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Photolytic behaviour of $[Co(NH_3)_4C_2O_4]$ in micellar and inverse micellar solutions

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Abstract

A comparative study of the charge transfer photochemistry of oxalatotetraamminecobalt(III) perchlorate in pure aqueous solution and in premicellar and micellar solutions of three different surfactants (anionic, cationic and non-ionic) has been undertaken. The results indicate the following. (1) The quantum yield of Co^{2+} ($\phi_{Co^{2+}}$) changes as the concentration of the surfactant changes with a concomitant change in the microenvironment of the probe. The manner in which $\phi_{Co^{2+}}$ varies depends on the nature of the surfactant used in the solution. The critical micellar concentration (CMC) of a surfactant can be determined from a plot of $\phi_{Co^{2+}}$ vs. $-\log[\text{surfactant}]$. (2) The photoaquation of ammonia does not take place in micellar solutions of sodium dodecylsulphate (SDS) and cetyltrimethylammonium bromide (CTAB), but occurs to a small extent in a micellar solution of Triton X-100. The photolysis of the complex has also been carried out in two different inverse micellar microemulsions. The results reveal that the efficiency of the intramolecular photoredox process, as manifested by the quantum yield of Co^{2+}, decreases as the size of the water pool of the microemulsions decreases. © 1997 Elsevier Science S.A. All rights reserved.

Keywords: Charge transfer photochemistry; $[Co(NH_3)_4C_2O_4]^+$; Micellar and inverse micellar solutions

1. Introduction

The study of photophysical processes and photochemical reactions in ordered molecular assemblies has added a new dimension to photochemical research [1,2]. Of the various ordered molecular assemblies, micellar systems have been thoroughly investigated. Micellar media, when used for chemical reactions, exhibit completely different features from those of non-aqueous and aqueous solvents. Micellar aggregates which are structurally well characterized can alter significantly the excited state chemistry and reactivity of the singlets and triplets. A photochemical reaction conducted in micellar media is influenced by the micellar environment, which results in the control and/or modification of the reactivity. The salient properties of micelles which influence the photochemical reactivity are cage and microviscosity effects, localization and compartmentalization effects, pre-orientational, polarity and counterion effects and the effect of the charged interface [3–8]. Micellar aggregates also exist in a variety of non-polar solvents. The aggregation occurs in an inverted manner with the polar headgroups collected together in an inner core and the hydrocarbon tails spread out into the non-polar oil phase. A distinguishing feature of these inverted micelles is their ability to solubilize an appreciable amount of water in the inner polar core. The size of the water pool and the properties of the water present in the inner core of inverted micelles can be controlled by varying the amount of water.

The photochemical reactivity in micellar and inverse micellar systems has been studied extensively, but few of these investigations have been concerned with the reactivity of inorganic complexes [9–14]. In this work, we have investigated the steady state photolysis of $[Co(NH_3)_4C_2O_4](ClO_4)$ in premicellar and micellar solutions of sodium dodecylsulphate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 (polyoxyethylene (E-10) tert-octylphenol). The same study has also been conducted in pure aqueous solution (in the absence of any surfactant) and by trapping the complex in the inner water core of AOT(sodium salt of diisooctyl sulfosuccinate)/heptane/water and CTAB/chloroform–isooctane/water microemulsions.

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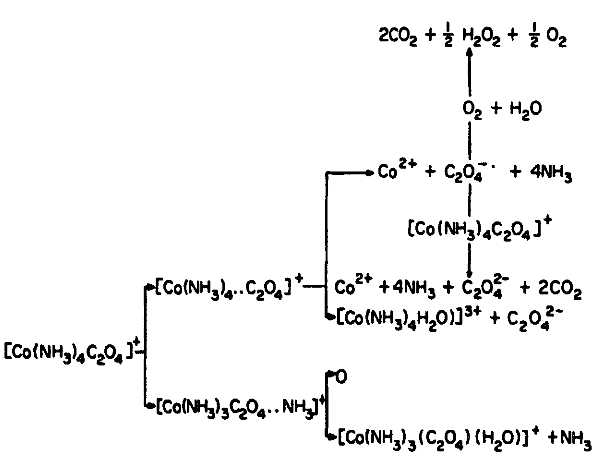
2. Experimental details

