Copper(II) Complexes of a Dicephalic Imidazole Surfactant. Tunable Organization of Metalloaggregates


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The complexation of two-headed (dicephalic) surfactant molecules (1) to copper(II) sulfate in aqueous dispersions at pH 5.5 and 9.5 leads to the generation of metalloaggregates of the general type Cu(Imidazole)$_2^{2+}$. At both pH values vesicles are observed which, however, consist of different complexes due to the dicephalic nature of the surfactant. At pH 5.5 four imidazole groups from two surfactant molecules coordinate to one copper center in a bidentate fashion, whereas at pH 9.5 a two-dimensional polymeric network is formed in which each copper(II) ion is surrounded by four imidazole groups from four different surfactant molecules. The aggregates formed exhibit different physical properties, which have been studied by electron microscopy, monolayer experiments, differential scanning calorimetry, and spectroscopic techniques.

Introduction

The design and construction of nanoscopic structures from transition metal containing building blocks has become a topic of increasing interest in recent years.1-3 Self-assembled amphiphilic systems with metal binding sites have been developed and successfully applied in catalysis and in material science.4-7

In this paper we describe a so-called dicephalic surfactant (1), which has two imidazole headgroups linked to a single paraffinic tail. This compound can complex metal ions in two different ways, viz., by forming a chelate...
yield (mp = 88 °C). IR (cm⁻¹, KBr): ν 3100 (w, CH–Im), 2910 (s, CH₃), 2840 (s, CH₃), 1740 (s, C=O), 1530–1490 (m, Im). MS (EI, m/z): 458 (M⁺), 214 (M⁺–OC(O)CH₃), 107 (175 – Im). NMR (CDCl₃): δ (ppm) 0.88 (t, J = 6.7 Hz, 3H, CH₃), 1.25 (m, 28H, CH₂(CH₂)₁₂CH₃), 1.56 (m, 3H, (O)CH₂CH₂), 2.31 (t, J = 7.5 Hz, 2H, C(O)CH₃), 4.07 (AXXY’ X, CH₂N), 5.33 (AXXY’ Y, 1H, CH–O), 6.92 (s, 1H, 5-ImH), 7.11 (s, 1H, 4-ImH), 7.47 (s, 1H, 2-ImH). Anal. Calcd for C₂₇H₄₆N₄O₂: C, 70.70; H, 10.11; N, 12.21. Found: C, 70.67; H, 10.20; N, 11.99.

Sample Preparation. Copper-free samples were prepared by vortexing 6 mg (0.013 mmol) of 1 in 2 mL of water for 30 min at 70 °C. Subsequently, the pH was adjusted to the desired value using aqueous 0.01 M sulfuric acid or aqueous 0.01 M sodium hydroxide and the samples were kept at 70 °C for another 30 min. For the preparation of the copper complexes the desired amount of an aqueous 1.0 mM CuSO₄ solution was added to the vortexed surfactant dispersions. The dispersion was titrated with sulfuric acid or sodium hydroxide to pH 5.5 or pH 9.5, respectively, and vortexed at 70 °C for 30 min.¹⁰

EPR Spectroscopy. Aqueous dispersions of the copper(II) complexes were prepared as described above and frozen in liquid nitrogen. EPR spectra were recorded at 7 ± 1 K using a Bruker ESR 300 spectrometer.

FT-IR Spectroscopy. IR samples were prepared by depositing 160 μL of the surfactant dispersion (see sample preparation) as a film on AgCl windows, using the isopotential spin-drying method.¹¹ FT-IR spectra were measured at ambient tempera-

Figure 1. Freeze fracture electron micrographs of dispersions of 1 prepared at (a) pH 5.5, 1 prepared at (b, c) pH 9.5 and (b) after 16 h and (c) after 1 week. (d) Idem for a 2:1 complex of 1 and CuSO₄ prepared at pH 5.5.
Results and Discussion

Inspection of a space-filling (CPK) model reveals that the cross section of the headgroup of 1 is much larger than the cross section of its lipophilic tail (Chart 1). It was expected, therefore, that this compound, according to the shape–structure concept, would form micelles after dispersion in water. To control the charge, and thereby the size of the hydrophilic part of the molecule, it is important to know the pKₐ values of 1. These were determined by potentiometric titration and amounted to pKₐ = 3.6 and = 7. In the following, experiments will be described which were carried out at fixed pH values, viz., at pH = 9.5 and pH = 5.5, corresponding to deprotonated and singly protonated molecules of 1, respectively.¹⁰

