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# EFFECTS OF ADDED DOTAB ON THE *cmc* AND ENTHALPY OF MICELLE FORMATION AT 298.2 K FOR CTAB(aq)

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## Abstract

In a titration calorimetric study an aqueous solution held in a syringe and containing hexadecyltrimethylammonium bromide (CTAB; $15.4\times10^{-3}$ mol dm$^{-3}$) is injected in aliquots ($5\times10^{-3}$ dm$^3$) into a sample cell containing initially water. Analysis of the data shows that the *cmc* equals $0.97\times10^{-3}$ dm$^{-3}$ and the enthalpy of micelle formation equals $-10.3$ kJ mol$^{-1}$. When the solution in the syringe is replaced by a mixed surfactant solution, CTAB + dodecyltrimethylammonium bromide, at the same total concentration of surfactant, the *cmc* of CTAB decreases gradually with increasing mole fraction of DOTAB but the enthalpy of CTAB micelle formation is hardly affected. We conclude, therefore, that incorporation of DOTAB monomers into the CTAB micelles stabilizes entropically the CTAB micelles.

**Keywords:** *cmc*, CTAB, DOTAB, enthalpy of micelle formation, micelles, titration calorimetry

## Introduction

Titration microcalorimetry is an important technique in the characterisation of amphipathic salts in aqueous solutions [1–3]. In principle, two pieces of information emerge from one experiment (at fixed temperature and pressure); (*i*) the critical micellar concentration (*cmc*) and (*ii*) enthalpy of micelle formation which for very dilute solution is approximately the limiting enthalpy of micelle formation, $\Delta_{mic}H^{\circ}$. The latter refers to the increase in enthalpy when one mole of monomer is incorporated into micelles. In the titration microcalorimetric method [2, 3] small aliquots of a solution containing an amphipathic salt at a concentration of surfactant above the *cmc* are injected into a sample cell containing initially water. Hence over the first set of injections the calorimeter records the impact of deaggregation. A stage is reached where the concentration

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of salt in the sample cell reaches and then exceeds the *cmc*. Over the next series of injections the calorimeter monitors the effect of dilution of the micellar solution in the syringe. For hexadecyltrimethylammonium bromide (CTAB), the two regimes, deaggregation of micelles and dilution of micellar solution, are clearly identified [3] leading to estimates of the *cmc* and $\Delta_{mic}H^{\infty}$, $0.95\times10^{-3}$ mol dm$^{-3}$ and $-10.3$ kJ mol$^{-1}$. Addition of NaBr(aq) up to 0.02 mol dm$^3$, of NaCl(aq) up to 0.1 mol dm$^3$ and EtOH(aq) up to a mole fraction of 0.0469 lowers [4] the *cmc* of CTAB. Similarly, addition of *n*-pentanol up to $13.1\times10^{-2}$ mol dm$^{-3}$ lowers the *cmc* and dramatically alters the recorded enthalpy of deaggregation from endo- to exothermic. These solutes are, compared to CTAB, relatively small molecules/ions. Here we report the impact on micelle formation by CTAB of adding dodecyltrimethylammonium bromide which has a cmc of $13\times10^{-3}$ mol dm$^{-3}$, a markedly higher concentration than that for CTAB. Significantly, the deaggregation of CTAB micelles is not dramatically affected by the presence of DOTAB.

## Experimental

### *Materials*

The surfactants CTAB and DOTAB were supplied and purified as described previously [3, 5].

### *Calorimeter*

A titration microcalorimeter [MicroCal Ltd., USA] was used as previously described [3, 5]. The volume of the sample cell was $1.4115\times10^{-6}$ m$^3$ and the volume of each injected aliquot was $5\times10^{-9}$ m$^3$. The temperature of the calorimeter was set to 298.2 K. The calorimeter operated by measuring the rates of heating as a function of time of sample and reference cells, the latter containing water in the study reported here. Using the ORIGIN software the recorded pulses, linked to a series of injections, are integrated to yield the heat of injection as a function of injection number. Knowing the concentration of CTAB in each injected aliquot, the calculated heat was readily re-expressed in terms of enthalpy of injection for one mole of CTAB.

In the experiments reported here, 50 aliquots of solution were injected into the sample cell. Each injection was made over a period of 5 seconds at 2 minute intervals. In all cases a short baseline was recorded between injections indicating that a series of equilibrium states were being tracked. In order words, no slow kinetic processes contributed to the recorded pattern.

Many preliminary experiments were carried out in which the two surfactants CTAB(aq) and DOTAB(aq) were placed together or separately in either the sample cell or syringe. Our concern was to minimise the contribution to the ob-

served heats of injection from the non-ideal (e.g. ionic strength) effects of the solutions. Further, we wanted to minimise the impact of changes in composition of micellar solutions on the changes in these ionic strength effects. Although effects based on the non-ideal properties of the micellar solutions [3] cannot be eliminated, the following protocol proved satisfactory. Two dilute solutions were prepared having the same concentration, $15.4\times10^{-3}$ mol dm$^{-3}$, of both CTAB and DOTAB. We assumed that for such dilute solutions the densities are equal such that by mixing volumes $V_1$ and $V_2$ of CTAB(aq) and DOTAB(aq), a series of solutions could be prepared at common surfactant concentration but containing different surfactant mole fractions.

