Monatsh Chem (2010) 141:309–316
DOI 10.1007/s00706-010-0253-0

ORIGINAL PAPER

Synthesis, characterization, and electron transfer reaction of some surfactant–cobalt(III) complex ions

K. Sasikala · S. Arunachalam

Received: 29 May 2009 / Accepted: 7 January 2010 / Published online: 12 February 2010

Abstract The surfactant complex ion *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$ (tmd = 1,3-propanediamine, $C_{12}H_{25}NH_2$ = dodecylamine) has been synthesized and characterized by elemental analysis and spectral data. In addition we have determined the critical micelle concentration of the surfactant–cobalt(III) complex and studied the kinetics and mechanism of the complex with ferrocyanide anion. The reaction is found to be second order, and the second-order rate constant increases with increasing initial concentration of the surfactant–cobalt(III) complex due to the presence of self-micelles formed by the complex itself. The thermodynamic parameters were determined. The results have been analyzed.

Keywords Surfactant–cobalt(III) complex · Self-micelles · Critical micelle concentration · Electron transfer

Introduction

Surfactants are often used in the formulations of pesticides and herbicides [1]. They have also found a wide range of applications because of their unique solution properties such as detergency, solubilization, and surface wetting capabilities in diverse areas such as chemical as well as biochemical research [2] and as catalysts in several organic and inorganic reactions [3]. Surface-active materials are major building blocks of many physical, chemical, and biological systems. They have been introduced into several commercial products such as antiseptic agents in cosmetics and as germicides [4], and have also found a wide range of applications in diverse areas such as mining, petroleum, and pharmaceutical industries. It has been observed that several redox reactions in micellar media were influenced by the hydrophobic and electrostatic forces and, for a given set of reactions, the observed rate depends on the extent of association between the reactants and micellar aggregates [5–9]. In the course of studies on the effects of metallosurfactants on chemical reactions, catalytic effects were observed above a critical micelle concentration (CMC). Such systems offered the possibility to investigate the effects of the local reactant concentrations in the micellar subphase, as well as the local microenvironment, on the reactivity [10–14]. Cobalt(III) complexes, by virtue of their abundance and diversity, have played a fundamental role in our understanding of the structural, spectroscopic, and electrochemical properties of coordination compounds. We have been interested in the synthesis and micelle-forming properties of cobalt(III) complexes containing lipophilic ligands for a long time [15–18]. Gaswick et al. have reported that the hexacyanoferrate(II) anion can reduce some pentaamine cobalt(III) complexes to cobalt(II) via an outer-sphere electron transfer step [19], and they have also reported that the substituted pentaaminecobalt(III) complexes could be reduced by hexacyanoferrate(II) with the formation of an ion pair [20]. It has been postulated that the ion pair was approached by $Fe(CN)_6^{4-}$ on the ammonia side of the cobalt(III) complexes. In spite of the great effort and success in the study of metallosurfactants of cobalt(III) complexes, such complexes still attract much attention due to their interesting properties and the relative simplicity of their synthesis. To the best of our knowledge no previous

---

K. Sasikala · S. Arunachalam (✉)
School of Chemistry, Bharathidasan University,
Tiruchirappalli 620 024, TN, India
e-mail: arunasurf@yahoo.com

K. Sasikala
e-mail: s.sasi1981@gmail.com

studies to find electron transfer reactions of surfactant–cobalt(III) complexes containing double-chain metallosurfactants with $Fe(CN)_6^{4-}$ have been published. Also the ligand 1,3-propanediamine reacts faster with cobalt(III) complexes than do other ligands such as triethylenetetramine, phenanthroline, and bipyridine. From this point of view the results presented herein are of interest. In the present study we have realized the synthesis, characterization, and CMC determination of a novel surfactant–cobalt(III) complex containing a single, long-chain amine as one of the coordinating ligands. Also we report our studies of electron transfer reactions of this surfactant–cobalt(III) complex with $Fe(CN)_6^{4-}$ under various conditions.

Results and discussion

Spectroscopic characterization

The surfactant–cobalt(III) complex synthesized in the present study was characterized by UV–Vis, IR, and NMR techniques. The purity of the complex was checked by Co, C, N, H analysis, and the results were found to be in good agreement with the calculated values.

