exchange map is often sufficient to obtain an order of magnitude indication of the involved exchange rates. The examples in this paper have been restricted to such a qualitative analysis. However, for a more quantitative determination of the rate constants, several exchange maps for different mixing times τ_m must be recorded. Of particular interest is the build-up of the cross-peak intensities for short mixing times in analogy to the determination of the nuclear Overhauser effect build-up rates.[6,27,28] It directly provides the individual rate constants.

Although 2D experiments are in general time consuming it should be remembered that thanks to the two-dimensional signal-averaging feature inherent in the 2D Fourier transformation a sensitivity not much lower than that in a one-dimensional spectrum recorded in the same total time can be achieved.[52]

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The Importance of Hydrophobic–Hydrophilic Factors in Binding of Charged Substrates to Micelles: The Use of Extramicellar Probe Luminescence to Monitor Association of Cations to the Micelle

Thomas K. Foreman, Warren M. Sobol, and David G. Whitten*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514.
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Abstract: The anionic metal complex **1**, RuL_3^{4-}, where L = 4,4′-dicarboxy-2,2′-bipyridine, has been used as an extramicellar luminescent probe to monitor the binding capacity of anionic sodium dodecylsulfate micelles for the quencher Cu^{2+} and several organic cations. Addition of surfactant attenuates the quenching activity of the cations toward **1** in each case. For Cu^{2+} the binding capacity, as monitored by the quenching of the extramicellar probe, is in good agreement with those determined for Cu^{2+} and other divalent metal ions, using quite different methods; curvature in the quenching plot as $[Cu^{2+}]$ increases is attributed to screening of the micellar charge by bound Cu^{2+}. For MV^{2+} quite different behavior is observed; the Stern–Volmer type quenching plot shows two good linear portions at any surfactant concentration. The portion with low slope at low $[MV^{2+}]$ is attributed to MV^{2+} binding to the organized surfactant; at higher $[MV^{2+}]$ the steeper plot has a slope essentially the same as that obtained in water in the absence of micelles. The absence of curvature suggests association of several MV^{2+} molecules does not inhibit binding of additional quenchers until nearly all the binding sites are occupied. This finding, combined with the relatively high binding capacity in terms of cation/SDS for MV^{2+} compared to metal ions, suggests that MV^{2+} binds at different sites and that other factors control its binding. Similar results have been obtained with other organic cations. The results are most consistent with a model whereby these bind at hydrocarbon–water interfaces and not primarily with the micelle head groups.

The surge of recent interest in chemical reactions occurring in organized assemblies such as micelles and vesicles has led to several investigations and some controversy concerning the nature, site, and extent of binding of various substrates with the assemblies.[2-5] Certainly one of the key features responsible for the numerous current studies of micellar phenomena is the remarkable ability of charged micelles to solubilize and concentrate a wide variety of reagents ranging from oppositely charged metal ions to hydrocarbons. Several investigations have established binding constants for different species; there have also been attempts to determine the limits to which a given substrate can bind or be solubilized. Studies with nonpolar solubilizates such as benzene and some aliphatic hydrocarbons, for example, indicate that in excess of 1 mol of substrate/mol of surfactant can be solubilized, in some cases without producing large effects on such micellar properties as the degree of aggregation or viscosity.[4,6-12] On the other hand, studies with uni- and divalent metal ions suggest many fewer than one ion/surfactant molecule can be accommodated.[13-17]

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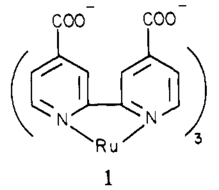
Polar solubilizates, which are generally believed to associate with the head groups of micelles and hence influence phenomena such as the sphere-to-rod transition point, can frequently be solubilized to an extent of greater than 1 mol of solubilizate/mol of surfactant.[6,11]

