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Hydrophobic and Entropic Factors in the Solubilization of Ionic Substrates in Micelles: Effects of Temperature, Surfactant Chain Length, and Added Surfactants[1]

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Abstract: The binding of the cations *N,N'*-dimethyl-4,4'-bipyridinium(2+) (MV^{2+}) and Cu^{2+} to anionic detergents in micellar solutions has been investigated by luminescence quenching studies employing an extramicellar probe. Effects of temperature, added alcohol, and surfactant chain lengths have been studied to more precisely define the type of binding solubilization that occurs for the two cations. For MV^{2+}, a moderately hydrophobic cation, the binding is entropically favored and the process can be regarded as similar to the micellization reaction itself in which the driving force for solubilization can be largely attributed to elimination of hydrocarbon–water interfaces. For the more hydrophilic Cu^{2+} the binding is enthalpically favored, indicating a more conventional Coulombic attraction to the micelle head groups.

Association equilibria (eq 1) are frequently characterized by negative enthalpies and entropies of reaction, especially when X and Y are of opposite charge but also in several cases when they are uncharged or even of the same charge.[2-7] A notable exception

$$X + Y \overset{K_A}{\rightleftharpoons} X\cdots Y \qquad (1)$$

to this is the micellization of surfactants in aqueous solution where the "hydrophobic effect" results in entropic control with a large positive entropy and (usually) relatively small values of $\Delta H°$.[8] An interesting process which might be expected to have intermediate or variable thermodynamic functions associated with it is the solubilization of various substrates by organized media such as micelles or vesicles. The ability to solubilize a wide variety of diverse reagents is probably the most important property of micelles and other surfactant assemblies.[8-19] An understanding of the range and specific microenvironments provided by different solubilization sites or regions in these assemblies appears prerequisite to understanding the role of various associated lipid or protein–lipid aggregates in biological systems. In recent investigations we have studied the binding of several charged metal complexes, metal ions, and organic cations to surfactant assemblies, especially anionic micelles such as those formed from sodium lauryl sulfate (SLS).[20-22] One of the most important aspects of these studies has been the finding that hydrophobic or hydrophobic–hydrophilic interactions play important roles in the binding of polar organics or organic cations.[20,21] While we have used several methods to investigate these interactions, one of the most useful has been to study luminescence quenching of an extramicellar probe by substrates capable of binding to the assemblies.[20,23] In a recent paper we reported on the use of the anionic ruthenium(II) complex RuL_3^{4-}, where L = 4,4'-dicarboxy-2,2'-bipyridine, as an extramicellar probe to measure the binding of cations such as Cu^{2+}, *N,N'*-dimethyl-4,4'-bipyridinium(2+) (MV^{2+}), *N,N'*-dibenzyl-4,4'-bipyridinium(2+) (BV^{2+}), 4-cyano-*N*-methylpyridinium(1+) (CMP^+), and 4-cyano-*N*-methylpyridinium (CBP^+) to anionic SLS micelles.[20] The attenuation of quenching of these ions by the addition of SLS above the cmc could be used to quantitatively measure the capacity of the surfactant assembly for the various cations; a key result of this study was the finding that the capacity of SLS was much greater for the larger and more hydrophobic ions such as MV^{2+} and CBP^+ than for small hydrophilic ions such as Cu^{2+}. In this paper we report an extension of this study which much more precisely delineates the role of hydrophobic–hydrophilic interactions in micelle solubilization processes. This study focuses on the effects produced by variation of surfactant chain length and temperature as well as by addition of cosurfactants. The results of the study clearly indicates that relatively hydrophobic ions such as MV^{2+} bind by an entropically favored process which presumably involves elimination of water–hydrocarbon interfaces similar to the micellization process itself. In contrast the binding of the small hydrophilic Cu^{2+} (and presumably other metal ions as well) involves a more "conventional" process, enthalpically controlled and presumably governed largely by Coulombic attraction.

Experimental Section

Materials. The synthesis and purification of RuL_3^{4-} has been previously described.[20] Sodium lauryl sulfate (SLS) was obtained from Bio-

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(1) Photochemical Reactivity in Organized Assemblies. 27. Paper 26: Cox, G. S.; Whitten, D. G., submitted for publication.

(2) Das, R. R.; Pasternak, R. F.; Plane, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 3312.

(3) Blumberg, W. E.; Peisach, J. *J. Biol. Chem.* **1965**, *240*, 870.

(4) Fuhrhop, J. H.; Wasser, P.; Riesner, D.; Mauzerall, D. *J. Am. Chem. Soc.* **1972**, *94*, 7996.

(5) Zachariasse, K. A.; Whitten, D. G. *Chem. Phys. Lett.* **1973**, *22*, 527.

(6) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 839.

(7) Forster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969.

(8) Tanford, C. "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", 2nd ed.; Wiley: New York, 1980.

(9) For recent reviews, see: Mittal, K. L., Ed. "Micellization, Solubilization and Microemulsions"; Plenum Press: New York, 1977; Vols. I and II and ref 10–19.

(10) Mittal, K. L., Ed. "Solution Chemistry of Surfactants"; Plenum Press: New York, 1979.

(11) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.

(12) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.

(13) Mukerjee, P. "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; pp 153–174.

(14) Bansal, K. M.; Patterson, L. K.; Fendler, E. J.; Fendler, J. H. *Int. J. Radiat. Phys. Chem.* **1971**, *3*, 321.