Visible absorption spectrum

The visible absorption spectrum (Fig. 1) of this complex shows a maximum at 503 nm with an extinction coefficient ε of 71 $mol^{-1}\ dm^3\ cm^{-1}$, comparing well with spectrum of the corresponding butylamine complex [21]. This shows that both the ordinary and the surfactant complexes have the same structure and the replacement of lower aliphatic amine ligands by long-chain aliphatic amines does not affect the symmetry of the surfactant complex.

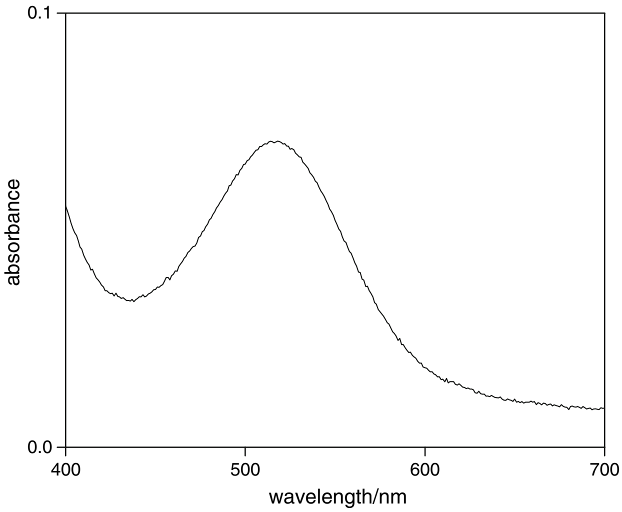


Fig. 1 Electronic absorption spectra of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$

IR spectrum

The infrared spectrum was used for the assignment of the geometrical configuration of the complex. Buckingham and Baldwin have studied the NH_2 deformation mode in the 1,700–1,500 cm^{-1} region, the CH_2 rocking mode in the 900–850 cm^{-1} region, and the Co–N stretching mode in the 610–500 cm^{-1} region to distinguish between *cis* and *trans* isomers of cobalt(III) ethylenediamine complexes [25–28], reporting that the important variations between the *cis* and *trans* isomers are found in the CH_2 rocking region 900–850 cm^{-1}. *Trans* isomers always show only one peak, and *cis* isomers occur as shoulders. Because of the lower-symmetry *cis* configuration, our complex (Fig. 2) shows two bands for NH_2 deformation in the 1,630–1,580 cm^{-1} region, two bands for NH_2 wagging in the 1,120–1,156 cm^{-1} region, the CH_2 rocking mode in the 940–830 cm^{-1} region, and two bands for Co–N stretching in the 760–550 cm^{-1} region.

^1H NMR spectra

In the ^1H NMR spectrum of our complex (Fig. 3a), the amine protons of 1,3-propanediamine appear as a singlet at 3.5 ppm and, due to the lower symmetry, the methylene protons of 1,3-propanediamine show a more complex absorption around 2.1–2.9 ppm. The methylene protons of the dodecylamine moiety give rise to a multiplet, usually at 1.2–1.8 ppm.

^{13}C NMR spectra

Oulaghan [21, 22] studied the ^{13}C NMR spectra of a number of cobalt(III) complexes with flexible tetraamine ligands, showing the expected six resonance signals for the tetraamine. They distinguished the *trans*- and *cis*-complexes by differences in their chemical shift, considering that these differences can be attributed to the different environments of the carbon atoms in the complex. In the ^{13}C NMR spectrum of our surfactant–cobalt(III) complex (Fig. 3b, c), for the 1,3-propanediamine six signals are observed. For dodecylamine, the aliphatic methylene carbons of all the complexes appear around 22–40 ppm and the terminal carbon atoms appear at 14 ppm.

Uniqueness of the surfactant–cobalt complex

The uniqueness of the surfactant–cobalt(III) coordination complex lies in the fact that the bond between the head

