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

Nico A. J. M. Sommerdijk,[†] Kees Jan Booy,[‡] Arthur M. A. Pistorius,[§]
Martinus C. Feiters,[‡] Roeland J. M. Nolte,^{*,‡} and Binne Zwanenburg^{*,‡}

Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld, 6525
ED Nijmegen, The Netherlands, Laboratory of Organic and Macromolecular Chemistry,
Eindhoven University of Technology, Eindhoven, The Netherlands, and Department of
Biochemistry, University of Nijmegen, Nijmegen, The Netherlands

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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 $\text{Cu}(\text{imidazole})_4^{2+}$. 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*⁸ 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

in which one or more molecules of **1** bind to one metal ion in a bidentate fashion or by binding two different metal ions generating a coordination polymer. Here we report that copper(II) binding of *dicephalic* surfactant **1** can be tuned by varying the pH, in such a way that both forms of complexation can be obtained separately. It will be demonstrated that although the mesoscopic morphology of the aggregates is maintained upon switching between the two binding modes, their molecular organization, and thereby their physical properties, change appreciably.

Materials and Methods

General. Electron microscopy, differential scanning calorimetry, powder diffraction, and monolayer experiments were performed according to procedures described previously.⁹

1,3-Bis(1-imidazolyl)-2-propyl octadecanoate (1). To a solution of imidazole (2.8 g, 4.1 mmol) in DMF (300 mL) was added NaH (1.1 g, 4.6 mmol). After being stirred at room temperature for 1 h, the solution was cooled to $-15\text{ }^\circ\text{C}$ and epibromohydrin (2.6 g, 1.0 mmol) dissolved in DMF (100 mL) was gradually added over a period of 4 h. The mixture was allowed to warm to room temperature and stirred for an additional 16 h. A solution of stearoyl chloride (6.0 g, 0.99 mmol) in DMF was added dropwise, and the reaction mixture was stirred for 24 h. After evaporation of the DMF in vacuo the reaction mixture was dissolved in ethyl acetate and washed several times with aqueous 10% NaHCO_3 in order to remove excess of imidazole. The organic layer was dried and concentrated in vacuo to yield a white solid. Stearic acid was removed by column chromatography (Silica gel, eluent: ethyl acetate/ethanol/triethylamine, 69/30/1, v/v/v), and after crystallization from ethyl acetate, **1** was obtained in 65%

[†] Laboratory of Organic and Macromolecular Chemistry, Eindhoven University of Technology.

[‡] Department of Organic Chemistry, University of Nijmegen.

[§] Department of Biochemistry, University of Nijmegen.