(15) Mukerjee, P.; Cardinal, J. R.; Desai, N. R. "Micellization, Solubilization and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; p 241.

(16) Smith, M. B.; Alexander, A. E. *Proc. Int. Congr. Surf. Act., 2nd* **1957**, *1*, 311.

(17) Eriksson, J. C.; Gillberg, G. *Acta Chem. Scand.* **1966**, *20*, 2019.

(18) McBain, M. E. L.; Hutchinson, E. "Solubilization and Related Phenomena"; Academic Press: New York, 1955.

(19) Elworthy, P. H.; Florence, A. T.; McFarlane, C. B. "Solubilization by Surface Active Agents and Its Application in Chemistry and the Biological Sciences"; Chapman and Hall: London, 1968.

(20) Foreman, T. K.; Sobol, W. M.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 5333.

(21) Schmehl, R. H.; Whitesell, L. G.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 3761.

(22) Schmehl, R. H.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1938.

(23) Russell, J. C.; Whitten, D. G.; Braun, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 3219.

0002-7863/82/1504-4215$01.25/0

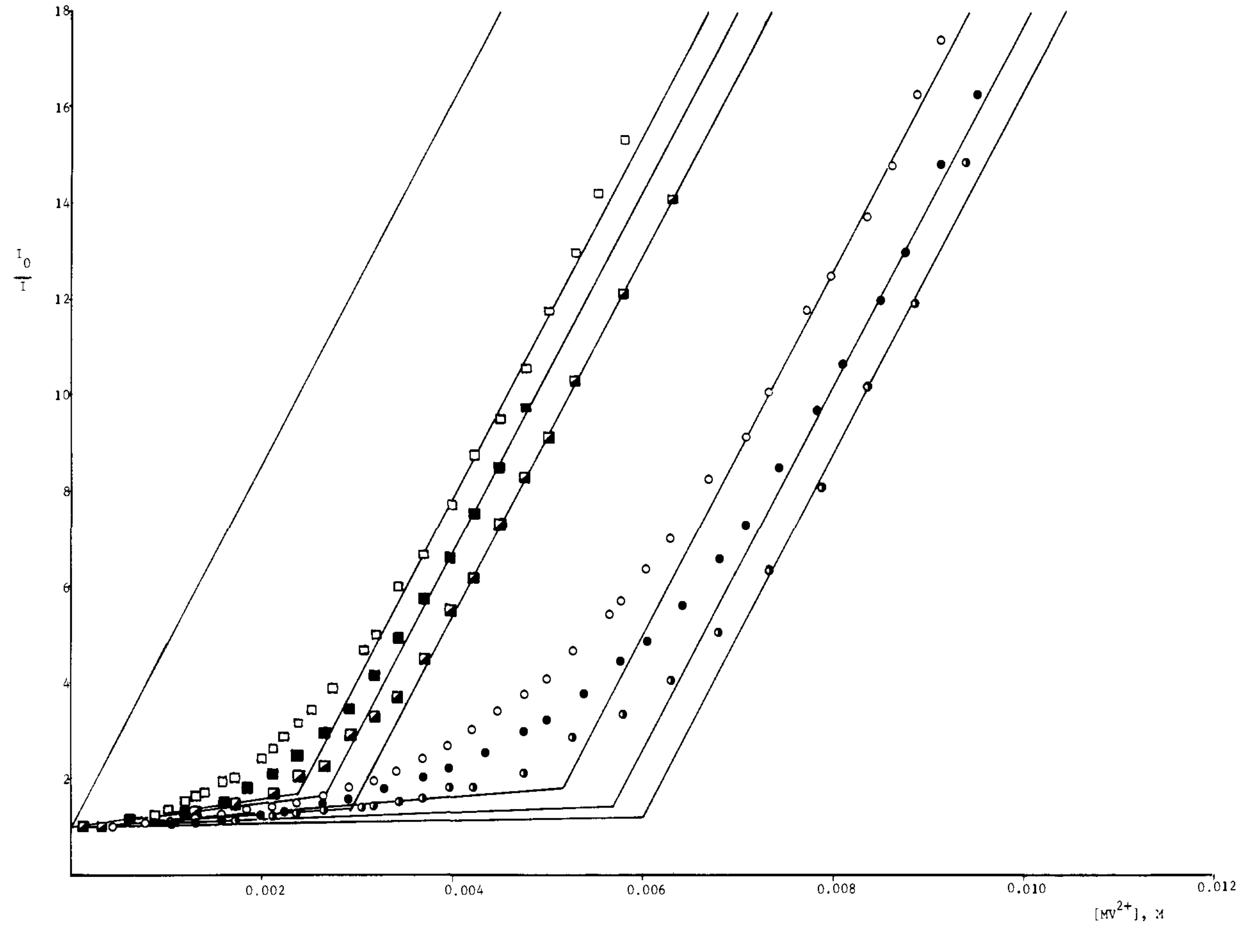

Figure 1. Luminescence quenching of RuL_3^{4-} by MV^{2+} as a function of added detergent at T = 45 °C: □, SLS (0.01 M); ■, STS (0.01 M); ◪, SCS (0.01 M); ○, SLS (0.02 M). ◑, SCS (0.02 M); ●, STS (0.02 M).