A considerable portion of recent work with micellar systems and other organized assemblies such as vesicles and liposomes has focused on photoreactions. Many of these studies have involved electron-transfer reactions where the quenching is either retarded or enhanced due to the solubilization of the excited substrate in the micellar pseudophase; in several cases the overall chemistry occurring is also modified compared to homogeneous solution due to enhanced or hindered charge separation following the quenching event.[18-23] In the present paper we report an investigation of the quenching of an excited metal complex, RuL_3^{4-}, (**1**), where L = 4,4′-dicarboxy-2,2′-bipyridine, by the dications Cu^{2+}, *N*,*N*′-dimethyl-4,4′-bipyridinium (MV^{2+}), *N*,*N*′-dibenzyl-4,4′-bipyridinium (BV^{2+}), and two organic monocations in aqueous micellar (SDS) and homogeneous solutions. In this study the anionic substrate is effectively excluded from the micellar pseudophase such that the dominant excited state quenching reactions occur between the substrate and quencher not bound to the micelle. In this case the observed quenching phenomena can be used to assess the binding of the cationic quencher to the anionic micelle; the results, which show quite different behavior for Cu^{2+} and the organic cations, suggest that hydrophobic–hydrophilic interactions may play a major role in the observed preferential binding of the latter cation and provide some new insights into micellar structure and binding properties.



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Experimental Section

Materials. Complex **1** was prepared by first synthesizing and purifying tris(4,4′-dicarbethoxy-2,2′-bipyridine)ruthenium(II)$^{2+}$ by previously described methods.[24] The ester groups were removed by saponification with 0.1 M NaOH; neutralization with HCl and precipitation several times from H_2O with acetone afforded pure **1**. Complete saponification was indicated by infrared spectroscopy; the anionic complex has absorption and emission maxima at 465 and 620 nm, respectively, in water at pH 7. Benzyl viologen dichloride was prepared by stirring stoichiometric amounts of benzyl chloride (Baker) and 4,4′-bipyridine (Aldrich) in acetonitrile for several hours. The resulting solid obtained was recrystallized several times from ethanol. Likewise, 4-cyano-*N*-methylpyridinium perchlorate was prepared with use of methyl iodide (Aldrich) and 4-cyanopyridine (Aldrich). The iodine salt was isolated and reacted with $AgClO_4$ in ethanol to obtain the perchlorate salt. The white pyridinium salt was recrystallized from ethanol several times. 4-Cyano-*N*-benzylpyridinium chloride was obtained in a similar manner with use of benzyl chloride instead of methyl iodide. All compounds gave satisfactory elemental analyses. All other reagents were purified prior to use.[25]

Spectroscopic Measurements. Emission intensities and lifetimes were obtained by exciting aerated solutions at 465 or 457 nm and monitoring the emission near its maximum. Emission intensities were measured on a Perkin-Elmer MPF-2A spectrophotofluorimeter; emission lifetimes were obtained by using a Molectron pulsed nitrogen dye laser as the excitation source.

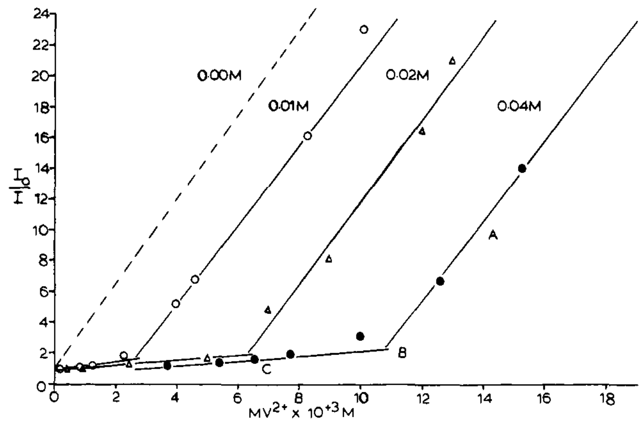

Figure 1. Stern–Volmer plots for quenching of the luminescence of **1** by methyl viologen at various surfactant concentrations. Concentrations of SDS (M) are indicated on the figure. The ordinate is I^0/I for all except the 0 M SDS where it is τ^0/τ. The abscissa is the molar concentration of methyl viologen × 10^3.

