

The occurrence of matrix relaxation above a transition temperature appears rather common to polymers including biological tissues. The matrix relaxation responsible for electron transfer should be taken into account in both interpretation of experimental results and construction of theoretical models, although such a relaxation has been neglected so far in the interpretation of the previous results on the temperature effects in biological systems.^{1,16,17,19,20}

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Enthalpies of Micellization of Quaternary Tetradecyl- and Cetyltrimethylammonium

Sergio Paredes,* Marianne Tribout,

Universite Libre de Bruxelles, Chimie Generale I, Faculte des Sciences, 1050 Bruxelles, Belgium

and Luis Sepulveda*

Departamento de Quimica, Facultad de Ciencias Basicas y Farmaceuticas, Universidad de Chile, Las Palmeras 3425, Casilla 653, Santiago, Chile (Received: February 18, 1983; In Final Form: August 4, 1983)

Direct enthalpies of micellization (ΔH_m°) of cetyltrimethylammonium salts (CTAX, X = OH⁻, F⁻, Cl⁻, Br⁻, and NO₃⁻) and tetradecyltrimethylammonium hydroxide (TTAOH) have been measured by using a microcalorimeter method. The dilution of the detergent solution was carried out in the calorimeter chamber in where heats of dilution were detected. The chamber was fed with two peristaltic pumps, one pump delivered the solvent and the other the detergent solution whose concentration varied continuously. The concentration gradient was obtained by inserting a flask containing solvent in the detergent pump path followed by a flask containing the detergent solution at a concentration about ten times its critical micelle concentration (cmc). When the dilution in the calorimeter chamber is done with water and the resulting solution is above the cmc of the given detergent, the heat detected arises from the heat of demicellization and the heat of micellar dilution. On the other hand, when the dilution is done with a solution just above the cmc, the heat detected would only correspond to the heat of micellar dilution. The standard enthalpies of micellization (ΔH_m°) obtained in this manner are discussed in terms of hydrophobic and electrostatic contributions. The ΔH_m° values and the standard free energies of micellization obtained from the cmcs were used to calculate the standard entropies of micellization (ΔS_m°). A linear trend between ΔS_m° and ΔH_m° was obtained which was interpreted in terms of dehydration of ions when they are transferred from the water to the micellar phase. It is concluded that the binding of small ions to micelles would be promoted mainly by entropic factors. It is also concluded that the thermodynamic behavior of micellar solutions is essentially determined by the nature and properties of the counterions.

Introduction

Heats of micellization (ΔH_m) have been usually obtained from the variation of the critical micelle concentration (cmc) with temperature. The reported values are often different from those obtained by direct calorimetric measurements.^{1,2} On the other hand, authors not only disagree on the magnitude but also on the sign of the heats of micellization^{1,3} and the models used for estimating the enthalpies of micellization from direct calorimetric experiments differ from one author to another.⁴⁻⁸

The heats of micellization obtained from the variation of the cmc with temperature are questionable considering that the large changes in temperature needed to observe changes in the cmc

might affect the micellar structure. The method also requires the application of a theory of micelle formation which is not well established in thermodynamic terms.

The above considerations make the obtainment of ΔH_m from direct calorimetric measurements desirable with an appropriate model for interpreting the results. Unfortunately, even the direct calorimetric data obtained in these systems are not so easily and unambiguously interpreted because of the superposition of the heats of dilution and the heats of demicellization.

In this work we have measured the total heats of dilution of micellar solutions trying to separate the contributions due to the heats of micellization from the heats due to micellar dilution.