Rad Laboratories and used after purification as described below. The sodium alkyl sulfates—sodium hexadecyl sulfate (SCS), sodium tetradecyl sulfate (STS), and sodium decyl sulfate (SDeS)—were prepared by treating the corresponding alcohols with chlorosulfuric acid. This reaction was carried out in ethereal solution at 20 °C as described by Kurz.[24] The *n*-alkylsulfuric acids were neutralized by addition of aqueous sodium hydroxide until a paste was obtained at pH 7; the paste was washed, dried, and recrystallized three times from 2-propanol. The products were further purified by Soxhlet extraction with refluxing hexane for 12 h. Finally each surfactant was recrystallized from ethanol and dried in vacuo over P_2O_5. Methyl viologen hydrate (Aldrich) was recrystallized twice from ethanol.

Spectroscopic Measurements and Techniques. A concentrated (ca. 3 × 10^{-4} M) stock solution of RuL_3^{4-} was prepared by dissolving a weighed sample of the complex in a solution of 0.05 M NaCl made from triply distilled water. The solutions for luminescence measurements were prepared by adding 0.5 mL of the above stock solution to a 5-mL volumetric flask containing freshly prepared solutions of the surfactant in triply distilled water containing 0.05 M NaCl; the mixture was then diluted with 0.05 M NaCl. Aliquots (3 mL) of these solutions were added to quartz fluorescence cuvettes thermostated at 25, 35, or 45 °C. Emission spectra were obtained on a Perkin-Elmer MPF-2A spectrophotofluorimeter with activation at 465 nm; for quenching studies successive aliquots of a concentrated stock solution of MV^{2+} (0.4 M) or $CuCl_2$ (0.3 M) were added to the sample cell via a calibrated Hamilton microliter syringe. The emission was measured after each addition was made and the solution mixed. The intensity values (I) were corrected for the dilution in the plots discussed below. Emission lifetimes were obtained by using a Molectron pulsed nitrogen dye laser as the excitation source.

Table I. Quenching Data for RuL_3^{4-}* by MV^{2+} in Aqueous and Detergent Solutions

[det]^a	T, °C	slopes A	slopes B	$C_D^{tot}/[MV^{2+}]$
0	25		2840	
0.03 M SDeS	25	242	2280	6.25
0.04 M SDeS	25	119	2200	5.40
0.03 M SLS	25	43.8	2300	3.80
0.04 M SLS	25	39	2570	3.67
0.02 M SLS^b	25	135	2270	3.51
0.03 M SLS^b	25	100	2140	3.82
0.04 M SLS	25	77	2140	3.64
0	45		3783	
0.01 M SLS	45	257	3783	4.25
0.02 M SLS	45	126	3700	3.88
0.01 M STS	45	253	3760	3.77
0.02 M STS	45	90	3613	3.52
0.01 M SCS	45	117	3771	3.41
0.02 M SCS	45	53	3790	3.33

^{a} 0.05 M NaCl added in each case. ^{b} Heptanol (0.02 M) added.

Results

Studies with Methyl Viologen. As previously reported,[20] addition of SLS above the cmc to aqueous solutions of RuL_3^{4-} containing the quenchers MV^{2+} or Cu^{2+} suppresses the luminescence quenching due to binding of the quencher cation to the SLS micelles. The behavior observed is fairly general, and characteristic plots are shown in Figure 1. Since several previous results suggested that MV^{2+} and other organic cations bind via hydrophobic interactions,[21-23] it appeared of interest to investigate quantitatively the efforts of surfactant chain length and temperature to precisely delineate these effects. Thus the effect of

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[24] Kurtz, J. L. *J. Phys. Chem.* **1962**, *66*, 2239.
[25] Mysels, K. J.; Kapauan, P. *J. Colloid Sci.* **1961**, *16*, 481.
[26] Flockhart, B. D. *J. Colloid Sci.* **1961**, *16*, 484.
[27] Schott, H. *J. Phys. Chem.* **1966**, *70*, 2966.
[28] Robinson, B. H.; White, N. C.; Mateo, C. *Adv. Mol. Relaxation Processes* **1975**, *7*, 321.
[29] Lessner, E.; Teubner, M.; Kahlweit, M. *J. Phys. Chem.* **1981**, *85*, 1529.
[30] Shick, M. J. *J. Phys. Chem.* **1964**, *68*, 3585.

