

The positive root corresponds to the pseudo-first-order rate constant for the faster process (mostly tautomerization) and the negative root corresponds to pseudo-first-order rate constant for the slower process (mostly decarboxylation).

Tautomerization is subject to general acid and base catalysis so each of the constants which pertain to a tautomerization rate in Scheme II is comprised of the sums of terms arising from various catalytic modes

$$k_i = k_{iH}[H^+] + k_{iHA}[HA] + k_{iA}[A] + k_{iH_2O}[H_2O] + \dots$$

Certain terms in the complete rate expression are kinetically indistinguishable owing to a proton ambiguity, e.g., those for the pathways $\text{Hoxac}^-_{\text{K}} + \text{H}_2\text{O} \rightarrow \text{Hoxac}^-_{\text{E}} + \text{H}_2\text{O}$, and $\text{oxac}^{2-}_{\text{K}} + \text{H}^+ \rightarrow \text{oxac}^{2-}_{\text{E}} + \text{H}^+$.

In analyzing the concentration and pH dependence of the $k_{i,\text{obsd}}$ values, only one of the terms in such an equivalent set was retained. Further simplifications could be made in a series of experiments with a given metal ion because not all possible

pathways were found to be present.

In performing the nonlinear curve fitting for a given data set, values of the rate constants for the various acid- and base-catalyzed enolization paths were estimated together with a value of K_M^{enol} for the particular metal ion complex. The rate constants for the ketonization paths were then calculated. For each data point, an overall distribution of species was then calculated with use of the equilibrium constants given in Table III. This overall distribution was broken down into the contributions of each of the keto and enol species to obtain the necessary fractional distributions. These values were then substituted into (7A) together with the estimates of the rate constants, and a value of $\lambda+$ was calculated for that data point. Repeating this process the sum-squares $\sum(k_{i,\text{obsd}} - \lambda_{+,\text{calcd}})^2$, for all the data points were calculated and minimized by adjusting the values of the unknown rate constants and K_M^{enol} .

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Rates of the Reactions of Uranium(VI) and the Hydrated Electron in Micellar Systems¹

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The rate of the reaction between e_{aq}^- and U(VI) decreases with increasing sodium dodecyl sulfate (SDS) concentrations ≤ 4 mM and then remains constant up to 0.1 M SDS. The results are interpreted by the postulate of the interaction between U(VI) and pre-micellar aggregates of SDS. The rate of the reaction between the tris(carbonato)dioxouranium(VI) ion and the hydrated electron goes through a minimum and then increases with increasing cetyltrimethylammonium bromide (CTAB) concentration. A plausible mechanism that accounts for these observations is presented.

Introduction

The adsorption processes that occur at the interface between a suspended colloid and solution are important in the distribution of trace metal ions in natural aquatic systems.² When the metal ions under consideration can undergo oxidation-reduction reactions, it is of interest to assess the effect of such adsorption on the reactivity patterns of the metal ions.

The use of a micellar-water interface provides an opportunity to study the reactions of adsorbed ions in which the interactions are predominantly electrostatic and the structure of the adsorbent is at least moderately well-defined. In addition, by studying the dynamics of the redox reaction in concentrations less than cmc, it is conceptually possible to demonstrate differences between the homogeneous and heterogeneous reaction systems. Indeed, considerable effort has been devoted to the understanding of the effect of such micellar systems on the kinetics⁴ of various processes.³ Electron transfer across the double layer between many donor-acceptor couples has been studied in detail, most commonly following photoexcitation.⁴ Similarly, reactions of aquated electrons,

produced by radiolysis of micellar solutions, with acceptors of different affinities to the micelles were thoroughly studied.⁵ Micellar effects on the rates of electron transfer to and from inorganic complexes have also been recently investigated.⁶⁻⁹

The results obtained in the present investigation use the reaction of e_{aq}^- with U(VI) to explore the above delineated areas of interest. The choice of U(VI) for the metal ion to be used was dictated by the interest in speciation of heavy metals in the aquatic environmental reservoir and the fact that the known chemistry of U(VI) permits a study of its interactions with both anionic and cationic micellar material.

