

## THERMOCHEMISTRY OF AQUEOUS MICELLAR SYSTEMS

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**Abstract** - Surfactants tend to aggregate above a certain concentration, called the critical micelle concentration, into large clusters or micelles. With modern calorimetric and other related techniques it is now possible to measure precisely and rapidly the thermodynamic properties of liquid systems over a wide range of concentration and temperature. An overview is given of data obtained in our laboratory for heat capacities, enthalpies, entropies and free energies of aqueous sodium decanoate, octylammonium hydrobromide, nonyl and decyltrimethylammonium bromide. The thermodynamic functions of micellization are derived and interpreted with a phase-separation model. The closely related microemulsions are also briefly discussed.

### INTRODUCTION

Micellar systems are very special types of macromolecular solutions. Amphiphilic molecules or ions tend to aggregate in solution into units which are comparable in size to biocolloids, and their properties can be studied with many of the standard techniques that are used for other types of macromolecules (1-5). They differ however in their stability. They form only above concentrations that are called critical micelle concentrations (CMC), and the aggregates, known as micelles, are in dynamic equilibrium with the singly-dispersed solute in the system. The investigation of thermodynamic properties of surfactants are primarily concerned with the study of various factors affecting this equilibrium.

The most common way of investigating the thermodynamics of micellar systems is to determine the changes in the CMC with temperature or in the presence of various additives or cosolvents. This is done through measurement of a property, such as conductance or surface tension, which shows a break in the micellization region. This approach is limited since the CMC is not always sharply defined, very high precision is required to extract the changes in heats and in heat capacities during micellization, there is no easy way of knowing if the observed changes are due to modification in properties of the singly-dispersed molecules, micellar units or both, and oversimplified models for micellization have to be used.

In the last ten years or so (6-11) we have undertaken very systematic studies of the direct measurement of thermodynamic properties of surfactants in water. Our aim was to measure all thermodynamic properties of well-characterized surfactants, over a wide range of concentration covering the pre and postmicellar regions, in order to predict the temperature and pressure dependence of various equilibrium properties and to test rigorously the main models and theories of micellization.

### EXPERIMENTAL

This paper is concerned with the thermochemical properties of aqueous surfactants. It is sufficient to mention that the heats of dilution and heat capacities per unit volume were measured with commercial versions (SODEV INC) of flow microcalorimeters that have been well-described in the literature (12-14). For heat capacities, simultaneous determination of densities are required, and these were measured with a SODEV flow densimeter (15). Finally these thermochemical data were used to calculate the temperature dependence of the activity data. The osmotic coefficients were measured by the freezing-point technique (16).

The longer the chain length of the surfactant the sharper are the changes in properties in the micellization region. Unfortunately most of our experimental techniques have a lower concentration limit of about 0.01 mol kg<sup>-1</sup> in water. This therefore limits our choice of surfactants to those having chain lengths up to a maximum of about 10 carbon atoms. The

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ionic systems that have now been well-investigated are the alkylamine hydrobromides (8,9,11), nonyl and decyltrimethylammonium bromides (7,10) and sodium decanoate (8,9). The details of the experimental procedure and experimental data are all given in the original references. The basic equations necessary to correlate all the thermodynamic functions of the surfactants are also given elsewhere (6).

#### THERMODYNAMIC FUNCTIONS

The method of extracting information of micellar systems can best be understood through an example, and for this purpose volumes are probably the easiest to visualize. The surfactant solution is considered a true solution and, from the experimental densities, the apparent molal volume  $\phi_V$  can readily be calculated as a function of the stoichiometric molality  $m$  of the solute. These data are shown for sodium decanoate (NaDEC) in Fig. 1. At low concentrations  $\phi_V$  changes in a regular fashion but, in the CMC region, increases more sharply and eventually levels off. If  $\phi_V$  are measured at fairly closely spaced concentrations, the partial molal volumes  $\bar{V}_2$  can readily be derived from a plot of  $\Delta(\phi_V m)/\Delta m$  against the mean molality as shown in Fig. 1. Much information can be extracted from these  $\bar{V}_2$ . At infinite dilution  $\bar{V}_2^0$  is a measure of the intrinsic volume of the solute or pair of ions and of all solute-solvent interactions. With most organic molecules or ions  $\bar{V}_2^0$  is lower than the molar volume  $V_2^0$  of the same (liquid) pure solute, since the alkyl chains seem to fit, at least partially, in the natural cavities of liquid water (17). At low concentrations the variation of  $\bar{V}_2$  with  $m$  reflects solute-solute interactions. These include long-range coulombic forces as calculated from the Debye-Hückel theory, all types of dimerization, structural interactions, etc. Beyond a certain concentration,  $\phi_V$  increases very sharply. The initial break is identified with the CMC and represents the concentration at which micelles begin to form. The high value of  $\bar{V}_2$  beyond the CMC is the volume of a surfactant solute in the micellar state. If the aggregation number of the micelle is known then the volume of the micelle is obtained. Or else, if the total volume of the micelle is known, e.g. from kinetic properties, the aggregation number can then be calculated. Since the interior of a micelle somewhat resembles an organic liquid,  $\bar{V}_2$  has, as a first approximation, the molar value of a corresponding liquid surfactant. Since micelles can interact with each other and with the counterions,  $\bar{V}_2$  in the post-micellar region will also vary to a small extent with  $m$ .

