SYNTHESIS, CHARACTERIZATION AND DETERMINATION OF CRITICAL MICELLE CONCENTRATION (CMC) VALUES OF SOME MIXED-LIGAND COMPLEXES OF COBALT(III)-DPPZ METALLOSURFACTANTS

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Abstract: Surface active mixed-ligand complexes of metallosurfactnt Cobalt(III) containing the chelating ligand dipyrido(3,2-a-2'-3'-c)phenazine (dppz) as equatorial and with different axial amine ligands (dodecylamine or cetylamine) were synthesised (cis-$[Co(dppz)_2AX]^{2+}$ and cis-$[Co(dppz)_2A_2]^{3+}$ (dppz = dipyrido(3,2-a-2'-3'-c)phenazine, A = Dodecylamine or Cetylamine, X = Cl)) and characterized by UV-Visible, IR, NMR and elemental analysis. The critical micelle concentration (CMC) values of these metallosurfactant complexes in aqueous solution were determined as a function of temperature using conductometric technique. The specific conductivity data (at 298, 303, 308 and 313 K) and thermodynamics of micellization (ΔG_m^0, ΔH_m^0 and ΔS_m^0) were evaluated.

Keywords: Metallosurfactants, Cobalt(III)-dppz, CMC, Micelles, Mixed-ligand complexes

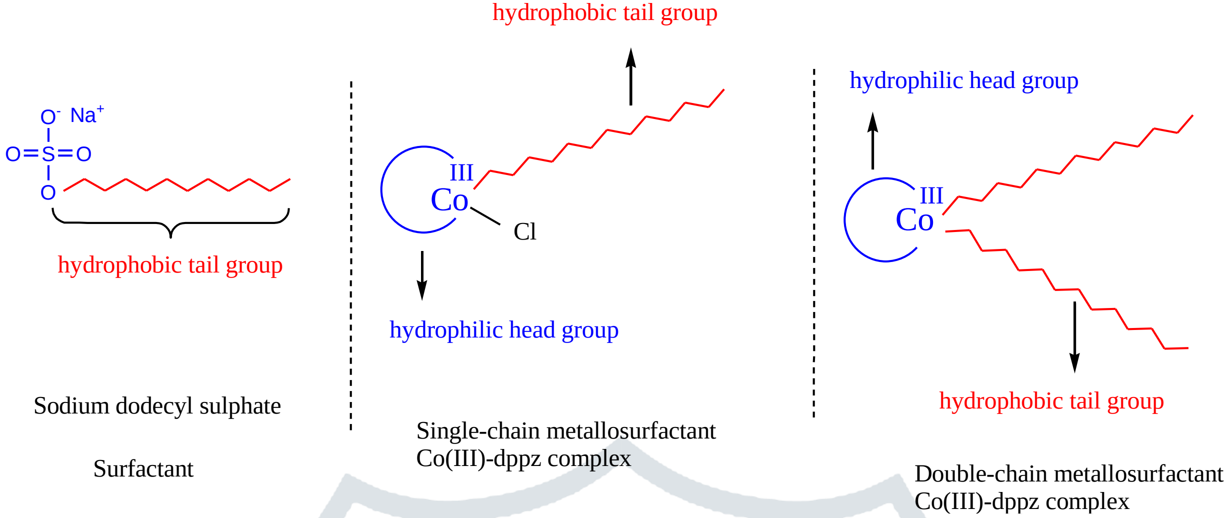
1. INTRODUCTION

Studies on the chemistry of metallosurfactant of cobalt-(III) complexes have received a substained high level of attention from the scientific community for the last few decades [1–6] due to their relevance in various redox processes in biological systems, and act as promising agents for anthelmintic [7], antiparasitic [8] and antibiotics [9] . Metallosurfactants are special type of surfactant where a coordination complex (containing a central metal ion with surrounding ligands coordinated to the metal) acts as the surfactant.