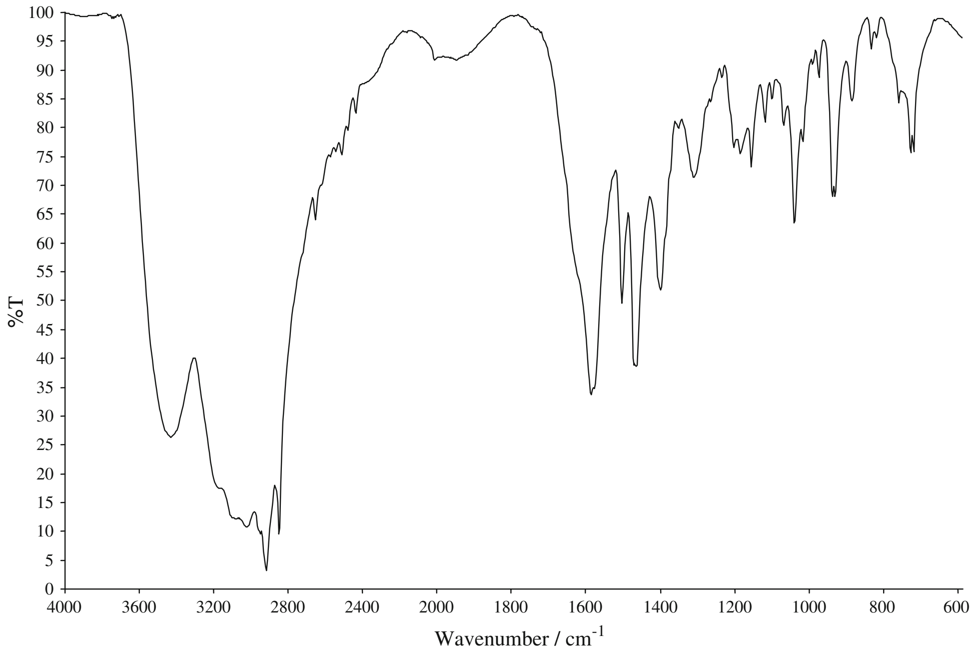


Fig. 2 IR spectrum of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$

group and the tail part of the surfactant–cobalt(III) complex is a coordinate bond and the surfactant contains a higher charge on the head group, unlike common surfactants such as sodium dodecyl sulfate. At the same time, like common surfactants, this surfactant–cobalt(III) coordination compound forms foams in aqueous solution when mechanically disturbed, e.g., by shaking, and this complex dissolves slowly in water, though sometimes we had to sonicate the solution to get a homogeneous solution.

Critical micelle concentration values

The CMC value of the surfactant–cobalt(III) complexes was computed from the plot of concentration of cobalt(III) complex versus specific conductance (Fig. 4). The complex concentration at which the micellization starts is evident from the change in the slope of the plot, and that particular concentration is the CMC under experimental conditions. The CMC value was determined by fitting the data points above and below the break to two equations of the form $y = mx + c$ and solving the two equations simultaneously to obtain the point of intersection. Least-squares analysis was employed, and correlation coefficients were greater than 99%. The CMC value thus obtained for our complex is 3.5×10^{-4} mol dm^{-3}.

