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Calorimetric Studies of The Association of Amphiphiles in Aqueous and Nonaqueous Solutions

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The use of modern high-precision solution calorimeters to study the association of amphiphiles in solution is discussed. Examples of studies made by the author and coworkers are given. The thermodynamic properties for micelle formation of poly(oxyethylene) alkyl ethers, C_nE_x, in water and formamide solutions are summarized. Studies of the association of sodium dodecylsulfate SDS in water and aqueous pentanol solutions made to test a thermodynamic model for the association of ionic amphiphiles are described.

Introduction

Amphiphilic systems attract much research interest both for the widespread technical use and for the intriguing and multifaceted features such systems display. Amphiphiles are substances with dual solvation characteristics as they consist of a nonpolar, hydrophobic part and a polar or ionic headgroup. One or two nonpolar groups, usually hydrocarbon chains, can be bound to the hydrophilic headgroup. In the following, only single chain amphiphiles will be discussed and the words amphiphile and surfactant will be used synonymously. In aqueous solutions, the low solubility of the hydrophobic chains will lead to self association and the formation of aggregates where the nonpolar groups are brought together in water-free micro-domains while the polar headgroups remain hydrated. At low concentrations, discrete aggregates called micelles are formed and at higher amphiphile content, various liquid crystalline phases appear. Physicochemical aspects of surfactant aggregation and particularly micelle formation are reviewed in *e.g.* references 1 – 7. The application of various calorimetric techniques to the study of surfactant association in aqueous solution has been discussed by Desnoyers *et al*[8].

The term *micelle* normally refers to a large aggregate formed in strongly cooperative association of amphiphilic compounds[2]. Micelle formation starts at a well defined concentration, called the critical micelle concentration, c.m.c., and aggregates of usually well defined size (or narrow size distribution) are formed. Strength of cooperativity, aggregation number and c.m.c. are interdependent and show for instance a regular variation with the size of the nonpolar group. The concept of c.m.c. is important in the field of surfactants but is not well defined[2]. Usually a true c.m.c.[9] is understood to mean a narrow concentration range below which all amphiphile is in the form of monomers and above which all additional amphiphile form micelles. This requires cooperative association to give micelles with an aggregation number of at least 20 and a c.m.c. below, say, 0.03 $mol{\cdot}dm^{-3}$. Sensitive calorimeters allowing precise measurements at low concentrations are needed to study the aggregation behaviour of amphiphiles with low c.m.c. Various solution

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calorimeters available at the author's laboratory are suited for such investigations and some studies we have made of micelle formation in aqueous and nonaqueous solutions will be discussed in this paper. Our aim has been to gain information about interactions in dilute binary and ternary surfactant systems. Most studies consisted of measurements of calorimetric titration curves with step-wise injections of small amounts of pure liquid amphiphile or concentrated amphiphile solution starting with pure solvent in the calorimeter vessel[10]. The resulting titration curves were good approximations of the partial molar enthalpy changes.

Calorimetric results of the high resolution we achieved had not been reported previously. Micelle formation in water of poly (ethylene oxide) alkyl ethers of the general formula $C_nH_{n+1}(OC_2H_4)_xOH$, abbr. C_nE_x, will be discussed firstly. Then a couple of studies of sodium dodecylsulfate, $C_{12}H_{25}SO_4Na$, made to test a theoretical model for the association of ionic surfactants, will be described. Finally, a study of the association of C_nE_x amphiphiles in formamide will be treated.

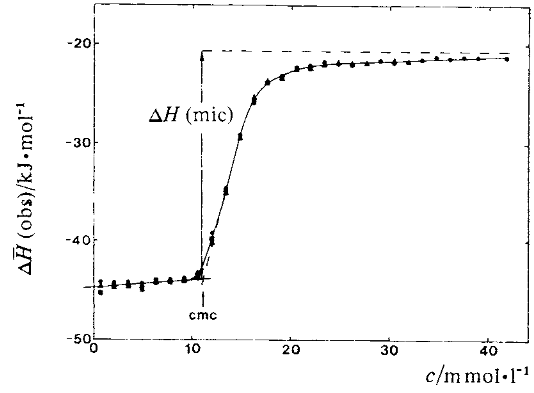

Fig. 1 Differential enthalpies of solution of C_8E_4 as function of molality at 10.00°C, ●, ■ and ▲, respectively, indicate the results of three different titration series. The result of each individual experiment is represented by a dot at the mean concentration. The change in molality was 1.4×10^{-3} mol·kg^{-1} in each step. (——) Calculated titration curve using the parameter values found from the best fit of the results to the mass-action law model of micelle formation; (- - -) $\Delta\bar{H}_{obs}$ of complete turnover.