The micellization of surfactant molecules under different experimental conditions continues to be of great interest, primarily on account of their wide range of industrial applications [10-14]. Surfactants, some times called surface-active agents or detergents, are among the most versatile chemicals available. Surfactants are amphiphilic molecules consisting of a hydrophilic head group and a hydrophobic (lipophilic) tail, and are thus able to interact with both polar and non-polar compounds (scheme 1). They are characterized by a wide variety of morphology of aggregates formed by the self assembly of surfactant molecules in aqueous solution to form micelles, where their properties are different from those of the nonaggregated monomer molecules. It is well-known from studies on single-chain surfactants that the counterion has a strong influence on the critical micelle concentration, aggregation number and size and shape of aggregates of ionic surfactant systems [15-19].

We are interested in the synthesis and micelle forming properties of several metal complexes containing lipophilic ligands for a long time [20-23]. As in biology, such compounds may exhibit novel physical and chemical properties with interesting and useful associated applications. A feature of modern coordination chemistry is its expanding ability to mimic form and structure in biology. This has largely been achieved using a principle which has itself been borrowed from biology: the self-assembly of well-defined and complex molecular entities from constituent subunits in solution. Unlike biology, however, self-assembly in coordination chemistry occurs through the formation of coordinate bonds rather than weak inter- or intramolecular interactions. Self-assembly in coordination chemistry consequently provides an important and powerful entry into supramolecular engineering and the associated fields of solid-state and crystal engineering [24-25].

A characteristic feature of transition metals is their ability to form complexes with a variety of neutral molecules such as 2,2'-Bipyridine (*bpy*) and 1,l0-phenanthroline (*phen*). They are simple polypyridine compounds which serve as effective chelating agents for metal ions; the photophysics and photochemistry of complexes of these ligands are under active investigation with particular interest in their application to solar energy conversion schemes. These are widely used as a classical N,N'-bidentate ligand to prepare mixed-ligand complexes in coordination chemistry. A common feature of these ligands is the presence of a vacant π orbital that can accept electron density from the metal ion to form a type of π bonding that supplements the σ bonding arising from the donation of lone pair of electrons. Most of the metal complexes containing *bpy* and *phen* chelators can act as potential anti-tumor agents [26] and a boost of interest because of their multiple applications in fields such as medicine [27], magnetic resonance imaging [28] and drug delivery [29]. Intensive investigations of the coordination chemistry of metallosurfactants with chelating ligands continue to be stimulated by interest for metallobiomolecules, the search for appropriate systems for binding and activating simple molecules, catalysis, and magnetic interactions [30]. In spite of the greatest effort and success in the study of metallosurfactants of cobalt(III) complexes, such complexes have still attracted much attention due to their interesting properties and the relative simplicity of their synthesis. As a part of our studies on transition metal-based surfactants [20-24, 30, 31] in this paper we report the synthesis, characterization and determination of critical micelle concentration values of some more novel metallosurfactant Co(III)-dppz complexes.



Sodium dodecyl sulphate

Surfactant

Single-chain metallosurfactant
Co(III)-dppz complex

Double-chain metallosurfactant
Co(III)-dppz complex

Scheme 1 : Structure of surfactant and metallosurfactant

2. EXPERIMENTAL

2.1. Materials

All the reagents were of analytical grade (Aldrich and Merck). Ultra pure water, obtained by deionising distilled water (conductivity < 10^{-6} S m^{-1}) using a Milli-Q Reagent Grade water system, was used for preparative work and to make up solutions for all physical measurements.

2.2. Physical measurements and methods

Electronic absorption spectra were taken in 10^{-3} M perchloric acid medium recorded in a Varian Cary 500 Scan UV-Vis-NIR spectrophotometer. Infrared (IR) spectra were recorded on a Jasco 460 plus spectrometer using the KBr discs method. ^{1}H NMR spectra were recorded in appropriate deuteriated solvents using a Bruker AC 300F (300 MHz) spectrometer with TMS as internal reference. C, H and N were estimated using a Perkin Elmer 2400 CHN instrument. Conductance measurements were carried out in aqueous solutions of complexes with a Elico conductivity bridge type CM 82 and a dip-type cell with a cell constant of 1.0.