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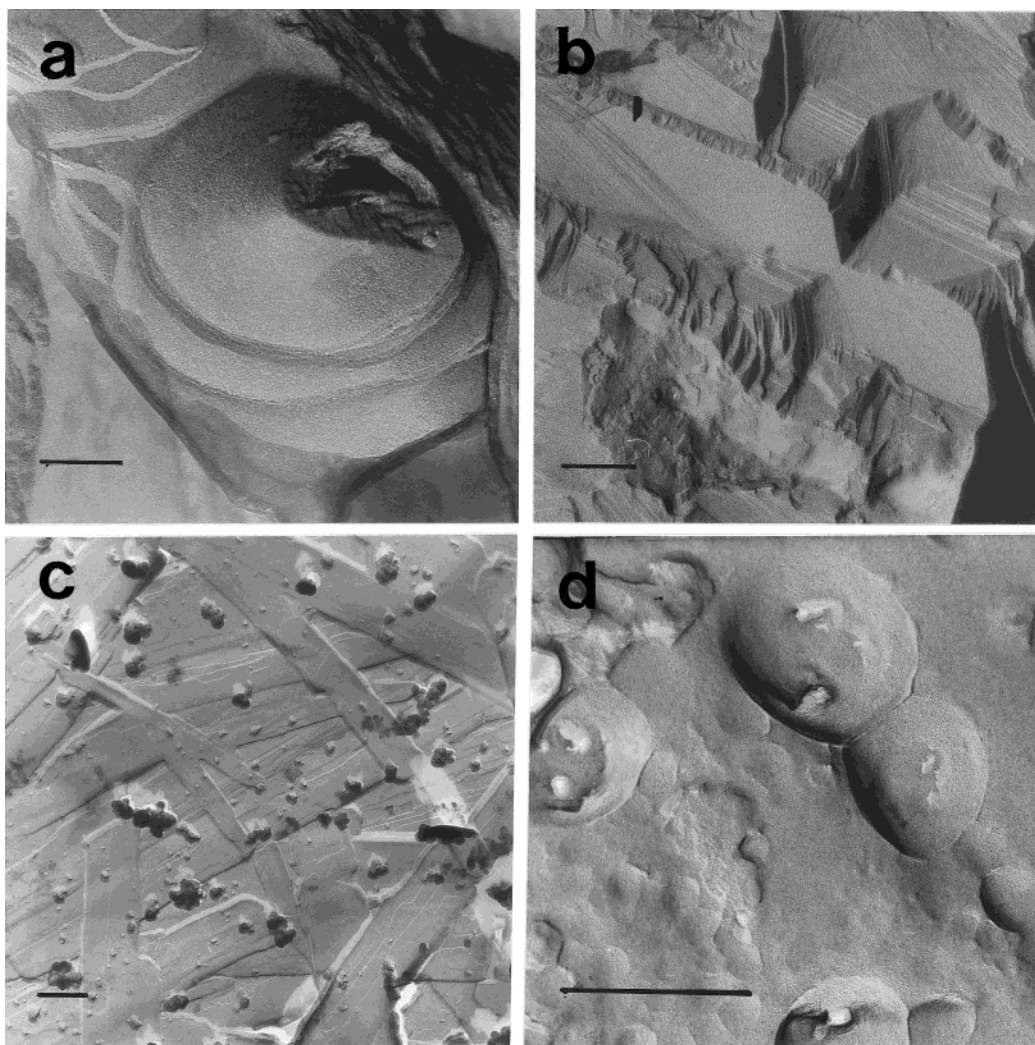
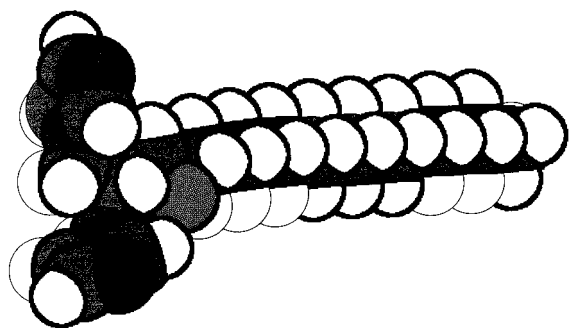
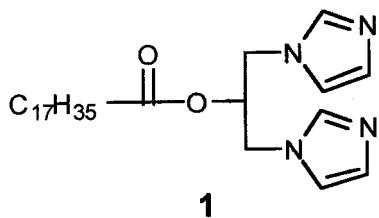


Figure 1. Freeze fracture electron micrographs of dispersions of **1** prepared at (a) pH 5.5, **1** prepared at (b, c) pH 9.5 and (b) after 16 h and (c) after 1 week. (d) Idem for a 2:1 complex of **1** and CuSO_4 prepared at pH 5.5.

Chart 1. Structure and Space Filling Model of Dicephalic Surfactant 1



yield (mp = 88 °C). IR (cm^{-1} , KBr): ν 3100 (w, CH-Im), 2910 (s, CH_2), 2840 (s, CH_3), 1740 (s, C=O), 1530–1490 (m, Im). MS (EI, m/z): 458 (M^+), 175 ($\text{M}^+ - \text{OC}(\text{O})\text{C}_{17}\text{H}_{35}$), 107 (175 - Im). NMR (CDCl_3): δ (ppm) 0.88 (t, $J = 6.7$ Hz, 3H, CH_3), 1.25 (m, 28H, $\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$), 1.56 (m, 3H, $\text{C}(\text{O})\text{CH}_2\text{CH}_2$), 2.31 (t, $J =$

7.5 Hz, 2H, $\text{C}(\text{O})\text{CH}_2$), 4.07 (AXX'YY', CH_2N), 5.33 (AXX'YY', 1H, $\text{CH}-\text{O}$), 6.92 (s, 1H, 5-ImH); 7.11 (s, 1H, 4-ImH), 7.47 (s, 1H, 2-ImH). Anal. Calcd for $\text{C}_{27}\text{H}_{46}\text{N}_4\text{O}_2$: 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 CuSO_4 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-

