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ENTHALPIES OF MICELLE FORMATION BY HEXADECYLTRIMETHYLAMMONIUM BROMIDE IN AQUEOUS SOLUTION CONTAINING PENTANOL

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Titration calorimetric data show a dramatic change from endo- to exothermic deaggregation when pentanol–hexadecyltrimethylammonium bromide (CTAB) mixed solutions are injected into an aqueous solution containing pentanol. The results are interpreted in terms of a change in the structures of the aggregates in solution from simple CTAB micelles to mixed amphiphilic microheterogeneities when pentanol is added.

INTRODUCTION

In aqueous solution at 298·2 K and ambient pressure, the amphipathic[1] salt hexadecyltrimethylammonium bromide (CTAB) forms micelles when the molality of CTAB exceeds 1×10^{-3} mol kg^{-1}, the critical micellar concentration (CMC).[1] The associated limiting enthalpy of micelle formation (see also below) expressed[2] in terms of 1 mol of CTAB is −9·.77 kJ mol^{-1}. With increase in concentration, new post-micellar phenomena are observed according to, for example, differential scanning microcalorimetry.[3] These phenomena are not examined here because we confine attention to solutions where the concentration of CTAB is around the cmc. An interesting and important feature of these systems is their ability to solubilize large amounts of organic compounds which otherwise have low solubility in water. Moreover, the solubilization can be very efficient, as shown[4] by the molar ratio at saturation of 5 : 1 for *n*-pentanol to alkyltrimethylammonium bromide surfactants and the incorporation$_5$ of 70 butanol molecules per micelle by CTAB. The enthalpy of transfer of *n*-pentanol from aqueous solution into CTAB micelles is endothermic, 6·42 kJ mol^{-1} as expressed for 1 mol of pentanol. Several models have been discussed for the solubilization.[6] One approach[7] places the adsorbed alcohols in the palisade layer rather than in the hydrophobic core. Another model stresses the role of surface sites.[8] A more dramatic change in micelle structure is envisaged in another description developing the concept of a mixed micelle.[9,10] Thus, as more alcohol is added, the micelles lose their form, the system moving towards different microaggregates of alcohol and surfactants.[4] These different models and explanations impinge on another important feature of micellar systems, namely micellar catalysis.[11] Thus, CTAB micelles in aqueous solution catalyse the alkaline hydrolysis of 2,4-dinitrochlorobenzene[12] (DNCB). However, the catalytic action is reduced when monohydric alcohols are added.[13]

To probe the interaction between pentanol and CTAB, we have used a titration microcalorimeter.[14,15] In the absence of pentanol, the deaggregation process of CTAB micelles to simple ions is endothermic (i.e. exothermic micelle formation). However, when pentanol was added, the endothermicity decreased, switching to an exothermic deaggregation. We also report on the shift in cmc for CTAB when pentanol is added. The magnitude of the enthalpy changes point to a dramatic change in CTAB micellar (microphase)[16] organization.

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EXPERIMENTAL

Materials. CTAB was used as described.[14] Pentanol (99%, Aldrich) was used as supplied. CTAB (Lancaster Synthesis) was dried overnight in an oven at <60 °C.

Titration calorimetry. In an Omega titration calorimeter[17] (MicroCal, MA, USA), a syringe is mounted above a sample cell, volume 1·4115 cm^3, and injects small aliquots (typically 10^{-2} cm^3) of a solution into a sample cell. The output from the calorimeter (displayed on a VDU) shows a series of pulses which characterize the rate of heating required to hold sample and reference cells on the same temperature gradient. The Origin software integrates each pulse to produce a plot showing heat $q(t)$ at injection number k (see below).

In the experiments reported here, stock aqueous solution was prepared containing a known molality of pentanol. Both sample and reference cells were filled with this aqueous pentanol solution. The same stock solution was used to prepare a CTAB solution of known molality, which was placed in the syringe. This protocol was the result of many preliminary studies. Originally, we had planned to put water into the sample cell and inject the CTAB + pentanol solution. The results were compared with calorimetric data where an aqueous solution of pentanol was injected into the sample cell, initially containing water. However, simple dilution of aqueous pentanol is strongly exothermic, throwing some doubt on the analysis of the data when $(CTAB + pentanol)_{aq}$ was injected into water. The compromise in which reference, initial solution in sample cell and solvent for CTAB in the syringe had the same molality of pentanol proved satisfactory.