2.3. Synthesis of single chain metallosurfactant cobalt(III)-dppz complexes

2.3.1. cis-$[Co(dppz)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$ and cis-$[Co(dppz)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$:

cis-$[Co(dppz)_2Cl_2]Cl$ [32], (3 g) was dissolved in water (10 mL). To this solution dodecylamine (1 mL) (1:1 ratio), where the amine used was not sufficiently miscible with (soluble in) water, was first mixed with ethanol (2 mL) and then added drop by drop over a period of 30 min. The dark brown colour solution gradually became pale during the reaction. The mixture was set aside at 313 K for 2 days until no further change was observed. Afterwards a saturated solution of sodium perchlorate in very dilute perchloric acid was added. Slowly a pasty solid mass was separated out and it was filtered off, washed with small amounts of alcohol followed by acetone, and then it was dried over air. The semi-dried solid was further dried in a drying pistol over fused calcium chloride and stored in vacuum desiccator. For the complex *cis*-$[Co(dppz)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$, cetylamine was used in the place of dodecylamine.

2.4. Synthesis of double-chain surfactants of cobalt(III)-dppz complexes

2.4.1. cis-$[Co(dppz)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2.2H_2O$ and cis$[Co(dppz)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2.2H_2O$:

This complex was synthesized by adopting the same method as described for the synthesis of complex *cis*-$[Co(dppz)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2.2H_2O$ except that in place of *cis*-$[Co(dppz)_2Cl_2]Cl$, *cis*-$[Co(dppz)_2Br_2]Br$ [33] was used.

2.4.2. cis-$[Co(dppz)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ and cis-$[Co(dppz)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$:

cis-$[Co(dppz)_2Br_2]Cl$ [33], (3.0 g), was dissolved in water (20 mL). To this solution a slightly more than the calculated amount of dodecylamine (4.3 mL) (1:2 ratio) in ethanol (3 mL) was added drop by drop over a period of 30 min. The dark purple solution gradually became lighter during the reaction and the mixture was set aside for 3 days at 313 K. Afterwards a saturated solution of sodium perchlorate in very dilute perchloric acid was added, filtered off and washed with alcohol followed by acetone and dried. For the complex *cis*-$[Co(dppz)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$, cetylamine was used in the place of dodecylamine.

Safety Note. Caution: Perchlorate salts of metallosurfactant Co(III)-dppz complexes containing organic ligands are potentially explosive! Although we have experienced no problems with the compounds reported in this work, they should only be handled in small quantities and never scraped from sintered glass frits nor heated in the solid state.

2.5. Elemental Analysis

The purity of the complexes was checked by the analysis of carbon, hydrogen, and nitrogen present in them. C, H and N were estimated using a Perkin Elmer 2400 CHN instrument.

2.6. Estimation of Cobalt

A known weight of the complex was taken in a clean dried conical flask and 5ml of concentrated hydrochloric acid was added to it along with a small piece of tin metal. The contents were heated until a blue colour was obtained. The contents were then transferred quantitatively to a 25ml standard flask and made up to the mark with concentrated hydrochloric acid. The cobalt concentration was found out from the absorbance value [34] by assuming the molar absorption coefficient of $[CoCl_4]^{2+}$ at 691 nm as 561 $M^{-1}cm^{-1}$.

2.5. Determination of CMC

CMC values of the complexes were calculated using electrical conductance data measured using a digital conductivity meter (Elico conductivity bridge type CM 82). The conductivity cell (dip-type with a cell constant of 1.0) was calibrated with KCl solutions in the appropriate concentration range. The cell constant was calculated using molar conductivity data for KCl published by Barthel et al. [35]. Various concentrations of metallosurfactant-Co(III)-dppz complexes were prepared in the range 10^{-6}–10^{-3} mol dm^{-3}. All measurements were performed in a double-walled glass container, which was maintained at the desired temperature (± 0.1 K) using a circulating water bath. The conductivity of these solutions was measured at 298, 303, 308 and 313 K. The conductance was measured after thorough mixing and temperature equilibrating at each dilution. The measurement was started with a dilute solution and the subsequent concentrated solutions were prepared by adding a previously prepared stock solution. The establishment of equilibrium was checked by taking a series of reading after 15-min intervals until no significant change occurred.

