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Classification of calorimetric titration plots for alkyltrimethylammonium and alkylpyridinium cationic surfactants in aqueous solutions

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Calorimetric titration plots for deaggregation of micelles formed by alkylpyridinium and alkyltrimethylammonium surfactants are classified into three types, A, B and C, depending on the shape of the plot of the enthalpy of dilution as a function of surfactant concentration. For Type A plots the recorded heat of injection q changes sharply between two parts of the titration curve over which the recorded heats are effectively independent of the composition of the solution in the sample cell. For Type B plots, the change is less sharp and both parts of the plot show dependences of heat q on solution composition, a pattern accounted for in terms of solute–solute interactions. Type C plots are complicated, in that no sharp change in q is recorded, the complexity of the plots being accounted for in terms of micelle–monomer equilibria over a range of surfactant concentrations and related enthalpies of deaggregation.

In the application of titration calorimetry towards understanding the properties of ionic surfactants in aqueous solution,[1–3] small aliquots (*e.g.* 5×10^{-9} m^3) of a solution containing a surfactant at a concentration greater than the critical (spherical) micellar concentration (c.m.c.) but lower than the critical rod-like (or worm-like) micellar concentration (c.r.c.) are injected into a sample cell (*e.g.* volume 1.411×10^{-6} m^3). Initially, the sample cell contains water and so the calorimeter senses the heat q accompanying micelle deaggregation. With increase in the number of aliquots injected into the sample cell, so the concentration of surfactant in this cell increases and eventually exceeds the c.m.c. The heat accompanying subsequent injected aliquots is associated with dilution of micelles into a micellar solution. A plot of heat q against concentration of surfactant in the sample cell shows a sharp step at the c.m.c. The titration calorimetric technique yields, therefore, in principle, both the limiting enthalpy of micelle formation $\Delta_{mic}H_m^{\infty}$ expressed in terms of a mole of monomer and the c.m.c. at defined temperature. Both the c.m.c. and $\Delta_{mic}H^{\infty}$ are important variables in the sense of identifying the possible factors in determining the driving force for micelle formation/monomer aggregation and deciding between proposed structures for micelles in aqueous solution; *e.g.* the classic Hartley model[4,5] and the more open Menger model.[6] In both cases, the core of a micelle is hydrophobic, head-group repulsion being reduced by counterions which accumulate between the charged head-groups.[7]

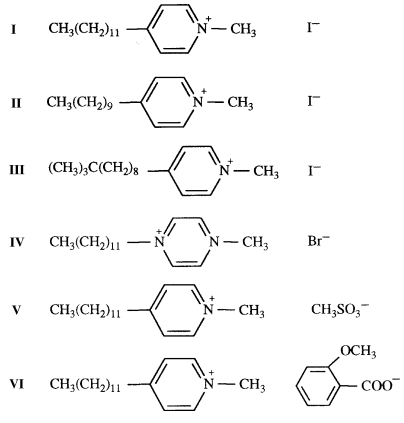
In the above, we used the words, in principle, because, in practice, a plot of heat q against the composition of the solution in the sample cell for a given surfactant does not always conform to the simple pattern described above.[3] Previously,[3] we accounted for the shape of the titration plots recorded for alkyltrimethylammonium bromides ($RN^+Me_3Br^-$ where R = $C_{16}H_{33}$, $C_{14}H_{29}$, $C_{12}H_{25}$ and $C_{10}H_{21}$) in terms of the dependences on solution composition of the activity coefficients for both the simple 1 : 1 salts $RN^+Me_3Br^-$ and the micelles, the latter being modelled as a macrosalt characterised by aggregation number N and the extent of counterion binding.[8]

An extensive study of the calorimetric titration curves produced by two groups of surfactants, alkyltrimethylammonium bromides and alkylpyridinium salts shows that the patterns which emerge can be classified into Types A, and B and C. Type A conforms to the textbook pattern discussed above, *e.g.* $C_{16}H_{33}$ $N^+Me_3Br^-$[= CTAB]. In cases classified as Type B, the solutions are sufficiently concentrated and the enthalpy of micelle formation sufficiently small that solute–solute interactions play a crucial role in determining the measured heat of injection. Calculations using a simple model for surfactant aggregation confirm the latter conclusion. The most complicated plots are classified as Type C where similar calculations show that aggregation to form micelles occurs over a range of surfactant concentrations.

Experimental

Materials

The surfactants were either purchased or synthesised as previously described.[2,3]



Scheme

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Calorimetry

Two titration microcalorimeters of the same design (MicroCal Ltd.) were used.[2,3] A computer-controlled syringe injected aliquots of an aqueous solution, volume (5–10) $\times 10^{-9}$ m^3, containing surfactant at a concentration typically 20 times the c.m.c. These aliquots were injected into a sample cell. The volume of the sample cell in the calorimeter at the University of Leicester was 1.411×10^{-6} m^3 whereas the volume of the sample cell at the University of Groningen was 1.3249×10^{-6} m^3. A reference cell having a similar volume was filled with water. The sample and reference cells were very slowly heated, the control system maintaining a constant small temperature difference between the two cells. Following injection, each recorded rate of heating was integrated to yield a plot showing the dependence of heat of injection q on either injection number or composition of the solution in the sample cell. The ratio of heat q to amount of surfactant injected yielded the enthalpy of injection per mole of surfactant, $\Delta_{inj}H$.