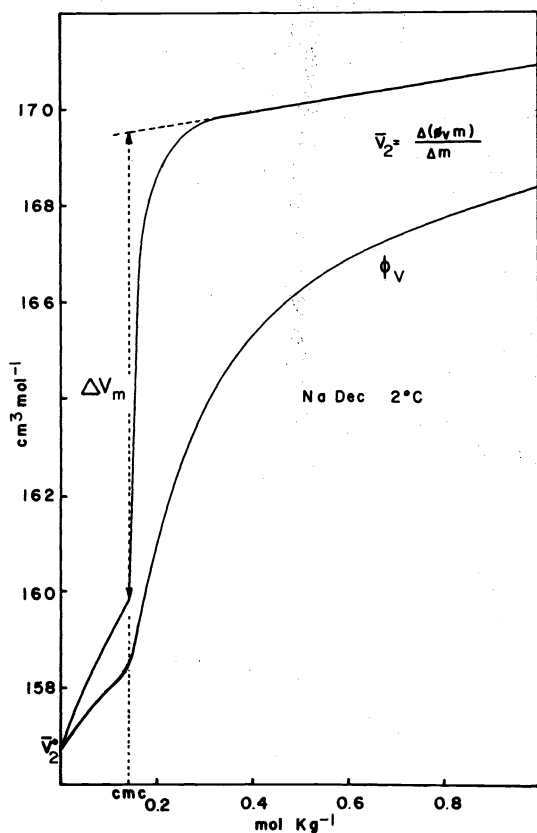


Fig. 1. The apparent and partial molal volumes of sodium decanoate in water at 2°C.

The molar change in volume during micellization  $\Delta V$  is calculated by measuring the difference in  $\bar{V}_2$  between the points obtained by extrapolation<sup>m</sup> of the regions above and below the CMC, to the CMC as illustrated in Fig. 1. The correctness of this procedure can readily be shown from a simple phase separation approach. The CMC is considered equivalent to a solubility, and the micelles act as a reservoir for singly dispersed surfactant molecules. Beyond the CMC the total volume of a solution is given by

$$\begin{aligned} V &= \sum n_i \bar{V}_i \\ &= 55.51 \bar{V}_w + \text{CMC} \bar{V}_s + (m - \text{CMC}) \bar{V}_m \end{aligned} \quad (1)$$

where  $\bar{V}_w$ ,  $\bar{V}_s$  and  $\bar{V}_m$  are the partial molal volumes of water and of the surfactant in the singly-dispersed and micellar states. This simple model assumes that the concentration of the singly-dispersed solutes remains constant beyond the CMC. In the premicellar region

$$V = 55.51 \bar{V}_w + m \bar{V}_s \quad (2)$$

Deriving Eq. (1) and Eq. (2) with respect to  $m$  the difference between  $\bar{V}_2^a$  and  $\bar{V}_2^b$ , above (a) and below (b) the CMC, is given by

$$\bar{V}_2^a - \bar{V}_2^b = \Delta V_m + (m - \text{CMC}) \partial \Delta V_m / \partial m \quad (3)$$

where  $\Delta V = \bar{V} - \bar{V}$ . At the CMC the second term of Eq. (3) drops out and  $\bar{V}_2^a - \bar{V}_2^b = \Delta V_m$ . Zana *et al.* (18) and Vikingstad *et al.* (19) have used a similar approach through apparent molal quantities. Above the CMC they assume that

$$\phi_V^a = \frac{\text{CMC}}{m} V_s + \frac{m - \text{CMC}}{m} V_m \quad (4)$$

and at the CMC  $\phi_V^b = V_s$ . Therefore it follows directly that

$$\phi_V^a - \phi_V^b = \frac{m - \text{CMC}}{m} \Delta V_m \quad (5)$$

Also, by differentiating Eq. (5) with respect to  $m$ , it can readily be shown that this equation becomes identical to Eq. (3) with the exception that  $\Delta V_m$  is now defined in terms of the apparent molal volumes  $V_m - V_s$  (8). In these idealized models it is obvious that the partial and apparent molal volumes of the components are identical, i.e.  $V_m - V_s = \bar{V}_m - \bar{V}_s$ .

This phase separation model implies that  $\bar{V}_2$  jumps from the value  $V_s$  to  $V_m$  at the CMC. With actual systems the changes are rarely as well defined, especially with short-chain surfactants. As seen in Fig. 1,  $\bar{V}_2$  attains the value of  $V_s$  at a concentration which is about twice the CMC. Micellization is therefore occurring over a range of concentration and, depending on the method used to measure the CMC, values anywhere in this range can be obtained. Also the second break is often called the second CMC. We feel that only the initial break is thermodynamically significant and will be used throughout this paper.