3. RESULTS AND DISCUSSION

The metallosurfactant cobalt(III)-dppz complexes synthesized in the present study were characterized by UV-Visible, IR and NMR spectra and checked by comparing the spectra with those for the corresponding ordinary complexes where one of the ligands is butylamine instead of dodecylamine/cetylamine and those reported earlier [36]. The purity of the complexes was checked by cobalt analysis [34], elemental, halide analyses, which were found to be in good agreement with that of calculated values (Table 1).

3.1. Spectroscopic characterization

3.1.1. Electronic absorption spectra

The wavelength of the first absorption maximum in aqueous perchlorate medium for each complex is given in Table 1. It has been observed that the absorption spectra [37, 38] of the *cis* and *trans* forms of $[M(en)_2(NH_3)Y]^{n+}$ cations (Y = Cl or H_2O) showed some differences in the longest-wavelength absorption band (d-d transition). The *trans* form showed a lower intensity ($\varepsilon < 50$ M^{-1} cm^{-1}) whereas the *cis* form showed a higher intensity ($\varepsilon > 70$ M^{-1} cm^{-1}). This observation can be used to determine the geometrical configuration of the present cations, whose longest-wavelength absorption maxima were shown in Table 1. Similarly, the position of λ_{max} suggests that the strength of the bidentate ligands follows the order bpy < phen. The lower λ_{max} values for the complexes containing the dppz ligand indicate that in these complexes the basal planes are comparatively more distorted than in the phen containing complexes. By comparing the spectra of the corresponding butylamine complexes it reveals that both the ordinary and the surfactant complexes have the same structure and the replacement of lower aliphatic amine ligands by long chain aliphatic amine ligands does not affect the symmetry of the surfactant complexes. Consequently, it does not seem that micellization greatly influences the structure of the polar head.

3.1.2. Infrared spectra

For the assignment of a geometrical configuration to these complexes, infrared spectroscopy was used. Several attempts have been made to relate differences in infrared spectra to geometrical configuration of complexes. Various workers have employed [39, 40] the NH_2 deformation mode in the 1700-1500 cm^{-1} region, CH_2 rocking mode in the 900-850 cm^{-1} and M-N stretching mode in the 610-500 cm^{-1} region to distinguish between the *cis* and *trans* isomers. Baldwin [39], suggested that the most consistent variations between the spectra of *cis*- and *trans*-isomers were found in the CH_2 rocking region (900-850 cm^{-1}). The *cis*-isomers always show two peaks, whereas the *trans*-isomers usually have only one. Hughes and McWhinnie [40] studied the infrared absorption spectra of several bis(ethylenediamine) complexes and obtained a satisfactory correlation in the 610-500 cm^{-1} region, where M-N stretching modes of the chelate ring occur. Here, no *trans*-isomers had more than three strong bands, while all *cis*-isomers had at least four, sometimes occurring as shoulders. The bands for the *trans* isomers were generally evenly distributed, while those for *cis*-complexes occurred in two groups with a wide separation between them. Because of the lower symmetry in the present study, the *cis* isomers show two bands for the NH_2 deformation, two bands for the NH_2 wagging modes, two bands for CH_2 rocking mode and four bands occurring as groups of two with wide separation for the M-N stretching mode. Complex of the type *cis*$[Co(dppz)X_2]^{n+}$ in the present study shows two bands for the NH_2 deformation in the region 1750-1500 cm^{-1}, two bands for the CH_2 or NH_2 twist mode in the region 1200-980 cm^{-1}, and the CH_2 rock mode in the region 945-850 cm^{-1} appeared as two bands [41]. Strukl et al. [42] and Schilt et al. [43] studied the infrared spectra of several bipyridyl and phenanthroline complexes. They observed that the spectral shape of the *bpy* and *phen* complexes were quite similar, taking into account the similarity of both ligands. In the spectra of the dppz complexes, strong bands were observed in three frequency region namely between 700 and 900 cm^{-1}, between 1100 and 1250 cm^{-1} and between 1400 and 1650 cm^{-1}. Strong bands in the 700-900 cm^{-1} region were attributed to the aromatic hydrocarbons of the dppz ring. The band near 725 cm^{-1} was assigned to the out of the plane motion of hydrogen atoms on the heterocyclic rings and the band near 830 cm^{-1} to the hydrogens on the centre ring. The multiple splitting which these bands exhibit in most of the spectra probably arise from out-of-plane hydrogen motion other than the one in which all atoms move in phase, and also possibly from overtones of low lying fundamentals in resonance.