Analysis

As commented in the introductory section, the calorimetric titration curves for ionic surfactants can be sub-divided into three types, A, B and C. We describe these in the following section. In this section we describe attempts to model the titration curves with the aim of understanding the phenomena which produce the three types. Here the emphasis is on patterns rather than attempts to reproduce the recorded heats of injection. We use approaches which build on two treatments of micelle formation:[9–11] (i) the pseudo-phase equilibrium model and (ii) the closed association model. We also consider a modification of the pseudo-phase equilibrium model, in which clustering of monomers to form micelles occurs over a range of surfactant concentrations.

Using the pseudo-phase equilibrium model we consider the impact of adding a small amount of surfactant X, δn^0_X to the sample cell producing a solution having concentration c^0_X where $c^0_X = k\delta n^0_X/V_R$ at injection number k into the sample cell, volume V_R. At a characteristic concentration, c.m.c., further added surfactant clusters form micelles, such that the concentration of monomers present as micelles equals [c^0_X − c.m.c.]. At all concentrations above the c.m.c. the concentration of non-aggregated monomers was assumed to be constant at a given c.m.c.

Using the closed association model,[9] when the concentration c^0_X exceeds the c.m.c., a chemical equilibrium is established between monomers and micelles: eqn. (I) where N is the aggregation number.

$$N\mathrm{X(aq)} \rightleftharpoons \mathrm{X}_N\mathrm{(aq)} \qquad \text{(I)}$$

For both models there are three important parameters in the context of calorimetric titrations: (i) aggregation number N; (ii) limiting enthalpy of micelle formation expressed in terms of one mole of monomer, $\Delta_{mic}H^\infty_m$; and (iii) the c.m.c.

We also examine the impact of solute–solute interactions in the aqueous solutions forming the injected aliquot from the syringe[2,3] and in the aqueous solution in the sample cell. Here, the key considerations centre on the extent to which the partial molar enthalpies of both micelles and monomers deviate from the corresponding limiting partial molar enthalpies, H^∞ (mic; aq) and H^∞ (mon; aq), respectively. Although, in general terms, compensation between entropic and enthalpic contributions often result in modest effects on the position of a chemical equilibrium as a consequence of solute–solute interactions, the latter play an important role in determining enthalpies and, hence, heats of deaggregation. Consequently, in order to calculate the composition of the sample cell following each injection of an aliquot, using eqn. (I) we assumed that the properties of the solutes are ideal. However, in calculating the corresponding heats, we took account of the possible effects of solute–solute interactions.

Pairwise solute–solute interactions

On the basis of pairwise solute–solute interactions,[12] the excess Gibbs energy of an aqueous solution at fixed temperature and pressure prepared using 1 kg of water is given by

$$G^E = [g_{jj}m_j^2 + 2g_{ij}m_i m_j + g_{ii}m_i^2](m^0)^{-2} \qquad (1)$$

Here g_{jj}, g_{ij} and g_{ii} are pairwise Gibbs energy interaction parameters for solutes i and j in an aqueous solution of molalities m_i and m_j. Taking, as example, solute j, the chemical potential of solute j in aqueous solution at molality m_j is given by eqn. (2) where the activity coefficient γ_j is defined such that at all T and p, limit ($m_i \to 0$; $m_j \to 0$) $\gamma_j = 1.0$.

$$\mu_j\mathrm{(aq)} = \mu^0_j\mathrm{(aq)} + RT\ \ln(m_j\gamma_j/m^0) \qquad (2)$$

Here μ^0_j (aq) is the chemical potential of solute j in an ideal solution where $m_j = m^0 = 1$ mol kg^{-1} and $\gamma_j = 1.0$. The activity coefficient γ_j is related[12] to G^E

$$\ln\ \gamma_j = [2/RT][g_{jj}m_j + g_{ij}m_i](m^0)^{-2} \qquad (3)$$

Application of the Gibbs–Helmholtz equation to eqn. (2) using eqn. (3) yields eqn. (4) where h_{ij} and h_{jj} are pairwise enthalpic interaction parameters characteristic of solutes i and j.

$$H_j\mathrm{(aq)} = H^\infty_j\mathrm{(aq)} + 2[h_{jj}m_j + h_{ij}m_i](m^0)^{-2} \qquad (4)$$

In the analysis described below, we concentrate attention on the homotactic term,[13] h_{jj}, so that the heterotactic terms h_{ij} are assumed to be zero. In a real solution the enthalpy of micelle formation described by eqn. (I) is given by

$$\Delta_{mic}H\mathrm{(aq)} = H(\mathrm{X}_N\ ;\ \mathrm{aq}) - NH(\mathrm{X};\ \mathrm{aq}) \qquad (5)$$