Micelles containing the same amphiphilic but different counterions might have a different ΔH_m because the counterions could be bound to a different extent and with different energy. In this way, the specificity of the binding could be best understood by knowing the enthalpic contribution to the total free energy for the transference of a given counterion from water to the micellar interface. In recent papers, the probable reasons by which different counterions are strongly or weakly bound have been analyzed.^{9,10} It has been concluded that the dehydration and location of the counterion in the Stern layer might play an important role. These

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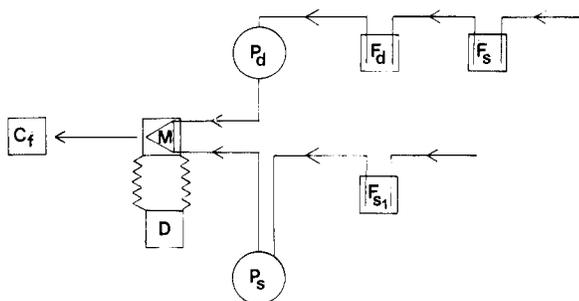


Figure 1. Arrangement of the apparatus for measuring the heats of micellar dilution. P_d and P_s are the peristaltic pumps delivering the detergent and solvent solutions, respectively. F_d is a flask containing the initial detergent concentration. F_s and F_{s1} are additional flasks containing the solvent for producing the concentration gradient and the dilution in M , respectively. D is the recorder and C_f is the final concentration produced by the mixing the solutions coming from F_d and F_{s1} .

factors should also be reflected in the heats of micellization. It follows that any attempt to establish the reasons by which a particular ion is preferentially adsorbed on a micellar surface will contribute to the understanding of the specificity of ion adsorption. Accordingly, we have measured the heats of micellization of cetyltrimethylammonium salts (CTAX) where $X = OH^-, Cl^-, F^-, NO_3^-,$ and Br^- and tetradecyltrimethylammonium hydroxide (TTAOH). The effects on ΔH_m produced by the addition of NaX on the corresponding CTAX solutions were also examined.

Experimental Section

Reagents. CTABr Merck was used after recrystallization from ethanol-ether mixtures. CTACl, Herga Industrias Quimicas, Rio de Janeiro, was purified as previously described.¹¹ CTANO₃ was prepared by mixing excess silver nitrate with CTABr with ethanol as solvent. After the mixture was stirred for several hours and then filtered for removal of the silver bromide and the excess of silver nitrate, the resulting solution was evaporated and the remaining solid was recrystallized from methanol-acetone mixtures. CTAOH was obtained by stirring a water solution of CTABr with an excess of silver oxide for several hours.

After filtration, a solution corresponding to an expected concentration of 0.5 M was obtained. Analysis of this solution by titration with 0.1 M HCl gave a concentration of 0.483 M. CTAF solutions were prepared by neutralization of CTAOH with HF. Tetradecyltrimethylammonium hydroxide (TTAOH) was purchased from Baker Chemical Co. as a 0.5 M aqueous solution. This product was labeled by Baker as CTAOH but the high cmc and further chromatographic analysis revealed that it was 99.6% TTAOH. Titration with HCl gave the same results.

CTAOH, CTAF, and CTANO₃ solutions were analyzed for their CTA content by precipitating them with an excess of potassium dichromate and, after filtration, determining at 430 nm the dichromate which did not react. The results indicated that the samples contained no less than 99% of CTA. Titration of CTAOH with HCl also gave a 99% OH⁻ content, indicating that excess of Ag₂O or complexes of Ag₂O with OH⁻ are absent. Another corroboration of the purity of the CTAOH used in this work was provided by its cmc (7.7×10^{-4} M) which is very close to that reported by Bunton et al. (8.6×10^{-4} M) for a CTAOH sample obtained by a completely different method in which Ag₂O is not used.¹² Generation of CTA and TTA carbonate was avoided by storing the solutions in a desiccator containing nitrogen. Dilutions and all other manipulations were done in an ambient of nitrogen.