Electron micrographs of samples prepared at pH = 5.5 revealed the presence of large multilamellar vesicles with diameters of approximately 1000 nm (Figure 1a). These vesicles displayed a broad phase transition at 19 °C, as determined by differential scanning calorimetry (DSC). Powder diffraction patterns of cast films of these vesicles indicated that they had intercalated bilayers with a periodicity of 30 Å, which suggests that the imidazole headgroups form arrays which are oriented parallel to the bilayer surface (Figure 2a).¹³ From CPK models it can be estimated that such an arrangement would require a headgroup area of approximately 70 Å². This is in good agreement with the results from monolayer experiments recorded on a subphase adjusted to pH 5.5 from which a molecular area of approximately 71 Å² was calculated by extrapolating the slope of Langmuir isotherms in the liquid condensed (LC) region (Figure 3). The possibility to form intermolecular hydrogen bonds between protonated and deprotonated headgroups would account for the unexpected generation of bilayer structures from 1.

Electron microscopy experiments, performed on samples prepared at pH = 9.5, revealed extended bilayer structures (Figure 1b) which displayed a gel to liquid crystalline phase transition at 41 °C in DSC. Powder diffraction experiments carried out on cast films of the aggregates showed Bragg reflections corresponding to bilayers with a periodicity of 63 Å. These data indicate that the molecules in the bilayers must be oriented parallel to the bilayer normal since the maximum molecular length of 1, as estimated from CPK models, amounts to approximately 30 Å (Figure 2b).

The stoichiometry of these complexes could not be determined using UV–vis spectroscopy because the solutions were too turbid or formed precipitates on standing. Two series of samples with varying Cu(II)/surfactant ratios were prepared at pH = 5.5 and pH = 9.5, respectively. EPR spectroscopy revealed identical signals for the two 2:1 surfactant/copper complexes at pH 5.5 and 9.5, indicating axial ligand symmetry of the copper ions in both cases (Figure 4a). The copper

Figure 2. Schematic representation of the most probable orientations of the surfactant molecules of 1 in bilayer structures prepared at (a) pH = 5.5 and (b) pH = 9.5.
hyperfine splitting could be measured on the g\textperp signal ($g_{\textperp} = 2.06$) despite the poor resolution. The line broadening is probably due to dipolar interactions because of small distances between the paramagnets. The unsplit $g_{\textparallel}$ signal ($g_{\textparallel} = 2.28$) was superimposed on the two right lines of $g_{\textparallel}$ ($g_{\textparallel} = 2.06$). Dilution of the copper centers using high surfactant/copper ratios did not improve the resolution.

In samples prepared at pH 5.5, an additional signal was observed when the imidazole/Cu(II) ratio was lower than 4 (Figure 4). This signal could be attributed to the presence of free copper sulfate, which suggests that \textbf{1} forms complexes of the type Cu(Imidazole)$_4^{2+}$. In samples prepared at pH 9.5, no additional signal or loss in resolution was observed at high copper(II) concentrations, which, at these high pH values, is probably due to the formation of electron paramagnetic resonance (EPR) silent copper oxide or hydroxide species.

Since coordination to copper(II) shifts the IR vibrations of the imidazole group to higher wavenumbers, it was possible to determine the stoichiometry of the complex with FT-IR.\textsuperscript{14} Oriented films were prepared from aqueous dispersions of \textbf{1} containing different amounts of copper sulfate using the isopotential spin drying method.\textsuperscript{13} For metal-free samples of \textbf{1}, prepared at pH = 5.5, two vibrations were observed for the imidazole group at 1506 and 1517 cm$^{-1}$, respectively. Addition of copper sulfate caused the appearance of an additional vibration at 1521 cm$^{-1}$, the intensity of which was proportional to the amount of coordinated imidazole groups, concomitant with the disappearance of the other two vibrations. Metal-free samples prepared at pH = 9.5 showed a vibration at 1509 cm$^{-1}$. In this case, upon addition of copper(II) sulfate an additional peak appeared at 1522 cm$^{-1}$. Peak areas of the vibrations assigned to free imidazole ($A_1$) and to Cu(II) coordinated imidazole ($A_2$) were determined using curve-fitting procedures. When the $A_1/A_2$ ratio was plotted against the Cu(II)/imidazole ratio, no changes were observed after the Cu(II)/imidazole had exceeded the ratio of 1:4. Moreover, when the imidazole/copper ratio exceeded 4:1, the appearance of a strong vibration at 1100 cm$^{-1}$ was observed at both pH 5.5 and pH 9.5, which could be assigned to free copper sulfate. These data indicate that at both pH 5.5 and 9.5 complexes of the type Cu(Imidazole)$_4^{2+}$ in both cases are formed from \textbf{1} and copper sulfate in accordance with the literature.\textsuperscript{14}