In each case, the *cmc* for the solution was calculated from the titration plot, by plotting $\sum_i q$ *vs.* injection number $i$ over the range of $k$ injections where $1 \leq i \leq k$. At low injection numbers, the data points fall on a straight line; at high injection numbers the data points fall on another straight line. The intersection of the two lines occurs at a concentration equal to the *cmc* [6].

## Results

The starting point for this study was a titration calorimetric plot for CTAB ($15.4\times10^{-3}$ mol dm$^{-3}$; aq), which confirmed the result reported in reference 3; $cmc = 0.97\times10^{-3}$ mol dm$^{-3}$ and $\Delta_{mic}H^{\circ} = -10.3$ kJ (monomer mol)$^{-1}$. This classic pattern was followed for a mixed surfactant ($15.4\times10^{-3}$ mol dm$^{-3}$; aq) where the CTAB mole fraction was, for example, 0.5; Fig. 1[A]. For DOTAB(aq), the *cmc* estimated by the same calorimetric method was $1.3\times10^{-2}$ mol dm$^{-3}$, with $\Delta_{mic}H^{\circ}$ equal to $-1.8$ kJ mol$^{-1}$.

The related $\Sigma\Delta H$ plot in Fig. 1[B] shows the anticipated pattern where the intersection of the two straight lines yields the critical micellar concentration. The latter can be expressed in terms of either the total concentration of surfactant (DOTAB and CTAB) or the concentration of CTAB, $0.69\times10^{-3}$ mol dm$^{-3}$. Similarly, the enthalpy of deaggregation can be expressed with respect to either the total surfactant or CTAB, i.e. either +5.7 kJ (surfactant monomer mol)$^{-1}$ or +11.4 kJ (CTAB monomer mol)$^{-1}$. Similar plots to those shown in Fig. 1 were obtained for [DTAB+CTAB] (aq; $15.4\times10^{-3}$ mol dm$^{-3}$) where the surfactant comprised CTAB with mole fractions at 0.1 intervals between 0.8 and 0.2. The results are summarised in Table 1 where we have expressed the derived molar quantities in terms of the solute CTAB.

## Discussion

Across the range of surfactant systems prepared using CTAB and DOTAB, the overall shape of the titration plots remained broadly similar even up to a system where the mole fraction of CTAB within the surfactant was only 0.2. We conclude therefore that the solutions in the syringe did not contain two types of

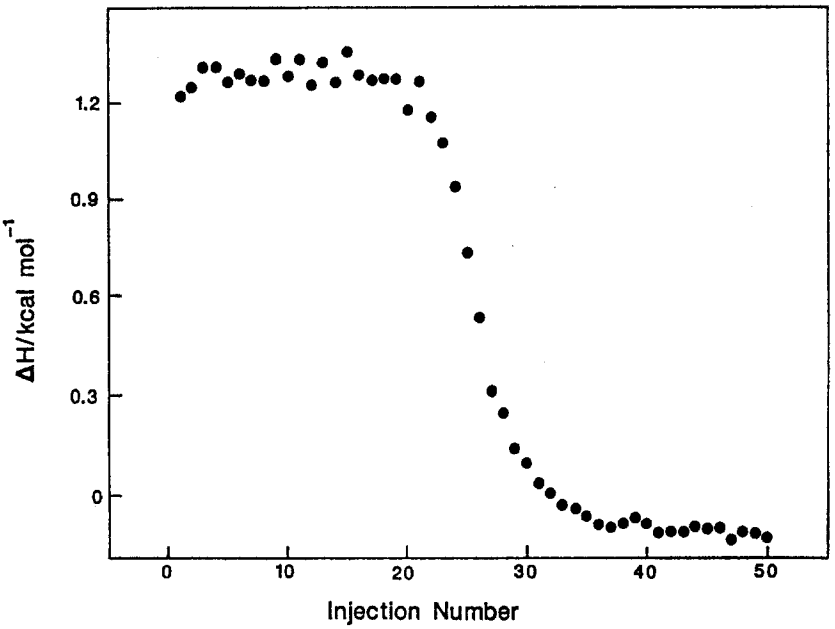


**Fig. 1** [A] Titration microcalorimetric plot for a surfactant ($15.4\times10^{-3}$ mol dm$^{-3}$; aq) comprising DOTAB+CTAB where mole fraction of CTAB equals 0.5. Plot of enthalpy change against injection number where the enthalpy change is expressed in terms of per mole of injected surfactant