Then, using eqn. (4)

$$\Delta_{mic}H\mathrm{(aq)} = [H^\infty(\mathrm{X}_N\ ;\ \mathrm{aq}) + 2h_{mic-mic}m_{mic}(m^0)^{-2}] - N[H^\infty(\mathrm{X};\ \mathrm{aq}) + 2h_{mon-mon}m_{mon}(m^0)^{-2}] \qquad (6)$$

Here subscript 'mic' refers to the micellar solute and subscript 'mon' refers to the monomeric solute. The equation corresponding to eqn. (4) but using apparent molar enthalpies $\phi(H_j)$ has the following form.

$$\phi(H_j) = H^\infty_j\mathrm{(aq)} + h_{jj}m_j(m^0)^{-2} \qquad (7)$$

Calorimetry

The enthalpy of a solution prepared using n_1 moles of water and n^0_X moles of surfactant X is given by eqn. (8) where ξ measures the extent of surfactant aggregation and where N is the aggregation number (at fixed temperature and pressure).

$$H\mathrm{(aq)} = n_1 H^*_1\mathrm{(l)} + (n^0_X - N\xi)\phi(H_{mon}) + \xi\phi(H_{mic}) \qquad (8)$$

Here $\phi(H_{mon})$ and $\phi(H_{mic})$ are the apparent molar enthalpies of monomers and micelles in solution having compositions characterised by n^0_X and ξ. H^*_1(l) is the molar enthalpy of pure water, substance 1. In the titration experiment the total amount of surfactant in the sample cell at injection number k equals kn^0_X and the extent of aggregation equals $\xi^{(k)}$. In each aliquot, the extent of chemical reaction is given by $\xi^{(l)}$. The change in enthalpy $\Delta H^{(k)}$ at injection number k is given

$$\Delta H^{(k)} = H(\mathrm{aq};\ k) - H(\mathrm{aq};\ k-1) - H(\mathrm{aq};\ \mathrm{aliquot}) \qquad (9)$$

At injection ($k - 1$), the amount of water in the sample cell is $n_1^{(k-1)}$ whereas at injection k, the amount of water equals $n_1^{(k)}$; the amount of water in the injected aliquot in $n_1^{(l)}$ such that

$n_1^{(k)} = [n_1^{(k-1)} + n_1^{(I)}]$. Eqn. (8) is used to describe, in turn, the three enthalpies introduced in eqn. (9).
Hence

$$\begin{aligned}\Delta H^{(k)} &= q^{(k)} \\ &= \xi^{(k)}\phi(H_{mic}\,;\,\text{cell};\,\xi^{(k)}) \\ &\quad + [kn_X^0 - N\xi^{(k)}]\phi(H_{mon}\,;\,\text{cell};\,\xi^{(k)}) \\ &\quad - \xi^{(k-1)}\phi(H_{mic}\,;\,\text{cell};\,\xi^{(k-1)}) \\ &\quad - [(k-1)n_X^0 - N\xi^{(k-1)}]\phi(H_{mon}\,;\,\text{cell};\,\xi^{(k-1)}) \\ &\quad - \xi^{(I)}\phi(H_{mic}\,;\,I;\,\xi^{(I)}) \\ &\quad - [n_X^0 - N\xi^{(1)}]\phi(H_{mon}\,;\,I;\,\xi^{(I)}) \end{aligned} \quad (10)$$

Here $\phi(H_{mic}\,;\,\text{cell};\,\xi^{(k)})$ and $\phi(H_{mon}\,;\,\text{cell};\,\xi^{(k)})$ are the apparent molar enthalpies of micelle and monomer in the sample cell where the extent of aggregation is represented by $\xi^{(k)}$. Similarly, $\phi(H_{mic}\,;\,\text{cell};\,\xi^{(k-1)})$ and $\phi(H_{mon}\,;\,\text{cell};\,\xi^{(k-1)})$ are the corresponding apparent molar enthalpies at extent of aggregation $\xi^{(k-1)}$ at injection number $(k-1)$ whereas the description $\xi^{(I)}$ refers to the composition of each aliquot injected. Where the concentration of surfactant in the sample cell (*i.e.* $c_X = n_X^0/V_R$) is less than the c.m.c. at both injections k and $(k-1)$, $\xi^{(k)}$ and $\xi^{(k-1)}$ are zero. In order to predict the pattern of the dependence of $q^{(k)}$ on injection number k a description is required of the aggregation process in order to calculate $\xi^{(k)}$, $\xi^{(k-1)}$ and $\xi^{(I)}$; eqn. (10). Using these estimates eqn. (7) is used to calculate, from the appropriate molalities, the corresponding apparent molar enthalpies of both micelles and monomers in the three solutions. The latter calculation requires estimates of the pairwise enthalpic interaction parameters as set out below. Calculation of $q^{(k)}$ also requires an estimate of the limiting enthalpy of micelle formation, $\Delta_{mic}H^{\infty}(aq)$ as described below. Eqn. (10) can then be used to calculate the ratio $[q^{(k)}/n_X^0]$, the heat produced per mole of surfactant injected into the sample cell. The remaining key required quantities are $\xi^{(k)}$, $\xi^{(k-1)}$ and $\xi^{(I)}$ and these depend on the model used.