C_nE_x in Water

Although quantitative, theoretical models describing the aggregation of nonionic amphiphiles in water are lacking, there are simple empirical models that can be used to describe the micellization process. Poly(ethyleneoxide) dodecyl ethers $C_{12}E_x$ with x between 5 and 8 have very low c.m.c. in water, 10^{-4} to 10^{-5} mol·dm^{-3}, and accordingly the micelle formation process shows high cooperativity. The (pseudo) phase-separation model gives for these surfactants a fully satisfactory description of the measured differential enthalpies of dilution of concentrated surfactant solutions[11]. It is assumed in this model that at concentrations below the c.m.c., the surfactant exists as hydrated monomers while above the c.m.c. a micellar pseudophase is formed. The difference between measured enthalpy changes for dilution below and above the c.m.c. gives the enthalpy of micelle formation ΔH(mic). For injections bridging the c.m.c. only a fraction of the injected micelles will break up to give monomers and from the measured enthalpy changes values of c.m.c. can be derived[11]. However, if the length of the alkyl chain is reduced, a tailing is seen in the titration curve indicating that micelle formation is not sharp but extends over a measurable concentration range. This is seen in the plot of differential enthalpies of solution of liquid C_8E_4 as function of molality, figure 1[12]. The curvature of the titration curve contains information about the micelle size, that is about the cooperativity of the aggregation process. The phase separation model is clearly not applicable but instead the mass-action law model[2,13] can be applied. In this model it is assumed that a single micellar species of aggregation number n is in equilibrium with the monomers: $n \cdot A \rightarrow A_n$; $K_n = [A_n]/[A]^n$. The calori-

Table 1 Thermodynamic properties for micelle formation at 25°C of poly(oxyethylene)alkyl ether surfactants.

	c.m.c.	ΔG°(mic)	ΔH(mic)	ΔS(mic)	ΔC_p(mic)
	mol•dm^{-3}	kJ•mol^{-1}	kJ•mol^{-1}	J•K•mol^{-1}	J•K•mol^{-1}
C_8E_4[a]	7.3×10^{-3}	−12.2	16.8 ± 0.2	97 ± 1	−392 ± 20
C_8E_5[b]	9.2×10^{-3}	−11.6	17.9 ± 0.2	99 ± 2	
C_8E_6[c]	10.1×10^{-3}	−11.4	20.1 ± 0.8	106 ± 3	
$C_{10}E_6$[c]	9.5×10^{-4}	−17.3	15.1 ± 1.3	109 ± 3	
$C_{12}E_5$[d]	5.8×10^{-5}	−24.2	13.5 ± 0.3	126 ± 2	−605 ± 50
$C_{12}E_6$[d]	6.5×10^{-5}	−23.9	14.8 ± 0.4	130 ± 2	−634 ± 40
$C_{12}E_8$[d]	9.0×10^{-5}	−23.1	16.3 ± 0.4	132 ± 2	−670 ± 75

[a] From ref. 12

[b] Measurements of c.m.c. and ΔH(mic) made at 30.0°C (0.0082 mol•dm^{-3} and 15.90 ± 0.20 kJ•mol^{-1}) recalculated to 25°C assuming the same ΔC_p(mic) as for C_8E_4. (G. Olofsson unpublished results)

[c] From ref. (14)

[d] From ref. (11)

metric results can then be evaluated by least squares fitting to give the aggregation number n, the enthalpy of micelle formation ΔH(mic) and K_n[12]. A couple of points worth noticing are revealed in figure 1. A) The c.m.c. is not unambigously defined but can be chosen in different ways. The choice indicated in the figure taking c.m.c. as the concentration at which micelles start to form (or more precisely: the concentration at which 1 % of the amphiphile is in micellar form) is used in this paper. Other choices can be made[2,13] so it is necessary to state explicitly how the c.m.c. is defined. B) The enthalpy of micelle formation ΔH(mic) can be defined in various ways. In figure 1 it is derived as the difference between the enthalpy content of the amphiphile in the micellar and monomer states at the c.m.c.: $\Delta H(\text{mic}) = \bar{H}\overset{\text{c.m.c.}}{(\text{mic})} - \bar{H}\overset{\text{c.m.c.}}{(\text{mon})}$. We have used this definition in most of our work but in some cases it has been more convenient to use the definition $\Delta H(\text{mic}) = \bar{H}\overset{\text{c.m.c.}}{(\text{mic})} - \bar{H}\overset{\infty}{(\text{mon})}$ where $\bar{H}\overset{\infty}{(\text{mon})}$ is the enthalpy content of monomer in infinitely dilute solution. The difference between numerical vaiues of ΔH(mic) defined in these two different ways is significant even for amphiphiles with fairly low c.m.c. as enthalpies of dilution in the premicellar region are not negligible. For C_8F_4 at 10°C, cf figure 1, the difference amounts to 0.89 kJ•mol^{-1} [12]. In order to determine the heat capacity changes for micelle formation ΔC_p(mic) of the C_nE_x amphiphiles, calorimetric measurements were made at various temperatures and ΔC_p(mic) were calculated from the temperature variation of ΔH(mic).