Heats of Micellization. The enthalpy of micellization (ΔH_m) was obtained in a L.K.B. 1007-1 microcalorimeter coupled with two L.K.B. peristaltic pumps. Figure 1 illustrates the general

arrangement of the total apparatus. One pump (P_s) delivered the solvent at a constant rate, V_s , and the other pump (P_d) delivered the detergent solution at a rate V_d . The mixing of detergent and solvent takes place in the mixing chamber (M) of the calorimeter where the heats produced by the dilution are detected. The detergent concentration changed continuously from a concentration C_0 (at about ten times the cmc) to a concentration which after being diluted in the calorimeter chamber reached a value corresponding to the cmc of the given detergent solution. The concentration gradient of the detergent solution was obtained by inserting in the detergent pump path a mixing flask (F_0) containing the detergent solution which was continuously diluted with solvent coming from another flask (F_s) connected in line with F_d and P_d . F_d initially contains a detergent solution of concentration C_0 which changes with time according to the relation

$$C_t = C_0 \exp\left(-\frac{V_d t}{m}\right) \quad (1)$$

where C_t is the concentration at time t and m is the mass of detergent solution in F_d . The actual concentration in M at a given time was known after previous calibration. The electrical signal coming from the calorimeter was registered in a Servogor RE 511 recorder calibrated by using the internal resistance and current intensity provided by the calorimeter and with the pumps working at the same rate of flow used in the heats measurements. Pump flow rates were measured in each experiment by weighing the amount of solvent or detergent solution delivered during the experiment. Considering all the runs, the average flow rates found were 0.510 ± 0.002 and 0.110 ± 0.002 g/min for V_s and V_d , respectively.

The precision of the measurements of the microcalorimeter device is related to the recorder sensitivity which was 0.093 and $0.037 \mu\text{cal/mm}$ with the recorder working at 50 and 20 mV, respectively. A typical run lasted 3-4 h and measured heights on the recorder paper were no less than 20 mm from the base line which was obtained with pure solvent delivered by both P_d and P_s (see Figure 1).

Heats of Micellar Dilution. The heats of micellar dilution were obtained in the same manner as ΔH_m , except that the P_s pump was fed with a detergent solution having a concentration just above the cmc of the given detergent. In this way there is no demicellization and the detected heats are only due to the dilution of all existing species.

Critical Micellar Concentrations. The critical micellar concentrations (cmcs) for the different detergent solutions were determined by the intersection of the lines obtained by plotting surface tension against the log of the molar concentration of the detergent solution. Surface tension measurements were determined by the drop method as described by Paredes et al.¹³

Results and Discussion

When the initial micellar solution after dilution gives as a result a solution that has a concentration still above the cmc, the heat exchanged in the process can be attributed to at least three contributions:

(a) **Heat of Demicellization ($-\Delta H_m$).** This heat effect is due to demicellization for maintaining a constant monomer concentration equal to the cmc. The heat involved in this process will be given by

$$Q_{\text{dem}} = V_s(\text{cmc})(-\Delta H_m) \quad (2)$$

where the product $V_s(\text{cmc})$ represents the number of moles of demicellized micelles expressed as moles of monomers.

(b) **Heat of Dilution of Demicellized Micelles (Q_d^b).** This heat contribution is given by

$$Q_d^b = V_s(\text{cmc})(\phi_f^\infty - \phi_i) \quad (3)$$

where ϕ_f^∞ stands for the apparent relative heat content at infinite

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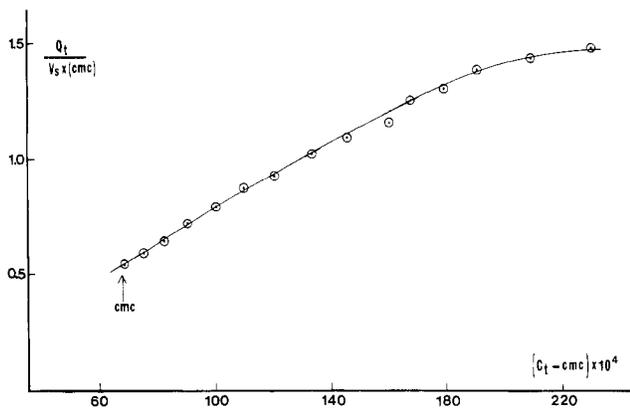


Figure 2. Heats of micellization (kcal/mol) of CTACl as a function of micellar concentration.