Closed association model

With reference to eqn. (I) applied to a solution having volume V and prepared using n_X^0 moles of surfactant X, the equilibrium amount of micelle is ξ and the equilibrium amount of monomer equals $[n_X^0 - N\ \xi]$ where N is the aggregation number. Then, for an ideal solution, the equilibrium constant K is given by

$$K = \xi V^{(N-1)}/[n_X^0 - N\xi]^N \quad (11)$$

Thus, for known K, V and aggregation number, eqn. (11) can, in principle, be solved to yield the extent of aggregation ξ. Unfortunately, for high aggregation numbers the arithmetic solution can only be obtained iteratively. In the study reported here eqn. (11) was re-expressed in logarithmic form.

$$\ln(\xi) + (N-1)\ln(V) = \ln(K) + N\ln[n_X^0 - N\xi] \quad (12)$$

A computer program (TURBO BASIC) was written which calculated the left- and right-hand sides of the equation as ξ is very gradually incremented. The required ξ corresponded to the point where the calculated difference between the right- and left-hand sides was zero. This calculation was used to obtain the equilibrium composition of the injected aliquots, $\xi^{(I)}$, in a solution having volume $V^{(I)}$. Similarly, the calculation was used to obtain the compositions of the sample cell $\xi^{(k)}$ and $\xi^{(k-1)}$ at injection numbers k and $(k-1)$. These extents of aggregation were used to calculate the corresponding concentrations and molalities of both monomer X(aq) and aggregate X_N(aq). (The assumption was made that the densities of the solutions were equal to the density of water at the same T and p.) Combination of eqn. (7) and (10) yielded an estimate of heat $q^{(k)}$ and $[q^{(k)}/n_X^0]$ at injection number k.

Pseudo-phase equilibrium

The analysis underlying this model is simpler than that based on the closed association model. For a solution having volume V containing n_X^0 moles of surfactant, the total concentration of surfactant c_X^0 is given by $[n_X^0/V]$. The c.m.c. is the concentration of monomeric surfactant X such that the concentration of monomers in the form of aggregates is given by $[(n_X^0/V) - \text{c.m.c.}]$. Then, for example, in the sample cell the amount of monomeric surfactant at injection k is given by (c.m.c. V_R) whereas the amount of aggregate is given by $\{[(k\ n_X^0/V_R) - \text{c.m.c.}]\ V_R\}$. Similar terms describe the composition of the sample cell at injection $(k-1)$ and the composition of each aliquot injected into the sample cell. In the calculations described below we assumed that both monomeric surfactants and micellar aggregates are ideal solutes. Then the heat $q^{(k)}$ at injection k is given by eqn. (14) (*cf.* eqn. (10).

$$\begin{aligned} q^{(k)} &= \{[(kn_X^0/V^{(R)}) - \text{c.m.c.}^{(k)}]V^{(R)}\}\phi^{\infty}(H_{mic}) \\ &\quad + [\text{c.m.c.}^{(k)}V_R]\phi^{\infty}(H_{mon}) \\ &\quad - \{[k-1)n_X^0/V^{(R)}] - \text{c.m.c.}^{(k-1)}\}V^{(R)}\phi^{\infty}(H_{mic}) \\ &\quad - [\text{c.m.c.}^{(k-1)}V^{(R)}]\phi^{\infty}(H_{mon}) \\ &\quad - \{[(n_X^0/V^{(I)}) - \text{c.m.c.}^{(I)}]V^{(I)}\phi^{\infty}(H_{mic}) \\ &\quad - [\text{c.m.c.}^{(1)}V^{(I)}]\phi^{\infty}(H_{mon}) \end{aligned} \quad (13)$$

Results

The analysis described above forms the backdrop to a consideration of the general characteristics for plots of measured $q^{(k)}$ against injection number k for a range of ionic surfactants. It is convenient to describe these plots as enthalpograms.

Type A enthalpograms

This type of enthalpogram is shown by, for example, *n*-hexadecyltrimethylammonium bromide in aqueous solution at 298.2 K and 4-*n*-dodecyl-1-methylpyridinium iodide (**I**) in aqueous solution at 303.2 K. The c.m.c.s are readily estimated by plotting $\Sigma q^{(k)}$ against concentration of surfactant in the sample cell. The points generate two straight lines which intersect at the c.m.c., a van Os plot.[14] The calculated c.m.c. is in good agreement with literature[15] and previously reported[3] estimates.

In this application, eqn. (10) was applied when the concentration of surfactant, $[kn_X^0/V_R]$ in the sample cell exceeds the c.m.c. In the limit of high injection number, $\xi^{(k)} = kn_X^0/N$, $\xi^{(k-1)} = (k-1)\ n_X^0/N$ and $\xi^{(I)} = n_X^0/N$. In the same limit, the apparent molar enthalpies of the micellar aggregates in the three solutions are approximately equal. Hence, the heat of injection approaches zero. Below the c.m.c. where the extents of aggregation $\xi^{(k)}$ and $\xi^{(k-1)}$ in the sample cell are zero, the heat of injection is given by

$$\begin{aligned} q^{(k)} &= kn_X^0\,\phi(H_{mon}\,;\,\text{cell};\,k) - (k-1)n_X^0\,\phi(H_{mon}\,;\,\text{cell};\,k-1) \\ &\quad - (n_X^0/N)\phi(H_{mic}\,;\,I) \end{aligned} \quad (14)$$