Thermodynamic properties of micelle formation at 25°C for seven C_nE_x surfactants that have been studied by calorimetric measurements are summarized in table 1. The c.m.c. and thus ΔG°(mic) decreases for constant X with increasing length of the alkyl chain. The change is about −3 kJ•mol^{-1} per CH_2-group in agreement with the change observed in the series $C_{10}E_8$ to $C_{15}E_8$[6]. An increase of the polar group gives a slight increase in c.m.c. corresponding to about 0.4 kJ•mol^{-1} in ΔG°(mic) per ethylene oxide group. The enthalpy of micelle formation ΔH(mic) decreases with increasing length of the alkyl chain but increases with the size of the polar group, about 1.1 kJ•mol^{-1} per ethylene oxide group. The changes in ΔS(mic) and heat capacity ΔC_p(mic) appear to be dominated by the change in properties of the alkyl chains and to be affected only to a minor extent by the size of the polar group. The sign and magnitude of ΔS(mic) and ΔC_p(mic) show that the dehydration of the alkyl groups upon aggregation gives the major contributions to these properties$^{11)}$. The enthalpy contribution from the aggregation of the alkyl chains can be expected to be small and exothermic$^{3,15)}$ so the observed endothermic ΔH(mic) are thought to indicate significant dehydration of ethylene oxide groups closest to the micelle surface$^{11)}$. The aggregation number of 23 ± 3 derived for C_8E_4 micelles at 25°C is compatible with the formation of spherical micelles having a radius of 12.4Å which is the length of an extended octyl chain$^{3)}$. However, a significantly higher aggregation number of 43 ± 7 was derived for C_8E_5. Both values refer to micelle formation at the c.m.c. In general, it appears that the size of C_nE_x micelles in aqueous solution varies in a complicated manner with temperature and composition, see *e.g.* references 16 – 18 and references therein. Calorimetric measurements of dilution of micellar C_nE_x indicate that such aggregate growth is accompanied by only minor enthalpy changes$^{11)}$.

Test of Theoretical Model for The Association of Amphiphiles

Hydrophobic interaction between the nonpolar chains will be the driving force for micelle formation of ionic surfactants like for nonionic but the dominating counteracting force will be the electrostatic repulsion between the charged head groups on the micelle surface. A satisfactory description of the micelle formation process can be made by extention of the mass-action law model to take into account the presence of ionic species, *cf* ref. 7. The most extensive and detailed studies have been made by Woolley and coworkers, refs 19 – 21 and therein. The micellar solution is treated as a mixed electrolyte by using the Guggenheim equations and a shielding factor is included to account for screening of the micellar charge. In this way good descriptions are made of thermodynamic properties such as osmotic capacities of alkyltrimethyl ammonium bromide capacities of alkyltrimethyl ammonium bromide solutions under varying conditions. However, more insight into interactions at a molecular level is provided by the thermodynamic model for the association of ionic amphiphiles in aqueous systems developed by B. Jönsson and H. Wennerström$^{22-24)}$. The model is based on expressions for the most important contributions to the free energy of the system and emphasizes a consistent treatment of the electrostatic effects.

An important feature is that the concentration dependence of the free energy is considered. The model has been extended to deal with surfactant-alcohol-water three-component systems$^{25)}$ and further refined and developed to describe solubilization of nonpolar additives$^{26,27)}$. This model has been successful in predicting phase-equilibria and to account for the aggregation behaviour around the c.m.c. To test the model we have used it to evaluate results of precise calorimetric measurements of differential enthalpies of dilution of micellar SDS solution$^{28)}$.