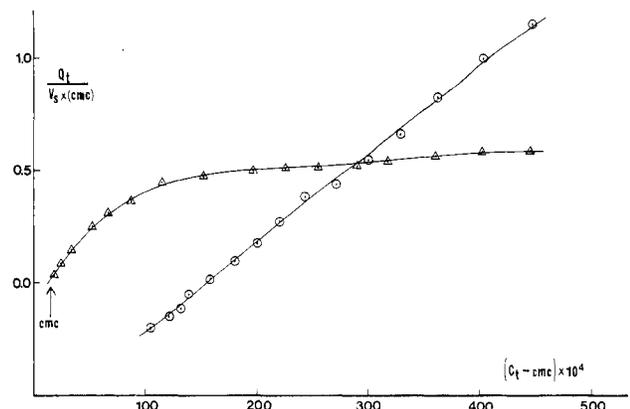


Figure 3. Heats of micellization (kcal/mol) of CTAF in water (O) and in a 0.05 M solution of NaF (Δ) as a function of CTAF molar concentration.

dilution, i.e., at the concentration of the final solution corresponding to the cmc. ϕ_i is the apparent relative heat content of the micellar solution at the concentration which enters to the mixing chamber M of the calorimeter.

(c) *Heat of Micellar Dilution (Q_d^m)*. This last contribution is due to the heat of dilution of the micelles which were not demicellized in the dilution process and it is expressed as

$$Q_d^m = [V_d(C_t - cmc) - V_s(cmc)](\phi_f - \phi_i) \quad (4)$$

where ϕ_f is now the apparent relative heat content of the micellar solution after dilution. The term in square brackets represents the number of moles of micelles diluted expressed as moles of monomers.

The total heat (Q_t) exchanged in the dilution process will then be given by

$$Q_t = Q_{dem} + Q_d^b + Q_d^m \quad (5)$$

Finally, eq 3-5 give

$$\frac{Q_t}{V_s(cmc)} = -\Delta H_m + \frac{V_d}{V_s(cmc)}(\phi_f - \phi_i)(C_t - (cmc)) + (\phi_f^\infty - \phi_i) \quad (6)$$

According to eq 6 the $Q_t/V_s(cmc)$ values will correspond to $-dH_m$ when the detergent solution at a micellar concentration ($C_t - (cmc)$) reaches after dilution in M (Figure 1) a solution with a concentration equal to the cmc of the given detergent (indicated by arrows in Figures 2-6). Under these conditions ϕ_f^∞ should be equal to ϕ_i .

In all the above treatments it has been assumed that the detergent monomer does not contribute to the heats of dilution since the heats of dilution were not detected with solutions at concentrations below the cmc. On the other hand when a given detergent

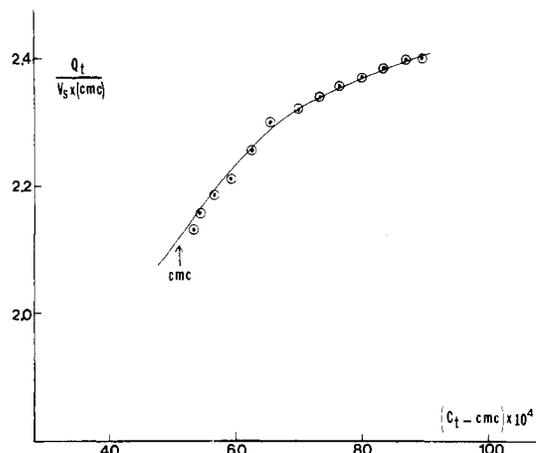


Figure 4. Heats of micellization (kcal/mol) of CTABr as a function of micellar concentration.