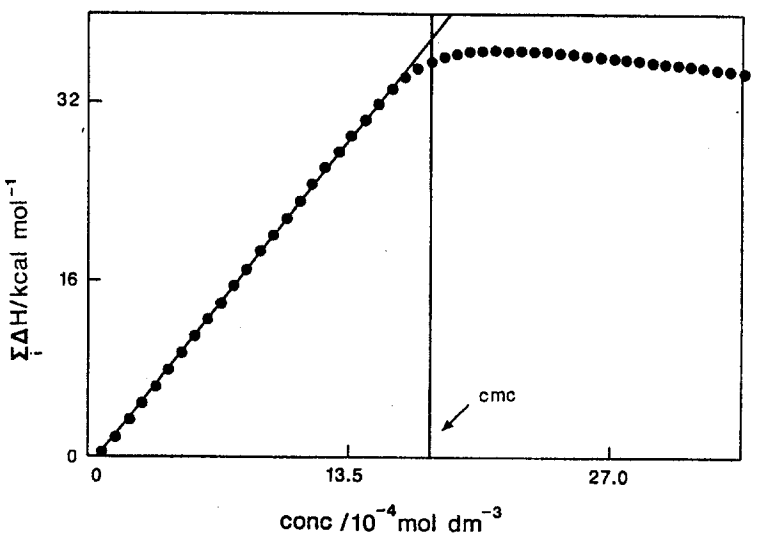


**Fig. 1** [B] Plot of $\sum_i \Delta H$ at each injection $i$ for the range $1 \leq i \leq k$: intersection of lines corresponds to a solution containing $1.38\times10^{-3}$ of surfactant or $0.69\times10^{-3}$ mol dm$^{-3}$ of CTAB

**Table 1** Titration calorimetric data for aqueous solutions at 298.2 K containing surfactant ($15.4\times10^{-3}$ mol dm$^{-3}$) comprising mixtures of CTAB+DOTAB

| Mole fraction CTAB | $\Delta_{mic}H^{\circ}/^{*}$ kJ (CTAB mol)$^{-1}$ | *cmc*/ 10–3×(CTAB mol)dm$^{-3}$ | $\Delta_{mic}G^{\circ}$/ kJ (CTAB mol)$^{-1}$ | $T\Delta_{mic}S^{\circ}$/ kJ (CTAB mol)$^{-1}$ |
|---|---|---|---|---|
| 1.0 | –10.3 | 0.97 | –34.4 | +24.2 |
| 0.8 | –9.29 | 0.91 | –34.7 | +25.4 |
| 0.7 | –11.3 | 0.82 | –35.2 | +23.9 |
| 0.6 | –10.9 | 0.80 | –35.4 | +24.5 |
| 0.5 | –11.4 | 0.69 | –36.1 | +24.7 |
| 0.4 | –10.9 | 0.54 | –37.3 | +26.4 |
| 0.3 | –12.6 | 0.35 | –39.5 | +26.9 |
| 0.2 | –10.5 | 0.23 | –41.5 | +31.0 |

*Enthalpy of micelle formation

micelles. If this had been the case, we would have expected to record two distinct steps as the two types of micelles deaggregated. Therefore, the properties of the micellar solutions are dominated by the CTAB surfactant. This observation prompted the calculation of derived parameters (cf. Table) in terms of the impact of DOTAB on the properties of CTAB. In other words, the calculated quantities characterise the changes in molar properties when CTAB forms micelles in the presence of DOTAB. The gradual decrease in *cmc* with decrease in mole fraction of CTAB points to either a stabilisation of the micelles or a destabilisation of the CTAB monomers in solution. The latter seems unlikely because it would require striking deviations of the properties of dilute salt solutions (comprising monomeric cations and bromide anions) from ideal. We had anticipated that the *cmc* of CTAB would increase when DOTAB was added on the grounds that the *cmc* for DOTAB is much higher, $15\times10^{-3}$ mol dm$^{-3}$. Therefore, the CTAB micelles appear to readily incorporate DOTAB. The relative insensitivity of the enthalpy of CTAB micelle formation [mean value –10.9 (±0.9) kJ mol$^{-1}$] to added DOTAB supports this view. From a thermodynamic standpoint these enthalpies describe the increase in enthalpy when one mole of CTAB monomer in the standard state in aqueous solution is incorporated into the micellar macrosalt [3] also in the solution standard state in aqueous solution. [For dilute aqueous solutions the standard state is the ideal solution where the molality of solute is 1 mol kg$^{-1}$.] Using these standard states, the corresponding increase in Gibbs energy is given by Eq. (1) [3].

$$\Delta_{mic}G^{\circ} = 2RT\ln(cmc/m^{\circ}) \quad (1)$$

The factor '2' emerges because the monomers are 1:1 salts when in solution below the *cmc*. Thus the decrease in *cmc* can be re-expressed (Table 1) in terms

of a decrease in $\Delta_{mic}G^{\circ}$ for CTAB consequent on addition of DOTAB. This decrease in $\Delta_{mic}G^{\circ}$ is accounted for by a gradual increase in the entropy of micelle formation. The increase is a consequence of the presence of the DOTAB 'impurity' in the CTAB micelles.

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