(10) As buffered solutions often contain components (e.g., amines, phosphate, borate, chloride, or acetate ions) that may compete with imidazole as ligands to copper(II), sodium hydroxide and sulfuric acid were chosen as pH-adjusting agents. Therefore it should be emphasized that at pH 5.5 sulfate ions and at pH = 9.5 hydroxy ions are present which may hydrogen bond to the surfactants or coordinate to the copper centers, thereby changing or influencing the molecular packing in the aggregates.

tures, using a Mattson Cygnus 100 single beam spectrometer, equipped with a liquid nitrogen cooled narrow band MCT detector. Acquisition parameters: were as follows: resolution, 4 cm^{-1} ; number of coadded interferograms, 128; moving mirror speed, 2.53 cm/s ; wavenumber range, $4000\text{--}750\text{ cm}^{-1}$; apodization function, triangle. Signal-to-noise ratios ($2000\text{--}2200\text{ cm}^{-1}$) were better than 4×10^3 . Data acquisition and analysis were performed using EXPERT-IR software (Mattson). Baselines were corrected, and peak positions were determined using second derivative spectra smoothed over 13 data points. Curve-fitting procedures were repeated several times (initial settings 10% Gauss/90% Lorenz; bandwidth 10 cm^{-1}), and the quality of the fitted spectra was checked by comparing the generated and original spectra before and after deconvolution.

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 concept¹² 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 pK_a values of **1**. These were determined by potentiometric titration and amounted to $pK_a = 3.6$ and ≈ 7 . In the following, experiments will be described which were carried out at fixed pH values, viz., at $\text{pH} = 9.5$ and $\text{pH} = 5.5$, corresponding to deprotonated and singly protonated molecules of **1**, respectively.¹⁰

Electron micrographs of samples prepared at $\text{pH} = 5.5$ revealed the presence of large multilamellar vesicles with diameters of approximately 1000 nm (Figure 1a). These vesicles displayed a broad phase transition at $19\text{ }^\circ\text{C}$, 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 \AA , 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 \AA^2 . This is in good agreement with the results from monolayer experiments recorded on a subphase adjusted to $\text{pH} 5.5$ from which a molecular area of approximately 71 \AA^2 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 $\text{pH} = 9.5$, revealed extended bilayer structures (Figure 1b) which displayed a gel to liquid crystalline phase transition at $41\text{ }^\circ\text{C}$ in DSC. Powder diffraction experiments carried out on cast films of the aggregates showed Bragg reflections corresponding to bilayers with a periodicity of 63 \AA . These data indicate that the molecules in the bilayers

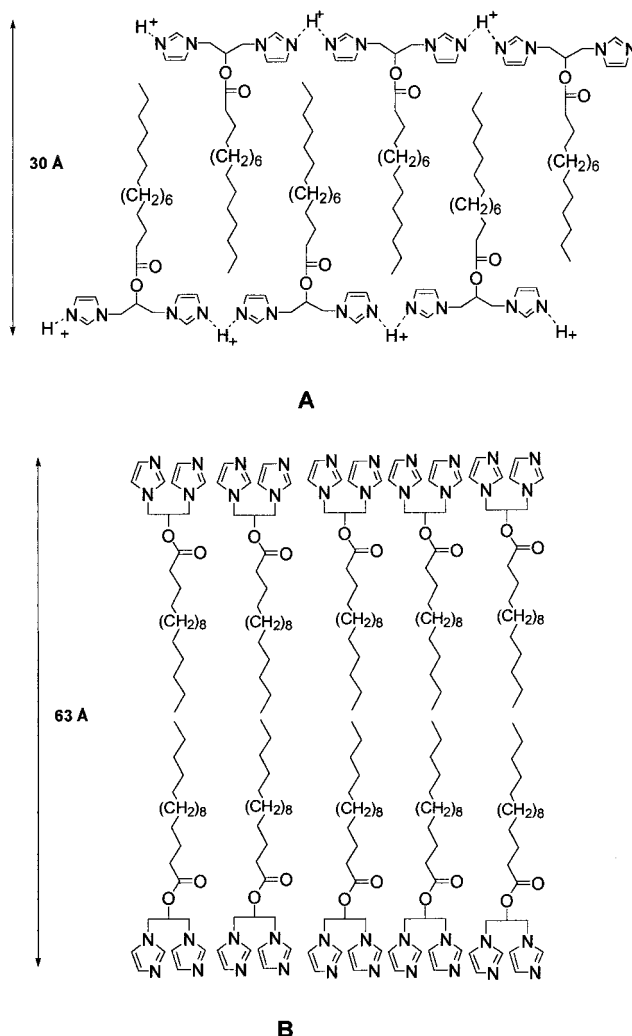


Figure 2. Schematic representation of the most probable orientations of the surfactant molecules of **1** in bilayer structures prepared at (a) $\text{pH} = 5.5$ and (b) $\text{pH} = 9.5$.