The enthalpic titration curves gave a detailed mapping of the micellization region. It was assumed that the micelle formation process is characterized by a single enthalpy value ΔH (mic) and accordingly that the shape of the titration curve reflected changes in the monomer and micelle concentrations as the total surfactant concentration increased. Above the c.m.c. of ionic surfactants the monomer concentration decreases with increasing total concentration. When the micelle concentration increases, the concentration of counterions also increases which leads to a screening of the electrostatic interactions and to a decrease in head-group repulsion at the micelle surface. The chemical potential of the amphiphile ion in the micelle is reduced and, therefore, a lower equilibrium concentration of monomer surfactant is required. The concentration changes during the titrations

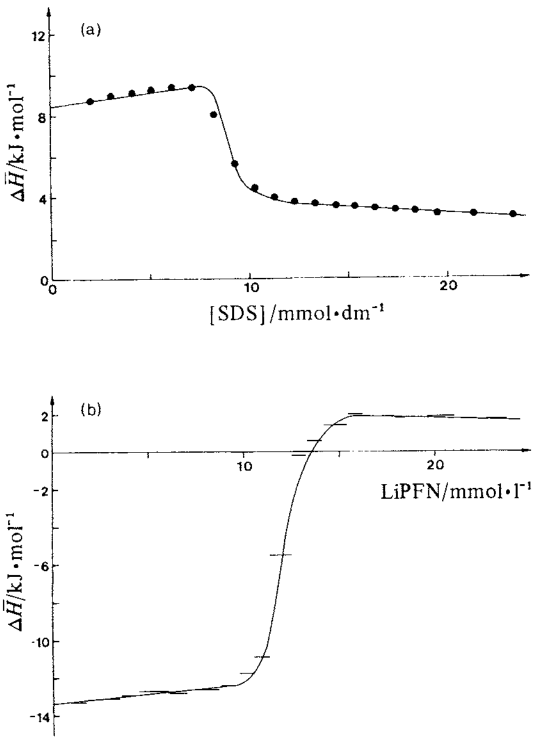

Fig. 2 a) Comparison between calculated (full line) and experimental (points) differential enthalpies of dilution of 28 wt% SDS solution at 35°C.
b) Differential enthalpies of dilution of 20 wt% lithium perfluorononate, LiPFN, solution against total LiPFN concentration. Comparison between calculated (full line) and experimental (bars) titration curves at 15°C. The length of the bars indicate the change in concentration in each titration step. (a) from ref. 28 and b) from ref. 29 with permission from the Royal Society of Chemistry.)

were calculated from the model and theoretical titration curves were derived. A comparison between calculated and experimental values of differential enthalpies of dilution of 28 wt% SDS solution in water at 35°C is shown in figure 2a. As can be seen the agreement is satisfactory. However, to reproduce the smooth bend in the curve, the aggregation number of micelles formed was allowed to increase from 50 at the c.m.c. (8.3 mmol) to 62 at 10.8 mmol and higher concentrations. In a similar study of the micelle formation of lithium perfluorononate[29], a constant aggregation number of 20 gave calculated curves that agreed well with the experimental curves as can be seen in fig. 2b. The good agreement seen between calculated and experimental titration curves shows that the thermodynamic model can give quantitative predictions of the composition of solutions of ionic surfactants in the c.m.c. region. As can be seen from fig. 2, ΔH(obs) increases significantly with concentrations below the c.m.c. This non-ideal behaviour of the monomer solutions is not taken into account in the theoretical model and the full-drawn lines below the c.m.c. are based on linear least-squares fits. The slope is much larger than expected for dilution of a simple 1:1 electrolyte[30,31] and as a similar effect is seen in the premicellar region of C_8E_4 (see fig. 1), pairwise interaction between the alkyl chains is the probable reason for this non-ideal behaviour. It can be noted that while this enthalpic non-ideality is noticeable, a corresponding deviation from simple electrolyte behaviour is not easily seen in activity measurements of ionic surfactants using for instance ion selective electrodes[32,33].

The decrease in monomer concentration for ionic amphiphiles above the c.m.c. in aqueous solution without extra salt is significant and must be taken into account when evaluating experimental results in the c.m.c. region, *cf* fig. 3. A commonly used definition of the change in a thermodynamic quantity for micelle formation ΔY(mic) is $\Delta Y(\text{mic}) = \bar{Y}(\text{mic}) - \bar{Y}(\text{mon})$ where $\bar{Y}$(mic) and $\bar{Y}$(mon) denote the partial molar quantity of the amphiphile at concentrations just above and below the c.m.c. If we apply this definition to our measured differential enthalpies of dilution ΔH(obs) we will derive an enthalpy change ΔH(op) as indicated in figure 4. The difference between ΔH(op) and the true ΔH(mic), denoted $\delta\Delta H$, is the additional enthalpy contribution from