A typical injection plot for aqueous CTAB in the absence of pentanol is shown in Figure 1. At the start of the experiment sample cell contains water and the syringe contains a solution in which the CTAB concentration is slightly above the cmc. In the first set of injections the micelles deaggregate to form effectively a dilute solution of a strong electrolyte, $RNMe_3^+(aq)$ and $Br^-(aq)$. For this system the injections produce endothermic peaks. With increase in the number of injections, the concentration of CTAB in the sample cell increases, approaching and then passing the cmc. In the latter case, further injections are athermal, the micellar solution simply being diluted on passing from syringe to sample cell. Two pieces of information emerge from the integrated plots, e.g. Figure 1(b). The first few peaks yield the enthalpy of deaggregation, $\Delta_{deagg}H$, and the cross-over from endothermic to athermal injection occurs at the cmc. At least three determinations were made on each solution and the reproducibility in the cmc was within ±3% and that in $\Delta_{deagg}H$ was within ±0·5 kJ mol^{-1}.

Each new solution was characterized by a new $\Delta_{deagg}H$ and a new cmc. Hence several preliminary

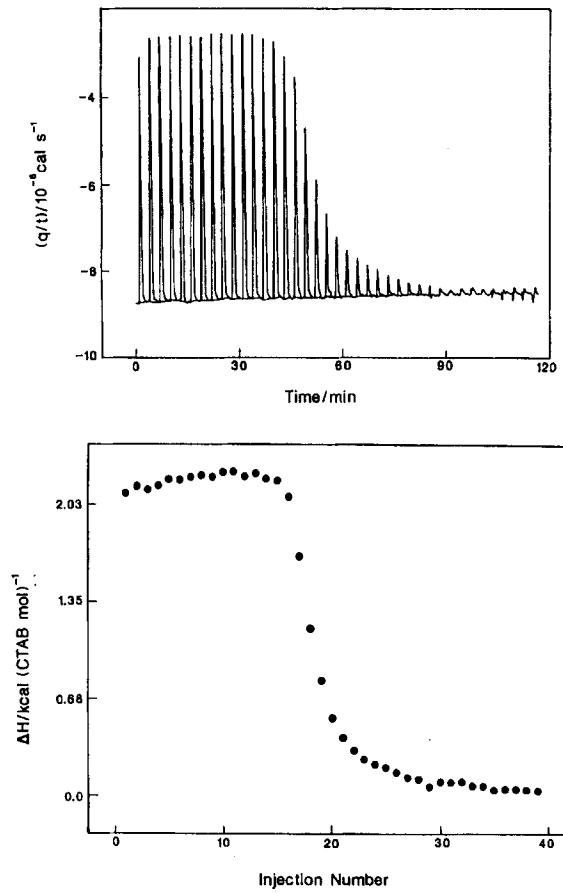

Figure 1. Titration calorimetric study using aqueous CTABi. (a) Injection plot showing rates of heating pulses as a function of time: concentration of aqueous CTAB in syringe = $14·8 \times 10^{-3}$ mol dm^{-3}. (b) Integrated plot showing dependence of enthalpy changes associated with each injection as a function of injection number

experiments were required to identify the amounts and volumes to be injected. With care it was possible to refill the syringe and continue the sequence of injections in a given experiment.

RESULTS

For aqueous solutions the titration calorimetric data (Figure 1) show a clear break in pattern near injection number 20, yielding an estimate of the cmc at $9·99 \times 10^{-4}$ mol dm^{-3}. The associated enthalpy change, assumed for such dilute solutions to be close to the limiting enthalpy change $\Delta_{mic}H^{\infty}$ for micelle formation, is −10·3 kJ mol^{-1}. Both estimates agree with published values,[2] −9·7 kJ mol^{-1}. When *n*-pentanol was added to both solutions in the syringe and sample cell (see

Experimental), the switch from endothermic to almost athermal injection occurred at a lower concentration of CTAB. Moreover, the dilution of the CTAB solution was less endothermic (Figure 2). With increasing molality of *n*-pentanol in the CTAB solution, the initial injections became less endothermic, eventually switching to exothermic (Figure 3).