must be oriented parallel to the bilayer normal since the maximum molecular length of **1**, as estimated from CPK models, amounts to approximately 30 \AA (Figure 2b). Inspection of CPK models revealed that the stacking of the imidazole groups was in accordance with the molecular area of 56 \AA^2 approximated from monolayer experiments (Figure 3).

Upon standing the extended bilayer structures observed at $\text{pH} 9.5$ transformed into platelets (Figure 1c) which were found to be polycrystalline by electron diffraction. DSC experiments revealed a sharp phase transition at $58\text{ }^\circ\text{C}$ for this material. The platelets were found to have a d spacing of 31 \AA , suggesting either a head to tail packing or an intercalation of the hydrocarbon chains. Heating of these platelets converts them back into the bilayered structures.

Complexation with Copper Sulfate. Blue complexes were formed upon addition of a copper sulfate solution to an aqueous dispersion of **1**. 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 $\text{pH} = 5.5$ and $\text{pH} = 9.5$, respectively. EPR spectroscopy revealed identical signals for the two 2:1 surfactant/copper complexes at $\text{pH} 5.5$ and 9.5 , indicating axial ligand symmetry of the copper ions in both cases (Figure 4a). The copper

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(13) An alternative model, which may explain the diffraction pattern, involves a tilted orientation of the surfactant molecules with respect to the bilayer normal. This would lead, however, to a distorted hexagonal packing of the hydrocarbon chains, indicated by a broadening of the reflection representing the d_s value. See: (a) Gulik-Krzywicki, T.; Rivas, T.; Luzzati, V. *J. Mol. Biol.* **1967**, *27*, 303. (b) Tardieu, A.; Luzzati, V. *J. Mol. Biol.* **1973**, *75*, 711. (c) Ranck, J. L.; Mathieu, L.; Sadler, D. M.; Tardieu, A.; Gulik-Krzywicki, T.; Luzzati, V. *J. Mol. Biol.* **1974**, *85*, 249. The occurrence in our samples of two sharp reflections corresponding to periodicities of 3.97 \AA and $3.97/\sqrt{3}\text{ \AA}$ (d_s and $d_s/\sqrt{3}$), respectively, indicates that the hydrocarbon chains in the vesicle bilayers are arranged in a well-defined hexagonal packing of the hydrocarbon chains, making a tilted orientation unlikely.

