

Figure 20. Comparison of line shapes calculated using the approximation described in the Appendix with those calculated using a complete calculation. The dimension of the largest complex non-Hermitian matrix which must be diagonalized in the approximate calculations is indicated in parentheses. For the complete calculation this dimension is 30×30 .

be treated using approximation B by making an appropriate correction to the diagonal elements of the exchange matrix χ . The corrected diagonal elements are given by

$$(\chi_{d_{ii}})_{\text{corr}} = \chi_{d_{ii}} + \left(\sum_j' \chi_{d_{ij}} \mathbf{M}_j^- \right) / \mathbf{M}_i^-$$

In the above equation the subscript d indicates that the indices vary only over those corresponding to a set of degenerate transitions and the prime on the summation symbol indicates that the term $\chi_{d_{ii}} \mathbf{M}_i^-$ is excluded. If C is set to a very small value no approximate factoring is found.

For intermediate values of C the degree of factoring will depend on the exchange rate(s). At slow rates the approximation will be equal to approximation B (including corrections for degenerate transitions). As the exchange rate is increased, the degree of factoring will decrease until at large exchange rates no approximate factoring will be found, and the complete calculation must be carried out. Figure 20 compares the results of exact and approximate simulation of the nmr line shapes for a trigonal bipyramidal A_2B_3X system in which the two axial spins (A) are simultaneously exchanging with two of the equatorial spins (B). In this particular case the constant C was chosen to have the value $1/20$. The slow exchange limit nmr parameters were the same as those used previously ($J_{AB} = 67.5$ Hz, $\delta_{AB} = 527$ Hz, $J_{AX} = 207$ Hz, $J_{BX} = 142$ Hz). In the present case the approximate calculation using the method outlined above gives better results than approximation B (neglect of all off-diagonal elements). However, the improvement is not dramatic. The utility of this approximation will depend on the nature of the exchange process and the spin system; the example given above probably does not represent a favorable case but was used here for comparison with the two other approximations described previously. Also, it represents a typical A_2B_3X spin system of the type with which this paper is concerned. The approximation described above and the approximation of neglect of all off-diagonal elements of $(\mathbf{R} + \chi - i\mathbf{L}_o(\omega))$ may be used in combination with omission of lines of very low intensity to reduce computation time still further.

Calorimetric and Counterion Binding Studies of the Interactions between Micelles and Ions. The Observation of Lyotropic Series

John W. Larsen* and Linda J. Magid¹

Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916. Received February 14, 1974

Abstract: Heats of transfer of a variety of salts from water to solutions of hexadecyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), and sodium dodecyl sulfate (NaLS) were measured. Lyotropic series for both cations and anions were observed for all soaps, the series for the two cationic soaps being almost identical. Linear plots of heats of transfer *vs.* the hydrated radius of the added counterion were observed. Using specific ion electrodes, the competition of tosylate, nitrate, and hydroxide with bromide ion for binding sites on the surface of CTAB micelles was studied. Both tosylate and nitrate bind to the micelle displacing bromide; ΔG , ΔH , and ΔS for the binding are reported. While addition of hydroxide decreases the amount of bromide bound to the micelle, no binding of hydroxide was observed.

The use of micelles to alter the rates of organic reactions has been vigorously explored by several workers.² There are several factors which affect the

size (number of monomers) and shape of micelles and hence their effectiveness in altering organic reaction rates. It is known that addition of salts lower the

(1) NSF Predoctoral Fellow, 1969–1972.
(2) (a) J. H. Fendler and E. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970), and references contained therein; (b) "Reaction Kinetics

in Micelles," E. H. Cordes, Ed., Plenum Press, New York, N. Y., 1973, and references contained therein; (c) L. J. Magid, Ph.D. Dissertation, University of Tennessee, 1973.

critical micelle concentration (cmc), increase the micellar size, and may have some effect on the degree of counterion binding for a given micelle. Salts have been found to both decrease³ and increase⁴ the rates of certain reactions catalyzed by micelles. The salt effects are generally explained using electrostatic arguments: adding a salt decreases the micellar surface charge density. The result is either a stabilization or destabilization of the transition state compared to the ground state of the reaction under consideration.

Although the foregoing explanation of salt effects in micellar catalysis is certainly attractive, experimental studies of counterion binding to micelles in the presence of added salts are not available for a wide variety of surfactants. Some data are available to support the idea that addition of salts to micellar solutions increases the amount of bound counterions (and hence decreases micellar charge).⁵ However, data are also available which indicate little effect of added salts on counterion binding. For example, Jones and Piercy,⁶ using light scattering to determine micellar charge, have observed that addition of NaBr has little effect on the binding of Br⁻ to micelles of dodecyltrimethylammonium bromide. The size of the micellar charge in the presence of salts has been used to rationalize both rate retardation^{2a,3} and rate enhancements^{3d,4} in reactions catalyzed by micelles.

Salt effects on the cmc, micellar size, and degree of dissociation for a given surfactant may follow a lyotropic series.^{7a} These series were first developed by Hofmeister,^{7b} who observed the effects of salts on the denaturation of euglobulins. Salts effective in denaturation were placed high in the series; series for both cations and anions could be constructed. An ion's position in a lyotropic series can be correlated with its charge and hydrated radius. Typical lyotropic series are as follows: anions, SO₄²⁻ < C₂H₃O₂⁻ < Cl⁻ < Br⁻ < NO₃⁻, ClO₄⁻ < I⁻ < CNS⁻; cations, (CH₃)₄N⁺ < NH₄⁺ < Rb⁺, K⁺, Na⁺, Cs⁺ < Li⁺ < Mg²⁺ < Ca²⁺ < Ba²⁺. Lyotropic series have been observed for the solubility of nonelectrolytes in aqueous salt solutions. In particular, salt effects on the cmc's of nonionic surfactants have been explained in terms of

salting-in and salting-out effects on the hydrophobic portions of the surfactants.⁸ If water-structure effects are important in salting in and salting out,^{7a,9} one might expect coions (ions of the same charge as the surfactant) as well as counterions to affect micellar size, shape, and cmc. For salt effects on the solubility of simple nonelectrolytes in water, the idea of internal pressure¹⁰ seems to work well.

For ionic surfactants, lyotropic series effects are also observed in the binding of the counterions to the micellar surface. A number of studies⁵ have indicated that the higher an ion is in a lyotropic series, the more effectively it will reduce micellar charge. Similar results have also been obtained for simple tetraalkylammonium salts in solution¹¹ and spread in monolayers.^{5a} A few examples of counterion binding competition experiments for cationic micelles have appeared previously.^{3d,5h,12}

We were interested in counterion binding for hexadecyltrimethylammonium bromide (CTAB), since it has been used extensively in the study of salt effects on micellar catalysis. In particular, does addition of an effective lyotropic salt result in reduced micellar charge? Does displacement of bromide ion occur when a second salt is added? What are the thermodynamics of binding of counterions to CTAB micelles? Our experimental approach includes the use of calorimetry and specific-ion electrodes. Some calorimetric work has also been carried out using sodium dodecyl sulfate (NaLS) and dodecyltrimethylammonium bromide (DTAB). The latter surfactant was selected to compare the effect of surfactant chain length and charge on micelle-salt interactions.

