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Polyhedron 25 (2006) 2452–2458

POLYHEDRON

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Studies on solvophobic interactions and micelle formation of some surface active Cr(III) complexes in non-aqueous solvents

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Received 30 January 2006; accepted 21 February 2006
Available online 28 March 2006

Abstract

Micelle formation of surface active Cr^{III} complexes of the type *cis*-$[Cr(en)_2(C_{12}H_{25}NH_2)X]^{2+}$ (where $X = F^-, Cl^-, Br^-$) have been studied in *n*-alcohol and in formamide at different temperatures by conductance measurements. Standard Gibbs free energy changes (ΔG^0_{mic}), enthalpies (ΔH^0_{mic}) and entropies (ΔS^0_{mic}) of micelle formation have been determined by studying the variation of the critical micelle concentration (CMC) with temperature. Critical micelle concentrations have also been measured as a function of percentage concentration of alcohol added. It is suggested that alcohol addition leads to an increase in formamide penetration into the micellar interface that depends on the alcohol chain length. The results are discussed in terms of increased hydrophobic effect (solvophobic interaction), dielectric constant of the medium, the chain length of the alcohols and the surfactant in the solvent mixture.

Keywords: CMC; Conductance; Metallosurfactants; Micellization; Solvent effect; Thermodynamic properties

1. Introduction

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. 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 non-aggregated monomer molecules. The concentration at which micelles appear in solution is termed the critical micelle concentration (CMC). The formation of micelles was often characterized by a discontinuity in system properties, such as conductivity, surface tension, light scattering, self-diffusion and the molality of dissolved compounds. Experimentally, the CMC can be determined from the inflection plots of some physical property of the solution as a function of concentration. The CMC can serve as a measure of micelle stability in a given state, and the thermodynamics of micellization can be determined from a study of the CMC–temperature dependence [1,2]. Cationic surfactants offer some additional advantages over other classes of surfactants. These substances, besides their surface activity, do show antibacterial properties and are used as cationic softeners, lubricants, retarding agents, antistatic agents and in some cases consumer use etc. In a previous paper [3], we have reported the influence of temperature on the behaviour of some novel Cr^{III} metallosurfactants in aqueous solution. Metallosurfactants have received a sustained high level of attention from the scientific community for the last few years due to their relevance in various redox processes in biological systems, and act as promising agents for anthelmintic [4], antiparasitic [5] and antibiotics [6].

The micelle formation in an aqueous solution is known to be effected by organic additives, and there have been many investigations concerning the effects of organic additives on the CMC of simple surfactants [7,8]. The micelle formation of metallosurfactants in non-aqueous solvents has attracted little attention [9,10] as compared to the vast

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doi:10.1016/j.poly.2006.02.022

number of extensive studies that have been reported in the literature dealing with the formation of micelles in aqueous surfactant solutions. Increasing attention is being devoted to the study of the incorporation or solubilization of neutral molecules into micelle in aqueous solution. The nature of a cosolvent determines the direction of changes in the CMC of surfactants. The effect of different cosolvents having an –OH group, such as PEG, sucrose, ethylene glycol and alcohols, on the micellization process has been studied [11,12]. Some of the most studied solubilizates are alcohols, because of the important role they have in the preparation of microemulsions. An excellent review of earlier work on the effect of *n*-alcohols on micellar solutions was given by Leung and Shah [13] and Zana [14]. Addition of alcohol can strongly influence the behaviour of the micelles and increase or decrease the micellar size depending upon the hydrophilic/hydrophobic character of alcohol [15,16]. Whereas the hydrophilic alcohols (methanol to propanol) mainly solubilize in aqueous solution and affect the micellization process by modifying the solvent, the more hydrophobic alcohol molecules (butanol, pentanol and higher alcohols) take part in the micellization process and become unique components of the micelle aggregate. To differentiate them from "inverted micelles which are formed in non-polar organic solvents, the term "solvophobic" has been applied by various researchers [17–20] to organic solvents, in analogy with the "hydrophobic interactions" causing micellization in aqueous media. The micelle formed due to a "solvophobic interaction" in polar non-aqueous solvents are similar in many respects to the micelles that are formed in aqueous media, although in general, micelle formation is not as favoured in non-aqueous solvents (with a low dielectric constant) as in water for a given surfactant [17–20].

In the present work, efforts have been made to study the effect of temperature variations on the CMC of metallosurfactants in non-aqueous solvents using a conductivity technique. Various aspects of the interaction of these surfactants in formamide during micelle formation in the presence of alcohols with various chain lengths are also discussed. In addition, the thermodynamic parameters, Gibbs free energy changes (ΔG^0_{mic}), enthalpies (ΔH^0_{mic}) and entropies (ΔS^0_{mic}), have also been estimated and analyzed for Cr^{III} metallosurfactants in non-aqueous solvents.

2. Experimental methods

2.1. Materials

Surface active Cr^{III} complexes, *cis*-$[\text{Cr(en)}_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)\text{F}](\text{ClO}_4)_2$, *cis*-$[\text{Cr(en)}_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)\text{Cl}](\text{ClO}_4)_2$ and *cis*-$[\text{Cr(en)}_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)\text{Br}](\text{ClO}_4)_2$ used in the present work were prepared similar to those complexes reported earlier [3]. Their purity was tested by UV–Vis spectroscopy and CHN analysis. All other chemicals were obtained from Fluka and were used without purification.

Safety note: caution. Perchlorate salts of Cr^{III} 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.

2.2. Determination of CMC

CMC values of the complexes were calculated using electrical conductance data measured using a digital conductivity meter (Metrohm 712). 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. [21]. Various concentrations of Cr^{III}–surfactant complexes were prepared in the range 10^{-6}–10^{-2} mol dm^{-3}. All the measurements were done in a jacketed vessel, which was maintained at the desired temperature (±0.1 °C) with a circulating water thermostat bath. The conductivity of these solutions was measured at 293–313 K. The conductance was measured after thorough mixing and temperature equilibrium 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. Establishment of equilibrium was checked by taking a series of readings after 15 min intervals until no significant change occurred.

3. Results and discussion

3.1. Temperature dependence of CMC

The CMC values of metallosurfactants in *n*-alcohol–formamide mixtures of different compositions and at various temperatures were determined from conductance measurements. Fig. 1. shows representative plots of specific conductivity corrected by that of the solvent k–k_{o}, as a function of the surfactant concentration at a fixed solvent composition and at different temperatures. Similar plots (not shown) were obtained in all the cases studied. The specific conductance of the solution in *n*-alcohol increases with increasing surfactant concentration. The increase seems to be due to the tendency of the metallosurfactants to form aggregates at higher surfactant concentration. It may be also attributed to the combined effect of ionic atmosphere, solvation of ions and decrease of mobility and ionization with the formation of micelles. When the conductivity of solutions with increasing concentration of surfactant is measured, the specific conductivity–surfactant concentration plots show two straight lines with different slopes. The first one corresponds to the concentration range below the CMC, when only monomers of surfactant exist in solution. Micelles start to form and a change of slope appears because the conductivity increases in a different manner. The intersection of these two straight lines was taken as the CMC value of the surfactant. The CMC values were computed from the slope of [Cr(III)] versus specific