Electron transfer kinetics

Nature of reaction

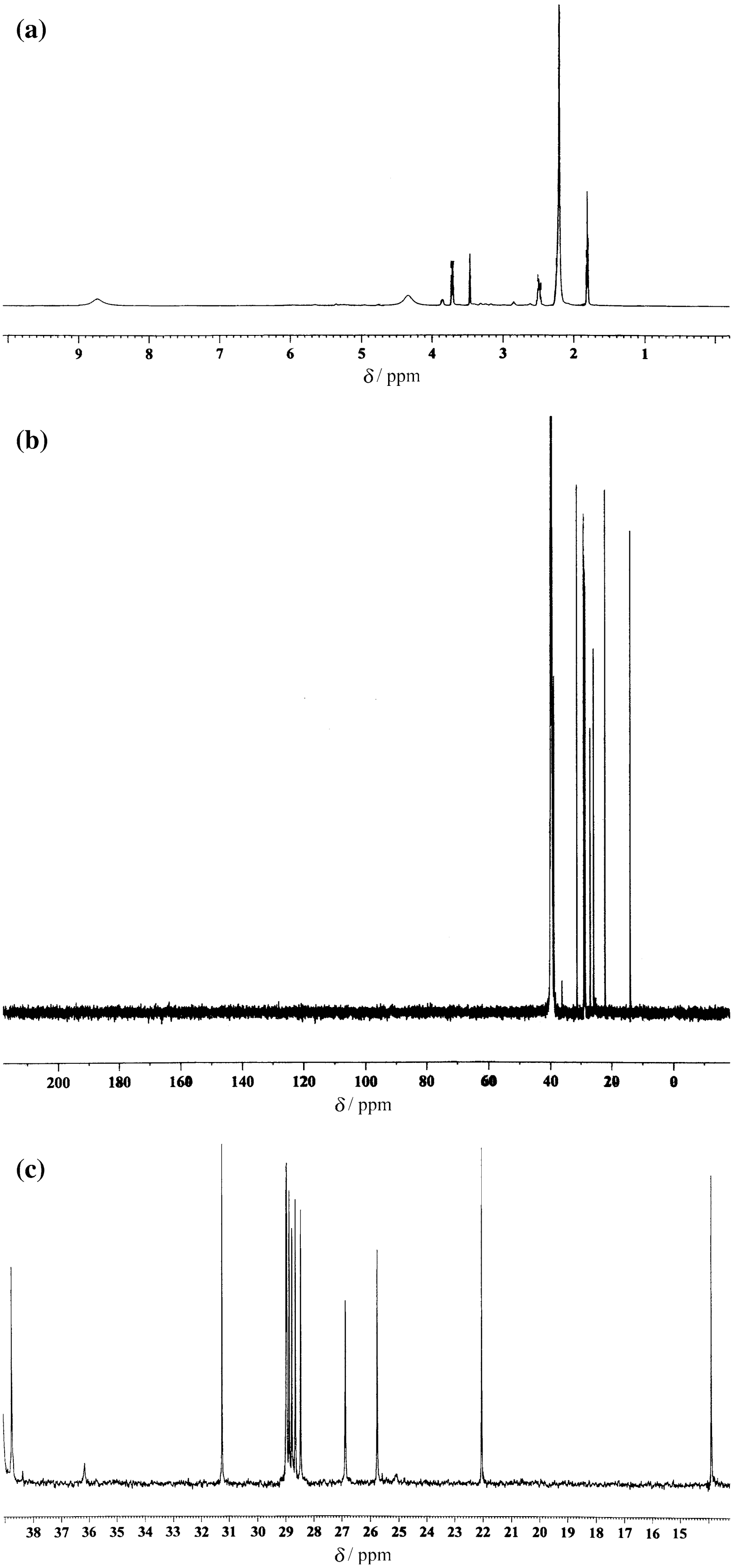
On mixing $Fe(CN)_6^{4-}$ and surfactant–cobalt(III) complex in aqueous solution a precipitate was formed and therefore homogeneous kinetic measurements were precluded. However when disodium dihydrogen ethylenediaminetetraacetate (Na_2H_2EDTA) was added to the solution, no precipitate was produced [19]. A repetitive scan of the spectrum during the reaction time at 25 °C is shown in Fig. 5, where an increase in absorbance is observed.

Effect of concentration

The electron transfer rate of the reaction is such that the process must be of outer-sphere type [19, 20, 29–34]. The most favorable mechanism for the second-order reaction is an outer-sphere electron transfer process which consists of three elementary steps (Scheme 1): ion pair formation (K_{ip}), electron transfer (K_{et}), and product successor dissociation.

The values observed for the second-order rate constants are summarized in Table 1. As seen from this table the rate constant increases with increasing initial concentration of the surfactant complex. All these values correspond to rate constant values in self-micelles formed from one of the reactant molecules themselves. Thus the surfactant–cobalt(III) complex molecules act both as one of the reactants as well as part of the micellar environment. So, when the concentration of the surfactant complex is increased above the CMC, the number of micelles also increases in the medium. This is the case at each concentration of the surfactant–cobalt(III) complex, because for different concentrations of micelles the medium environment can be considered as different. So in our case we encounter this peculiar behavior of dependence of the rate constant of the reaction on the initial concentration of one of the reactants, namely the surfactant–cobalt(III) complex.

Fig. 3 **a** ^{1}H NMR spectrum of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$. **b** ^{13}C NMR spectrum of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$. **c** ^{13}C NMR spectrum of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$ (range = 15–38 ppm)



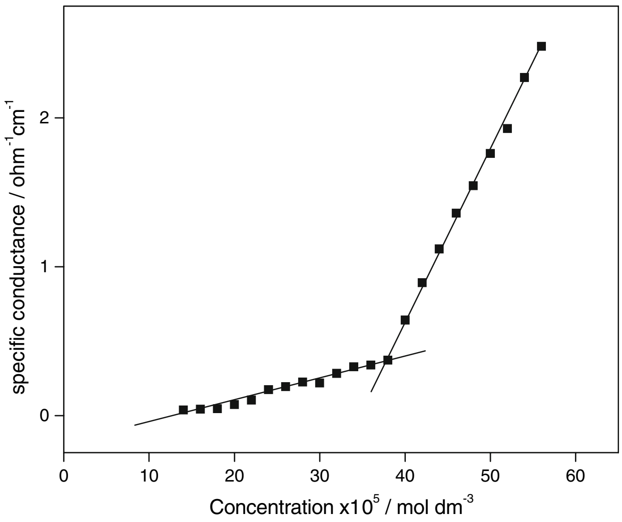


Fig. 4 CMC plot: specific conductance versus concentration of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$ in aqueous solution at 298 K