We feel calorimetry is superior to the temperature dependence of counterion binding for determining heats of binding of counterions to micelles, since temperature changes affect cmc's and micellar sizes.^{2a} Furthermore, calorimetric studies also enable the study of the effects of coions. In order to convert heats of transfer for ions into heats of ion-micelle binding, it is necessary to know what fraction of ions added to a micellar solution actually binds to the micelles. Some data of this kind have been obtained for CTAB solutions using specific ion electrodes to determine binding.

Specific-ion electrodes were selected for the study of counterion binding to CTAB because they permitted monitoring the binding of the different ions individually rather than only the overall micellar charges. These electrodes have been employed to determine the cmc's and the degree of counterion dissociation at the cmc for a number of surfactants, including sodium alkyl sulfates,¹³ alkyltrimethylammonium bromides,^{2c,13f,14}

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and other classes of surfactants.^{13a,c,15} Bunton¹⁶ has investigated the binding of H⁺ to sodium dodecyl sulfate micelles and OH⁻ to CTAB micelles. Competition between Br⁻ and organic solutes for binding sites on CTAB micelles has been studied using a Br⁻ specific ion electrode.^{2c,17}

Experimental Section

Materials. All salts used in calorimetry and counterion binding studies were reagent grade, dried to constant weight where necessary, and stored in a desiccator over Drierite or P₂O₅ until used.

Dodecyltrimethylammonium Bromide (DTAB). The surfactant DTAB was prepared from 1-bromododecane (Matheson Coleman Bell, 97%) and trimethylamine (Eastman, 25% aqueous solution) by the method of Scott and Tartar.¹⁸ Dry trimethylamine was obtained by distillation from the 25% aqueous solution. The resulting DTAB was recrystallized from acetone-ethanol mixtures. Nice white flakes were obtained; these were dried *in vacuo* for 24 hr at 60°, yield 59.5 g, 41%, mp 245°. Titration with AgNO₃ gave a molecular weight of 311 (actual 308.3). The cmc was 1.05×10^{-2} M by surface tension and 1.45×10^{-2} M by bromide ion specific electrode ($\log a_{\text{Br}^-}$ vs. $\log C$). Literature values cluster around 1.45×10^{-2} M.¹⁹

Hexadecyltrimethylammonium Bromide (CTAB). The surfactant CTAB (City Chemical Corp.) was slurried with CCl₄ and filtered by suction filtration, and the filtrate was warmed to produce a clear solution. CTAB crystallized from this solution as fine white needles; it was dried *in vacuo* for at least 24 hr at 60°.

The CTAB used had a cmc of 8×10^{-4} M by surface tension and 9.1×10^{-4} M using a bromide ion specific electrode. Titration of the CTAB using AgNO₃ gave a molecular weight of 363 (actual 364.5).

The use of other recrystallization techniques gave less satisfactory results. Recrystallization from 2-butanone gave a marked dip in the surface tension vs. $\log C$ plot at concentrations near the cmc. Addition of 2% hexadecanol (2% of CTAB on a concentration basis) gave the same behavior.

Sodium Dodecyl Sulfate (NaLS). NaLS was prepared from 1-dodecanol (Eastman, Technical) and chlorosulfonic acid (Eastman, Practical) according to the method of Kurz^{20a} and Dreger, *et al.*^{20b} The 1-dodecanol was purified by distillation at reduced pressure through a Nestor-Faust spinning-band column. The center cut showed only one peak on gc analysis. The resulting NaLS was recrystallized from 1-butanol. During collection of the crystals copious washing with diethyl ether was performed to remove any unreacted 1-dodecanol. Drying *in vacuo* at 55° for 24 hr gave 25.2 g of NaLS, 39% yield.

This material had a cmc of 6.7×10^{-3} M as measured by surface tension (lit. value 8.2×10^{-3} M).¹⁹ When the cmc was determined using NaLS solutions which were 72 hr old, a dip in the γ vs. $\log C$ plot occurred near the cmc. This is thought to be due to 1-dodecanol produced by hydrolysis of NaLS.²¹

Calorimetric Procedure. The construction and operating principles of the calorimeter used have been described.²² In a typical run twin calorimeters were each filled with 200 ml of solvent, delivered by volumetric pipet. When the solvent was a 0.04 M solution of

NaLS, the solution was prepared just prior to placing it in the calorimeter. Solutions of CTAB frequently had to be warmed to 26° in order to get all of the CTAB into solution, then cooled below 25° prior to introduction into the calorimeter. For temperatures around 25° no temperature control was usually necessary; (25 ± 1)° could easily be achieved by holding the ambient temperature at 22°. For solutes having highly exothermic ΔH_s values, the calorimeter was inserted into a metal can, and the can was placed in a water bath at 10°.

After the solvents were allowed to equilibrate with stirring for about 15 min, the solute injection procedure was begun. The samples were injected by means of a 3-cm plastic Jelco syringe with the tip cut off and replaced by a silicone rubber septum. After weighing each sample into a syringe, the syringes were stored in a desiccator containing either Drierite or P₂O₅. Hygroscopic solutes were handled in a drybox or glove bag, except for actual weighing of the filled syringes.

Counterion Binding. The reference electrode used (except for pH measurements) was the Orion Model 90-02 double junction reference electrode. The inner chamber was filled with solution 90-00-02 and the outer chamber was filled with solution 90-00-03, 10% KNO₃, except for measurements of NO₃⁻ and Br⁻ competition, where 10% KCl was used. For studies of CTAB in NaOH, the pH of the 10% KNO₃ was adjusted. These filling solutions were changed every 1-2 weeks. The specific-ion electrodes used were the Orion Model 94-35 bromide ion electrode, the Orion Model 94-17 chloride ion electrode, and the Orion Model 92-07 nitrate ion electrode (liquid membrane type). All emf measurements were recorded using the Orion Model 701 pH/mV meter.

The measured potential of a solution containing X⁻ using an electrode sensitive to X⁻ is given by eq 1. The term E_a is due to the choice of reference electrode and internal filling solutions for that reference electrode.

$$E = E_a + 2.3RT/nF(\log a_{X^-}) \quad (1)$$

The measured potentials of a series of standard solutions containing varying concentrations of the salt NaX were plotted against $\log a_{X^-}$ (obtained using activity coefficients (γ) for NaX from Latimer,²³ with interpolation where necessary). For NaOH the activity coefficients for NaCl were used. In practice the plots had slopes slightly less than theoretical (*ca.* -58 mV). Least-squares analysis was not applied to the calibration plots because of their good quality.