### Enthalpies.

The best functions to represent changes in enthalpy of micellar solutions are the apparent and partial molal relative enthalpies,  $\phi_L$  and  $\bar{L}_2$ . These functions are based on infinite dilution as the reference state and are readily derived from enthalpies of dilution, of solution or of mixing (20). The present data were all obtained from enthalpies of dilution.  $\bar{L}_2$  are shown for NaDec, octylamine hydrobromide (OABr) nonyl and decyltrimethylammonium bromides (NTABr, DTABr) at 25°C in Fig. 2. The values of  $\phi_L$  (dashed lines) are also shown for NaDec and NTABr. The transition is fairly well defined for NaDec and, although the interactions in the postmicellar region are large, the enthalpy of micellization can be deduced readily. As we will show later the transitions are even sharper at lower temperatures.

The situation becomes much more complicated with the other surfactants, and in this respect DTABr is an extreme case. The small hump which was apparent with NaDec now becomes a pronounced maximum. The CMC corresponds to the small inflection point and not to the maximum in  $\bar{L}_2$ . A reasonable value for  $\Delta H_m$  can still be obtained by extrapolating the relatively linear pre and postmicellar regions to the CMC. The experimental  $\Delta H_m$  of DTABr turns out to be very small at 25°C. At other temperatures the determination of  $\Delta H_m$  of this surfactant is less ambiguous.

The phase transition model can be readily extended to thermochemical properties. Corresponding to Eq. (4) the apparent molal enthalpy above the CMC is given by

$$\phi_H^a = \frac{\text{CMC}}{m} H_s + \frac{m - \text{CMC}}{m} H_m \quad (6)$$

Adding and subtracting  $\bar{H}_s^0$ , the standard partial molal enthalpy (at infinite dilution), Eq. (6) can be written as apparent molal relative enthalpies

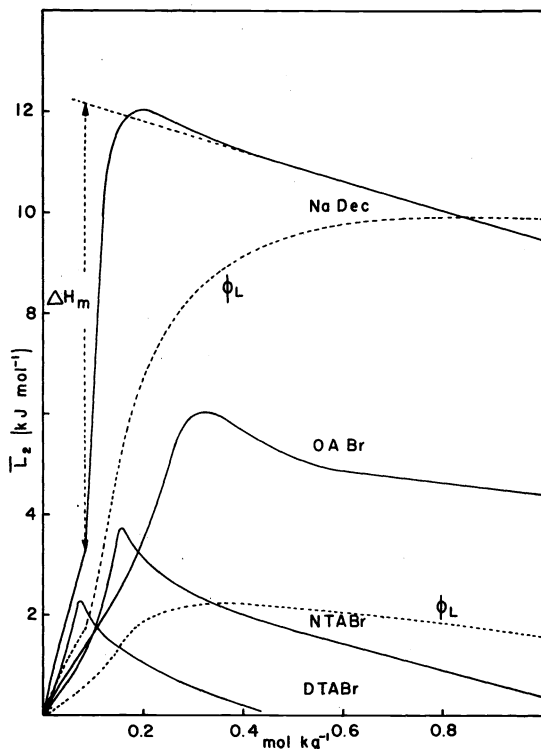


Fig. 2. The apparent and partial molal relative enthalpies of sodium decanoate, octylamine hydrobromide, nonyl and decyltrimethylammonium bromides at 25°C.

$$\phi_L^a = \frac{\text{CMC}}{m} L_s + \frac{m - \text{CMC}}{m} L_m \quad (7)$$

Below the CMC  $\phi_L^b = L_s$ . Differentiating with respect to  $m$ , the difference in partial molal enthalpies is then given by

$$\bar{L}_2^a - \bar{L}_2^b = \Delta H_m + (m - \text{CMC}) \partial \Delta H_m / \partial m \quad (8)$$

The phase separation model predicts that the shape of  $\bar{L}_2$  should be qualitatively similar to  $\bar{V}_2$  for endothermic  $\Delta H_m$ . The concentration dependence of  $\bar{L}_2$  deviates much more than  $\bar{V}_2$  from this idealized model especially when  $\Delta H_m$  is small. It is therefore obvious that micellization is occurring over a broad concentration region and phase separation models give an oversimplified view of micellization. Micelles do not form instantaneously at the CMC. Smaller aggregates probably form and grow in size as more surfactant is added until the optimum size is reached. A close analysis of  $\bar{L}_2$  should help in finding some of these intermediate structures through better models such as mass-action models.

Many attempts have been made in the literature (3,4,21-24) to determine  $\Delta H_m$  calorimetrically, but the values obtained vary enormously and often even differ in sign when they are small. The main reason for this disagreement is that it was not always realized that ionic surfactants have important solute-solute interactions which cause a rather large concentration dependence of  $\bar{L}_2$  above and below the CMC. Integral enthalpies of dilution or of mixing were generally used and different definitions of  $\Delta H_m$  were applied. For example it is obvious from Fig. 2 that, if  $\Delta H_m$  is deduced from  $\phi_L$ , e.g. enthalpies of dilution or of mixing, quite different values of  $\Delta H_m$  will be obtained depending on where the initial and final concentrations are taken. With NaDec the correct sign would be obtained in all cases but  $\Delta H_m$  would generally be too small. With NTABr and DTABr even the sign could be wrong. We will show later that the present method of defining  $\Delta H_m$  is self-consistent and predicts correctly the temperature dependence of the CMC.