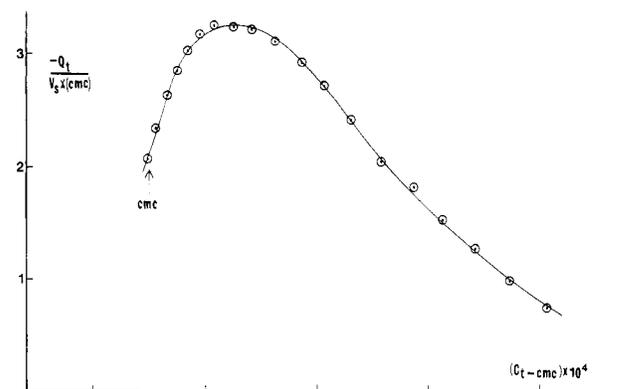


Figure 5. Heats of micellization (kcal/mol) of CTAOH as a function of micellar concentration.

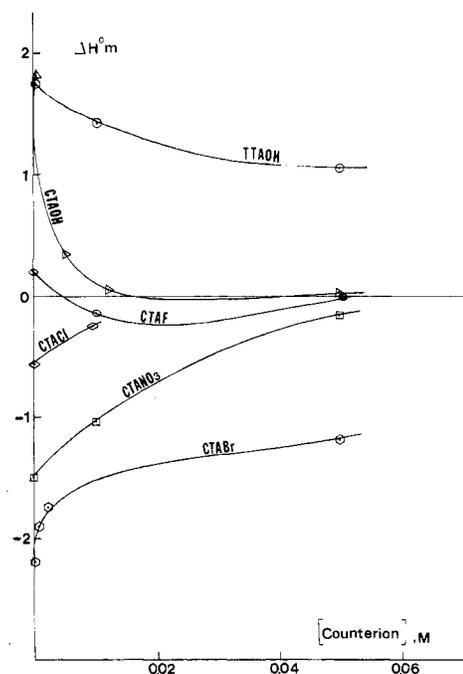


Figure 6. Heats of micellization (kcal/mol) of alkyltrimethylammonium salts as a function of the molarity of added counterions.

solution at a concentration well above the cmc is diluted with another detergent solution at a concentration just above the cmc, there is no demicellization and the detected heat should only correspond to the heat of micellar dilution Q_d^m , as expressed by eq 5.

TABLE I: Cmc's and Standard Enthalpies (ΔH_m°), Free Energies (ΔG_m°), and Entropies (ΔS_m°) of Micellization for Tetradecyl- and Cetyltrimethylammonium Salts in Water and in Presence of Added Counterions^a

detergent	$10^4 \times$ (cmc), M	ΔH_m° , kcal/ mol	ΔG_m° , kcal/ mol	ΔS_m° , cal/ (mol K)	additives
TTAOH	37.1	1.78 (2.88)	-5.8	25.4	
	26.4	1.44	-6.0	25.0	0.01 M NaOH
	21.3	1.09	-6.0	23.8	0.05 M NaOH
CTAOH	7.7	1.83 (2.70)	-6.7	28.6	
	3.06	0.36	-12.2	42.1	0.005 M NaOH
	2.76	0.08	-12.3	41.3	0.01 M NaOH
	2.24	0.00	-12.4	41.6	0.02 M NaOH
	2.22	0.00	-6.2	20.8	0.05 M NaOH
CTAF	19.5	0.20 (0.12)	-6.1	21.1	
	12.0	-0.11	-6.4	21.1	0.01 M NaF
	2.79	0.00	-7.8	26.2	0.05 M NaF
CTANO ₃	8.13	-1.48 (-2.53)	-6.7	17.5	
	1.77	-1.02	-7.5	21.7	0.01 M NaNO ₃
	1.47	-0.16	-7.6	25.0	0.05 M NaNO ₃
CTACl	13.2	-0.55 (-0.43)	-6.4	19.6	
	2.95	-0.22	-7.8	25.4	0.01 M NaCl
CTABr	8.9	-2.19 (-2.10)	-6.6	14.8	
	4.09	-1.85	-7.0	17.3	0.002 M NaBr
	2.30	-1.72	-7.4	19.5	0.005 M NaBr
	1.24	-1.17	-7.8	22.2	0.05 M NaBr

