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**THE THERMODYNAMICS OF SURFACTANT AGGREGATION AND
ADSORPTION AT THE CLAY-WATER INTERFACE**

The University of Oklahoma

PH.D.

1982

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE THERMODYNAMICS OF SURFACTANT AGGREGATION
AND ADSORPTION AT THE CLAY-WATER INTERFACE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

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degree of

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BY

RANDAL MYRON HILL

Norman, Oklahoma

1982

THE THERMODYNAMICS OF SURFACTANT AGGREGATION
AND ADSORPTION AT THE CLAY-WATER INTERFACE

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The completion of
this dissertation is dedicated to
my wife
with all my love.

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THE THERMODYNAMICS OF SURFACTANT AGGREGATION

AND

ADSORPTION AT THE CLAY-WATER INTERFACE

CHAPTER I

INTRODUCTION

i. General

The physical properties of solutions of amphiphilic molecules possess a peculiar concentration dependence. The purpose of this research has been to elucidate the details of the processes responsible for this unusual behavior. Amphiphilic molecules, or molecules with both lyophobic (poorly solubilized by the solvent) and lyophilic (well solubilized by the solvent) functional groups physically separated within the molecule tend to exhibit strongly cooperative association.

This causes an abrupt change in many physical properties at a certain concentration which is called the critical micelle concentration (cmc). Some typical examples of this discontinuity for a number of physical properties are shown in Figure I-1. Surfactants are among such substances, and are of intense interest for both theoretical and

practical reasons (1,2). Some examples of typical amphiphilic substances are given in Figure I-2. They are among the most important compounds made and used by the chemical industry.

A very important area of application of surfactants is their use in enhanced oil recovery (EOR). The importance of enhanced recovery of petroleum cannot be exaggerated in view of the fact that 65-70 % of the petroleum in a formation remains in place after conventional production is exhausted (3). The use of surfactants is one of several means under study for recovering a substantial portion of this remaining oil.

The residual oil is believed to exist as 'ganglia' trapped in the pores of the rock formation by capillary forces. It ought to be possible to force this oil out of the pores once the interfacial tension across the oil/brine interface has been reduced sufficiently. In situ this interfacial tension is about 20-30 dynes/cm (3). Addition of an appropriate surfactant system can lower it to about $10^{-3} - 10^{-4}$ dynes/cm (3). This is done by injecting a surfactant 'slug' into four wells at the corners of a square. Figure I-3 illustrates this procedure. The surfactant solution is followed by a viscous water soluble polymer solution which provides mobility control (pressure to force the oil out). The oil which is forced out of the pores is recovered at a well in the center of the square.

Much remains unclear about this process. In order to optimize the characteristics of the surfactant slug a detailed understanding of surfactant association behavior is needed. Surface active substances such as amphiphiles adsorb on convenient surfaces. Unfortunately, oil

is found in rock formations which are at least partially composed of clay minerals which have an enormous surface area. Thus it would be highly desirable to understand the interactions between surfactants and clay mineral surfaces.

Surfactants find application in virtually every area of industrial chemistry from detergents, emulsifiers and foamers to the manufacture of paper, fibers and fabrics as well as catalysis, corrosion and coatings, to name but a few. Theoretically, amphiphiles are of interest for at least three reasons: (i) as surface active substances they are of interest in themselves, (ii) their behavior constitutes a classic case of hydrophobic bonding (vide infra), and (iii) they are widely studied as models of biological systems.

Because each molecule possesses parts which are solubilized well in water and parts which are not (generally an alkyl chain, or some other hydrocarbon group) it is thermodynamically favorable for the molecule to be found in a region where both tendencies may be satisfied. Such a region occurs at an interface and surfactants experience a decrease in activity coefficient (resulting in an increase in number concentration relative to the bulk phase) by proximity to such a region. Solutions of amphiphilic molecules may also be stabilized by self-association in such a way that the hydrophobic parts of the molecule cluster together leaving the 'solvent loving' parts in contact with the solvent. This phenomenon is in fact only another manifestation of surface activity - the surface is now the closed surface of a sphere surrounded by the bulk phase. Together, these two

phenomena and their attendant energetics produce the abundance of phenomena characteristic of surfactant solutions.

The self-association of amphiphilic molecules into colloidal aggregates is well known and the clusters so formed are called micelles. The term 'micelle' (from Latin 'micella', which means 'small bit') was introduced by J.W. McBain in 1913 (4) to describe the formation of colloidal particles by detergents and soaps. The term is used with a different meaning in biology and colloid chemistry. As used in this context it will refer to the association of amphiphilic molecules into large (>10) aggregates characterized by strongly cooperative behavior. This has the consequences that the cmc will be reasonably well defined (sharp) and the size distribution of species will have a shape similar to that in Figure I-4, i.e., a minimum and a maximum will be observed (5, 6).

Although the general features of amphiphilic association have been known for some time, the thermodynamics of amphiphilic association remains one of the most active areas of research in physical chemistry. In spite of this frenetic activity the theoretical analysis is still rather incomplete (7). There is, of course, disagreement, even about major features of the phenomenon, and only recently has unambiguous evidence begun to provide clear answers to some questions.

ii. Micelle formation

A description of the general features of micelle formation must include consideration of the aggregation process and the structure of the aggregate, the disposition of the counterions (if any), the relationship between the aggregate and the solvent and the influence of other solutes.

a. The Aggregation Process

A wide range of aggregation behavior has been observed among amphiphiles (8, 9). Some amphiphiles undergo a very sharp change in many physical properties in the cmc region while others change less abruptly. The differences between the pre-cmc and the post-cmc regions are greater for some surfactants and some properties than for others. These effects are due to differences in the details of the association equilibria. The precise concentration identified as the cmc also depends on which property is selected for study as well as how the cmc is defined. This is partially due to mathematically and physically different averaging processes (10).

It is generally accepted that the hydrophobic moiety controls the aggregation behavior (11). The hydrophilic group serves mostly to effect sufficient solubility to permit large aggregates to form. The primary determining factor in micelle formation is the physical size of

the hydrophobic group. For instance, the logarithm of the cmc is linearly proportional to the number of carbon atoms for many classes of amphiphiles. Factors, such as branched chains, double bonds and polar groups which limit the efficiency of the hydrophobic association generally raise the cmc, working against association.

On the other hand, changes in the nature of the hydrophilic group have only minor effects on the aggregation (6), and may increase or decrease the aggregation in comparison with some polar group ideally matched to a given hydrophobic moiety. The head group must be polar enough (and hence hydrophilic enough) to effect sufficient solubility for aggregates to form. However, increasing polarity results in solubilization and electrostatic repulsion effects which counter the tendency to aggregate as is shown by the fact that ionic surfactants have higher cmc's than the corresponding non-ionics. For example, the cmc of C12 nonionic surfactants is typically about 10^{-4} M, whereas it is about 10^{-2} M for ionic C12 surfactants (12). Polar groups (e.g. phosphine oxide) generally give a lower cmc than more highly solubilized ionic groups. Among ionic groups, slight changes are seen corresponding to the strength of interaction with solvent water.

The effects of counterions on aggregation are mainly a function of the valence of the counterion. Divalent ions result in a lower cmc relative to monovalent ions, and the effect is greater for cationic surfactants than for anionics. It should however, be realized that divalent cations also usually shift the Krafft point to near or above 298 K (and hence render the surfactant insufficiently soluble at room temperature to form large aggregates). That the effect is more

pronounced for cationic surfactants is probably because of greater interactions between water and the positive amphiphile ion. Organic counterions can lower the cmc dramatically due to the formation of mixed micelles (13).

The temperature dependence of the cmc is rather weak, at least at room temperature (14). Most hydrophobic interactions have a maximum in the equilibrium constant as a function of temperature (vide infra). A minimum in the cmc (and hence a maximum in K) near room temperature has been observed for a number of surfactants (11, 16, 17). Thus the derivative ($d\ln K/dT$) will be zero near room temperature, and this accounts for the oft stated maxim that the enthalpy change for amphiphilic association processes is essentially zero.

Other solutes influence micelle formation in a variety of ways. Salts depress the cmc, though the effect is several orders of magnitude greater for ionic amphiphiles than for nonionic. Nonionic polar solutes can lower the cmc, as in the case of medium chain alcohols (6), or raise the cmc and even destabilize micelle formation altogether at high concentrations as in the case of urea (11). Except for strongly hydrophilic organic substances, the tendency is to lower the cmc, and to increase the size of the micelle (18).

A related topic is the formation of non-micellar aggregates, particularly in the region before micelles begin to form. Several systems are thought to exhibit pre-micellar association, from dimers to octamers (11, 16). It seems likely from studies of other hydrophobic interactions that such aggregates might form (19, 20, 21). Most of the experimental methods currently in use would not be particularly

sensitive to such aggregates, however. It is also likely that the low cmc's of the commonly studied surfactants preclude observation of pre-micellar association in any case since very little will have formed before micelles begin to appear and swamp out the effects (16). This is an area of ongoing debate which will be discussed in more detail below (cf. Discussion).

b. Models

Two models often employed in this field may be mentioned here, the phase separation model (PSM) and the multiple equilibrium model (MEM). The PSM treats micelle formation in analogy with a classical phase separation, while the MEM defines a set of chemical equilibria and determines the interaction coefficients (16).

The PSM considers the aggregation of amphiphiles as the formation of a separate pseudo-phase, similar to, for instance, crystal precipitation. The formation of micelles is described as the 'precipitation' of a micellar pseudo-phase at a saturation concentration of monomers that may be calculated from a 'solubility product'. The effects of counterions may be included by allowing the pseudo-phase to be charged (the charged phase model), although this complicates the treatment (11).

There are examples of classical phase separation processes where aggregate sizes may be limited to a narrow range (22), but they are always limited by kinetic factors. Micelles, however, are thermodynamically stable. Without consideration of ionic effects, the PSM predicts that the activity of the free amphiphile should become

constant above the cmc. However, surface tension results (23) and recent work with surfactant selective ion electrodes (24, 25) have demonstrated clearly that the monomer activity decreases significantly beyond the cmc. In spite of all this the model remains attractive, primarily because of its simplicity, and it is reasonably successful in predicting the behavior of certain types of amphiphiles, particularly nonionics with low cmc's. It is also the only model which can handle the complexities which arise in mixtures of surfactants and cosurfactants (26, 27).

The MEM defines a set of equilibria and determines equilibrium constants or interaction coefficients (vide infra). It is most useful for systems with large cmc's and small aggregation numbers. It can easily include the counterion, and does in fact predict the observed decrease in activity of the free amphiphile ion above the cmc. Some form of this model is probably necessary in order to account realistically for the details of micelle formation. Unfortunately, it gets prohibitively complex when more than two or three equilibria must be considered and cannot easily manage a distribution of equilibria. There are fundamental questions about how to handle activity coefficient effects and how properly to represent the long range forces associated with electrostatic interactions (11). This type of model is most appropriate for the short range forces characteristic of molecular complex formation (e.g. hydrophobic forces). The results, being more precise, may be of more use to the theoretician, but are of less use to the engineer.

c. Micelle Structure

In order to understand the behavior of micelle forming amphiphiles it would be useful to study the structure of the micelle itself. Pertinent information about the micelle structure includes the size and shape of the micelle, the conformation and mobility of the hydrophobic groups in the interior of the micelle, the nature of the environment in the interior and the distribution of counterions (if any) around the micelle.

Unfortunately, all approaches to micelle size and shape must assume some model in order to interpret the data. The most direct approach is to fit some physico-chemical data using the MEM and extract the mean aggregation number from the fit. Some studies done this way indicate that the distribution is asymmetric about the mean (29), but other work (30) is consistent with a narrow Gaussian distribution. Mukerjee (31) has discussed micelle size and shape in some detail. For many systems, it appears that polydispersity is low as shown by the near equality of number average and weight average methods (32). A significant observation is that although the cmc depends only weakly on head group structure and counterion, micelle size can vary a great deal (11). Micelle size usually decreases with increasing temperature and increases with added electrolyte.

Actual physical sizes and shapes may be inferred from light scattering techniques (33, 34, 35) (although with the qualification above). Correlating these with aggregation numbers it is found that the molar volume of the hydrophobic group is roughly equal to the molar

volume of the equivalent liquid hydrocarbon. The radius of the micelle turns out to be about equal to the length of the extended hydrocarbon chain, indicating that the chain is, on average, about half extended. This is in agreement with NMR studies of alkyl chain conformation inside the micelle (36). It is generally agreed (11, 16, 37) that up to concentrations of several times the cmc micelles assume a spherical shape, although there are important exceptions to this, and in view of the rapid kinetics of the system a spherical shape can only represent a dynamic average.

If the hydrocarbon chain is half extended in the micelle this would indicate a slightly more open structure than in the corresponding liquid hydrocarbon (11). However, the motion of the chains in the interior appears to be somewhat constrained (36), an observation which is consistent with any of several aspects of micelle structure (vide infra). Solubilization of nonpolar substances is most consistent with a liquid-like interior, but this interior seems to be more similar to the corresponding alcohol than the alkane.

The force required to bring a large number of charged ionic head groups together would completely prevent micelles from forming if the charge were not largely (60-70%) neutralized by closely-bound counterions. These counterions should not be thought of as chemically bound to specific sites, but rather, as composing a continuous radial distribution, or atmosphere around the micelle. It is convenient to discuss the disposition of the counterions in terms of a simple two state model, but it should be kept in mind that there is no unambiguous distinction between bound and free counterions. It is therefore not

surprising that B , the fraction of counterions 'bound' to the micelle is not experimentally well defined.

Obviously, the classical approach to calculating electrostatic interactions in solution on the basis of the linearized Poisson-Boltzmann equation breaks down rather badly when micelles begin to form. Elaborate models have been devised for counterion binding including charged spheres with specific sites and calculations of electrostatic interactions based on numerical solutions of the Poisson-Boltzmann equation (7, 38-41).

As far as this work is concerned the important features are that B is not strongly dependent on concentration or temperature. B may be somewhat dependent on micelle size. The aggregation number of a given amphiphile determines the volume of the sphere which is the micelle. The charge is distributed over the surface area of the sphere, however, not the volume. Hence it would be reasonable to argue that if a certain surface charge density is stable, then the smaller the sphere (keeping in mind that the size of the sphere is determined by the aggregation number) the smaller the fraction of counterions which must be adsorbed to reach that stable surface charge density. Thus the shorter chain amphiphiles ought to have smaller values of B , decreasing to the limit of non-micelle forming species which have no binding. This has in fact been observed (11).

B is primarily a function of micelle diameter, with some consideration of the hydration of the headgroup and the counterions which would limit the closest approach of the counterions and hence the surface charge neutralization per counterion. This argument is

consistent with the recent theoretical developments by Wennerström, Lindman and coworkers (7, 38-41).

iii. Thermodynamics

The structure of the micelle immediately suggests that the minimization of hydrocarbon-water contact is crucial to micelle formation. The molecular organization of the micellar system is the result of a delicate balance of thermodynamic forces. The tendency to replace hydrocarbon-water interactions with the more favorable combination of hydrocarbon-hydrocarbon and water-water interactions favors association (the hydrophobic effect). Repulsive forces between polar/ionic head groups, and solubilization of polar groups by solvent water hinder association. This interplay of forces is also responsible for numerous extremely important phenomena in biological systems (42). Surfactants are widely used as model systems in experimental studies of biophenomena. A thermodynamical description of micellar solutions thus has wider implications than merely an understanding of surfactant behavior.

A thermodynamical description of micelle formation should include the hydrophobic character of the association, electrostatic interactions within the system, the measurement of thermodynamic quantities and the formulation of a theory to account for the results. The availability of relevant thermodynamic information is essential for testing theoretical models as well as for understanding the details of the molecular interactions involved (6).

a. The Hydrophobic Effect

The tendency to exclude water-hydrocarbon contact by molecular association in aqueous solution is called the hydrophobic effect. The hydrophobic effect has been the subject of numerous reviews, most notably by Franks (21). Similar phenomena may also occur in non-aqueous solvents and are referred to in general as solvophobic effects (43). There are certain salient features which distinguish association brought about by hydrophobic effects from other types of association phenomena.

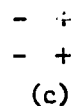
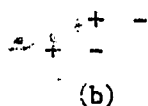
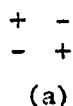
As is typical of hydrophobic bonding the thermodynamics of micelle formation is dominated by the increase in entropy accompanying association. This simply means that the entropy term ($T\Delta S$) makes a larger contribution to the free energy (and hence K , the equilibrium constant) than does the enthalpy, (but see below concerning the temperature dependence of the enthalpy). This needs to be qualified by the realization that entropy and free energy calculations always involve arbitrary choices of standard states and hence arbitrary magnitudes. There is also a great deal of confusion about the significance of the enthalpy contribution, and the origin of the entropy term.

The large positive entropy which accompanies hydrophobic association is usually attributed to increased structure in the shell of water immediately surrounding the hydrophobic moiety as compared with bulk liquid water. Ideally all possible hydrogen bonds are formed in ice, and a small fraction of these are broken in the liquid phase.

There appears to be a shell surrounding a hydrophobic moiety with an intermediate fraction of broken hydrogen bonds. This may be a consequence of increased structuring, and not the cause since solvophobic effects appear to occur in non-hydrogen bonding solvents also. The association of hydrophobic species would lead to a decrease in the shell volume occupied by water resulting in a decrease in structure and hence an increase in entropy. It might well be pointed out that researchers have found it very difficult to adduce unambiguous evidence for this structuring beyond the increase in entropy it was originally proposed to explain. This explanation is problematical because the conceptual link between disorder and entropy is not rigorously definable (44).

Even if the detailed structure cannot be determined yet, it may be assumed that the alkyl chain of an amphiphile monomer in aqueous solution is surrounded by layer of water structured by hydrogen bonding (6). Except for thermodynamic observations (21), this is supported by observations of large effects of surfactants on the water molecular motion (rotational and translational) below the cmc (45, 46). The polar head of the amphiphile interacts with water in a normal way (6). A detailed description of the micelle, including interactions with water (i.e. penetration, hydration) is at present a topic of considerable debate (6). A related point is that it is hard to see why the decrease in disorder due to the formation of a highly structured entity ought not to largely offset the increase due to the disappearance of structure in the water.

Calculations of intermolecular interactions indicate that the interaction between polar species should result in a lower energy than the interaction between a polar and a nonpolar species (43). Polar groups are thus more stable adjacent to each other than adjacent to nonpolar groups. Note that this assumes that the dipoles may freely orient with respect to each other and may therefore assume the most favorable orientation a.



In the micelle the polar groups are not free to orient this way and must assume the less favorable b or c. Thus there is not as large a contribution to stabilization of the micelle due to proximity of polar groups as might be expected. The more structured (sometimes called the 'iceberg') form of water around a nonpolar group would have both a lower enthalpy and entropy as compared with bulk liquid water (43). Another proposed source of the entropy increase is an increased freedom of motion of the hydrocarbon chain in the interior of the micelle as compared with the aqueous environment. The hydrocarbon chain may fit so snugly into the water 'lattice' that its freedom of motion is considerably restricted. This would contribute to the total entropy increase; however, evidence concerning the relative freedom of motion of alkyl groups inside the micelle and in the aqueous phase is rather difficult to interpret and the issue remains open.

The notion seems to be common that since hydrophobic association is entropy 'driven', the enthalpy change must be positive

or zero, and is of negligible importance. This is not true. Enthalpies of hydrophobic association equilibria have an unusually strong temperature dependence, being positive at lower temperatures, passing through zero and becoming negative at higher temperatures. It just happens that for many surfactants the enthalpy is positive and near zero at room temperature. Therefore, the value and the sign of the enthalpy for some particular association depend on what the temperature is. Other considerations, such as solubility limit the values actually observable.

The unusual temperature dependence of the enthalpy points to what is in fact the most fundamental characteristic of hydrophobic association: the change in heat capacity (ΔC_p) associated with the process is always large and negative (17, 47, 48). This could, of course, also be due to structuring of water around the hydrophobic group. A large negative ΔC_p implies that the enthalpy of many hydrophobic processes will become exothermic at temperatures not too far above room temperature. At the temperature at which the enthalpy passes through zero heat capacity measurements indicate that the structured water shell is still intact (49), hence association is still hydrophobic. Thus the relative dominance of the entropy or enthalpy is not the essential feature of hydrophobic association.

It might be helpful to think of this association in terms of classical surface chemistry. The association occurs because there is a large interfacial energy (or tension) in water-hydrocarbon contact which may be minimized by decreasing this costly surface area. Since interfaces are usually thought of in terms of continuum concepts, it may

be difficult to define what is meant by interfacial tension on a microscopic scale. However, interfaces are actually composed of individual intermolecular contacts. The macroscopic property of interfacial tension has its basis in microscopic interactions. Viewing hydrophobic interactions as a special case of interfacial energy could well advance our understanding of the microscopic basis of solution and interfacial properties. It is just as reasonable to seek a physical rationale for the large macroscopic water/hydrocarbon interfacial energy as it is to try to explain the unfavorability of water-hydrocarbon molecular contact by a structuring of solvent water. Insight into the latter may yield important insights into the former if they are indeed related phenomena (50).

Amphiphile aggregation is a complex process with the hydrophobic interaction being only one contribution to the total free energy. The hydrophobic interior of micelles appears from NMR and solubility studies to be less like a hydrocarbon liquid than might be expected (51, 52, 53). This has been attributed to penetration of water into the interior, the proximity of polar groups and a region of high dielectric constant, a solid or semi-crystalline state of the interior, and to the effects of Laplace pressure (due to the highly curved interface) (52, 53). It may also be pointed out that the micelle is a structured entity; the hydrocarbon chains are attached to polar groups which are confined to the surface of the micelle.

Because of competition between hydrophobic association and solvation of the polar head group it is likely that water penetrates to some extent into the micelle, thus increasing the water-hydrocarbon

contact area. This will modify free energy calculations based on measurements using alkanes because the appropriate chain length will depend on the extent of hydrocarbon-water contact. The extent of this penetration is controversial, and different experimental techniques give different results (37).

b. Electrostatic and Solvation Effects

The solvation of the head group by water and the electrostatic repulsion between the polar/ionic head groups at the surface of the micelle tend to hinder the aggregation. A quantitative treatment of these effects continues to be a major area of research effort. Essentially the problem is that the equations defining the electrostatic energy cannot be solved analytically. Numerous attempts have been made to find approximations permitting the problem to be solved, but even though some of these have been worked out in much detail, none adequately accounts for observed phenomena (6). In recent years Lindman, Wennerström and coworkers (7, 38-41) at Lund in Sweden have put together contributions by many researchers and developed an approach which is the current state of the art. After discussing some background their model (the PB model) will be described.

The distribution of charge due to other ions about a central ion may be defined by the charge density:

$$\rho_i(r) = \sum_j n_j z_j e g_{ij}(r) \quad (1)$$

where n_j is the mean number density of ionic species j , $z_j e$ the charge

on that species, and $g_{ij}(r)$ the radial distribution of species j about the central ion i . There will be an electrostatic potential due to interaction between the central ion and the distribution which must satisfy the Poisson equation:

$$\vec{\nabla} \cdot \vec{\nabla} \phi_i(r) = - \frac{\rho_i(r)}{\epsilon_r \epsilon_0} \quad (2)$$

where the charge density is defined for $r \geq a_i$, the radius of the central ion. The distribution of ions about the central ion may be assumed to be of the form of the Boltzmann distribution:

$$g_{ij}(r) = \exp\left(-\frac{z_j e \phi_i}{kT}\right) \quad (3)$$

The combination of Eqns. 1-3 forms the Poisson-Boltzmann (PB) equation which is the fundamental equation of electrolyte thermodynamics.

In principle the PB equation may be solved to obtain the electrostatic potential. Thermodynamic quantities are calculated by summing the electrostatic potential over all the ions in the solution (54). Unfortunately, the PB equation cannot be solved analytically in spherical symmetry without making certain simplifying assumptions. The exponential term in Eqn. (3) is usually expanded and the expansion terminated after two terms. In spherical coordinates:

$$\begin{aligned} \nabla^2 \phi_i &= \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi_i}{dr} \right) = \frac{e}{\epsilon_r \epsilon_0} \sum z_j n_j \left(1 - \frac{z_j e \phi_i}{kT} \right) \\ \nabla^2 \phi_i &= \kappa^2 \phi_i - \frac{e}{\epsilon_r \epsilon_0} \sum z_j n_j \end{aligned} \quad (4)$$

The second term on the RHS of Eqn. (4) is identically zero due to electroneutrality requirements, so the equation is reduced to:

$$\nabla^2 \phi_i = \kappa^2 \phi_i \quad (5)$$

This is called the linearized PB equation. The parameter, κ , is defined to be:

$$\kappa^2 = \frac{e^2}{\epsilon_r \epsilon_0 kT} \sum n_j z_j^2$$

Equation (5) may be solved analytically to give (for $r > a_i$):

$$\phi_i = \frac{z_i e \exp[-\kappa(r-a_i)]}{4\pi \epsilon_r \epsilon_0 r(1+\kappa a_i)}$$

from which may be obtained:

$$kT \ln \gamma_i = - \frac{(z_i e)^2}{8\pi \epsilon_r \epsilon_0} \frac{\kappa}{1+\kappa a_i}$$

In the limit of infinite dilution this reduces to the Debye-Huckel limiting law (DHLL):

$$\ln \gamma_i = A c^{1/2}$$

Gunnarsson, Jönsson and Wennerström (7) have made use of the cell model (43) to calculate electrostatic effects in micellar solutions by numerically solving the non-linearized PB equation (Eqns. 1-3). This approach had previously been successfully used in the treatment of polyelectrolyte systems (references given in 7). In the cell model the solution is divided into cells, each containing a micelle and sufficient water and electrolyte to give the correct concentration. In their use of the cell model the cells and the micelles are assumed to be spherical, and the charges are located at

the micelle surface (surface charge density σ) and in the aqueous region (see Figure I-5).

In spherical coordinates the PB equation for the case of two oppositely charged monovalent ions is (7):

$$\epsilon_r \epsilon_0 \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = -F [c_{+0} \exp\left(-\frac{e\phi}{kT}\right) - c_{-0} \exp\left(\frac{e\phi}{kT}\right)]$$

where c_{+0} and c_{-0} are the (volume) concentrations of positive and negative ions at the cell boundary. The electrostatic free energy is calculated by separately determining the energy of ion-ion interactions, and the entropy due to the non-uniform distribution of ions. The free energy is the sum:

$$G_{el} = E_{el} - TS_{el}$$

Expressions for each of these terms are given in 7. At infinite dilution, a numerical solution of Eqn. (6) is straight forward, but at finite concentrations, c_{+0} and c_{-0} must be determined consistent with the boundary conditions. This was accomplished by guessing initial values of c_{+0} and c_{-0} and solving Eqn. (6) by a fourth order Runge-Kutta method.

Closed form expressions for chemical potentials were derived and then used to determine the dependence of the cmc on electrolyte concentration, alkyl chain length, and counterion valency. Gunnarsson, et al. (7) also demonstrated that amphiphile monomer activity ought to decrease above the cmc. Using the results of their model, they show that a single specific formal degree of ion binding is predicted by the

PB equation. This is a very important point because it provides justification for using the mass action approach (vide infra).

In view of the fact that the PB equation neglects ion-ion correlation effects (the location of a third ion is not independent of the presence of two others) and finite ion size effects, the results obtained may be questionable, especially at high salt concentrations. However, the predictions of this model are conceptually in excellent agreement with current views of micelle formation and in reasonable quantitative agreement with experimental work insofar as calculations have been carried out.

Linse, Gunnarsson and Jönsson (55) have compared the results of the PB treatment with the results of a Monte Carlo simulation. The MC treatment made use of the same cell model described above except that ions were given a finite size. The MC simulation, within the statistical uncertainties due to a finite summation, avoids the major conceptual difficulties inherent in the PB approach. The PB equation proved to be a good approximation when applied to highly charged aggregates (i.e. larger micelles) with monovalent counterions. The discrepancies between the PB and MC results could almost always be rationalized in terms of the neglect of ion-ion correlation in the PB equation.

iv. Thermodynamic Measurements

The thermodynamics of micellar systems may be (and usually has been) derived from investigations of temperature, pressure and co-solute effects on the aggregation equilibrium (6, 14, 45). Alternatively, thermodynamic quantities may be measured directly, as for instance by calorimetry (14). In both cases the complexity of the association is such that it is essential that the process to which a quantity refers be carefully defined. This is no simple matter, and as there is little consistency in the literature with regard to definitions, comparison of results is often difficult and sometimes pointless.

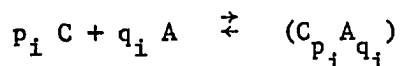
Direct measurements have the advantage that the data are obtained unambiguously and with a high degree of accuracy. The data in the equilibrium approach usually consist of the dependence of the cmc on some particular variable. The cmc must be obtained from the dependence of some physical property on concentration, and the actual number obtained depends on the particular definition of the cmc used. Unfortunately this is an arbitrary choice and in addition it is necessary to make several other assumptions in order to simply relate the cmc and the equilibrium constant, which is the quantity of interest. Stenius, Backlund and Ekwall have recently published an

excellent review which includes a valuable tabulation of thermodynamic data (47).

a. Equilibrium Measurements

If micellization is modelled as an association process, or as a phase transition, then changes in thermodynamic functions can be derived from van't Hoff type relations (11,56). The effect of temperature on the cmc is very small, and the best obtainable precision must be used to determine it (16). The cmc itself is sensitive to the presence of very small amounts of surface active impurities, but these are hoped to have little effect on changes with temperature, and it is the derivative with respect to temperature which gives the desired quantity.

A complete description of the aggregation process must account for a series of association equilibria:



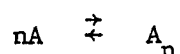
where C is the counter ion, A the amphiphile ion and q_i is the i-th aggregation number. The most common values of q_i lie between 20 and 80, while the fraction of counterions bound to the aggregate,

$$r_i = q_i/p_i$$

lies between 0.4 and 0.8 (47). It is usually sufficient to describe the thermodynamics of micelle formation in terms of average quantities defined on the basis of some model of aggregation. In order for quantities measured by different investigators to be compared it is

essential that the association model, the choice of standard states and the units used be clearly stated. The data published so far represent diverse choices (often unstated) of these details, and include much work of questionable quality (47).

The most basic example of this approach is based on a single equilibrium between neutral (nonionic) monomers and micelles:



in which A and A_n represent monomer and micelle respectively. The thermodynamic equilibrium constant is

$$K = \frac{[A_n]}{[A]^n}$$

where the brackets indicate the appropriate activities. In the discussion of the calorimetric results (vide infra) we will return to a more complex form of this model (the mass action model) which takes account of the contributions of the individual ions. It is often assumed (the phase separation model) that above the cmc the activity of the micellar species is constant and the monomer activity is equal to the cmc. Hence

$$K \propto 1/[\text{monomer}]^n$$

Therefore K is usually approximated by

$$\ln(\text{cmc}) = -\ln K / n$$

A number of excellent discussions of this method of calculating thermodynamic quantities exist (16, 56, 57). It appears to be

sufficient to approximate the standard free energy of micelle formation by (16):

$$\Delta G_M^0 = RT \ln (\text{cmc}) - \frac{RT}{n} \ln X_n$$

where X_n is the mole fraction of micelles. Differentiation with respect to temperature and pressure leads to

$$\Delta H_M^0 = RT^2 \frac{d \ln (\text{cmc})}{dT} + \frac{RT^2}{n} \frac{d \ln X_n}{dT}$$

$$\Delta V_M^0 = RT \frac{d \ln (\text{cmc})}{dP} - \frac{RT}{n} \frac{d \ln X_n}{dP}$$

The aggregation number, n , is often not known precisely, for which reason most investigators neglect the second term on the rhs of all three expressions (16). This probably results in only a relatively small error in the calculated values since n is usually large (6). Standard entropies of micelle formation are calculated from

$$\Delta G_M^0 = \Delta H_M^0 - T \Delta S_M^0$$

Enthalpies and heat capacity changes may also be obtained from calorimetric measurements, and it is of interest to compare the results obtained by the two approaches, although at the present time there do not appear to be any systematic trends in the differences (vide infra). A few thermodynamic quantities for some representative surfactants are listed in Table I-1 (47).

As Rosenholm, Burchfield and Hepler (57) and Muller (56) have pointed out, these equations are directly applicable only to

equilibrium constants expressed as functions of activities defined in terms of temperature independent measures of composition. Examples are mole fraction and molality, but not molarity. Probably the most serious difficulty with applying the van't Hoff equation to micellar equilibrium is that the nature of the equilibrium may change with parameters like temperature. For instance it is thought that n , the mean aggregation number, varies with temperature (6, 33, 56). Also it may be necessary to consider multiple equilibria of type (1) in order to properly account for observed behavior. Muller (56) has discussed the dependence of n on temperature in some detail and described a method of dealing with it.

The assumption that activity coefficients are unity is an acceptable approximation for dilute solutions of nonionic surfactants (57), many of which have very low cmcs anyway. For ionic surfactants, counterion binding and electrostatic effects are certain to complicate the problem at much lower concentrations (cf. 7).

Surfactant solutions exhibit very abrupt changes in most solution properties over a very narrow concentration range. However, the abruptness or degree of discontinuity of the change may vary several orders of magnitude within the range of substances generally classified as surfactants. In addition, the nature (shape) of the discontinuity and hence the values of thermodynamic quantities derived from its behavior vary depending on the property under consideration even for a single surfactant. Thermodynamic values obtained this way are in fact in substantial disagreement (see Table I-1) and direct calorimetric measurement of thermodynamic quantities over a wide range

of concentrations is obviously a more promising approach. It is certainly more difficult.

b. Direct Measurements

Enthalpies and heat capacities are commonly determined directly from calorimetric measurements. Volume data are often obtained as a result of the necessity of knowing accurate densities in order to do good calorimetry. Free energies, expansibilities and compressibilities may also be measured directly.

Free energies of surfactant solutions are derived from measurements of the activity of the solute (or solvent). Any colligative property measurement can be used to calculate activities. Christian and co-workers (19, 20) have determined activities of solubilizates from extremely accurate automated vapor pressure measurements. A relatively new development which has an enormous potential is the use of surfactant selective ion electrodes, such as the work of Kale, Cussler and Evans (25), Sasaki, et al. (58), and Cutler, Meares and Hall (24, 59). Much useful information about the aggregation process is obtainable from selective ion electrodes specific to some anionic or cationic surfactant monomer. Free energies, of course, can be calculated directly from the EMF data.

Most microcalorimeters or precision solution calorimeters can be used to determine enthalpies. Cell type instruments have been used (60), but flow microcalorimeters have the advantage of being faster (61). A large number of direct enthalpies of micellization have

been reported in the past (16), but in view of the complexity of the aggregation process which is now emerging it is doubtful whether many of these are actually reliable.

Heat capacities may be calculated from the variation of enthalpy with temperature or they may be measured directly with a flow microcalorimeter. Volume data are almost always calculated from density measurements. A flow version of the vibrating tube density meter may be connected in series with a flow microcalorimeter, thus permitting all three quantities to be determined simultaneously. Expansibilities are obtained from variation of density with temperature and compressibilities are generally obtained from sound velocity data.

