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INTERFACIAL PROPERTIES OF ZWITTERIONIC SURFACTANTS: N-DODECYLBETAINE

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SUMMARY

The interfacial properties and adsorption of a zwitterionic surfactant, n-dodecylbetaine, were investigated in interfacial tension and calorimetric studies.The enthalpy of micellization was directly obtained from calorimetric curve of surfactant dilution measurements and changed as expected.Adsorption onto silica gel showed mechanisms dependent on amphiphile concentration and temperature.

INTRODUCTION

In spite of the wide applicability of zwitterionic surfactants and their increasing commercial use,it is clear from literature,that their theoretical aspects have received far less attention than those of nonionic or ionic surfactants.

Recent studies have concerned phase diagrams (ref.1),micellization (ref.2), the upper consolute temperature (ref.3),the surface properties (refs.4,5,6),and microemulsion systems (refs.7,8).

Zwitterionic surfactants have the following general formula:$RR'R''N^+(CH_2)_mA^-$, where R,R' and R'' represent aliphatic groups,R' and R'' being methyl or ethyl, the anionic group A^- may be sulfate,sulfonate,carboxylate ...

Generally,the enthalpies of micellization have been calculated from studies of the temperature dependence of the critical micelle concentration (cmc).The purpose of our work is to obtain those of betaines in aqueous solutions directly from experimental calorimetric measurements,as has already been done for ionic surfactant systems (ref.9).

Three alkyl betaines $h(CH_2)_nN^+(CH_3)_2CH_2COO^-$ with n=12 ,14 and 16 of high purity have been synthetized and their surface properties studied.The enthalpy micellization of n-dodecylbetaine,its isotherms and its differential molar heat of adsorption onto silica gel were investigated.

EXPERIMENTAL

Surfactants

Two methods were employed to obtain the following betaines:

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a) n-dodecylbetaine was prepared using the method of Tori and Nakagawa (ref.10) as described elsewhere (ref.2). Several recrystallizations from dry acetone were performed to eliminate sodium chloride, a by-product of the reaction, followed by treatment of the aqueous solutions with an ion exchange resin. The aqueous solutions were subsequently liophilized.

b) A single step reaction was optimised starting from commercially available N-N dimethylglycinehydrochloride*:

$$(CH_3)_2\text{-N-}CH_2\text{-COOH, HCl} \quad + \quad RX \xrightarrow{Na_2CO_3} R\text{-}N^+(CH_3)_2\text{-}CH_2\text{-}COO^-$$

The reaction was carried out by refluxing the reactants in methanol for 48 H. After cooling, the reaction mixture was filtered and evaporated under vacuum and then dissolved in acetone. The salt was filtered off and the resulting alkylbetaines were obtained after several recrystallisations in acetone.

The structure of n-alkylbetaines was confirmed by direct inspection of their ^1H and ^{13}C NMR spectra and the purity of the compounds obtained from microanalyses.

Adsorbent

The silica gel adsorbent was a specimen SPHEROSIL XOB 015 ,manufactured by IBF-Rhone-Poulenc France. The measurements of the surface area of this adsorbent were carried out by using the BET method and Harkins-Jura method (ref.15), giving 24,6 and 25 m^2g^{-1} respectively. The latter value has been used in our calculations. The adsorption isotherm was determined by measuring the surfactant concentration before and after adsorption. The bulk solution concentration was measured by means of the differential refractometer Waters R 403 .

Measuremets

The surface tension measurements of the betaine solutions were made by applying the WILHELMY method and using a PROLABO tensiometer.

The calorimetric curves of the differential molar enthalpy of dilution $\Delta_{dil}H$ were obtained by means of the calorimeter developed by Partyka et al. (ref.13). The water and the surfactant stock solution, with an initial concentration of about 20 times higher than that corresponding to cmc, were placed into the calorimetric cell. When the thermal equilibrium was reached, the experiment was carried out in the following way:

0.2 g of the surfactant stock solution containing a definite quantity of surfactant (monomers+micelles), was injected by the pump into the water. The quantity injected was chosen so that the equilibrium concentration at the bottom of the calorimetric cell be smaller than cmc. The accompanying thermal effect was recorded.