The complex $[Co(NH_3)_4C_2O_4](ClO_4)$ was prepared following the procedure of Mori et al. [15] and the purity of the compound was checked by chemical analysis. The surfactants SDS, CTAB, Triton X-100 and AOT were of high purity grade (Sigma). Generally, analytical grade reagents were used. A low-pressure mercury vapour lamp (Thermal Syndicate T/M5/594-110 W) was used to generate radiation at a wavelength of 254 nm. All the photolyses were carried out in quartz vessels. The temperature of the system was maintained at 35 °C by circulating water using a thermostatic control device. The lamp output was observed before and after each experiment by ferrioxalate actinometry [16]. The photoreleased Co^{2+} ions were estimated by Kitson's method [17].

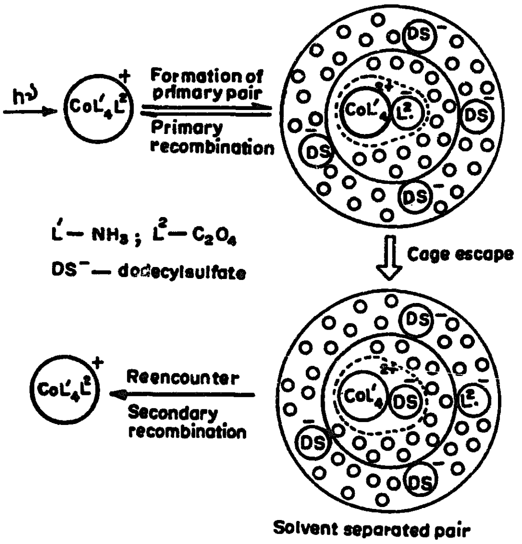
The concentration of NH_3, a photoproduct, was determined by a colorimetric method using Nessler's reagent.

3. Results and discussion

The experimental results can be interpreted in terms of Scheme 1, which is similar to that proposed by Vogler and Adamson [18] in connection with the photochemistry of the complex *trans*-$[Co(en)_2(NCS)Cl]^+$. This scheme suggests that $C_2O_4^{\cdot -}$ (radical anion) is formed due to primary homolytic splitting of the complex. The radical anion can induce secondary thermal reaction of $[Co(NH_3)_4C_2O_4]^+$ leading to the increased production of Co^{2+} ions. The results given in Table 1 indicate that $\phi_{Co^{2+}}$ increases as the concentration of SDS (anionic surfactant) increases in the premicellar range of concentration. The quantum yield of Co^{2+} reaches a maximum at a concentration equal to (or slightly greater than) the critical micellar concentration (CMC) of SDS. In postmicellar solutions of SDS, $\phi_{Co^{2+}}$ decreases as the concentration of SDS increases. For CTAB, $\phi_{Co^{2+}}$ is practically independent of the surfactant concentration in the premicellar region, but decreases with increasing surfactant concentration in the postmicellar range. The manner in which the quantum yield of Co^{2+} varies as the concentration of Triton X-100 changes is similar to that for SDS.



Scheme 1.



Scheme 2.

The observed trends in the results can be explained with the help of Scheme 2.

UV irradiation produces ligand to metal charge transfer (LMCT) states; geminate pairs consisting of $Co(NH_3)_4^{2+}$ and $C_2O_4^{\cdot -}$ are formed due to homolytic splitting of the complex. The efficiency of the electron transfer reaction is deter-

Table 1

$\phi_{Co^{2+}}$ as a function of the concentration of surfactant in acetate buffer (pH 4.63) (excitation wavelength, 254 nm; time of irradiation, 5 min; temperature, 35 °C; concentration of complex, 1×10^{-4} mol dm^{-3})