Both samples and standards were placed in a constant temperature bath 30 min prior to taking readings. A series of standards or samples were always read in order of increasing concentration. Because the millivolt readings do drift slowly toward a constant value with time, a waiting period of up to 10 min was sometimes necessary before a reliable reading could be obtained. The electrodes were either rinsed with distilled water and blotted with a tissue or simply blotted when changing solutions. Readings on sample solutions were frequently taken interspersed with readings on standard solutions, because of the problem of electrode drift with time. Reproducibility to within ± 1 mV was generally possible for the samples; reproducibility was better for the standards.

For the work on OH⁻ binding in 0.1 M CTAB solutions, pH readings were obtained for a series of NaOH solutions and plotted against $\log a_{\text{OH}^-}$. The resulting straight line had a slope close to one. Values of a_{OH^-} for the sample were then obtained from this straight line by interpolation.

When using the nitrate ion specific electrode in solutions containing Br⁻, corrections to the observed $a_{\text{NO}_3^-}$ had to be made because Br⁻ interferes with the nitrate ion electrode according to eq 2.²⁴

$$E_{\text{obsd}} = E_a - 2.3RT/F(\log [a_{\text{NO}_3^-} + 0.13a_{\text{Br}^-}]) \quad (2)$$

These corrections were necessary for 0.01 and 0.1 M CTAB solutions studied in the presence of NaNO₃. The necessary a_{Br^-} for each sample was obtained using the bromide ion specific electrode, which is not susceptible to interference by nitrate ion. A calibration plot of E_{obsd} vs. $\log a_{\text{NO}_3^-}$ (standards) was used to get the quantity ($a_{\text{NO}_3^-} + 0.13a_{\text{Br}^-}$) for each sample.

Results

Calorimetric Data.

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Table I. Enthalpies of Transfer for Salts from Water to 0.1 M CTAB Solution at $(25 \pm 1)^\circ$

Salts	$\Delta\bar{H}_s(0.1 M \text{ CTAB}), \text{ kcal/mol}$	$\Delta\bar{H}_s(\text{H}_2\text{O}), \text{ kcal/mol}$	$\Delta H_{\text{trans}}, \text{ kcal/mol}$
Na ₃ C ₆ H ₅ O ₇ · 2H ₂ O	5.02 ± 0.47	1.97 ± 0.32	3.05 ± 0.57
Na ₂ CO ₃	-2.07 ± 0.11 ^a	-4.541 ± 0.090 ^b	2.47 ± 0.14
Na ₂ SO ₄	1.49 ± 0.12	-0.560 ± 0.010 ^c	2.05 ± 0.12
NaC ₂ H ₃ O ₂	-3.09 ± 0.18	-4.140 ± 0.050 ^d	1.05 ± 0.19
NaF	1.10 ± 0.04 ^a	0.218 ± 0.010 ^d	0.88 ± 0.04
NaOH	-9.84 ± 0.02	-10.637 ± 0.010 ^d	0.80 ± 0.02
NaHCO ₃	0.878 ± 0.059	0.203 ± 0.024	0.68 ± 0.06
NaCl	1.32 ± 0.02	0.928 ± 0.005 ^d	0.39 ± 0.02
NaNO ₃	3.93 ± 0.20	4.900 ± 0.050 ^d	-0.97 ± 0.20
NaBr	-1.43 ± 0.12	-0.144 ± 0.015 ^d	-1.29 ± 0.12
NaSO ₃ C ₇ H ₇	0.663 ± 0.265	2.54 ± 0.21	-1.50 ± 0.11
KBr	4.08 ± 0.27	4.750 ± 0.020 ^d	-0.67 ± 0.27
LiBr	-12.4 ± 0.1 ^a	-11.670 ± 0.050 ^d	-0.71 ± 0.15
(CH ₃) ₄ NBr	4.80 ± 0.18	5.800 ± 0.100 ^d	-1.00 ± 0.20
NH ₄ Br	2.41 ± 0.06 ^a	4.010 ± 0.100 ^d	-1.60 ± 0.12
MgBr ₂	-39.6 ± 1.8	-37.7 ± 0.8	-1.9 ± 1.9
CaBr ₂	-25.9 ± 1.0	-23.3 ± 0.7	-2.6 ± 1.0

^a Extrapolated to infinite dilution using linear least-squares analysis. (These data, *i.e.*, $\Delta\bar{H}_s$ as a function of C , may be found in the microfilm edition.) ^b Linear least-squares analysis (ΔH vs. $I^{1/2}$) on the data of J. P. Rupert, H. P. Hopkins, and C. A. Wulff, *J. Phys. Chem.*, **69**, 3059 (1965). ^c K. S. Pitzer and L. V. Coulter, *J. Amer. Chem. Soc.*, **60**, 1310 (1938). ^d V. B. Parker, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 2* (1965).

Table II. Enthalpies of Transfer for Salts from Water to 0.075 M DTAB Solution at $(25 \pm 1)^\circ$

Salts	$\Delta\bar{H}_s(0.075 M \text{ DTAB}), \text{ kcal/mol}$	$\Delta H_{\text{trans}}, \text{ kcal/mol}$
Na ₂ CO ₃	-0.830 ± 0.147 ^a	3.71 ± 0.17
Na ₂ SO ₄	0.996 ± 0.117	1.56 ± 0.12
NaC ₂ H ₃ O ₂	-3.20 ± 0.07	0.94 ± 0.09
NaHCO ₂	0.617 ± 0.170	0.41 ± 0.17
NaNO ₃	4.44 ± 0.09	-0.46 ± 0.10
NaBr	-0.955 ± 0.082 ^a	-0.81 ± 0.08
NaSO ₃ C ₇ H ₇	0.990 ± 0.123	-1.55 ± 0.24
LiBr	-11.6 ± 0.2	≈ 0
NH ₄ Br	3.61 ± 0.13	-0.40 ± 0.17
KBr	4.20 ± 0.10	-0.55 ± 0.10
(CH ₃) ₄ NBr	5.01 ± 0.22	-0.79 ± 0.25
CaBr ₂	-24.2 ± 0.3	-0.9 ± 0.7
MgBr ₂	-38.6 ± 0.3	-0.9 ± 0.8

^a Extrapolated to infinite dilution using linear least-squares analysis. The original data may be found in the microfilm edition. ^b See Table I for $\Delta\bar{H}_s(\text{H}_2\text{O})$.

from water to aqueous surfactant solution for the salts studied are presented in Tables I-III. All of the counterion data collected represent competition between two different counterions. In order to make quantitative comparisons of the heats of binding for various counterions, it would be necessary to correct the observed heats of transfer for (1) the fraction of added counterions which are actually bound to the micelles and (2) the dissociation of sodium ions (NaLS) or bromide ions (CTAB, DTAB) already on the micelles. The latter processes are endothermic.^{5g,6,14b} In cases where the counterion is held constant but the coion is varied, MBr with CTAB or DTAB for example, the observed heats of transfer do not of course arise from coion binding.