The basic equations of dilute solution thermodynamics may be found in any classical thermodynamics textbook (e.g. Klotz (62) or Harned and Owen (54)). Apparent molar quantities are the most conveniently accessible experimentally. Partial molar quantities are calculated from the apparent molar quantities. The relevant equations will be illustrated for the case of the relative partial molar enthalpy. The partial molar enthalpy is defined as

$$\bar{H}_2 = (\partial H / \partial n_2)_{T,P,n_1}$$

Since absolute enthalpies, $\bar{H}_2$, (unlike volumes) cannot be measured, the relative partial molar enthalpy is introduced

$$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^\circ$$

The apparent relative partial molar enthalpy is defined by

$$L_2 = \frac{L - n_1 \bar{L}_1^\circ}{n_2} = \frac{L}{n_2}$$

where L is the total quantity and $\bar{L}_1^\circ$ is the relative partial molar enthalpy of the solvent in its standard state (pure phase, 1 atm and 298.15 K). ($\bar{L}_1^\circ$ is zero by definition for the relative partial molar enthalpy, but has been included to give the equation the correct form.) The relative partial molar enthalpy is related to the apparent relative partial molar enthalpy by

$$\bar{L}_2 = \frac{d}{dn_2} (n_2 \phi L_2)$$

Molality, m , and mole fraction, n_2 , are equivalent in aqueous solutions.

The apparent relative partial molar enthalpy is obtained from heat of dilution or heat of solution experiments. For example:

$$\Delta H_{\text{dil}} = \phi L_2(\text{final}) - \phi L_2(\text{initial})$$

Once ϕL_2 is known as a function of composition $\bar{L}_2$ can be calculated. Unfortunately in the region where micellization occurs ϕL_2 is changing rapidly and it is nearly impossible to represent ϕL_2 by a polynomial and quite hazardous to try to differentiate such a polynomial to obtain $\bar{L}_2$. In this region calorimetrists often still resort to graphical methods, or their computer equivalents.

The standard functions for volume, $\bar{V}_2$, expansibility, $\bar{E}_2$, compressibility, $\bar{K}_2$, and heat capacity, $C_{p,2}^\circ$, reflect intrinsic properties of solute molecules and of solute-solvent interactions. These functions appear to show excellent group additivity. These results have been summarized recently by Desnoyers (14).

Below the cmc most apparent molar quantities (for ionic solutes) may be fitted to an extended form of the Debye-Huckel equation:

$$\phi Y = \phi Y^\circ + a_0 c^{\frac{1}{2}} + a_1 c + \dots$$

where ϕY° is the standard state value, a_0 is the theoretical slope predicted by Debye-Huckel theory. There has been much discussion about the significance of a_1 . The trends and theories are summarized by Desnoyers (14).

The shape of the $\bar{L}_2$ curve appears to be rather similar for several surfactants. There is no adequate theory at present to account for the behavior of $\bar{L}_2$ once aggregation begins. This is a major area of development in the field, and one of the primary concerns of this research.

Such data might be used for the study of amphiphile association in the region below the cmc, for insight into the micelle formation process itself, and for the study of micelle-micelle, micelle-monomer and micelle-counterion interactions in the region above the cmc. A fair amount of calorimetric data exists for a number of surfactants. Unfortunately, most of these results have been manipulated prior to publication using models which do not correctly include such effects. For some reason, investigators seem more interested in determining some specific quantity, such as the enthalpy of micellization, and its implications for some particular model than in presenting (or determining) quantities of general usefulness such as partial molar quantities.

v. Surfactant Adsorption

An understanding of the adsorption behavior of amphiphilic substances is of interest to numerous disciplines (63), an excellent example of which is the enhanced oil recovery problem referred to above.

The adsorption of anionic surfactants on mineral oxide surfaces has been observed to display a characteristic adsorption isotherm (64, 65, 66). This isotherm is composed of four regions, representing different interaction regimes. The four regions are (i) an initial Henry's law region, (ii) a region of rapidly increasing adsorption (positive second derivative), (iii) a region of more gradually increasing adsorption (negative second derivative) and (iv) a plateau (64, 66, 67, 68). The transition from region iii to region iv generally occurs very near to the cmc. Much of the effort in this area in the past has dealt with mixtures of surfactants which were not isomerically pure. This circumstance is responsible for the often unusual results reported in the older literature (e.g. maxima and minima in the isotherm) (66). This has complicated the development of thermodynamic models to describe the phenomena.

The existence of a plateau region has been rationalized in terms of the phase separation model. The PSM predicts that the

monomer concentration above the cmc is constant and equal to the cmc (66, 69). Since micelles should not interact significantly with the surface, the adsorption must also become constant. It might seem reasonable to assume that the plateau corresponds to monolayer coverage of the surface. However, work using a variety of techniques indicates that coverage is not necessarily complete, and that the adsorbed species is structured into bilayers rather than monolayers (66).

The structure of the bilayer is thought to be that of Figure I-5 with the ionic head groups located next to the solid surface and in contact with the aqueous phase and the hydrocarbon groups forming a hydrophobic region in between. Interfacial densities of alkylsulfate/sulfonate surfactants fall in a range of about 0.02 to 0.03 molecules/A² (67). The interfacial density corresponds to a monolayer. Calculating adsorption densities of the bilayer on the basis of these densities compares quite well with measured adsorption densities (66).

The surface potential of mineral oxides is dependent on pH (70). Hence the strength of the interaction between an ionic species and the charged surface will vary with pH. The surface potential of alumina is nearly zero, or slightly positive at neutral pH (6.5 - 7.5), while that of montmorillonite is negative in this range (66, 70). Anionic surfactants would therefore be expected to interact strongly with alumina, but only weakly with montmorillonite at neutral pH. The surface potential becomes increasingly positive at lower pH, and it is thought that complete surface coverage only occurs under these conditions (66). However, the observed variation with pH is not large,

and it will be assumed in this work that complete coverage has been reached.

Lewis and Rehfeld (71) have measured heats of adsorption of several anionic, cationic and nonionic surfactants on various mineral oxide surfaces and their results indicate that anionic surfactants do interact much more vigorously with alumina than with montmorillonite. This is obviously an area in which a great deal of work might be done. Since calorimetric methods have proven to be productive means of studying surfactant behavior it was thought that an investigation of heats of adsorption might also yield important insights. For this reason some measurements were made using surfactants already well characterized and some typical mineral oxide surfaces in order to determine to what extent useful insight into adsorption of surfactants at solid surfaces might be obtained by this method. The results are described below.

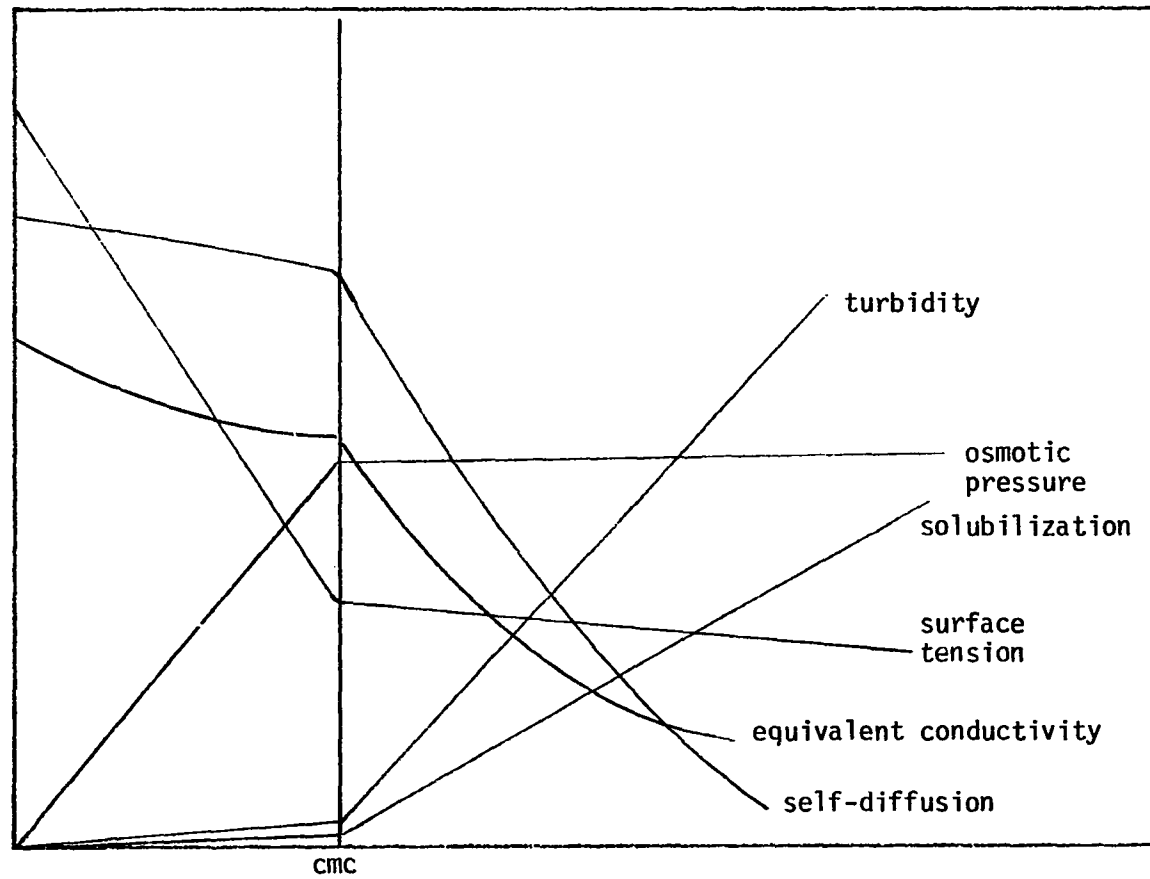


Figure I-1: Schematic diagram of the concentration dependence of several common physical properties showing the abrupt change at the cmc. From Ref. 8.

sodium octylsulfate
sodium octylsulfonate
sodium octylbenzenesulfonate
sodium octanoate

dodecylpyridinium bromide
cetyltrimethylammonium bromide

n-dodecyl methylsulfoxide
n-dodecyl dimethylphosphineoxide

sodium deoxycholate

Figure I-2: Some typical examples of micelle forming amphiphiles. The first four are anionic, the next two are cationic, the next two are nonionic, while the last is a biological amphiphile which forms micelles somewhat differently from the rest.

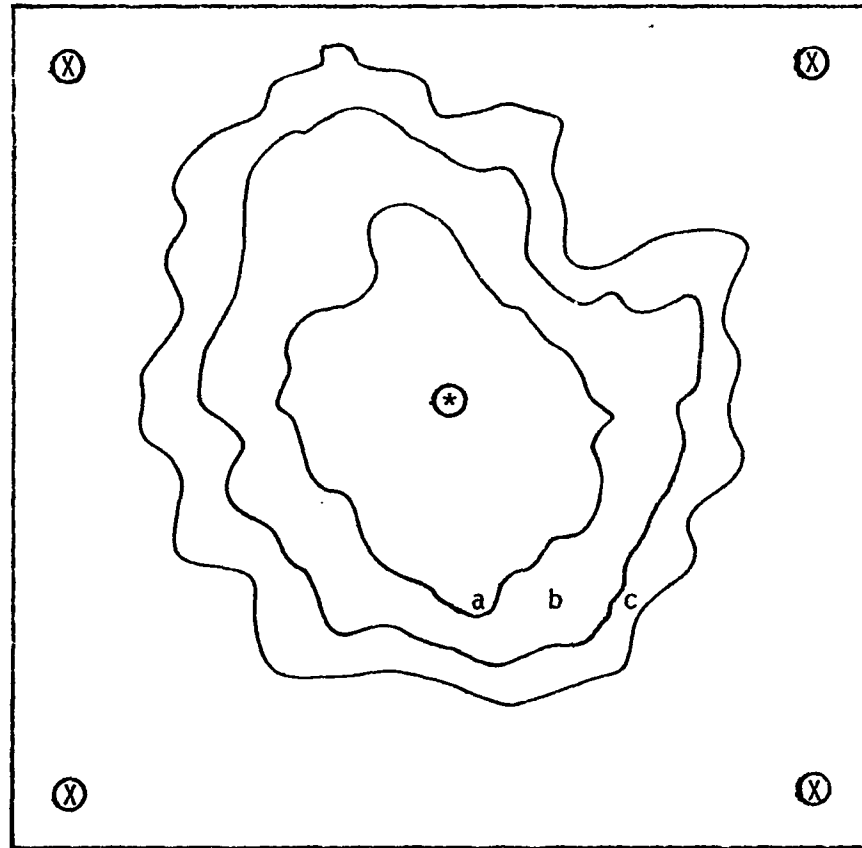


Figure 1-3: Illustration of the method of enhanced oil recovery by injection of a surfactant slug followed by a polymer slug. The four injection wells are marked X and the production well is marked *. The advancing oil is marked a, the surfactant solution b, and the polymer c.

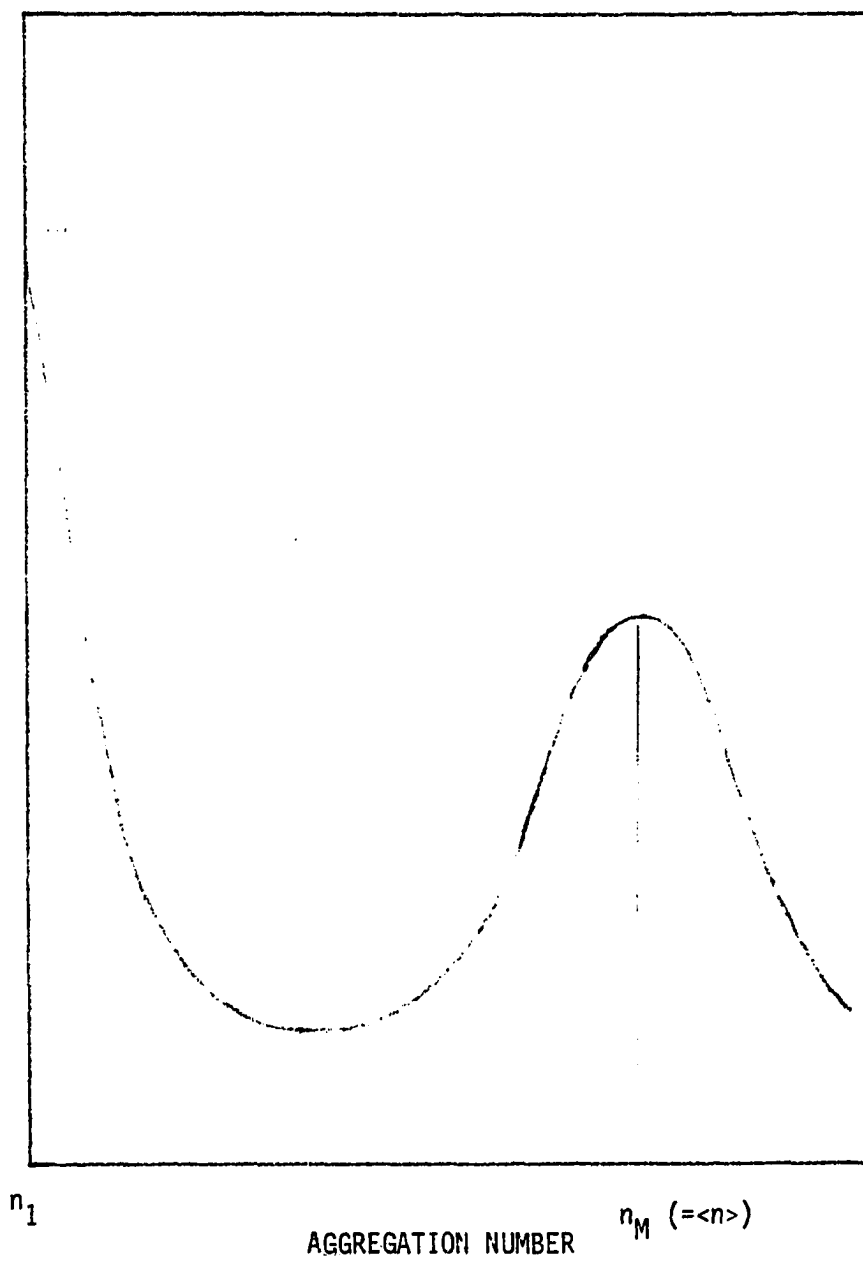


Figure I-4: Distribution of species in a micellar solution.

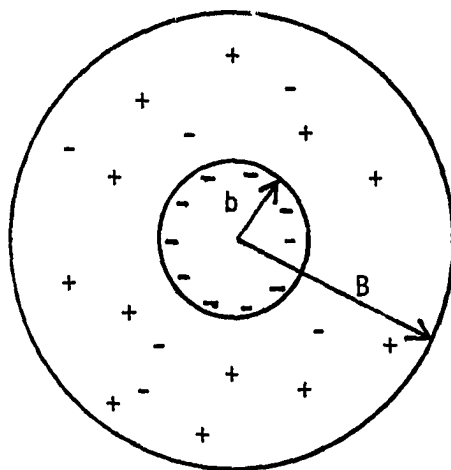


Figure I-4: Diagram of the cell model used in the PB model (7). Spherical micelle of radius b in a spherical cell of radius B . From Ref. 7.

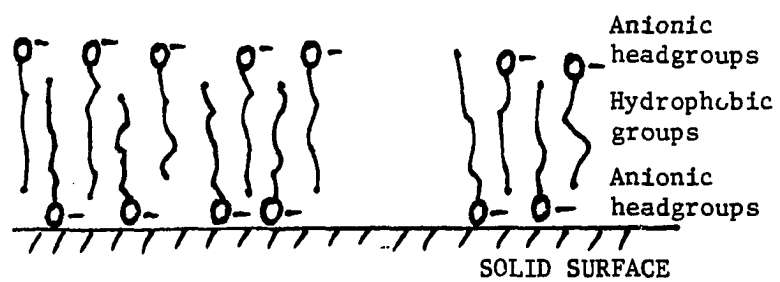


Figure I-5: Diagram of bilayer structure of surfactant adsorbed at solid surface. After Ref. 66.

Amphiphile	T (K)	ΔH_m (kJ/mol)
Na dodecylsulfate	298	2.51
	298	-4.2
	298	-0.38
	303	-2.76
	303	-1.26
	303	-3.31
	303	-2.09
	303	-2.09
dodecyltrimethyl- ammonium bromide	298	-1.39 (cal)
	298	-1.58 (cal)
dodecylpyridinium bromide	298	-4.06
	298	-3.47 (cal)
	303	-5.48
	303	-5.56 (cal)
	308	-6.57
	308	-7.32 (cal)

Table I-1: Selection of representative heats of micelle formation (from 47). Values determined calorimetrically are marked (cal).

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CHAPTER II

OBJECTIVES AND APPROACH

The four objectives of this research are:

- (1) To provide accurate relative molar enthalpy data for sodium octylsulfate, sodium octylsulfonate and sodium octylbenzenesulfonate in aqueous solution at 298.15 K and 308.15 K.
- (2) To develop insight into amphiphile aggregation over a range of concentrations including pre-micellar aggregation, micelle formation and post-cmc interactions
- (3) To provide heat of adsorption data for the adsorption of these three surfactants on alumina, and montmorillonite at 298.15 K.
- (4) to provide insight into the adsorption of amphiphiles at the solid-liquid interface.

The method of approach to achieve these objectives will be to make heat of dilution and heat of solution measurements with a precision solution calorimeter. Heats of immersion will be used to determine adsorption enthalpies. Heats of dilution will be extrapolated to infinite dilution to obtain relative apparent partial molar enthalpies.

Assumptions used in treating the relative partial molar enthalpy data in order to elucidate amphiphilic aggregation behavior include:

(1) Deviations from Debye-Huckel limiting law behavior are entirely due to hydrophobic association.

(2) The micelle may be modelled using an average aggregation number, $\langle n \rangle$, and a single, formal degree of counterion binding.

In treating heat of adsorption data it will be assumed that:

(1) Adsorption occurs at concentrations high enough to consider bilayer coverage to be complete.

(2) The orientation of the surfactant molecule on the surface is such that its cross-sectional area may be calculated from headgroup dimensions.

CHAPTER III

EXPERIMENTAL

i. General

Enthalpy data were measured using a Tronac 450/550 precision solution calorimeter. This instrument has been described in the literature (1, 2, 3). The 450/550 model may be operated in the isoperibol (constant surroundings) mode or the isothermal mode. Heats of dilution and heats of solution of three surfactants were measured in water at 298.15 K and 308.15 K. The three surfactants were sodium octylsulfate (SOS, $\text{cmc} = 0.14$ molal, 4, 5), sodium octylsulfonate (SOSN, $\text{cmc} = 0.18$ molal, 5), and sodium octylbenzenesulfonate (SOBSN, $\text{cmc} = 0.0128$ molar, 6). Densities of all three were measured at 298.15 K and 308.15 K. Heats of solution and densities were measured over a concentration range from 0 to 0.7 molal for SOS and SOSN and from 0 to 0.2 molal (limit of solubility) for SOBSN. In addition heats of adsorption on aluminum oxide and natural and sodium exchanged homoionic montmorillonite were measured at 298.15 K.

ii. Calorimeter

The Tronac calorimeter basically consists of a glass dewar reaction vessel (RV) immersed in a constant temperature water bath. Figure III-1 is a diagram of the calorimeter. The water bath is stable over a short period of time (hours) to within 0.0001 C, and over a long period of time (weeks) to within 0.0005 C. The Tronac cooled heater design requires a source of chilled water at a reasonably constant temperature. This was provided by using a Coolflow-25 water chiller to cool the water in a 15 gal Coleman ice chest, which was then pumped through the Tronac. The temperature of the bath was set using a mercury in glass thermometer accurate to within 0.005 deg C. The bath temperature was monitored using a Hewlett-Packard 2804A quartz thermometer. The bath temperature was the temperature at which the experiment was performed since in these experiments actual temperature changes were very small (<0.01 deg C). Thus the temperatures at which the experiments were performed were 298.15 K and 308.15 K within 0.01 K.

The RV and its contents will be referred to as 'the system'. The RV used in this work had a capacity of 50 ml. The contents of the RV are stirred by a constant speed motor (400 rpm) The glass stirring rod supplied with the instrument was replaced by a stainless steel one

made by the Physics Department Instrument Shop. It was constructed of a special cryogenic tubing which is so thin that longitudinal heat flow is nil. This stirring rod was not used in corrosive solutions. A thermistor and a resistor extend down into the liquid (see Figure III-2). A 2.5 ml Gilmont precision buret partially submerged in the water bath provides the titration capability. The stirring rod may be substituted with one which has a cradle and hammer assembly for holding and crushing glass ampoules and thereby measuring heats of solution and heats of immersion.

The resistor is used as a heater to electrically calibrate the system. It is wired in series with a precision resistor ($R=100.03$ ohms) which is immersed in the constant temperature water bath. The voltage across both of these resistors may be measured (HTRI and HTRV respectively). The electrical energy dissipated in a time interval, t , may be calculated from:

$$H_e = (HTRI)(HTRV)t/100.03$$

The temperature of the contents of the RV is monitored by the thermistor, which is wired into a Wheatstone bridge. The measured quantity is the so-called 'out-of-balance' voltage of this Wheatstone bridge as the resistance of the thermistor changes. Over small temperature intervals the resistance of a thermistor is linearly proportional to temperature. Over small voltage intervals the out-of-balance voltage of a Wheatstone bridge is linearly proportional to the change in resistance of the variable element. Both of these effects are included in the electrical calibration as well as the

titration/run, and therefore, as long as the magnitude of the change in temperature during the electrical calibration is close to that of the titration/run any non-linear effects should cancel out.

The balance point of the bridge may be adjusted by varying the resistance of a set of potentiometers on the front panel of the 450 electronics. The bridge is balanced (set to zero voltage) at the bath temperature, T_b , with the thermistor immersed in the bath. For careful work the bridge must be zeroed every day. The potentiometer resistances are slightly dependent on room temperature. It is therefore desirable that the room be kept at a reasonably constant temperature (within 2 deg C). The response time of the thermistor is fast (< 0.1 sec), and thus, to the extent that the system may be considered to be adiabatic, the shape of the thermogram (plot of temperature vs. time or titrant volume) may be interpreted in terms of specific equilibria.

iii. Computer Interface

I have interfaced the Tronac calorimeter to an Apple II computer for two reasons: to allow a very precise clock to control the time-base of the experiments, and to permit the data to be processed directly by the computer, thus eliminating the error-prone and tedious procedure of manually processing such data. Figure III-3 is a diagram of the complete system. Experimental control of the calorimeter means that the computer operates two switches in the calorimeter: the on/off switch of the buret, and the on/off switch of the electrical calibration heater. The circuitry is already in place for these switches to be controlled electronically. The relevant part of the circuit diagram of the 450 electronics is reproduced in Figure III-4 along with a circuit diagram of the interface. Essentially, there are two opto-isolators which are operated by logic level voltages: +5 V is on and 0 V is off. The Apple II has a game port which includes four terminals which may be set high (+5 V) or low (0 V) by software commands (for instance POKE-16295,0 sets terminal AN0 high). However, these cannot be connected directly to the opto-isolators in the Tronac electronics because the Apple II cannot provide enough current to drive the opto-isolators.

The standard solution to this problem is to insert a transistor switch between the computer and the device. The UCN4401A chip was chosen because it incorporates four such switches in one simple integrated circuit. The other two switches may be used to provide software control of the switch which selects the output to the voltmeter. This chip draws only a very small current from the computer, but can provide more than enough current to drive the opto-isolators in the Tronac. Because the UCN4401A is an open collector device, and the Tronac has been wired with the two ground terminals of its opto-isolators tied together it was necessary to insert an additional opto-isolator between the Tronac and the UCN4401A. This harmless complexity would be avoided if a standard transistor switch, such as that described in the Apple II manual were used (8).

The data of an isoperibol experiment consist of the variation of the out-of-balance voltage across the thermistor with time. The timebase for the experiment is provided by a realtime clock manufactured by Mountain Hardware. Two schemes for making use of the clock are possible: the computer could read the clock and pair voltages with time readings, or time intervals. By far the more efficient method is to make use of the interrupt capabilities of the 6502 microprocessor (7). The 6502 μ P (the heart of the Apple II) is capable of being interrupted by an external device. That is, when a certain signal comes in it will stop what it is doing and proceed to a designated task. The Mountain Hardware clock is capable of sending such a signal. When the 6502 μ P stops what it is doing it will jump to an address in memory which is stored at memory location 03FE-03FF.

The routine stored at that location will be executed and the μP will resume what it was doing.

Two routines then, are required: one to set up the interrupt capability, and one to do something when the interrupt occurs. The binary routines to carry out these tasks are listed in Figure III-5. The set up routine stores the address of the second routine at 03FE-03FF, opens the 'gates' on the μP and the clock board to allow the interrupt through, then monitors the contents of memory location 0339 until it becomes 1. Control is then returned to the BASIC program. The second routine simply stores a 1 at 0339 and returns to the first routine. This round-about is necessary because there is no simple means to return from a second routine to the point in a BASIC program which called the first routine. The BASIC program reads the voltage and then repeats the process. With the exception of memory location 03FE-03FF the addresses were chosen on the basis of convenience.

It should be realized that the clock is generating interrupt signals all the time. They only reach the μP when both 'gates' are open. Thus, after reading the voltage the computer can do any necessary calculations or other needed tasks as long as the interrupt is reenabled before the next interrupt is issued by the clock. On a computer time scale there is a tremendous amount of time available for calculations between interrupts. As long as it always gets back to the clock before the next interrupt occurs the timebase of the experiment is unaffected. Obviously the sequence of events between the interrupt and the voltage reading actually being taken requires some time. The point is that this time is always the same (to within 0.001 sec) and

the interval between readings is therefore always 1.000 sec. This would be more satisfying if it were more elegant, if, say, the voltage could be read by a machine language routine.

The voltages are measured with a Hewlett-Packard 3455A voltmeter which is interfaced to the Apple II by means of an IEEE-488 (GPIB) interface manufactured by California Computer Systems. This interface has some very nice features to it, among them the ability to connect some 14 instruments to the computer with one interface. Unfortunately, the manual supplied by the interface manufacturer is almost completely useless.

The interrupt capability must be completely re-enabled after every voltage reading. This is because the GPIB interface makes use of the 6502's interrupt ability also, changing, among other things, the contents of memory location 03FE-03FF. The operation of the voltmeter is such that it may be set up to allow the computer to trigger a reading (an A to D conversion), which will be sent to the computer as soon as it is available. This particular voltmeter scales every reading taken; thus even if the voltage changes by several orders of magnitude it requires only one cycle to shift scales.

iv. Experimental Methods

Each experiment consists of seven segments: (1) lead, (2) heat, (3) trail, (4) titration/run, (5) trail, (6) heat, (7) trail (see Figure III-6). Each titration/run is thus bracketed by two electrical calibrations. The parameters (the slope and intercept) of a linear fit of each lead/trail segment are calculated at the end of that segment from the appropriate sums (9, 10). These sums are calculated during the segment as each voltage reading is made, although only every tenth voltage reading is stored in memory, later to be transferred to disk for permanent storage. This means that for a 300 second segment, 300 points are used to calculate the slope and intercept, but only 30 are stored. This improves the certainty of the fit (decreases the rmsd) without making permanent data storage for archival purposes unmanagable.

It is desirable for theoretical reasons to pick the magnitude, sign and shape of the electrical calibration to match the chemical reaction being measured. Unfortunately, only the first of these is practical. The Tronac calorimeter is in fact isoperibol, not adiabatic - there is a substantial heat leak between the RV (the system) and the bath (the surroundings). Therefore the heat capacity measured by an electrical calibration will be a complicated function of

the heat of stirring, the self-heating of the thermistor, the heat leak, the heat capacity of the components and the thermal history of the experiment. Heat flow between the system and the surroundings is slow, even if substantial. Thus the thermal gradient does not reach a steady state for some time after the temperature in the RV has been substantially disturbed. This is part of the reason why it is necessary to allow a minimum of three hours for thermal equilibration before the experiment is begun. This is also part of the reason why it may be observed that the slope of the voltage vs. time curve at some voltage (above bath temperature) is rather dependent on the immediate thermal history of the apparatus. It is also dependent on such factors as the precise placement of the RV with respect to the stirrer.

The apparent heat capacity is obviously dependent on the quantity of material in the RV. The addition of material during a titration will add mass to the system, and hence increase its heat capacity. It will also increase the area of the walls of the RV in contact with the liquid, which will increase the rate of heat flow between the system and surroundings. Tronac asserts that these effects are linear with volume, which is nearly true. It should be pointed out that if the liquid level approaches, or passes the junction between the neck (one thick wall) of the RV and the dewar (two thin walls), strange and decidedly non-linear effects may occur. For the purposes of this work this region was carefully avoided, and it was assumed that the linear average of the before and after heat capacities could be equated to the actual heat capacity at the midpoint of the titration/run.

The heat capacities are calculated by extrapolating the linear fits of, for instance, segments 1 and 3 to the midpoint of segment 2. The change in voltage at the midpoint is calculated and the ratio of the electrical energy to the change in voltage (temperature) is the heat capacity.

The observed enthalpy change is calculated by extrapolating the linear fits of segments 3 and 5 to some point in segment 4 and the change in voltage calculated. This point is chosen on the basis of the shape of the curve. Theoretically the area above and below the midpoint should be equal (see Figure III-7). For a linear titration curve this obviously equals the geometric midpoint. For a non-linear curve the problem is best solved by numerically finding the point of balance. For some types of reactions (heats of immersion and heats of solution for instance) the shape of the curve is determined by first order kinetics (diffusion). This leads to a thermogram with an exponential shape. In this case the midpoint may be analytically calculated and turns out to be about:

$$t_0 + 0.37(t_f - t_0)$$

where t_0 is the point at which the reaction begins and t_f is the point at which it is essentially complete. The software can handle either of these alternatives.

It is obvious from an examination of Figure III-6 that the temperature of the contents of the RV will not, except by coincidence, equal that of the bath at the midpoint of the run. Since the titrant is kept at the bath temperature there will be a temperature

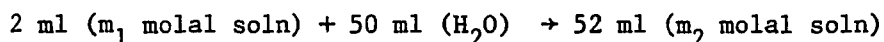
differential between the titrant and the RV contents during the titration which will give rise to an apparent heat effect which must be corrected for. Essentially, the temperature change on mixing two samples at different temperatures is a function of the respective volumes and heat capacities, and the temperature differential. The average temperature differential may be equated to the voltage at the midpoint of the titration since the bath 'temperature' is 0 V. However, only an apparent heat capacity is known, and only for the RV and contents. Furthermore, it is probable that the titrant undergoes viscous heating by flowing through the small bore teflon tubing, and this may not be very reproducible because of the irregularity of the bore. Nevertheless a correction of the form:

$$Q_c = -V(C_p - C_{p,rv})(E_{mid} - T_c)/(50 + V/2)$$

was tried. V is the volume of titrant, C_p is the average apparent heat capacity (average of C_p before and after the run), $C_{p,rv}$ is the heat capacity of the reaction vessel, E_{mid} is the temperature (mV) at the midpoint of the run, T_c is the temperature rise due to viscous heating and $50+V/2$ is the total volume in the RV at the midpoint. This was fit using a least squares method to the results of a series of water into water titrations in order to determine the best values of $C_{p,rv}$ and T_c . This correction turned out to be the major source of the uncertainty in the calculated enthalpies of dilution. For this reason it is felt that it could be improved upon.

Heats of dilution were measured by titrating 2 ml of

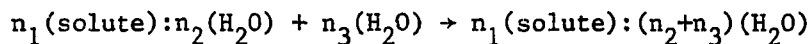
concentrated solution into 50 ml of a less concentrated solution, usually pure solvent (water). This experiment may be represented by:



The heat measured will be the heat to dilute 2 ml at concentration m_1 to 52 ml at concentration at m_2 . The two concentrations are related by:

$$m_1 = 26 m_2$$

If concentrations and volumes are converted to moles, the experiment may be represented by:



All solutions were prepared by weight for accuracy. The weight of the water was corrected for bouancy.

The precision buret was rinsed three times with 1.5 ml of the solution and then filled. The teflon tube was connected, 0.5 ml of solution flushed through it and the buret refilled. For subsequent runs with the same solution the buret had only to be refilled. The RV was then filled and attached under the chimney with a clamp. After centering the RV the stirrer was turned on and the insert assembly lowered into the water bath. The RV contents were heated to about 3 mV below the bath temperature (the thermistor zero). This provided about three hours for the system to reach thermal equilibrium before the experiment is begun at +0.1 mV. These numbers are arbitrary, but were used consistently to avoid unnecessary problems. Equilibration for at

least three hours is essential, as was discussed above. After the system has reached thermal equilibrium the experiment is begun. The computer control and experimental procedure has been discussed above. Each experiment was repeated twice more and the three values averaged.

Heat of solution and heat of immersion experiments were performed very similarly to this except that the buret was deactivated. The solute or immersant was loaded through a funnel fashioned from a disposable pipet into the glass ampoules purchased from Tronac. The ampoule was sealed and placed in the cradle. The remainder of the experiment was the same as before. Equilibration was less critical and, of course, no correction for temperature differentials had to be made. The heat of crushing was negligible for all the work reported here.

v. Chemical Calibration

A number of chemical standards are available for the calibration of calorimeters. For the purpose of calibrating a solution calorimeter the heat of protonation of tris(hydroxymethyl)aminomethane (tris, or THAM) with hydrochloric acid is recommended (11). THAM is a primary standard base, and may be obtained in very high purity. This reaction was performed as well as measuring heats of dilution of sodium chloride solutions. The procedure developed for titration of HCl into a solution containing an accurately weighed amount of THAM was such that the thermogram displayed a clearly defined endpoint. This permitted the concentration of the HCl to be determined very accurately without relying on an external standardization. The results were in excellent agreement with the literature (11). The heats of dilution of sodium chloride were not as successful partially because the heats in the lower concentration range were so small as to be insufficiently accurate to permit extrapolation of the results to infinite dilution. The higher concentration values were, however, in good agreement with Parker's data (12).

vi. Chemicals

Sodium octylsulfate was obtained from Kodak. It was purified by twice recrystallizing it in 2-propanol. The 2-propanol had previously been distilled from 99% 2-propanol on a 30 plate Oldershaw column. The SOS was subsequently washed twice with diethyl ether to remove the 2-propanol and allowed to dry in the hood. After air drying it was placed in the oven for 15 minutes and then kept under vacuum for 48 hours to eliminate the last traces of solvent. The yield was about 85%. The product was freely pouring white flakes which could be ground to pass a 100 mesh sieve. The surface tension after purification showed no significant dip in the vicinity of the cmc. This indicates that surface active impurities have been eliminated (13).