Experimental Section

Reagents. The uranyl perchlorate stock solution was prepared by dissolving U_3O_8 in perchloric acid and recrystallizing and standardized by the usual gravimetric techniques. Sodium carbonate solutions were prepared by weight from an ultrapure solid. G. F. Smith perchloric acid was diluted and standardized by the usual techniques. Sodium

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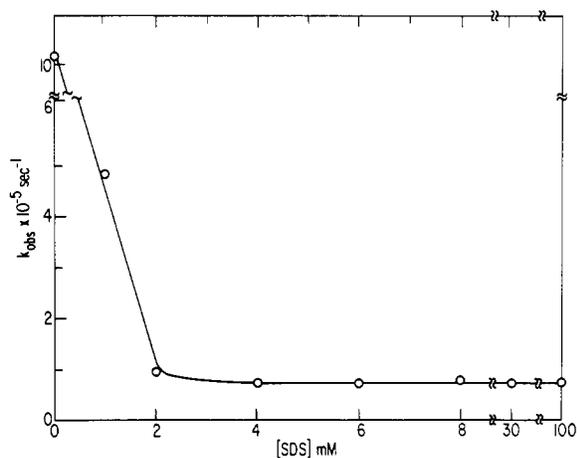


Figure 1. Effect of [SDS] on the rate of the reaction of e_{aq}^- with UO_2^{2+} ; $[\text{UO}_2^{2+}] = 1 \times 10^{-4} \text{ M}$, pH 5.8.

dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were purified by repeated recrystallization from ethanol-ether solutions. All reactions were carried out in triply distilled water.

Procedures. Solutions of U(VI) were saturated with He by using the conventional syringe technique. Solutions of the surfactants were deoxygenated by use of a vacuum system, and appropriate volumes of surfactant solution were then introduced into the syringes containing the metal ion.

Pulse Radiolysis. The Chemistry Division linear electron accelerator provided pulses of 2–10 ns which produced ca. 10^{-6} M concentration of e_{aq}^- in 5-cm length cells. The spectrophotometric detection of the e_{aq}^- , data collection, and treatment have been described previously.^{10a}

Results and Discussion

Reaction of U(VI) with e_{aq}^- in SDS-Containing Solutions.

The effect of the variation of SDS concentration on the reaction of e_{aq}^- with U(VI) was studied over a range of SDS concentrations below and above the cmc (1–100 mM SDS). The observed first-order rate parameter in solutions of 0.1 mM U(VI), pH 5.8, as a function of SDS concentrations is presented in Figure 1. The rate parameters are corrected for the slow reaction of e_{aq}^- ($k = 5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) with SDS measured in blank solutions.

The rate of reaction 1, in aqueous perchlorate media, pH



5.3, is $k_1 = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This rate is essentially independent of solution composition and/or complexing of the uranyl ion. Thus, for example, the $\text{UO}_2(\text{CO}_3)_3^{4-}$ species reacts with the hydrated electron at a rate that is nearly diffusion controlled ($k = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).^{10b} It is therefore interesting to note (Figure 1) the marked variation in the rate of the reaction in solutions containing SDS. This decrease in the rate parameter occurs even at concentrations of SDS substantially below the cmc.

From 4 mM concentrations of SDS the rate of disappearance of e_{aq}^- remains constant up to 0.1 M SDS. The rate parameter over this range of substrate concentration is similar to that measured for the rate of disappearance of e_{aq}^- in the absence of U(VI) and is not changed by variation of the initial U(VI) concentration. We therefore conclude that the rate of reaction 1, in solutions containing SDS above the cmc, is reduced to such an extent that the U(VI) ions do not effectively compete with other decay modes of e_{aq}^- .

Numerous studies have demonstrated that di- and trivalent cations interact strongly with negatively charged micelles. The

closest example to the system presently studied is probably the vanadyl ion in SDS micellar solutions.¹¹ Since the uranyl ion behaves as if there were a charge of 3+ on the U atom with respect to complex ion formation,¹² it is to be expected that there will be a strong attractive electrostatic interaction between this ion and the head groups of the SDS. Thus, for VO^{2+} , complete binding to SDS micelles was observed slightly above the cmc.¹¹ Bhalekar and Engberts⁶ have also concluded that for bivalent ions the electrostatic binding that dominates the hydrophobic interactions will ensure complete association with the micellar interface. This high-negative-potential field would at the same time act to repulse the hydrated electron. From the reduction in k_{obs} with increase in SDS concentrations, we can conclude that at $[\text{SDS}] > 4 \times 10^{-3} \text{ M}$, less than 1% of the UO_2^{2+} ion is in the bulk of the solution. Apparently, the binding constant of UO_2^{2+} to SDS micelles is extremely high; however, any estimate of this constant is not feasible because of the reduction of the cmc (vide infra).