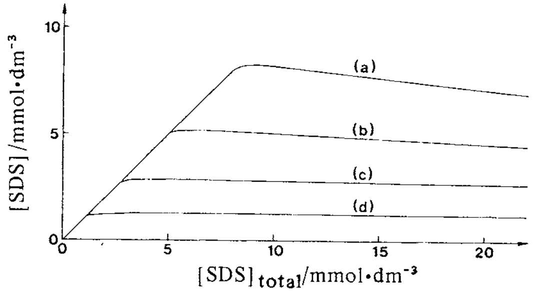

Fig. 3 Concentration of SDS in monomer state as a function of total SDS concentration in (a) pure water, (b) 0.010 mol•dm^{-3} NaCl, (c) 0.030 mol•dm^{-3} NaCl and (d) 0.10 mol•dm^{-3} NaCl.

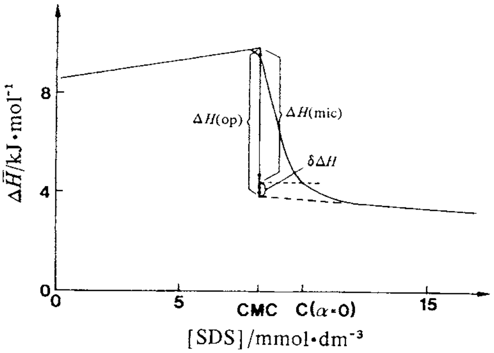

Fig. 4 Comparison between the 'true' ΔH(mic) and operational ΔH(op) enthalpy of micelle formation; $\delta\Delta H$ indicates the additional enthalpy contribution from micelle formation due to decreasing monomer concentration in the post-micellar region. (From ref. 28 with permission from the Royal Society of Chemistry.)

Table 2 Values of the NaCl concentration, C_{salt}, the critical micelle concentration, c.m.c., the enthalpy of micelle formation, $\Delta H'$(mic) and the differential enthalpy of dilution, ΔH(dil), of 28 wt% SDS solution at 35°C.

C_{salt}	c.m.c.	$\Delta H'$(mic)	ΔH(dil)
mol•dm^{-3}	mmol•dm^{-3}	kJ•mol^{-1}	kJ•mol^{-1}
0	8.2	−4.1 ± 0.2	4.4 ± 0.2
0.010	5.0	−4.8 ± 0.2	3.7 ± 0.2
0.030	2.5	−5.6 ± 0.2	3.0 ± 0.2
0.100	1.2	−6.6 ± 0.2	1.9 ± 0.2

micelle formation due to the decreasing monomer concentration above the c.m.c. Neglect of this decrease leads to an error in derived values of ΔH(mic) of about 10%. Addition of extra salt leads to a lowering of the c.m.c. and the monomer concentration will become more constant above the c.m.c., see fig. 3[34,35]. The enthalpy of micelle formation is also affected and becomes more exothermic with increasing salt concentration[35]. Results of measurements of differential enthalpies of dilution of 28 wt% SDS solution in NaCl solutions are summarized in table 2. $\Delta H'$(mic) is defined here as the difference between the enthalpy content of SDS in the micelle state at the c.m.c. and in the monomer state at infinite dilution. The enthalpy of dilution ΔH(dil) denotes the difference between the enthalpy content of micellar SDS at the c.m.c. and in the 28 wt% solution. The sum ΔH(dil) + $[-\Delta H'(\text{mic})]$ = 8.5 kJ•mol^{-1} which is the enthalpy of dilution to infinitely dilute solution is independent of salt concentration.

Calorimetric measurements were also made of differential enthalpies of dilution of concentrated SDS solution into aqueous solutions containing varying amounts of pentanol[36]. In micellar solutions pentanol is solubilized to form mixed SDS – pentanol micelles whose composition is determined by the composition of the solution. Calorimetric titration curves of dilution of 10 wt% SDS solution in water and three pentanol solutions are shown in fig. 5. The composition of the solutions and micellar phases as function of total SDS concentration were calculated from the theoretical model. In addition, quantitative estimates were derived of enthalpy contributions in the formation of the mixed micelles. The solid lines in figure 5 represent the calculated curves derived using only one adjustable parameter. As can be seen, the agreement between the theoretical and the experimental curves is satisfactory which illustrates the predictive value of the model.