With reference to eqn. (14) we have also assumed that all the surfactant in the injected aliquot is in the aggregated form. If the solution in the sample cell is sufficiently dilute that $\phi(H_{mon}\,;\,\text{cell};\,k)$ equals $\phi(H_{mon}\,;\,\text{cell};\,k-1)$ which then equals $\phi^{\infty}(H_{mon})$ then $q^{(k)}$ is given by

$$q^{(k)}/n_X^0 = \{\phi^{\infty}(H_{mon}) - [\phi(H_{mic}\,;\,I)/N]\} \quad (15)$$

Moreover, if the micellar solution in the syringe is ideal then $\phi(H_{mic}$; I) in eqn. (15) can be replaced by the corresponding limiting property, $\phi^{\infty}(H_{mic})$. Then, under the conditions described above $(q^{(k)}/n_X^0)$ is zero at high k and constant at low k, yielding, according to eqn. (15) the limiting enthalpy of micelle formation per monomer, eqn. (16), $\Delta_{mic}H_m^{\infty}$.

$$\Delta_{mic}H_m^{\infty} = \{\phi^{\infty}(H_{mic})/N\} - \phi^{\infty}(H_{mon}) \quad (16)$$

In other words, the quantity $(q^{(k)}/n_x^0)$ at low k equals $-\Delta_{mic}H_m^{\infty}$. Consequently, the calculated titration calorimetric curve has an abrupt change at the c.m.c. Moreover, if the limiting enthalpy of micelle formation is exothermic, the enthalpies of injection [*cf.* eqn. (15) and (16)] are endothermic. The results of a calculation based on these assumptions are summarised in Fig. 1 which shows the endothermic enthalpies of injection below the c.m.c., independent of injection number and the absence of an enthalpy of injection above the c.m.c.

The pattern shown in Fig. 1 closely resembles that previously reported[2] for CTAB ($n_X^0 = 7.77 \times 10^{-8}$ mol; $c_{inj} = 1.54 \times 10^{-2}$ mol dm^{-3}) injected into, initially, water at 298.2 K. The same pattern is observed for 4-*n*-dodecyl-1-methylpyridinium iodide in aqueous solution at 303 K, Fig. 2. In view of the nature of the surfactant, there is always the possibility that these solutes are adsorbed on the cell walls and/or accumulate at the air/water interface. If these complicating features are important in the operation of the titration calorimeter, there is the possibility that the measured enthalpies of micelle formation depend on the rate of stirring. This was shown not to be the case. The measured enthalpies $\Delta_{mic}H^{\infty}$/kJ (mol monomer)$^{-1}$ were −15.9, −16.1, −16.4 and −16.0 at stirring speeds of 200, 350, 500 and 650 rev min^{-1}. The variation is within estimated error limits in the measurement of $\Delta_{mic}H^{\infty}$ of 0.1–0.2 kJ (mol monomer)$^{-1}$. A gradual decrease in $\Delta_{mic}H^{\infty}$ was recorded when the concentration of injected aliquot was increased, *e.g.* from −16.1 to −17.1 kJ (mol monomer)$^{-1}$ when the concentration of surfactant in the injected aliquot was increased from 50.1 to 90.5 × 10^{-3} (mol monomer) dm^{-3}. As discussed below, we attribute this increase to the fact that the properties of the solutions show increasing deviations from ideal (in a thermodynamic sense) with increase in surfactant concentration.

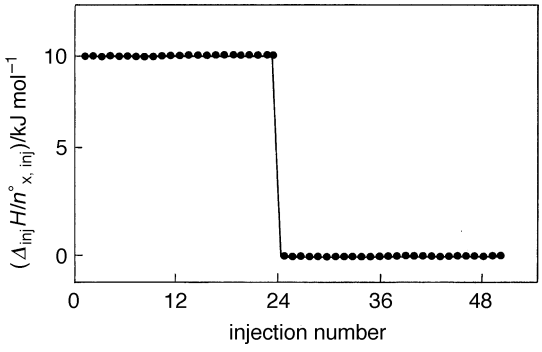

Fig. 1 Calculated dependence of enthalpy of injection per mole of monomer on injection number; input parameters are $\Delta_{mic}H^{\infty} = -10.0$ kJ mol^{-1}, c.m.c. = 1.0 mol m^{-3} and $N = 50$ where volume of sample cell = 1.4115 × 10^{-6} m^3, volume of injected aliquot = 1.0 × 10^{-9} m^3; 1 kcal ≡ 4.184 kJ

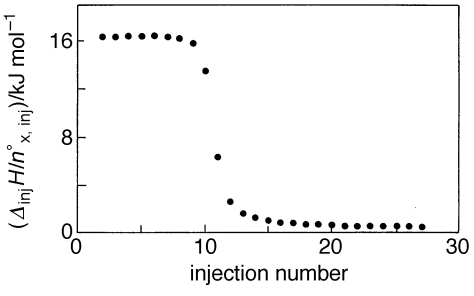

Fig. 2 Calorimetric titration curve for 4-*n*-dodecyl-1-methylpyridinium iodide (**I**), $\Delta_{mic}H^{\circ} = -16.1$ kJ (mol monomer)$^{-1}$; c.m.c. = 4.27 × 10^{-2} mol dm^{-3}

Comparison of the calculated curve in Fig. 1 and recorded titration in Fig. 2 indicates that this type of titration curve is favoured by: (i) a large standard enthalpy of micelle formation; (ii) a high aggregation number; and (iii) a low c.m.c. Conditions (i) and (ii) result in an intense pulse of heat (either exothermic or endothermic) for detection by the calorimeter.