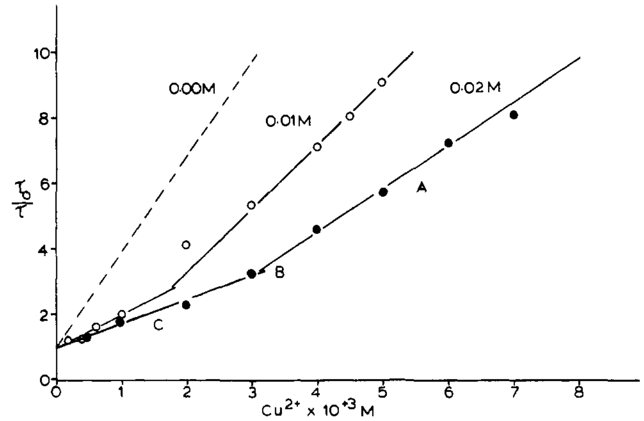

Figure 2. Stern–Volmer plots for quenching of the luminescence of **1** by Cu^{2+} at various surfactant concentrations. Concentrations of SDS (M) are indicated on the figure. The ordinate is τ^0/τ and the abscissa is the molar concentration of Cu^{2+} × 10^3.

Table I. Quenching Data for 1 with Cu^{2+} and MV^{2+} in Aqueous and Micellar Solution

quencher	[SDS],[a] M	K_{SV} (A) (correlation)	K_{SV} (C)	$[SDS]_m/[Q]$[d] (B)
MV^{2+}	none	2840[c] (1.000)		
MV^{2+}	0.01	2580[b] (1.000)	209	3.4
MV^{2+}	0.02	2660[b] (0.987)	140	3.0
MV^{2+}	0.04	2570[b] (0.999)	149	3.6
BV^{2+}	none	3890[b] (0.999)		
BV^{2+}	0.02			<3.0
Cu^{2+}	none	2900[c] (0.998)		
Cu^{2+}	0.01	1950[c] (0.998)	1150	5.5
Cu^{2+}	0.02	1330[c] (0.998)	735	6.3
CBP^+	none	2210[b] (1.000)		
CBP^+	0.01	2180[b] (1.000)	284	2.0
CBP^+	0.02	2030[b] (0.996)	160	2.0
CMP^+	none	2770[b] (0.999)		

[a] 0.05 M NaCl added, in triply distilled water. [b] Obtained from luminescence intensity quenching plot. [c] Obtained from lifetime quenching plot. [d] $[SDS]_m$ calculated by subtracting cmc from total [SDS]. A, B, and C are the defined regions shown in Figures 1 and 2.

Results and Discussion

Quenching of the luminescence of **1** by MV^{2+} in homogeneous solution gives coincident lifetime and intensity Stern–Volmer plots

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(25) SDS (Biorad, electrophoresis grade) was purified by several recrystallizations from ethanol. Water was triply distilled in all cases.

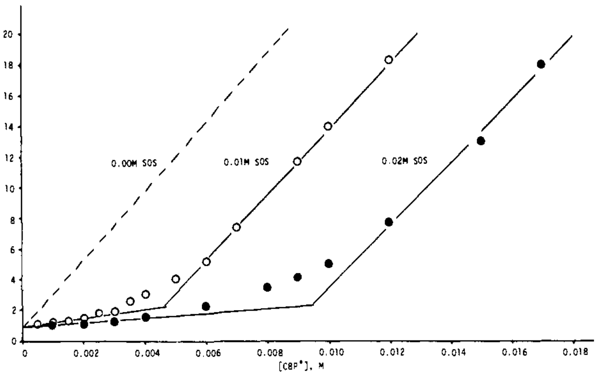

Figure 3. Stern–Volmer plots for quenching of the luminescence of **1** by 4-cyano-*N*-benzylpyridinium at various surfactant concentrations. Concentrations of SDS (M) are indicated on the figure. The ordinate is I^0/I and the abscissa is the molar concentration of CBP^+.