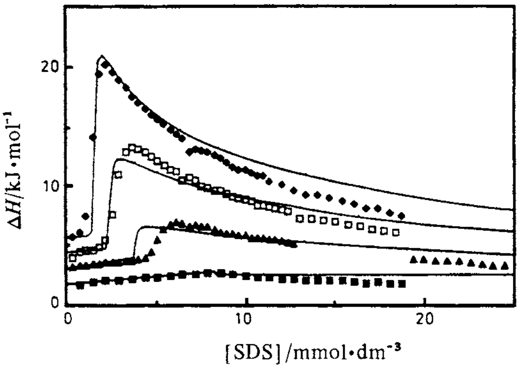

Fig. 5 Differential enthalpies of dilution of a 10 wt% SDS solution as a function of total SDS concentration. Initial calorimeter solution: ■, pure water and ▲, 0.059; □, 0.118; ◆, 0.176 mol·dm^{-3} pentanol solution at 25°C. The solid lines represent calculated curves. (From ref. 36 with permission from the Royal Society of Chemistry.)

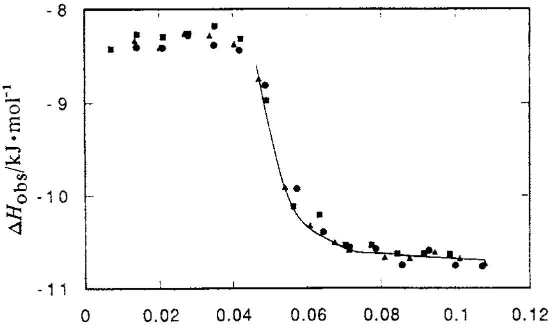

Fig. 6 Differential enthalpies of solution of liquid $C_{12}E_4$ in formamide as function of molality at 40.1°C; ▲, ● and ■ indicate the results of three different titration series. The full curve was calculated using the parameter values found from the best fit of the results to the mass-action law model of aggregation. (From ref. 28 with permission from the Royal Society of Chemistry.)

C_nE_x in Formamide

Aggregate formation of amphiphilic molecules to give for instance liquid crystalline phases is not unique to aqueous systems but can take place in other solvents with strong cohesive forces. The gradual change of the association behaviour with solvent properties is nicely revealed by the phase diagrams of alkyltrimethylammonium halides in various solvents$^{37)}$. To get further information about aggregation in solution, the author made a titration microcalorimetric study of three nonionic amphiphiles in dilute formamide solution$^{38)}$. The calorimetric results $\Delta\bar{H}$(obs) were in the form of differential enthalpies of solution of liquid amphiphile for $C_{12}E_4$ and $C_{12}E_6$ and differential enthalpies of dilution of concentrated micellar solution for $C_{16}E_8$. There were pronounced drops in the enthalpy curves at a certain concentration (except for $C_{12}E_x$ at 25°C) as exemplified by the results for $C_{12}E_4$ at 40°C in fig. 6. Allowing for the difference in sign, the titration curve for $C_{12}E_4$ in formamide shows the same general features as the curve for C_8E_4 in water, fig. 1. Therefore, it was natural to assume micelle formation and to apply the mass-action law model to evaluate ΔH(mic), c.m.c. and aggregation number N in the same way as for C_8E_4 in water. The resulting values are summarized in table 3. Measurements were made at 25 and 40°C and ΔC_p(mic) was calculated from the difference in ΔH(mic) at the two temperatures. The values of c.m.c. for C_nE_x in water are *ca* three powers of ten lower than in formamide, (*cf* table 1) and the aggregation number about 60 or larger. ΔH (mic) in water are fairly endothermic and the strong association is due to large, positive entropy changes. The positive entropy contribution arises from the dehydration of the hydrocarbon chains and micelle formation is considered a manifestation of the hydrophobic effect$^{3)}$. In formamide the enthalpy changes are only slightly exothermic or zero ($C_{12}E_6$ at 25°C) but still aggregation takes place and it is clear that

Table 3 Thermodynamic properties for micelle formation of poly(oxyethlene) alkyl ether surfactants in formamide at 25°C.

	c.m.c. mol·dm^{-3}	ΔH(mic) kJ·mol^{-1}	ΔS(mic)^a J·K^{-1}·mol^{-1}	ΔC_p(mic) J·K^{-1}·mol
$C_{12}E_4$	5.2·10^{-2}	−1.35 ± 0.10	47 ± 1	−80 ± 7
$C_{12}E_6$	4.9·10^{-2}	0 ± 0.05	(52)^b	−76 ± 5
$C_{16}E_8$	8.5·10^{-3}	−3.45 ± 0.10	55 ± 1	−98 ± 10

[a]: The relation $\Delta G°(\text{mic}) = RT \ln X_{\text{mic}}$ was used.
X_{mic} is mole fraction at the c.m.c.