In order to observe the set of exothermic injections in Figure 2, the concentration of CTAB in the syringe had to be reduced significantly. Athermal injection was only recorded after a sequence of endothermic injections. Finally, the pulses refer to a series of equilibrium states. As shown by the injection pattern in Figure 4 (cf. Figure 3), a small 'baseline' was recorded between each injection.

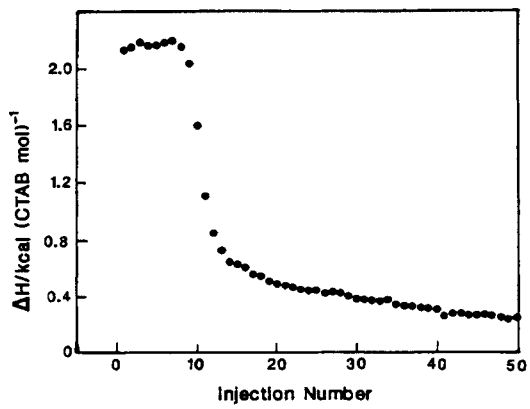

Figure 2. Integrated plot showing dependence of enthalpy of dilution as a function of injection number for aqueous CTAB (0·023 mol dm^{-3}) and aqueous *n*pentanol (0·018 mol kg^{-1})

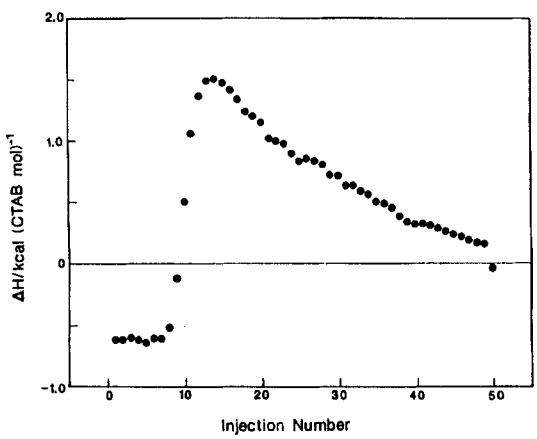

Figure 3. Integrated plot showing dependence of enthalpy of dilution as a function of injection number for aqueous CTAB (0·004 mol dm^{-3} and aqueous *n*-pentanol (0·111 mol kg^{-1})

The effect of added *n*-pentanol on CTAB micelles was characterized using two quantities. An effective cmc was recorded as the concentration of CTAB in the sample cell at which the titration enthalpy was half the titration enthalpy (independent of sign) over the first few injections (Table 1). In these terms, the cmc decreases with increase in *n*-pentanol concentration, a pattern consistent with the generalization that amphiphilic solutes such as monohydric alcohols depress the cmc.[18] The corresponding enthalpy term expressed in terms of 1 mol of CTAB monomer was estimated from the enthalpy changes accompanying the first few injections

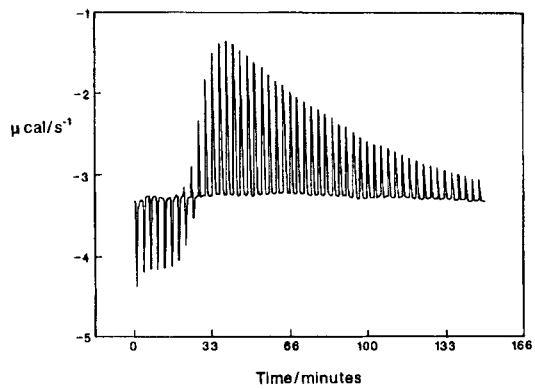

Figure 4. Recorded output from titration microcalorimeter showing rate of heating of sample/reference to attain same rate of increase in temperature as a function of time during which injections are made. The syringe contained aqueous CTAB (4×10^{-3} mol dm^{-3}) and aqueous *n*-pentanol (0·111 mol kg^{-1}); the sample cell contained aqueous *n*-pentanol (0·111 mol kg^{-1}); total number of injections = 50