(Figure 1) with added NaCl above 0.1 M; at lower NaCl concentrations the intensity plots are slightly curved, indicating a small amount of association between **1** and the quencher. The value for the quenching constant, $k_q = 5.6 \times 10^9$ M^{-1} s^{-1}, from the linear plots is fairly close to that obtained for $Ru(bpy)_3^{2+}$ with the same quencher;[26] this suggests that the net effect of the ligand COO^- groups on the excited state redox potential is relatively small.[27] For Cu^{2+} as a quencher in homogeneous solution, a lifetime Stern–Volmer plot shows good linearity (Figure 2) and gives a quenching constant of $k_q = 5.8 \times 10^9$ M^{-1} s^{-1}. Addition of SDS to aqueous solutions above the cmc attenuates the quenching of both cations (Figures 1 and 2) as would be anticipated due to binding of the cations to the anionic micelles. The behavior for the **1**-MV^{2+} system is especially striking and clear-cut: addition of the surfactant results in I^0/I vs. $[MV^{2+}]$ plots having two distinct linear portions with a sharp break (Figure 1). The "early" portion has a much lower slope (Table I) than the later portion; the later portion has a slope essentially identical with that obtained in homogeneous solution. The point at which the two linear portions intersect is at a remarkably low surfactant/quencher ratio which is roughly constant with varying surfactant concentration. The behavior of the **1**-Cu^{2+} system is different; the separation into two linear regions is less clearly demarcated (Figure 2) and the point at which two "linear" plots would intersect occurs at much higher surfactant/quencher ratios (Table I).[29]

Three other organic cations have also been examined under similar conditions. Two of them, BV^{2+} and CBP^+ (Figure 3), show very similar behavior to that observed with MV^{2+}. The third, CMP^+, shows different behavior (Figure 4) but also indicates some attenuation of the quenching process.

The results obtained with the various quenchers in SDS solution can be explained in terms of the binding sites and capacities of the anionic surfactant for the two dications. Previous studies have shown that both MV^{2+} and Cu^{2+} have high association constants with SDS micelles.[14-17,23,30] The attenuation of Cu^{2+} quenching of **1** at low $[Cu^{2+}]$ is attributed to initial association of Cu^{2+} with the micelles; as the concentration of Cu^{2+} increases there is an upward curvature of the τ^0/τ vs. $[Cu^{2+}]$ plot until a limiting linear region with a slope nearly equal to that for homogeneous solution is attained. The fact that the initial slopes *decrease* for both quenchers with increase in [SDS] suggests that the low initial quenching observed is due to reaction between free quencher and excited substrate and not to collisions between the latter and micelle-bound quencher. The intersection point from the two approximately linear portions gives a SDS_m/Cu^{2+} ratio of ca. 6:1; this value is very close to those obtained for the binding capacity of SDS determined for Cu^{2+}, using quite different methods,[13-15] and compares well with binding capacities obtained for other divalent metal ions such as Ni^{2+}, Zn^{2+}, and Mn^{2+}.[13,14,31] The curvature of the plot (Figure 2) can clearly be attributed to a screening of the micellar charge as increasing numbers of Cu^{2+} ions associate with the anionic head groups.