Surfactant	Concentration of surfactant (mol dm^{-3})	$\phi_{Co^{2+}}$	Surfactant	Concentration of surfactant (mol dm^{-3})	$\phi_{Co^{2+}}$	Surfactant	Concentration of surfactant (mol dm^{-3})	$\phi_{Co^{2+}}$
SDS	0	0.52	CTAB	0	0.52	Triton X-100	0	0.52
	1×10^{-4}	0.54		1×10^{-5}	0.59		2.4×10^{-5}	0.57
	1×10^{-3}	0.56		1×10^{-4}	0.61		1.9×10^{-4}	0.65
	6×10^{-3}	0.64		8×10^{-4}	0.59		2.4×10^{-4}	0.67
	8×10^{-3}	0.66		1×10^{-3}	0.59		3×10^{-4}	0.63
	1×10^{-2}	0.67		5×10^{-3}	0.54		2.4×10^{-3}	0.56
	5×10^{-2}	0.62		1×10^{-2}	0.50			
	0.1	0.60						

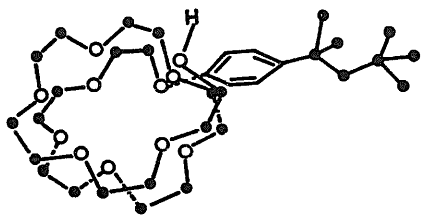


Fig. 1. Molecular model of Triton X-100.

mined by the competition between diffusive separation and recombination (primary and secondary) reactions of the radical pairs. If the solution contains an anionic surfactant, such as SDS, the DS$^-$ ions can replace $C_2O_4^{\cdot -}$ ions in the first coordination shell, resulting in an inhibition of the recombination reaction. The encounter frequency between $Co(NH_3)_4^{2+}$ and DS$^-$ increases as the concentration of SDS increases, and leads to an increase in the value of $\phi_{Co^{2+}}$ with increasing SDS concentration in the premicellar region. The decrease in $\phi_{Co^{2+}}$ at postmicellar concentrations of SDS may be ascribed to two different factors. First, in postmicellar solutions, all the complex ions (being positively charged) are bound to the negatively charged interfaces of the anionic micelles, and the solvent molecules (being polar) are highly structured in the microenvironment of the complex ions owing to the intense electric field of the charged micellar aggregates. This leads to a large increase in the microviscosity of the environment and, eventually, the recombination reaction of the radical pair is favoured. Second, in postmicellar solutions of SDS, the complex ions are bound to the micelles and $C_2O_4^{\cdot -}$ ions are located in the bulk of the solution; naturally, $C_2O_4^{\cdot -}$ ions cannot induce secondary thermal reaction.

The quantum yield of Co^{2+} is independent of the surfactant concentration in premicellar solutions of CTAB; this is due to the fact that cetyltrimethylammonium ions cannot replace $C_2O_4^{\cdot -}$ in the first coordination shell. In postmicellar solutions of CTAB, the radical anions are bound to the positively charged micelles, so that the secondary thermal reaction is hindered, resulting in a decrease in the value of $\phi_{Co^{2+}}$. In postmicellar solutions of CTAB, the complex ions remain in the bulk of the solution and the change in bulk viscosity (due to micellization) is not large enough to reduce the quantum yield of Co^{2+}.

The variation in $\phi_{Co^{2+}}$ with the concentration of Triton X-100 indicates that the electrically neutral micelles of Triton X-100 resemble the negatively charged micelles of SDS to some extent. The molecular model of Triton X-100 (Fig. 1) shows that the hydrophilic moiety of the molecule has a crown ether-like structure; the oxygen spiral of the non-ionic micellar interface can encage the positively charged complex ions owing to ion–dipole interactions and the water molecules in the immediate vicinity of the micelles are highly structured due to dipole–dipole interactions. This is why the effects of Triton X-100 are similar to those of SDS.

In an earlier study [19], we noted some changes in the spectral characteristics of the oxalatoamminecobalt(III) complexes in micellar and inverse micellar solutions; these changes were due to binding, encaging, etc. of the positively charged complex ions.