Sodium octylsulfonate was obtained as the monohydrate from Aldrich. A small amount was recrystallized in absolute ethanol. However a subsequent determination of surface tension indicated no significant dip in surface tension either before or after purification. Thereafter it was used as supplied for the calorimetric experiments.

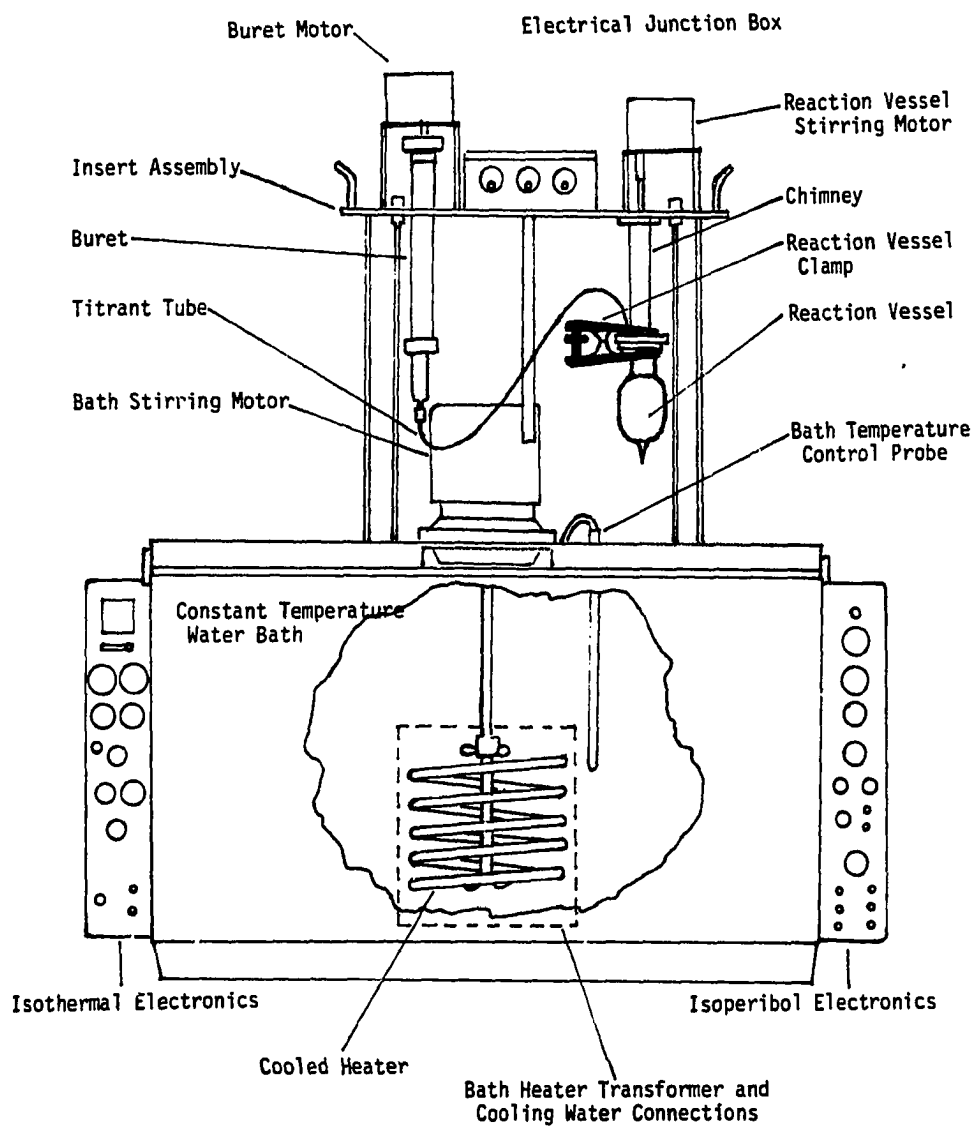
Sodium octylbenzenesulfonate was obtained from Fairfield Chemical Company. As supplied it contained a substantial quantity of extraneous material such as hairs and plastic fibers. SOBSN has a

Krafft point of 18 deg C (6) and hence is not very soluble in water at room temperature. It becomes very soluble at higher temperatures. Therefore it was dissolved in boiling water and filtered hot through a coarse glass frit. On cooling slowly to room temperature and then to 0 deg C in an ice water bath about 90% of the material recrystallized. This was filtered out and excess water removed under vacuum. At this point it still showed a significant dip in surface tension in the vicinity of the cmc. For this reason it was twice recrystallized in absolute methanol and dried under vacuum. Yield was about 85%. After this treatment it no longer showed evidence of the surface tension dip and was considered adequately pure for calorimetric experiments.

SAZ-1 montmorillonite was obtained from the Source Clay Minerals Repository. As supplied it was about 80% in the calcium form (14). In order to convert it to the sodium form 20 g were suspended in water in a 2 liter glass stoppered mixing cylinder. Two moles of NaCl were added and the suspension stirred vigorously overnight. Then the clay was allowed to settle to the bottom and the supernatant liquid siphoned off. It was washed twice more in this way with 1 M NaCl. Then it was washed with distilled water until the clay deflocculated. At this point it was washed three more times with distilled water and centrifuged in between to remove the water. This removed the excess electrolyte. The clay was dried in the oven overnight at 110 deg C and ground in an agate mortar and pestle to pass a 100 mesh sieve. In preparation for calorimetric experiments it was loaded dry into the Tronac ampoules and stored unsealed in a closed chamber over saturated sodium oxalate. This gives a relative humidity of 76% at 20 deg C

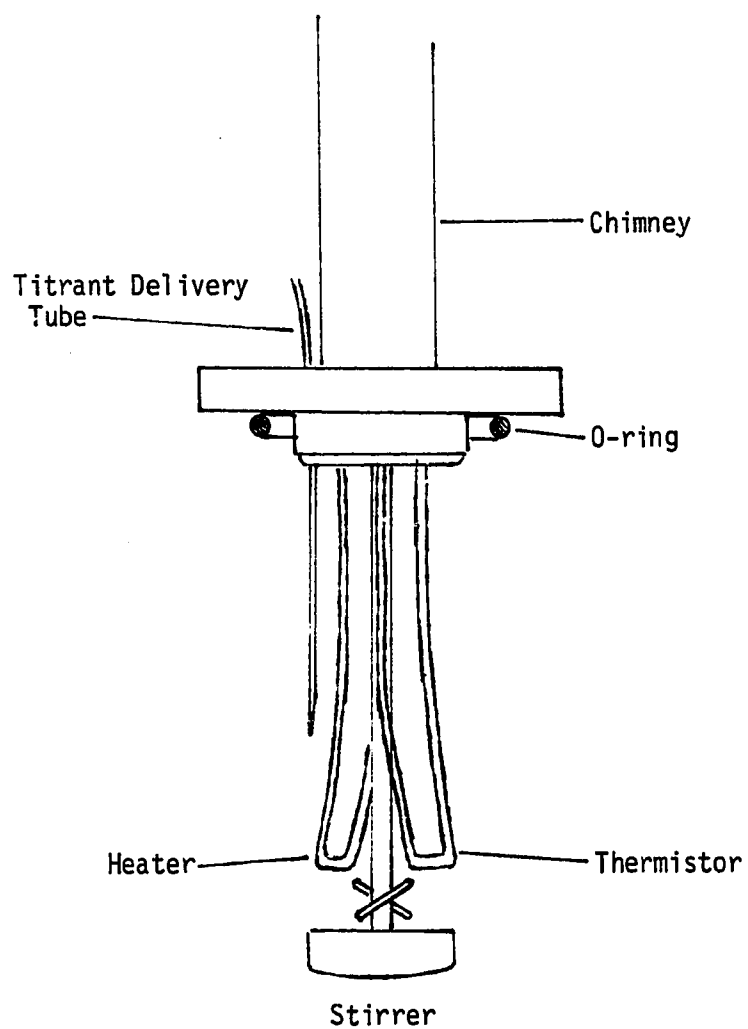
(15). This was done because it is much easier to accurately weigh the clay in a hydration state similar to that in air at ambient conditions. In addition the hydrated clay has a much smaller heat of immersion than does very dry clay. Isotherm data available in the literature (15) indicates that at about 75% R.H. the isotherm is relatively flat and the clay contains about 20% water by weight. This was confirmed by drying the clay in the oven at 110 deg C overnight, and then in vacuo at 100 deg C until its weight was constant, and comparing the wet and dry weights.

Alumina (Al_2O_3) was kindly furnished by Tom Burchfield at the Bartlesville Energy Technology Center. It was Fisher Reagent, cat. no. A-591, lot no. 530704. It was dried in the oven at 110 deg C overnight, then loaded into the Tronac ampoules. After it was weighed it was stored in a closed chamber at 76% humidity for one week. This was done to minimize the heat of immersion. It was weighed once more to determine the amount of water adsorbed, sealed and loaded into the calorimeter.



TRONAC 450/550 Calorimeter Components

Figure III-1: Diagram of the Tronac 450/550 batch calorimeter. From Tronac, Inc. operating manual, 1979.



Calorimeter Chimney With Reaction Vessel Removed

Figure III-2: Diagram of calorimeter chimney.
From Tronac 450/550 operating manual, 1979.

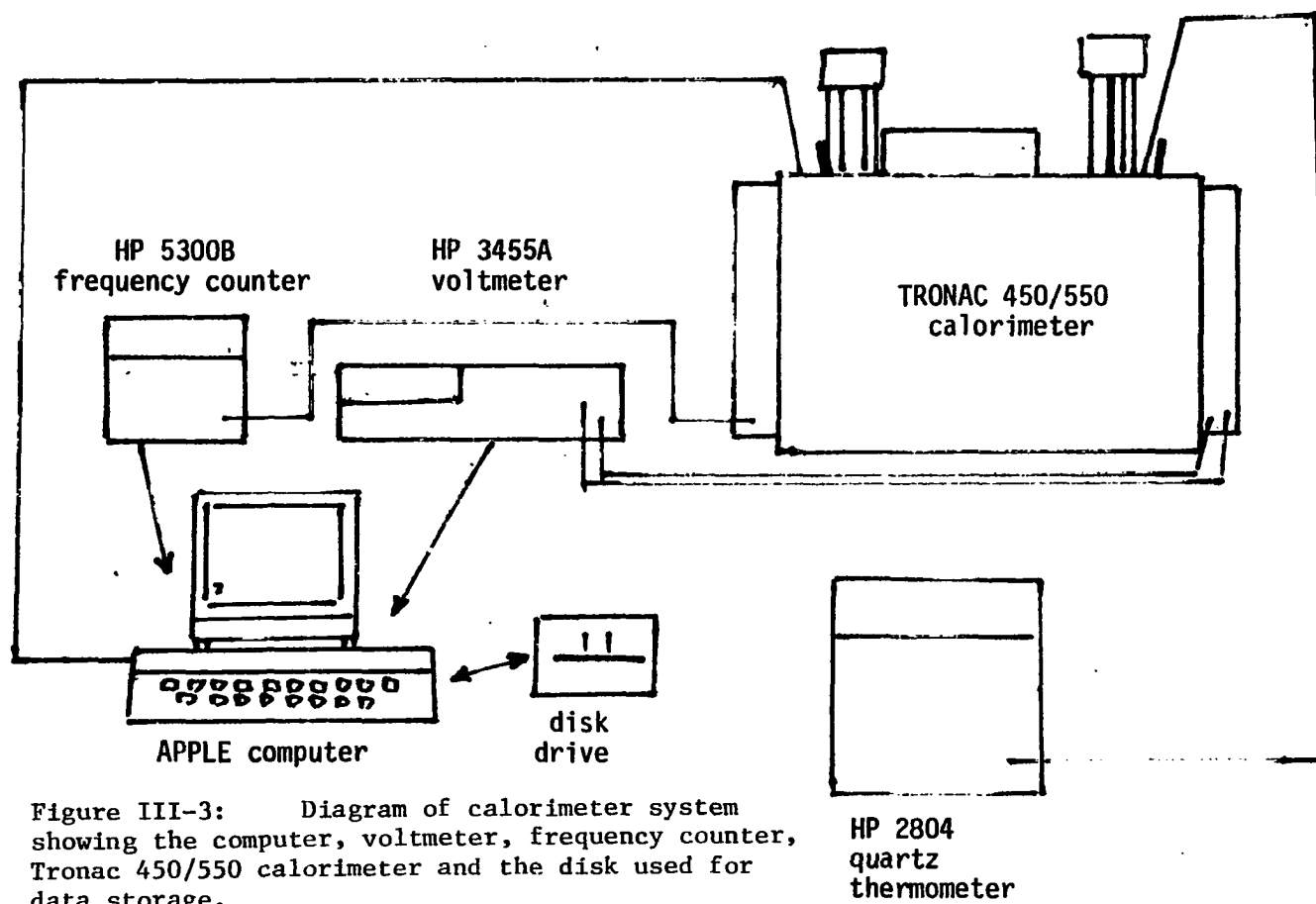


Figure III-3: Diagram of calorimeter system showing the computer, voltmeter, frequency counter, Tronac 450/550 calorimeter and the disk used for data storage.

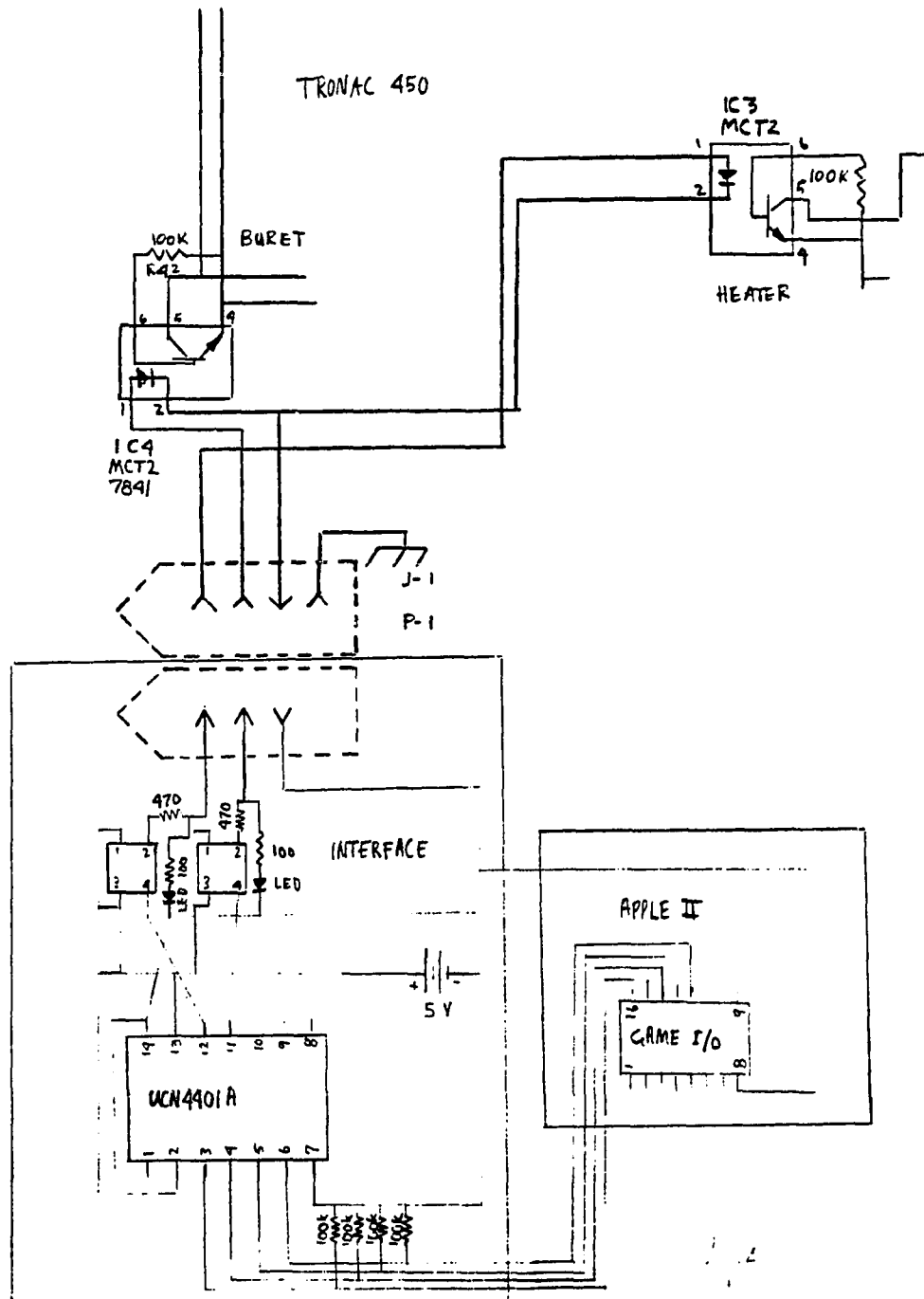


Figure III-4: Circuit diagram of the interface which was built for the APPLE II/TRONAC 450/550 calorimeter. The part of the diagram showing the Tronac 450 electronics was taken from blueprints provided by Tronac, Inc. with the instrument.

```

0300- 48          PHA
0301- 78          SEI
0302- A9 30       LDA  #$30
0304- 8D FE 30    STA  $03FE
0307- A9 03       LDA  #$03
0309- 8D FF 03    STA  $03FF
030C- A9 00       LDA  #$00
030E- 8D 2D 03    STA  $032D
0311- A9 01       LDA  #$01
0313- 8D D9 C0    STA  $COD9
0316- 58          CLI
0317- A9 01       LDA  #$01
0319- CD 2D 03    CMP  $032D
031C- D0 F9       BNE  $0317
031E- A9 00       LLA  #$00
0320- 8D D9 C0    STA  $COD9
0323- AD D7 C0    LDA  $COD7
0326- AD D8 C0    LDA  $COD8
0329- 68          PLA
032A- 60          RTS

```

(a)

```

0330- 48          PHA
0331- AD D7 C0    LDA  $COD7
0334- A9 01       LDA  #$01
0336- 8D 2D 03    STA  $032D
0339- 68          PLA
033A- 40          RTI

```

(b)

Figure III-5: Binary subroutines which set up clock interrupt, wait for interrupt, and act on interrupt. See text.

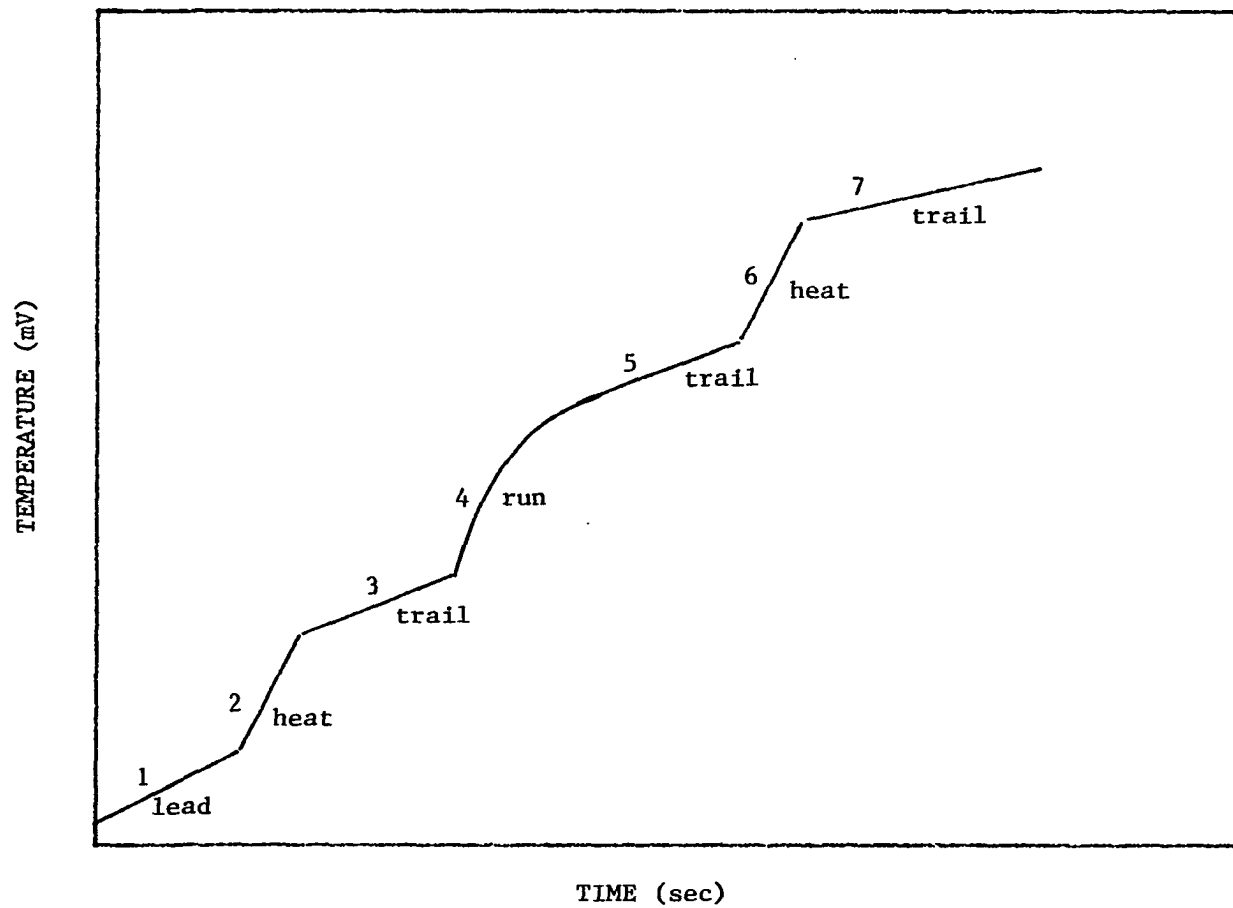


Figure III-6: Diagram of a typical calorimetric experiment consisting of a run/titration bracketed by electrical calibrations.

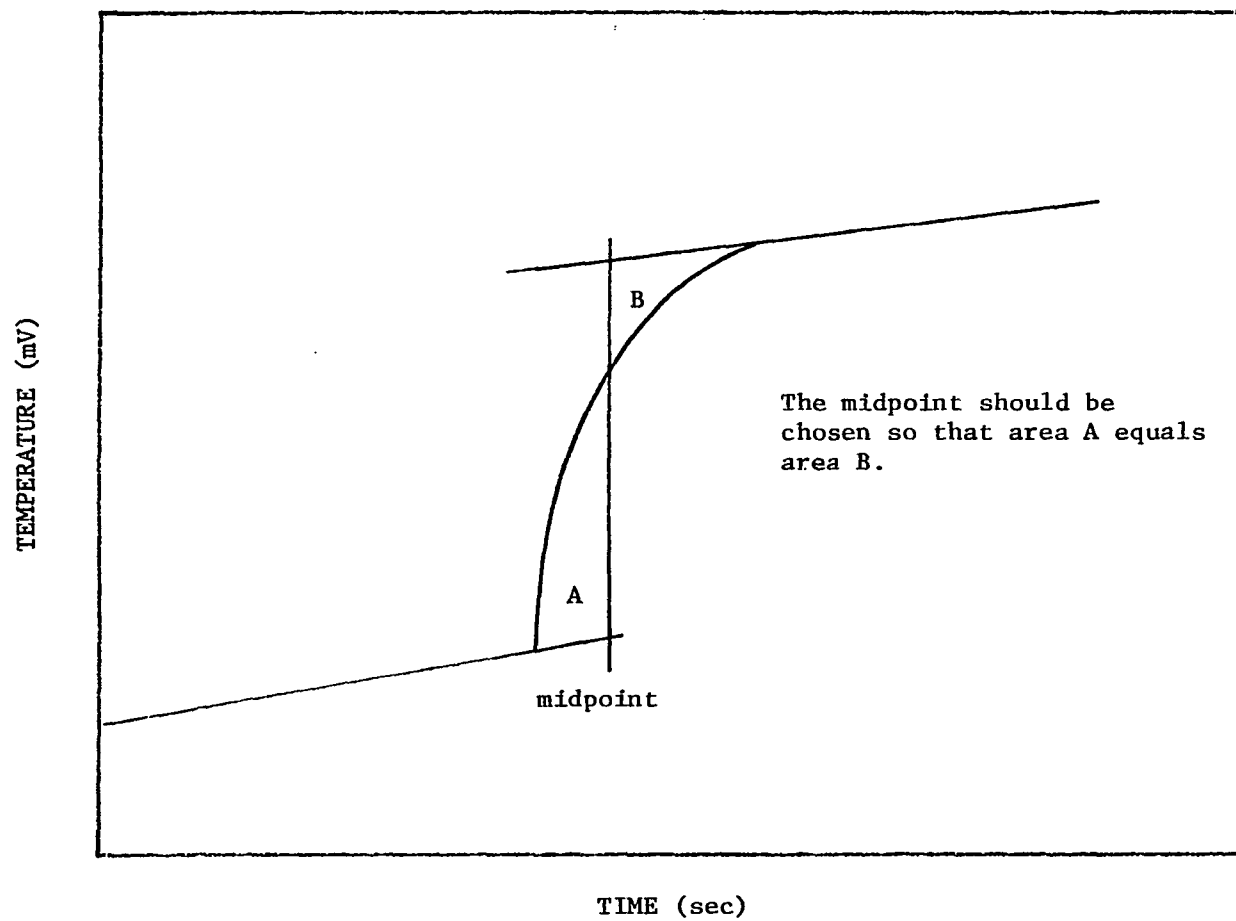


Figure III-7: Diagram of run/titration segment showing the method of determining the midpoint.

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CHAPTER IV

RESULTS

1. Sodium Octylsulfate

a. Density

In the calorimetric experiments the titrant (diluent) is dispensed by volume from a precision buret. However, it is much more accurate, and convenient, to prepare solutions by weight. Therefore it is necessary to have access to accurate density data.

The density of sodium octylsulfate at a few concentrations was measured at 298.15 K using the Mettler/Paar DMA 40 digital density meter. The measured values agreed with data reported by Musbally, Perron and Desnoyers (1) within experimental error. Therefore their data were fit using a least squares procedure to an expression of the form:

$$d = d_0 + 10^{-3} (a_1 m + a_2 m^2 + a_3 m^3) \quad (1)$$

and this expression was used in all subsequent calculations. Values of the parameters are given in Table IV-1. Densities were measured at

308.15 K over the range of the calorimetric experiments since no data has been reported in the literature at this temperature. The results are tabulated in Table IV-2, and the parameters of the fit to Eqn. (1) are given in Table IV-1.

b. Enthalpy

Integral heats of dilution of sodium octylsulfate in aqueous solution were measured with the Tronac calorimeter over the range 0 to 0.7 molal at 298.15 K and 308.15 K. The dilution factor was always 1:25. The data at 298.15 K is given in Table IV-3 and the data at 308.15 K in Table IV-4. Molar integral heats of dilution were calculated using the density results referred to above. Molar integral heats of dilution are also tabulated in Tables IV-3 and IV-4 and are plotted in Figure IV-1. Because the Debye-Huckel formalism is most conveniently written in terms of molar concentration units molalities were converted to molarities which are included in Tables IV-3 and IV-4.

The integral heat of dilution is related to the relative apparent partial molar enthalpy, ϕL_2 , by:

$$\Delta H_d = \phi L_2(\text{final}) - \phi L_2(\text{initial}) \quad (2)$$

For electrolyte solutions ϕL_2 may conveniently be expressed as the sum of a square root term (the Debye-Huckel limiting law, DHLL) and higher

order terms which account for nonideality (7):

$$\phi L_2 = a_0 c^{\frac{1}{2}} + a_1 c + a_2 c^2 \quad (3)$$

Where a_0 is the DHLL slope and is equal to 1975 at 298.15 K and 2248 at 308.15 K (the units are J/mol/(mol/L)^{1/2}, 2). A number of terms were tried as corrections to DHLL behavior including $c^{3/2}$, $c^{5/2}$ and c^3 . The combination of a linear term and a quadratic term was ultimately used because it gave the best fit of the data. The precise significance of a_1 and a_2 is open to debate. In this work it will be assumed that all deviations from DH behavior are due to association effects. On this interpretation a_1 and a_2 are interaction coefficients of dimerization and trimerization respectively (3). Thus a_1 and a_2 are not considered to be due to electrostatic effects (but see Chapter V and Ref. 4).

Using Eqn.'s (2) and (3) the pre-cmc heat of dilution data was fit using a least squares procedure from which a_1 and a_2 were determined, a_0 was not permitted to vary. The resulting parameters are listed in Table IV-5. Values of ϕL_2 ($= \phi L_2(\text{pre-cmc})$) were calculated at all final concentrations using Eqn. (3) and this quantity added to the measured heat of dilution to give the heat of dilution to infinite dilution. This is, of course, equal to ϕL_2 at the initial concentration. Figure IV-2 is a plot of the data in the pre-cmc region at 298.15 K along with the function representing the best fit to the data. The data and the best fit function at 308.15 K are plotted in Figure IV-3. Note that all final concentrations were well below the cmc. Thus it is reasonable to calculate the heat of dilution from the

final concentration to infinite dilution from $\phi L_2(\text{pre-cmc})$, even for solutions which have an initial concentration well above the cmc. Values of ϕL_2 are tabulated in Tables IV-6 and IV-7 and are plotted in Figure IV-4.

$\bar{L}_2$ is obtained from ϕL_2 by differentiation. Numerical differentiation is always hazardous, hence it was decided to smooth the data in the post-cmc region by fitting it to some mathematical function, and calculate the derivative analytically. Examination of the post-cmc region of both relative apparent partial enthalpy curves reveals that a convenient mathematical function with the same general behavior is an exponential function of the form:

$$\phi L_2 = a_1 + a_2(c - \text{cmc}) - a_3 \exp(-a_4(c - \text{cmc})) \quad (4)$$

The cmc of sodium octylsulfate is taken to be 0.14 mol/L (5, 6). The post-cmc data were fit to this equation and the parameters are given in Table IV-7. Figure IV-5 is a plot of ϕL_2 at 298.15 K along with the function representing the best fit of the post-cmc data. The results at 308.15 K are plotted in Figure IV-6.

The relative partial molar enthalpy is related to the relative apparent partial molar enthalpy by:

$$\bar{L}_2 = \frac{d}{dn_2} (n_2 \phi L_2)_{n_1} = \phi L_2 + m \frac{d\phi L_2}{dm} \quad (5)$$

where the derivative is taken with respect to mole fraction, or equivalently, molality. However, since the above relative apparent partial molar enthalpy is written in terms of molarity it is necessary to include another factor:

$$\bar{L}_2 = \phi L_2 + m \frac{d}{dc} \frac{dc}{dm} \phi L_2$$

Molarity is related to molality by:

$$c = m\rho / (1 + m \text{ FW}/1000)$$

$$m = c / (\rho + c \text{ FW}/1000)$$

where c is the molarity, ρ is the density in g/cm³, and FW is the formula weight in grams. The correction term may be calculated as follows:

$$\frac{dc}{dm} = \frac{\rho}{1 + m \frac{\text{FW}}{1000}} - \frac{m\rho \frac{\text{FW}}{1000}}{\left(1 + m \frac{\text{FW}}{1000}\right)^2}$$

$$\text{Let } A = m \text{ FW}/1000$$

$$= c \text{ FW}/1000 / (\rho - c \text{ FW}/1000)$$

$$B = c \text{ FW}/1000$$

$$\text{Then } A = B / (\rho - B)$$

$$\text{and } \bar{L}_2 = \phi L_2 + \frac{c}{\rho - A} \frac{d\phi L_2}{dc} \left(\rho / (1 + A) - \rho A / (1 + A)^2 \right) \quad (6)$$

$\bar{L}_2$ was calculated using the density given by Eqn. (1) and ϕL_2 given by Eqn. (3) in the pre-cmc region and Eqn. (4) in the post-cmc region.

Figure IV-7 is a plot of $\bar{L}_2$ at 298.15 K (obtained as described as above) as a function of concentration. Because the slope of ϕL_2 is changing rapidly in the vicinity of the cmc, $\bar{L}_2$ has been determined near the cmc with only limited confidence. It is likely that a maximum somewhat lower than that observed is more realistic. In order to check the reasonableness of this procedure the ϕL_2 data was expanded (points interpolated between measured data points using a fifth order polynomial and sets of seven points) and differentiated numerically. The results of one such calculation is shown in Figure IV-8. It may be readily observed that while the general features are similar, the analytical procedure eliminates much roughness and the artifact of the tail-off at high concentrations. The results at 308.15 K are plotted in Figure IV-9.

The enthalpy of micellization may be obtained from $\bar{L}_2$ by a procedure described by Desnoyers, et al. (7). The relative partial molar enthalpy well above and well below the cmc is extrapolated to the cmc and the difference between the two at the cmc is taken to be the enthalpy of micellization. This presumes that there is a relatively linear portion of the curve in the regions above and below the cmc. This has been done at both temperatures and the results are diagrammed in Figures IV-10 and IV-11.

It may be observed from the plots of the relative apparent partial molar enthalpy at both temperatures that the changes with temperature in the pre-micellar region are minor. The significance of this to the interpretation of the pre-micellar data in terms of hydrophobic association will be discussed in Chapter V. For whatever

reason, it is apparent that the dramatic change occurring with temperature is related to micelle formation, specifically the enthalpy of micelle formation. With this in mind, the change in heat capacity associated with micellization may be calculated from the difference between the ϕL_2 curves at the two temperatures:

$$\Delta C_{p,mic} = [\phi L_2(308.15) - \phi L_2(298.15)]/10 \quad (7)$$

The functions representing the data in the post-cmc region were inserted into this equation and the excess heat capacity calculated. The results are plotted in Figure IV-12.

This curve represents the change in heat capacity due to micelle formation. If the amount of amphiphile in micellar form at each concentration were known the excess heat capacity at each concentration could be divided by the fraction in the micelle to give the change in heat capacity per mole of micelle. The result should be a flat curve at $\Delta C_{p,mic}$. This will be done in Chapter V. Since the fraction in the micelle is approaching one, the measured curve ought to be approaching $\Delta C_{p,mic}$. The measured curve appears to be approaching a limiting value of about -300 J/K/mol. This is in excellent agreement with Musbally, Perron and Denoyers (1). Since their data was obtained with a differential device at 298.15 K, it is interesting to note that heat capacities are not in fact temperature dependent. Thus enthalpy data of amphiphile solutions may safely be extrapolated over a substantial temperature interval using known heat capacity results.

ii. Sodium Octylsulfonate

a. Density

Densities of sodium octylsulfonate solutions were measured in the range 0 to 0.7 molal at 298.15 K and 308.15 K using the DMA 40 digital density meter. No density data have been reported in the literature for octylsulfonate at either 298.15 K or 308.15 K. The measured densities are tabulated in Tables IV-8 and IV-9. The results were fit to Eqn. (1) using a least squares procedure. The parameters obtained from the fit are listed in Table IV-10. Eqn. (1) with these values of the parameters was used in all subsequent calculations where the density was required.

b. Enthalpy

Integral heats of dilution of sodium octylsulfonate in aqueous solution were measured with the Tronac calorimeter over the range 0 to 0.7 molal at 298.15 K and 308.15 K. The dilution factor was always 1:25. The measured heats are tabulated in Tables IV-11 and IV-12. Molar integral heats were calculated using the density results and are

also given in Tables IV-11 and IV-12. The molar integral heats of dilution are plotted in Figure IV-13.