It is apparent from the data presented in Figure 1 that the rate of the reaction between e_{aq}^- and U(VI) decreases markedly even at SDS concentration well below the cmc of 8 mM. This effect can be rationalized if one postulates that premicellar aggregation occurs in these systems. Such behavior has been previously inferred from the effect of amphiphilic compounds on rates of reactions of a variety of multivalent ions.^{8,13,14} On the other hand, EPR relaxation time measurements for VO^{2+} in SDS solutions indicate no change in its correlation time at $[\text{SDS}] < \text{cmc}$.¹¹ The premicellar aggregation induced by such ions seems therefore to have little effect on the rate of the local motions of the ions. Alternatively, if these premicellar aggregates are substantially smaller than the micellar aggregates, motions that involve the aggregate itself along with the counterion may contribute to the motions that average the anisotropy of the EPR parameters. In such a case, kinetic effects on reaction rates can still be observed while relaxation times will hardly be affected. It is impossible to decide on the basis of our kinetic measurements whether the average aggregate size in this region of [SDS] is the same or smaller than that of the micelles in the absence of the highly charged ions. However, since the changes involved in the correlation times of VO^{2+} occur at [SDS] close to the cmc,¹¹ we may conclude that no significant reduction of the cmc induced by U(VI) occurs in the presently studied system. Rather, the multivalent ions provide nucleation centers for smaller aggregates. We have previously noted, however, that the rate of the reaction between e_{aq}^- and U(VI) complex ions is rather insensitive to the formal charge on the U(VI). Therefore, the effect observed at low SDS concentrations is very probably caused by association between aggregates of SDS and U(VI) rather than between dimers of SDS of the type discussed by Mukerjee et al.¹⁵

Reaction of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ with e_{aq}^- in CTAB Micellar Solutions. The rate of the reaction between the hydrated electron and the tris(carbonato)dioxouranium(VI) ion was measured in 0.05 M Na_2CO_3 solutions over a range of CTAB concentrations (1–50 mM). The values of the first-order parameter as a function of [CTAB] are presented graphically for two concentrations of the uranium complex (4 and $8 \times 10^{-5} \text{ M}$) in Figure 2. The high concentration of Na_2CO_3 ensures preservation of the ionic strength and pH along the whole series of these experiments.

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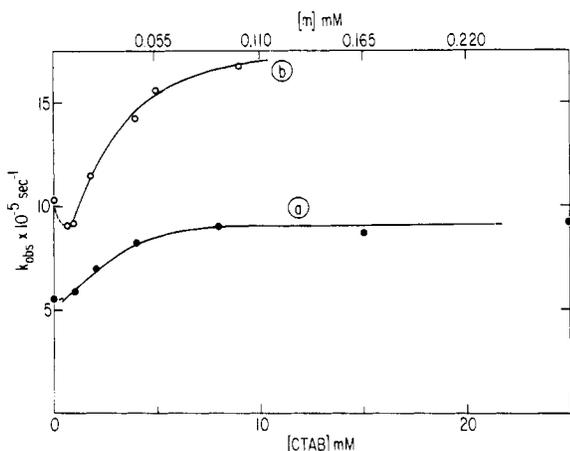
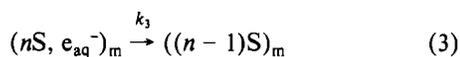
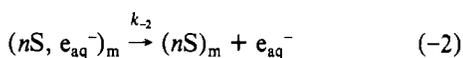


Figure 2. Effect of [CTAB] on the rate of the reaction of e_{aq}^- with $[UO_2(CO_3)_3^{4-}]$: (a) $[UO_2(CO_3)_3^{4-}] = 4 \times 10^{-5} M$; (b) $[UO_2(CO_3)_3^{4-}] = 8 \times 10^{-5} M$ (all in 50 mM Na_2CO_3 at pH 11). Solid curves were calculated by taking $\alpha = 1.8$.

These data show that at low [CTAB] (albeit above the cmc under these experimental conditions) the rate of the reaction apparently goes through a minimum and then increases with increasing CTAB concentration. The rate of the reaction then becomes invariant at the lower initial concentration of the uranium complex, and an indication of a yet unattained plateau region can be seen for the higher $[UO_2(CO_3)_3^{4-}]$ as well (Figure 2). This behavior may be contrasted with similar studies of the rate of the reaction of e_{aq}^- with several pyrene derivatives solubilized in CTAB micelles.^{4,5d} In these studies as well as in previous studies,^{5a} trapping of e_{aq}^- in the potential field of the CTAB micelles was invoked to explain the reduction in the rate of reaction of e_{aq}^- with the various scavengers. In the present system, due to the high concentrations of carbonate employed, detrapping of e_{aq}^- from that field rapidly occurs. As delineated in the mechanism proposed below, the competing reactions of detrapping and intramicellar electron transfer are no more the rate-determining steps while the diffusion toward the micelles assumes that role. Under such conditions the rate of the reaction of e_{aq}^- with the U(VI) complex is expected to increase with increasing concentration of micelles.

