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# Titration microcalorimetry of micelle formation in aqueous solutions containing alkylpolyoxyethylene glycol ethers, $C_{12}H_{25}(OCH_2CH_2)_mOH$ where $m = 3$, 4 and 5, and octadecyltrimethylammonium bromide

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Titration microcalorimetric results are reported for alkylpolyoxyethylene glycol ethers, $C_{12}H_{25}(OCH_2CH_2)_mOH$ where $m = 3$, 4 or 5 at ambient pressure and 298.2 K. The enthalpograms yield estimates of critical micelle concentrations (c.m.c.) which for these surfactants cover the range from $3.25(\pm0.22) \times 10^{-5}$ to $5.26(\pm0.49) \times 10^{-5}$ mol dm$^{-3}$ with increasing integer $m$. The enthalpograms are complicated. Although the recorded enthalpies of injection are exothermic, the dominant process accompanying injection of an aliquot into the sample cell is not simple micelle deaggregation. Rather these surfactant solutions above the c.m.c. contain both micelles and higher aggregates. In a similar fashion, enthalpograms for aqueous solutions containing octadecyltrimethylammonium bromide, $C_{18}H_{37}N^+$ $Me_3Br^-$ (OCTAB) do not follow the previously reported pattern for n-hexadecyltrimethylammonium bromide (CTAB), pointing to the dramatic impact of an additional methylene group in the alkyl chain of the cationic surfactant on the aggregation of this surfactant in aqueous solution.

## Introduction

Important information concerning the properties[1,2] of ionic surfactants in aqueous solutions has been obtained using titration microcalorimetry. In the latter technique small aliquots (*e.g.* $5 \times 10^{-6}$ dm$^3$) of a concentrated surfactant solution are injected into a sample cell, volume approx. 1.5 cm$^3$, containing, initially, water. The recorded enthalpogram in the case of, *e.g.*, CTAB[3] shows a series of strongly endothermic dilutions over the first set of injections. The recorded heat decreases dramatically to almost zero when the concentration of surfactant in the sample cell equals or exceeds the c.m.c. Consequently the recorded enthalpogram yields estimates of both the c.m.c. and the limiting enthalpy of micelle formation, $\Delta_{mic}H^\infty$ which, for CTAB, is exothermic.

In an extension of this research programme,[3,4] we turned our attention to the properties of surfactants in aqueous solutions[5] concentrating attention on alkylpolyoxyethylene glycol ethers. Generally the c.m.c.'s for nonionic surfactants are lower than the c.m.c.'s for an analogous ionic surfactant as a result of reduced repulsive headgroup interactions.[5] Significantly in the context of microcalorimetry, micelle formation by nonionic surfactants is often endo- rather than exo-thermic as in the case of ionic surfactant.[6] The expectation was therefore that the recorded enthalpograms for these glycol ether surfactants would be essentially mirror images of those previously recorded[3,4] for ionic surfactants. Olofsson studied[7] similar nonionic surfactants where $m = 5$, 6 and 8. Olofsson used an LKB-titration calorimeter which involved a sample cell having a volume 100 cm$^3$, the volume of injected aliquots being between 5 and 25 mm$^3$. The calorimetric results were complicated. The intention in the study reported here was to exploit the sensitivity of a titration microcalorimeter where the volume of the sample cell is approx. 1.5 cm$^3$ and the volume of the injected aliquot is of the order $10^{-6}$ dm$^3$. The expectation was therefore that the calorimetric results would be relatively simple to interpret. In the event this expectation was not fulfilled. The enthalpograms are complicated indicating an underlying complexity absent for the ionic surfactants at concentrations above their c.m.c.'s.[3,4] Interestingly, the enthalpograms recorded for aqueous solutions containing OCTAB resemble the pattern set by nonionic surfactants.

The results show that these nonionic surfactant systems associate to form micelles above characteristic c.m.c.'s but apparently the micelles cluster to form higher aggregates. As a consequence a reasonable estimate of the c.m.c. for a given surfactant is obtained but serious difficulties arise in estimating the corresponding enthalpy of micelle formation.

## Experimental

### Calorimetry

A titration microcalorimeter (MicroCal Ltd.) was used as described previously.[2–4] The volume of the sample cell was 1.411 cm$^3$; the volume of each injected aliquot was $5.0 \times 10^{-6}$ dm$^3$. The temperature of the sample cell and aliquots was 298.2 K. Injection of aliquots and recording of the associated heats were controlled by a PC. For each experiment, the recorded quantity was the rate of heating as a function of time. These results were processed to yield a plot of the ratio of recorded heat to the amount of surfactant X injected into the sample cell, $[q/n_X^0(\text{inj})]$.