In general, the variation of $\phi_{Co^{2+}}$ with the change in concentration of the surfactant is due to the change in the microenvironment of the substrates. The microenvironment changes drastically as micelles are formed in the system, and

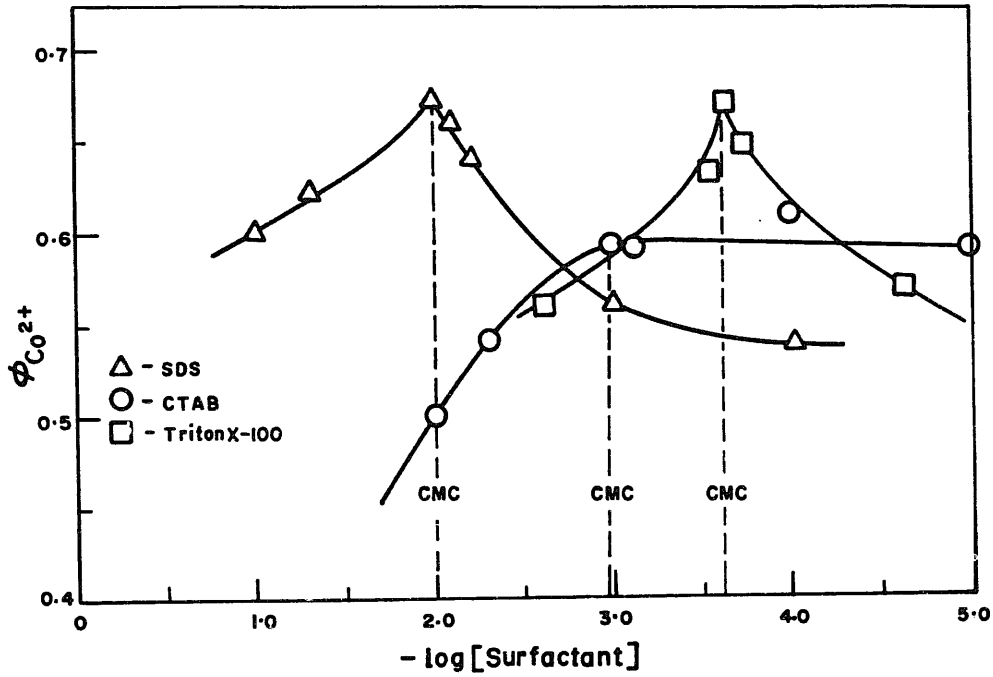


Fig. 2. Plots of $\phi_{Co^{2+}}$ vs. – log(surfactant) for $[Co(NH_3)_4C_2O_4]ClO_4$ on 254 nm irradiation. △, SDS; ○, CTAB; □, Triton X-100.

therefore it is natural that the CMC of a surfactant can be determined from a plot of $\phi_{Co^{2+}}$ against $-\log[\text{surfactant}]$ (Fig. 2). Horvath et al. [20] also reported that a plot of the quantum yield of photo-oxidation of $Fe(bipy)_2(CN)_2$ vs. [SDS] provides information on the CMC of SDS.

3.1. Micellar control of the photoaquation of the NH_3 ligand

Scheme 1 suggests the following. (1) The complex undergoes two reactions, i.e. redox decomposition and photosubstitution. (2) The expected value of the ratio $\phi_{NH_3}/\phi_{Co^{2+}}$ is equal to four if the photoaquation of NH_3 does not occur; the same ratio exceeds four when the ligand NH_3 is photosubstituted by H_2O molecules. The results presented in Table 2 indicate that, irrespective of the pH of the solution, the complex undergoes NH_3 aquation in surfactant-free aqueous solution and in premicellar solutions of SDS, CTAB and Triton X-100. The aquation of ammonia relative to the redox process decreases in premicellar solutions of surfactants compared with that in pure aqueous solution. The photoaquation of NH_3 does not take place in micellar solutions of SDS and CTAB, but occurs to a small extent in micellar solutions of Triton X-100. In general, the photoaquation of NH_3 is hindered in micellar solutions of all three surfactants used. This is one of the striking observations of this investigation but, at present, we are not in a position to provide any explanation.