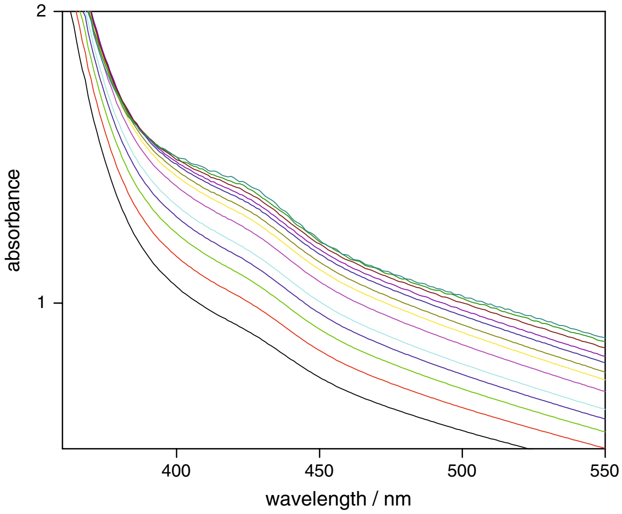
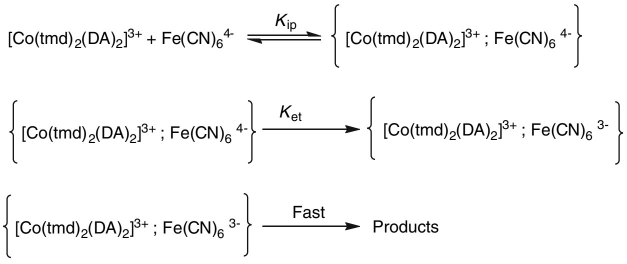


Fig. 5 Repetitive scan for the reduction of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$ by $Fe(CN)_6^{4-}$ at 298 K, [complex] = 4 × 10^{-4} mol dm^{-3}, $[Fe(CN)_6^{4-}]$ = 0.01 mol dm^{-3}, cycle time = 60 s



Scheme 1

Table 1 Second-order rate constants for the reduction of [Co(III)] by $[FeCN_6^{4-}]$ in aqueous solution at 298 K

Oxidizing agent	[Co(III)] × 10^4 (mol dm^{-3})	*k* (mol^{-1} dm^3 s^1)
cis-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$	4	0.8
	5	1.8
	6	2.6
	7	3.7
	8	5.6

Table 2 Thermodynamic parameters

Oxidizing agent	[Complex] × 10^4 (mol dm^{-3})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1})
cis-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$	4	8.3	−79.4
	5	20.9	−38.8
	6	26.1	−20.4

The increase in the rate constant of the outer-sphere electron transfer reaction with increasing concentration of the complex may be attributed to aggregation of this metal complex in its own self-micelles. As this reaction is considered equivalent to intramolecular electron transfer reactions (rather than collisional contact electron transfer) with larger average separation between the reactants due to the statistical distribution of $Fe(CN)_6^{4-}$ ions in the Stern layer of the self-micelles of the cobalt(III) complex, a higher number of micelles at higher initial concentration of the cobalt(III) complex enhances the rate constant of the reaction.

Effect of temperature

The effect of temperature on the rate was studied at three different temperatures (303, 308, and 313 K; Table 2) in order to obtain the activation parameters for the reaction between cobalt(III) surfactant complexes and $Fe(CN)_6^{4-}$. Figure 6 shows that increasing the temperature increases the rate of the electron transfer reactions of the surfactant–cobalt(III) complexes.