## Materials

The surfactants, obtained from Nikkol Chemical Co. (Tokyo, Japan), were used as received. Aqueous solutions were prepared by dissolving the required amounts of surfactants in water. An important consideration with respect to the prepared aqueous solutions is the clouding point. According to the compilation in ref. 6 [see Table 11.1.2], the clouding temperature for $C_{12}E_5$ is 26 °C at low wt.% surfactant composition. For the titration calorimetric experiments the prepared solutions at 25 °C were clear. Ref. 6 reports that for $C_{12}E_4$, the clouding temperature is around 5 °C. The solutions used for the titration calorimetric experiments were very slightly cloudy. Ref. 6 reports that for $C_{12}E_3$ the clouding temperature is below 0 °C. In the experiments reported here, the solutions cleared on degassing. The latter is a required procedure in all titration calorimetric experiments. We also point out that experiments examining clouding points are usually concerned with the properties of nonionic surfactants + water systems over the composition range, 0 to 100 wt.% surfactants; *e.g.* ref. 8. In the experiments reported here the compositions for the surfactant solutions are less than 0.01 wt.%.

## Analysis of recorded enthalpograms

In a calorimetric investigation of the properties of nonionic surfactants each aliquot from the microsyringe adds $n_X^0$ moles of surfactant X to the sample cell. For the purpose of developing the argument, we assume that the surfactant is in the form of both micelles and monomers. We also assume that the thermodynamic properties of both micellar and aqueous phase are ideal. Hence the c.m.c. of a given surfactant is independent of the total amount of surfactant in a given system. If the volume of each injected aliquot is $V$(inj), the amount of monomeric surfactant in the injected aliquot equals [$V$(inj)c.m.c.] mol. The amount of surfactant in the form of micelles is therefore [$n_X^0$(inj) − $V$(inj)c.m.c.] mol where $n_X^0$(inj) is the total amount of surfactant in each aliquot.

According to the pseudo-separate phase model[9] for micellar solutions an equilibrium is established between X(aq) in the aqueous phase and X(mic) in the micellar phase. If the thermodynamic properties of the two phases are ideal, the equilibrium can be characterised by the following equation where $\mu_X^*$(mic) is the chemical potential of pure micellar surfactant and $\mu_X^0$(aq) is the reference chemical potential of surfactant X in an ideal solution having unit concentration at the same $T$ and $p$. [Here $R$ is the gas constant and $c_r = 1$ mol dm$^{-3}$.]

Thus

$$\mu_X^0(\text{aq}) + RT\ \ln(\text{c.m.c.}/c_r) = \mu_X^*(\text{mic}) \quad (1)$$

By definition

$$\Delta_{\text{mic}}G_X^0 = \mu_X^*(\text{mic}) - \mu_X^0(\text{aq}) \quad (2)$$

Here $\Delta_{\text{mic}}G_X^0$ is the increase in chemical potential when one mole of surfactant transfers from the ideal aqueous solution at unit concentration to the pure micellar phase.

Hence, from eqn. (1) and (2),

$$\Delta_{\text{mic}}G_X^0 = RT\ \ln(\text{c.m.c.}/c_r) \quad (3)$$

In analogous form the enthalpy of formation of the micellar phase can be expressed as follows.

$$\Delta_{\text{mic}}H_X^0 = H_X^*(\text{mic}) - H_X^0(\text{aq}) \quad (4)$$

The contribution to the enthalpy of each injected aliquot, $H$(inj) is given therefore by eqn. (5) where $V$(inj) is the volume of each injected aliquot and $n_X^0$(inj) is the amount of surfactant in each aliquot.

$$H(\text{inj}) = V(\text{inj})\text{c.m.c.}H_X^0(\text{aq}) + [n_X^0(\text{inj}) - V(\text{inj})\text{c.m.c.}]H_X^*(\text{mic}) \quad (5)$$

At low injection number $I$, the micelles break up to form monomers X(aq). At injection number $I$, the total amount of surfactant in the sample cell equals [$In_X^0$(inj)], having enthalpy [$In_X^0$(inj)$H_X^0$(aq)]. Similarly at injection number ($I$ + 1), the corresponding enthalpy is given by [($I$ + 1)$n_X^0$(inj)/$H_X^0$(aq)]. At injection number ($I$ + 1) the calorimeter records heat $q$($I$ + 1) [= $H$($I$ + 1) − $H$($I$) − $H$(inj)]. The ratio [$n_X^0$(inj)/$V$(inj)] equals the concentration of surfactant in the injected aliquot, $c_X^0$(inj). From eqn. (4) and (5), the ratio [$q/n_X^0$(inj)] at injection number ($I$ + 1) is given by eqn. (6).