3.2. Photolytic behaviour of the complex in inverse micellar microemulsions of AOT/heptane/water and CTAB/chloroform–isooctane/water

The results given in Table 3 reveal that the efficiency of the photoredox process decreases sharply if the complex ions remain trapped in the inner polar core of inverse micellar systems. The water in the inner core of inverted micelles is always biphasic: phase I is structured and phase II is bulk water; the relative amounts of the two phases depend on the water content of the system. Fluorescence probe analysis of the micellar core has indicated a very rigid interior state with a viscosity of over 40 cP [21]. The diffusive separation of the radical pair generated by primary homolytic bond splitting is strongly inhibited in the rigid inner core and, as a consequence, the quantum yield of formation of Co^{2+} ions decreases sharply if the photolysis of the complex is carried out in inverse micellar microemulsions. The complex ions

Table 2

Photolysis of $[Co(NH_3)_4C_2O_4](ClO_4)$ (excitation wavelength, 254 nm; time of irradiation, 5 min; temperature, 35 °C); quantum yields[a] (ϕ) of Co^{2+} and NH_3 in surfactant-free aqueous solution and in premicellar and micellar surfactant solutions

Medium	Surfactant	Environment	pH of the medium (bulk)	Concentration of complex (mol dm^{-3})	Concentration of surfactant (mol dm^{-3})	$\phi_{Co^{2+}}$	ϕ_{NH_3}	$\phi_{NH_3}/\phi_{Co^{2+}}$
Acetic acid–acetate buffer	–	Homogeneous	4.63	1×10^{-4}		0.52	3.39	6.52
			3.72			0.54	3.57	6.61
			3.42			0.54	3.67	6.80
Acetic acid–acetate buffer	SDS	Micellar	4.63	1×10^{-4}	0.1	0.60	2.45	4.08
		Micellar	4.63		1×10^{-2}	0.67	2.70	4.03
			3.72			0.72	2.90	4.03
			3.42			0.75	2.96	3.95
		Premicellar	4.63		1×10^{-3}	0.56	2.88	5.14
			3.72			0.59	3.02	5.12
			3.42			0.60	3.06	5.10
Acetic acid–acetate buffer	CTAB	Micellar	4.63	1×10^{-4}	1×10^{-2}	0.50	2.06	4.12
		Micellar	4.63		1×10^{-3}	0.59	2.37	4.02
			3.72			0.64	2.57	4.02
			3.42			0.66	2.65	4.01
		Premicellar	4.63		1×10^{-4}	0.61	3.34	5.47
			3.72			0.64	3.43	5.34
			3.42			0.65	3.51	5.40
Acetic acid–acetate buffer	Triton X-100	Micellar	4.63	1×10^{-4}	2.4×10^{-3}	0.56	2.62	4.68
			3.72			0.61	2.87	4.70
			3.42			0.63	3.03	4.81
		Micellar	4.63		2.4×10^{-4}	0.67	3.10	4.63
			3.72			0.71	3.35	4.72
			3.42			0.73	3.43	4.70
		Premicellar	4.63		2.4×10^{-5}	0.57	3.19	5.60
			3.72			0.60	3.30	5.50
			3.42			0.62	3.44	5.55

[a] For the quantum yields of the products (ϕ values), averages of at least three independent experiments are reported in all the tables.

Table 3
Photolysis of $[Co(NH_3)_4C_2O_4](ClO_4)$ encaged in the inner water core of inverted micelles (excitation wavelength, 254 nm; time of irradiation, 5 min; temperature, 35 °C). $\phi_{Co^{2+}}$ as a function of the water content of inverse micellar systems