#### Heat capacities.

The partial molal relative heat capacities of NaDec, OABr, NTABr and DTABr, obtained from volumetric specific heats and densities, are shown in Fig. 3. Organic solutes in water all have very large  $\bar{C}_{p2}^o$  (given in Fig. 3), characteristic of hydrophobic hydration (17). Inside the micelle most of the aliphatic chains of the surfactants are no longer in contact with water and  $\bar{C}_{p2}$  now has approximately the value of an organic liquid. However, in the CMC region,  $\bar{C}_{p2}$  has a very pronounced hump for NaDec and OABr while a maximum is observed for

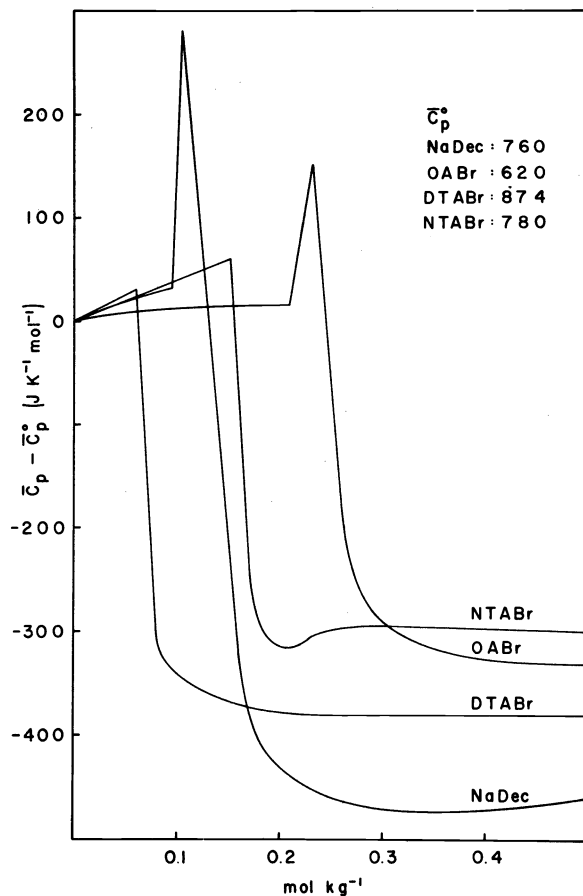


Fig. 3. The partial molal relative heat capacities of sodium decanoate, octylamine hydrobromide, nonyl and decyltrimethylammonium bromides at 15°C.

NTABr and DTABr. These humps are also observed for  $\phi_C$  as shown in Fig. 4.

The hump in  $\phi_C$  can be predicted with the simple phase-separation approach. From Eq. (6) it readily follows from  $\phi_C = \partial\phi_H/\partial T$  that

$$\phi_C = \frac{CMC}{m} C_{Ps} + \frac{m - CMC}{m} C_{Pm} - \frac{\Delta H_m}{m} \frac{\partial CMC}{\partial T} \quad (9)$$

For a phase-separation model (5,25)

$$\frac{\partial CMC}{\partial T} = - \frac{1}{(1 + \beta)RT^2} \Delta H_m \quad (10)$$

where  $\beta$  is the degree of association of the counterions. If  $\beta$  varies with temperature (8) then an extra term must be added to Eq. (10). The difference in  $\phi_C$  above and below the CMC becomes

$$\phi_C^a - \phi_C^b = \frac{m - CMC}{m} \Delta C_m + \frac{CMC(\Delta H_m)^2}{(1 + \beta)mRT^2} \quad (11)$$

The predicted concentration dependence of  $\phi_C$  for an ideal typical micellar system is shown in Fig. 5. From Eq. (11) it is obvious that at the CMC

$$\phi_C^a - \phi_C^b = \frac{(\Delta H_m)^2}{(1 + \beta)RT^2} \quad (12)$$

The second term of Eq. (11) or Eq. (12) is called the relaxation contribution to heat capacities (26-38) and occurs whenever an equilibrium is involved in the system. Although the phase-separation model is an oversimplified one, the predicted height of the hump is of the correct order of magnitude (8).