A very small portion of the observed heats of transfer may also be due to additional surfactant undergoing micellization. The small heats of micellization observed for NaLS and DTAB make the last correction unnecessary. For CTAB, Czerniawski²⁵ reports the heat of micellization to be -3.77 kcal/mol, but because of CTAB's low cmc very little additional surfactant will

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Table III. Enthalpies of Transfer for Salts from Water to 0.04 M NaLS Solution at $(25 \pm 1)^\circ$

Salts	$\Delta\bar{H}_s(0.04 M \text{ NaLS}), \text{ kcal/mol}$	$\Delta H_{\text{trans}}, \text{ kcal/mol}$
NaSO ₃ C ₇ H ₇	1.56 ± 0.21	-0.98 ± 0.30
NaC ₂ H ₃ O ₂	-4.33 ± 0.07 ^a	-0.19 ± 0.08
NaNO ₃	4.36 ± 0.16 ^a	-0.54 ± 0.17
Na ₂ SO ₄	-1.70 ± 0.08 ^a	-1.14 ± 0.08
LiBr	-11.1 ± 0.2	0.6 ± 0.2
NaBr	-0.333 ± 0.077	-0.19 ± 0.08
NH ₄ Br	3.65 ± 0.15	-0.36 ± 0.18
KBr	3.94 ± 0.22 ^b	-0.81 ± 0.22
(CH ₃) ₄ NBr	3.40 ± 0.15 ^a	-1.40 ± 0.18
CaBr ₂	-24.9 ^c	-1.6

^a Extrapolated to infinite dilution using linear least squares analysis. The original data may be found in the microfilm edition. ^b Precipitation of surfactant occurred at $\leq 0.0175 M$ KBr (fourth injection). ^c Based on one injection. Addition of further CaBr₂ caused precipitation of surfactant. ^d See Table I for $\Delta\bar{H}_s(\text{H}_2\text{O})$.

be micellized during the course of salt addition. Estimates on enthalpies for structural changes in the micelles have not been made with any reliability.

Lacking the necessary data on fraction of counterions bound for all the salts investigated, the salts studied have been arranged in lyotropic series based on their observed heats of transfer; see Tables I-III. One ion is more effective than another (and hence is placed higher in the lyotropic series) if the ΔH_{trans} for the more effective ion is the more negative.

For CTAB the observed anionic lyotropic series on the basis of the ΔH_{trans} in Table I is citrate < CO₃²⁻ < SO₄²⁻ < C₂H₃O₂⁻ < F⁻ < OH⁻ < HCO₂⁻ < Cl⁻ < NO₃⁻ < Br⁻ < SO₃C₇H₇⁻. The series for DTAB is the same, although it does cover fewer anions. Both series closely parallel the typical anion series for protein denaturation. Being able to observe such a lyotropic series for observed ΔH_{trans} (no corrections applied) is indeed gratifying. The series seems to reflect the binding ability of the anions. The closer the approach of the ion to the micelle surface, the more favorable ΔH_{trans} should be. Hydrophobic interactions with the head groups may also be important in certain cases, *e.g.*, tosylate ions. Indeed, a plot of ΔH_{trans} vs. Stokes'

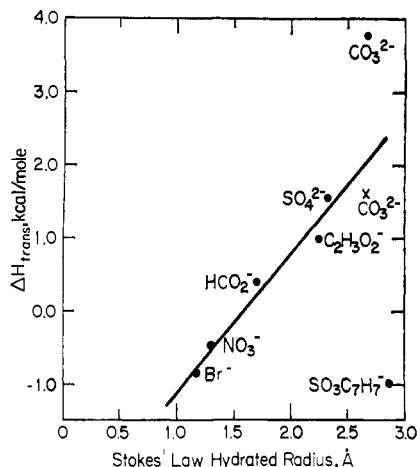


Figure 1. ΔH_{trans} (to 0.1 M CTAB) for NaX vs. the Stokes' law hydrated radii for the anions.

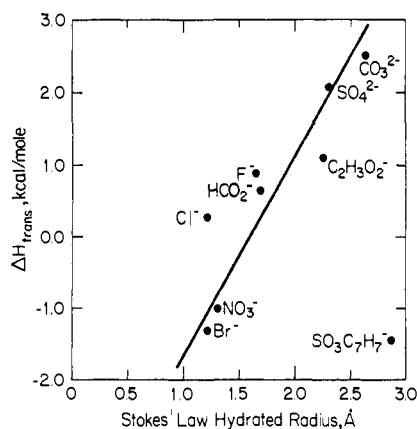


Figure 2. ΔH_{trans} (to 0.075 M DTAB) for NaX vs. the Stokes' law hydrated radii for the anions.

law hydrated radii²⁶ (omitting OH^- because of its high equivalent conductivity) for the anions studied gives a reasonable straight line; see Figures 1 and 2. Only tosylate ion is a significant distance off the line. The Stokes' law hydrated radius for the benzoate ion was used to approximate the tosylate ion's radius.

Strictly speaking, ΔH_{trans} should be plotted against the distance of closest approach, a , for the anions and the charged trimethylammonium head groups. The parameter a may be obtained from the Debye-Hückel formula for activity coefficients, but this would require knowledge of the activity coefficient of CTAB in aqueous solution. Since a is related to the sum of the radii (including some water of solvation) of the cation and anion but the cation does not change in our studies with CTAB and DTAB, the variation in Stokes' law radii for the anions should be a reasonable reflection of the variation in a .

Since 0.075 M DTAB contains only 65% as many micelles as 0.1 M CTAB (assuming similar aggregation numbers for the surfactants in the absence of salt), one might expect the ΔH_{trans} value for an anion in DTAB to be 65% of what it is in CTAB (this of course also assumes that the enthalpy of binding for the anions is independent of surfactant chain length). With the

(26) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1968, pp 124-126 and App. 6.1, 6.2.

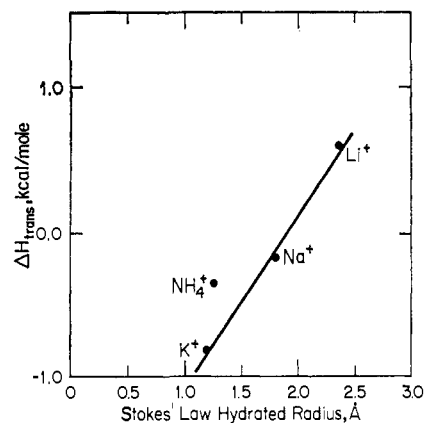


Figure 3. ΔH_{trans} (to 0.04 M NaLS) for bromide salts of alkali metals vs. the Stokes' law hydrated radii for the cations.

exception of Na_2CO_3 , the ΔH_{trans} for DTAB are 47-89% of the corresponding ΔH_{trans} values for CTAB. This seems to indicate that the binding characteristics of the two micellar surfaces are not radically different.