Isokinetic temperature and activation parameters ($\Delta S^{\#}$ and $\Delta H^{\#}$)

From the transition-state theory, the values of $\Delta S^{\#}$ and $\Delta H^{\#}$ were determined by plotting ln(*k*/*T*) versus 1/*T*. The results obtained are shown in Table 2.

$$\ln k/T = \ln K_\mathrm{B}/h + \Delta S^{\#}/R - \Delta H^{\#}/RT.$$

The activation parameters were calculated from *k* at 303, 308, and 313 K using the Eyring relationship by the method of least squares and are collected in Table 2. From the slope the value of $\Delta H^{\#}$ was calculated and from the intercept the value of $\Delta S^{\#}$ was calculated. The negative value of $\Delta S^{\#}$ is due to the more ordered structure of the transition state that is a compact ion pair (step 1 in Scheme 1), in which the opposite charges, namely 3+ on

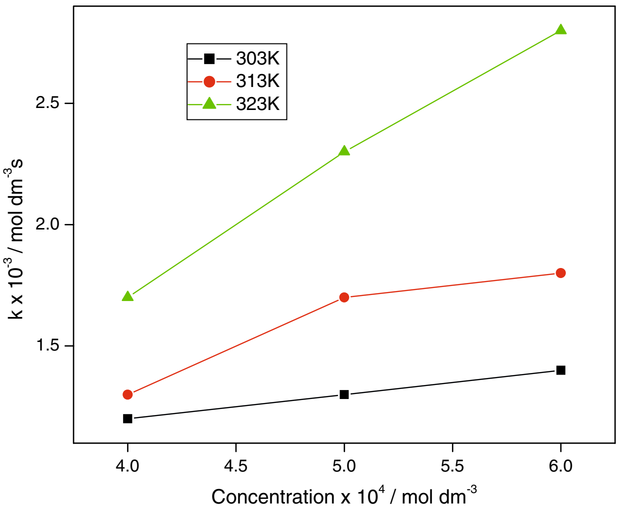


Fig. 6 Plot of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$ versus k at 303, 308, and 313 K. $[Fe(CN)_6^{4-}] = 0.01$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3}

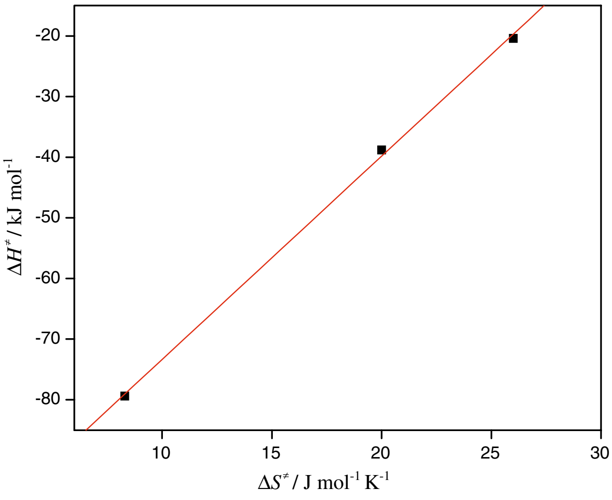


Fig. 7 Isokinetic plot of the activation parameters for the reduction of *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2]^{3+}$ by $Fe(CN)_6^{4-}$

the surfactant–cobalt(III) complex and 4− on the $Fe(CN)_6^{4-}$, reside in one single entity (of the ion pair). Hence, such a situation leads to more attraction of surrounding solvent molecules around the positive and negative charges on the ion pair, itself resulting in the loss of freedom of movement of the solvent molecules in the transition state, thus exhibiting electrostriction as reflected in the $\Delta S^{\#}$ values.

This proposed mechanism is confirmed by the isokinetic plot (Fig. 7). The isokinetic temperature can be calculated from the slope of the following equation:

$$\Delta H^{\#} = \Delta H^{0} + \beta \Delta S^{\#}.$$

The isokinetic temperature is the temperature at which all compounds react fast. Also, at the isokinetic temperature, variation of substituent has no influence on the free energy of activation. In an isoentropic oxidation, the isokinetic temperature lies at infinity and only the enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic reaction, and the reactivity is determined by the entropy of activation [35]. In the present reduction reaction the enthalpy of activation is linearly related to the entropy of activation, and the isokinetic temperature is 335 K. Below this temperature the reaction is controlled by the enthalpy of activation $\Delta H^{\#}$, and above this temperature the reaction is controlled by the entropy of activation $\Delta S^{\#}$. From the isokinetic plot it is concluded that a common mechanism exists, and it was evident that the reaction of surfactant–cobalt(III) complex and the ferrocyanide anion is an outer-sphere electron transfer reaction.

Conclusion

The presence of a metal complex in the hydrophobic part of an amphiphile increases the ability for aggregation. The CMC value of the surfactant–cobalt(III) complex is very small compared with that of the simple organic surfactant dodecylammonium chloride (CMC = 1.5×10^{-2} mol dm^{-3}) [15, 16]. We therefore conclude that the surfactant–metal complexes have greater capacity to associate with themselves.