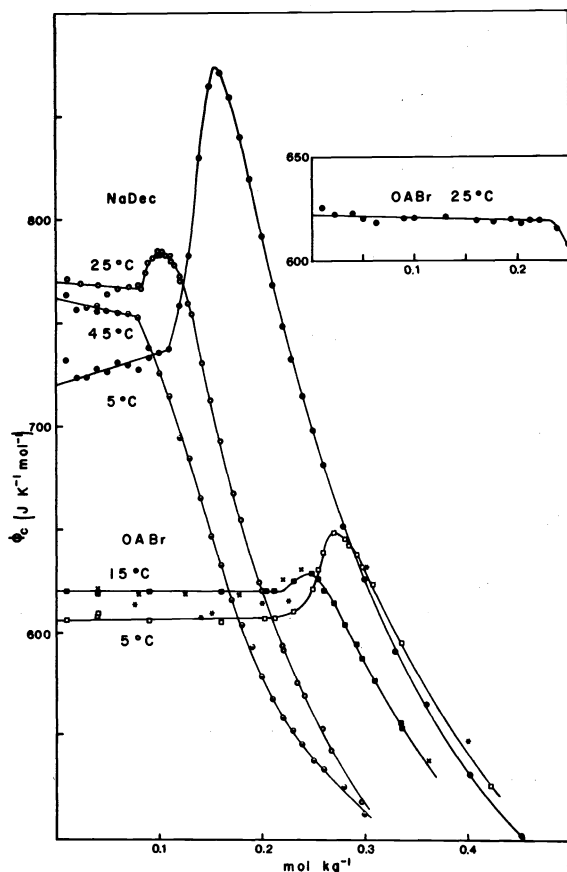


Fig. 4. The apparent molal heat capacities of sodium decanoate and octylamine hydrobromide at various temperatures. Reproduced with permission from Can. J. Chem. (8).

The relaxation contribution to  $\bar{C}_{p2}$  can also be calculated by differentiating Eq. (11) with respect to  $m$ , i.e.  $\bar{C}_{p2} = \partial(\phi_C^m)/\partial m$ . The relaxation term is now proportional to  $\Delta H (\partial \Delta H / \partial m)$  and for an ideal micellar system this term should vanish; only a discontinuity should be observed at the CMC. The hump in  $\bar{C}_{p2}$  observed in Fig. 3 should therefore be ignored in evaluating  $\Delta C_m$ . On the other hand the profile of the hump contains much information since it is related to the micellization process and can in principle be used in conjunction with other functions to calculate the various equilibria leading to micellization. It is also interesting to note that there is no hump in the case of DTABr but a maximum. This immediately suggests that the equilibria leading to micellization are more complex in this case. Probably dimerization occurs in the pre-micellar region. Once a proper theory of micellization is available it is probable that the kind of equilibria involved in micellization will be deducible from the shape of all the thermodynamic functions in the micellar region. Such theoretical approaches are presently being investigated in our laboratory.

#### Free energies and entropies.

Free energies of micellar systems can readily be measured from colligative properties (7,9) or from electromotive forces (29-31). Then, from the experimental free energies and enthalpies, the partial molal entropies of the surfactant solutions can also be calculated as a function of concentration (6).

The osmotic coefficients of the present surfactants were measured at the freezing point (7,9). Knowing the corresponding thermochemical properties as a function of temperature it will be shown in the next section that it is relatively easy to calculate the osmotic coefficients,  $\phi$ , the mean activities,  $a_{\pm}$ , the mean activity coefficients,  $\gamma_{\pm}$ , and the non-ideal free energies,  $\bar{G}_2^{ni} = \nu_2 RT \ln \gamma_{\pm}$ , at any temperature. The relative chemical potential,  $\bar{G}_2 - \bar{G}_2^0 = \nu_2 RT \ln a_{\pm}$ , and its ideal and non-ideal contributions are shown in Fig. 6 for NaDec at 25°C. The ideal contribution, which corresponds to the free energy of mixing, increases continuously. Beyond the CMC phase-separation models predict a nearly constant activity (32). The concentration of singly-dispersed surfactants should remain constant. The non-ideal

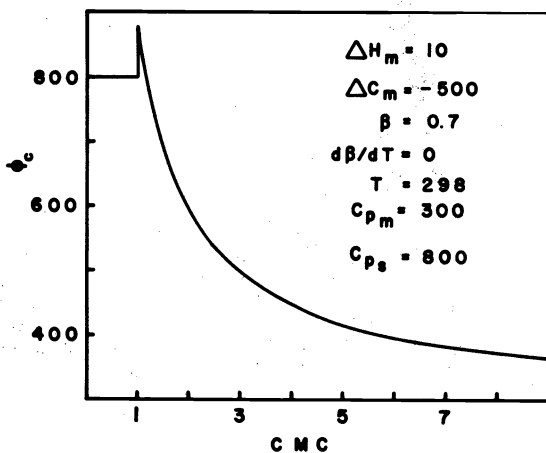


Fig. 5. Predicted apparent molal relative heat capacity for an ideal typical surfactant in water. The units of enthalpies and heat capacities are in  $\text{kJ mol}^{-1}$  and  $\text{JK}^{-1} \text{mol}^{-1}$ .

contribution should therefore reflect the decrease in total concentration due to micellization. This  $\bar{G}_2^{\text{ni}}$  is shown for various surfactants in Fig. 7. In the premicellar region various solute-solute interactions, primarily long-range coulombic forces, cause a negative contribution. Beyond the CMC there is a further decrease due to micellization. Phase-separation models would predict a well-defined single break in  $\bar{G}_2^{\text{ni}}$ .

The non-ideal contributions to the partial molal entropies of various surfactants are shown in Fig. 8. The shape of these curves are qualitatively similar to  $\bar{L}_2$  and can be used to measure  $\Delta S_m$  graphically, although better results are obtained from  $\bar{S}_2 - \bar{S}_2^0$  (7). As it will be shown later  $\Delta H_m - T\Delta S_m = 0$  as is expected for any system at equilibrium.