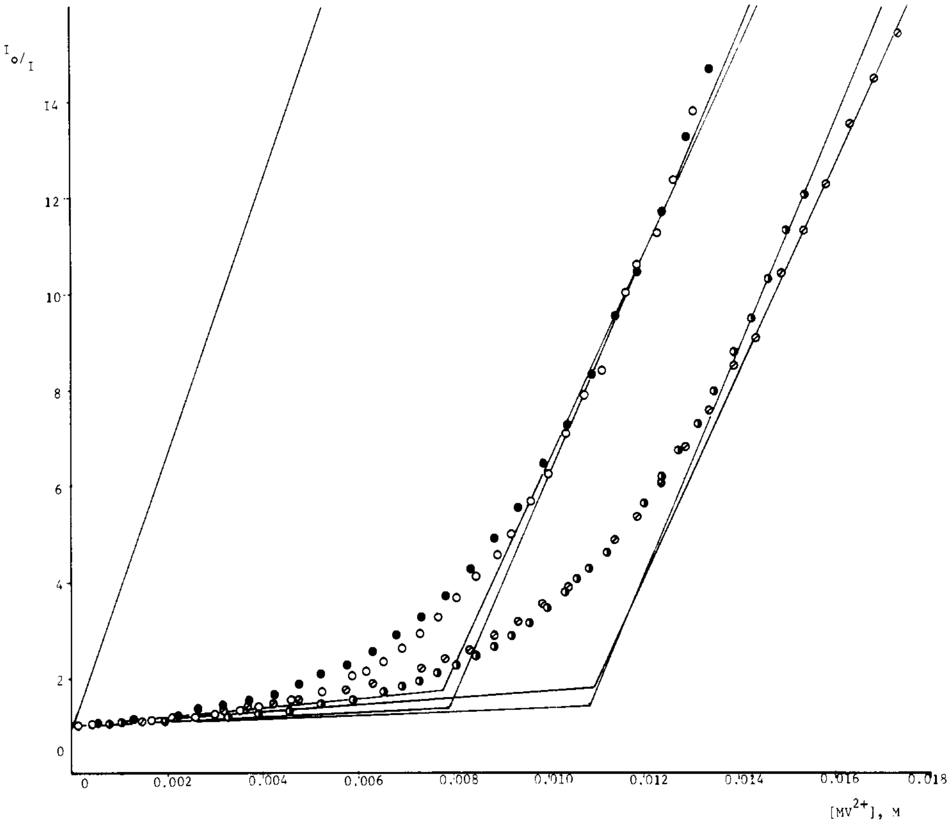

Figure 2. Luminescence quenching of RuL_3^{4-} by MV^{2+} as a function of added detergent with and without added 1-heptanol at $T = 25$ °C: ○, SLS (0.03 M), NaCl (0.05 M), and heptanol (0.02 M); ●, SLS (0.03 M), NaCl (0.05 M), and heptanol (0.02 M); ◑, SLS (0.04 M) and NaCl (0.05 M); ⊖, SLS (0.04 M), NaCl (0.05 M), and heptanol (0.02 M).

surfactant addition on the quenching of RuL_3^{4-} by MV^{2+} was investigated for the series $CH_3(CH_2)_{n-1}SO_4Na$ for n = 10, 12, 14, and 16. For all of these surfactants behavior similar to that for SLS was observed. Due to limitations on the solubility of SCS in water at 25 °C, it is not easy to compare all four surfactants at a single temperature; however as is clearly shown in Figure 1, increasing the surfactant chain length shifts the plots of I_0/I vs. MV^{2+} in such a way as to indicate an increase in the capacity of the surfactant to bind the viologen as the chain length is increased. Data listed in Table I include the slope for these plots at low (MV^{2+}) (slope A), the limiting slope obtained at higher (MV^{2+}) (slope B), and the value $C_D^{tot}/(MV^{2+})$ where C_D is the total concentration of surfactant at point where the two lines intercept for the different surfactants at several temperatures.

Several aspects of these experiments are interesting. The increasing slopes for the detergent-free solutions probably reflect a composite of a small decrease in the excited-state lifetime of RuL_3^{4-*} with a moderate increase in the near diffusion-controlled rate of quenching. The Stokes–Einstein relationship predicts k_{diff} should vary with T/η which over the temperatures 25, 35, 45 °C increases with relative values of 1, 1.28, and 1.59, respectively; the actual increases (Table I) are slightly lower but nonetheless substantial. We have previously used the limiting value (CD/MV^{2+}) where the two "linear" plots intersect to estimate the capacity of the micelle for binding the quencher. In our earlier studies at lower temperatures the two plots showed very little deviation from linearity except for the region near the intersection point. In the present study we find that at elevated temperatures the departure from linearity is more pronounced, indicating less of a sharp break in the micelle–viologen binding.

It is probably reasonable to assume that only assembly-bound surfactant has a high binding affinity for the quencher cation MV^{2+}. Thus a relationship (eq 2) should exist with $C_D/[Q]$ being

$$C_D^{mic}/[Q] = \frac{C_D^{tot} - cmc}{[Q]} \tag{2}$$

constant for any surfactant at a given temperture provided either that the aggregation number of other micelle characteristics do not vary appreciably with change in C_D. It is possible either to use eq 2 with previously determined cmc values or to estimate cmc values from the measured intersection points. As Table II indicates, the measured data yield cmc values in reasonable agreement with those obtained from the literature. For the cases where no cmc values are available, those estimated by using the intersection points obtained at different C_D's are reasonable and the values of $C_D^{mic}/(Q)$ are mostly constant (at constant temperature) within experimental error over the range of surfactant concentrations employed.

In several recent studies we and others have investigated reactions occurring in "swollen micelles" which generally consist of mixtures of detergents such as SLS with alcohols such as

Table II. Calculated and Literature Values for the cmc's of Sulfate Detergents at Different Temperatures

[det][a]	cmc(lit.)	cmc(calcd)	$C_D^{mic}/[Q]$	T, °C
0.03 M SDeS	0.0150[d]	0.011 54	3.846	25
0.04 M SDeS	0.0150	0.011 54	3.846	25
0.03 M SLS[b]	0.00816[e]	0.008 07	3.41	25
0.04 M SLS[b]	0.00816[e]	0.008 07	3.41	25
0.02 M SLS[c]		0.005 08	3.62	25
0.03 M SLS[c]		0.005 08	3.18	25
0.04 M SLS[c]		0.005 08	3.18	25
0.03 M SLS	0.0032[f]	0.003 67	3.33	25
0.04 M SLS	0.0032	0.003 67	3.33	25
0.01 M SLS	0.0015[g]	0.001 60	3.57	45
0.02 M SLS	0.0015	0.001 60	3.57	45
0.01 M STS	0.0011[h]	0.001 22	3.31	45
0.02 M STS	0.0011	0.001 22	3.31	45
0.01 M SCS	0.0006[i]	0.000 49	3.250	45
0.02 M SCS	0.0006	0.000 49	3.250	45

[a] 0.05 M NaCl except as otherwise stated. [b] No added NaCl. [c] 0.05 M NaCl plus 0.02 M 1-heptanol. [d] Reference 25. [e] Reference 26. [f] Reference 27. [g] Reference 28. [h] Reference 29. [i] Reference 30.