The lyotropic series observed for cations with CTAB is $\text{K}^+ < \text{Li}^+ < (\text{CH}_3)_4\text{N}^+ < \text{NH}_4^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$; for DTAB it is $\text{Li}^+ < \text{NH}_4^+ < \text{K}^+ < (\text{CH}_3)_4\text{N}^+ < \text{Na}^+ < \text{Ca}^{2+} \approx \text{Mg}^{2+}$. Since the cations are not bound to the CTAB or DTAB micellar surface, with the possible exception of $(\text{CH}_3)_4\text{N}^+$, where hydrophobic interactions in the sense of mixed micelle formation may play a role, the observed order must be rationalized in terms of indirect effects. The results in Tables II and III for DTAB and NaLS were obtained at surfactant concentrations of five times the cmc in both cases, in an attempt to utilize solutions containing about the same number of micelles.

The cationic results for NaLS give $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < (\text{CH}_3)_4\text{N}^+ < \text{Ca}^{2+}$. The reported ΔH_{trans} for Ca^{2+} is based on a single injection, since addition of CaBr_2 causes NaLS to precipitate. The same problem, to a lesser extent, was observed with KBr . It is assumed that ΔH_{trans} is measuring the binding of some fraction of the added cations to the NaLS micellar surface, with the cations which can approach the head groups most closely giving the most favorable ΔH_{trans} . A plot of ΔH_{trans} for the alkali metal cations vs. their Stokes' law hydrated radii supports this contention (Figure 3). The alkaline earth cations would not necessarily be expected to fall on the same line, since the magnitude of an ion's charge will also influence ΔH_{trans} .

The anion results with NaLS gives the following series: $\text{C}_2\text{H}_3\text{O}_2^- < \text{NO}_3^- < \text{SO}_3\text{C}_7\text{H}_7^- < \text{SO}_4^{2-}$. This result will be considered in terms of water structure effects in the Discussion section.

Counterion Binding. Tables IV-VI give the results of competitive counterion binding studies using CTAB and NaNO_3 and NaOH and $\text{NaSO}_3\text{C}_7\text{H}_7$. Lack of a tosylate ion specific electrode precluded a direct study of tosylate binding.

The competition between NO_3^- and Br^- for binding sites on CTAB micelles was examined at two concentrations of CTAB; the results are presented in Table IV. The activities of free NO_3^- and Br^- were determined using nitrate and bromide ion specific electrodes respectively, with appropriate corrections being made

Table IV. Competitive Counterion Binding for CTAB: Bromide Ions vs Nitrate Ions

[NaNO ₃], M	[CTAB], ^a M	Bound [Br ⁻], M	Bound [NO ₃ ⁻], M	1 - α ^b
0.0400	0.00996	0.0018	0.0070	0.89
0.0200	0.00993	0.0024	0.0058	0.83
0.0100	0.00988	0.0035	0.0043	0.79
0.0048	0.00980	0.00495	0.0027	0.78
0.0020	0.00965	0.0061	0.0014	0.78
0.0010	0.00950	0.0066	0.00077	0.78
0.0315	0.1000	0.0568	0.0228	0.81
0.0200	0.1000	0.0626	0.0157	0.78
0.0100	0.1000	0.0670	0.0088	0.76
0.0048	0.1000	0.0720	0.0045	0.77
	0.1000	0.0770		0.77

^a Concentration of CTAB in micellar form. ^b Includes both kinds of ions: $1 - \alpha = (\text{bound}[\text{NO}_3^-] + \text{bound}[\text{Br}^-]) / [\text{CTAB}]$.

Table V. Competitive Counterion Binding for 0.1 M CTAB: Bromide Ions vs. Hydroxide Ions

[NaOH], M	Bound [Br ⁻], M	Bound [OH ⁻], M	1 - α ^a
0.0497	0.0714	0.0290	0.71
0.0398	0.0719	0.0116	0.72
0.0298	0.0722	0.0095	0.72
0.0199	0.0734	0.0165	0.73
0.00995	0.0754	0.0090	0.75

^a Includes both kinds of ions: $1 - \alpha = (\text{bound}[\text{OH}^-] + \text{bound}[\text{Br}^-]) / [\text{CTAB}]$.

Table VI. Competitive Counterion Binding for CTAB: Bromide Ions in the Presence of Sodium Tosylate

[NaSO ₃ C ₇ H ₇], M	[CTAB], ^a M	Bound [Br ⁻], M	1 - α
0.0120	0.1000	0.0680	0.68
0.0100	0.1000	0.0702	0.70
0.0080	0.1000	0.0720	0.72
0.0052	0.1000	0.0750	0.75
0.0040	0.1000	0.0757	0.76
0.0020	0.1000	0.0770	0.77
	0.1000	0.0785	0.78
0.0125	0.00618 ^b	0.0000	
0.0200	0.00620 ^b	0.0000	

^a Concentration of CTAB in micellar form. ^b These solutions are very viscous.

for Br⁻ interference with the nitrate electrode. It was assumed that ions bound to the micellar surfaces do not contribute to the observed readings. Initial concentrations of free NO₃⁻ and Br⁻ were obtained from the observed activities using standard activity coefficients for each ion separately.²³ The resulting concentrations were then added together and new activity coefficients determined for NO₃⁻ and Br⁻ using these total salt concentrations. This second set of activity coefficients was then divided into the appropriate observed activities ($a_{\text{NO}_3^-}$ and a_{Br^-}) to get concentrations of free NO₃⁻ and Br⁻. The concentrations of free NO₃⁻ and free Br⁻ were then subtracted from total added NO₃⁻ and Br⁻ to get the values for bound NO₃⁻ and Br⁻, respectively. For 0.01 M CTAB the concentration of free counterions due to monomers was taken into account, as was the effect of added salt on the cmc.^{2c} There has been some criticism^{13b} of neglecting the effect of the surfactant on the activity coefficients of free counterions. While recognizing that CTAB will have such an effect^{2c} on both NO₃⁻ and

Br⁻, we contend that the effect will be similar for the two ions. The amounts of bound NO₃⁻ and Br⁻ have been added together in order to compute the fraction of the CTAB micellar charge which is neutralized in each case; the results are expressed as $1 - \alpha$ values, where α is defined as the degree of counterion dissociation. Thus $1 - \alpha$ is the degree of counterion-micelle association.

As the results in Table IV show, adding NO₃⁻ to CTAB solutions results in part of the added NO₃⁻ binding to the micelles; this binding is accompanied by some displacement of Br⁻. For 0.01 M CTAB $1 - \alpha$ consistently gets larger as the concentration of NO₃⁻ increases; for 0.1 M CTAB $1 - \alpha$ remains almost constant as the concentration of NO₃⁻ is increased.