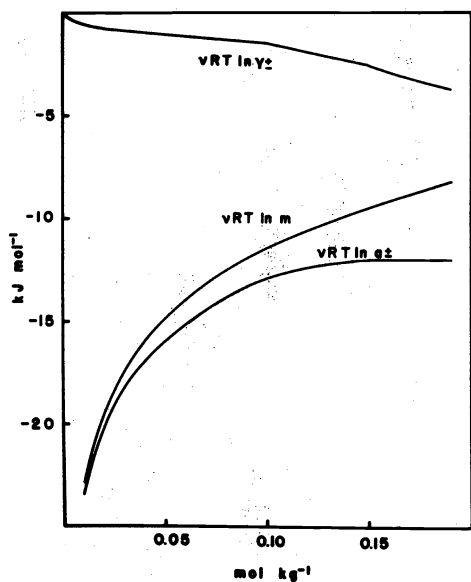


Fig. 6. The relative chemical potential and ideal and non-ideal contributions of sodium decanoate in water at  $25^\circ\text{C}$ .

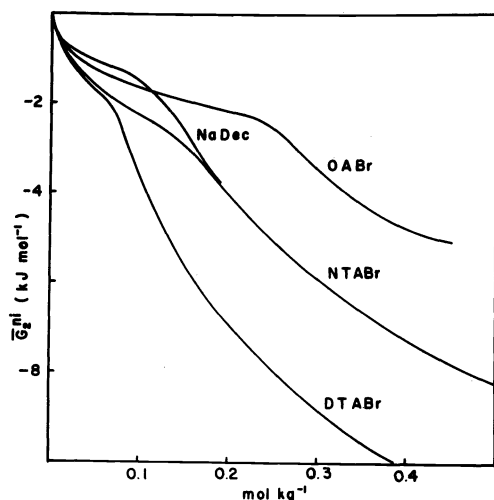


Fig. 7. The non-ideal free energies of sodium decanoate, octylamine hydrobromide, nonyl and decyltrimethylammonium bromides in water at 25°C.

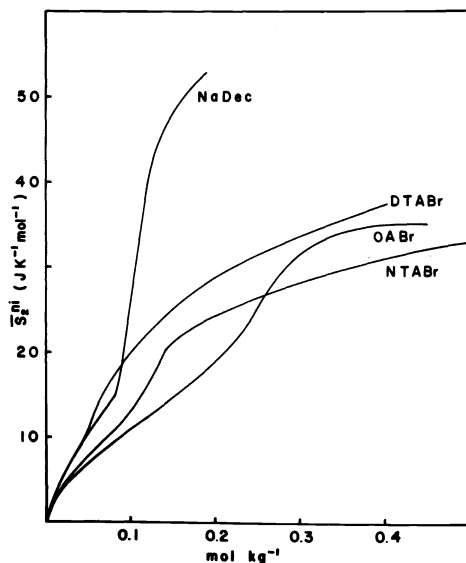


Fig. 8. The non-ideal partial molal entropies of sodium decanoate, octylamine hydrobromide, nonyl and decyltrimethylammonium bromides in water at 25°C.

#### TEMPERATURE DEPENDENCE OF FUNCTIONS

The heat capacities were measured as a function of temperature and the enthalpies and free energies at a single temperature. Through simple thermodynamic relations (6) it is thus possible to calculate enthalpies, entropies and free energies also as a function of temperature. The dependence on  $T$  and on  $m$  of  $\bar{C}_{P2}$ ,  $\bar{L}_2$ ,  $\bar{S}_2 - \bar{S}_2^0$  and  $\bar{G}_2^{ni}$  of NaDec is shown in Figs 9 to 12.

The temperature dependence of the hump in  $\bar{C}_{P2}$  are well seen in Fig. 9; it disappears at high temperatures but goes through a maximum between 2 and 5°C. These humps in  $\bar{C}_{P2}$  are ignored for the determination of  $\Delta C$  but are taken into account in the prediction of the temperature dependence of  $\bar{L}_2$ . Since  $\Delta H_m$  reaches a value close to zero near 45°C it is expected that the hump in  $\phi_C$  (or  $\bar{C}_{P2}$ ) should disappear. On the other hand  $\Delta H_m$  becomes more endothermic the lower the temperature. It is therefore surprising that the hump in  $\phi_C$  should go through a maximum somewhere between 2 and 5°C. Obviously some of the interactions involved in micellization or some of the properties of the micelles are slightly different near the freezing temperature and are reflected in the hump of  $\bar{C}_{P2}$ .