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The equilibrium state of the calorimeter is characterized by the return to the initial base line.Then, the next injection is made,and so on.Each new injection allows us to attain a higher equilibrium concentration of surfactant and is followed by a consistent thermal effect.After many injections of the stock solution into the water, the water solution concentration reaches the cmc value. The next injections of the stock solution into that micellar solution are accompanied by smaller and smaller thermal effects,which are due to the dilution of the stock solution (20 times cmc).

Initially, the surfactant in solution exists in monomeric form.After reaching the cmc, the concentration of monomers becomes constant as determined previously in diffusion studies (ref.2).

The $\Delta_{mic}H$ of micellization at different temperatures was calculated from the calorimetric curves of dilution of C_{12}-betaine by extrapolation to the cmc region.The same calorimetric method was used (ref.13) for the measurements of the differential molar heat of adsorption ($\Delta_{ads}H$).This time,however,silica gel particles were placed at the bottom of the calorimetric cell.After injecting a given quantity of surfactant solution into the water suspension of particles, a part of the injected surfactant molecules is adsorbed and another one remains in water.Then, the accompanying thermal effect is recorded.Each new injection leads to a higher surface coverage of the silica particles.

RESULTS AND DISCUSSION

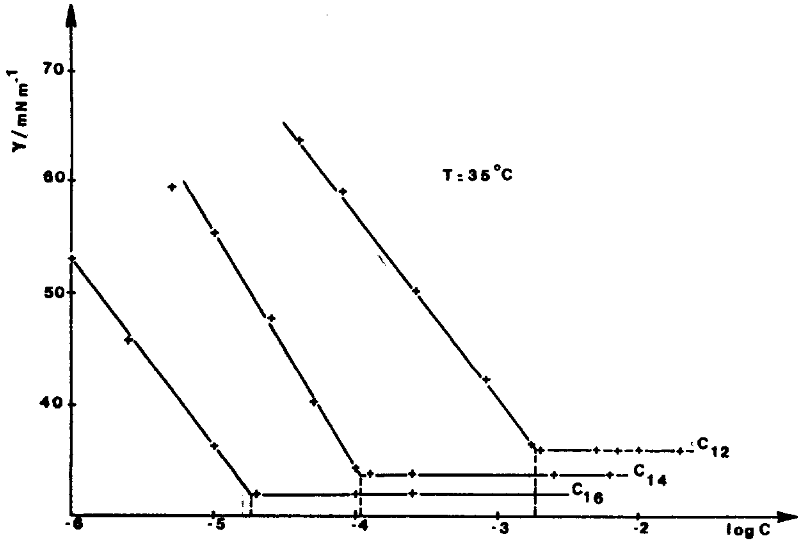

Fig.1 Surface tension γ versus concentration log of n-alkylbetaines in aqueous solution ,n=12, 14 and 16 .T=25°C

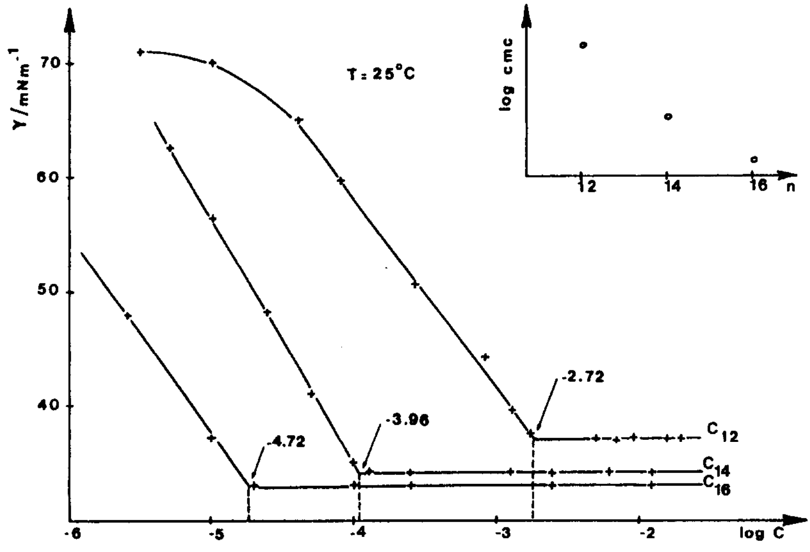

Fig.2 Surface tension γ versus concentration log of n-alkylbetaines in aqueous solution, n=12, 14 and 16.T=35 C .