$$\{[q/n_X^0(\text{inj})] \text{ at } (I+1)\} = -\Delta_{\text{mic}}H_X^0 + [\text{c.m.c.}/c_X^0(\text{inj})]\Delta_{\text{mic}}H_X^0 \quad (6)$$

Under normal operational conditions [c.m.c./$c_X^0$(inj)] is of the order 0.1 so that the main contribution to {[$q/n_X^0$(inj)] at ($I$ + 1)} is $\Delta_{\text{mic}}H_X^0$ such that if micelle formation is exothermic, for example, {[$q/n_X^0$(inj)] at ($I$ + 1)} is positive and constant over the first series of injections. At some stage the concentration of surfactant in the sample cell exceeds the c.m.c. such that at injection number ($I$ + 1) and $I$ the contributions of the surfactant to the enthalpies of the sample cell are given by: (i) $V$(sc)c.m.c.$H_X^0$(aq) + [($I$ + 1)$n_X^0$(inj) − $V$(sc)c.m.c.)]$H_X^*$(mic), and (ii) $V$(sc)c.m.c.$H_X^0$(aq) + [$In_X^0$(inj) − $V$(sc)c.m.c.)]$H_X^*$(mic), respectively, where $V$(sc) is the volume of the sample cell. Then following the argument described above the ratio [$q/n_X^0$(inj)] at a high injection number is given by eqn. (7).

$$\{[q/n_X^0(\text{inj})] \text{ at } (I+1)\} = [\text{c.m.c.}/c_X^0(\text{inj})]\Delta_{\text{mic}}H_X^0 \quad (7)$$

Then the difference between [$q/n_X^0$(inj)] at low ($I$ + 1) and high ($I$ + 1) yields the required estimate for $\Delta_{\text{mic}}H_X^0$. The pattern anticipated for enthalpograms characterising surfactant systems having ideal thermodynamic properties is a sharp step in [$q/n_X^0$(inj)] at the point where the concentration of surfactant in the sample cell exceeds the c.m.c.

Thus,

$$\{[q/n_X^0(\text{inj})] \text{ at low } (I+1)\} - \{[q/n_X^0(\text{inj})] \text{ at high } (I+1)\} = -\Delta_{\text{mic}}H_X^0 \quad (8)$$

It is important in this analysis to note the emphasis on 'differences'; *e.g.* eqn. (8). The ratio [$q/n_X^0$(inj)] is a ratio of two extensive variables. Then, for example, [$q/n_X^0$(inj)] at a low injection number for a given aqueous solution is constant. Then the difference given by eqn. (8) yields a molar intensive property. The resulting idealised titration calorimetric plot for this type of investigation forms a sharp step at the c.m.c.; see Fig. 4 in ref. 1. In the next section we show that the corresponding plots for the systems described here differ considerably from such an idealised plot.

## Results

The analysis described in the previous section leading to eqn. (8) predicts that enthalpograms recorded using different amounts of surfactants in the injected aliquot lead directly to estimates of c.m.c. and $\Delta_{\text{mic}}H_X^0$. Significantly, the enthalpograms recorded for experiments using different concentrations in the injected aliquots should be superimposable if the underlying model for micelle deaggregation is correct. In fact the general pattern of enthalpograms for a set of related nonionic surfactants turns out to be quite different.

In the examples shown for $C_{12}E_5$ in Fig. 1, [$q/n_X^0$(inj)] is strongly exothermic at low injection numbers, becoming less exothermic with increase in surfactant concentration in the injected aliquots. Significantly, even at high injection numbers, [$q/n_X^0$(inj)] is strongly exothermic whereas the model described in the previous section anticipates that [$q/n_X^0$(inj)] would be essentially zero. Titration plots were reproducible for the same system as judged by [$q/n_X^0$(inj)] at low injection numbers. Similar plots were recorded for related surfactants where