In the spectra, only one strong band was observed in this region as expected for two identical groups of four hydrogen atoms each. Not much can be said about the bands in the 1100-1250 cm^{-1} region expect that they may arise from in-plane hydrogen deformation motions or possibly ring vibrations. The metallosurfactant Co(III)-dppz complexes, strong bands were observed in three frequency regions namely between 700 and 900 cm^{-1}, between 1100 and 1250 cm-^{1}and between 1400 and 1650 cm^{-1}. Strong bands in the 700–900 cm^{-1} region were attributed to the aromatic hydrocarbons of the dppz ring. The band near 720 cm^{-1} was assigned to the out of the plane motion of hydrogen atoms on the heterocyclic rings and the band near 840 cm^{-1} to the hydrogens on the centre ring. The multiple splitting which these bands exhibit in most of the spectra probably arise from out-of-plane hydrogen motion other than the one in which all atoms move in phase, and also possibly from overtones of low lying fundamentals in resonance. Only three strong bands are present, one near 750 ascribed to out of plane bending of ring hydrogens, and one near 1450 cm^{-1} which is probably a ring frequency, and a ring frequency near 1600 cm^{-1}. Numerous weak bands were observed between 900 and 1350 cm^{-1}. The C=C and C=N stretching vibrations of the heterocyclic ring stem exhibits in the region viz. at 1409, 1446, 1540 and 1567 cm^{-1}. Perchlorate bands at ca. 1100, 920, 625 and 460 cm^{-1} belong to an ionic species; this means that this counter-ion is not involved in the metal-ligand coordination [44]. The IR spectroscopic data therefore clearly indicate a *cis* configuration for the metallosurfactant cobalt(III)-dppz complexes.

3.1.3. ^{1}H NMR spectra

The ^{1}H NMR spectra of the metallosurfactant Co(III)-dppz complexes exhibit patterns similar to those of the bipyridine complexes. The aromatic protons of dppz ligand of the two complexes appeared in the region 7-10 ppm and assigned in a manner similar to the case of their respective parent complexes. [45,46] The methylene protons of the long chain moieties (dodecylamine/cetylamine) give rise to a multiplet usually at 1.2-1.8 ppm, whereas the terminal methyl group of the hydrocarbon chain substituent gives a triplet at 0.85 ppm. The ^{1}H NMR spectral data for the metallosurfactant cobalt(III)-dppz complex three signals were observed three signals at 7.0 to 8.5 ppm, which correspond to dppz ligands and the highly intensive peak appeared at around 2.5 ppm assignable to dppz moiety and exhibit signals in the region 2.3-3.0 ppm attributable to the –CH$_2$ group of the dodecylamine or cetylamine, thus confirming the structure of the complex. It is well established that bis-type metallosurfactant cobalt(III)-dppz complexes of dipyrido(3,2-a-2'-3'-c)phenazine take only the *cis*-configuration because of the repulsion between the ligands. The *cis* configuration of all the present complexes was confirmed by the ^{1}H NMR.