Experimental

Materials

Cobaltous chloride hexahydrate and dodecylamine used for the synthesis of the surfactant–cobalt(III) complex were purchased from Merck, India. Sodium perchlorate was obtained from Fluka and was used as such. $K_4[Fe(CN)_6]$ and EDTA (disodium salt) of AR grade were obtained from Merck. Milli-Q water was used in all our studies.

Synthesis of the surfactant–cobalt(III) complex

The surfactant–cobalt(III) complex *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2](NO_3)_3$ was synthesized from the precursor complex, *trans*-$[Co(tmd)_2Cl_2]ClO_4$ by a similar method to the same type of ordinary complexes reported in the literature [21, 22], except in the place of lower amines, dodecylamine was used. *Trans*-$[Co(tmd)_2Cl_2]ClO_4$ (3.0 g) was dissolved in 20 cm^3 water. To this solution slightly more than the calculated amount of dodecylamine (4.3 cm^3) in 3 cm^3 ethanol was added dropwise over a period of 30 min. The green solution gradually became red and the mixture was set aside at 40 °C for 2 days until no further change was observed. Afterwards a saturated solution of sodium nitrate was added. Slowly the complex *cis*-$[Co(tmd)_2(C_{12}H_{25}NH_2)_2](NO_3)_3$ was separated as a pasty solid mass and was filtered off, washed with small amounts of alcohol and acetone, and then dried over air. The semidried solid was further dried in a drying pistol over fused calcium chloride and stored in a vacuum desiccator. UV–Vis: $\lambda_{\max}(\varepsilon) = 503$ (71) nm (mol^{-1} dm^3 cm^{-1}); IR (KBr): $\bar{\nu} = 1{,}630-1{,}580$ (NH_2 deform), 1,120–1,156 (NH_2 wagging), 940–830 (CH_2 rock mode), 760–550 (Co–N stretch) cm^{-1}.

Instrumentation and physical methods

CHN analysis of the sample was carried out at SAIF, Lucknow, India. UV–Vis absorption spectra were recorded on a Varian cary 500 scan UV–Vis–NIR spectrophotometer using cuvettes of 1 cm path length, and the FT-IR spectra were recorded on a FT-IR Perkin Elmer spectrophotometer with samples prepared as KBr pellets. NMR spectra were recorded in appropriate deuterated solvents using a Bruker AC 500F (500 MHz) spectrometer with TMS as internal reference. Conductivity measurements were taken using a Elico conductivity bridge-type CM 180 and dip-type cells with cell constant of 1.0.

CMC determination

The critical micelle concentration value of the surfactant–cobalt(III) complex was measured conductometrically. Various concentrations of surfactant–cobalt(III) complexes were used in the range of 1×10^{-5} to 1×10^{-1} mol dm^{-3} in aqueous solution. The conductivity cell was calibrated with KCl solutions in the appropriate concentration range.

Kinetic measurements

The rate of the reaction was measured spectrophotometrically using a Varian cary 500 scan UV–Vis–NIR spectrophotometer equipped with a water Peltier system (PCB 150). The temperature was controlled within ±0.01 °C. A solution containing the desired concentration of potassium ferrocyanide, sodium nitrate, and disodium ethylenediaminetetraacetate (Na_2H_2EDTA) in oxygen-free water was placed in a 1-cm cell, which was then covered with a serum cap fitted with a syringe needle. This cell was placed in a thermostated compartment in the spectrophotometer and then the solution containing the surfactant–cobalt(III) complex was added anaerobically using the syringe. The absorbance at 420 nm was recorded as a function of time. The second-order rate constant, *k*, for the Fe(II) reduction of the cobalt(III) complex defined by $-d[Co(III)]/dt = k[Co(III)][Fe(CN)_6^{4-}]$ was calculated from the concentration of iron(II) and the slope of the $\log(A_t - A_\alpha)$ versus time plot, which is equal to $-k[Fe(CN)_6^{4-}]/2.303$, where A_t is the absorbance at time *t*, A_α is the absorbance after all the cobalt(III) complex has been reduced to cobalt(II), and *k* is the second-order rate constant. Usually the value of A_α was measured at times corresponding to ten half-lives. All the first-order plots were substantially linear for at least five half-lives, with a correlation coefficient of >0.999. Each rate constant reported is the average result of triplicate runs. Rate constants obtained from successive half-life values within a single run agreed to within ±5%. The stoichiometry of the reaction was determined by measuring spectrophotometrically the concentrations of Fe(III) and Co(II) ions produced from equimolar mixtures of the reactants after completion of reaction.