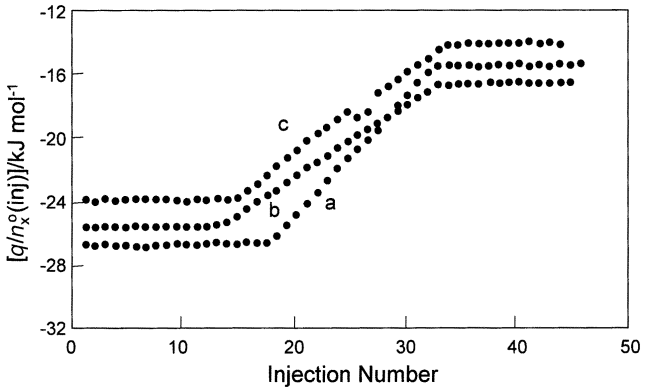


**Fig. 1** Three enthalpograms for alkylpolyoxyethylene glycol ethers, $C_{12}H_{25}(OCH_2CH_2)_5OH$ in aqueous solutions where the concentration of surfactant in the injected aliquot are (a) 5, (b) 6 and (c) $7 \times 10^{-4}$ mol dm$^{-3}$.

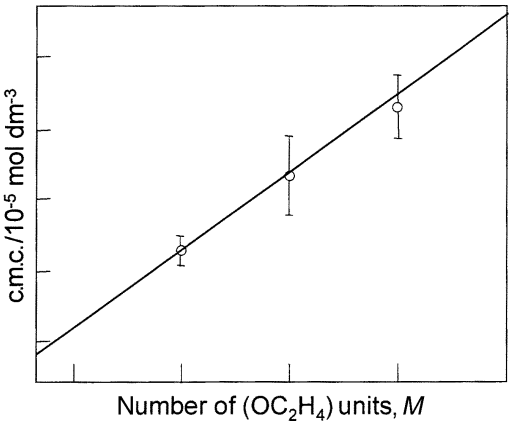


**Fig. 3** Dependence of c.m.c. on $m$ for $C_{12}H_{25}(OCH_2CH_2)_mOH$ in aqueous solution.

$m = 3$ and 4. Each enthalpogram was used to construct van Os plots[10] in which $\sum_{j=1}^{j=I}[q/n_x^0(\text{inj})]$ is plotted as a function of injection number $I$. As shown by the typical example in Fig. 2, the calculated points form two straight lines which intersect at the c.m.c.; Table 1. The estimated c.m.c.'s are in good agreement with those reported previously[6] and indicate a linear dependence on the integer $m$; Fig. 3.

Nevertheless, the change in overall pattern for each system with change in concentration of surfactant in the injected aliquot meant that it was not possible to obtain satisfactory estimates of the enthalpies of micelle formation. Ref. 6 [see Table 11.1.8] reports endothermic enthalpies ranging from 5.9 kJ mol$^{-1}$ for $C_{12}E_3$ to 13.5 kJ mol$^{-1}$ for $C_{12}E_5$. This range covers the ranges estimated from the enthalpograms reported here but we hesitate to be more specific.

Previously[3] we showed that the enthalpograms for the surfactant, CTAB follow the classic pattern described in the previous section. However the enthalpograms for the structurally related OTAB, Fig. 4, resemble those for the nonionics, as shown in Fig. 1. The difference is that over the first few injections $[q/n_x^0(\text{inj})]$ is endothermic, which suggests that micelle formation for OTAB, as for CTAB, is exothermic. However the enthalpograms are not superimposable. Comparison of the titration calorimetric plots for OTAB(aq) at different concentrations in the injected aliquots shows that the recorded $[q/n_x^0(\text{inj})]$ at the same low injection number (*e.g.* $I = 10$ in Fig. 4) changes sign. If the properties of OTAB(aq) resembled those of CTAB(aq), both the sign and magnitude of $[q/n_x^0(\text{inj})]$ would have been effectively constant.[1] The change in the nature of the titration plots shows the remarkable impact of adding a methylene group to the alkyl chain in CTAB to form OTAB. Nevertheless the van Os plots provided satisfactory estimates of the c.m.c. for OTAB: Table 1.

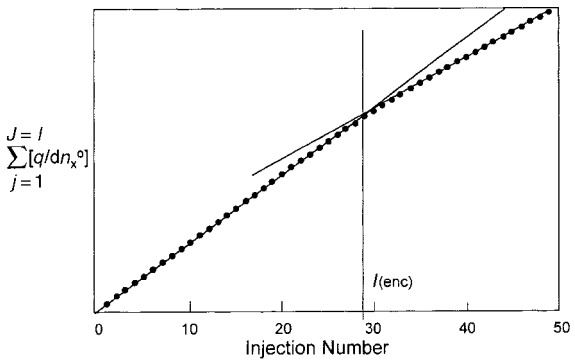


**Fig. 2** Van Os plot calculated from the enthalpogram for $C_{12}H_{25}(OCH_2CH_2)_4OH$ in aqueous solution ($4 \times 10^{-4}$ mol dm$^{-3}$).