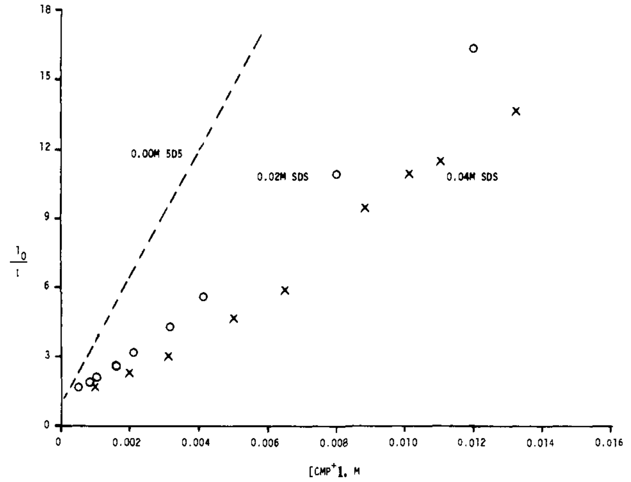

Figure 4. Stern–Volmer plots for quenching of the luminescence of **1** by 4-cyano-*N*-methylpyridinium at various surfactant concentrations. Concentrations of SDS (M) are indicated on the figure. The ordinate is I^0/I and the abscissa is the molar concentration of CMP^+.

The behavior observed for MV^{2+}, BV^{2+}, and CBP^+ quenching of **1** in the presence of SDS is quite different. Here, as with Cu^{2+}, there is an early attenuation of the quenching which can be attributed to initial association of the cation with the micelles. The finding that these plots show little upward curvature and are virtually linear until the break point is noteworthy and indicates that the binding of additional cation quenchers to the micelles is not very much retarded until a limiting capacity is reached. The limiting capacity, indicated by the SDS_m/quencher ratio at the break in the plots, is clearly much higher than that for metal ions used in other studies. Yet, the fact that there is a clearly indicated limiting capacity for the cations in contrast to the essential free partitioning observed for many uncharged solutes[3,6] suggests there are discrete binding sites for these ions. These two pronounced differences in behavior suggest very strongly that the binding of the relatively hydrophobic cations to the micelles is quite different from that occurring with metal ions or with neutral organics. A reasonable explanation appears to be that the binding of these ions to the micelle is governed chiefly by hydrophobic–hydrophilic interactions whereas the metal cation binding is due primarily to Coulombic association with the charged head groups. Such an explanation is in accord with increasing evidence[4,6,32,33] that there is a large surface–volume ratio for the micelle and, perhaps more importantly, a large micelle (i.e., hydrocarbon)–water interface region. Thus the charge on the bound cations should play a relatively minor role in inhibiting binding of additional quenchers, rather it is the elimination of hydrophobic–hydrophilic interfaces that provides the chief driving force and enables the association of higher numbers of the larger organic cations.

The contrast between the behavior of CBP^+ and CMP^+ in this regard is worth noting. Although both quenchers are water soluble and quench the excited state of **1** efficiently in homogeneous aqueous solution, the quenching by CMP^+ is clearly less attenuated by adding the anionic surfactant. This clearly runs counter to what would be expected on the basis of simple electrostatic interactions. The observation of what appears to be only a weak

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partitioning in the case of this relatively small hydrophilic monocation compared to the distinct binding observed with the larger, more hydrophobic CBP$^+$ underlines the role of hydrophobic factors and once again reinforces the idea that these cations as well as probably many other polar organic molecules are solubilized or interact with micelles by binding at hydrophobic-hydrophilic interfaces.

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Catalytic Water Reduction at Colloidal Metal "Microelectrodes". 2. Theory and Experiment

Deborah S. Miller,[†] **Allen J. Bard,**[‡] **George McLendon,***[†] **and J. Ferguson**[†]

Contribution from the Departments of Chemistry, University of Rochester, Rochester, New York 14627, University of Texas at Austin, Austin, Texas 78712.