In competition studies using OH⁻ and Br⁻, a pH combination electrode was used to measure free [OH⁻]. Briefly, hydroxide ion does not seem to be bound to CTAB micelles (Table V), in agreement with other work.^{12c,16} As Table V indicates, Br⁻ binding to CTAB did decrease slightly as [NaOH] was increased. We experienced a great deal of difficulty in obtaining reproducible pH readings in solutions containing CTAB and NaOH. It is possible that liquid junction potential problems are severe with the glass electrode. If no OH⁻ is bound to CTAB micelles, the observed enthalpy of transfer for NaOH from H₂O to CTAB solutions is due entirely to Br⁻ displacement from the micelles. However, this would give an enthalpy of displacement of about 8 kcal/mol, an unreasonable value when compared to the 2 kcal/mol value for displacement of Br⁻ from dodecyltrimethylammonium bromide micelles.^{6,14b}

Table VI presents the effect of tosylate ion on Br⁻ bound to the CTAB micelles in 0.1 M CTAB. Lack of a tosylate ion specific electrode prohibited a complete study of this system; no data on the amount of tosylate bound to the micelles were obtained. Tosylate ion is very effective at freeing Br⁻ from the CTAB micellar surfaces. It is so effective that the largest possible $1 - \alpha$ value for the micelles in these systems is 0.80, assuming 100% of the added tosylate ion is bound. Bunton,²⁷ using kinetic data and treating tosylate ion as an inhibitor, found that about 75% of the tosylate present was bound (this was for 0.003 M CTAB). Because of tosylate ion's interaction with the surfactant head groups,^{2b} it should be very effective at reducing the micellar charge density by spreading the head groups apart. When the molar ratio of tosylate to CTAB is greater than one, very viscous solutions are observed; the micelles actually bear a negative charge.^{2b,4} It is found that under these conditions there is no Br⁻ bound to the CTAB micelles.

We also unsuccessfully attempted to study competition between Cl⁻ and Br⁻ for binding sites on CTAB micelles. Patterson^{12b} has observed that Cl⁻ is rather inefficient at displacing Br⁻ from CTAB micelles by observing the dependence of fluorescence lifetimes for anthracene and perylene solubilized in the micelles on the concentration of added NaCl.

The effectiveness of the ions studied in this work at displacing Br⁻ from the CTAB micellar surface follows a lyotropic series: OH⁻ < NO₃⁻ < SO₃C₇H₇⁻. We

(27) C. A. Bunton, E. J. Fendler, L. Sepulveda, and K.-U. Yang, *J. Amer. Chem. Soc.*, **90**, 5512 (1968).

feel that some OH⁻ is bound, giving rise to the small observed displacement of Br⁻. The effect of the ions on α , the degree of micellar dissociation, does not follow a lyotropic series, however, because tosylate is very good at displacing Br⁻ from the micelles. Tosylate may in fact be a special case since hydrophobic interactions may play a role.^{2b, 4, 28}

Our data do support increased counterion binding when NO₃⁻ is added to CTAB solutions, but the effect is certainly not as large as expected for an ion high in a lyotropic series. We wonder whether salt effects on the rates of micellar reactions should not also take into account changes in structure of the micelles induced by the added salts.

Specific adsorption potentials for counterions at a charged surface have been reported to be quite large.²⁹ It is possible to determine the difference in specific adsorption potentials for the binding of pairs of counterions using $\Delta G = -RT \ln f$, where f is a selectivity ratio obtained by dividing the ratio of bound concentrations of the two ions by the ratio of their free concentrations.^{12a} We used $f = ([Br^-]_{bound}/[X^-]_{bound})/([Br^-]_{free}/[X^-]_{free})$, so that an f value less than one means that X⁻ is bound in preference to Br⁻. We have calculated ΔG values from the binding observed in our competitive counterion studies; the results appear in Table VII. If the specific adsorption potential for Br⁻ is

Table VII. Differences in Specific Adsorption Potentials for Binding of Counterions to CTAB Micelles

[NaX], M	[CTAB], M	Bound ratio ^a	Bulk ratio ^b	f^c	ΔG , cal/mol
0.0400 NaNO ₃	0.00996	0.257	0.248	1.04	-23
0.0200	0.00993	0.414	0.535	0.774	150
0.0100	0.00988	0.814	1.14	0.714	200
0.0048	0.00980	1.83	2.40	0.763	160
0.0020	0.00965	4.36	6.39	0.682	230
0.0010	0.00950	8.57	14.8	0.579	320
0.0315 NaNO ₃	0.1000	2.49	4.98	0.50	410
0.0200	0.1000	3.99	8.70	0.459	460
0.0100	0.1000	7.61	27.5	0.277	760
0.0048	0.1000	16.0	93.3	0.171	1100
0.0120 NaSO ₃ C ₇ H ₇	0.1000			0.71 ^d	160
0.0100	0.1000			0.79 ^d	140
0.0080	0.1000			0.86 ^d	89
0.0052	0.1000			1.0 ^d	0
0.0040	0.1000			1.04 ^d	-23
0.0020	0.1000			1.12 ^d	-67

^a Bound ratio = $[Br^-]_{bound}/[X^-]_{bound}$. ^b Bulk ratio = $[Br^-]_{free}/[X^-]_{free}$. ^c f = bound ratio/bulk ratio. ^d Assumed $[SO_3C_7H_7^-]_{bound}/[SO_3C_7H_7^-]_{free} = 3$; $f = [Br^-]_{bound}/3[Br^-]_{free}$.

arbitrarily set at zero, a positive ΔG in our convention means that the other ion is preferentially bound. On this basis, NO₃⁻ is bound in preference to Br⁻. Tosylate is also bound in preference to Br⁻, but the ΔG values are much smaller than expected when the thermodynamics of binding to CTAB micelles for these two ions are considered (*vide infra*). The reason for the small ΔG value for tosylate may be our assumption that 75% of the added tosylate ions are bound in each case. As Table VII indicates, the differences in specific adsorption potentials for pairs of ions are certainly not

large. This does not necessarily mean that the actual values for these potentials cannot be large, however.

Using observed ΔH_{trans} values, the counterion binding results, and the heat of displacement for Br⁻ from cationic micellar surfaces (2 kcal/mol^{6, 14b}), true heats of binding to CTAB micelles in 0.1 M CTAB for NO₃⁻ and SO₃C₇H₇⁻ could be calculated. The calculation procedure is shown in Table VIII; it is based on the amount of solution used in the calorimetric runs.