A large $|\Delta_{mic}H^{\infty}|$ for ionic surfactants is favoured by a large N and a high degree of counterion binding such that, in the case of, for example, cationic micelles deaggregation of micelles over the first injection numbers releases bound counteranions into the solution. Condition (iii) means that the properties of the solutions in both sample cell and syringe are close to ideal. The lower the c.m.c., the greater is the tendency of the plots before and after the c.m.c. to comprise horizontal lines where the heat of injection is effectively independent of injection number. Consequently, for surfactants which produce Type A titration plots, the determination of c.m.c. and limiting enthalpy of micelle formation is reasonably straightforward. Examples include surfactants **II** and **III** where the limiting molar enthalpies of micelle formation are −12.9 and −12.6 kJ mol^{-1}, respectively. Exceptions to this statement would describe cases where micelle formation is solely entropy driven and so the calorimeter would be insensitive to changes in composition of the sample cell as the concentration changed from below to above the c.m.c. Otherwise, the c.m.c. for surfactants producing a Type A titration plot is conveniently determined using a van Os plot[14] in which the sum of $\Delta_{inj}H$ from $k = 1$ to k is plotted against the concentration of surfactant in the sample cell. The data points fall on two distinct straight lines[2] which intersect at a concentration corresponding to the c.m.c.

Type B enthalpograms

These surfactants which produce Type A injection plots offer textbook cases. Nevertheless, close examination of, for example, the titration plots[2] for CTAB(aq) shows a slight tendency for the enthalpies of injection to increase over injections below the c.m.c. This pattern is not surprising in that the same titration calorimeter can be used to probe solute–solute interactions for simple neutral solutes in dilute aqueous solutions.[16]

In general terms, the c.m.c. of ionic surfactants increase with a decrease in alkyl chain length.[10] Consequently, in order that the concentration of surfactant in the simple cell changes from below to above the c.m.c. at an injection number comparable to that shown in Fig. 2, a higher concentration of surfactant is required in each aliquot. Consequently, the properties of the solution in the syringe and, with increasing injection number, in the sample cell, cannot be assumed to be ideal. A further consequence of a decrease in alkyl chain length in the surfactant is a decrease in the $|\Delta_{mic}H^{\infty}|$ for micelle formation and so the trend is for the magnitude of the heat associated with each injection to fall.

The foregoing qualitative comments are supported by the results of a calculation based on eqn. (I), (7), (10) and (12). We have introduced an element of thermodynamic non-ideality by setting h_{jj} and h_{ii} as non-zero. The results of a typical calculation are given in Fig. 3. With increase in the enthalpic coefficients [*cf.* eqn. (7)] particularly the coefficient describing the non-ideal properties of the micelles in the injected aliquot, so the dependence of $\Delta_{inj}H/n_X^0$ on injection number below the c.m.c. becomes more marked.

Two recorded titration curves for ionic surfactants (Fig. 4) are similar to the calculated curve in Fig. 3, leading to the

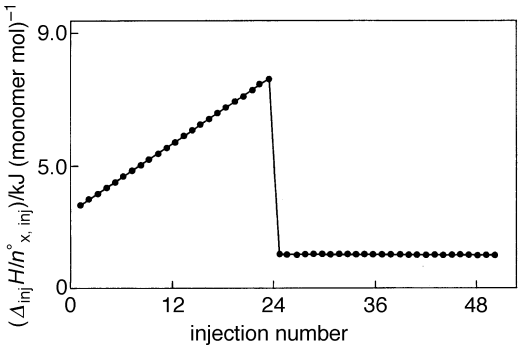

Fig. 3 Calculated titration calorimetric plot for the dependence of enthalpy of injection per mole of surfactant; $\Delta_{mic}H^{\infty} = -1.0$ kJ (mol monomer)$^{-1}$; c.m.c. = 10 (mol monomer) m^{-3}; $N = 50.0$; $h_{ii} = h_{jj} = 100$ kJ mol^{-1}

classification of such plots as Type B. The plot for tetradecyltrimethylammonium bromide (MTAB) shows a slightly steeper rise at low injection numbers than the plot for 4-dodecyl-1-methylpyridinium bromide (**IV**). Nevertheless, the change from Type A to Type B plots can be understood in terms of increasing importance of the non-ideal component of the thermodynamic properties of surfactants in solution.

Using the titration plots, the c.m.c. can be estimated using the method proposed by van Os and co-workers[14] and discussed above for Type A injection plots. The difference is that the calculated points for $\Sigma\Delta_{inj}H$ when plotted against the concentration of surfactant in the sample cell often fall on a smooth linking curve in the region of a c.m.c.