Stoichiometry

The stoichiometry of the reactions was determined by estimating Fe(III) and Co(II) present in the product mixture. Fe(III) was determined spectrophotometrically by Kitson's method [23], and Co(II) was determined [24] as $[CoCl_4]^{2-}$ at 690 nm in an excess of HCl. The ratio of Fe(III) to Co(II) was found to be 1:1 in the reactions studied, indicating 1:1 stoichiometry.

Acknowledgments We are grateful to the UGC-SAP & COSIST and DST-FIST programmes.

References

1. Scramm LL, Stasiuk EN, Marangoni DG (2003) Annu Rep Prog Chem Sect C 99:3
2. Rosen MJ (2004) Surfactants and interfacial phenomenon, 3rd edn. Wiley, New Jersey
3. Fendler JH, Fendler EJ (1975) Catalysis in micellar and macromolecular systems. Academic, New York
4. Tadros TF (2005) Applied Surfactants, 1st edn. Wiley-VCH, Germany
5. Majumdar T, Mahapatra A (2005) Colloids Surf A 302:360
6. De la Vega R, Tejeda PP, Cornejo PL, Sanchez F (2004) Langmuir 20:1558
7. Cornejo PL, Perez P, Garcia F, de la Vega R, Sanchez F (2002) J Am Chem Soc 124:5154
8. Cornejo PL, Hernandez M, Tejeda PP, Perez F, Gotor RP, Sanchez F (2005) J Phys Chem B 109:1703
9. Gotor RP, Jimenez R, Lopez P, Perez P, Herrera CG, Sanchez F (1998) Langmuir 14:1539
10. Qiu L, Xie J, Shen YH (2006) J Mol Catal A Chem 244:58
11. Ying M, Jiang F, Wei H, Meng X, Yu X, Zeng X (2006) J Dispers Sci Technol 27:15

12. Xie J, Cheng S, Jiang B, Juan D, Hu C, Zeng X (2004) Colloids Surf A 235:137
13. Yan X, Jiang B, Zeng X, Xie J (2002) J Colloid Interface Sci 247:366
14. Santhakumar K, Kumaraguru N, Arunachalam S, Arumugham MN (2006) Int J Chem Kinet 38:98
15. Arumugam MN, Arunachalam S (1997) Indian J Chem 36A:84
16. Arumugam MN, Arunachalam S (1997) Indian J Chem 36A:315
17. Santhakumar K, Kumaraguru N, Arunachalam S, Arumugham MN (2006) Polyhedron 25:1507
18. Kumaraguru N, Arunachalam S, Arumugham MN, Santhakumar K (2006) Transition Met Chem 31:250
19. Gaswick D, Haim A (1971) J Am Chem Soc 93:7347
20. Miralles AJ, Szecsy AP, Haim A (1982) Inorg Chem 21:697
21. Oulaghan BM, House DA (1978) Inorg Chem 17:2197
22. Arulsamy N, Bohle DS, Goodson PA, Jaeger DA, Reddy VB (2001) Inorg Chem 40:836
23. Kitson RE (1950) Anal Chem 22:664
24. Linck RG (1970) Inorg Chem 9:2529
25. Buckingam DA, Jones D (1965) Inorg Chem 4:1387
26. Baldwin ME (1960) J Chem Soc 4369
27. Kipp EB, Haines RA (1969) Can J Chem 47:1073
28. Morris ML, Busch DH (1960) J Am Chem Soc 82:1521
29. Holder AA, Dasgupta TP (2002) Inorg Chim Acta 331:279
30. Bansch B, Martinez P, Van Eldik R (1992) J Phys Chem 96:234
31. Miralles AJ, Armstrong RE, Haim A (1977) J Am Chem Soc 99:1416
32. Kustin K, Epstein IR (1990) J Chem Soc Dalton Trans 971
33. Poonkodi SPR, Anbalagan K (2001) Transition Met Chem 26:212
34. Karthikeyan G, Anbazalagan K, Elango KP (2000) Transition Met Chem 25:213
35. Karunakaran C, Chidambaranathan V (2001) Croat Chem Acta 74:51