Table VIII. Calculation of the Enthalpies of Binding of Nitrate and Tosylate to Micelles in 0.1 M CTAB Solutions

Quantity	Numerical value	
	for NaNO ₃	For NaSO ₃ C ₇ H ₇
[NaX] under calorimetric conditions	0.03148	0.0120
$\Delta \bar{H}_s(0.1 M CTAB)$, kcal/mol, for NaX	3.93 ± 0.20	0.663 ± 0.265
Moles of NaX added under calorimetric conditions ^a	0.00631	0.0024
Observed heat, in cal, for solution of NaX in 200 ml of 0.1 M CTAB ^b	24.8	1.59
Moles of X ⁻ bound in 200 ml of 0.1 M CTAB ^c	0.00442	0.0018
$\Delta \bar{H}_s(H_2O)$, kcal/mol, for NaX	4.900 ± 0.050	2.54 ± 0.21
Observed heat, in cal, for solution of NaX in H ₂ O ^d	30.9	6.10
Moles of Br ⁻ displaced in 200 ml of 0.1 M CTAB solution ^e	0.0040	0.0021
Estimated heat, in cal, of displacement ^f	8.1	4.2
Calculated heat, in cal, of binding of X ⁻ to the micelles in 200 ml of 0.1 M CTAB solution ^g	-14.2	-8.7
ΔH of binding, kcal/mol, for NaX ^h	-3.22	-4.83

^a [NaX], M \times 0.2, since the calorimeter operates with 200 ml of solution. In all cases the value of [NaX] corresponds to a concentration at which counterion binding studies have been carried out. ^b $\Delta \bar{H}_s(0.1 M CTAB)$ for NaX, x moles of NaX added. ^c Determined by multiplying percentage of counterions bound (as determined by binding studies) by moles of NaX bound under calorimetric conditions. Percentages are NO₃⁻ 70% and SO₃C₇H₇⁻ 75%. The tosylate value comes from C. A. Bunton, E. J. Fendler, L. Sepulveda, and K.-U. Yang; *J. Amer. Chem. Soc.*, **90**, 5512 (1968). ^d $\Delta \bar{H}_s(H_2O)$ for NaX, x moles of NaX added. ^e Determined from counterion binding data, NO₃⁻, 0.077-0.0568 M are displaced, for SO₃C₇H₇⁻ 0.0785-0.0680 M. Each of these numbers was then multiplied by 0.2. ^f Calculated using $\Delta H_{displacement} = 2$ kcal/mol, T. Ingram and M. N. Jones, *Trans. Faraday Soc.*, **65**, 297 (1969). ^g Heat of solution of NaX in H₂O + heat of displacement of Br⁻ + heat of binding of X⁻ = observed heat for solution of NaX in 0.1 M CTAB. ^h (Calculated heat of binding for X⁻/1000)/moles of X⁻ bound.

To determine the free energies and entropies of binding to CTAB micelles for NO₃⁻ and SO₃C₇H₇⁻, the observed amounts of bound ions were first corrected to reflect the actual concentrations of the counterions in the micellar phase. The correction involved dividing the observed bound concentrations in each case by the volume fraction of solution taken up by the micelles' Stern layers. It was assumed that all the counterions which are not measurable with the specific ion electrodes are bound in the Stern layer. For spherical CTAB micelles, we calculate the Stern layer to be 49.4% of the total micellar volume; for rods the figure is 36.5% (see Appendix). Since the partial specific

(28) L. Sepulveda, *J. Colloid Interface Sci.*, **46**, 372 (1974).

(29) J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York, N. Y., 1961.

Table IX. Free Energies and Entropies of Binding of Various Ions to CTAB Micelles in 0.1 M CTAB Solutions

Ion	Bound [ion], M	Free [ion], M	[Ion] _{mic} , ^a M	K ^b	ΔG, ^c kcal/mol	ΔH, kcal/mol	ΔS, eu
NO ₃ ⁻	0.0228	0.00868	1.27	146	-2.95	-3.22	-0.91
SO ₃ C ₇ H ₇ ⁻ for rods:	0.009	0.003	0.50	167	-3.03	-4.83	-6.0
NO ₃ ⁻			1.71	197	-3.13	-3.22	-0.30
SO ₃ C ₇ H ₇ ⁻			0.677	226	-3.21	-4.83	-5.4

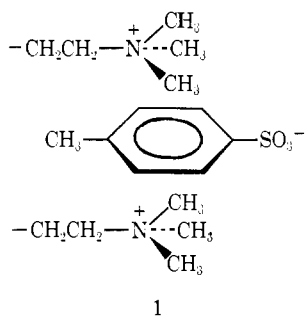
^a [Ion]_{mic}, M = bound [ion], M/volume fraction of the Stern layer in 0.1 M CTAB; for spherical micelles the volume fraction is 0.0180; for rods it is 0.0133. ^b K = [ion]_{mic}/free [ion]. ^c ΔG = -RT ln K.

volume of CTAB in 0.1 M CTAB is approximately 1 ml/g,^{2c} CTAB micelles occupy a volume fraction of 0.0364 in 0.1 M CTAB. The Stern layer volume fractions corresponding to spheres and rods are then 0.0180 and 0.0133, respectively. We realize that the existence of spherical micelles is open to some doubt³⁰ but adopt them as one useful model for calculation purposes.

The results of these calculations are presented in Table IX. Free energies were calculated using equilibrium constants for the counterion binding of the form $K = [\text{ion}]_{\text{mic}}/[\text{ion}]_{\text{free}}$. Activity coefficient effects were neglected; since the concentration of the ions in the micellar phase will be quite high, this introduces an error into the calculations of the free energies of binding. For comparison Rehfeld³⁶ has found ΔG = -3.4 kcal/mol, ΔH = -1.09 kcal/mol, and ΔS = 7.8 eu for the binding of Na⁺ to NaLS micelles, using a hypothetical one molar solution as standard state.

Discussion

The dependence of the observed heats of transfer for anions from H₂O to CTAB and DTAB solutions and for cations from H₂O to NaLS solutions on the hydrated radii of the ions involved supports the contention that favorable binding of counterions depends on how closely they can approach the charged micellar surfaces. Poorly solvated ions show the strongest binding, in general; they are also the most effective protein denaturants.³¹ Only for tosylate ion do significant non-electrostatic effects seem to be important. We agree with Bunton's interpretation of the mode of binding of the tosylate ion, depicted in 1.



The positions of citrate and tosylate in the ΔH_{trans} series are in agreement with the positions that Jencks and Robinson³² found for them in studying their effects on the solubility of the tetrapeptide acetyltetraglycyl ethyl ester. We observed a smaller ΔH_{trans} for NO₃⁻

than for Br⁻ with both CTAB and DTAB; Cohen^{5b} found that NO₃⁻ was less effective than Br⁻ at lowering the cmc of CTAB. However, for the related surfactant tetradecyltrimethylammonium bromide, Wan³³ found a different order of effectiveness of ions in cmc lowering.

The ΔH_{trans} values for cations with NaLS are in agreement with the effects of these cations in decreasing the cmc^{5e,33} and degree of counterion dissociation^{5e,5f} for NaLS. Goddard^{5f} found that cation effects on the decrease in cmc for NaLS correlate very well with the distance of closest approach of the ions to the charged head groups.