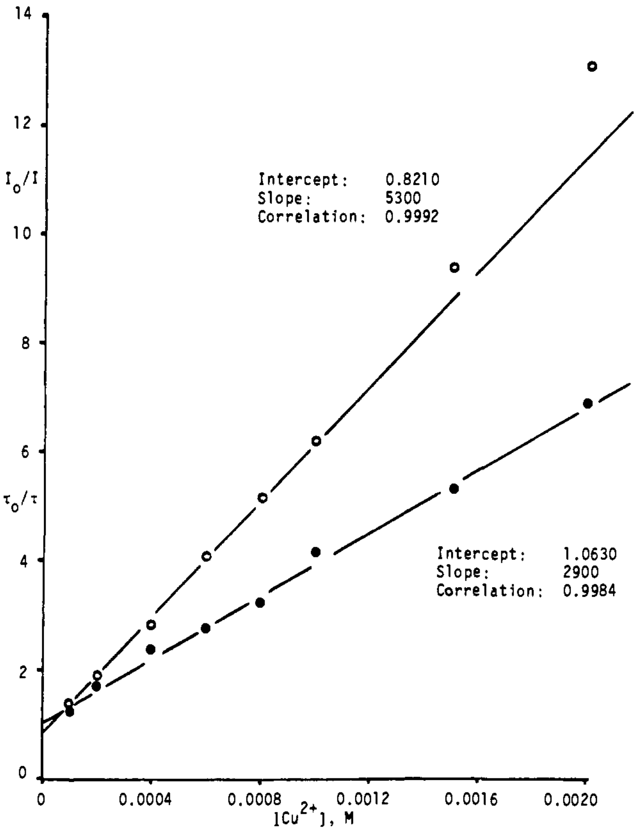

Figure 3. Luminescence intensity and lifetime quenching of RuL_3^{4-} by Cu^{2+} in 0.05 M NaCl aqueous solution: ○, I_0/I; ●, τ_0/τ. pH was greater than 6.0.

1-pentanol, 1-hexanol, or 1-heptanol.[31-34] Figure 2 compares the quenching of RuL_3^{4-} luminescence by MV^{2+} in the presence of SLS with that obtained in 1-heptanol–SLS mixtures. The plots are in fact very similar for the two systems, suggesting that addition of water-insoluble 1-heptanol does little to either enhance or suppress binding of MV^{2+} to the micelle. However since the heptanol increases the total volume of the surfactant assemblies, the net result is actually a small decrease in the partitioning of the viologen between the assembly and aqueous phase.

Studies with Cu^{2+}. While MV^{2+} shows a relatively low tendency to associate with RuL_3^{4-} in the ground state (all the quenching is essentially dynamic with 0.05 M NaCl added), the quenching of RuL_3^{4-} luminescence by Cu^{2+} clearly consists of static and dynamic components. Thus a study of lifetime vs. intensity quenching in detergent-free solution shows marked differences (Figure 3) which can be ascribed to eq 3 and 4, where K_{sv} is the

$$I_0/I = 1 + (K_{sv}\tau + \beta K_A)[Q] + K_{sv}\tau\beta K_A[Q]^2 \qquad (3)$$

$$\tau_0/\tau = 1 + K_{sv}\tau[Q] \qquad (4)$$

"lifetime" Stern–Volmer quenching constant, K_A is the ground-state association constant between Cu^{2+} and RuL_3^{4-} and β is the ratio of extinction coefficients between free RuL_3^{4-} and the RuL_3^{4+}–Cu^{2+} association complex. Since both plots of I_0/I and τ_0/τ vs. $|Cu^{2+}|$ are linear in the range 0–0.002 M, it can be assumed that the terms in $[Q]^2$ are negligible and values of K_{sv} = 2900 M^{-1} and K_A = 2400 M^{-1} are obtained at 25 °C. The former is nearly the same as that obtained for MV^{2+} and probably very close to the diffusion-controlled limit for this system.

Table III. Quenching of RuL_3^{4-} by Cu^{2+} in the Presence of Detergents

[det]	T, °C	slopes A	slopes B	C_D^{tot}/Cu^{2+} at intercept
0.01 M SLS	25	1183	4875	5.18
0.01 M SLS	35	1200	5326	5.60
0.01 M SLS	45	1459	5888	6.15
0.02 M SLS	45	900	5888	5.63
0.01 M STS	35	977	5722	4.54
0.01 M STS	45	1092	5662	5.17
0.02 M STS	45	771	5315	5.47

Table IV. Calculated and Literature Values for cmc's from Experiments with Cu^{2+}

[det]	T, °C	cmc(lit.)	cmc(calcd)	$C_D^{mic}/[Q]$
0.01 M SLS	35	0.002 00	0.002 47[a]	4.48
0.01 M SLS	45	0.001 56	0.001 4[b]	5.19
0.02 M SLS	45	0.001 56	0.001 4[b]	5.19
0.01 M STS	35	0.001 0	0.000 97[a]	
0.01 M STS	45	0.001 0	0.001 09[a]	5.26
0.02 M STS	45	0.000 8	0.001 09[a]	5.26

[a] Reference 29. [b] Reference 28.