The transitions in  $\bar{L}_2$  and  $\bar{S}_2$  near the CMC become larger and sharper at lower temperatures (Figs 10 and 11). The functions  $\Delta H_m$  and  $\Delta S_m$  can be determined graphically as discussed previously. The temperature dependence of  ${}^m\Delta H_m$  and  $\Delta S_m$  can also be predicted from  $\Delta C_m$ , i.e.

$$\Delta H_m^T = \Delta H_m^{298} + \int_{298}^T \Delta C_m dt \quad (13)$$

$$\Delta S_m^T = \Delta S_m^{298} + \int_{298}^T \frac{\Delta C_m}{T} dT \quad (14)$$

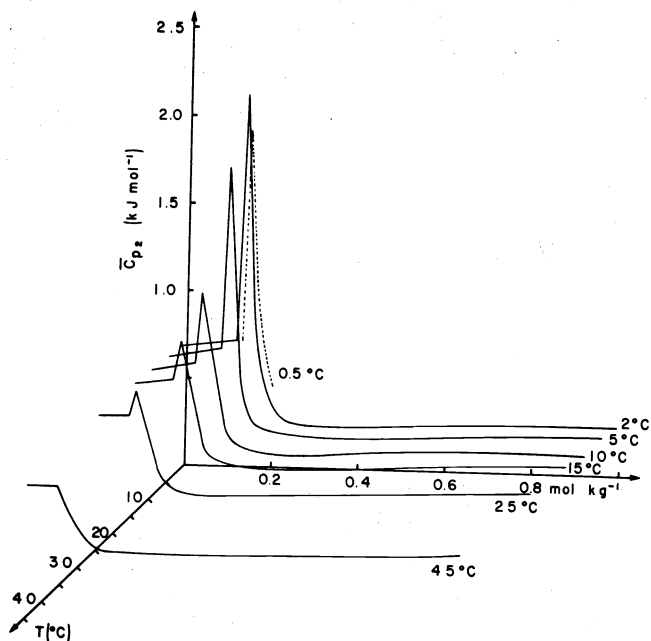


Fig. 9. Concentration and temperature dependence of  $\bar{C}_{p2}$  of sodium decanoate.

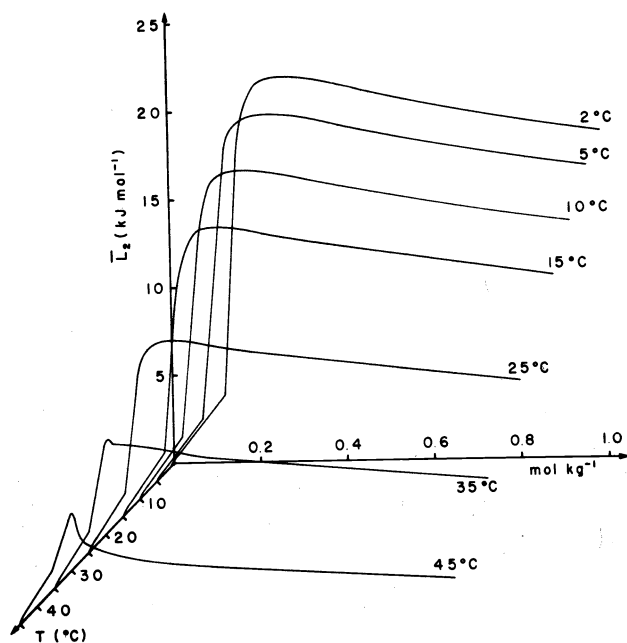


Fig. 10. Concentration and temperature dependence of  $\bar{L}_2$  of sodium decanoate.

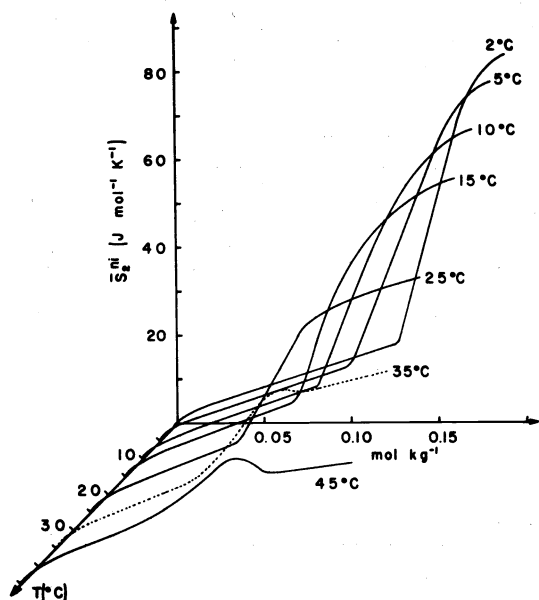


Fig. 11. Concentration and temperature dependence of  $\bar{S}_2^m - \bar{S}_2^0$  of sodium decanoate.

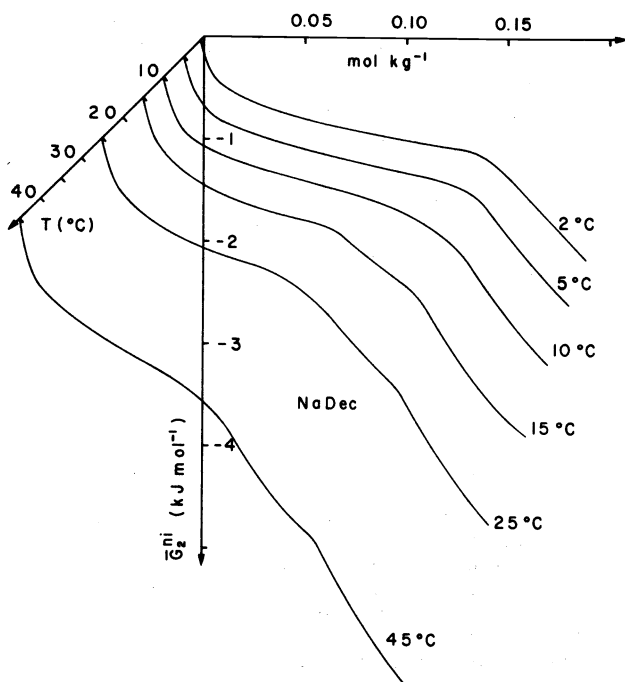


Fig. 12. Concentration and temperature dependence of  $\bar{G}_2^{ni}$  of sodium decanoate.