## Discussion

The recorded enthalpograms for the nonionic surfactants $C_{12}H_{25}(OCH_2CH_2)_mOH$ where $m = 3$, 4 or 5 ( and OTAB) confirm the complexities previously reported by Olofsson.[7] In

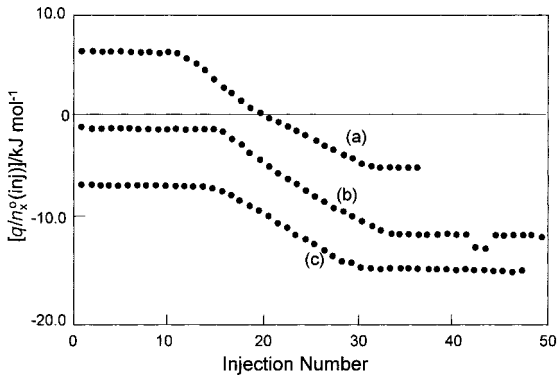


**Fig. 4** Three enthalpograms for aqueous solutions of OTAB at concentrations (a) $2.0 \times 10^{-3}$ (b) $1.0 \times 10^{-3}$ and (c) $0.8 \times 10^{-3}$ mol dm$^{-3}$.

**Table 1** Critical micellar concentrations for four surfactants in aqueous solutions at 298.2 K

| Surfactant[a] | Concentration of injected aliquots[b]/$10^{-4}$ mol dm$^{-3}$ | c.m.c./$10^{-5}$ mol dm$^{-3}$ | | |
|---|---|---|---|---|
| | | Expt. | Literature | |
| $C_{12}E_3$ | 3.0–6.0 | $3.25 \pm 0.22$ | 5.5[c] | 5.2[e] |
| $C_{12}E_4$ | 3.0–6.0 | $4.31 \pm 0.55$ | 4.6[c] | 6.4[e] |
| $C_{12}E_5$ | 5.0–8.0 | $5.26 \pm 0.45$ | 5.78[c] | 6.4[e] |
| OCTAB | 8.0–30 | $11.7 \pm 2.8$ | 29.2[d] | — |

[a] $m = 3$, 4 and 5 for $C_{12}E_m$; $C_{12}H_{25}(OCH_2CH_2)OH$. [b] For each system 12 enthalpograms were recorded. [c] From ref. 6. [d] At 30 and 40 °C. [e] From ref. 11 using Wilhelmy plate technique to measure surface tensions.

other words the results can be understood in terms of extensive clustering of surfactant micelles above the c.m.c. for each surfactant. Because the concentration of surfactant in the injected aliquot is significantly above the c.m.c. (as required by the technique), the extent of clustering is a function of the concentration. Nevertheless, over the first few injections at the start of an experiment, the solution in the sample cell of the calorimeter comprises monomeric solutes. Beyond the c.m.c., complexities arising from clustering mean that the difference $\{[q/n_X^0(\text{inj})]$ at low $(I+1)\} - \{[q/n_X^0(\text{inj})]$ at high $(I+1)\}$ does not yield directly the enthalpy of micelle formation. Nevertheless the van Os plots highlight the changeover from below to above the c.m.c. and hence yield directly the c.m.c. at the point where micelles and higher clusters appear, the derived values being in reasonable agreement with previous reported values; Table 1. The higher clusters are probably in the form of a multi-lamellar phase, taking account of the clouding points discussed above.

In conclusion, we have shown how the sensitivity of a modern titration microcalorimeter highlights the complexity of apparently simple nonionic surfactants. The disadvantage, common to most calorimetric studies, is that calorimetry does not readily yield detailed molecular models for such complex systems.

The dramatic difference in the enthalpograms for CTAB and OTAB highlights the impact of one more methylene group in the extended alkyl chain. Thus for the series $RN^+Me_3\ Br^-$ where $R < C_{16}H_{33}$ the c.m.c. decreases and $\Delta_{mic}H^0$ becomes more exothermic with increase in length of the alkyl chain.[3] Up to CTAB, the overall characteristics of the surfactants are dominated by the polar–$N^+Me_3$ head groups and bromide counterions. Clearly introduction of one more $CH_2$ group produces surfactants for which other effects start to play an important role and the polar groups play a secondary role. Again, large clusters may take the form of vesicles in bilayer structures.

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