It is not possible to explain the observed ΔH_{trans} values for ions of the same charge as the surfactant in terms of binding to the micellar surfaces, unless appreciable opportunity for hydrophobic bonding exists (*i.e.*, (CH₃)₄N⁺ with CTAB and DTAB). The coions may be affecting, *via* their effects on water structure, the amount of the hydrocarbon chains exposed at the micellar surfaces and the organization of the micelles' water of hydration.

Coions are known to affect the cmc of cetylpyridinium bromide (CpBr); these data have been explained using a water structure argument. Tetramethylammonium bromide is known to decrease the cmc of CTAB at concentrations up to 0.09 M; thereafter the cmc increases. This result has been explained³⁴ using water structure also; in this case mixed micelle formation may be occurring.

Changes in water structure caused by ions have been monitored in a number of different ways.^{7a} On the basis of the effect of the ions on the near-ir of HOD the following order represents ability to increase water structure: K⁺ < Na⁺ < Li⁺ < (CH₃)₄N⁺ < Ca²⁺ < Mg²⁺. Looking at Table I, the observed order of ΔH_{trans} for cations with CTAB roughly follows this order, with Na⁺ and NH₄⁺ out of line. The cation results with DTAB do not correspond to the water structure order at all, except in the grossest sense. More disturbing, of course, is the difference in results with CTAB and DTAB, which we are unable to explain.

Solutes which alter water structure also may alter the heat of micellization.³⁵ Since the observed ΔH_{trans} for cations with CTAB and DTAB are most favorable for structure-making ions, it is hard to imagine that the ΔH_{trans} represent enthalpy effects resulting from structural changes in the micellar water of hydration. It would seem that this water would already be highly structured by the micelles themselves.³⁶

(30) (a) C. Tanford, *J. Phys. Chem.*, **76**, 3020 (1972); (b) H. Schott, *J. Pharm. Sci.*, **60**, 1594 (1971); (c) H. Schott, *ibid.*, **62**, 162 (1973).

(31) R. P. Taylor and I. D. Kuntz, *J. Amer. Chem. Soc.*, **94**, 7963 (1972).

(32) (a) D. R. Robinson and W. P. Jencks, *J. Amer. Chem. Soc.*, **87**, 2470 (1965); (b) P. K. Nandi and D. R. Robinson, *ibid.*, **94**, 1299, 1308 (1972).

(33) L. S. C. Wan and P. K. C. Poon, *J. Pharm. Sci.*, **58**, 1562 (1969).

(34) J. Steigman, I. Cohen, and F. Spingola, *J. Colloid Sci.*, **20**, 732 (1965).

(35) (a) L. Espada, M. N. Jones, and G. Pilcher, *J. Chem. Thermodyn.*, **2**, 1 (1970); (b) M. N. Jones, G. Pilcher, and L. Espada, *ibid.*, **2**, 333 (1970).

(36) T. S. Sarma and J. C. Ahluwalia, *Chem. Soc. Rev.*, **2**, 203 (1973).

Anions also affect water structure, but, since ΔH_{trans} values to NaLS were obtained for only four anions, it is not really possible to say whether there are water-structure effects operative for NaLS or not. The observed ΔH_{trans} order $\text{C}_2\text{H}_3\text{O}_2^- < \text{NO}_3^- < \text{SO}_3\text{C}_7\text{H}_7^- < \text{SO}_4^{2-}$ is inconclusive.

From Table IX, and the assumption that ΔH for Br^- binding to CTAB micelles is -2 kcal/mol,^{6,14b} we see that the actual heats of binding for NO_3^- and $\text{SO}_3\text{C}_7\text{H}_7^-$ follow a lyotropic series. The entropies of transfer for binding of nitrate and tosylate may be related to these ions' position in a lyotropic series. Refeld^{5g} has observed a positive entropy of transfer for Na^+ ions binding to NaLS micelles. Although it is frequently considered that there is no loss of solvation when a counterion binds to a micelle,³⁷ loss of solvation might be a possible explanation for the observed entropies. Nitrate ion and tosylate ion, although poorly solvated in aqueous solution and not expected to show an increase in solvation upon binding, may be very tightly bound to the CTAB micellar surfaces. This seems to be reflected in their ΔS values, especially in the case of tosylate ion. The ions will of course lose some translational entropy upon binding. It must also be pointed out that the ΔG 's do not necessarily refer to precisely the same standard state, because the added ions in each case may be binding to micelles containing different amounts of Br^- already on the micellar surface.

Conclusions

It is clear that a lyotropic series similar to that existing for proteins exists for ion binding to micelles. The controlling factor in this binding seems to be the distance of closest approach of the ion to the micelle, although polarizable organic ions may be exceptions. Chain length has little effect on binding. There is a definite effect on the micelle of ions having the same charge as the micelle. Its source is unknown.

It is felt that the work discussed here has established

(37) (a) D. Stigter, *J. Phys. Chem.*, **68**, 3603 (1964); (b) P. Mukerjee, *J. Colloid Sci.*, **19**, 722 (1964).

the usefulness of calorimetric investigation and the use of ion-specific electrodes for characterizing surfactant systems containing more than one species of counterions. For example, using fluorescence quenching^{12b,c} of an organic solute in micelles having Br^- for the counterion as a probe for displacement of Br^- by other counterions says nothing about the binding of the other counterions. While great advances have been made in understanding the mechanism of micelle catalyzed reactions, more knowledge about the state of the micelle, the counterions bound to it and its structure in the presence of organic solutes is necessary for a complete picture of its catalytic behavior.

Appendix

The core radius for a CTAB micelle, assuming that no hydrocarbon is exposed to bulk water, is 20.4 \AA .^{30a} This corresponds to a core volume of $3.56 \times 10^4 \text{ \AA}^3$. For the thickness of the Stern layer we have included the radius of $(\text{CH}_3)_4\text{N}^+$, 3.47 \AA ,²² one-half a $\text{CH}_2\text{-N}$ bond length (estimated at 0.73 \AA) and 1 \AA additional thickness to account for water of hydration and possible roughness of the micellar surface. This gives a total thickness of 5.2 \AA and a total micellar radius of 25.6 \AA which corresponds to $V = 7.03 \times 10^4 \text{ \AA}^3$. The Stern layer volume is thus $3.47 \times 10^4 \text{ \AA}^3$, or 49.4% of the total micellar volume.

Similarly, for a CTAB rod of indefinite length, using $r_{\text{core}} = 20.4 \text{ \AA}$ and $r_{\text{total}} = 25.6 \text{ \AA}$, the Stern layer volume is 36.5% of the total volume.

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Supplementary Material Available. A table listing concentration dependence of heats of solution will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche ($105 \times 148 \text{ mm}$, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5774.