3.2. Critical Micelle Concentration Values (CMC)

The CMC values were computed from the slope of [Co(III)] versus specific conductance data. The complex concentration at which the micellization starts was evident from the change in the slope of the plot and that particular concentration is the CMC under the experimental conditions. The CMC values were determined at three different temperatures (298, 303, 308 and 313K). At all temperatures a break in the conductance versus concentration plots, characteristic of micelle formation was observed. The CMC values were determined by fitting the data points above and below the break to two equation 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 0.98 in all the cases. The conductivity measurements at three different temperatures were repeated three times and the accuracy of the CMC values (Table 2) was found with in ± 3% error. Fig. 1 illustrates the plot for the complex *cis*-$[Co(dppz)_2(C_{12}H_{25}NH_2)_1Cl](ClO_4)_2$; similar plots (not shown) were obtained for all the remaining complexes. It is observed that dodecylamine to cetylamine, CMC decreases. It may be due to the increase in the size of the coordination sphere, which makes more weakly hydrated. Weakly hydrated can be adsorbed more readily in the micellar surface that decreases the charge repulsion between the polar groups and thus facilitates the micellization. Further with the increase in the alkyl chain on polar head group, the CMC again shows a decrease. This may be due to an increase in hydrophobic character of the molecule in the coordination sphere with that of dodecyl/cetylamine.

3.3. Thermodynamics of micellization

The study of CMC versus temperature is often undertaken to obtain information on hydrophobic and head group interactions. This involves deriving various thermodynamic parameters of micelle formation. Two models are generally used, the mass-action or equilibrium model and the phase separation or pseudo-phase model. The mass-action model assumes that an equilibrium exists between the monomeric surfactant and the micelles. The phase separation model, assumes that the aggregates have their counterions in the surrounding atmosphere in a separate phase [47-49]. According to these models, the standard Gibbs free energy of micelle formation per mole of monomer, ΔG_m^0, is given by

$$\Delta G_m^0 = RT\,(2-\alpha_{ave})\ \ln CMC \qquad (1)$$

where R,T and α_{ave} are gas constant, absolute temperature and average degree of micellar ionization, respectively.

The enthalpy of micelle formation can be obtained by applying the Gibbs-Helmholtz equation to the equation (1)

$$\Delta H_m^0 = -RT^2\ (2-\alpha_{ave})\ d\ln CMC / dT \qquad (2)$$

Once the Gibbs free energy and the enthalpy of micelle formation are obtained, obviously, the entropy of micelle formation can be determined by

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)\ /\ T \qquad (3)$$

The thermodynamic parameters of micellization for the cationic surfactant are compiled in Table 2. The observed more negative Gibbs free energy of micellization indicates more favored micellization for the system under study when compared to hexadecyltrimethylammonium bromide (CMC = 9.0×10^{-4} mol dm^{-3}). Moreover, since the changes of CMC with temperature are small, the value of ΔH_m^0 and ΔS_m^0 must be rather inaccurate and should be considered as only approximate. Nuselder and Engberts [50] have suggested that for negative ΔH_m^0 values, London-dispersion forces play major role in the micelle formation. Positive values of ΔS_m^0 clearly indicate that the micellization of the studied surfactants in aqueous solution is governed mainly by hydrophobic interactions between the surfactant cations resulting in the breakdown of the structured water surrounding the hydrophobic groups and indicates that the cationic surfactants formation is entropy driven process. The observed increase in the entropy values indicates that increasing head group polarity favors the micellization process. As mentioned in our previous reports [40-42], the CMC values for metallosurfactant cobalt(III)-dppz in the present study are also very low compared to that of simple organic surfactants. Thus it is suggested that these metal surfactant complexes have more capacity to associate themselves forming aggregates compared to those of ordinary synthetic organic surfactants. Moreover, introduction of a metal complex to the hydrophilic part of the amphiphile can remarkably enhance the ability of aggregation.