Relative apparent partial molar enthalpies in the pre-cmc region were determined by extrapolating the data to infinite dilution. The extrapolation was carried out by fitting the pre-cmc heat of dilution data to Eqn. (2) and (3) as above. All final concentrations were well below the cmc. The parameters of the least squares fit of the data are listed in Table IV-13. The coefficients of the linear and quadratic terms will be considered to be due to pre-micellar association rather than to electrostatic effects. The data in the pre-cmc region along with the functions representing the best fit at 298.15 K and 308.15 K are plotted in Figures IV-14 and IV-15 respectively.

The relative apparent partial molar enthalpy was calculated at all concentrations by adding the heat of dilution from the final concentration to infinite dilution ($= \phi L_2$ at the final concentration) to the measured heat of dilution from c_i to c_f . This is, of course, exactly equal to ϕL_2 at the initial concentration. The results are tabulated in Tables IV-14 and IV-15. Figure IV-16 is a plot of the relative apparent partial molar enthalpy at both temperatures.

In order to facilitate differentiation of ϕL_2 to obtain $\bar{L}_2$ the post-cmc data were smoothed by fitting it to a convenient mathematical function. An exponential of the type shown in Eqn. (4) was used as above. The parameters obtained from the least squares fit are given in Table IV-16. The relative apparent partial molar enthalpy of sodium octylsulfate shows a clear break at 0.14 M, especially at 308.15 K.

This corresponds very well with values of the cmc reported in the literature (5, 6). The literature reports a cmc of 0.18 M for sodium octylsulfonate (6). However, the break in the relative apparent partial molar enthalpy obtained in this work occurs at 0.15 M (see Figure IV-17). Therefore in this work a cmc of 0.15 M was used for sodium octylsulfonate. The data and the function representing the best fit of the post-cmc data are plotted in Figures IV-18 and IV-19.

Since the definition of $\bar{L}_2$ is in terms of mole fraction/molality it was necessary to use the density measurements to calculate the correction to Eqn. (4) as above. $\bar{L}_2$ was calculated by analytically differentiating the functions representing the pre-cmc and the post-cmc data. $\bar{L}_2$ at 298.15 K is plotted in Figure IV-20 and at 308.15 K in Figure IV-21. The enthalpy of micellization was calculated from the $\bar{L}_2$ curves using the Desnoyers definition (7) as above. The results are diagrammed in Figures IV-22 and IV-23. The heat capacity change associated with micellization was calculated from the difference in the two ϕL_2 curves at the two temperatures and is plotted in Figure IV-24. As the fraction in the micelle approaches one the excess heat capacity approaches -325 J/K/mol. There are not, to my knowledge, any enthalpy or heat capacity data reported in the literature for sodium octylsulfonate.

iii. Sodium Octylbenzenesulfonate

The cmc of sodium octylbenzenesulfonate occurs at a much lower concentration (0.0128 M, 9) than that of the other two surfactants being considered. In addition, the solubility is limited at room temperature (usually 22 deg C in this laboratory) by the proximity of the Krafft temperature (18 deg C, 9). Therefore relative apparent partial molar enthalpies in the pre-cmc region could not be obtained from heats of dilution using the Tronac calorimeter. Instead heats of solution were measured over a range of (final) concentrations by breaking ampoules of surfactant into water. Unfortunately, a problem with this method is that the fragments of the glass ampoule create an abnormally noisy heat of stirring unless the ampoule is well shattered.

For this reason some of the data taken could not be used. In addition, it should be remembered that the quantity of interest is only a small part of the measured value.

It has also been pointed out that heat of solution measurements are sometimes dependent on the crystalline state of the material being considered (10). This can be affected by recrystallization procedures and by such things as grinding. For this reason all heat of solution measurements were made using ampoules prepared from a single homogeneous sample. The absolute value of the

standard heat of solution must therefore be viewed with some skepticism until this point is established.

Some heat of dilution values were measured at higher concentrations at 308.15 K to supplement the data, and to provide a check of the validity of the heat of solution data. The data at 298.15 K and 308.15 K are tabulated in Tables IV-17 and IV-18.

The heat of solution at a finite concentration is equal to:

$$\Delta H_s = \Delta H_s^\circ - \phi L_2(c_f) \quad (8)$$

where ΔH_s° is the standard heat of solution at infinite dilution, and $\phi L_2(c_f)$ is the relative apparent partial molar enthalpy at the concentration of the final solution. The relative apparent partial molar enthalpy of the aqueous surfactant in the pre-micellar region may be written:

$$\phi L_2 = a_0 c^{\frac{1}{2}} + a_1 c \quad (9)$$

Since the cmc occurs at so low a concentration it might seem that the single term of the DHLL ought to be sufficient. However, the data cannot be interpreted using only the square root term in ϕL_2 .

There is a large deviation from DHLL behavior, with a linear coefficient of the order of 4×10^5 . Dimerization constants of up to 100 L/mol have been calculated from conductivity measurements (11) for Cl2 ionic surfactants in the pre-cmc region. Since octylbenzenesulfonate acts much like a Cl2 surfactant a dimer interaction coefficient of 4×10^5 is not at all unreasonable. This point will be discussed in Chapter V, but suffice it to say here that

it is hard to imagine the physical basis of a very large electrostatic correction to the DHLL below 0.01 M.

The linear term in Eqn. (9) was calculated from the pre-cmc data, and the heat of solution at infinite dilution determined. Values of these quantities are listed in Table IV-19. The heat of solution at infinite dilution was subtracted from the measured heat of solution to obtain ϕL_2 at all concentrations. The relative apparent partial molar enthalpies are listed in Tables IV-20a and IV-20b and are plotted in Figure IV-25.

It may be seen from the plot that the behavior of sodium octylbenzenesulfonate is very similar to the others except that the effects are much larger.

iv. Adsorption

As surface active substances it would be expected that amphiphiles would adsorb strongly on available surfaces. Such surface area is found in abundance in clay minerals. Heats of adsorption of these surfactants were measured on aluminum oxide (as a pure surface) and on natural and homoionic sodium-exchanged montmorillonite. All heats of adsorption were measured at concentrations high enough to ensure that complete coverage had been reached (12, 13, 14).

Montmorillonite possesses a negative surface charge at neutral pH due to substitutions within the crystal lattice (15). Since the surfactants under consideration are anionic surfactants it follows that they should not interact strongly with the surface. This is borne out by the data. Heats of adsorption of sodium octylbenzenesulfonate on Na-SAz-1 montmorillonite are listed in Table IV-21. Heats of immersion of natural SAz-1 montmorillonite are given in Table IV-22 along with heats of immersion in sodium octylsulfate solutions at several concentrations. The small variation with concentration is near the experimental error of the instrument and is most likely due to interactions with calcium (the predominant cation present in the natural sample) rather than surface interactions.

The surface area may be calculated from the heat of immersion in water by the Harkins and Jura method (16):

$$\Delta H_i = A(\gamma + T \frac{d\gamma}{dT})$$

This turns out to be 813 m²/g which is about what the surface area ought to be (17), but is higher than would be expected considering the basis of the Harkins-Jura method. Since most of this area is interlayer area it would not be accessible to surfactant molecules. Assuming that the surfactant molecules adsorb only on the external surface of the clay, the N₂ BET surface area of 80 m²/g (17) may be used as the area available to surfactant molecules. Assuming complete bilayer coverage and a cross-sectional area of the surfactant molecules of about 34.84 square angstroms (calculated from molecular dimensions of the head group, 12) the enthalpy of adsorption per mole adsorbed was calculated. These results are listed in Table IV-23.

Heats of adsorption on aluminum oxide were measured by immersing a sample of alumina in the surfactant solution. Heats of immersion in water and in surfactant solutions are listed in Table IV-24. The Harkins-Jura surface area of the alumina was 4.43 m²/g. Surface areas of aluminas can vary from 0.1 m²/g to several hundred m²/g depending on the preparation of the sample and the method used to measure the surface area. In particular, these variations are largely due to micropores in the particles. The Harkins & Jura method would mask these micropores, giving a small area. However, the calculated value of 4.43 m²/g is not unreasonable, and probably represents a good

estimate of the surface area the surfactant molecules would 'see' since their size precludes adsorption into small micropores.

Assuming complete bilayer coverage and a cross-sectional area of 34.84 square angstroms, molar heats of adsorption were calculated. These are listed in Table IV-23. Obviously heats of adsorption are much larger for adsorption on alumina than on montmorillonite. This is in agreement with other measurements made on similar systems (12, 13, 14, 18, 19). It would be expected that cationic and nonionic surfactants would show much larger effects on the montmorillonite.

T (K)	d_0 (g/cm ³)	a_1	a_2	a_3
298.15	0.997043	60.466957	-35.584581	21.91137
308.15	0.994029	55.563063	-18.510380	0.0

Table IV-1: Parameters of Eq. (1) for sodium octylsulfate at 298.15 K and 308.15 K.

d (g/cm ³)	c (mol/kg)
0.99670	0.0508
0.99732	0.0604
0.99830	0.0798
0.99907	0.0973
1.00000	0.1109
1.00093	0.1317
1.00134	0.1396
1.00227	0.1558
1.00310	0.1700
1.00330	0.1795
1.00402	0.1905
1.00454	0.1996
1.00495	0.2105
1.00526	0.2179
1.00681	0.2514
1.01311	0.3990
1.01715	0.4978

Table IV-2: Densities of sodium octylsulfate
at 35 °C.

m_i (mol/kg)	ΔH_d (J)	ΔH_d (J/mol)	c_i (mol/L)	c_f (mmol/L)	mmol
0.0509	-0.0764	-759.34	0.0503	1.937	0.1006
0.0903	-0.2158	-1217.3	0.0886	3.421	0.1773
0.1010	-0.2987	-1509.2	0.0990	3.821	0.1979
0.1105	-0.3406	-1575.5	0.1081	4.176	0.2162
0.1208	-0.4213	-1785.8	0.1180	4.559	0.2359
0.1307	-0.4940	-1938.7	0.1274	4.927	0.2548
0.1407	-0.5933	-2166.7	0.1369	5.297	0.2738
0.1504	-0.6982	-2389.3	0.1461	5.656	0.2922
0.1587	-0.7780	-2526.8	0.1540	5.961	0.3079
0.1710	-0.9579	-2893.5	0.1655	6.414	0.3311
0.1791	-1.0478	-3026.1	0.1731	6.711	0.3463
0.1914	-1.1708	-3170.8	0.1846	7.160	0.3692
0.2011	-1.2870	-3323.0	0.1937	7.514	0.3873
0.2152	-1.4185	-3430.9	0.2067	8.026	0.4135
0.2256	-1.5333	-3544.0	0.2163	8.403	0.4327
0.2365	-1.638	-3618.3	0.2264	8.797	0.4527
0.2551	-1.778	-3653.0	0.2434	9.466	0.4867
0.2999	-2.138	-3765.5	0.2839	11.064	0.5678
0.4052	-2.933	-3893.0	0.3767	14.745	0.7534
0.5000	-3.622	-3958.7	0.4574	17.972	0.9149
0.6035	-3.819	-3518.2	0.5427	21.409	1.0855
0.6997	-4.181	-3374.0	0.6196	24.534	1.2392

Table IV-3: Integral heats of dilution of sodium octylsulfate at 25 °C.

m_i (mol/kg)	ΔH_d (J)	ΔH_d (J/mol)	c_i (mol/L)	c_f (mmol/L)	mmol
0.0508	-0.08239	-823.12	0.0500	1.921	0.1001
0.0604	-0.1035	-871.14	0.0594	2.281	0.1188
0.0702	-0.1535	-1113.5	0.0689	2.648	0.1379
0.0798	-0.2040	-1304.0	0.0782	3.007	0.1564
0.0897	-0.2245	-1278.9	0.0878	3.376	0.1755
0.1000	-0.2765	-1415.5	0.0977	3.759	0.1953
0.1109	-0.3395	-1570.1	0.1081	4.163	0.2162
0.1203	-0.4096	-1749.2	0.1171	4.510	0.2342
0.1317	-0.4847	-1894.5	0.1279	4.931	0.2558
0.1396	-0.5663	-2091.1	0.1354	5.221	0.2708
0.1558	-0.6954	-2307.3	0.1507	5.815	0.3014
0.1700	-0.7466	-2275.9	0.1640	6.334	0.3281
0.1795	-0.7766	-2245.8	0.1729	6.680	0.3458
0.1905	-0.8090	-2208.6	0.1832	7.079	0.3663
0.1996	-0.8648	-2256.9	0.1916	7.409	0.3832
0.2105	-0.9016	-2235.3	0.2017	7.802	0.4033
0.2179	-0.9678	-2320.9	0.2085	8.069	0.4170
0.2514	-1.0640	-2224.5	0.2392	9.270	0.4783
0.3036	-1.1958	-2089.0	0.2862	11.118	0.5724
0.3981	-1.3965	-1891.1	0.3692	14.398	0.7384
0.4978	-1.4871	-1638.4	0.4538	17.763	0.9077
0.5951	-1.3590	-1273.5	0.5336	20.952	1.0671
0.7005	-1.2830	-1040.0	0.6169	24.298	1.2337

Table IV-4: Integral heats of dilution of sodium octylsulfate at 35 °C.

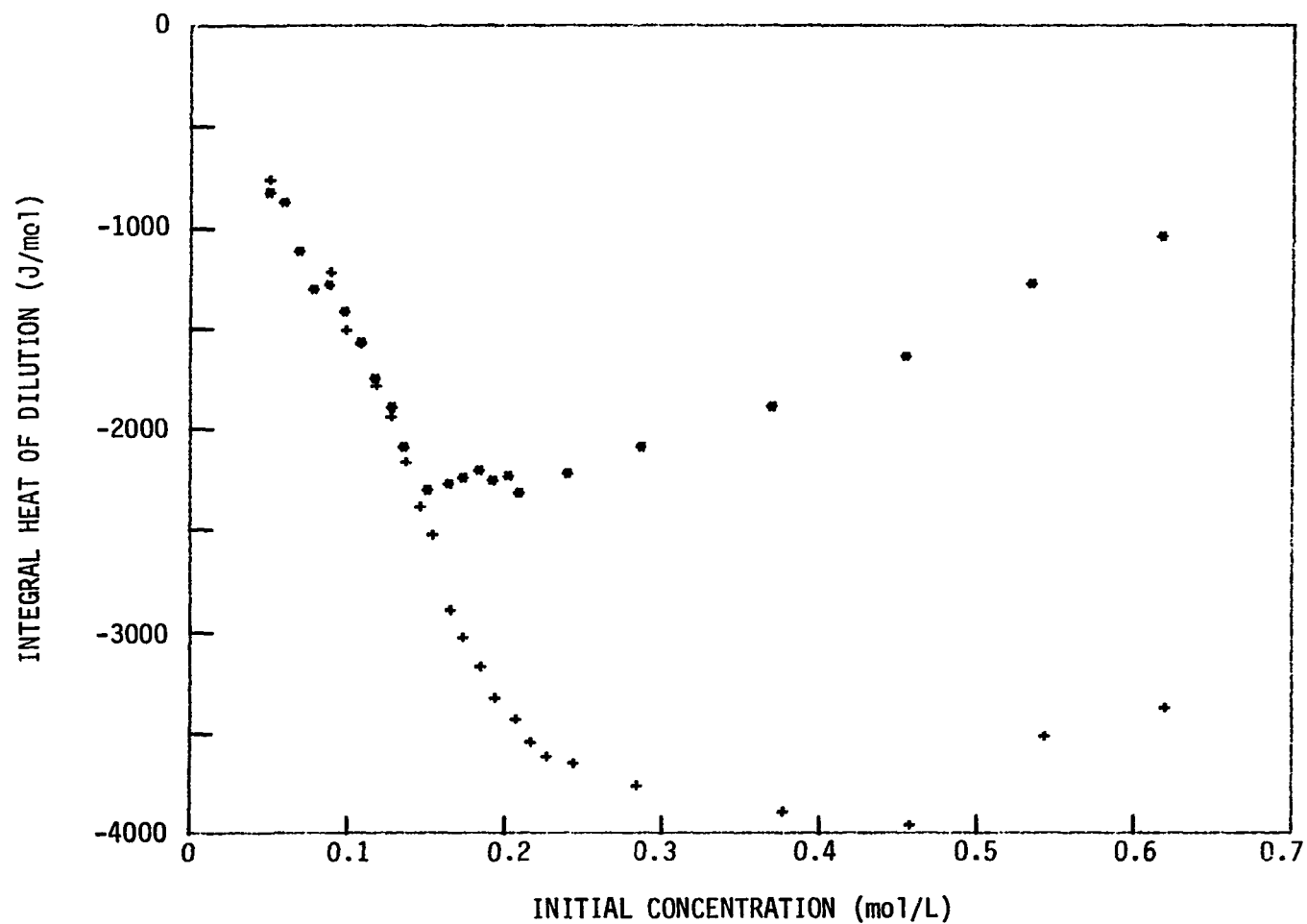


Figure IV-1: Integral heats of dilution of sodium octylsulfate. 298.15 K (+), 308.15 K (*). Dilution factor = 1:25.

T (K)	a_0	a_1	a_2
298.15	1975	5378.8691	44446.9015
308.15	2248	7575.05073	18877.5131

Table IV-5: Parameters of Eqn. (3). a_0 is the Debye-Huckel limiting slope.

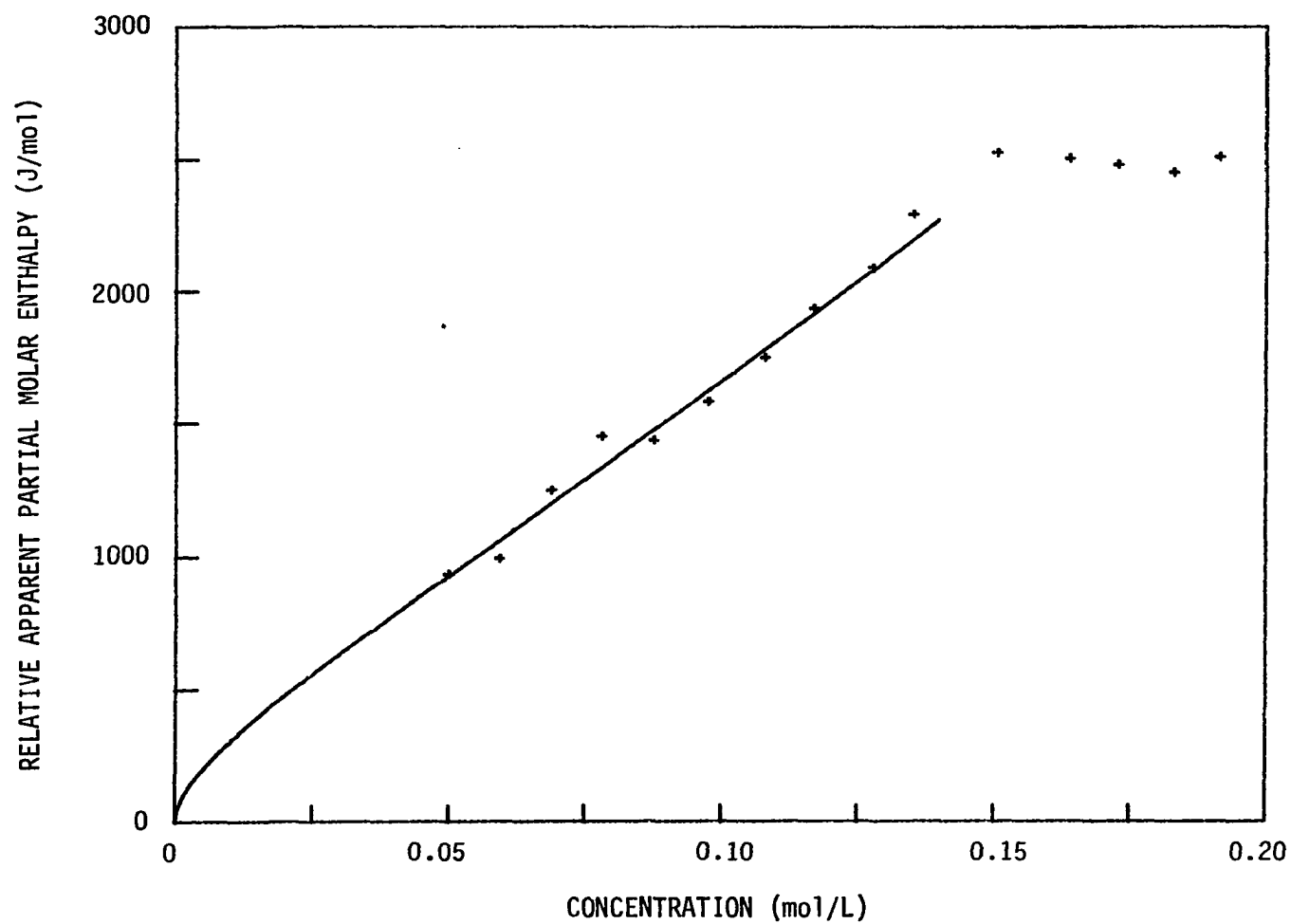


Figure IV-3: Relative apparent partial molar enthalpy of sodium octylsulfate at 308.15 K. Plot of the function representing the best fit of the data.

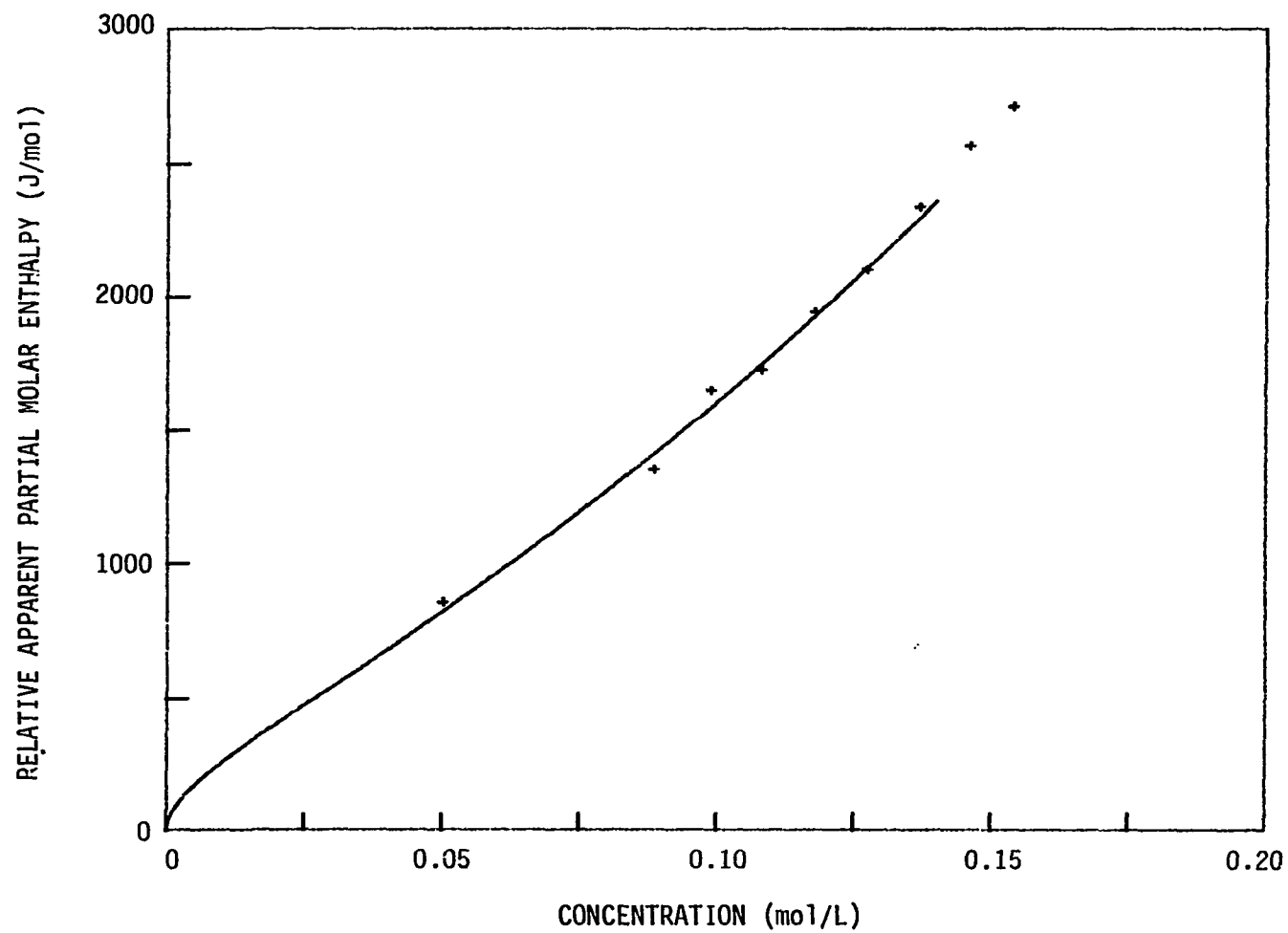


Figure IV-2: Relative apparent partial molar enthalpy of sodium octylsulfate at 298.15 K. Plot of the function representing the best fit of the data.

c_i (mol/L)	ϕL_2 (J/mol)
0.0503	856.85
0.0886	1351.7
0.0990	1652.4
0.1081	1726.4
0.1180	1944.6
0.1274	2104.9
0.1369	2340.1
0.1461	2569.7
0.1540	2712.9
0.1655	3087.9
0.1731	3226.0
0.1846	3378.7
0.1937	3537.1
0.2067	3653.9
0.2163	3773.4
0.2264	3854.3
0.2434	3900.0
0.2839	4038.2
0.3767	4221.8
0.4574	4334.5
0.5427	3942.7
0.6196	3842.0

Table IV-6: Relative apparent partial molar enthalpies of sodium octylsulfate at 25 °C.

c_i (mol/L)	ϕL_2 (J/mol)
0.0500	936.28
0.0594	995.90
0.0689	1249.4
0.0782	1450.3
0.0878	1435.3
0.0977	1582.0
0.1081	1747.0
0.1171	1934.7
0.1279	2090.2
0.1354	2293.6
0.1507	2523.4
0.1640	2503.5
0.1729	2480.9
0.1832	2452.3
0.1916	2507.5
0.2017	2494.1
0.2085	2585.2
0.2392	2512.8
0.2862	2412.6
0.3692	2273.9
0.4538	2078.5
0.5336	1765.9
0.6169	1585.6

Table IV-7: Relative apparent partial molar enthalpies of sodium octylsulfate at 35 °C

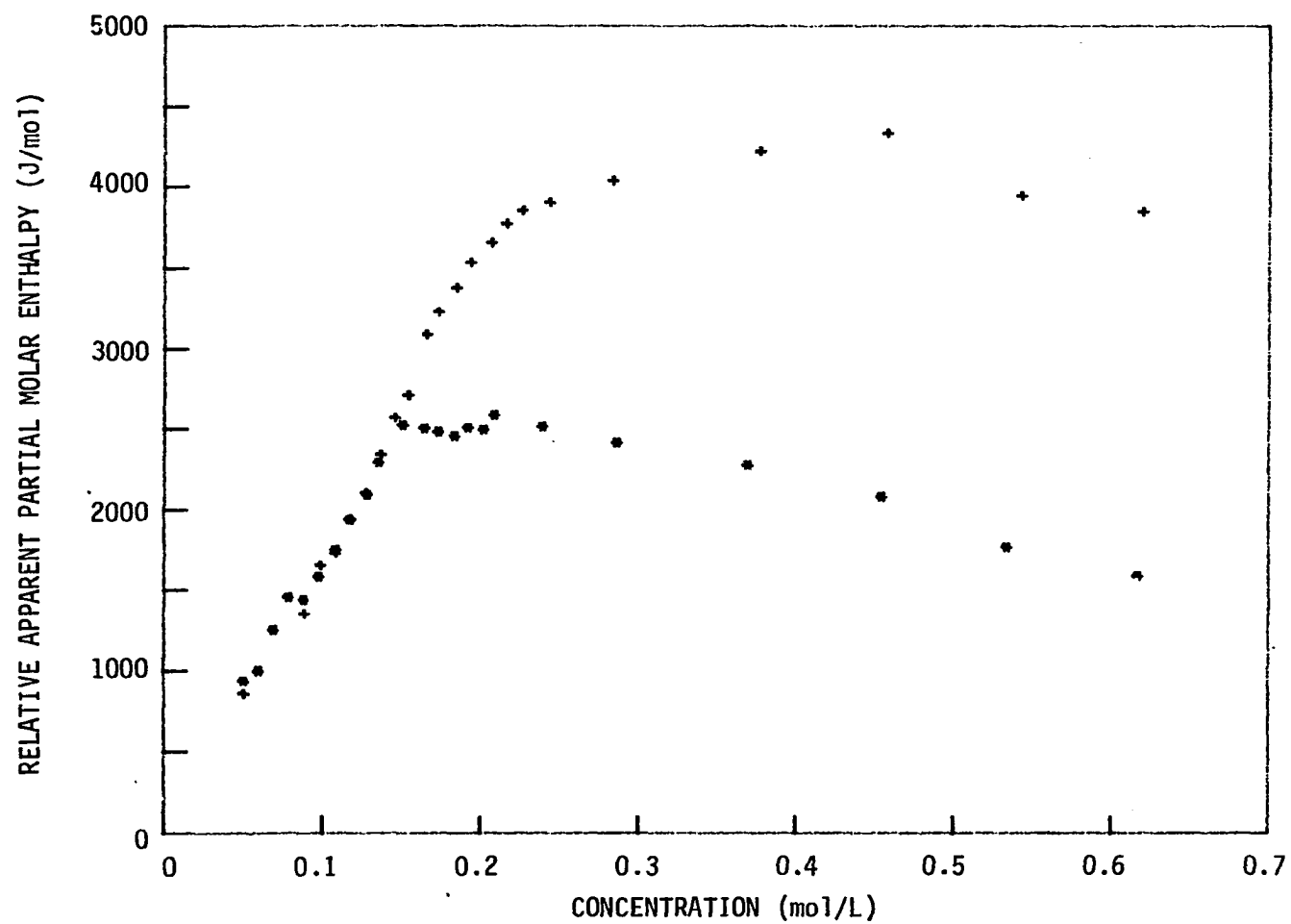


Figure IV-4: Relative apparent partial molar enthalpy of sodium octylsulfate at 298.15 K (+) and 308.15 K (*).

T (K)	a_1	a_2	a_3	a_4
298.15	4870.1473	-2087.34346	2436.56367	12.205859
308.15	3149.18697	-3282.29016	676.55065	7.2369278

Table IV-7a: Parameters of Eqn. (4) for sodium octylsulfate at 298.15 K and 308.15 K.

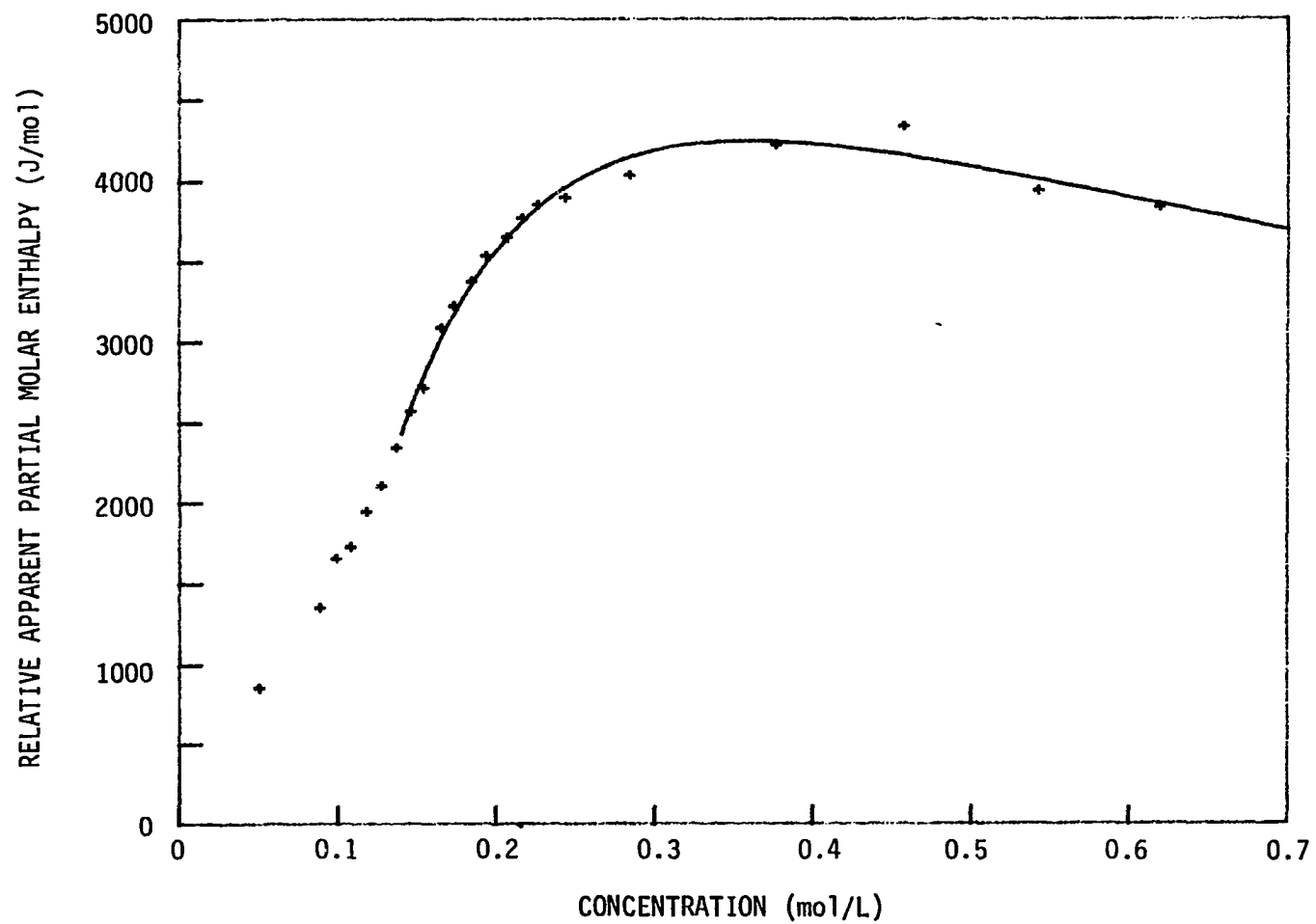


Figure IV-5: Relative apparent partial molar enthalpy of sodium octylsulfate at 298.15 K. Plot of the function representing the best fit of the data in the post-cmc region.