Figures 1 and 2 show the surface tension γ plotted as a function of the log of the surfactant concentrations in the final solution at two temperatures. This method is widely used to determine cmc, since it can be applied for a variety of ionic and nonionic surfactants.On the contrary, conductivity measurements are restricted to surfactants carrying a charged polar head.In the case of zwitterionic surfactants, we have shown, that the aggregates of dodecylbetaine have a net charge equal to zero. (ref.2) at pH=6,7 .Thus, the cmc value in this case cannot be obtained from conductivity measurements.The cmc value determined by us is this way was also confirmed in density and refractive index measurements.At T=25°C ,the cmc value was found to be $2.0 \cdot 10^{-3}$ mole kg^{-1} , in agreement with the literature data (ref.11) .

In Fig.1 ,the plot of γ as a function of logC ,(C is the molar concenration) shows a net break at the cmc of the betaines studied.For n-dodecyl betaine, a value of $1.9 \cdot 10^{-3}$ mole kg^{-1} was found.

In all cases, the shape of the γ curves around cmc shows that the three surfactants studied were pure.

The values of cmc,and the areas occupied by the polar heads at the liquid/ /gas interface are listed in Table I .The area occupied by one polar head was calculated from the slope of the γ = f(logC) curves, using the following relationship,

$$\Gamma = \frac{1}{2.303\ RT} \left(\frac{-\delta\gamma}{\delta \log C}\right)_T \qquad \text{and} \qquad A = \frac{10^{14}}{N\Gamma}$$

where Γ is the surface excess concentration in mol cm^{-2}, A is the area per molecule in nm^2, and N is Avogadro number.

BETAINE	T/(°C)	cmc/(mole kg^{-1})	δ/(Å)^2
C_{12}	25	$1.9\cdot10^{-3}$	57
	35	$1.8\cdot10^{-3}$	59
C_{14}	25	$1.1\cdot10^{-4}$	44
	35	$1.05\cdot10^{-4}$	46
C_{16}	25	$1.9\cdot10^{-5}$	55
	35	$1.9\cdot10^{-5}$	57

TABLE 1. The experimentally estimated cmc values,and the cross-sectional areas at the liquid/air interface

C_{12} and C_{16} betaines have cmc and the surface area occupied by the polar head in agreement with the literature data reported (ref.12).On the contrary, the cmc value for C_{14} betaine estimated by us is smaller than expected on the basis of the evolution of betaine series cmc with chain length.So far,we have not studied yet calorimetrically the C_{14} and C_{16} betaines, due to their low cmc values.

Micellization is an interfacial effect.The enthalpy of micellization is composed of two main contributions:(1) the transfer of the aliphatic part of betaine from the bulk solution to the hydrophobic core of the micelle,(2) the transfer of the polar group from the bulk solution to the micellar environment. The effect of temperature on the enthalpy of micelle formation results from the interfacial interactions.The sum of the enthalpies of these processes is given by the measured values of the heat of dilution of the betaines.

Figure 3 shows the curves corresponding to the heats of dilution of betaine C_{12} per mole at 25 and 35°C respectively.