Type C enthalpograms

Comparison of the calculated (Fig. 3) and observed (Fig. 4) titration plots shows that the plots differ in the region of the c.m.c. Mehrian *et al.*[17] reported a similar endothermic extremum near the c.m.c. for 4-*n*-decylpyridinium chlorides (aq) at 318 K. The surfactant, disodium 2,2-di-*n*-octyl-1,3-propanediyl bisulfate (aq; 298 K) shows the same pattern,[18] in that the

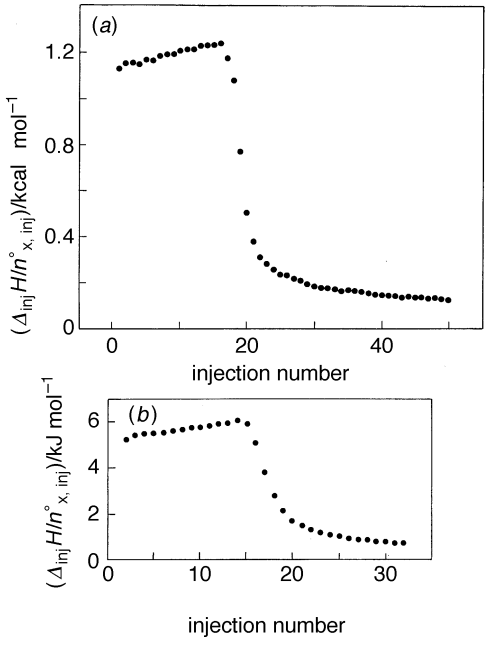

Fig. 4 Titration calorimetric plots classified as Type B: (*a*) tetradecyltrimethylammonium bromide (aq; 298.2 K); volume of aliquot = 5.0×10^{-6} dm^3, concentration = 62.6×10^{-3} (mol monomer) dm^{-3}. (*b*) 4-*n*-dodecyl-1-methylpyridinium bromide (**IV**) at 303 K; $\Delta_{mic}H^{\infty} = -5.48$ kJ (mol monomer)$^{-1}$

c.m.c. estimated from electrical conductivity data (*i.e.* 9.1×10^{-3} mol dm^{-3}) does not correspond either to the concentration in the sample cell at the maximum in $\Delta_{mic}H$ or the concentration in the sample cell corresponding to the most rapid change in $\Delta_{mic}H$ plotted as a function of injection number, *k*.

The computer program forming the basis of the pattern shown in Fig. 3 was written in such a way that, only at the point where the concentration of surfactant in the sample cell exceeds the c.m.c. is a sub-routine based on eqn. (12) used to calculate the composition of the sample cell. Therefore, a sharp change in heat of injection is anticipated at the c.m.c. The implicit assumption is, therefore, that the c.m.c. for a given surfactant (at defined *T* and *p*) is a unique and well defined concentration. In the absence of experimental information, the impact of heterodispersity of micelles[14] is difficult to judge in terms of the shape of the titration plots. Many authors (*e.g.* ref. 19) have suggested that, particularly with an increase in c.m.c. (and decrease in alkyl chain length), the c.m.c. is less sharply defined. In other words, the c.m.c. is itself dependent on surfactant concentration.

The possibility that the effective c.m.c. changes as the concentration of surfactant in the sample cell changes was explored in a modification of the computer program described above. The c.m.c. was defined as the concentration at which the surfactant started to aggregate. In one typical calculation (Fig. 5), the c.m.c. was increased gradually over the next seven injections. Consequently, the c.m.c. at injection $(k + 1)$ was higher than at injection number *k*. In other words, an element of cooperative clustering was incorporated into the calculation but, otherwise, the solutes, monomer and micelle were treated as ideal solutes. The increment[20] in c.m.c. (Fig. 5) decreased with increase in injection number. The outcome was a short range of injection numbers over which the heats of injection are more endothermic than when just monomers are present in the sample cell. Following the maximum there was a gradual decrease in calculated heat of injection, eventually reaching a constant value.

If, in addition to an incremental c.m.c., account is taken of possible non-ideal properties of both monomers and micelles, the calculated injection plots become quite complicated. Nevertheless, the possibility of complexities arising from a distribution of c.m.c. values is raised, leading to injection plots which we have classified as Type C.

Turning to experimental data, the above model accounts, in part, for the injection plots recorded for a number of ionic surfactants. In practice, the plots are more complicated than shown in Fig. 5 because of the dependences of apparent molar enthalpies of both monomers and micelles on the composition of the solution. The latter are particularly important because,

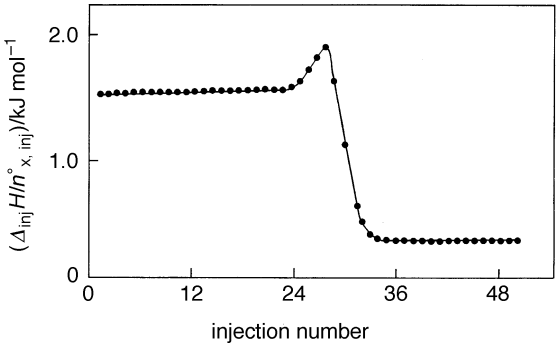

Fig. 5 Calculated titration calorimetric plot for the case where the c.m.c. for the solution in the sample cell depends on the total concentration of surfactant; $\Delta_{mic}H^{\infty} = 1.0$ kJ mol^{-1}; c.m.c. = 10.0 mol m^{-3}; $N = 50$. At injection numbers beyond the initial c.m.c., effective c.m.c.s increased by 4.5, 8.5, 12, 15, 17, 18, 18.5 and 18.7%; pseudo-phase equilibrium model.