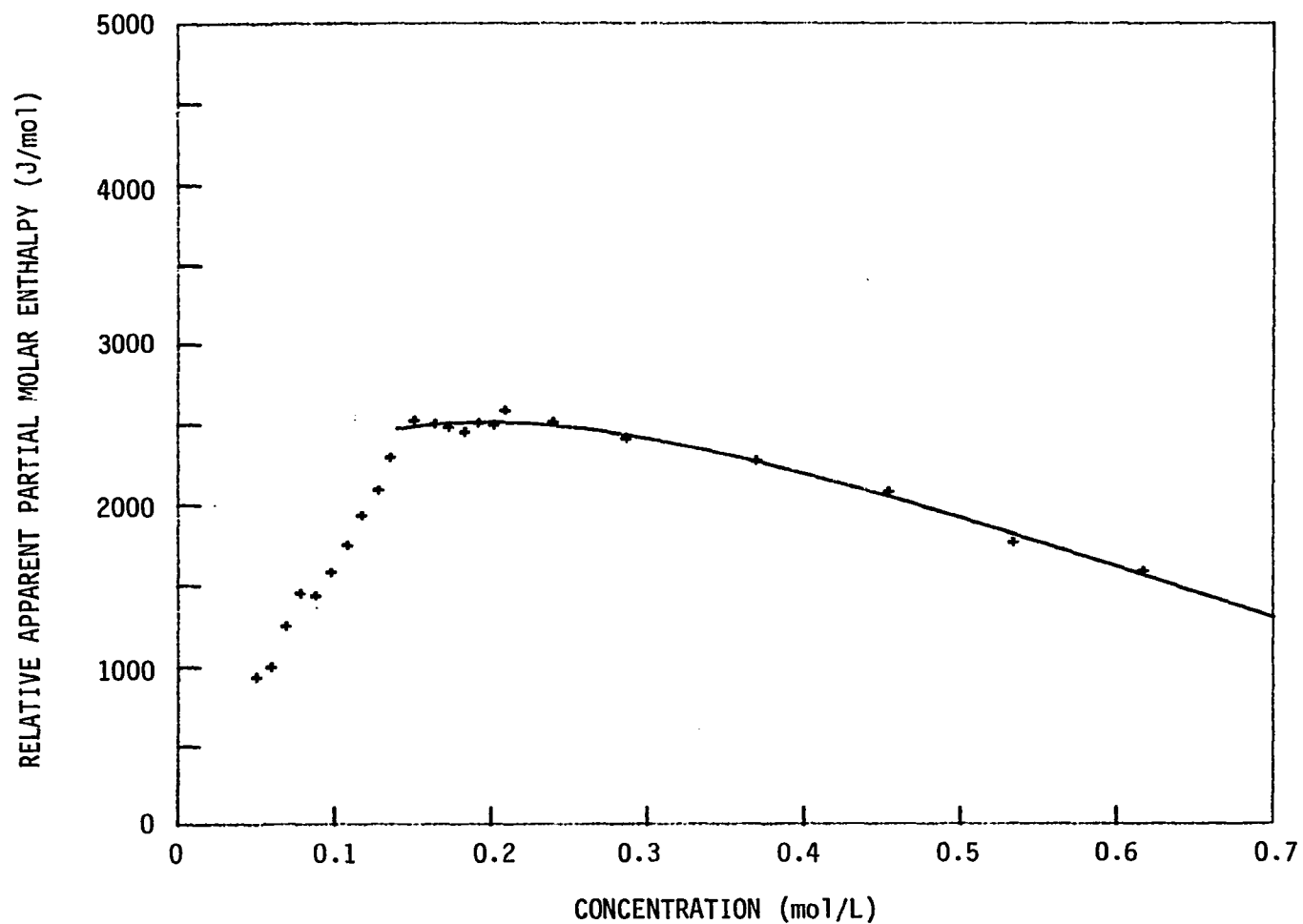


Figure IV-6: Relative apparent partial molar enthalpy of sodium octylsulfate at 308.15 K. Plot of the function representing the best fit of the data in the post-cmc region.

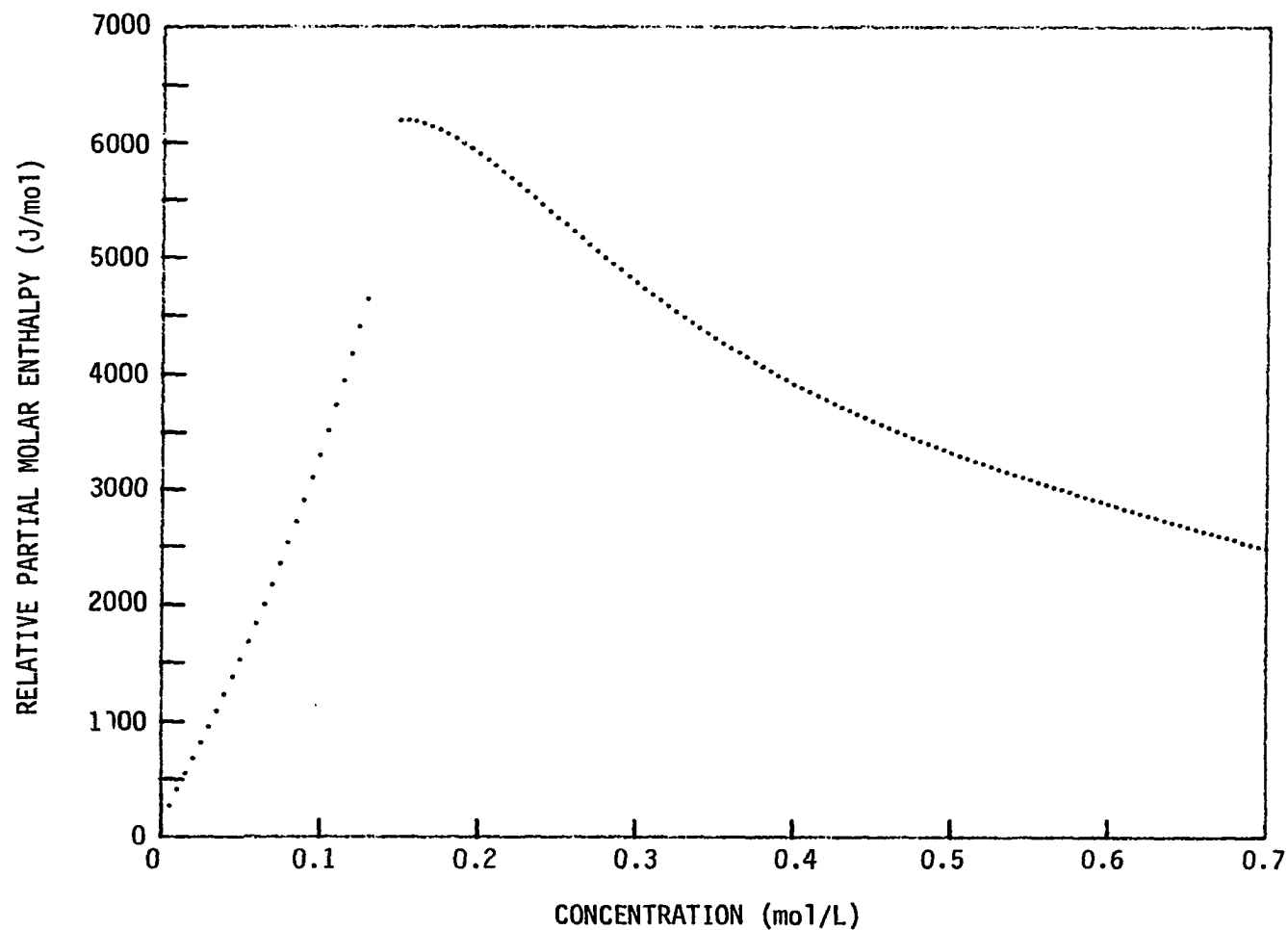


Figure IV-7: Relative partial molar enthalpy of sodium octyl-sulfate at 298.15 K. Derived by smoothing the pre-cmc and post-cmc data and analytically differentiating the resulting functions.

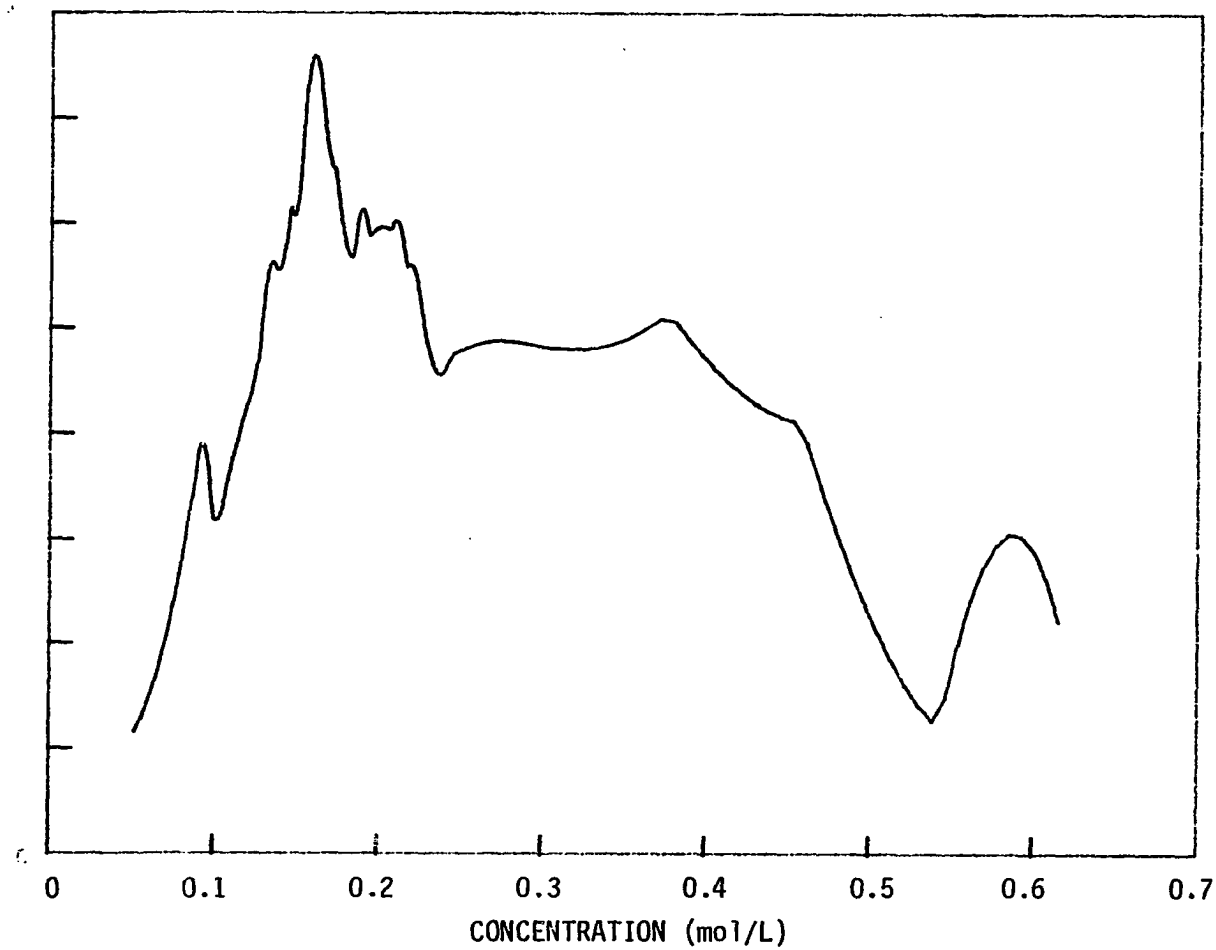


Figure IV-8: Relative partial molar enthalpy of sodium octyl-sulfate at 298.15 K. Derived by expanding the data by interpolating using sets of seven points and a fifth order polynomial.

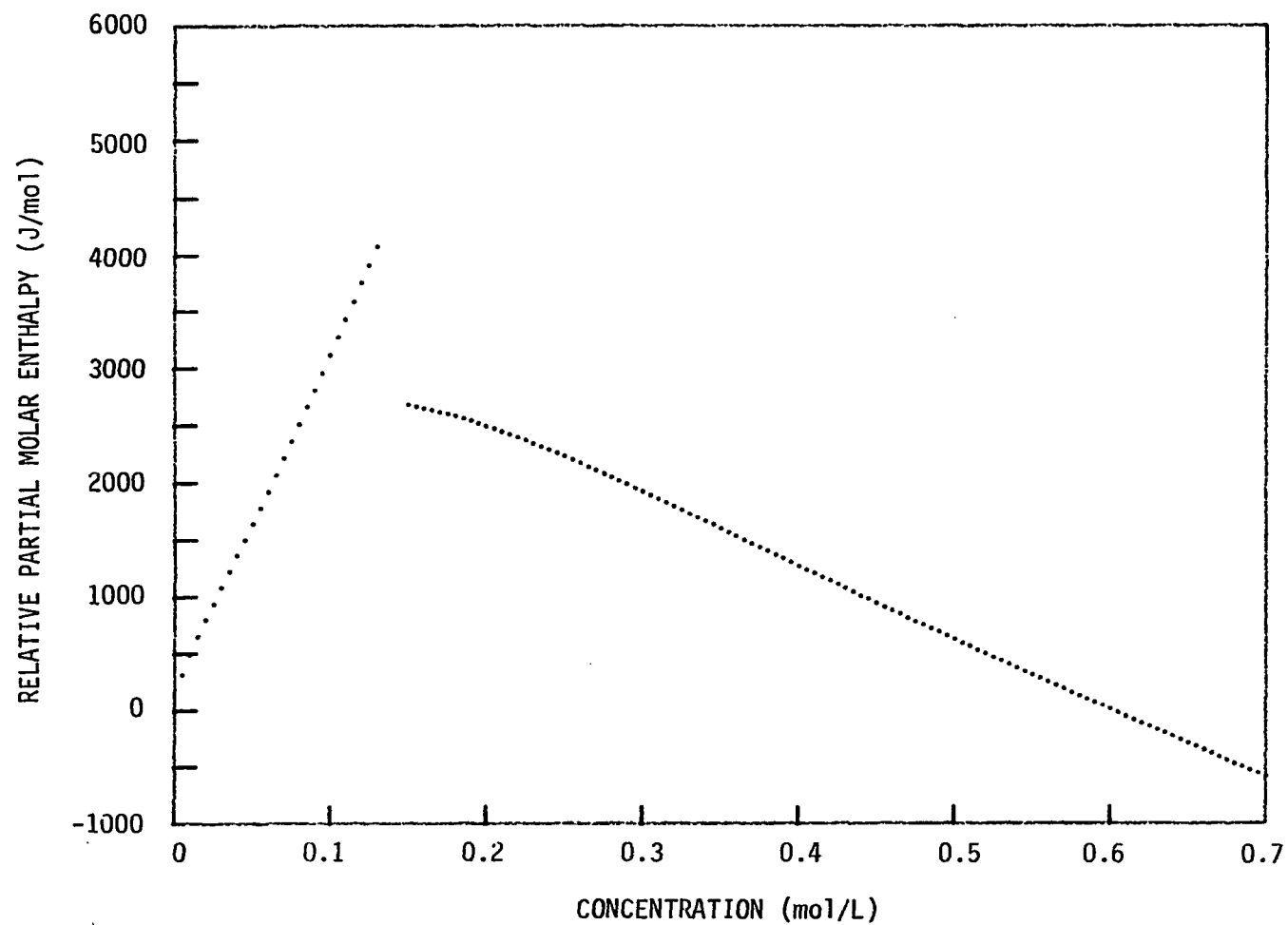


Figure IV-9: Relative partial molar enthalpy of sodium octyl-sulfate at 308.15 K.

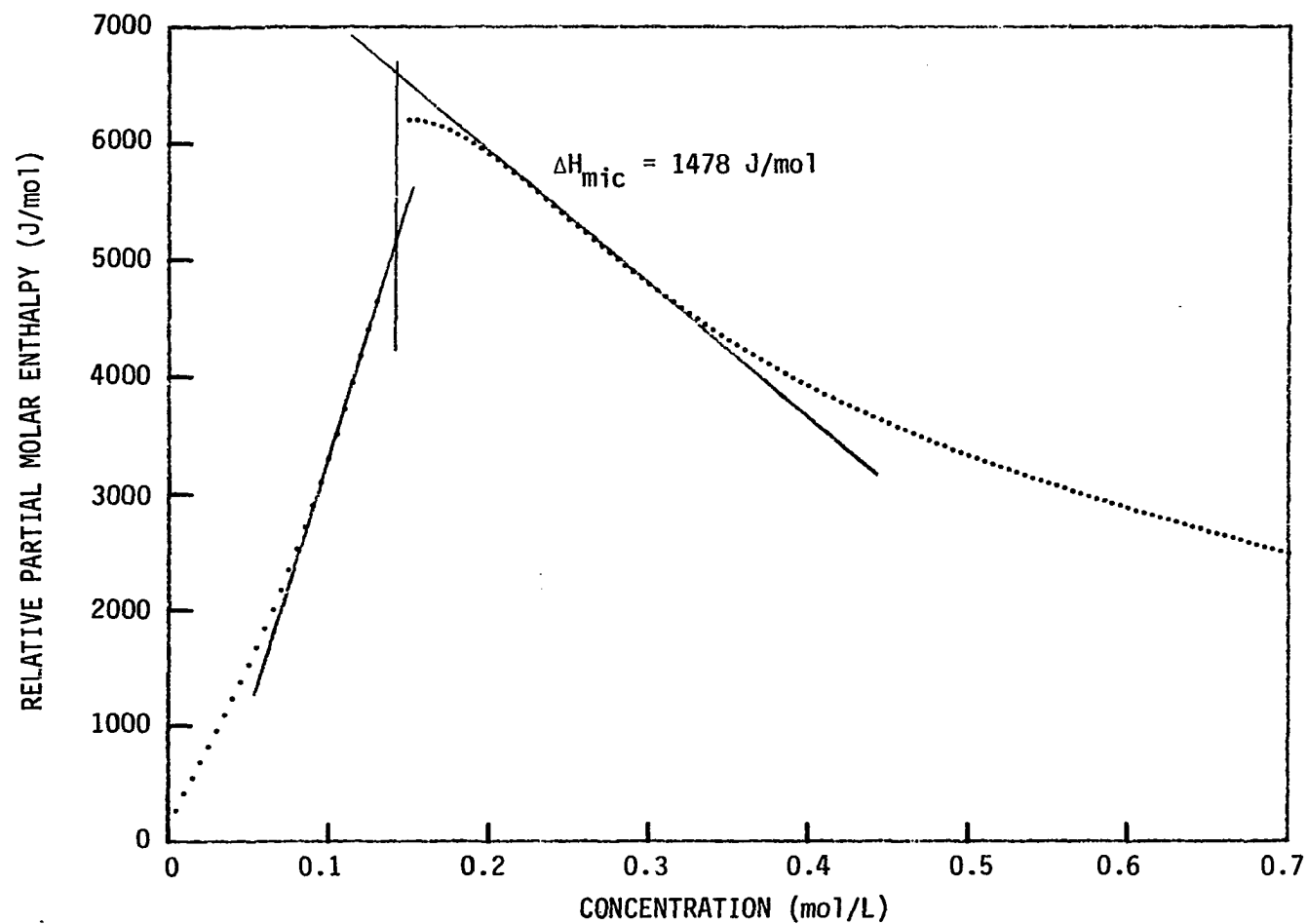


Figure IV-10: Relative apparent partial molar enthalpy of sodium octylsulfate at 298.15 K showing the determination of the enthalpy of micelle formation. $\Delta H_{mic} = 1478 \text{ J/mol}$.

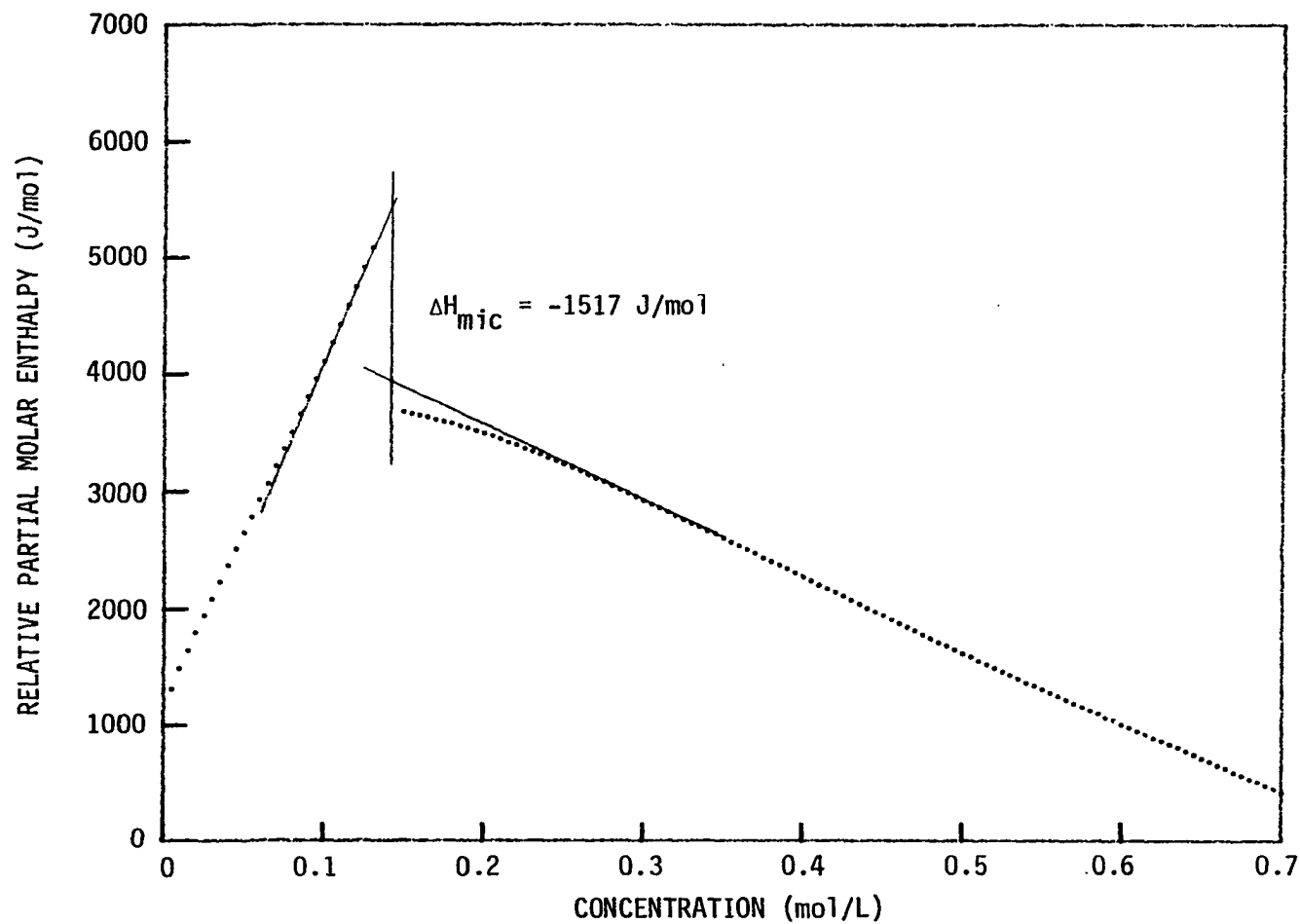


Figure IV-11: Relative apparent partial molar enthalpy of sodium octylsulfate at 308.15 K showing the determination of the enthalpy of micelle formation. $\Delta H_{mic} = -1517 \text{ J/mol}$.

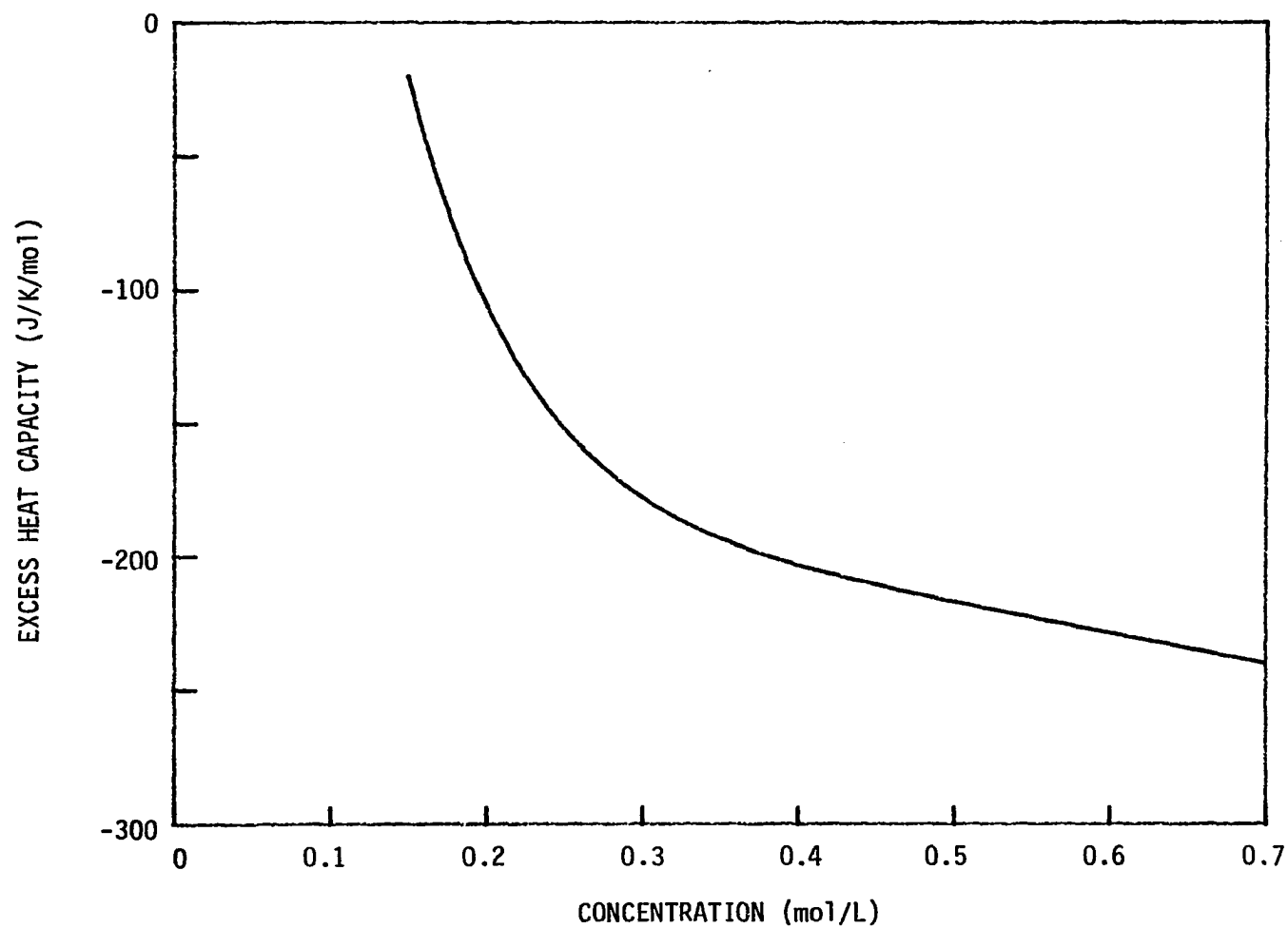


Figure IV-12: Excess heat capacity of sodium octylsulfate. Temperature range was from 298.15 K to 308.15 K. The limiting value is $\Delta C_{p,mic}$ and is equal to -300 J/K/mol.

c (mol/kg)	d (g/cm ³)
0.04993	0.99967
0.05832	0.99977
0.09978	1.00188
0.1299	1.00348
0.1495	1.00451
0.1695	1.00544
0.1794	1.00596
0.1901	1.00642
0.1999	1.00678
0.2296	1.00802
0.2489	1.00880
0.3965	1.01474
0.4952	1.01815
0.5923	1.02172
0.6902	1.02519

Table IV-8: Densities of sodium octyl-sulfonate at 298.15 K.

c (mol/kg)	d (g/cm ³)
0.04985	0.99608
0.1013	0.99882
0.1494	1.00093
0.1969	1.00268
0.2501	1.00495
0.3018	1.00722
0.3985	1.01084
0.4967	1.01446
0.5978	1.01798

Table IV-9: Densities of sodium octyl-sulfonate at 308.15 K.

T (K)	d_0 (g/cm ³)	a_1	a_2	a_3
298.15	0.997043	53.7755142	-29.678693	15.63109
308.15	0.994029	47.1516664	-13.104041	2.07116

Table IV-10: Parameters of Eq. (1) for sodium octylsulfonate at 298.15 K and 308.15 K.

m_i (mol/kg)	ΔH_d (J)	ΔH_d (J/mol)	c_i (mol/L)	c_f (mmol/L)	mmol
0.0242	-0.01908	-396.94	0.0240	0.9240	0.04807
0.0583	-0.09819	-852.37	0.0576	2.218	0.1152
0.0998	-0.25939	-1325.0	0.0978	3.777	0.1958
0.1299	-0.42993	-1695.3	0.1268	4.899	0.2536
0.1495	-0.58936	-2025.8	0.1455	5.626	0.2909
0.1695	-0.80438	-2446.6	0.1644	6.363	0.3288
0.1794	-0.93813	-2700.3	0.1737	6.726	0.3474
0.1901	-1.1043	-3005.0	0.1837	7.118	0.3675
0.1999	-1.2588	-3262.7	0.1929	7.476	0.3858
0.2296	-1.6869	-3825.3	0.2205	8.556	0.4410
0.2489	-1.9360	-4062.6	0.2383	9.253	0.4765
0.2997	-2.6276	-4617.5	0.2845	11.07	0.5691
0.3965	-3.7717	-5089.4	0.3705	14.47	0.7411
0.4952	-4.8694	-5345.4	0.4555	17.85	0.9110
0.5923	-5.7708	-5378.7	0.5365	21.09	1.073
0.6902	-6.5856	-5348.4	0.6157	24.28	1.231

Table IV-11: Integral heats of dilution of sodium octyl-sulfonate at 298.15 K.

m_i (mol/kg)	ΔH_d (J)	ΔH_d (J/mol)	c_i (mol/L)	c_f (mmol/L)	mmol
0.04985	-0.06973	-709.53	0.0491	1.886	0.0983
0.1013	-0.2778	-1403.1	0.0990	3.807	0.1980
0.1494	-0.5810	-2005.7	0.1448	5.582	0.2897
0.1969	-0.9886	-2610.0	0.1894	7.313	0.3788
0.2501	-1.4530	-3046.8	0.2385	9.227	0.4769
0.3018	-1.8826	-3299.0	0.2853	11.06	0.5707
0.3985	-2.4931	-3361.2	0.3709	14.43	0.7417
0.4967	-2.9743	-3268.4	0.4550	17.77	0.9100
0.5978	-3.3689	-3125.9	0.5389	21.11	1.0778
0.7001	-3.6290	-2921.9	0.6210	24.40	1.2420

Table IV-12: Integral heats of dilution of sodium octyl-sulfonate at 308.15 K.

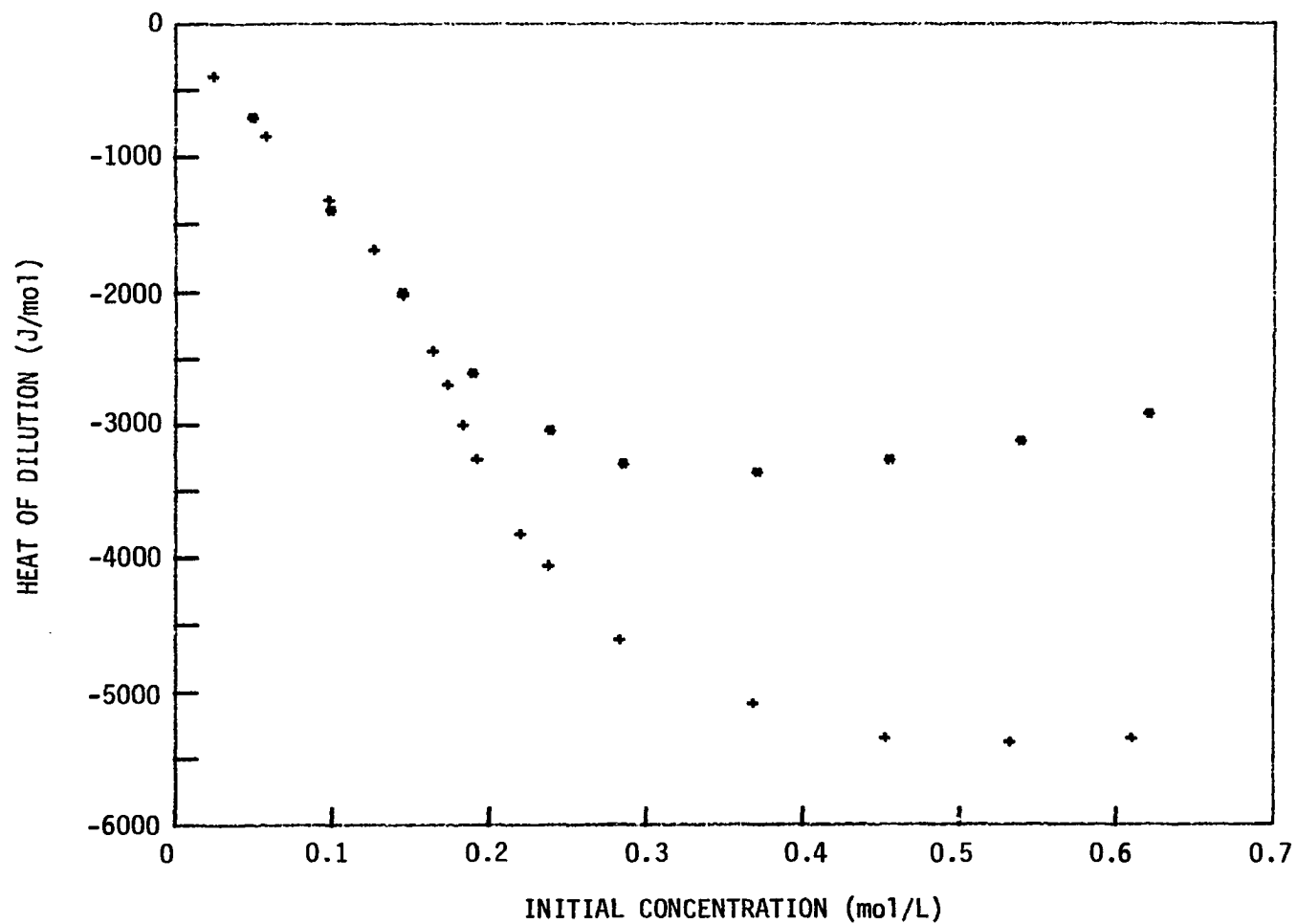


Figure IV-13: Integral heats of dilution of sodium octylsulfonate at 298.15 K (+) and 308.15 K (*). Dilution factor = 1:25.

T (K)	a_0	a_1	a_2
298.15	1975	5983.52112	27173.3427
308.15	2248	6762.06456	18081.2698

Table IV-13: Parameters of Eq. (3). a_0 is the Debye-Hückel limiting slope.