[b]: Phase separation model not applicable.
Estimated aggregation numbers at 40°C:
$C_{12}E_4$ = 30 ± 5, $C_{12}E_6$ = 12 ± 3, $C_{16}E_8$ ~ 70.

positive entropy contributions are decisive for aggregation. The association tendency is weaker in formamide as evidenced by the higher c.m.c. but if C_nE_x surfactants in water are compared to $C_{n+4}E_x$ surfactants in formamide they show a similar association behaviour in solution and formation of liquid crystalline phases. It is well established from studies of dissolution in water of hydrocarbons and molecules containing hydrocarbon groups that the hydration of hydrocarbon groups is characterized by large and negative entropy changes and large and positive heat capacity changes$^{3,15,39)}$. The concept hydrophibic hydration usually refers to these unusual solvation properties of non-polar groups the origin of which is still much debated$^{39)}$. A striking feature of the thermodynamics of micelle formation in water is the strong response to temperature changes as evidenced by the large, positive ΔC_p(mic). However, it is clear that the peculiar solute – water interactions giving rise to these anomalous heat capacity effects are not a prerequisite for micelle formation. The association of $C_{12}E_4$ and $C_{16}E_8$ in formamide has all the characteristics of micelle formation still the values of ΔC_p(mic) are small, about 1/8 of the values in water. Neither are any anomalous heat capacity changes found for the dissolution of liquid amphiphiles$^{38)}$ nor for n-alkanols$^{40)}$ in formamide. For instance, ΔC_p for dissolution of liquid propanol and pentanol were found to be 35 ± 6 J·K^{-1}·mol^{-1} in formamide at 25°C$^{40)}$ for both alcohols while they are 210 and 324 J·K^{-1}·mol^{-1} in water$^{41)}$. Thus the strong cohesive forces in formamide give rise to a solvophobic effect that promotes micelle formation but lacks the peculiar solute – solvent interactions giving anomalous heat capacity effects. The solvophobic effect of hydrocarbon groups is probably somewhat weaker in formamide than in water. The calorimetric study supports the conclusion reached by Jonströmer *et al*$^{42)}$ from their NMR study of C_nE_x surfactants that exchanging water for formamide leads to a change in degree but not in character of amphiphile association.

References

1) H. Wennerström and B. Lindman, *Phys. Rep.* 52, 1 (1979).

2) B. Lindman and H. Wennerström, *Topics in Current Chemistry* 87, 1 (1980).

3) C. Tanford, *The hydrophobic Effect: Formation of Micelles and Biological Membranes* (John Wiley, New York, 2nd ed. 1980).

4) P. Stenius, S. Backlund and P. Ekwall, in *Thermodynamic and Transport Properties of Organic Salts* P. Franzosini and M. Sanesi

eds IUPAC Chemical Data Series No. 28 (Pergamon, Oxford, 1980) Chap 3, 2.

5) D.G. Hall and G.J.T. Tiddy, in *Anionic Surfactants. Physical Chemistry of Surfactant Action* E.H. Lucassen-Reynders ed. Surfactant Science Ser. vol. 11 (Marcel Dekker, New York, 1981) Chap. 2.

6) K. Meguro, M. Ueno and K. Esumi, in *Nonionic Surfactants. Physical Chemistry* M.J. Schick ed. Surfactant Science Ser. vol. 23 (Marcel Dekker, New York, 1987) Chap. 3.

7) R. Zana, in *Cationic Surfactants. Physical Chemistry* D.N. Rubingk and P.M. Holland eds Surfactant Science Ser. vol. 37 (Marcel Dekker, New York, 1991) Chap. 2.

8) J. Desnoyers, G. Perron and A. Roux, in *Surfactant Solutions. New Methods of Investigation.* R. Zana ed. Surfactant Science Ser. vol. 22 (Marcel Dekker, New York, 1987) Chap. 1.

9) W. Binana-Limbele and R. Zana, *Colloid Polym. Sci.* **267**, 440 (1989).

10) The injected volumes were of the order of 10 mm^3 and the volumes of the calorimetric vessels varied between 3 and 100 cm^3. Further descriptions of equipment, experimental procedure etc. can be found in references to our work given below.

11) G. Olofsson, *J. Phys. Chem.* **89**, 1473 (1985).