^a ΔH_m° in parentheses correspond to those values obtained by dilution of a given detergent concentration with the same detergent at a concentration just above its cmc.

Some typical plots of $Q_d/(V_s(\text{cmc}))$ vs. $(C_r - (\text{cmc}))$ are shown in Figures 2-5. It is seen that the dependences of the heats of dilution on the concentration are determined by the nature of the counterions. In fact, while CTACl and CTAF (Figures 2 and 3) show an almost linear pattern, CTAOH shows a maximum (Figure 5). The heats of micellization are very sensitive to the values of the cmcs which were only precise for detergents diluted with water but not when an excess of counterion was added. In these cases a region rather than a point was obtained at the intersection of the lines of surface tension against the log of surfactant concentration. This behavior will be discussed in detail in a future publication. The experimental value of ΔH_m° is taken now as the standard enthalpy of micellization (ΔH_m°) since it corresponds to the change in heat content when monomers at practically infinite dilution (cmc) associate to form micelles.¹⁴

Table I summarizes all the results. In the ΔH_m° column of Table I are also shown in parentheses some values of ΔH_m° obtained from experiments where the dilution was done with a solution having a concentration just above the cmc. In this way, only heats of micellar dilution (Q_d^m) are expected and they were subtracted from the total heat exchanged when a detergent solution of the same concentration was diluted with water. The difference should then correspond to ΔH_m° . The agreements in ΔH_m° obtained from these two methods are good for CTAF, CTACl, and CTABr but are poor for TTAOH and CTAOH probably because these last systems show a heat of micellar dilution too high compared with the heats of micellization. For example, when a 50 mM TTAOH solution is diluted with a 5 mM TTAOH solution (cmc = 3.7 mM) the heat evolved is -71 μcal while the heat evolved (cmc = 3.7 mM) the heat evolved is -71 μcal while the heat evolved when the same solution is diluted with water is -152 μcal . In the first case, there is no demicellization and the heat evolved might correspond only to the heat of micellar dilution. In the second case, both heat of demicellization and micellar

dilution might be present. This example also illustrates the importance of the heats of micellar dilution as compared with the total heat which includes the heat of micellization according to eq 5 and 6.

From the above results it might be concluded that our interpretation of the heats of micellar dilution is more correct than that given by Eatough and Rehfeld⁵ who attribute the changes in heats of dilution of a micellar solution to changes in the degree of micellar ionization (α). According to their model, a maximum in the heat evolved by dilution is not to be expected because α might also reach a maximum as the concentration of surfactant increases.

The only calorimetric value for the heats of micellization with which our results can be compared are those reported by Jolicoeur et al.¹⁵ who give a value of -2.21 for CTABr as compared with our value of -2.12 kcal/mol.

The values of ΔH_m° obtained for the different counterions follow the same pattern shown by the free energies of transference of the counterions from water to the surface of cationic micelles,¹⁰ suggesting that the enthalpic contribution greatly contributes to the specificity of the binding of the different counterions.

