the alkyl chain and methylene tether group, respectively.

The solution properties of the above zwitterionic surfactants have been shown to be strong functions of the type of negatively charged center (carboxylate vs. sulfonate) and the number of methylene groups separating the charged sites [10]. For similar structures, differences such as the higher solubility and critical micelle concentration of the betaine relative to the sulfobetaine can be explained as a direct result of the carboxylate headgroup being more hydrophilic than the sulfonate. The hydrophilicity of the headgroup with increasing tether length is a complex balance between the hydrophobic effect induced by the increasing number of carbons vs. the hydrophilic effect of the increasing dipole moment. This results in maxima in the cmc and solubility at n equal to 3 or 4.

The effect of the above two parameters on the enthalpy of micellization in aqueous solution and the enthalpy of adsorption onto silica gel has been studied [12] for a series of n -12 carboxybetaines and n -12 sulfobetaines; where $n=1, 2, 3$. Some basic results are presented in Figs 2 and 3.

Synthetic silica gel in the form of spherosil XOBO15 was supplied by Rhone-Poulenc (France). This macroporous powdered substrate with spherical particles of diameter between 40 to 100 μm had a specific surface area of 25 m^2/g [B.E.T./nitrogen gas adsorption and the Harkins-Jura method/immersion in water]. Zwitterionic surfactants were synthesized in the laboratory [12]. All water for solution preparation was deionized and dust-free. In a neutral aqueous environment solid adsorbent is well above its point of zero charge and therefore carries a negative charge. At this pH a polar head group of both the carboxybetaines exists as a zwitterion [10].

Figure 2 shows three calorimetric curves of dilution of a micellar stock solution, the molality of which is above the corresponding cmc values, for 1–12 and 3–12 carboxybetaine, and 3–12 sulfobetaine at 298 K. The shape of each curve is consistent with a dilution of a micellar solution containing quite monodisperse micelles. At low molalities, the constant enthalpy effect results from destruction of micelles and dilution of unmicellized species. It is a direct measure of the molar enthalpy of micelle formation, because the dilution of micelles from the stock solution is an athermal process (the second plateau on the curve). The experimental enthalpies of micellization are the following:

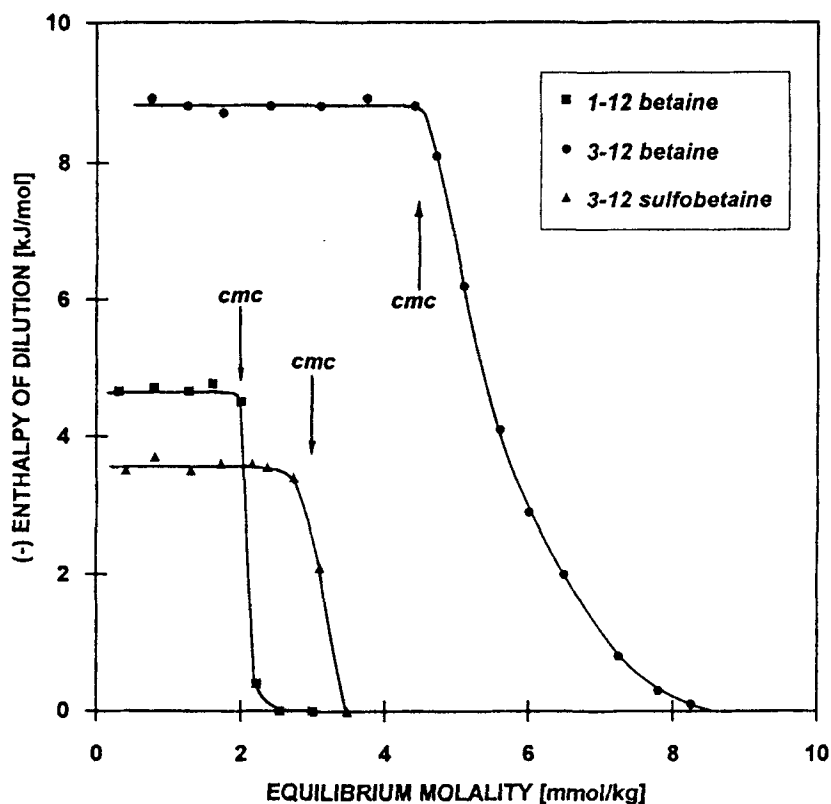


Fig. 2 Differential molar enthalpies of dilution for three zwitterionic surfactants in water at 298 K

4.7 $\text{kJ}\cdot\text{mol}^{-1}$ (1-12 betaine), 8.8 $\text{kJ}\cdot\text{mol}^{-1}$ (3-12 betaine), and 3.6 $\text{kJ}\cdot\text{mol}^{-1}$ (3-12 sulfobetaine). It is evident that the effect of micellization becomes less endothermic (favoured energetically to a greater extent) with decreasing hydrophilicity of the headgroup (i.e., shorter interchange bridge and sulfonate anionic group).