Freeze fracture electron micrographs were taken from dispersions of 2:1 \textbf{1}/Cu(II) complexes prepared at pH 5.5 and pH 9.5. In both cases vesicles with diameters ranging from 50 to 250 nm were observed (Figure 1d). Although at both pH values the vesicles were similar in size, DSC measurements revealed a remarkable difference in their phase behavior: a phase transition was observed at 15°C for the dispersions prepared at pH 5.5 and at 62°C for the dispersions prepared at pH 9.5. Powder diffraction patterns obtained from the respective complexes showed

\hspace{1cm}(14) Reedijk, J. J. Inorg. Chem. 1971, 33, 179.
bilayer periodicities of 32 Å (pH = 5.5) and 37 Å (pH = 9.5), respectively, suggesting interdigitation of the alkyl chains in both cases.

Langmuir monolayer experiments were carried out on an aqueous subphase containing 1.2 mM CuSO₄. When 1 was spread on a sub-phase adjusted to pH = 5.5, a transition to a more compressible state was observed at \( \Gamma = 26 \) mN/m (Figure 3). The molecular areas, both before and after the transition, were determined by extrapolation to zero pressure and amounted to 74 and 83 Å², respectively. The occurrence of a transition to a state with a higher compressibility at lower molecular area is remarkable but can be explained in the following way: Due to the compression of the monolayer, the local imidazole concentration increases and causes a change in the number of imidazole ligands coordinated to the Cu(II) ions. We propose that at high areas per molecule, i.e., at low local surfactant concentrations, a 1:1 complex of surfactant 1 and copper sulfate is formed, favored by the fact that the two imidazole groups in the surfactant molecules are preorganized (Figure 5a). At lower molecular areas, and thus at higher local surfactant concentrations, a 2:1 surfactant 1/copper complex is favored. This requires, however, equatorial positions for the imidazole groups, which means that the plane of the complex must lie flat on the air–water interface (Figure 5b). This complex will be more compressible than the complex of Figure 5a that is located perpendicular to the air–water interface.

When solutions of compound 1 were spread on a subphase containing 1.2 mM CuSO₄, adjusted to pH =
9.5, no phase transition was observed in the isotherms (Figure 3). Brewster angle microscopy revealed that already at low surface pressures domains were present. This suggests that at pH 9.5 a preorganized complex is formed of which the structure does not change when the local surfactant concentration is altered. The molecular area occupied by the complex was determined by extrapolation of the slope of the isotherm to zero pressure and amounted to 77 Å² (Figure 3). These data are in agreement with a complex in which the imidazole groups of one surfactant molecule coordinate to different copper centers. A possible structure for this complex is depicted in Figure 5c.

**Conclusion**

The complexes generated upon addition of copper sulfate to aqueous dispersions of 1 at pH 5.5 and pH 9.5 appear to possess similar stoichiometries and symmetries. Their aggregates, however, although nearly identical in shape and dimensions, are quite different with regard to their molecular organization. Langmuir monolayer experiments reveal differences in compressibilities and molecular areas for the two cases, implying that the type of complex formed depends on the pH. On the basis of these experiments different ligand arrangements are proposed, which are in agreement with the observed differences in phase behavior, e.g., the thermal stability of the bilayer structure is higher for the polymeric two-dimensional network at pH 9.5 than for the assembly of individual complexes at pH 5.5.

We conclude that dicephalic surfactants are a new interesting class of amphiphilic compounds, which have the possibility to form either bidentate chelates or polymeric complexes. By variation of the pH, the type of complex that is formed can be controlled and thereby the physical properties of the material.