The most probable contributions to the total ΔH_m° are the hydrophobic effect (ΔH_h°), the electrostatic contribution (ΔH_e°) due to the association of the counterions, and the repulsion of the charged head groups (ΔH_r°). Thus

$$\Delta H_m^\circ = \Delta H_h^\circ + \Delta H_e^\circ + \Delta H_r^\circ \quad (7)$$

ΔH_e° can be negative if only electrostatic interactions are considered. For the same reason, the heat effect arising from the repulsion of the surface charges not neutralized by counterions can be positive¹⁶ and small because α is normally small. Finally, ΔH_h° is a negative contribution in accordance with the origin of the hydrophobic effect.¹⁷ The above considerations lead one to expect a total negative ΔH_m° , particularly in those cases in which counterions such as NO₃⁻, Br⁻, and Cl⁻ are strongly bound to micelles. On the other hand, the positive values of ΔH_m° found for CTAOH, TTAOH, and CTAF can be explained on the basis that these systems have a large degree of ionization¹² which would account for an endothermic ΔH_r° and an exothermic ΔH_e° .

In all the systems studied the increase in concentration of the counterions tends to produce a decrease in ΔH_m° when it is positive and an increase when it is negative (Table I and Figure 6). The first effect can be rationalized by assuming that α decreases by increasing the counterion concentration. This effect has been invoked by Bunton and Romsted to explain some kinetic results.¹²

However, the above explanation cannot be applied to the increase of negative ΔH_m° on addition of counterions like NO₃⁻ to CTANO₃, since a decrease in α might have the same effect as for the positive ΔH_m° . The $-\Delta H_m^\circ$ values should be even more negative in order to account for these changes in ΔH_r° and ΔH_e° . As α is not expected to increase on addition of counterions, other factors like hydration of both counterions and micelles could be responsible for the effect. The ionic strength increases results in a decrease of repulsion between the head groups which results in the squeezing of water from the micellar surface. This rupture of the water-head groups interactions would contribute endothermically to ΔH_m° .

The values of the cmcs obtained in this work allow the calculation of the standard free energies of micelle formation (ΔG_m°) through the relation¹⁴

$$\Delta G_m^\circ = RT \ln X(\text{cmc}) \quad (8)$$

where $X(\text{cmc})$ is the mole fraction of detergent at the cmc and therefore the unitary system has been chosen as the standard state.¹⁴ The corresponding standard entropies (ΔS_m°) can then be obtained by combining the ΔG_m° with the ΔH_m° values here

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(16) However, Etough and Rehfeld⁵ consider that this contribution is negative. It is well-known that the repulsion of the charged heads is a factor that is opposite to micellization and therefore must contribute positively to the free energy of micellization.

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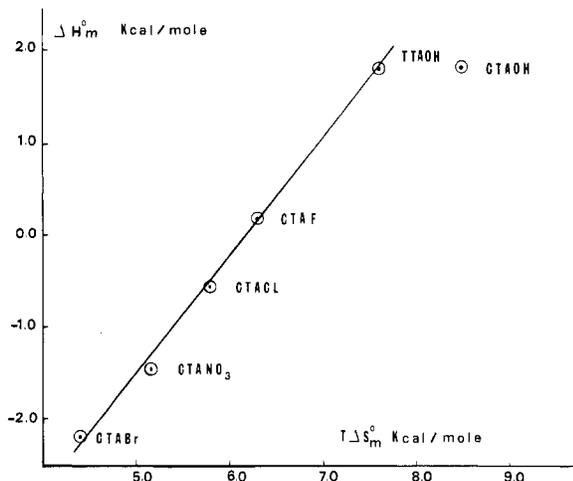


Figure 7. Relationship between standard heats of micellization and standard entropies of micellization.

obtained. The values obtained for ΔG_m^0 and ΔS_m^0 are also shown in Table I.

As expected, the driving force for micelle formation is in all cases determined by the positive entropy of micellization which is almost independent of the sign and magnitude of ΔH_m^0 .