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Abstract: A simple theory based on electrochemical principles is presented which predicts some of the catalytic properties of the widely used colloidal metal dispersions. The theory has been specifically applied to the case of photocatalytic water reduction to H_2. The model assumes that the kinetic properties of the system are governed by the current-potential curves of the half-reactions and that the reaction velocity can be determined by finding the common potential at which the current attributable to the mediator (e.g., methyl viologen) oxidation is equal to that for proton reduction at the metal surface. The effects of pH, mediator potential, and colloid size and composition can be predicted. These predictions have been experimentally verified with methyl viologen radical cation generated electrochemically and photochemically (via the Ru(bpy)$_3^{2+}$–*N*-phenylglycine system) and with other mediators at colloidal dispersions of several metals.

The catalytic reactions of metal colloids have been the subject of long and fruitful study.[1-6] Interest in these systems has been further increased by their use as necessary cocatalysts in photocatalytic water reduction schemes.[7-9] This latter use has prompted preliminary investigations of the mechanisms by which these metal particles facilitate water reduction by a reduced mediator, like methyl viologen radical cation (MV$^{+}\cdot$). Analogy suggests that these colloids may act as "microelectrodes", with a potential determined by the photoreduced mediator.[2,4,8] Using this analogy, several groups have quite recently presented kinetic studies of methyl viologen dependent H_2 production at dispersed Pt, Au, and other metals.[2,4,10,11] Grätzel has reported some empirical determinants of colloidal catalyst efficiency, including the effects of colloid size and protective agents. Limiting rates for the catalyst reaction with MV$^{+}\cdot$ were also reported.[4] More mechanistic approaches have been taken by other groups. Kopple et al. have reported isotope effect studies of H_2 production on Au colloids.[2] The observed isotope effects are quite similar to those observed at bulk electrodes, supporting the microelectrode analogy. Miller and McLendon have reported extensive rate studies of colloidal catalysis of water reduction with different metals and varying mediator potential.[10] In the studies of Meisel and Heinglein,[3] the observed rate data were treated with the use of microscopic kinetic models. While this approach is interesting, it suffers from a limited ability to predict quantitatively the effects of reaction variables on catalytic efficiency. To date, no such predictive theory is available for the important catalytic water reduction reaction, nor are sufficient experimental results available for a definitive test of any theory.

The suggestion that heterogeneous catalysis of electron transfer reactions at metals or carbon can be interpreted in terms of the electrochemical behavior of the reactants involved in the process has been discussed previously,[6,12] based on a model first proposed for corrosion reactions.[13] Most recently Spiro[12] has discussed the special cases of (a) two totally irreversible reactions in the absence of mass transfer effects and (b) a totally irreversible reaction coupled with a mass transfer limited one in the limiting current regime. General models have apparently not been proposed, however, nor have attempts been made to use these in a more predictive way in homogeneous photocatalytic processes involving heterogeneous catalysts. In the present manuscript, a general model is proposed and quantitatively extended which predicts a wide variety of experimental data for colloidal catalysis of water reduction. It is the purpose of this manuscript to present explicitly this predictive model for colloidal catalysis in the hydrogen evolution reaction. In this model, the colloidal "microelectrode", like a bulk electrode, serves several functions. It provides a medium by which the number of electrons (or equivalents) of the two half-reactions can be matched. It also provides a surface for lowering the activation energy of one or both of the half-reaction processes. In the process under consideration here, the one-electron oxidation of the donor MV$^{+}\cdot$ is matched to the overall two-electron process producing H_2. Moreover, the adsorption of hydrogen atoms on the surface of the metal lowers the energy required for the reduction step H$^+$

[†] University of Rochester.

[‡] University of Texas at Austin.

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(10) (a) D. S. Miller and G. McLendon, *Inorg. Chem.*, **20**, 950–953 (1981). (b) In principle, the ratio of MV$^{+}\cdot$/MV^{2+} may change in the course of catalysis so that the position of the anodic curve would shift rather than remaining fixed in Figure 1. In practice, this shift is small under the (common) experimental conditions reported here; the total shift of pH$_{1/2}$ due to the changing ratio of MV$^{+}\cdot$/MV^{2+} is <0.1 pH unit.

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