Several phenomenological kinetic models were developed to describe scavenging reactions in micellar systems on short time scales.¹⁶⁻¹⁹ The following reaction scheme shown by (2), (-2), and (3) describes the processes for the disappearance of the hydrated electron in the present systems. $(nS)_m$ designates



a micelle containing n molecules of the electron scavenger S (in this case the $UO_2(CO_3)_3^{4-}$ anion). Reaction 2 is then the trapping of the hydrated electron in the Stern region. The hydrated electron can then either diffuse back to the bulk solution or react with $UO_2(CO_3)_3^{4-}$. Reaction -2 is therefore

the detrapping process and will include exchange reactions with other anions (in this case carbonate primarily). The rate of reaction 3 is usually assumed to be directly proportional to the occupation number, n , of scavengers in the micelle, and k_3 is a "unimolecular" rate constant for this reaction.¹⁶⁻¹⁹ Two assumptions are then undertaken with regard to the reactants in this system. The first assumption is that all of the $UO_2(CO_3)_3^{4-}$ ions occupy the Stern region of the micelles. Because of the high negative charge on the uranium complex this assumption is likely to be valid even at the high ionic strength employed in this study. The second assumption is that the uranium complex remains in the Stern region during the lifetime of the hydrated electron ($\leq 1 \mu s$). If a steady state for the CTAB-adsorbed e_{aq}^- , $(nS, e_{aq}^-)_m$, is assumed, the rate of disappearance of the hydrated electron (in bulk solution and in association with the micelle) by those micelles containing n scavengers, r_n , is given by eq 4. Since $k_2[(nS)_m] \ll (k_{-2}$

$$r_n = \frac{nk_2k_3[(nS)_m][(e_{aq}^-)_{tot}]}{k_2[(nS)_m] + k_{-2} + nk_3} \quad (4)$$

+ nk_3), eq 4 can be simplified to eq 4a.

$$r_n = \frac{k_2[(nS)_m][(e_{aq}^-)_{tot}]}{1 + k_{-2}/nk_3} \quad (4a)$$

The rate of disappearance of e_{aq}^- with all micelles containing all the various numbers n of scavengers is then $\sum_{n=0}^{\infty} r_n$. To calculate $[(nS)_m]$, we assume a Poisson distribution of scavengers among the micelles $[(nS)_m] = \bar{N}^n e^{-\bar{N}} [m] / n!$, where $[m] = (C_0 - cmc) / \eta$ is the concentration of micelles ($\eta = 82$) and $\bar{N} = [S] / [m]$ is the average number of scavengers associated with the micelles. Substitution of the Poisson distribution for $(nS)_m$ in eq 4a yields expression 5 for the observed first-order

$$k_{obsd} = \left(\sum_{n=0}^{\infty} \frac{1}{1 + k_{-2}/nk_3} \frac{\bar{N}^n e^{-\bar{N}}}{n!} \right) k_2 [m] \quad (5)$$

rate parameter k_{obsd} . A similar result was obtained by Atik and Singer for fluorescence quenching in micellar solutions.¹⁹ The observed rate constant is then a composite of the two effects, the rate of diffusion to the micelle, which will increase linearly with $[m]$, and the probability of the intramicellar electron-transfer reaction.

An analysis of these experimental results requires estimates of the effect of the added Na_2CO_3 on the cmc and the aggregation number.²¹

We can calculate that the effect of the ionic strength²² of the sodium carbonate solutions will decrease the cmc to a value much less than the C_0 of our experiments and can therefore be neglected. We estimate a value of $\eta = 82$ based on the results presented by Jones and Reed²³ for the effect of Na_2SO_4 on the micelles of tetradecyltrimethylammonium bromide. It should be noted that the values derived for K_b and k_{-2} are markedly affected by the value estimated for this parameter.