Looking for a correlation between ΔH_m^0 and ΔS_m^0 , we found a linear relationship for the different detergents with water as a solvent (Figure 7). Such a correlation implies that ΔH_m^0 is directly involved in the ΔS_m^0 values. ΔS_m^0 can now be separated into two contributions: one constant contribution independent of the counterion concentration due to the hydrophobic effect produced by the transfer of the hydrocarbon chain from water to the micelle (ΔS_{mH}^0) and other due to the binding of the

counterions to the micellar charged surface ($\Delta S_{m_b}^0$). An attempt was made to calculate ΔS_{mH}^0 from the values reported by Tanford¹⁴ for the transference of an hydrocarbon from water to the interior of a sodium dodecyl sulfate micelle (NaLS). Although there is an almost linear trend between ΔS_{mH}^0 and the number of carbon atoms of ethane, propane, butane, and pentane, the extrapolation to C_{16} gives a ΔS_{mH}^0 value of about 4.8 cal/(mol K). This value is rather low and unexpected because it would then be necessary to attribute all the remaining entropic contributions to the dehydration of the bound counterions (Table I). From Table 6-1 of ref 14, a linear relationships was also obtained between the number of carbon atoms of the hydrocarbons and their heats of transfer (ΔH_{mH}^0) from water to NaLS micelles. The extrapolation to a C_{16} hydrocarbon molecule gave a ΔH_{mH}^0 value of -11.2 kcal/mol which cannot be explained by using our experimental results. In this way the extrapolation of thermodynamic properties beyond five carbon atoms of the hydrocarbon chain appears to be unwarranted.

The differences in ΔS_m^0 shown in Table I for the different counterions could be explained in terms of changes of hydration in going from water to the micellar interface. It is clear from Figure 7 and Table I that the more hydrated ions like OH^- , F^- , and Cl^- have the highest entropic and the lowest enthalpic contribution to the transfer of these anions from water to cationic micelles. It can be concluded that the factors involved in the binding of small anions to cationic micelles are entropic rather than enthalpic.

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Measurements of Diffusion Coefficients in Liquids at Atmospheric and Elevated Pressure by the Chromatographic Broadening Technique

John G. Atwood* and Jane Goldstein

The Perkin-Elmer Corporation, Norwalk, Connecticut 06856 (Received: May 4, 1983;
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Diffusion coefficients of solutes were measured in a series of six liquid chromatography mobile phases based on *n*-alkanes from pentane to decane with about 5% ethyl acetate modifier. Results for 18 solutes in the hexane-based mobile phase and 2 solutes in all 6 mobile phases are reported at near atmospheric pressure. Results for anisole, benzyl acetate, hexamethylbenzene, and didecyl phthalate in the hexane- and decane-based mobile phases at pressures up to 21 MPa are reported, with pressure and temperature coefficients of diffusion coefficients. The chromatographic method, in which the broadening of a solute peak injected into a long capillary tube is measured, was used. Theory is developed to estimate the effect of experimental nonideality on the accuracy of the method and to design the instrumentation to give accurate results in the shortest time. It is shown that, if the volume and length of the diffusion tube and the transit time of the sample in it are known accurately, the accuracy of the method is relatively insensitive to small variation of cross-sectional area along the tube, to small variation of flow rate during the transit time, and to small noncircularity of the tube's cross section. The number of theoretical plates in the tube must be 30 or greater, and the flow rate must lie within the range for which increase of peak variance per unit length is exactly proportional to flow rate. For coiled capillary tubes, a transition flow rate was found which must not be exceeded for accurate results. Minimum bandwidth, hence modern small-volume liquid chromatographic equipment, is advantageous in practicing the technique.

Introduction

In the chromatographic broadening technique, a small sample is injected into steady flow in a long capillary tube. From the measured dispersion of the sample as it leaves the tube, its diffusion coefficient in the liquid can be calculated. Pratt and Wakeham¹

and Grushka and Kikta² introduced the technique for measuring diffusion coefficients in liquids. These authors have described some of the advantages of the technique. It is an absolute method, requiring no calibration. It works especially well to determine diffusion coefficients near infinite dilution, yet it can also be used

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