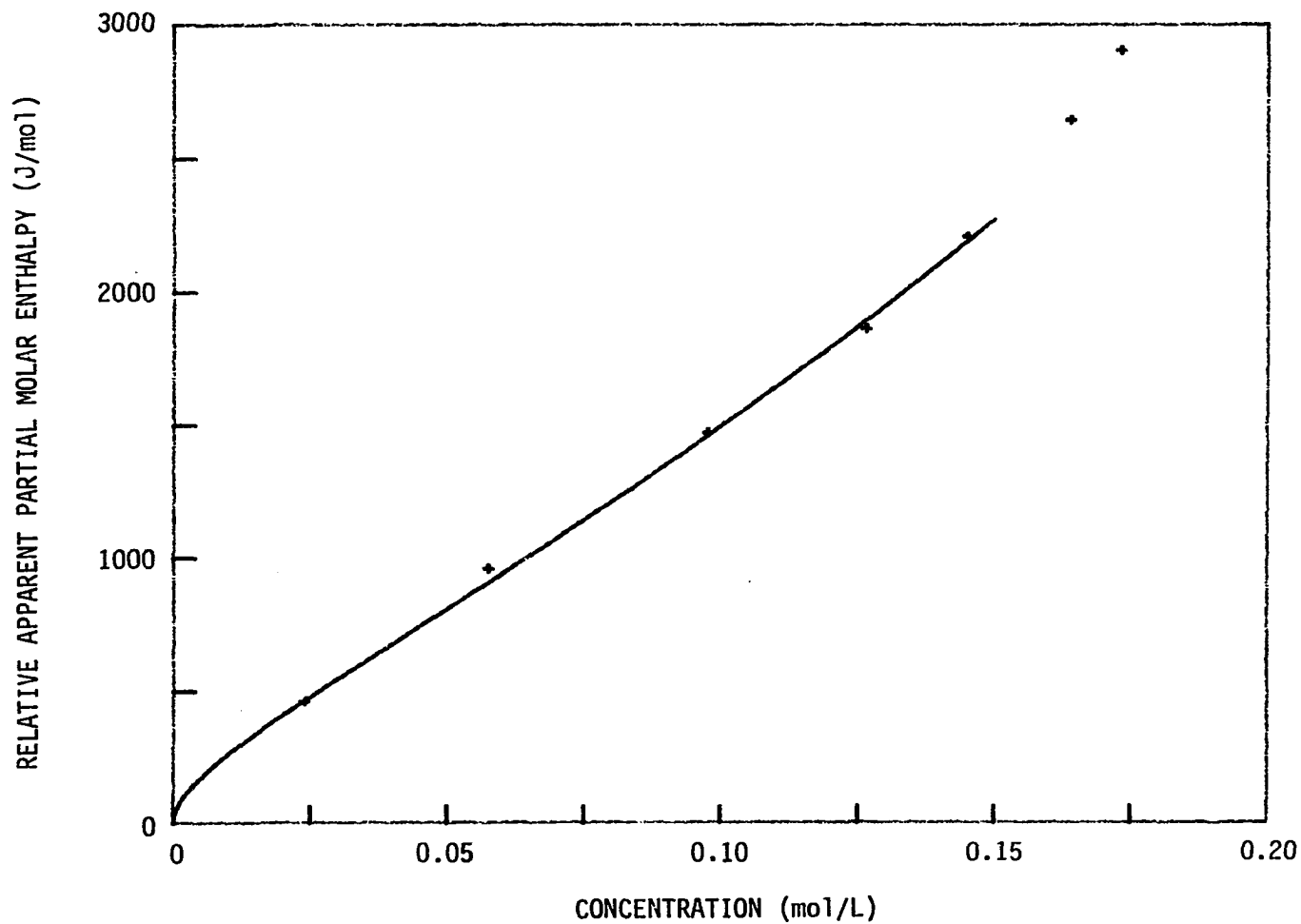


Figure IV-14: Relative apparent partial molar enthalpy of sodium octylsulfonate at 298.15 K. Plot of the function representing the best fit of the data in the pre-cmc region.

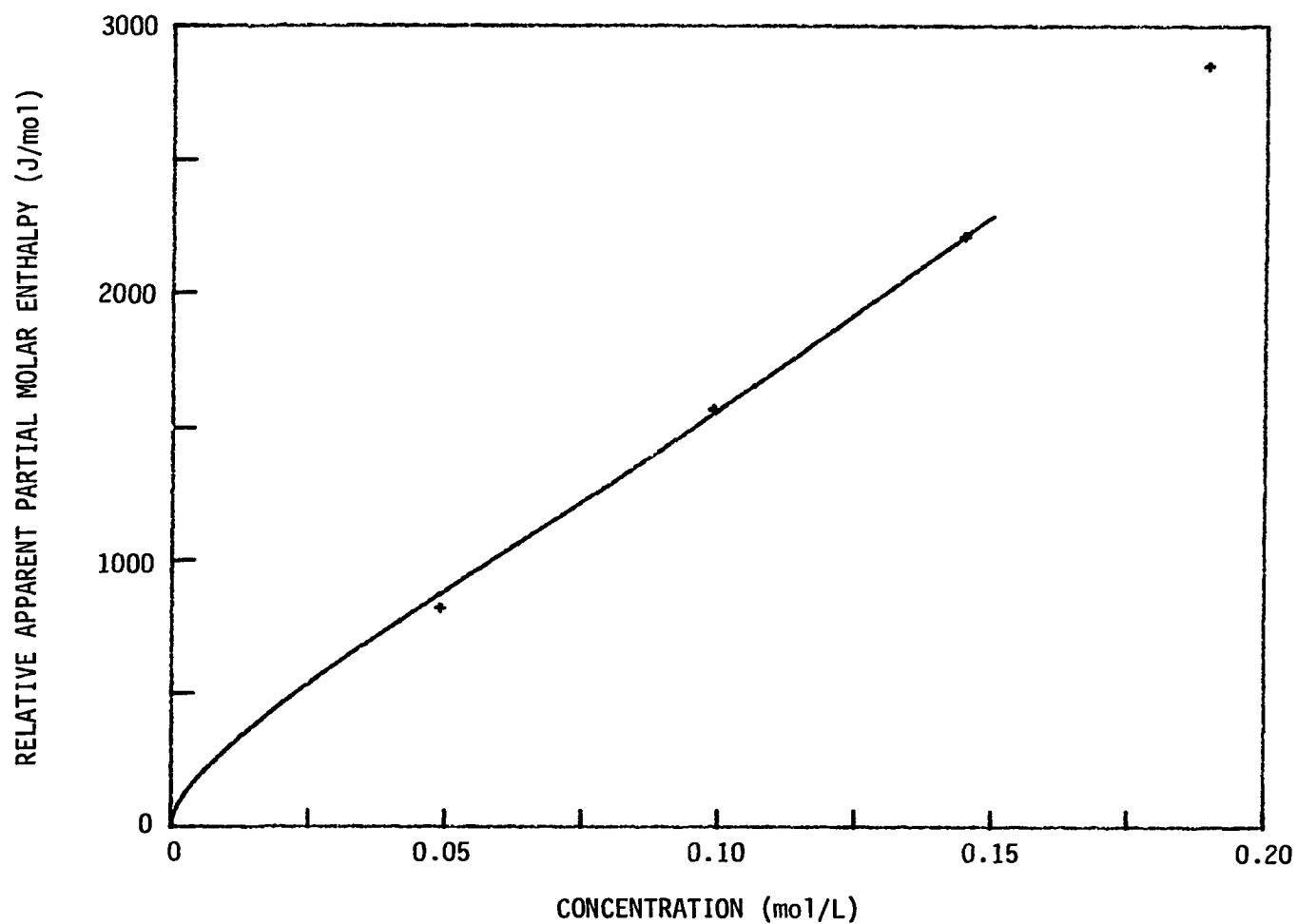


Figure IV-15: Relative apparent partial molar enthalpy of sodium octylsulfonate at 308.15 K. Plot of the function representing the best fit of the data in the pre-cmc region.

c_i (mol/L)	ϕL_2 (J/mol)
0.0240	462.53
0.0575	958.79
0.0977	1469.4
0.1265	1863.5
0.1451	2208.4
0.1640	2643.3
0.1732	2903.8
0.1832	3215.6
0.1923	3479.7
0.2197	4061.2
0.2374	4310.2
0.2833	4894.8
0.3684	5419.2
0.4522	5724.6
0.5320	5803.6
0.6098	5817.3

Table IV-14: Relative apparent partial molar enthalpy of sodium octylsulfonate at 298.15 K.

c_i (mol/L)	ϕ_{L_2} (J/mol)
0.0491	819.96
0.0990	1567.8
0.1448	2211.9
0.1894	2852.6
0.2385	3326.7
0.2853	3612.5
0.3709	3732.6
0.4550	3693.8
0.5389	3603.3
0.6210	3448.8

Table IV-15: Relative apparent partial molar enthalpy of sodium octylsulfonate at 308.15 K.

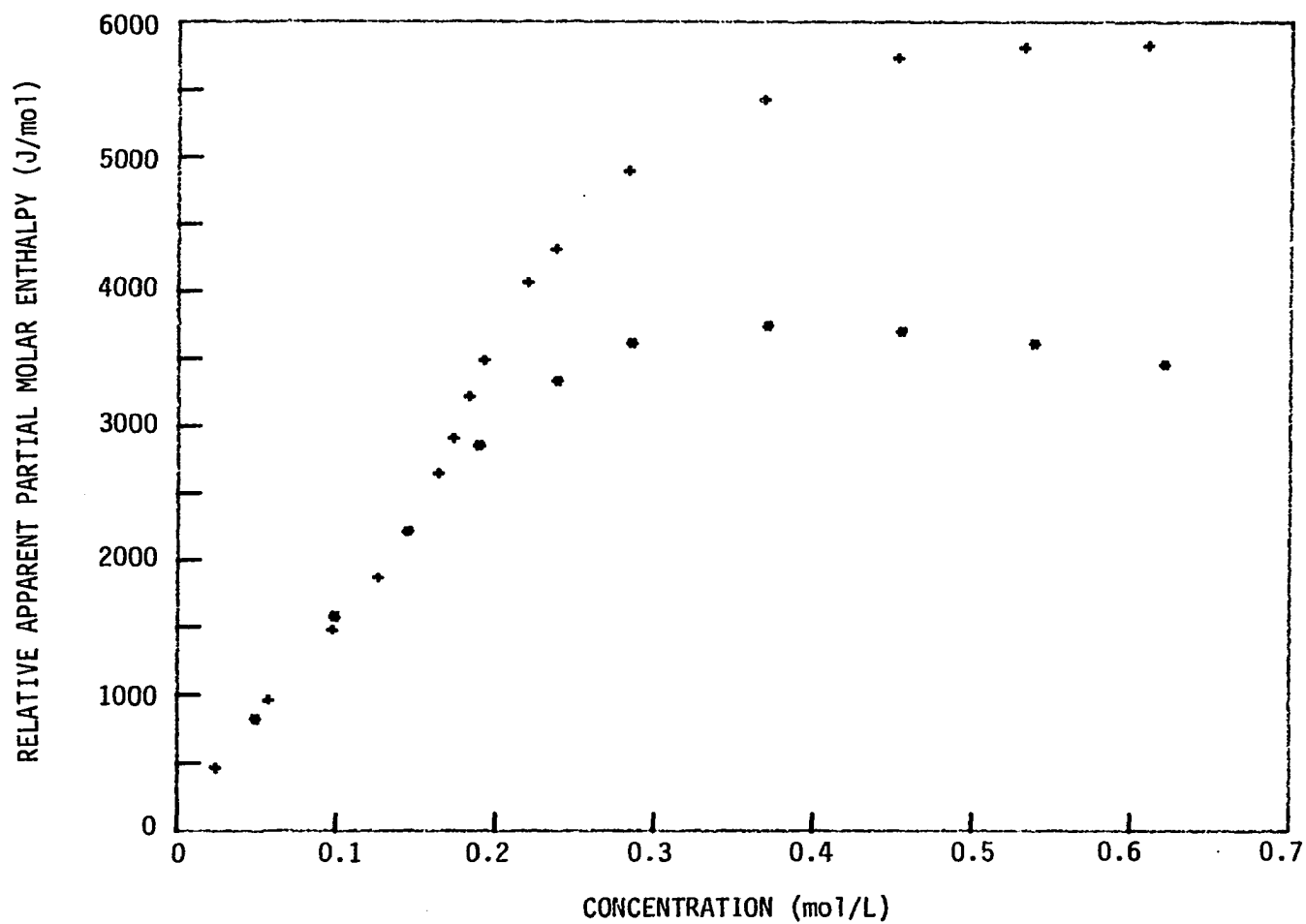


Figure IV-16: Relative apparent partial molar enthalpy of sodium octylsulfonate at 298.15 K (+) and 308.15 K (*).

T (K)	a_1	a_2	a_3	a_4
298.15	5833.20831	78.1463395	3680.55582	10.2188204
308.15	4381.76909	-1939.75939	2209.26533	10.5781299

Table IV-16: Parameters of Eq. (4) for sodium octylsulfonate at 298.15 K and 308.15 K.

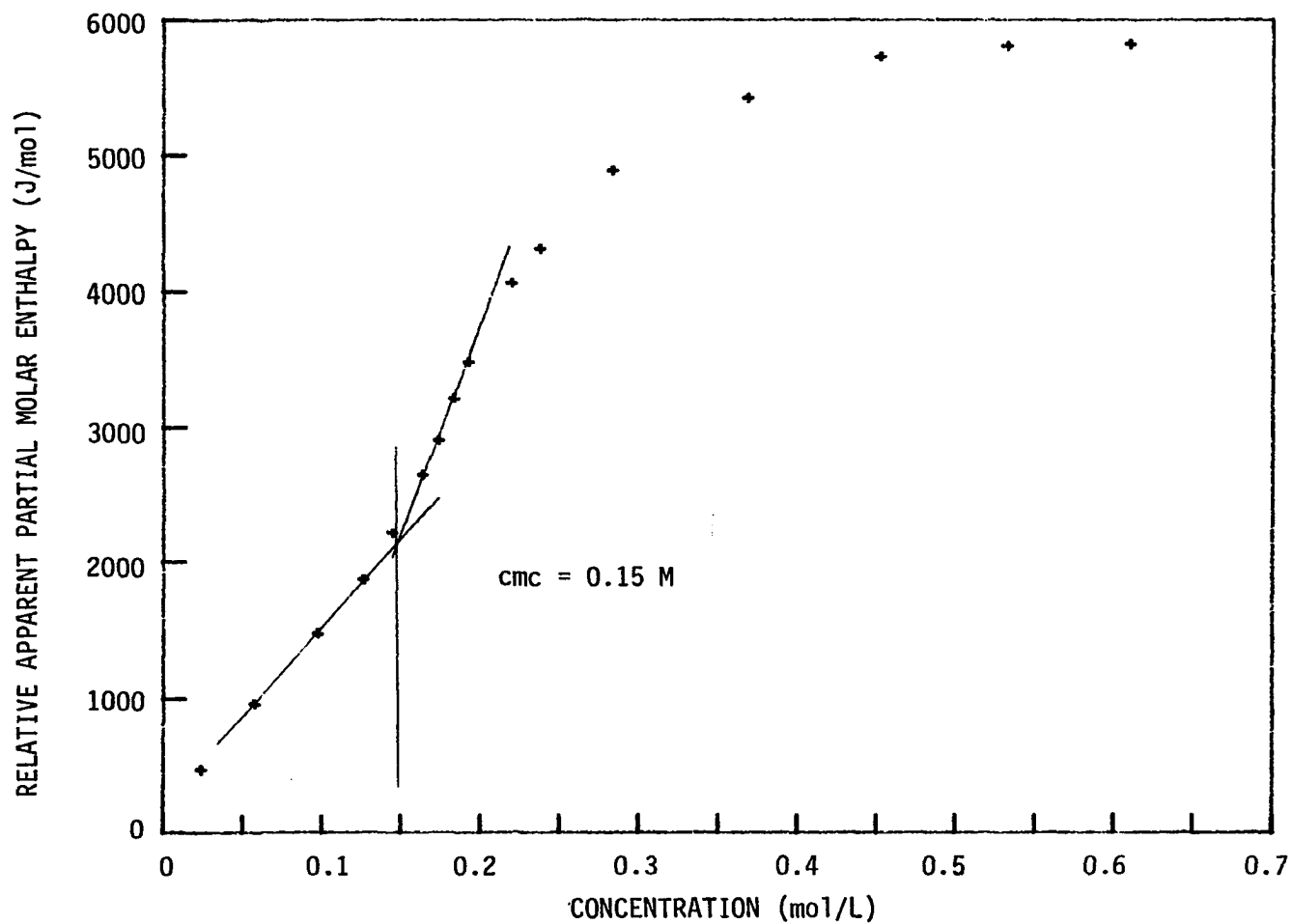


Figure IV-17: Plot of the relative apparent partial molar enthalpy of sodium octylsulfonate at 298.15 K showing how the cmc was determined.

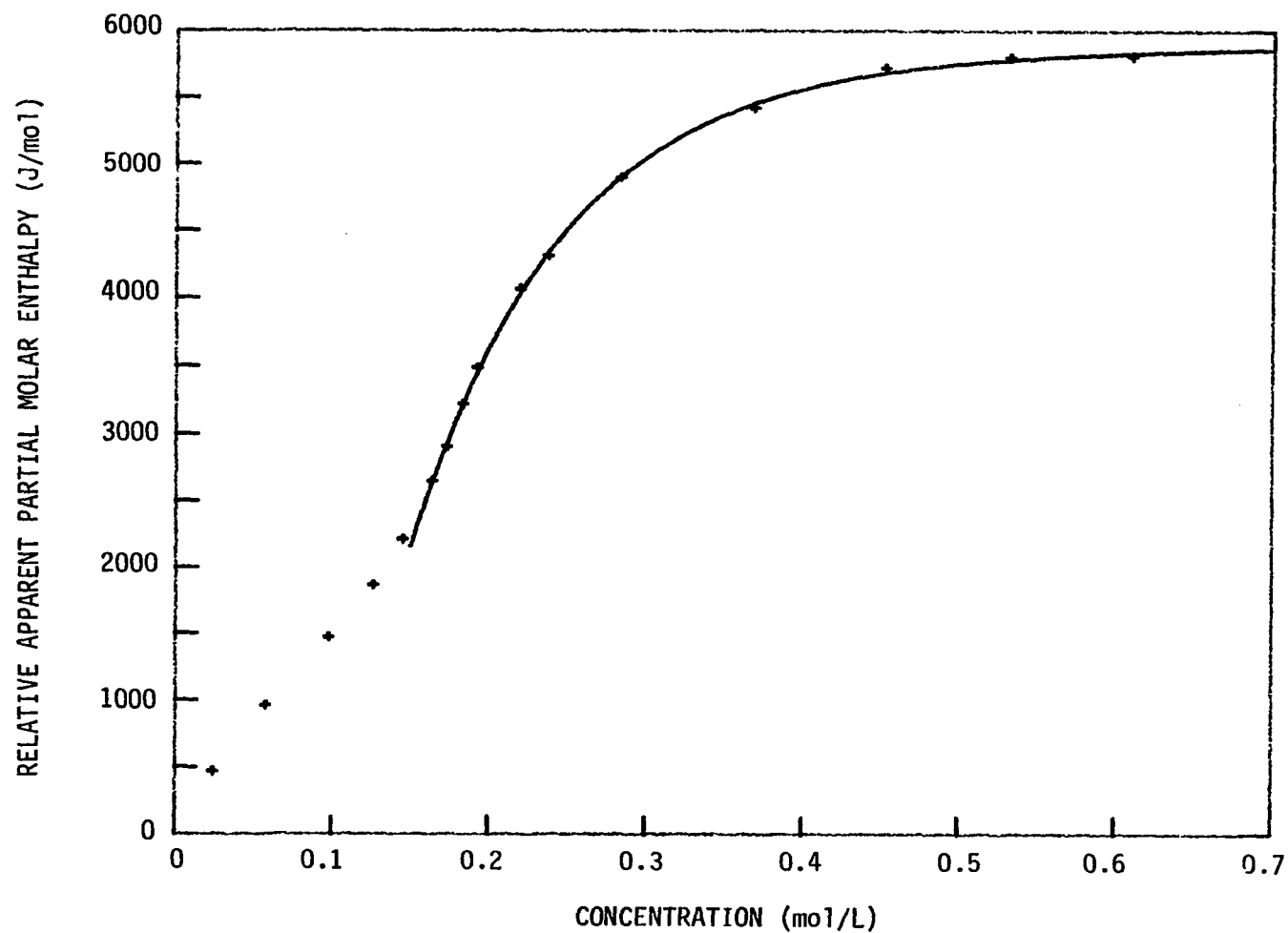


Figure IV-18: Relative apparent partial molar enthalpy of sodium octylsulfonate at 298.15 K. Plot of the function representing the best fit of the data in the post-cmc region.

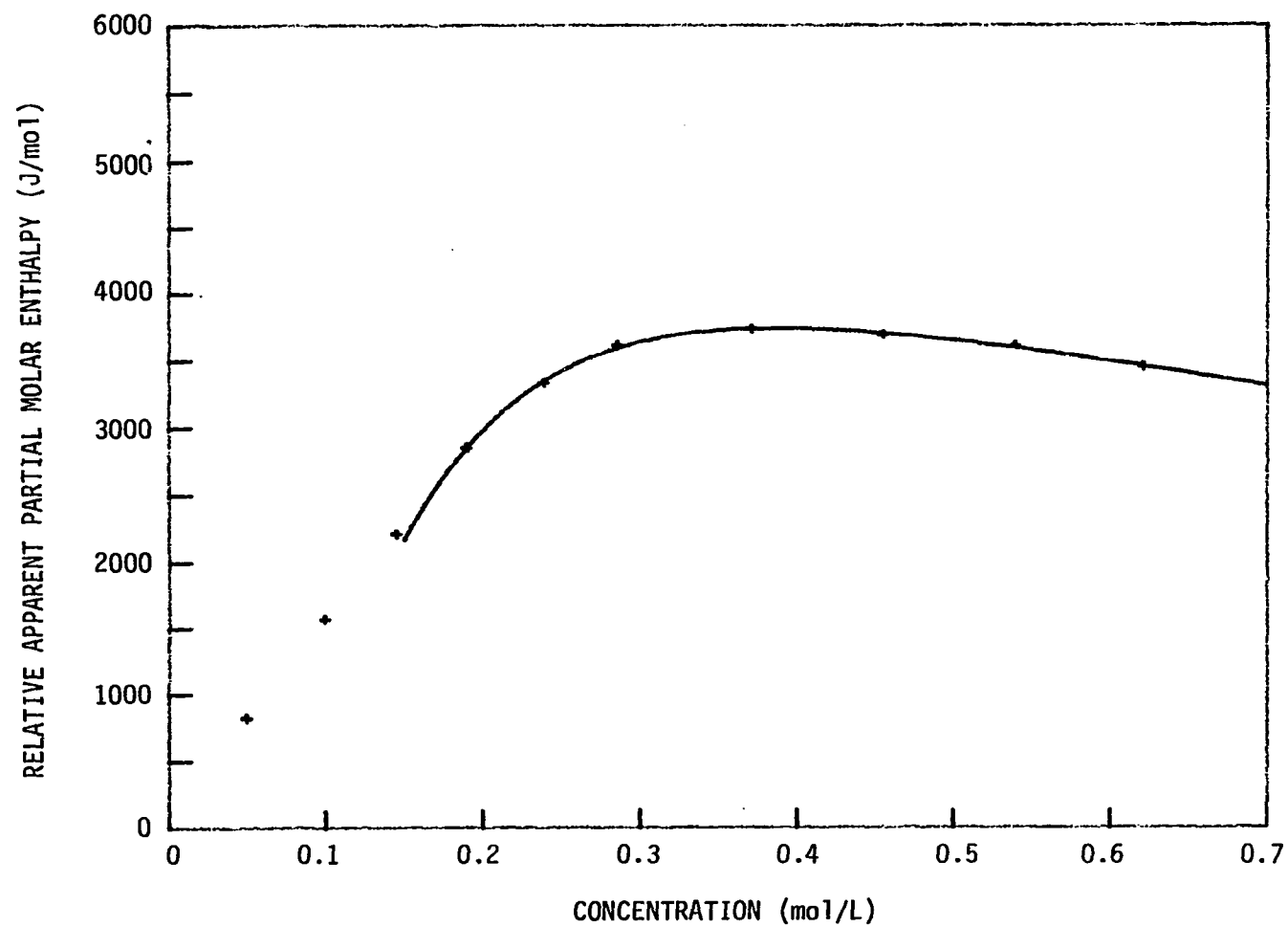


Figure IV-19: Relative apparent partial molar enthalpy of sodium octylsulfonate at 308.15 K. Plot of the function representing the best fit of the data in the post-cmc region.

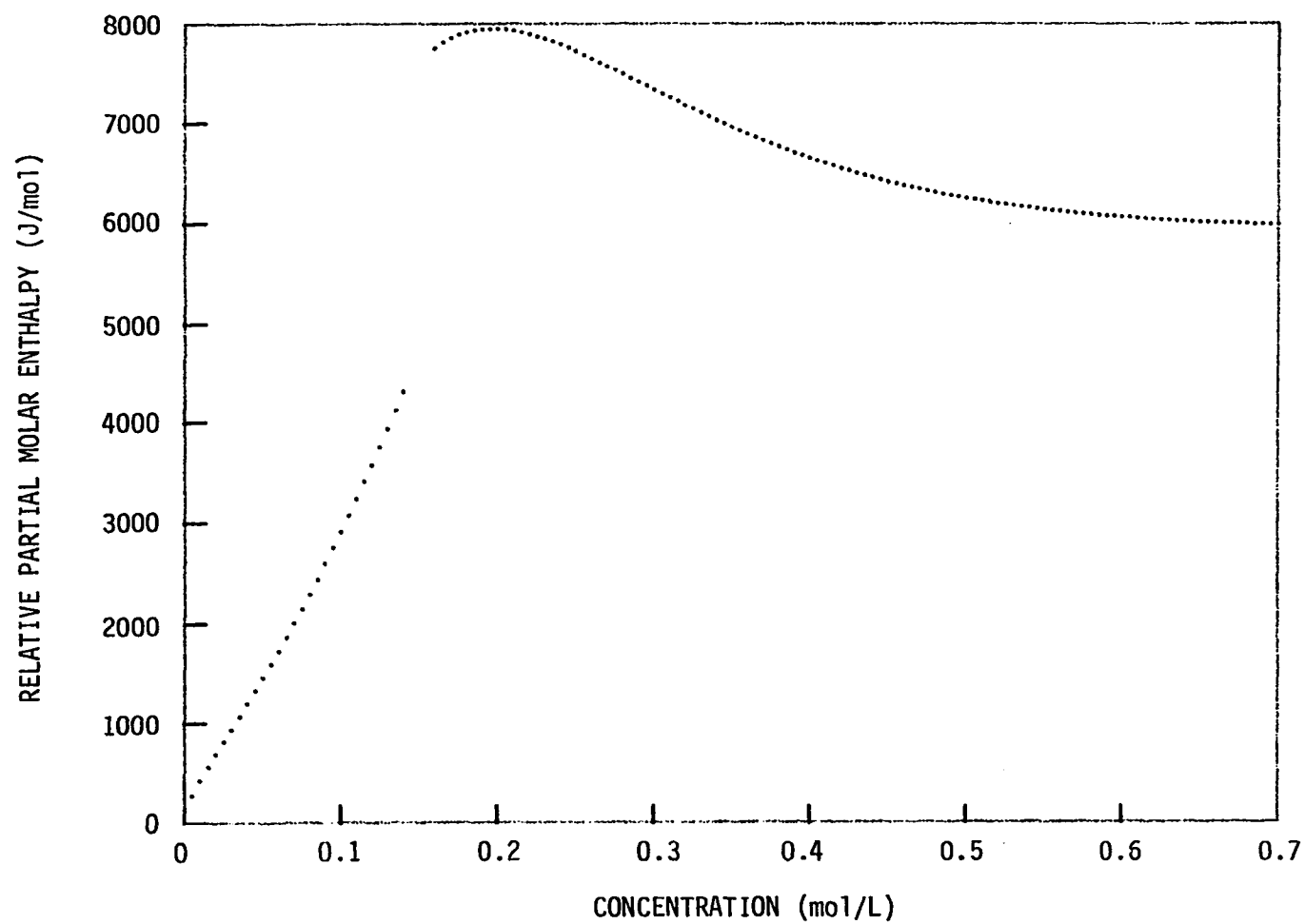


Figure IV-20: Relative partial molar enthalpy of sodium octyl-sulfonate at 298.15 K.

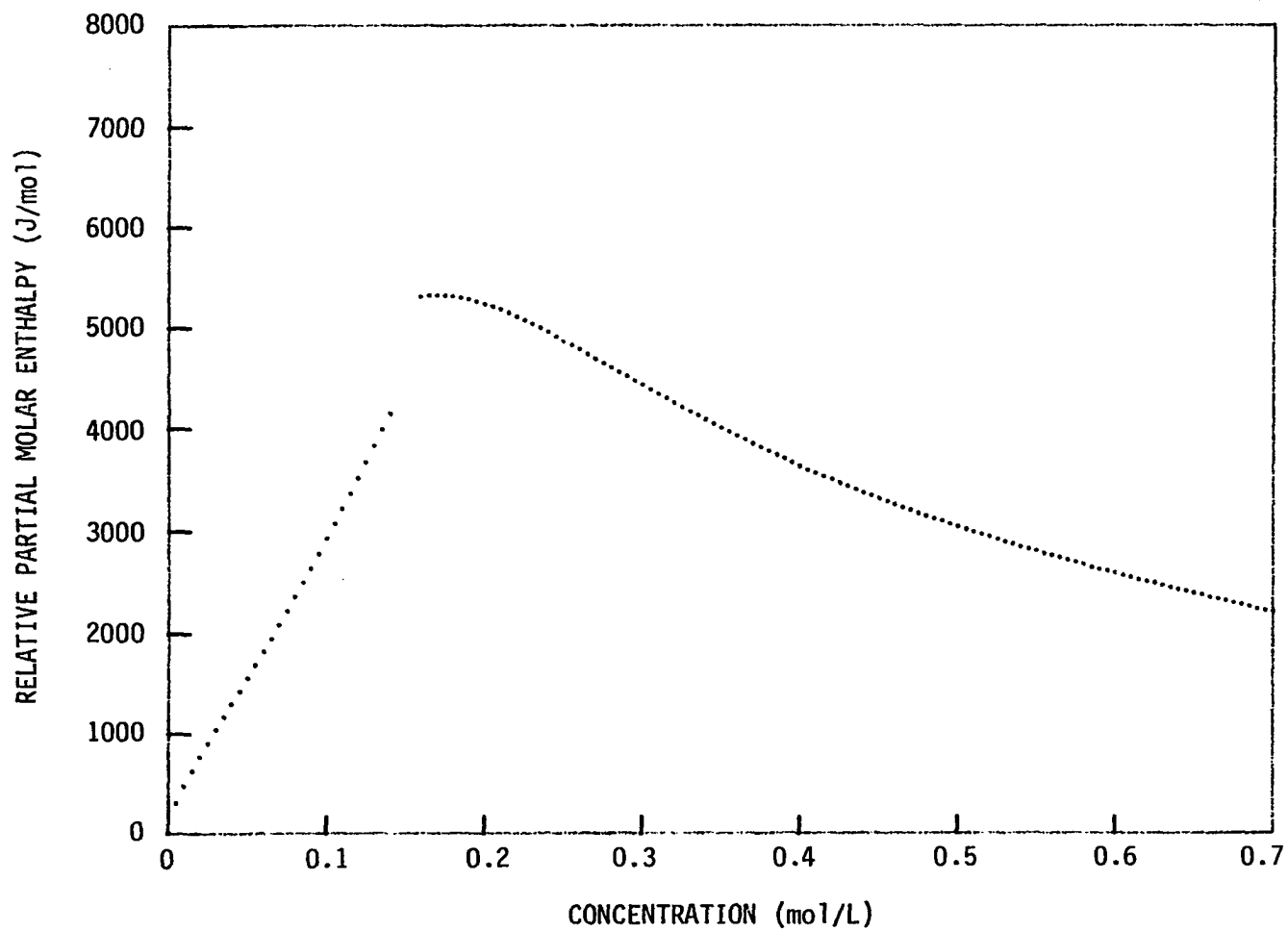


Figure IV-21: Relative partial molar enthalpy of sodium octyl-sulfonate at 308.15 K.

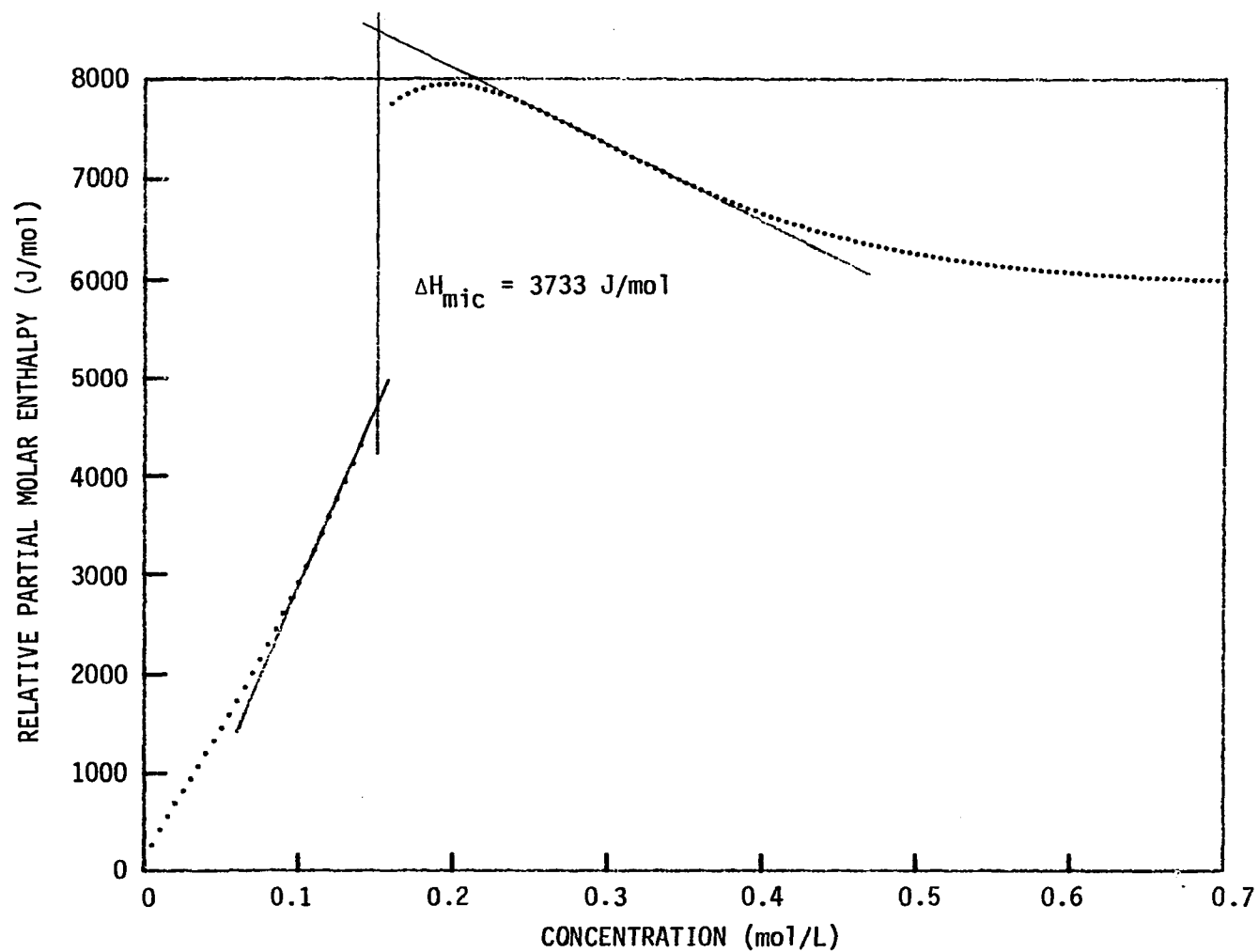


Figure IV-22: Relative apparent partial molar enthalpy of sodium octylsulfonate at 298.15 K showing the determination of the enthalpy of micelle formation. $\Delta H_{mic} = 3733 \text{ J/mol}$.