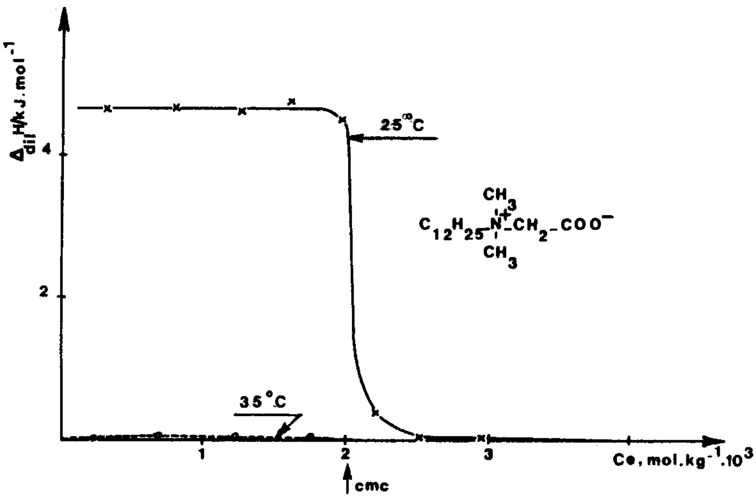

Fig.3 N-dodecylbetaine enyhalpy of dilution $\Delta_{dil}H$ at T=25°C and T=35°C as a function of the equilibrium concentration.

At the lower temperature (25°C), and below cmc, the enthalpy of dilution is constant, but in the cmc region it decreases dramatically to almost a zero value. At 35°C, the enthalpy of dilution of C_{12} betaine is very close to zero. From the last experiment we were not able to evaluate the very small value for $\Delta_{mic}H$.

The decrease in $\Delta_{mic}H$ when temperature increases could be explained by the variation of the iceberg structure of water around the alkyl chain of the free monomers. During micellization, that structure is disrupted and the flexibility of the alkyl chain increases.

The second, much more important enthalpic contribution is due to the hydration of the polar part of molecules ($-N^+(CH_2)_2CH_2-COO^-$) . That hydration usually decreases with increasing temperature. Thus, one should not be surprised by the very small values of $\Delta_{mic}H$.

The comparison between the measured $\Delta_{mic}H$ for C_{12} betaine at 25°C and the literature data (ref.14), obtained by the indirect method, shows significant differences (4.7 and 5.85 kJ mole^{-1} respectively).

Our present calorimetric data provide us only with the total enthalpy effect accompanying the micelle formation. Experiments on homologous series of betaines with various polar groups and different chain lengths are in progress in our laboratory now. We hope that these experiments will allow us to separate the energetic contributions to the enthalpy of micellization coming from aliphatic chains and polar heads.

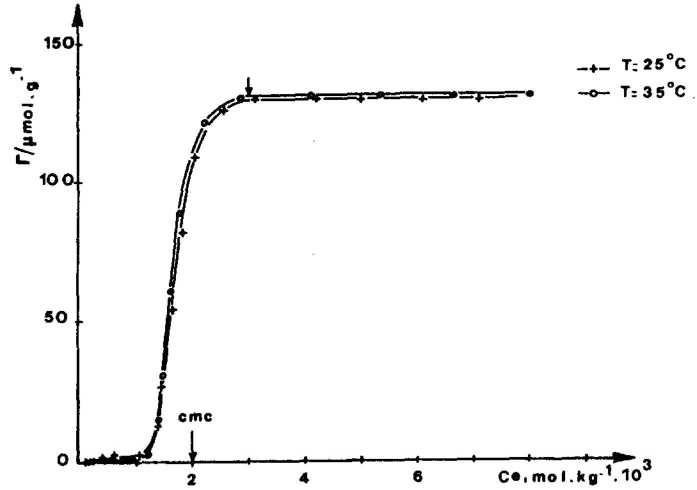

Fig.4 Experimental adsorption isotherms of n-dodecylbetaine on Spherosil at 25 and 35^oC .

Figure 4 shows the isotherms of adsorption of C_{12} onto silica gel measured at two temparatures.At the low surface coverages $\Theta < 0.05$ ($\Theta = \Gamma/\Gamma^*$, where Γ^* is the adsorbed quantity at plateau),the adsorbed amount increases slowly with the bulk concentration increasing.A few surface sites are opened to direct anchorage of the surfactant molecules.This direct "gaseous" adsorption constitues the background for a further adsorption step.As shown by the shape of the steeper parts of the isotherms, the increase in equilibrium concentration brings about structuring increase of the adsorption.Adsorption continues above cmc ,and the plateau is reached at an equilibrium concentration of about $3.1 \cdot 10^{-3}$ mole kg^{-1} .Such a plateau formation,far enough from the cmc region,is not typical for a nonionic surfactant adsorbed onto hydrophilic surfaces (ref.16).