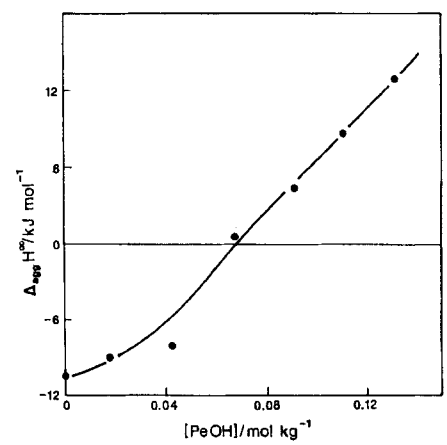

Figure 5. Dependence on *n*-pentanol concentration of the enthalpy of aggregation for CTAB in aqueous solutions containing *n*-pentanol

Table 1. Effect of added *n*-pentanol on CTAB micelles in aqueous solution at 298·2 K

Syringe solution			
[CTAB]/10^{-2} mol dm^{-3}	[*n*-pentanol]/10^{-2} mol dm^{-3}	cmc/10^{-4} mol dm^{-3}	ΔH^{m}/kJ mol^{-1}
2·56	0	9·99	−10·3
2·31	1·82	8·59	−9·0
2·05	4·29	6·89	−8·1
1·86	5·59	5·56	−6·9
1·20	6·73	4·56	0·5
0·71	9·13	3·57	4·4
0·40	11·1	2·83	8·8
0·40	13·1	1·88	12·3

(Table 1). These enthalpy quantities showed a gradual change from exothermic to endothermic for aggregation (micelle formation) of the CTAB monomers, i.e. the reverse of the deaggregation accompanying injection (Figure 5).

DISCUSSION

The key question centres on the nature of the aggregate contained in the solution held in the syringe when that aqueous solution is prepared using CTAB and *n*-pentanol. In the last example recorded in Table 1, the deaggregation process following injection into water is exothermic, 12·3 kJ (mol CTAB)$^{-1}$ (cf. Figure 3). The latter characterizes release of free alkylammonium ions, bromide ions and *n*-pentanol from the aggregates into an aqueous solution. The first entry in Table 1 shows that deaggregation of CTAB micelles is endothermic, +10·3 kJ mol^{-1}. In these terms, the release of *n*-pentanol from the CTAB aggregates is exothermic, −22 kJ (mol CTAB)$^{-1}$. De Lisi *et al.* quote −6·42 kJ (mol *n*-pentanol)$^{-1}$ for the transfer of *n*-pentanol from CTAB micelles into aqueous solution. This exothermicity is consistent with a model which stresses the hydrophobic nature of *n*-pentanol and the interior of the CTAB micelles.[19] Nevertheless, the arithmetic indicates that the aggregate in the syringe has a stoichiometry of approximately 3 PeOH·CTAB. If this is the case, a model based on incorporation of *n*-pentanol into a slightly modified CTAB micelle is unrealistic. Moreover, the complexity in the titrations cannot be accounted for in these terms, especially the switch from exothermic to endothermic to approximately athermal as shown in Figure 3. A better description is in terms of the model suggested by Quirion and Desnoyers,[9] which treats, for example, both CTAB and *n*-pentanol as amphiphiles. A CTAB + *n*-pentanol system comprises mixed aggregates with a predominance of CTAB or *n*-pentanol microstructures depending on the CTAB/*n*-pentanol molar ratio. The term comicellizes is used by Perron *et al.*[10] in a comparable case to describe the interaction between the two components. We then attribute the complex patterns in the titration calorimetry to a sequence of microstructures (microheterogeneous clusters) as the titration proceeds. The switch from exo- to endothermic deaggregation signals a switch from deaggregation dominated by *n*-pentanol release to deaggregation dominated by CTAB. Gradually, however, the structures in the syringe and sample cell must become identical because in the limit of an infinite number of injections the solutions have the same composition. We also note that within the time-scale of the experiment the information obtained refers to a series of equilibrium states.

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