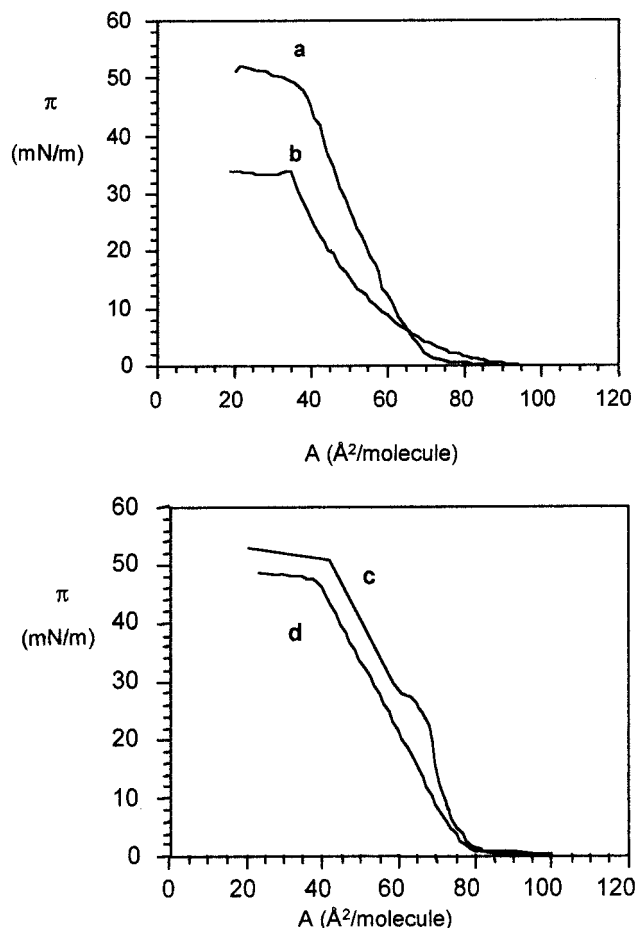


Figure 3. Langmuir monolayer isotherms of **1** recorded at 20 °C on a subphase containing water adjusted to (a) pH 9.5 and (b) pH 5.5 and on a subphase containing aqueous 1.2 mM copper sulfate adjusted to (c) pH 5.5 and (d) pH 9.5.

hyperfine splitting could be measured on the g_{\parallel} signal ($A_{\parallel} = 171$ G), despite the poor resolution. The line broadening is probably due to dipolar interactions because of small distances between the paramagnets. The unsplit g_{\perp} signal ($g_{\perp} = 2.06$) was superimposed on the two right lines of g_{\parallel} ($g_{\parallel} = 2.28$). 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 **1** forms complexes of the type $\text{Cu}(\text{Imidazole})_4^{2+}$. 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.¹⁴ Oriented films were prepared from aqueous dispersions of **1** containing different amounts of copper sulfate using the isopotential spin drying method.¹¹ For metal-free samples of **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

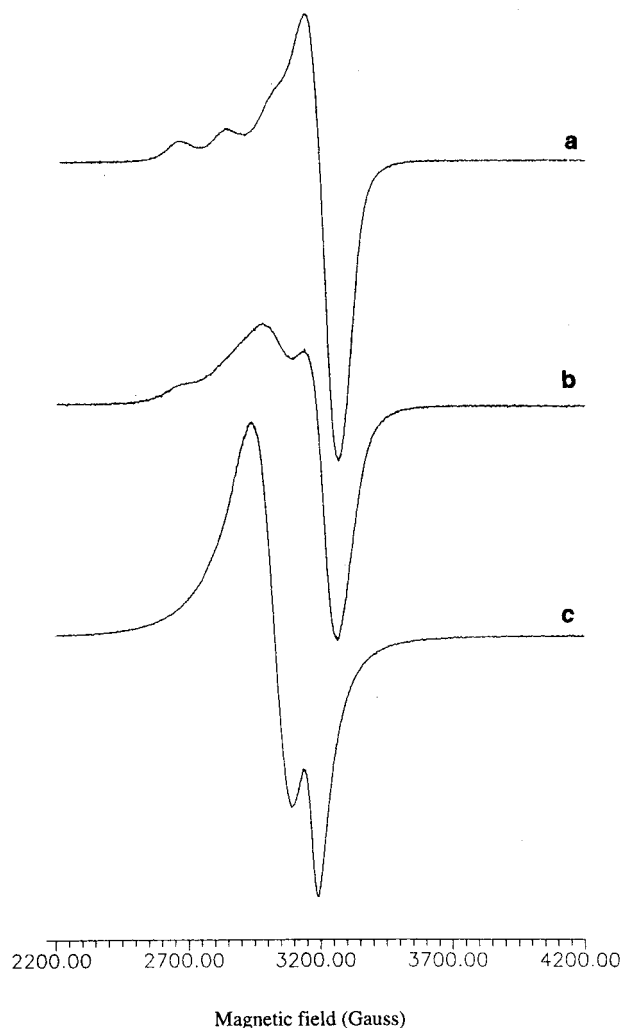


Figure 4. EPR spectra of (a) 2:1, (b) 1:1, and (c) 1:2 complexes of **1** and copper sulfate prepared at pH 5.5.