The cross-sectional area of one admolecule calculated from the plateau of adsorption isotherm is equal to 33 Å^2 .The same value calculated for the air--water solution interface yelds 58 Å^2 per molecule.(Ref.6).The influence of temperature on adsorption is negligible.

Direct calorimetric measurements of differential molar heats of adsorption $\Delta_{ads}H$ seem to provide a further support for the above interpretation.

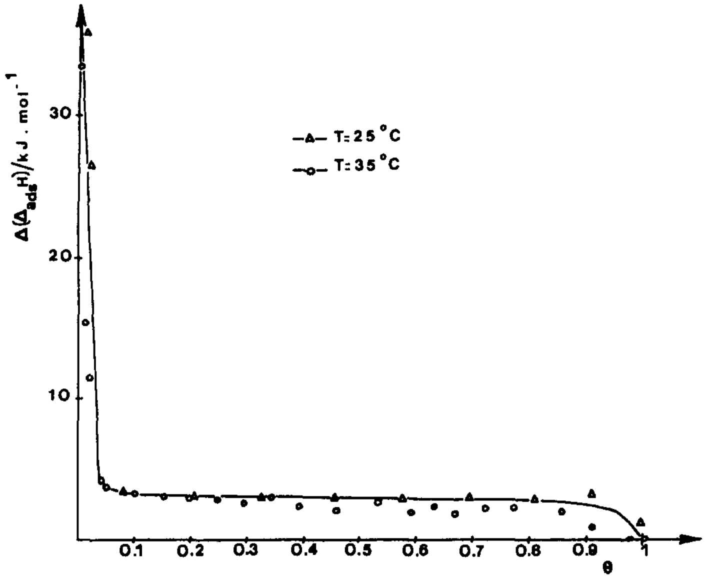

Fig.5 Differential molar enthalpies ($\Delta_{ads}H$) of adsorption of n-dodecylbetaine ,versus θ at 25 and 35^{o}C .

Figure 5 shows that,at small bulk equlibrium concentrations of betaine, one observes a strong interaction between individual molecules and isolated sites of silica surface.Interactions between adsorbed molecules are negligible. The $\Delta_{ads}H$ values are relatively large;(Fig.5).

When the surface coverage θ exceedes a value of about 0.05 , $\Delta_{ads}H$ becomes constant and very low.(About 3.5 kJ per mole).This would indicate a physical adsorption.It seems,that the betaine molecules are adsorbed around individual betaine molecule already anchored on the water molecules ,well structured by the silica gel surface.

CONCLUSIONS

Isotherm and calorimetric data suggest the following structure for the adsorbed layer at the saturation plateau.

At the first stage, the molecules are attached individually by the polar head ($-N^{+}(CH_3)_2CH_2COO^{-}$) to the sites of silica gel ($0 < \theta < 0.05$).The exotermic heats of adsorption seem to be a convincing experimental proof for that adsorption mechanism.

Adsorption then progresses due to hydrophobic interactions between aliphatic parts of betaine on the silica gel surface homogenized by strongly bonded water molecules.This kind of ice-water structure can give a relatively homogeneous solid surface.

Beginning from Θ =0.05 up to 1, the values of $\Delta_{ads}H$ are very small. (3.5 kJ mol^{-1}).Calorimetric experiments give the sum of the enthalpic exchange between the exit of monomer from bulk solution and the adsorption of this monomer in the interfacial surfactant structure.It would be desirable to estimate separately the various enthalpic contributions due to the different parts of surfactant molecules.Perhaps it might be feasible by studying the adsorption of the same kind of surfactant molecules with various aliphatic parts.

The experimental cross-sectional area of one molecule calculated from the saturation plateau,σ,was 33 Å^2.The same quantity calculated for the solution--air interface was found to be about 58 Å^2.The theoretical surface occupied by polar head of betaine ($-N^+(CH_3)_2CH_2COO^-$) in one of different possible configurations is 55.9 Å^2.That calculation,and the measured calorimetric data suggest that the adsorbed molecules have a bilayer structure.

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