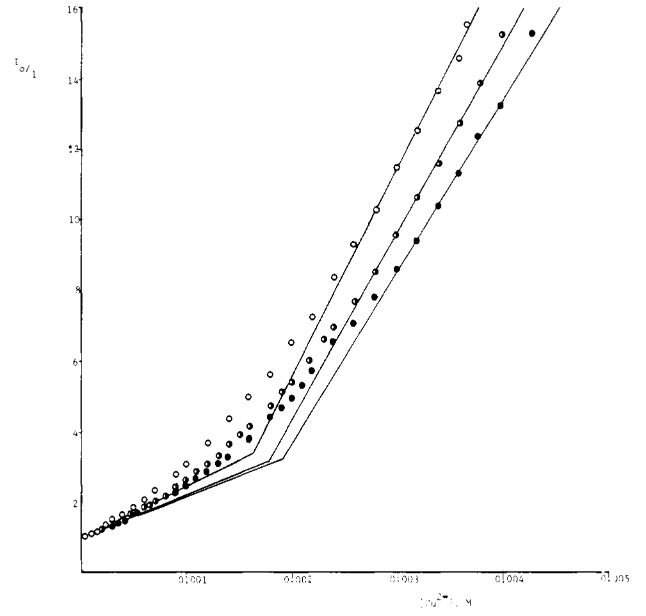

Figure 4. Luminescence intensity quenching of RuL_3^{4-} by Cu^{2+} in SLS at various temperatures: ○, 25 °C; ◑, 35 °C; ●, 45 °C.

Lifetime quenching studies with Cu^{2+} were not carried out over a temperature range; however the intensity quenching values obtained (Table III) show a small increase with temperature. The smaller increase observed with Cu^{2+} compared to MV^{2+} undoubtably reflects the partially offsetting increase in k_{diff} and decrease in K_A. Addition of the various detergents to solutions containing RuL_3^{4-} and Cu^{2+} results in a suppression of the luminescence quenching similar to that observed with MV^{2+} but smaller in magnitude. Values for the two slopes and the intersection points are listed in Table III for the various surfactants at different temperatures. Figure 4 shows intensity quenching plots in the presence and absence of detergent. The effect of surfactant chain length on Cu^{2+} binding was not as extensively investigated as for MV^{2+}. However, the data in Table IV suggest that the capacity, as indicated in $C_D^{mic}/[Q]$, changes very little on changing from SLS to STS.

Discussion

The main objective of this study has been to further investigate the factors governing the binding (or partitioning) and capacity

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(31) Russell, J. C.; Whitten, D. G. *J. Am. Chem. Soc.*, in press.

(32) Thomas, J. K. *ACS Symp. Ser.*, in press.

(33) Jain, A. K.; Singh, R. P. B. *J. Colloid Interface Sci.* **1981**, *81*, 536.

(34) Almgren, M.; Löfroth, J. E. *J. Colloid Interface Sci.* **1981**, *81*, 486.

(35) The possibility that some of the quenching observed could be due to collision of micelle-associated quencher with RuL_3^{4-*} appears remote since an estimate of the maximum K_{sv} obtainable at "normal" aggregation numbers is ca. 0.3, a value much lower than observed. Furthermore the fact that the slope A values decrease upon increase in surfactant concentration indicates that there is little or no contribution from this.

Table V. Equilibrium Constants and Thermodynamic Parameters for Binding of Cations to Anionic Micelles

	T, °C	$\Delta G°$, cal/mol	$\Delta H°$, cal/mol	$\Delta S°$, eu	K
			MV^{2+}		
SDes					
0.04 M	25	−4500 ± 41	+4870 ± 22	+32 ± 4	2000 ± 100
0.05 M	25	−4560 ± 42	+4870 ± 21		2210 ± 110
0.04 M	35	−4840 ± 8	+4870 ± 22		2710 ± 35
0.05 M	35	−4850 ± 8	+4870 ± 22		2780 ± 36
SLS					
0.02 M	25	−4990 ± 46	+3610 ± 35	+28.9 ± 1	4590 ± 390
0.03 M	25	−4920 ± 45	+3690 ± 36		4040 ± 315
0.04 M	25	−4880 ± 45	+4300 ± 36		3820 ± 300
0.01 M	35	−5160 ± 33	+3730 ± 36		4600 ± 245
0.02 M	35	−5237 ± 33	+3660 ± 35		5207 ± 280
0.04 M	35	−5223 ± 33	+3674 ± 35		5090 ± 280
0.01 M	45	−5520 ± 11	+3660 ± 35		6230 ± 109
0.02 M	45	−5500 ± 11	+3690 ± 36		6010 ± 106
STS					
0.01 M	35	−5490 ± 88	−820 ± 100	+15.2 ± 0.7	7890 ± 1075
0.02 M	35	−5391 ± 86	−722 ± 87		6700 ± 910
0.04 M	35	−5290 ± 85	−620 ± 75		5640 ± 770
0.01 M	45	−5440 ± 10	−630 ± 80		5610 ± 830
0.02 M	45	−5640 ± 10	−821 ± 100		7550 ± 1100
			Cu^{2+}		
SLS					
0.01 M	25	−4500	−5560 ± 56		1980
0.01 M	35	−4530	−5630 ± 57	−3.6 ± 0.4	1640
0.01 M	45	−4570	−5590 ± 58		1380
STS					
0.01 M	35	−4610	−6770 ± 69	−7.0	1870
0.01 M	45	−4680	−6910 ± 70		1650