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 $\text{Cu}(\text{imidazole})_4^{2+}$ in both cases are formed from **1** and copper sulfate in accordance with the literature.¹⁴

Freeze fracture electron micrographs were taken from dispersions of 2:1 **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

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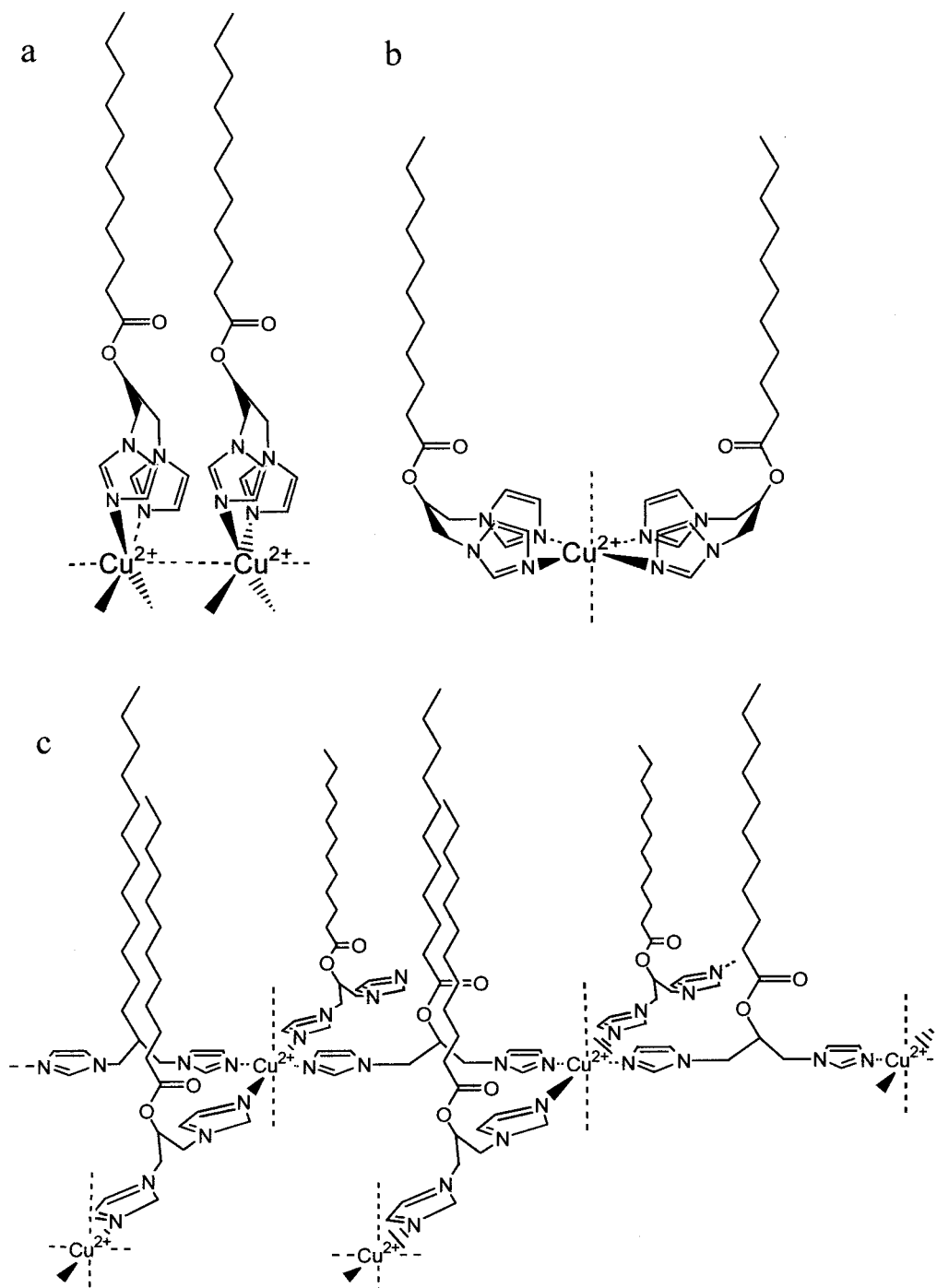


Figure 5. Proposed orientations of **1** in monolayers on a CuSO_4 subphase adjusted to (a, b) pH 5.5 [(a) is before and (b) is after the phase transition] and (c) on a CuSO_4 subphase adjusted pH 9.5.

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 CuSO_4 . When **1** was spread on a sub-phase adjusted to pH = 5.5, a transition to a more compressible state was observed at $\Pi = 26$ 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 CuSO_4 , 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 \AA^2 (Figure 3). These data are in agreement with a complex in which the imidazole groups of one surfactant molecule **1** 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.

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