Figure 3 illustrates the variations of the differential molar enthalpies of adsorption onto silica gel from water at 298 K. Two characteristic regions can be distinguished. The first region is characterized by the decreasing exothermicity of the process. Its domain is limited to very low surface coverage ratios. The decreasing tendency in the exothermic differential enthalpy of adsorption can be related with the direct solid-adsorbate interaction and is usually explained in terms of surface heterogeneity [5, 6]. It is probable that individual zwitterions are localized on the negatively charged silica surface with the quaternary nitrogen as the surface binding site and the anionic group away from the surface or extended on it.

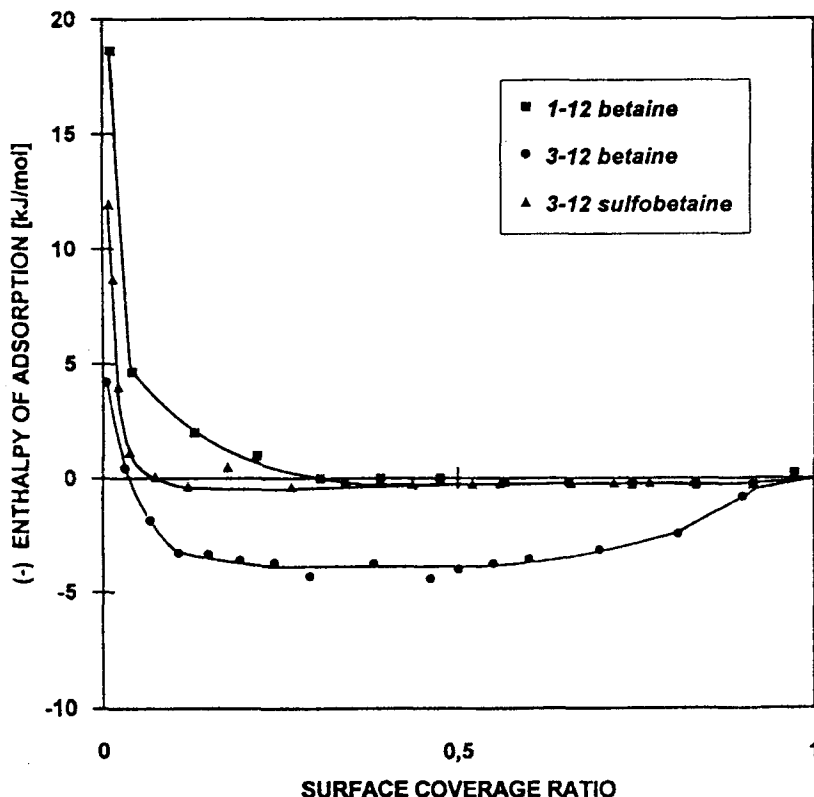


Fig. 3 Differential molar enthalpies of adsorption for three zwitterionic surfactants onto silica gel from water at 298 K

In the second region, the enthalpy of surfactant adsorption is a constant function of the surface coverage ratio; the enthalpic value was found to be about $0.3 \text{ kJ}\cdot\text{mol}^{-1}$ (1-12 betaine), $4.1 \text{ kJ}\cdot\text{mol}^{-1}$ (3-12 betaine), and $0.2 \text{ kJ}\cdot\text{mol}^{-1}$ (3-12 sulfobetaine). This endothermic molar enthalpy decreases with decreasing hydrophilicity of the zwitterionic headgroup in a similar way as the enthalpy of micellization in the bulk solution does. This supports the hypothesis of aggregation at the solid/solution interface at higher surface coverages. Adsorption in this region can be interpreted as the formation of three-dimensional-like micelles of surface. Surfactant association of this type is less endothermic on the surface than in the bulk phase owing to the differential energetic state of monomers at the interface.

It can be noted that although the enthalpic curves have the same shape in the first adsorption region, the corresponding values are, however, shifted down by vectors, of which the lengths increase with decreasing headgroup hydrophilicity. This observation, supplemented by the perfect continuity of the enthalpic ef-

fect on transition from region 1 to region 2, permits to suppose that surface aggregates begin to form already at low surface coverages and contribute to the total heterogeneity of the system.

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Zusammenfassung — Die Wichtigkeit der kalorimetrischen Methoden bei Untersuchungen von Kolloiderscheinungen wurde anhand der Analyse der experimentellen Verdünnungs- und Adsorptionenthalpien für wäßrige Lösungen dreier zwitterionischer oberflächenaktiver Substanzen gezeigt: 1-12 Betain, 3-12 Betain und 3-12 Sulfobetain. Das zur Bestimmung dieser Daten eingesetzte Mikrokalorimeter "Montcal 3" wird ebenfalls beschrieben. Es wurde gezeigt, daß die molaren Mizellisierungsenthalpien und die differentiellen molaren Enthalpien der Adsorption an Kieselgel eine Funktion der Hydrophilität der endständigen Gruppe ist, festgelegt durch den Typ des negativ geladenen Zentrums und die Anzahl Methylengruppen zwischen den geladenen Punkten.