Concentration of complex (mol dm^{-3})	Medium	Microenvironment	Water content (v/v) (%)	$[H_2O]/[AOT]$ or $[CTAB]$	$\phi_{Co^{2+}}$
1×10^{-4}	AOT/heptane/water microemulsion	Inner core of inverted micelles filled with acetic acid–acetate buffer	2.0	11.5	0.22
			2.8	16.0	0.27
			4.0	23.1	0.29
1×10^{-4}	CTAB/chloroform–isooctane/water microemulsion (volume ratio of chloroform and isooctane, 2 : 1)	Inner core of inverted micelles filled with acetic acid–acetate buffer	1.1	8	0.30
			1.3	10	0.33
			1.7	12	0.37
1×10^{-4}	Acetic acid–acetate buffer (pH 4.63)	Homogeneous (bulk aqueous phase)	–	–	0.52

remain trapped in the inner water pool of inverse micellar systems and, as a result, the local concentration of the complex is 25–50 times the apparent overall concentration of 1×10^{-4} mol dm^{-3}. Therefore a considerable fraction of the excited complex ions dissipate energy via self-quenching and this factor may be partly responsible for the decreased quantum yield of Co^{2+} in inverse micellar systems.

The size of the water pool in the centre (core) is controlled by the ratio $[H_2O]/[AOT]$ or $[H_2O]/[CTAB]$; the pool size increases as the ratio increases. The increase in $\phi_{Co^{2+}}$ with increasing pool size or water content is due to the fact that, at higher water contents, there are more free water molecules so that the water properties resemble those of ordinary/bulk water. From this viewpoint, the quantum yield of Co^{2+} in inverse micellar microemulsions may be considered as a sensor of the rigidity of the inner water core.

4. Conclusion

The photolytic behaviour of $[Co(NH_3)_4C_2O_4]^+$ is extremely sensitive to the presence of surfactants in the medium.

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References

[1] D.G. Whitten, R.C. Russel and R.H. Schmehl, *Tetrahedron, 38* (1982) 2455.

[2] J.K. Thomas, *Chem. Rev., 80* (1980) 283.

[3] N. Ramnath, V. Ramesh and V. Ramamurthy, *J. Photochem., 31* (1985) 75.

[4] N.J. Turro, *Proc. Natl. Acad. Sci. USA, 80* (1983) 609.

[5] J.C. Russel, S.B. Costa, R.P. Seiders and D.G. Whitten, *J. Am. Chem. Soc., 102* (1980) 5678.

[6] N.J. Turro and M. Aikawa, *J. Am. Chem. Soc., 102* (1980) 4866.

[7] K. Kalyanasundaram, F. Grieser and J.K. Thomas, *Chem. Phys. Lett., 51* (1977) 501.

[8] C.A. Backer, J.R. Corvan-Cowdery, S.P. Spooner, B. Amritage, G.L. McLendon and D.G. Whitten, *J. Surf. Sci. Technol., 6* (1990) 59.

[9] D.A. Lerner, M.B. Quintal, P. Maillard and C. Giannotti, *J. Chem. Soc., Perkin Trans. 2, 7* (1990) 1105.

[10] L. Papula, O. Horvath and S. Papp, *J. Photochem. Photobiol. A: Chem., 54* (1990) 205.

[11] W.J. Dressick, K.W. Raney, J.N. Demas and B.A. DeGraff, *Inorg. Chem., 23* (1984) 875.

[12] S.J. Atherton, *J. Phys. Chem., 88* (1984) 2840.

[13] R.H. Schmehl and D.G. Whitten, *J. Phys. Chem., 85* (1981) 473.

[14] K. Chandrasekaran, T.K. Foreman and D.G. Whitten, *Nouv. J. Chim., 5* (1981) 275.

[15] M. Mori, M. Shabita, E. Kyuno and K. Hoshiyana, *Bull. Chem. Soc. Jpn., 31* (1958) 291.

[16] C.G. Hatchard and C.A. Parker, *Proc. R. Soc. London, Ser. A, 235* (1956) 518.

[17] R.E. Kitson, *Anal. Chem., 22* (1950) 664.

[18] A. Vogler and A.W. Adamson, *J. Phys. Chem., 74* (1970) 67.

[19] S. Saha, Photochemistry of cobalt(III) complexes in microheterogeneous media, *Ph.D. Thesis*, University of Calcutta, India, 1993.

[20] O. Horvath, L. Papula, B. Kraut and S. Papp, *J. Photochem. Photobiol. A: Chem., 47* (1989) 91.

[21] M. Wong, J.K. Thomas and M. Gratzel, *J. Am. Chem. Soc., 98* (1976) 2391.