In order to calculate values for the parameters in eq 5, we measured the rate of disappearance of the hydrated electron at constant m and varying $UO_2(CO_3)_3^{4-}$ concentrations. The statistical adjustment of these data by a least-squares routine resulted in the values $\alpha = k_{-2}/k_3 = 1.8 \pm 0.5$ and $k_2 = (10 \pm 2) \times 10^{10} M^{-1} s^{-1}$. The data and the least-squares adjustment of the data are presented in Figure 3. The same values of the parameters α and k_2 are then used to calculate the smooth curves through the experimental data points in Figure

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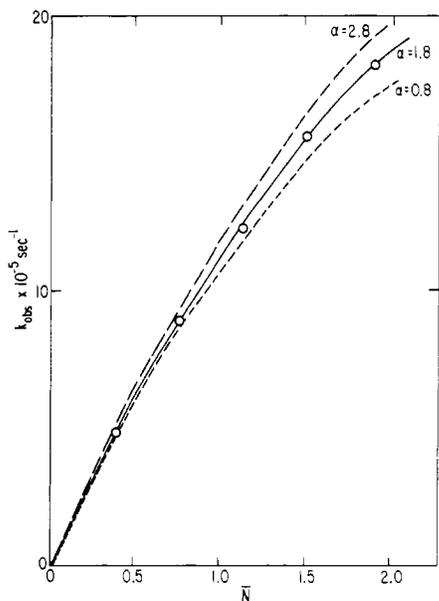


Figure 3. Dependence of k_{obs} on the average number of $\text{UO}_2(\text{CO}_3)_3^{4-}$ ions per micelle, \bar{N} : O, experimental results; —, calculated curve, $\alpha = 1.8$, $k_2 = 1.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$; - - -, calculated curves, $\alpha = 1.8 \pm 1$, $k_2 = 1.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. Experimental results were obtained with $[\text{CTAB}] = 5 \text{ mM}$ and $[\text{Na}_2\text{CO}_3] = 50 \text{ mM}$, at pH 11.

2. These two values of the parameters seem then to fit the complete set of experiments reasonably well.

The value of k_2 is close to that expected for a diffusion-controlled rate constant for the formation of a complex between the hydrated electron and the bulky micelle. The value of α indicates that the probability of the hydrated electron escaping the micellar interface is twice as great as the probability that the associated electron will react with $\text{UO}_2(\text{CO}_3)_3^{4-}$ if the micelle contains a single molecule of that scavenger.

An estimate of the binding constant for the association between the hydrated electron and CTAB micelles can be calculated on the basis of simple electrostatic interaction from the relation

$$K_b = \eta \bar{V} e^{-Z\psi/25.69} \quad (6)$$

where \bar{V} is the partial molar volume of surfactant in the micelle

with a value of 0.363 M^{-1} , Z is the ionic charge of the reactant e_{aq}^- , and ψ is the surface potential of the micelle in mV. A reasonable estimate of 10 mV can be made for the value of this surface potential on the basis of the results calculated for an analogous system.²³ The calculated value of $K_b = 44 \text{ M}^{-1}$ (eq 6) and this value in conjunction with the value determined for k_2 allow an estimate of $k_{-2} \approx 2.3 \times 10^9 \text{ s}^{-1}$. This estimate of k_{-2} and the above determined value of $\alpha = 1.8$ allow an estimated value of $k_3 \approx 1.3 \times 10^9 \text{ s}^{-1}$. This can be converted to a bimolecular rate constant of $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ if one assumes a radius of closest approach of 20 \AA ^{5d} and that the reaction occurs in a Stern region of 4-\AA width. This rate constant is an order of magnitude higher than the recent estimate of Schmehl and Whitten²⁰ for the diffusion rate constant for a reaction believed to occur on the micellar interface. Apparently, the present reaction takes place in an environment that is very similar to that of water.

Conclusions

As could be expected for a reaction between two oppositely charged species, the rate of reaction between e_{aq}^- and UO_2^{2+} is drastically inhibited by negatively charged micelles. This reduction however is apparent already at concentrations much below the critical micellar concentration. Premicellar aggregation of relatively large particles is believed to be induced by the large added cation. These results emphasize the point that rates of redox reactions in natural aquatic systems may well be altered by adsorption on suspended particulate matter. On the other hand, when the rate of reaction between similarly charged reactants (e_{aq}^- and $\text{UO}_2(\text{CO}_3)_3^{4-}$) is studied in the presence of oppositely charged micelles (CTAB), two opposing effects can be expected. At low occupancy of the micelles by the probe reactant, the reaction rate will drop with increasing micellar concentration due to the increased residence time of one of the reactants in micelles free of the other reactant. At high occupancy however the opposite effect of increased micellar concentration is to be expected.

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Registry No. UO_2^{2+} , 16637-16-4; $\text{UO}_2(\text{CO}_3)_3^{4-}$, 17372-00-3; SDS, 2386-53-0; CTAB, 57-09-0.