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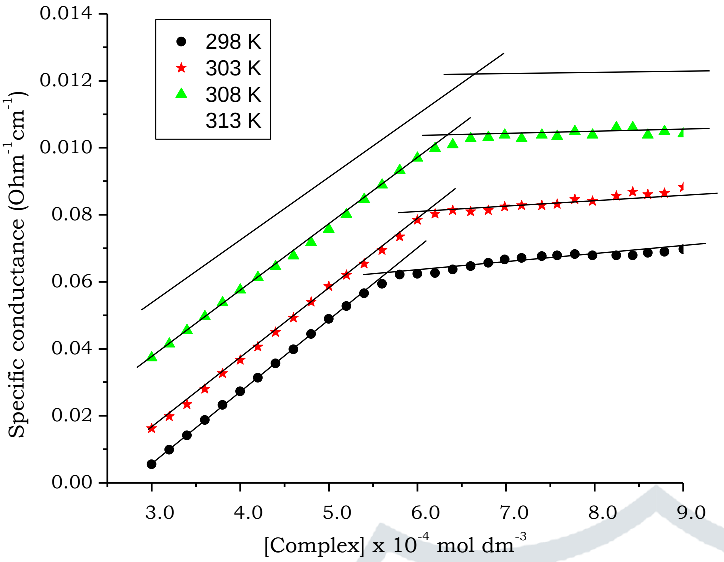

Figure 1. Electrical conductivity *vs* [Co(III)]-dppz complex in aqueous solution

Table 1. Microanalysis and visible spectra of some metallosurfactant Cobalt(III)-dppz complexes

Surfactants	λ_{max} (ε)[a]	Yield (%)	% Calculated (Found)			
			Co	C	H	N
cis-$[Co(dppz)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$	452 (87)	62	5.61 (5.71)	55.28 (55.43)	4.54 (4.63)	12.08(12.17)
cis-$[Co(dppz)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	455 (96)	67	4.76 (4.83)	58.67 (58.75)	6.07 (6.11)	10.26 (10.33)
cis-$[Co(dppz)_2(\ C_{16}H_{33}NH_2)Cl](ClO_4)_2$	451 (92)	65	5.32 (5.46)	56.88(56.91)	5.04 (5.10)	11.47 (11.60)
cis-$[Co(dppz)_2(\ C_{16}H_{33}NH_2)_2)_2](ClO_4)_3$	453 (110)	71	4.16 (4.22)	58.15 (58.24)	6.45 (6.51)	9.97 (10.04)

[a] λ in nm; ε in $M^{-1}cm^{-1}$.

Table 2. CMC values of some metallosurfactant cobalt(III)-dppz in aqueous solution

Complexes	CMC (mol dm^{-3})				ΔG^0_{mic} (kJ mol^{-1})	ΔH^0_{mic} (kJ mol^{-1})	$T\Delta S^0_{mic}$ (kJ mol^{-1})
	298 K	303 K	308 K	313 K			
cis-$[Co(dppz)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$	5.67 x 10^{-4}	6.08 x 10^{-4}	6.37 x 10^{-4}	6.66 x 10^{-4}	−29.15 ± 0.2	−16.79 ± 0.1	19.18 ± 0.2
cis-$[Co(dppz)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	8.55 x 10^{-4}	8.96 x 10^{-4}	9.12 x 10^{-4}	9.27 x 10^{-4}	−31.46 ± 0.1	−19.54 ± 0.3	21.63 ± 0.1
cis-$[Co(dppz)_2(\ C_{16}H_{33}NH_2)Cl](ClO_4)_2$	6.15 x 10^{-4}	6.67 x 10^{-4}	6.97 x 10^{-4}	7.15 x 10^{-4}	−35.29 ± 0.1	−23.47 ± 0.2	16.94 ± 0.3
cis-$[Co(dppz)_2(\ C_{16}H_{33}NH_2)_2)_2](ClO_4)_3$	3.63 x 10^{-5}	4.05 x 10^{-5}	4.66 x 10^{-5}	4.84 x 10^{-5}	−39.27 ± 0.2	−28.92 ± 0.3	13.38 ± 0.2