12) B. Andersson and G. Olofsson, *J. Chem. Soc. Faraday Trans* 1, **84**, 4087 (1988).

13) J.E. Desnoyers, G. Caron, R. DeLisi, D. Roberts, A. Roux and G. Perron, *J. Phys. Chem.* **87**, 1397 (1983).

14) J.M. Corkhill, J.F. Goodman and J.R. Tate, *Trans. Faraday Soc.* **60**, 996 (1964).

15) S.J. Gill and I. Wadsö, *Proc. Natl. Acad. Sci. USA* **73**, 2955 (1976).

16) P.-G. Nilsson, H. Wennerström and B. Lindman, *J. Phys. Chem.* **87**, 1377 (1983).

17) W. Brown and R. Rymdén, *J. Phys. Chem.* **91**, 3565 (1987).

18) T. Kato, S.-i. Anzai, S. Takano and T. Seimiya, *J. Chem. Soc. Faraday Trans* 1, **85**, 2499 (1989).

19) T.E. Burchfield and E.M. Woolley, *J. Phys. Chem.* **88**, 2149 (1984).

20) E.M. Woolley and M.T. Bashford, *J. Phys. Chem.* **90**, 3038 (1986)

21) L.V. Dearden and E.M. Woolley, *J. Phys. Chem.* **91**, 4123 (1987).

22) G. Gunnarson, B. Jönsson and H. Wennerström, *J. Phys. Chem.* **84**, 3114 (1980).

23) B. Jönsson and H. Wennerström, *J. Colloid Interface Sci.* **80**, 482 (1981).

24) B. Jönsson, G. Gunnarsson and H. Wennerström, *Solution Behaviour of Surfactants: Theoretical and Applied Aspects,* eds. K.L. Mittal and E.J. Fendler (Plenum Press, New York, 1982) vol. 1, p. 317.

25) B. Jönsson and H. Wennerström, *J. Phys. Chem.* **91**, 338 (1987).

26) M. Aamodt, M. Landgren and B. Jönsson, *J. Phys. Chem.* In press.

27) M. Landgren, *Thermodynamic Modelling of Ionic Surfactant Systems. PhD Thesis* (University of Lund, 1990).

28) I. Johnson, G. Olofsson and E. Jönsson, *J. Chem. Soc. Faraday Trans* 1 **83**, 3331 (1987).

29) I. Johnson and G. Olofsson, *J. Chem. Soc. Faraday Trans* 1 **84**, 551 (1988).

30) B.J. Birch and D.G. Hall, *J. Chem. Soc. Faraday Trans* 1 **68**, 2350 (1972).

31) R.L. Berg, BERC/TPR-7713, Bartlesville Energy Research Center, Bartlesville, Oklahoma (1977).

32) S.G. Cutler, P. Meares and D.G. Hall, *J. Chem. Soc. Faraday Trans* 1 **74**, 1758 (1978).

33) K.M. Kale, E.L. Cussler and D.F. Evans, *J. Solution Chem.* **11**, 581 (1982).

34) M. Landgren, (Results of calculations using the thermodynamic model reported in ref. 35).

35) I. Johnson, *Thermodynamic Study of Micelle Formation in Water and Alcohol Solutions. PhD Thesis* (University of Lund, 1989).

36) I. Johnson, G. Olofsson, M. Landgren and

B. Jönsson, *J. Chem. Soc. Faraday Trans* 1 **85**, 4211 (1989).

37) T. Wärnheim and A. Jönsson, *J. Colloid Interface Sci.* **125**, 627 (1988).

38) G. Olofsson, *J. Chem. Soc. Faraday Trans.* **87**, 3037 (1991).

39) N. Muller, *Acc. Chem. Res.* **23**, 23 (1990).

40) D. Berling and G. Olofsson, unpublished results.

41) D. Hallén, S.-O. Nilsson, W. Rothschild and I. Wadsö, *J. Chem. Thermodyn.* **18**, 429 (1986).

42) M. Jonstömer, M. Sjöberg and T. Wärnheim, *J. Phys. Chem.* **94**, 7549 (1990).

要　旨

溶液中での両親媒性物質の会合の研究に使用した高精度溶液用カロリメーターについて述べられている。著者達が行った研究例として水およびホルムアミド溶液中でのポリ（オキシエチレン）アルキルエーテルのミセル形成に関する熱力学的性質について考察されている。イオン性界面活性剤の会合に関する熱力学的モデルの検証のために行われた水およびペンタノール水溶液中でのドデシル硫酸ナトリウムの会合について述べられている。