for different ionic solubilizates in simple micelles. Cu^{2+} and MV^{2+} may be regarded as prototype hydrophilic and moderately hydrophobic ions, respectively. The binding of these ions to anionic micelles may be most conveniently assessed by evaluating the thermodynamics associated with the partitioning of the ions between aqueous and micellar phases (eq 5). Thus, if we assume

$$Q_{H_2O} \overset{K_A'}{\rightleftharpoons} Q_{mic} \tag{5}$$

$$K_A' = [Q_{mic}]/[Q_{H_2O}] \tag{6}$$

that all of the quenching observed in the presence of surfactant at low quencher concentration (slope A) is due to quencher present in the aqueous phase, the ratio of slope A to the K_{sv} obtained in the absence of surfactant gives the fraction of quencher in the aqueous phase. From this assumption and the use of densities, molecular weights, concentration, etc., it is quite easy to evaluate K_A', $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the binding of Cu^{2+} and MV^{2+} to SLS and other detergents. Table V compares the values thus obtained;[36] the striking feature here is once again the different trends observed for MV^{2+} and Cu^{2+}. For Cu^{2+} it is clear that the negative entropies and enthalpies indicate a "classical" type of association equilibrium, probably governed largely of Coulombic attraction. For MV^{2+} the controlling *positive* entropies and relatively small enthalpies indicate a fundamentally different type of association. While it is certainly clear that Coulombic factors play a role in the binding of MV^{2+} to the anionic detergents (i.e., MV^{2+} clearly does not associate with cationic assemblies such as CTAB micelles),[22] the relatively large positive entropies and small enthalpies are fairly similar to those associated with micellization itself.[8] In the latter process, the positive entropy is usually associated with the elimination of hydrocarbon–water interfaces and thus the freeing of water molecules from a highly structured environment.[8] A similar interpretation of the thermodynamics of binding of MV^{2+} to the anionic assemblies certainly seems reasonable and is in accord with our previous suggestions that polar organics and moderately hydrophobic ions bind by hydrophilic–hydrophobic interactions in which the driving force for solubilization is elimination of hydrocarbon–water interfaces.[20,23]

A further point underlining the importance of the "hydrophobic effect" in the binding (or solubilization) process for charged or polar but moderately hydrophobic reagents is the large increase in K with surfactant chain length exhibited for MV^{2+} but not for Cu^{2+} (Table V). Thus the equilibrium constant for binding of Cu^{2+} is scarcely affected by chain length while that for viologen steadily increases as the chain length of the alkyl sulfonate increases from 10 to 16 carbons.[37]

It is interesting and perhaps useful to evaluate these results in terms of current ideas on micelle structure and dynamics. Following years of general acceptance of the so-called "oil-drop" model of a micelle in which the aggregate is assumed to have a roughly spherical droplet structure with a clearly demarcated inner liquid hydrocarbon "core" and an outer contact or "Stern" layer containing the charged or polar head groups and associated water and counterions; an increasing array of results from various types of experiments have indicated deficiencies of this model and in turn to the proposal of alternate models.[11,38–40] While there are certainly fundamental differences in the several models recently proposed, a common feature of most models is the presence of a considerably greater hydrocarbon–water interface area than would be predicted in the "classical" model and a fairly consistent view that solubilization of most, if not all, organic solutes occurs in highly polar regions most likely at or near the "micelle–water interface".[40–43]

From our present and previous studies of the binding of hydrophobic ions such as MV^{2+} and 4-cyano-*N*-benzylpyridinium to SLS micelles, it is clear that there is a limiting ratio of ca. one cation per two to three surfactant molecules in the assembly.[20]

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(36) It should be pointed out that the K_A' values listed here are not identical with the K_{ex} values defined in an earlier paper[21] where the exchange between different cations at the micelle–water interface was examined.

(37) Studies with sodium cetyl sulfate show a pronounced increase in K for MV^{2+} compared to STS; however since SCS can only be studied at higher temperatures, it is not possible to make meaningful quantitative comparisons.

(38) Fromherz, P. *Chem. Phys. Lett.* **1981**, *77*, 460.

(39) Fromherz, P. *Ber. Bunsenges Phys. Chem.*, in press.

(40) Dill, K. A.; Flory, P. *J. Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 676.

(41) Mukerjee, P. "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; pp 153–174.

(42) Mukerjee, P.; Cardinal, J. R. *J. Phys. Chem.* **1978**, *82*, 1614–1620.

(43) Mukerjee, P.; Mysels, K. J.; Kapauan, P. *J. Phys. Chem.* **1967**, *71*, 4166.