Also, since the system is at equilibrium,  $\Delta G_m = 0$  by definition. Therefore there is a third way of calculating  $\Delta H_m$ , i.e.

$$\Delta H_m = T\Delta S_m \quad (15)$$

These various ways of calculating  $\Delta S_m$  and  $\Delta H_m$  at different temperatures offer a severe test of self-consistency for the definition of the micellization process. Such a comparison is made for NTABr in Table 1 and the agreement is excellent.

TABLE 1. Entropies and enthalpies of micellization of nonyltrimethylammonium bromide in water.

T(°C)	$\Delta S_m$ (JK <sup>-1</sup> mol <sup>-1</sup> )		$\Delta H_m$ (kJ mol <sup>-1</sup> )		
	(a)	(b)	(a)	(c)	(d)
5	29	29.2	8.70	8.60	8.07
15	14	13.7	4.20	4.25	4.03
25	0	---	0.25	---	0
35	-12	-12.9	-3.60	-3.65	-3.70
45	-25	-25.4	-7.70	-7.55	-7.95

(a) graphically

(b) from  $\Delta S_m^T = \Delta S_m^{298} + \int_{298}^T \frac{\Delta C_m}{T} dT$

(c) from  $\Delta H_m^T = \Delta H_m^{298} + \int_{298}^T \Delta C_m dt$

(d) from  $\Delta H_m^T = T\Delta S_m$

The temperature dependence of  $\bar{G}_2^{n1}$  of NaDec is shown in Fig. 12. At low temperatures, where the measurements were made, a single break is observed at the CMC. At higher temperatures a double break seems to be present. We thought originally (6) that this double break might be related to the two CMC's that have often been reported in the literature. However, direct measurements of  $\bar{G}_2^{n1}$  by EMF methods (9,29) do not confirm the existence of these two breaks. A close examination of the present data suggests that the double break is an artifact and

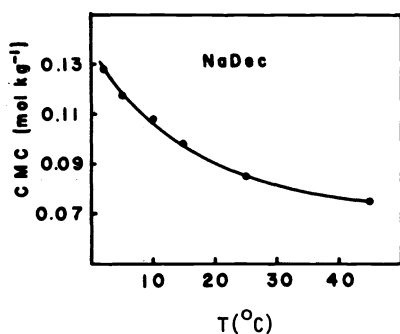


Fig. 13. Temperature dependence of the CMC of sodium decanoate in water.

occurs because the hump in  $\bar{C}_{p2}$  does not vary in a regular fashion with temperature and concentration. Heat capacity data at every two degrees or so would probably be required at low temperatures to predict the correct temperature dependence of  $\bar{G}_2^{n1}$ . While it is generally true that it is preferable to measure heat capacities as a function of temperature to calculate the temperature dependence of free energies rather than extract heat capacities from the temperature dependence of free energies, in the case of complicated systems such as surfactants, it could be advantageous to measure both the temperature dependence of free energies and of heat capacities.

Finally the CMC can readily be calculated as a function of temperature from Eq. (10) provided the degree of association  $\beta$  is known (10). Or else, from the experimental CMC, (see Fig. 13)  $\Delta H_m$  and  $\Delta C_m$ , all known as a function of temperature, the parameter  $\beta$  can be deduced as a function of temperature. In general  $\beta$  is maximum near the freezing point and decreases with temperature (8). With NaDec  $\beta \approx 0.7$  at low temperatures in agreement with other estimates of this parameter (33).

#### MICROEMULSIONS

The thermodynamic techniques can also be used to study the so-called microemulsions, which are mixtures of oil, water, alcohol and surfactants (34). The heat capacities of many

aqueous solutions of polar nonelectrolytes, such as amines and alcohols (35,36), show transitions which are quite similar to surfactants even though molecules like tert-butanol or triethylamine can hardly be called surfactants. The transitions in the systems are sharper if surfactants are added to the system. These systems have the ability of dissolving rather large quantities of oil, thus their name microemulsion. From a study of the thermodynamic properties of suitable probes much information can be obtained on the stability of these systems and on the local environment of the probe (36). Much work is presently being done on these systems in view of their potential use in oil recovery.

#### CONCLUSION

In this paper an attempt was made to summarize the concentration and temperature dependences of the thermochemical and activity data for four ionic surfactants that have been studied extensively in our laboratory. While not reported here the volumetric properties (volumes, expansibilities and compressibilities) were also investigated. While it is quite tedious to measure all these data, especially in the micellization region, we believe that it is primarily through such studies that proper theories on micellization will eventually be developed.

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