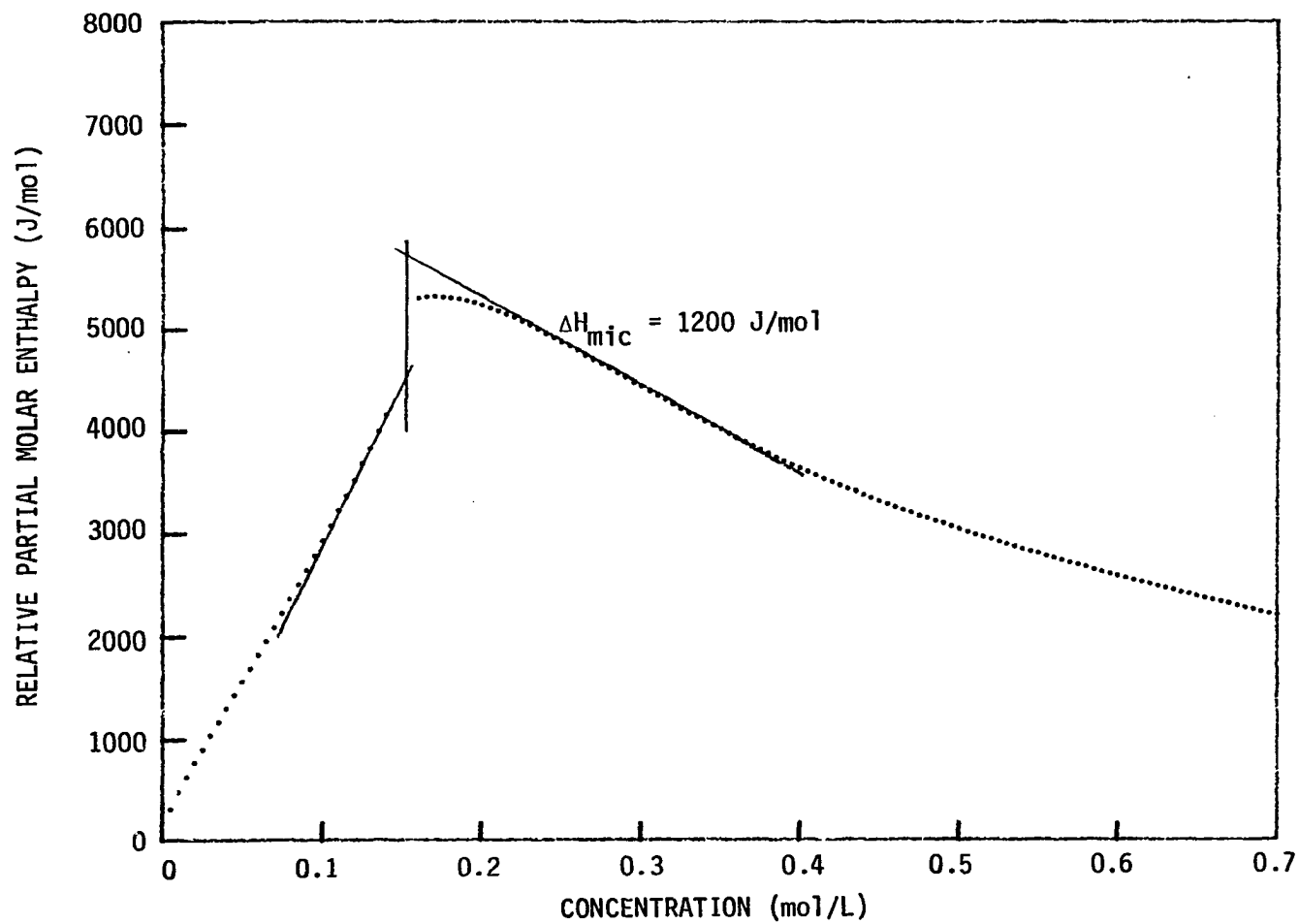


Figure IV-23: Relative apparent partial molar enthalpy of sodium octylsulfonate at 308.15 K showing the determination of the enthalpy of micelle formation. $\Delta H_{mic} = 1200 \text{ J/mol}$.

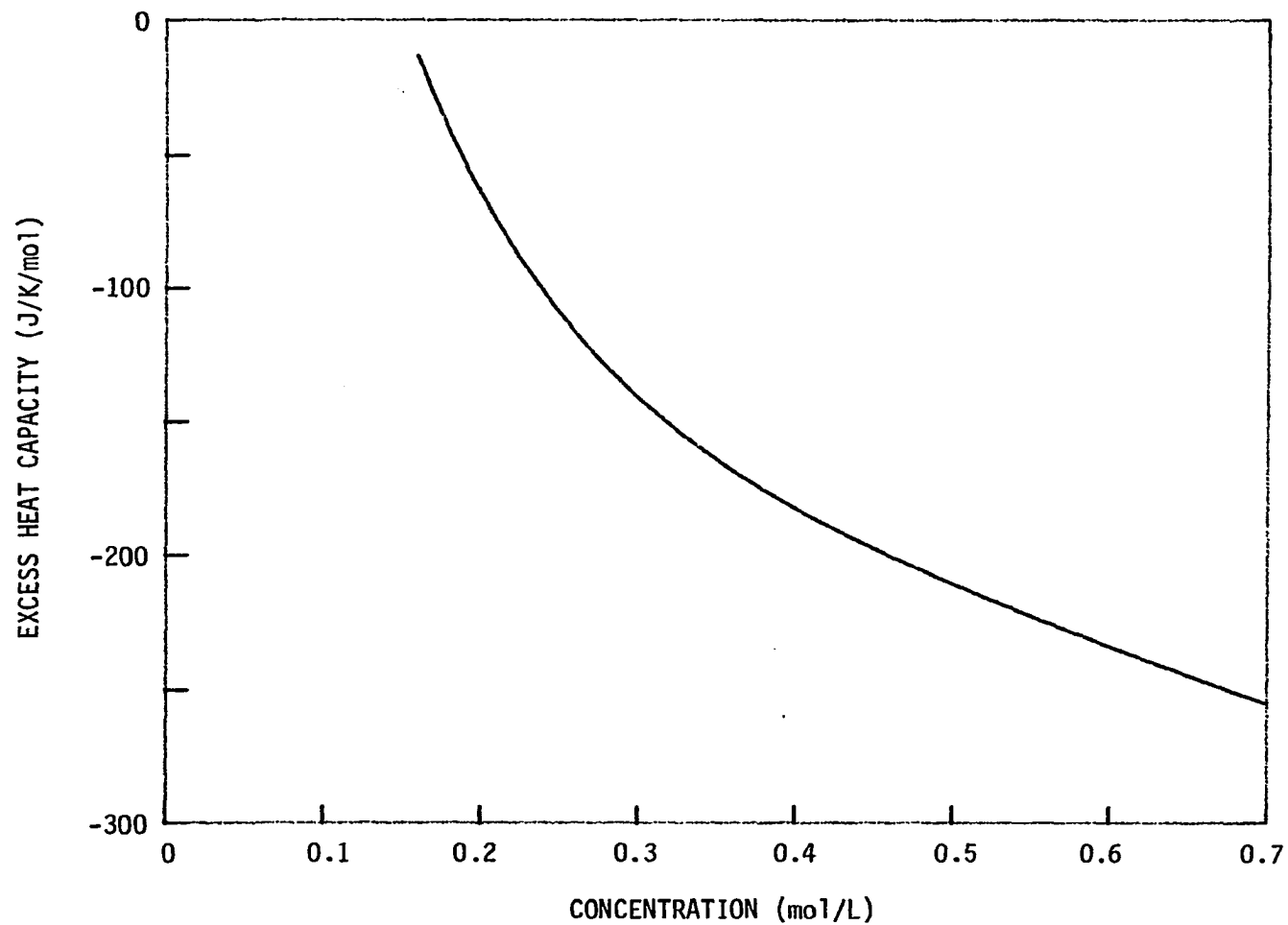


Figure IV-24: Excess heat capacity of sodium octylsulfonate. Temperature range was from 298.15 K to 308.15 K. The limiting value is $\Delta C_{p,mic}$ and is equal to -350 J/K/mol.

SOBS (g)	c_f (mol/L)	mmol	ΔH_s (J)	ΔH_s (J/mol)
0.0273	0.00187	0.0934	-1.738	-18.61
0.0933	0.00639	0.3192	-6.627	-20.76
0.1457	0.00998	0.4984	-11.22	-22.52
0.5332	0.0365	1.824	-42.22	-23.15
0.5599	0.0384	1.915	-45.32	-23.67

Table IV-17: Heats of solution of sodium octylbenzene-sulfonate in water at 298.15 K.

SOBS (g)	c_f (mol/L)	mmol	ΔH_s (J)	ΔH_s (J/mol)
0.0576	0.00395	0.1970	-5.759	-29.24
0.1483	0.01016	0.5073	-16.14	-31.82
0.2401	0.01645	0.8213	-22.21	-27.05
0.5277	0.03615	1.8051	-44.52	-24.66

Table IV-18a: Heats of solution of sodium octylbenzene-sulfonate in water at 308.15 K.

m_i (mol/kg)	ΔH_d (J)	c_i (mol/L)	c_f (mol/L)	mmol	ΔH_d (J/mol)
0.0217	-0.1068	0.0216	0.00083	0.0432	-2472.2
0.1035	-1.1773	0.1004	0.00387	0.2008	-5863.0

Table IV-18b: Heats of dilution of aqueous sodium octylbenzenesulfonate at 308.15 K.

T (K)	ΔH_S° (kJ/mol)	a_1
298.15	-17.64	4.6795×10^5
308.15	-27.51	4.0161×10^5

Table IV-19: Heat of solution at infinite dilution and dimer interaction coefficient of sodium octylbenzenesulfonate at 298.15 K and 308.15 K.

c (mol/L)	ϕL_2 (J/mol)
0.00187	970
0.00639	3120
0.00998	4880
0.0365	5510
0.0384	6030

Table IV-20a: Relative apparent partial molar enthalpies of sodium octylbenzenesulfonate at 298.15 K.

c (mol/L)	ϕL_2 (J/mol)
0.00395	1730
0.01016	4310
0.01645	-460
0.0216	-2074
0.0362	-2850
0.1035	-4169

Table IV-20b: Relative apparent partial molar enthalpies of sodium octylbenzenesulfonate at 308.15 K.

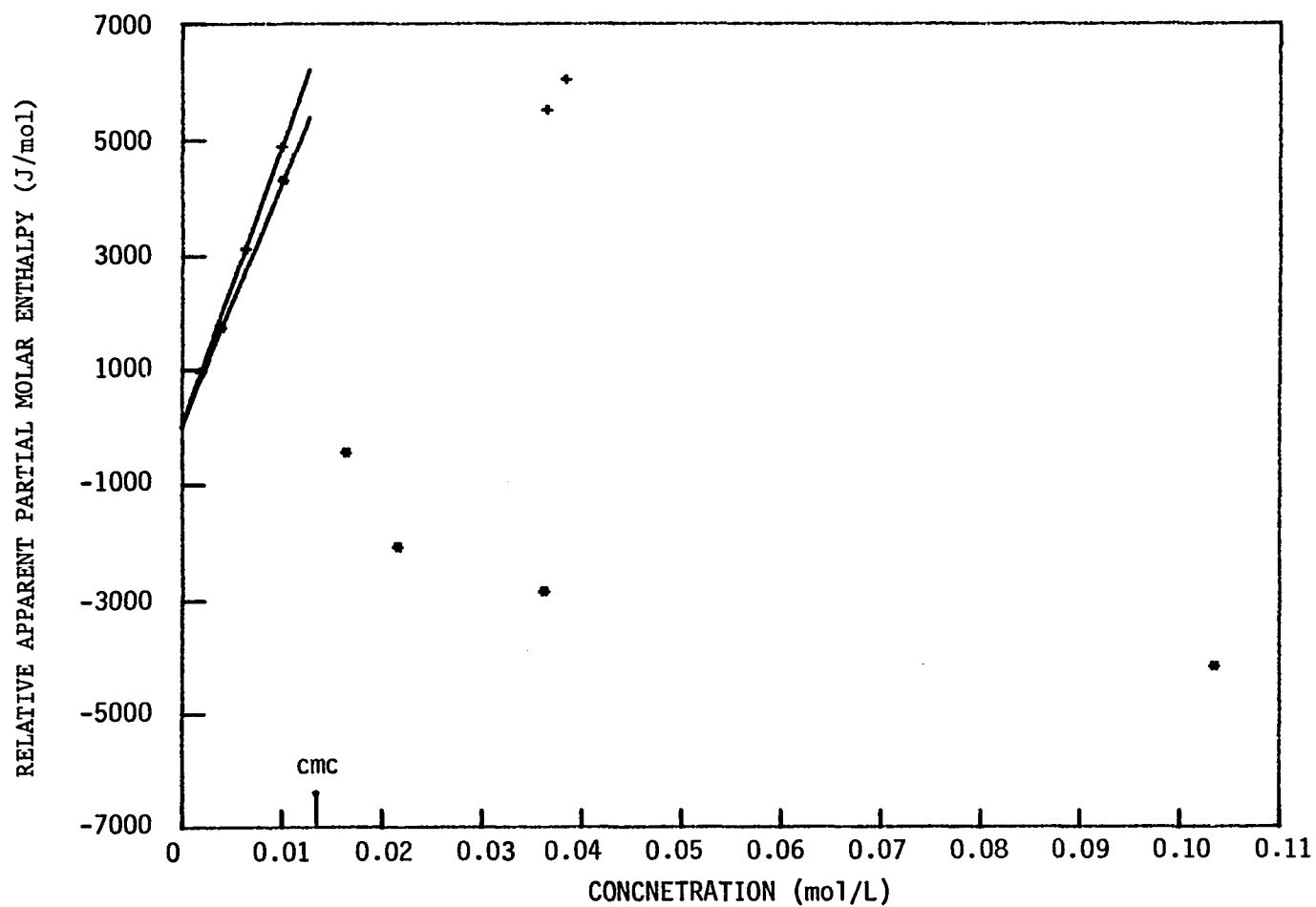


Figure IV-25: Relative apparent partial molar enthalpy of sodium octylbenzenesulfonate at 298.15 K (+) and 308.15 K (*). The lines are plots of the function representing the pre-cmc region at 298.15 K (upper) and at 308.15 K (lower).

SOBS (g)	c (mol/L)	ϕL_2 (J/mol)	ΔH_s (J)	$\Delta H_s(\text{obs})$ (J)	ΔH_{ads} (J)	SAz-1 (g)	ΔH_{ads} (J/g)
0.5303	0.0363	-5510	-41.99	-35.68	6.31	1.1176	5.65
0.5302	0.0363	-5510	-41.99	-32.34	9.65	1.6851	5.73

Table IV-21: Heats of adsorption of sodium octylbenzenesulfonate on Na-SAz-1 montmorillonite at 298.15 K.

SAz-1 (g)	$\Delta H_i(\text{obs})$ (J)	ΔH_i (J/g)	ΔH_i (J)	ΔH_{ads} (J)	c (mol/L)	ΔH_{ads} (J/g)
0.8754	85.94	98.17				
0.8923	86.10	96.49				
1.3000	102.68		100.25	2.43	0.1132	2.359
1.2047	96.16		93.80	2.36	0.1586	2.446
1.2270	98.06		95.54	2.52	0.2030	2.568

Table IV-22: Heats of immersion of nat-SAz-1 in water and heats of adsorption of sodium octylsulfate on nat-SAz-1 at several concentrations at 298.15 K.

Al_2O_3 (g)	$\Delta H_i(\text{obs})$ (J)	ΔH_i (J/g)	ΔH_{ad} (J/g)	c (mol/L)	amphiphile
1.0917	-0.5700	-0.5220			
1.1306	-0.6177	-0.5460			
1.2528	-1.403	-1.120	-0.590	0.0869	SOBS
1.3125	-1.172	-0.8930	-0.363	0.4980	SOS
1.2595	-1.164	-0.9242	-0.394	0.4954	SOSN

Table IV-24: Heats of immersion of alumina in water and heats of adsorption of sodium octylsulfate, sodium octylsulfonate and sodium octylbenzenesulfonate on alumina at 298.15 K.

Adsorbent	Adsorbate	ΔH_{ads} (J/mol)
Al_2O_3	SOBS	13.95
Al_2O_3	SOS	8.58
Al_2O_3	SOSN	9.32
Na-SAz-1	SOBS	7.45
nat-SAz-1	SOS	3.21

Table IV-23: Heats of adsorption of sodium octylbenzenesulfonate, sodium octylsulfate and sodium octylsulfonate on alumina, sodium-homoionic SAz-1 montmorillonite and natural SAz-1 montmorillonite at 298.15 K.

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V. DISCUSSION

i. General

The primary objective of this work was to elucidate the details of the aggregation behavior of amphiphilic molecules. As will be demonstrated in the following analysis of the heat of dilution results, enthalpy data for surfactant systems can yield valuable insight into amphiphilic aggregation behavior. The data have been modelled using the mass action model; the model and the results will be discussed in detail. It has been possible to draw significant conclusions about association in the pre-micellar region, the details of micellar aggregation, and the relative importance of electrostatic interactions throughout the range of concentration.

These questions have been addressed before, but the enthalpy data provide a unique perspective not easily obtained by other means. In addition, the development of a model for the behavior of the partial molar enthalpy of amphiphilic solutions (making use of the mass action approach), while not the final stage, represents an important advance in our understanding of surfactant solutions. In view of the confusion that exists with regard to enthalpies of micellization the results of the model are of especial value in giving us an accurate indication of

the various terms which contribute to the enthalpy and their relative importance.

The limited objectives of the study of surfactant-solid surface interactions were to determine the quantitative magnitude of the interaction, and to determine the feasibility of the calorimetric approach to the study of these problems. The results are in good agreement with qualitative knowledge concerning adsorption of surfactants at mineral oxide surfaces (1, 2, 3). No similar measurements have been reported. In addition it may be concluded that the calorimetric approach shows a great deal of promise for systematic study of this problem.

ii. Modelling

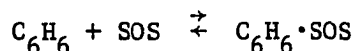
As was stated above, some form of the MEM is probably essential in order realistically to account for the association behavior of surfactants, especially those with a relatively small aggregation number and a high cmc. Since the cmc occurs at a relatively high concentration there ought to be an ample concentration range in which to observe pre-micellar association (should any occur). It should also be possible to detect the features of the micelle formation process, and post-cmc interactions.

Hydrophobic solutes typically display association into small aggregates. For example, a dimerization constant of 0.5 L/mol and a dimerization enthalpy of 10 kJ/mol (at 298 K) are typical (4, 5, 6). This would correspond to about five percent dimer at a concentration equal to the cmc of sodium octylsulfate, 0.14 M, an amount that would be more than enough to cause a substantial enthalpy effect, and hence ought to be easily observable.

When the data for SOS and SOSN were fitted to Eqn. (IV-1) above, a number of terms and combinations of terms were tried as corrections to DHLL behavior, including, for example, $c^{3/2}$, $c^{5/2}$, and c^3 . A linear term and a quadratic term were ultimately used because this combination gave the best (least-squares) fit of the data. Considering

the interpretation of these parameters as interaction coefficients, this indicated that dimer and trimer formation were contributing significantly to the enthalpy in the pre-micellar region. In addition, the relative magnitude of the coefficients indicated that dimerization and trimerization are of about equal significance and in fact contribute more to ϕL_2 , even at low concentrations, than the DHLL term.

There are two reasons for considering these terms to be due to hydrophobic association rather than electrostatic effects. First, hydrophobic systems involving no ionic species typically display aggregation into small aggregates with equilibrium constants and enthalpies sufficient to account for the effects observed (4). For instance, the association constant for the benzene-SOS interaction:



is about 0.5 L/mol (4). Second, most of the theoretically based corrections to the DHLL are in the opposite direction to the observed deviations in enthalpy. That is, they tend to screen electrostatic interactions especially at higher concentrations. For example, there is a slight negative deviation from the DHLL enthalpy for NaCl at a concentration equal to the cmc of SOS (7). The large positive deviations observed with ionic amphiphiles, however, would require some kind of dramatic enhancement of electrostatic interactions at very low concentrations. It seems much more reasonable to assume that these large positive effects are due to hydrophobic association.

There are, of course, numerous empirical corrections to the DHLL which are capable of accounting for positive deviations. The

usual procedure is to add a linear term, and any other higher order terms which are deemed necessary in order to fit the data (7, 8). It is readily acknowledged that no unambiguous distinction can be made (at this time) between such empirical 'electrostatic' corrections and corrections due to association (7); both consist operationally of exactly the same thing: adding higher order terms to the DHLL. Whether they are in fact due to electrostatic or hydrophobic effects cannot be finally determined at present on the basis of enthalpy data.

In defense of my choice to call the pre-micellar interactions hydrophobic consider the relative magnitudes of the coefficients. In dealing with simple strong electrolytes a linear term contributing 5-10% to the relative apparent partial molar enthalpy may be required in order to account for data at higher concentrations (although it should also be kept in mind that for strong electrolytes the coefficient of this term would be negative). However, the coefficients obtained here represent a much larger departure from ideal behavior, on the order of five times the magnitude of the DH term. In fact, in the case of octylbenzenesulfonate the departure is even larger. This cannot, in my opinion, be attributed to electrostatic effects. It may well be true that a portion of the higher order terms is due to electrostatic effects, but it is claimed here that the unusual magnitude and the positive sign of the terms are due to hydrophobic association.

Mukerjee (9) and others (10) have discussed the problem of pre-micellar association on the basis of conductivity data. It is argued that dimerization would increase the conductivity because the

dimer would have a smaller hydrodynamic radius than two monomers (9). On the other hand, any kind of increased interaction between oppositely charged ions (e.g. a decreased distance of closest approach, or ion pairing) would have the effect of decreasing the conductivity. The meaning of the data has been subject to some controversy, and it is not clear which phenomenon is actually occurring (10). However, some writers (particularly Mukerjee) maintain that conductivity data definitely indicate association in the pre-cmc region.

Assuming the formation of dimers and trimers the equilibria will be:



The total concentration will be:

$$c = c_1 + 2c_2 + 3c_3$$

where the subscript indicates the state of aggregation. Mass balance thus requires that:

$$c_2 = K_2 c_1^2$$

$$c_3 = K_3 c_1^3$$

Therefore:

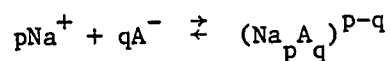
$$c = c_1 + 2K_2 c_1^2 + 3K_3 c_1^3$$

This concentration will henceforth be referred to as the 'free'

concentration; meaning the total concentration of amphiphile not in micelles.

$$c_F = c_1 + 2c_2 + 3c_3$$

With the onset of micelle formation, a further equilibrium must be considered:



for which the thermodynamic equilibrium constant will be:

$$K_M = \frac{a_{(\text{Na}_p\text{A}_q)^{p-q}}}{a_{\text{Na}}^p a_{\text{A}}^q}$$

The average aggregation number, $\langle n \rangle$, is equal to q . The fraction of counterions 'bound' to the micelle surface is $r=p/q$. Mass balance requires that:

$$c = c_F + qc_M$$

$$c = c_{\text{Na}} + rqc_M$$

from which qc_M may be eliminated to yield:

$$c_{\text{Na}} = (1-r)c + rc_F$$

The equilibrium constant becomes:

$$K = \frac{c_M \gamma_M}{((1-r)c + rc_F)^p c_1^q \gamma_{\pm}^{p+q}} \quad (1)$$

The activity coefficient of the micelle will be assumed to be

essentially unity. This may be justified by pointing out that the actual concentration of micelles remains very small throughout most of the concentration range considered. The mean activity coefficient of the ions is defined as:

$$\ln \gamma_{\pm} = \frac{-A\sqrt{I}}{1+B\sqrt{I}}$$

where A is the DH coefficient, equal to 0.5091 at 298.15 K and 0.5189 at 308.15 K (8, 11); B is an ionic size parameter. The ionic strength is defined as:

$$I = \sum c_i z_i^2$$

$$I = \frac{1}{2}((1-r)c + rc_F) + \frac{1}{2}c_F + \frac{1}{2}(c - c_F)(p-q)^2/q$$

This equation would treat the micelle as if it were a very highly charged point charge, which is most unrealistic. For this reason, a screening factor was inserted in front of the micellar charge:

$$I = (1-r)c/2 + (1+r)c_F/2 + (c - c_F)(sf(p-q))^2/2q$$

in order to account for both the large size (which will tend to decrease the effect of the charge) and the screening due to the distribution of counterions in the vicinity of the micelle.

Note also that it has been assumed that amphiphile found in dimers and trimers contributes to the ionic strength as though it were free. This is because such small aggregates almost certainly orient

themselves with the charged head groups far apart, since this would still permit substantial contact of the hydrocarbon groups. (Remember that these are pairs of like-charged molecules, not ion-pairs.) In this orientation the charges will not be much closer to each other than in the free aqueous state, or at least the change in free energy will be only a small fraction of what it would be if the ionic head groups were adjacent to each other, and only a small fraction of the energy gained by association of the hydrophobic groups.

Gustavsson and Lindman (11, 12) studied the interactions between sodium and octylsulfate using NMR relaxation. Among other results they concluded that sodium does not bind to any pre-micellar aggregates which would support my assumption that the formation of pre-micellar aggregates does not greatly disturb the electrostatic energy.

Activity coefficients have not been included in the expressions for dimer and trimer formation. This amounts to assuming that the ratio of the dimer activity coefficient to the square of the monomer activity coefficient is essentially unity, and similarly for the trimer. This is certainly an approximation, as is the assumption above that the formation of dimers and trimers does not affect the electrostatic energy. The significance of these approximations and the question of how they affect the result will be discussed below. It may also be stated that the enthalpy of dimerization obtained in this way may well contain an element due to electrostatic interactions, as does the enthalpy of micellization. In any case the data are not

sufficiently precise to permit the entire distribution of equilibrium constants and activity coefficients to be determined.

The concentration of micelles will be:

$$c_M = K_M((1-r)c + rc_F)^p c_1^q \gamma_{\pm}^{p+q}$$

and the total concentration becomes:

$$c = c_F + qc_M$$

A function, f , may be defined as:

$$f = c_1 + 2c_2 + 3c_3 + qc_M - c$$

Given a value of c , and an initial guess of c_1 , the best value of c_1 consistent with a given set of association constants may be found by iteration using a Newton's method:

$$c_1' = c_1 - f/f'$$

This strategy was used to calculate the monomer concentration, given values of the dimer, trimer and micelle constants. The fractions in the dimer, trimer and micelle were calculated from the monomer concentration.

The enthalpy results may be considered to be the sum of an electrostatic term (a modified DHLL to take into account electrostatic screening at the higher concentrations) and terms accounting for the enthalpy of association (14):

$$\phi L_2 = \frac{a_0 \sqrt{I}}{1+B/I} + a_2 \Delta H_2 + a_3 \Delta H_3 + a_M \Delta H_M \quad (2)$$

where a_0 is the DH limiting slope given above for Eq. IV-(3), and a_2 , a_3 and a_M represent the fractions of amphiphile in the form of dimer, trimer and micelle respectively:

$$a_2 = 2c_2/c$$

$$a_3 = 3c_3/c$$

$$a_M = qc_M/c$$

A modified DH relation has been used here because (i) the equation is in terms of ionic strength, and (ii) it proved to be essential to moderate the ionic strength dependence at higher concentrations. Dividing the simple DHLL by $1+B\sqrt{I}$ accounts in large part for electrostatic screening in more concentrated electrolyte solutions.

In the context of this model the enthalpies represented by $\Delta H_{2,3}$, and ΔH_M refer to rigorously defined physical processes, namely the equilibria defined above. The standard state is, of course, the hypothetical standard state at unit activity.

The relative apparent partial molar enthalpy data were modelled using these equations. The resulting parameters are listed in Table V-1. Tables V-2, V-3, V-4 and V-5 list the calculated values of the enthalpy, the monomer concentration, and the fraction in the micelle at each concentration. Figures V-1, V-2, V-3 and V-4 are plots of the calculated enthalpy and the data for SOS and SOSN at 298.15 K and 308.15 K showing the fit of the model to the data.

Values of the dimer, trimer and micelle constants were chosen to be 0.5 L/mol, 2 L²/mol² and 21 respectively for both surfactants at both temperatures. (The value given for the micellization constant is

the q th root of the quantity defined by Eq. (1). The units of the concentration terms on the rhs of Eq. (1) are molarity.) The degree of counterion binding was assumed to be 0.6 throughout (12). The screening factor was set equal to 0.3 (the micelle was treated as though it had three tenths of its formal charge) because this value appeared to provide about the right degree of attenuation of the micellar charge. The ionic size parameter was chosen to be 7, which is a typical value for large organic ions (7).

There has been some debate in the literature about whether the fraction of counterions bound to the micelle is constant over a range of concentrations. Eatough and Rehfeld (15) assumed a varying degree of counterion binding in order to interpret heat of dilution data for sodium dodecylsulfate. However, other work (16, 17) indicates that this fraction is essentially constant over a wide range of conditions. Gunnarsson, Jönsson and Wennerström (18) (vide supra) reached this same conclusion from their development of the theory of electrostatic interactions in micellar solutions. On the basis of this theory and experimental data it was decided to use a single formal degree of counterion binding throughout.

During the course of developing the model, numerous values of the dimer, trimer and micelle constants were tried. The dimer and trimer constants were even allowed to be varied by the program in order to see what values would be produced by the least squares procedure. The resulting observation was that the particular values of K_2 and K_3 used determined the values of the dimer and trimer formation enthalpies, but not the goodness of the fit. This is due to the

coupling of the equilibrium constants and the enthalpies - which is a feature of this kind of data. The product of the equilibrium constant and the enthalpy could be determined quite well, but they could not be determined independently. If the dimer and trimer constants and enthalpies were all allowed to vary simultaneously, spurious results were obtained, with the least squares procedure usually failing to converge. This is a problem of fitting and does not reflect a physical feature except the high degree of coupling inherent in the quantities. Therefore, reasonable values of K_2 and K_3 were chosen consistent with studies of related hydrophobic systems, and the enthalpies were extracted from the least squares fit.

In addition one further consideration affected the choice of values of K_2 and K_3 . Activity data are available for SOS, from which monomer activities over a range of concentrations may be calculated (19). The micelle constant and the dimer and trimer constants were chosen so as to most nearly match these results, and to predict the correct cmc.

Hydrophobic enthalpies and constants are usually very dependent on temperature. It is therefore necessary to discuss why the values of the dimer, trimer, and micelle constants were not varied with temperature. The use of the same set of constants for both surfactants also requires some comment.

SOS and SOSN have slightly different values of the cmc. Strictly speaking, SOS should therefore have a slightly larger micelle formation constant than SOSN. However, in the context of this model the micelle constant cannot be determined with any great degree of

precision. The small change expected is within the uncertainty in K_M , and since the two constants would not be experimentally distinguishable it was thought best simply to use the same quantity for both. It simply made no difference to the fit if 20.5 were used instead of 21.

Small variations with temperature of the dimer and trimer enthalpies were detected by the model. However, these quantities would be expected to vary more than was observed if indeed they were due to hydrophobic association. That they did not is also due to the coupling of the equilibrium constant with the enthalpy. Positive enthalpies would result in a decrease in K with increasing temperature, hence the decrease in K could nearly balance the increase in ΔH . In order to elucidate this point further it is essential that additional work be done over a wider range of temperatures, particularly at the temperature at which the enthalpy becomes zero. This would make it possible to de-couple K and ΔH and would therefore be extremely useful.

The enthalpy of micelle formation also changes with temperature, but the accompanying change in K is much smaller and is not detectable. It may be observed from the plots that some features of the experimental data are not reproduced well by the model. However, the overall behavior is accounted for quite well up to a concentration of about twice the cmc.

Table V-6 summarizes the enthalpy of micellization results including the results of the Desnoyers method (vide supra). Perhaps the most noticeable feature of the numbers is that the MEM results are always more positive than the values obtained from the Desnoyers method. In the case of SOS at 308.15 K there is even a difference of

sign. That the numbers are not equal for the two methods is a consequence of the different definitions of standard enthalpies involved.

An examination of all the MEM plots (Figures V-1, 2, 3, 4) demonstrates that in every case the enthalpy calculated by the model tends to become nearly constant at high concentrations. On the other hand the experimental values show a definite tendency to decrease at the highest concentrations. This is related to the reason for why the enthalpy of micelle formation of SOS at 308.15 K turns out not to be negative.

According to the model the monomer, (and hence the dimer and trimer) concentration decreases quite rapidly beyond the cmc. This decrease will be accompanied by a corresponding decrease in the contribution to the enthalpy due to the DH term, as well as terms due to dimerization and trimerization. It is simply a feature of this model that the decreases in the electrostatic, dimer and trimer enthalpies are exactly balanced by the increase in the micelle enthalpy, leading to a constant enthalpy at high concentrations. Obviously, if the relative apparent partial molar enthalpy is to remain nearly constant above the cmc (even if it does begin to decrease at much higher concentrations) the micelle enthalpy must be positive.

This argument is somewhat dependent on what the DH term is expected to do. The DH term is a function of the ionic strength, which in turn is dependent on the concentrations and charges of all the species present. At higher concentrations some of these interactions are attenuated due to electrostatic screening (accounted for by the

$1/(1+B\sqrt{I})$ term). However, it proved impossible to account for the data using any expression for the ionic strength which increased rapidly beyond the cmc (due to the highly charged micelles). Only a substantial screening factor moderated the charge of the micelles sufficiently to model the data, but this resulted in an ionic strength which did not increase rapidly enough above the cmc to force the micellization enthalpy to become negative in the case of SOS at 308.15 K.

I think that this interplay of effects is in fact duplicating a real characteristic of the system; that the enthalpy of micellization is being determined correctly, but that another, unaccounted for effect is responsible for the failure at high concentrations. Another observation which supports this conclusion is that substantial changes in the non-varying parameters did not greatly affect the value of the micellization enthalpy; instead such changes usually resulted in deteriorating the fit.

The model fails correctly to account for the data in two significant ways. It is very difficult to force the model to reproduce the sharp change at the cmc, and the model cannot account for the observed behavior at high concentrations. The first failure is probably due to weakness in the treatment of electrostatic effects and assumptions made about the contribution to the electrostatic picture due to association into small aggregates. At high concentrations it is common for the treatment of electrolyte solutions to become very complex. Thus it is not surprising that the model does not adequately treat phenomena in this region. The specific physical cause of the

behavior is probably long-range electrostatic interactions between the highly charged micelles.

At high concentrations the fraction of amphiphile in micelles approaches unity, and the concentration of micelles becomes large enough for micelle-micelle interactions to become substantial, especially considering their large electrostatic charge. Another possible explanation (cf. Ref. 15) is that varying interactions between the micelle and the counterions are responsible for the high concentration behavior.

iii. Comparisons With the Literature

Goddard, Hoeve and Benson (20) reported heat of dilution data for sodium octylsulfate at 298.15 K in 1957. Their experimental method consisted of diluting a volume of 2.9761 molal sodium octylsulfate to various final concentrations. This procedure is fairly analogous to the method which I have used. It may be seen from the plots of heats of dilution presented above that if the downward trend of the data continues the measured heat of dilution will have become negative by the time a concentration of 3 molal has been reached. This is in fact what Goddard, et al. observed. Their heat of dilution (as a function of final concentration) curve has the same shape and relative magnitude as that obtained in this work. Goddard, et al. did not derive values of the relative apparent partial molar enthalpy, but they do give values of the function:

$$\bar{H}_2 - \text{const.} \propto \bar{L}_2$$

which is related to the relative partial molar enthalpy, although the constant is arbitrary, and therefore the absolute magnitude of the quantity is arbitrary. The behavior of this function is very similar to the behavior of the relative partial molar enthalpy derived above. Goddard, et al. do not report any data at higher temperatures.

Goddard, et al. calculated a standard heat of micelle formation from their data of 3.35 kJ/mol at 298.15 K. Benjamin (21) recalculated Goddard, et al.'s data to obtain a standard heat of micellization of 6.3 kJ/mol. The definition of the standard heat of micellization used by Benjamin was:

$$\Delta H_M^\circ = \bar{H}_2(\text{just above the cmc}) - \bar{H}_2(\text{infinite dilution})$$

This is a different definition than that employed by Goddard, et al. Neither definition refers to a well defined physical process and hence the numbers cannot easily be compared to the values obtained from the MEM. They are substantially larger than the values I obtained using the Desnoyers method, although once again the relation between the definitions is unclear.