If we assume the usual aggregation number (60) of SLS is unchanged, this indicates ca. 20–30 ions can bind per micelle. From tabulation of bond distances, an approximate surface area for the ions is estimated as ca. 50 Å^2. This indicates a requirement ranging from 900 to 1550 Å^2 for the binding of these ions to the assembly. Various spherical droplet models for micelle structure recently proposed suggest a sphere radius of 18–21 Å for 12-carbon surfactants;[11,38,41] these values yield surface areas of 4070 and 5600 Å^2, respectively. Using combinations of minimum and maximum values, these areas give a range of 16–38% for the proportion of the surface occupied by the ions if it is assumed they bind with the molecular plane of the cation on the surface of the sphere with no interpenetration. In comparison, the recently proposed surfactant block model[38,39] suggests a more-or-less cubic structure having an edge length of 36 Å; this yields a surface area of ca. 7800 Å^2 of which 12–19% would be covered by the ions if the same assumptions are made. A principal difference between the "larger" sphere model[11] and the surfactant block model is the presumed resistance to penetration of the latter model. Thus while the former model should allow some penetration of molecules such as MV^{2+} into gaps, the surfactant block model would suggest the ions should indeed be in one or more of the various sites indicated at the assembly–water interface.

From the above calculations it would seem that the observed results could be accommodated reasonably well by most of the models recently proposed but not by the more classical "two-state" model. The major conclusion from the present results is that the micelle must present a variety of binding sites where ready exchange of ions can occur. Some of these sites are clearly highly hydrophilic such that binding of ions can be largely governed by enthalpy while others are moderately hydrophobic such that entropic effects are predominant.

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Registry No. MV^{2+}, 4685-14-7; Cu, 7440-50-8; RuL$_3^{4-}$, 78338-26-8.

Synthesis with Tin Templates. A New Family of Diastereomeric Macrocycles

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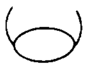
Abstract: The synthesis and properties of a new family of diastereomeric macrocyclic compounds are described which span two different types of internal cavities. The compounds are characterized by a polylactone ring and functionalized side chains arranged in either a "syn" or an "anti" configuration. The method of synthesis involves the use of cyclic tin–oxygen compounds as covalent templates and provides either of the diastereomers with high regio- and stereospecificity. Extensive spectroscopic data are given (NMR and X-ray analyses) and evidence for the different binding properties of the diastereomers for europium ions. The relationships of these compounds with naturally occurring ionophores is discussed and their possible application for the design of ion carriers or catalysts indicated.

In recent years considerable effort has been made to design synthetic complexing agents for metal ions and charged molecules.[1-4] Major emphasis has been given to systems which span a well-defined environment around the guest ion such as macrocyclic polyethers,[2] cryptands,[3] and spherands.[4] While the crown ethers delineate a two-dimensional environment, the cryptands and spherands span a three-dimensional one, providing systems with high binding efficiency and selectivity. Additional compounds capable of forming three-dimensional cavities have recently been introduced with macrocyclic polyaza- and oxo compounds containing ligating side chains.[5-8] The binding properties of the latter family of compounds are intermediate between those of the crown ethers and cryptands. Specificially, macrocyclic compounds with ligating side chains are more efficient binders than nonfunctionalized marocycles.[5-9] On the other hand, they are likely to show more favorable exchange kinetics than cryptands. In addition, macrocycles with ligating side chains offer themselves for the design of two different types of cavities: considering compounds with two side chains, two diastereoisomers are possible: structures where the side chains assume a "syn" configuration (structure A), and structures where the side chains assume an "anti" configuration (structure B). In the "syn" isomer (A) one


A


B

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(1) R. M. Izatt and J. J. Christensen, Eds., "Synthetic Multidentate Macrocyclic Compounds", Academic Press, New York-San Francisco-London, 1978. G. A. Melson, Ed., "Coordination Chemistry of Macrocyclic Compounds", Plenum Press, New York-London, **1979**. F. Voegtle and E. Weber, *Kontakte, 11*, 1 (1977); J. S. Bradshaw, G. E. Mass, R. M. Izatt, and J. J. Christensen, *Chem. Rev.*, **79**, 375 (1979).

(2) C. J. Pedersen, *J. Am. Chem. Soc.*, **87**, 7017 (1967); C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

(3) B. Dietrich, J. M. Lehn, and J. Simon, *Angew. Chem., Int. Ed. Engl.*, **13**, 406 (1974); J. M. Lehn, *Acc. Chem. Res.*, **11**, 49 (1978); J. M. *Lehn, Struct. Bonding (Berlin)*, **16**, 1 (1973).

(4) D. J. Cram, T. Kaneda, R. C. Helgeson, and G. M. Lein, *J. Am. Chem. Soc.*, **101**, 6753 (1979); D. J. Cram., T. Kaneda, G. M. Lein, and R. C. Helgeson, *J. Chem. Soc., Chem. Commun.*, 948 (1979); D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **11**, 8 (1978).

(5) C. K. Chang and T. G. Traylor, *J. Am. Chem. Soc.*, **95**, 5810, 8475, 8477 (1973).

(6) K. Bowman, D. P. Riley and D. H. Busch, *J. Am. Chem. Soc.*, **97**, 5036 (1975).

(7) J. A. Kaden, in "Coordination Chemistry 20", D. Danerjea, Ed., 1980, p 71.

(8) G. W. Gokel, D. M. Dishong, and C. J. Diamond, *J. Chem. Soc. Chem. Commun.*, 1053 (1980).

(9) J. F. Riordan and B. L. Vallee, *Adv. Exp. Med. Biol.*, **48**, 33 (1974).

0002-7863/82/1504-4220$01.25/0