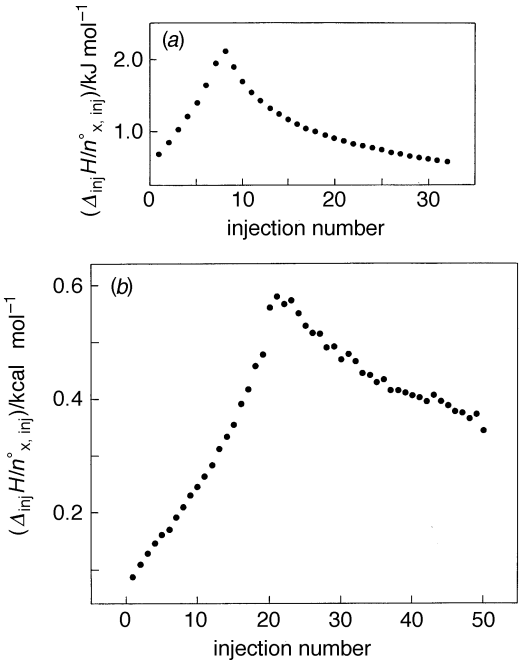

Fig. 6 Recorded titration calorimetric plots for two ionic surfactants: (*a*) d-dodecyl-1-methylpyridinium methylsulfonate in aqueous solution at 303 K. Estimated $|\Delta_{mic}H^{\circ}/n^{\circ}_{x_{inj}}| = -1.8$ kJ mol; maximum in heat of injection at 8.8×10^{-3} (mol monomer) dm^{-3}. (*b*) Decyltrimethylammonium bromide (aq) (**V**) at 298.2 K; volume of injected aliquot = 5×10^{-6} dm^3 having concentration 1.0 mol dm^{-3}.

for surfactants classified as Type C, the alkyl chain lengths are shorter and hence the c.m.c. values are higher. Consequently, concentrated solutions are used in the titration experiments. Moreover, $|\Delta_{mic}H^{\infty}|$ for micelle formation is smaller and hence the contribution from the non-ideal properties to the measured heat of injection is more significant than for Type A and Type B systems. The two examples shown in Fig. 6 are typical of Type C systems.

A Type C injection plot does not readily yield a satisfactory estimate of an effective c.m.c. Typical van Os plots (see above) have complex shapes. A rough estimate of a c.m.c. is possible by calculating the concentration of surfactant in the sample cell at the maximum in the heat of injection but this method is unsatisfactory. The maximum arises because the overall shape is a consequence of both micelle deaggregation during the injection process and the non-ideal thermodynamic properties of the solutions.

Discussion

The fact that solute–solute interactions play an important role in titration calorimetric studies of ionic surfactants is not surprising. Nevertheless, the identification of three types of plots pinpoints those important features which determine the patterns that emerge. The two key considerations centre on the magnitude of the limiting enthalpy of micelle formation and the c.m.c. With increase in c.m.c., the technique requires the use of more concentrated solutions. As a consequence the role of solute–solute interactions and their dependence on solute concentration becomes increasingly important. In some cases, it may be possible to overcome this concentration dependence by using a relatively high concentration of added salt in combination with a strong endo- or exothermicity of micelle formation. In the case of **IV** at 303 K, the curve type changes from Type B to Type A when the concentration of NaBr is increased to 0.1 mol dm^{-3}; (i) [NaBr] = 0, c.m.c. = 10.8×10^{-3} (mol monomer) dm^{-3} and $\Delta_{mic}H^{\infty} = -5.2$ kJ (mol monomer)$^{-1}$ and (ii) [NaBr] = 0.1 mol dm^{-3}, c.m.c. = 2.2×10^{-3} (mol monomer) dm^{-3} and $\Delta_{mic}H = -6.0$ kJ (mol monomer)$^{-1}$. Similarly, for surfactant **V** the titration curve changes from Type C at 303 K through Type B at 313 and 323 K to borderline Type A/B at 333 K. For this surfactant the change in curve type is a consequence of an increase in the exothermicity of micelle formation estimated as -1.8 at 303 K and -16.1 kJ (mol monomer)$^{-1}$ at 333 K. In the case of surfactant **VI** the enthalpogram changes from Type B at 303.15 and 313.15 K to Type A at 323.15 and 333.15 K, again a consequence of a more striking limiting exothermic enthalpy of surfactant aggregation;[21] *e.g.* -15.8 kJ mol^{-1} at 303.15 and -33.7 kJ mol^{-1} at 333.15 K.

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