Kresheck and Hargraves (22) performed calorimetric measurements similar to those of Goddard, et al. and obtained values of the standard heat of micelle formation for several systems using a definition similar to Benjamin's. For sodium octylsulfate they report values of 4.81 kJ/mol and 1.46 kJ/mol at 298.15 K and 308.15 K respectively. These numbers are very similar to the values I have obtained from the mass action model, although this must be fortuitous in light of the difficulty of relating the definition of the standard enthalpy of micelle formation used by Kresheck and Hargraves to the definition used in the MEM. Kresheck and Hargraves also reported a value of $\Delta C_{p,\text{mic}}$ of -309.6 J/K/mol which is in excellent agreement with my results. This points up the fact that while it is often difficult to relate various reported values of enthalpies of micellization at any

one temperature, differences with temperature often turn out to be remarkably similar regardless of definitions of micellization enthalpies.

Flockhart (23) determined the enthalpy of micelle formation of sodium octylsulfate from the temperature dependence of the cmc (ignoring the effects of counterion binding). He obtained values of 0.84 kJ/mol and -1.68 kJ/mol at 298.15 K and 308.15 K respectively. (I have interpolated Flockhart's data to obtain these values; his numbers were given at 10 degree intervals beginning at 10 deg C.) The equation which Flockhart used to calculate the enthalpy of micelle formation was:

$$\Delta H_M^\circ = -RT^2 \, d\ln(\text{cmc})/dT$$

Moroi, et al. (24) obtained 2.51 kJ/mol and -4.06 kJ/mol at 298.15 K and 308.15 K using another formula which includes counterion binding:

$$\Delta H_M^\circ = -RT^2(1+p/n) \, d\ln(\text{cmc})/dT$$

(I have also interpolated Moroi's data to obtain points at 5 deg intervals.) These values are substantially more negative than those obtained in this work, but once again, the difference with temperature turns out to be quite similar. The significance of these quantities is difficult to ascertain. The definition of the standard enthalpy of micellization which was used is of dubious value, especially considering the probability of pre-micellar association. As Mukerjee (9) points out, the identification of the monomer concentration with the cmc (which underlies the two above equations) cannot be made if

significant quantities of pre-micellar aggregates exist. Nevertheless, the trends in these data also show the tendency towards increasingly negative enthalpies with increasing temperature which is always observed.

To my knowledge, no enthalpy data exist in the literature for sodium octylsulfonate. There is a great deal of similarity between the results for SOS and SOSN which lends considerable confidence to the measurements. It is thought that the oxygen atom in the C-O-S linkage in alkylsulfates behaves like an extra half carbon (25). Since the sulfonate lacks this oxygen it might be expected that it would behave much like a 7.5 carbon alkylsulfate. This is borne out by the observation that the cmc is slightly lower for the sulfate than for the sulfonate. It is also consistent with the heat data. The shorter chain alkylsulfates show increasing partial molar enthalpies as the chain length gets shorter (26, 27), and at a given concentration, the relative partial molar enthalpy (as well as the relative apparent partial molar enthalpy) of sodium octylsulfonate is always above the value for sodium octylsulfate (in the post-cmc region).

It may also be pointed out that the temperature at which the enthalpy of micellization becomes zero is evidently a little higher for the sulfonate than for the sulfate since the enthalpy of micellization, while decreasing with increasing temperature, is larger at a given temperature than the value for the sulfate. Which would be consistent with our understanding of hydrophobic systems (10). Kresheck (10) gives some data on the temperature at which ΔH becomes zero for a few surfactants. The value for C8 sulfate is 29 deg C, while for C12

sulfate it is 29 deg C and for C14 sulfate it is 21 deg C. This trend indicates that the zero enthalpy temperature increases with decreasing chain length. If octylsulfonate may be considered equivalent to 7.5C sulfate in ought to have a higher zero enthalpy temperature than octylsulfate, which is what was observed.

The behavior of the octylbenzene sulfonate results are very typical of longer chain anionic surfactants (26, 27). Assuming that the benzene group is equivalent to 3.5 CH_2 , octylbenzenesulfonate ought to be very similar to dodecylsulfate. In fact enthalpies of micellization reported for both are very near zero (28, 29) at room temperature. Jolicoeur and Philip (28) report an enthalpy of micelle formation of 0.13 kJ/mol for sodium octylbenzenesulfonate at 295 K. A value of 0.13 kJ/mol (hence, positive and nearly zero) would be consistent with my observation that the relative apparent partial molar enthalpy of SOBS appears to become nearly constant above the cmc. (cf. the discussion above concerning ϕL_2 of SOS becoming constant above the cmc.) If this is true then it would imply a large negative enthalpy of micellization at 308.15 K, which would be consistent with data for SDS (29).

Birch and Hall (7) have measured heats of dilution of several alkylsulfates in the pre-cmc region. They also observe large deviations from DHLL behavior in the pre-cmc region, and an increase in the magnitude of the deviation with increasing alkyl chain length. The heats of dilution which they report for sodium octylsulfate were somewhat larger at very low concentrations than the values which I would extrapolate. The differences could be accounted for if there

were an error in the correction term used in the calculation of the measured enthalpy (see Experimental section). However, Birch and Hall's data were all at concentrations well below the range of the Tronac calorimeter, which may account for the difference, because in this range the error in the measured heat is greater than the value which would be measured. The difference is toward a greater deviation from DHLL behavior, and would therefore tend to increase my pre-micellar association enthalpies.

Birch and Hall (7) attempted to model this behavior both in terms of dimer formation, and in terms of electrostatic effects. The effect which they invoked involved a large dependence of the effective ionic radius on temperature (the derivative of the effective ionic radius with respect to temperature appears in the expression for an extension of the DHLL). They rationalized this on the basis of a dependence of the degree of hydrophobic hydration on temperature. The large dependence on temperature which is required seems unrealistic to me. It may also be pointed out that the hydrophobic hydration probably does not decrease significantly with temperature (see above concerning the hydrophobic effect). In any case they conclude that both explanations have some value, and that it is not possible at the present time to finally answer the question of which is the correct explanation. This is in agreement with my conclusions above, although I think that there is more good reason to consider such deviations from DHLL enthalpies as due to hydrophobic association than otherwise.

iv. Conclusions

Accurate relative apparent partial molar enthalpies and relative partial molar enthalpies have been obtained for SOS, SOSN and SOBS at two temperatures, 298.15 K and 308.15 K. The data for SOS and SOSN have been modelled using the MEM and the results clearly lead to three important conclusions concerning amphiphilic aggregation.

First, the model strongly indicates that association into small (dimers and trimers were chosen in the modelling) aggregates occurs in the pre-cmc region. Although the evidence is not unequivocal, it is, I believe, strong. This is in contradiction to the position that short chain amphiphiles do not form dimers (19, 25), and supportive of the position that pre-micellar association is very important and must be taken into account in order to properly understand the behavior of surfactant solutions (9).

Second, the formation of micelles should be considered in terms of the multiple equilibrium model, particularly for those systems which have a small aggregation and a high cmc. It will, however, be necessary to develop a more realistic characterization of the electrostatic interactions in order to make full use of the power of the MEM. This should be along the lines of the theoretical work done by Wennerstrom, Lindman and co-workers (18 and other references given

in Chapter I). The MEM proved to be capable of duplicating the general features of the relative apparent partial molar enthalpy through the cmc and up to about twice the cmc. There were significant features of the behavior in the immediate vicinity of the cmc which were not properly accounted for. Considering the limitations of the electrostatic model used the MEM accounted for the behavior of the systems remarkably well.

Third, the failure of the model at high concentrations indicates that complications of the electrostatic picture due to the presence of highly charged micelles have become very important. Thus, it may be concluded that micelle-micelle long-range electrostatic interactions are very important to the behavior of more concentrated surfactant solutions. The failure of the model may also have been partially due to variations in interactions between the micelles and their counterions.

Another conclusion which may be drawn from this work is that the heat of dilution from some concentration well above (or just above) the cmc to infinite dilution is not a measure of the enthalpy of micelle formation. The relative apparent partial molar enthalpy at some concentration well above the cmc includes several terms in addition to the monomer dilution term and the micelle formation term. In order to properly determine the portion due to micelle formation a rather detailed knowledge of the numerous interactions involved must be obtained. Calorimetric data and modelling such as that presented in this paper provide an excellent means to obtain knowledge of such details.

The enthalpy data which have been obtained are very similar in features to data obtained by other workers for these and similar systems (26, 27, 29). The magnitudes of the enthalpies compare well with what little calorimetric data exist for these surfactants, although some of these report only an enthalpy of micelle formation, which makes a detailed comparison impossible.

Heats of adsorption on alumina and montmorillonite were measured and the values obtained are consistent with other information concerning these interactions (1, 2, 3). It may be concluded that the calorimetric approach to the study of surfactant adsorption at solid surfaces shows enormous promise. Very little concerning the detailed adsorption processes at the solid surface may be concluded from my measurements, except that their behavior follows the lines of existing theory. A systematic calorimetric study of a variety of surfaces using a set of homologous surfactants under various conditions of temperature, salinity and pH would be very rewarding (3).

The approach to surfactant aggregation and adsorption through calorimetric measurements proved to be a rewarding and productive means of elucidating their behavior. It is sincerely to be hoped that further details of the behavior of these systems will continue to be the subject of calorimetric investigations.

	SOS/298.15	SOS/308.15	SOSN/298.15	SOSN/308.15
Aggregation Number	18	18	18	18
Fraction of Counterions Bound	0.6	0.6	0.6	0.6
Screening Factor	0.3	0.3	0.3	0.3
Size Parameter	7	7	7	7
Dimerization Constant (L/mol)	0.5	0.5	0.5	0.5
Dimerization Enthalpy (J/mol)	6843.45	7037.47	6092.30	6017.95
Trimerization Constant (L ² /mol ²)	2	2	2	2
Trimerization Enthalpy (J/mol)	24239.9	22981.9	20161.1	22889.7
Micellization Constant (qth root, molarity units)	21	21	21	21
Micellization Enthalpy (J/mol)	5283.42	1654.95	6883.77	3963.60

Table V-1: Parameters of MEM model used to fit the relative apparent partial molar enthalpy data for sodium octylsulfate (SOS) and sodium octylsulfonate (SOSN) at 298.15 K and 308.15 K.

	$\Delta H1$ (J/mol)	$\Delta H2$ (J/mol)	T (K)
SOS	5283.42	1478	298.15
SOS	1654.95	-1517	308.15
SOSN	6883.77	3733	298.15
SOSN	3963.60	1200	308.15

Table V-6: Enthalpies of micellization for sodium octylsulfate (SOS) and sodium octylsulfonate (SOSN) at 298.15 K and 308.15 K determined by MEM model ($\Delta H1$) and by the Desnoyers method ($\Delta H2$).

PLM (J/MOL)	PLC (J/MOL)	ERROR	C (MOL/L)	CI	AM
8.5685E+02	7.8645E+02	7.0401E+01	5.0307E-02	4.7418E-02	1.6546E-13
1.3517E+03	1.4964E+03	-1.4472E+02	8.8642E-02	7.9347E-02	3.2998E-07
1.6524E+03	1.7005E+03	-4.8090E+01	9.8962E-02	8.7336E-02	5.1531E-06
1.7264E+03	1.8833E+03	-1.5697E+02	1.0809E-01	9.4198E-02	4.5621E-05
1.9446E+03	2.0823E+03	-1.3773E+02	1.1796E-01	1.0138E-01	3.8483E-04
2.1649E+03	2.2742E+03	-1.6930E+02	1.2741E-01	1.0791E-01	2.3956E-03
2.3401E+03	2.4677E+03	-1.2756E+02	1.3692E-01	1.1365E-01	1.1260E-02
2.5697E+03	2.6493E+03	-7.9577E+01	1.4611E-01	1.1763E-01	3.3384E-02
2.7129E+03	2.7933E+03	-8.0338E+01	1.5395E-01	1.1973E-01	6.2252E-02
3.0879E+03	2.9833E+03	1.0465E+02	1.6553E-01	1.2138E-01	1.1281E-01
3.2260E+03	3.0942E+03	1.3176E+02	1.7313E-01	1.2191E-01	1.4719E-01
3.3787E+03	3.2444E+03	1.3434E+02	1.8462E-01	1.2220E-01	1.9783E-01
3.5371E+03	3.3496E+03	1.8751E+02	1.9365E-01	1.2217E-01	2.3548E-01
3.6505E+03	3.4854E+03	1.6852E+02	2.0672E-01	1.2186E-01	2.8607E-01
3.7734E+03	3.5746E+03	1.9879E+02	2.1632E-01	1.2150E-01	3.2026E-01
3.8543E+03	3.6597E+03	1.9462E+02	2.2635E-01	1.2104E-01	3.5342E-01
3.9600E+03	3.7884E+03	1.1168E+02	2.4336E-01	1.2012E-01	4.0428E-01
4.0382E+03	4.0341E+03	4.0662E+00	2.8389E-01	1.1757E-01	5.0275E-01
4.2218E+03	4.4048E+03	-1.8302E+02	3.7670E-01	1.1121E-01	6.4992E-01
4.3345E+03	4.6109E+03	-2.7637E+02	4.5744E-01	1.0589E-01	7.2827E-01

Table V-2: Calculated values of the relative apparent partial molar enthalpy (PLC), the monomer concentration (CI), and the fraction in the micelle (AM) as a function of concentration for sodium octylsulfate at 298.15 K.

PLN (J/MOL)	PLC (J/MOL)	ERROR	C (MOL/L)	C1	AM
9.3628E+02	7.9863E+02	1.3766E+02	5.0647E-02	4.7187E-02	1.3654E-13
9.9590E+02	9.5820E+02	3.7701E+01	5.9405E-02	5.5326E-02	1.1615E-11
1.2494E+03	1.1274E+03	1.2195E+02	6.8924E-02	6.3379E-02	5.5925E-10
1.4503E+03	1.2980E+03	1.5226E+02	7.6216E-02	7.1023E-02	1.5234E-08
1.4553E+03	1.4774E+03	-4.2110E+01	8.7769E-02	7.8660E-02	2.4166E-07
1.5620E+03	1.6666E+03	-8.4619E+01	9.7671E-02	8.6350E-02	3.4572E-06
1.7470E+03	1.8683E+03	-1.2123E+02	1.0811E-01	9.4212E-02	4.2917E-05
1.9347E+03	2.0419E+03	-1.0718E+02	1.1708E-01	1.0076E-01	3.0088E-04
2.0902E+03	2.2464E+03	-1.5623E+02	1.2792E-01	1.0827E-01	2.4667E-03
2.2936E+03	2.3721E+03	-7.8536E+01	1.3541E-01	1.1288E-01	8.5426E-03
2.5234E+03	2.5233E+03	8.2087E-02	1.5070E-01	1.1914E-01	4.7215E-02
2.5035E+03	2.5469E+03	-4.3335E+01	1.6402E-01	1.2147E-01	1.6388E-01
2.4609E+03	2.5350E+03	-5.4082E+01	1.7290E-01	1.2215E-01	1.4392E-01
2.4523E+03	2.5090E+03	-5.6708E+01	1.8315E-01	1.2247E-01	1.8919E-01
2.5075E+03	2.4828E+03	2.4733E+01	1.9159E-01	1.2249E-01	2.2479E-01
2.4941E+03	2.4492E+03	4.4915E+01	2.0167E-01	1.2231E-01	2.6482E-01
2.5852E+03	2.4261E+03	1.5908E+02	2.0849E-01	1.2211E-01	2.9034E-01
2.5128E+03	2.3277E+03	1.8509E+02	2.3915E-01	1.2069E-01	3.9026E-01
2.4126E+03	2.2063E+03	2.0635E+02	2.8601E-01	1.1775E-01	5.0582E-01
2.2739E+03	2.0682E+03	2.0569E+02	3.6923E-01	1.1206E-01	6.3948E-01
2.0785E+03	1.9890E+03	8.9443E+01	4.5384E-01	1.0647E-01	7.2432E-01
1.7659E+03	1.9456E+03	-1.7976E+02	5.3357E-01	1.0162E-01	7.7824E-01
1.5856E+03	1.9186E+03	-3.3305E+02	6.1685E-01	9.7012E-02	8.1842E-01

Table V-3: Calculated values of the relative apparent partial molar enthalpy (PLC), the monomer concentration (C1), and the fraction in the micelle (AM) as a function of concentration for sodium octylsulfate at 308.15 K.

PLM (J/MOL)	PLC (J/MOL)	ERROR	C (MOL/L)	C1	AM
4.6253E+02	3.5017E+02	1.1236E+02	2.4024E-02	2.3399E-02	5.5120E-22
9.5879E+02	8.0845E+02	1.5034E+02	5.7545E-02	5.3727E-02	5.4224E-12
1.4694E+03	1.4571E+03	1.2276E+01	9.7727E-02	8.6393E-02	3.7724E-06
1.8635E+03	1.9524E+03	-8.8850E+01	1.2654E-01	1.0734E-01	2.0481E-03
2.2084E+03	2.3357E+03	-1.2730E+02	1.4513E-01	1.1729E-01	3.0335E-02
2.6433E+03	2.7949E+03	-1.5163E+02	1.6396E-01	1.2123E-01	1.0572E-01
2.9038E+03	3.0115E+03	-1.0772E+02	1.7323E-01	1.2191E-01	1.4764E-01
3.2156E+03	3.2289E+03	-1.3335E+01	1.8321E-01	1.2219E-01	1.9175E-01
3.4797E+03	3.4124E+03	6.7373E+01	1.9232E-01	1.2219E-01	2.3005E-01
4.0612E+03	3.8859E+03	1.7527E+02	2.1972E-01	1.2135E-01	3.3179E-01
4.3102E+03	4.1385E+03	1.7171E+02	2.3737E-01	1.2046E-01	3.8712E-01
4.6748E+03	4.6560E+03	2.3885E+02	2.8325E-01	1.1761E-01	5.0140E-01
5.4192E+03	5.2845E+03	1.3468E+02	3.6839E-01	1.1177E-01	6.3980E-01
5.7246E+03	5.6749E+03	4.9661E+01	4.5224E-01	1.0622E-01	7.2412E-01
5.8036E+03	5.9316E+03	-1.2793E+02	5.3198E-01	1.0136E-01	7.7824E-01
5.8173E+03	6.1161E+03	-2.9882E+02	6.0981E-01	9.7041E-02	8.1626E-01

Table V-4: Calculated values of the relative apparent partial molar enthalpy (PLC), the monomer concentration (C1), and the fraction in micelles (AM) as a function of concentration for sodium octylsulfonate at 298.15 K.

PLM (J/MOL)	PLC (J/MOL)	ERROR	C (MOL/L)	C1	AM
8.1996E+02	7.3777E+02	8.2189E+01	4.9138E-02	4.6386E-02	8.4696E-14
1.5678E+03	1.6098E+03	-4.2046E+01	9.8997E-02	8.7362E-02	4.8733E-06
2.2119E+03	2.4470E+03	-2.3503E+02	1.4484E-01	1.1730E-01	2.8243E-02
2.8526E+03	2.9017E+03	-4.9070E+01	1.8939E-01	1.2250E-01	2.1568E-01
3.3267E+03	3.1597E+03	1.6698E+02	2.3846E-01	1.2073E-01	3.8825E-01
3.6125E+03	3.3190E+03	2.9349E+02	2.8533E-01	1.1781E-01	5.0399E-01
3.7326E+03	3.5107E+03	2.2189E+02	3.7087E-01	1.1195E-01	6.4152E-01
3.6935E+03	3.6355E+03	5.8077E+01	4.5501E-01	1.0639E-01	7.2526E-01
3.6033E+03	3.7265E+03	-1.2327E+02	5.3888E-01	1.0131E-01	7.8121E-01
3.4489E+03	3.7945E+03	-3.4592E+02	6.2100E-01	9.6794E-02	8.2011E-01

Table V-5: Calculated values of the relative apparent partial molar enthalpy (PLC), the monomer concentration (C1), and the fraction in micelles (AM) as a function of concentration for sodium octylsulfonate at 308.15 K.

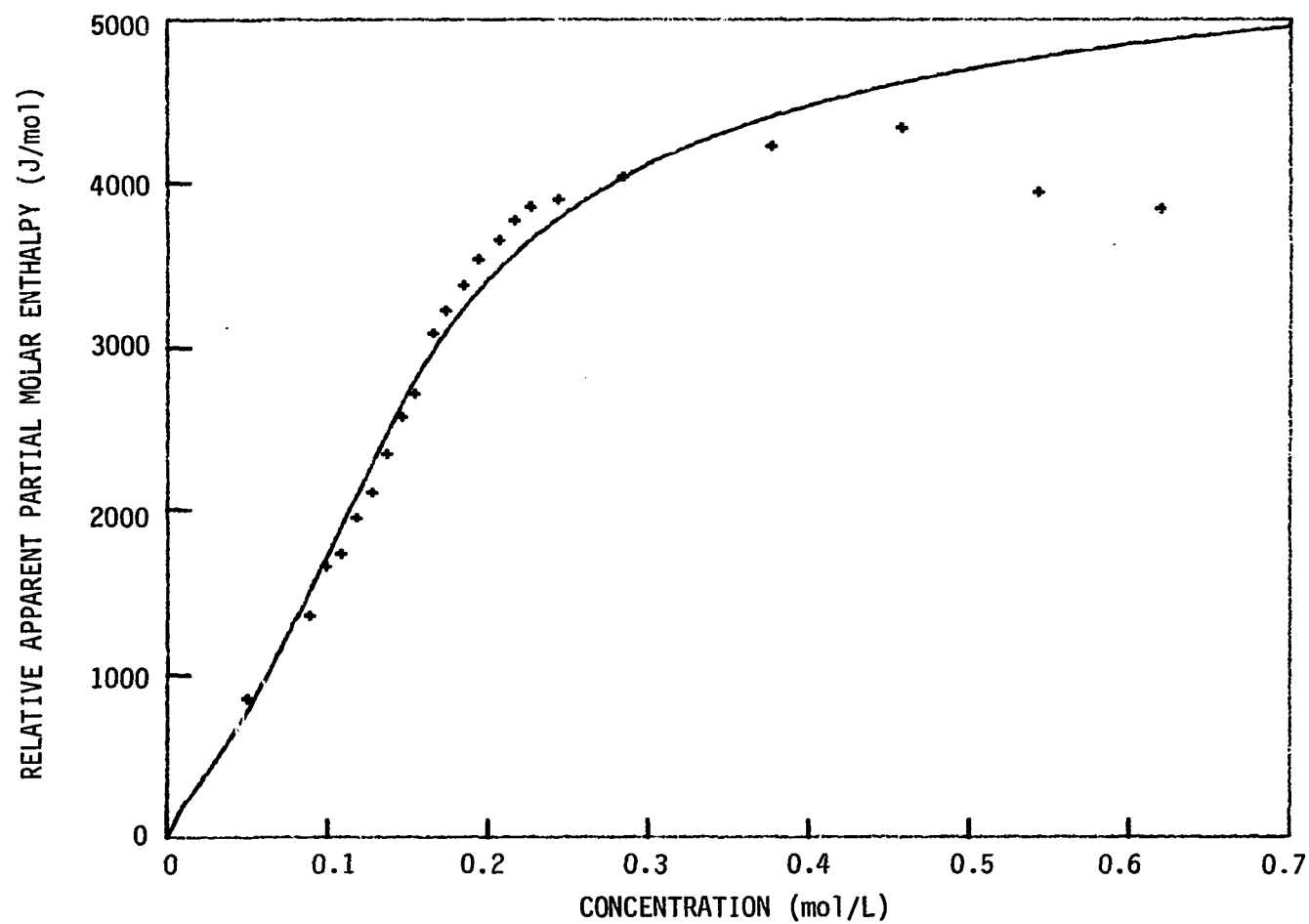


Figure V-1: Relative apparent partial molar enthalpy of sodium octylsulfate at 298.15 K. The curve is a plot of the enthalpy calculated from the model.

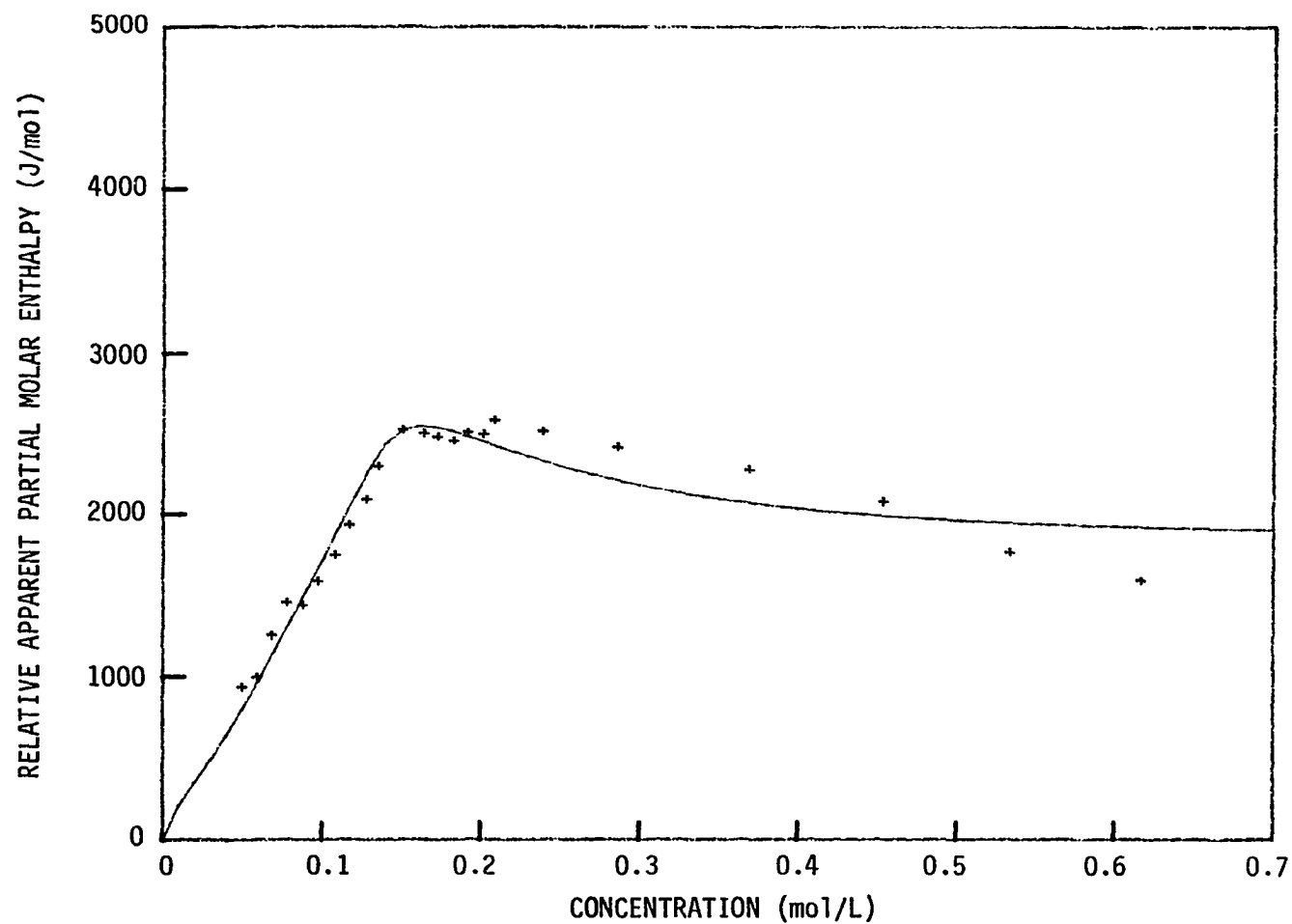


Figure V-2: Relative apparent partial molar enthalpy of sodium octylsulfate at 308.15 K. The curve is a plot of the enthalpy calculated from the model.

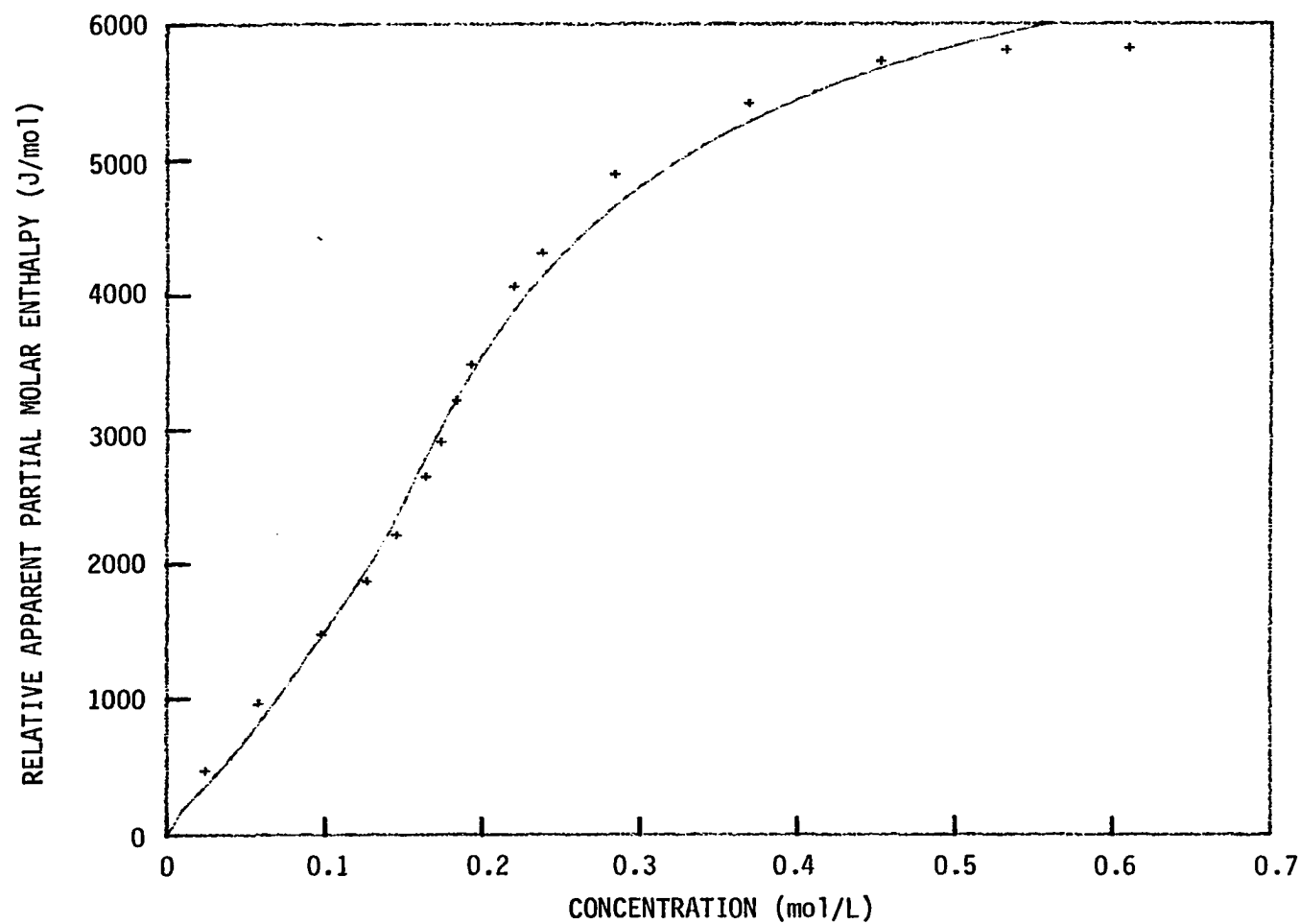


Figure V-3: Relative apparent partial molar enthalpy of sodium octylsulfonate at 298.15 K. The curve is a plot of the enthalpy calculated from the model.

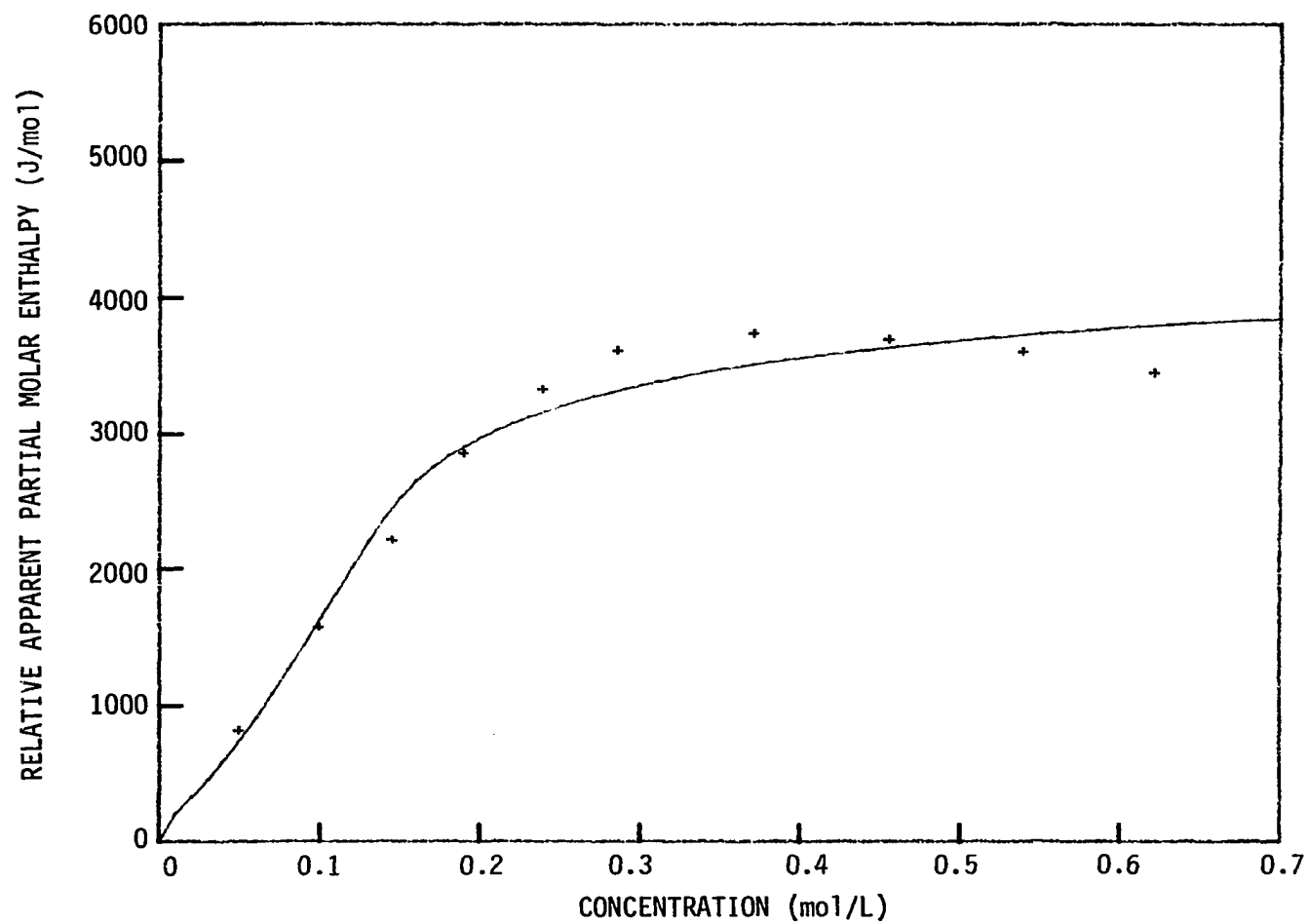


Figure V-4: Relative apparent partial molar enthalpy of sodium octylsulfonate at 308.15 K. The curve is a plot of the enthalpy calculated from the model.

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