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Influence of copper(II) ions on the structure and properties of octodecyl propylenediamine vesicles

Hongtao Guo, Xiaohai Zhou *, Jinfeng Dong, Gaoyong Zhang, Xinlin Hong

School of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

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Abstract

The amphiphiles of octodecyl propylenediamine could self-assemble into vesicles in pure water and aqueous solution of $CuCl_2$ or $Cu(NO_3)_2$. It has been found that the structure and properties of vesicles are quite different when the copper(II) salt is added to the solution. The self-aggregate structure and properties of the vesicles have been characterized by means of UV–vis spectra, transmission electron microscopy, dynamic light scattering, small-angle X-ray diffraction, differential scanning calorimetry and surface tension. The results show that the Cu^{2+}-coordinated amphiphiles adopt compressed tetrahedral structures and the partially interdigitated chain-packing model in bilayer membranes, which was influenced not only by the counterions but also by the ligands.

Keywords: Octodecyl propylenediamine; Copper(II) ions; Vesicle; Bilayer membrane; Coordinated structure

1. Introduction

Vesicles are hollow spherical structures with bilayer membranes formed by the self-assembly of surfactants, lipids, or block copolymers in aqueous solutions. Vesicles have long been a scientific curiosity because of their structural resemblance to primitive biological cells. More importantly, vesicles are of technological interest for applications ranging from drug delivery and controlled release to bioseparations and sensing [1]. In recent years, synthetic amphiphiles that can self-organize into vesicles in dilute aqueous solutions have been reported with different chemical structures and composition of headgroups and hydrophobic tails. It has been shown that, for synthetic amphiphiles, double chained surfactants can easily assemble into vesicles [2], and bolaform ones can self-organize into monolayered vesicles, which are highly stable over time to the variation of temperature and ionic strength changers [3]. Otherwise, surfactant/cosurfactant mixtures and ion-pair amphiphiles could form vesicles upon sonic dispersal in water [4–6]. It is usually considered that a rigid segment is essential for a pure single-chain amphiphile to form stable bilayer membranes in dilute aqueous dispersion, except for very few cases, such as amphiphiles with a hyperextended alkyl chain or a perfluorinated chain or monoglycerides [7–10]. Recently, a new mechanism of bilayer membrane formation from simple single-chain amphiphiles without rigid segment was proposed [11]. It demonstrated that the interaction between hydrophilic headgroups through hydrogen bond, ionic bond, and metal complex induces a parallel packing of the corresponding hydrophobic chains. It has been reported that vesicles formed from a series of simple amphiphiles with monoalkyl chains in common length and without rigid segment in aqueous solutions [11,12]. Metal ions can be also used to induce modified vesicles to form higher-level self-assemblies, which can be controlled artificially and reversibly by adjusting the concentration of metal ions in the solution [13]. On the other hand, the formation and collapse of vesicles is controlled by the existing balance between polar headgroup and hydrophobic tail, alteration of the metal ion's charge state of headgroups can be controlled, for example by redox-switching, which in turn permits regulation of aggregate formation [14–16]. Metal ions inducing and controlling the structures of self-assembly has become a topic of increasing interest.

Monoalkylethylenedimaine amphiphiles ($C_{18}H_{37}NHCH_2CH_2NH_2$), which are readily coordinated with metal ions, could self-assemble into stable bilayer membranes in pure water [17].

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* Corresponding author. Fax: +86 27 87218534.
E-mail address: surfactant@sina.com (X. Zhou).

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When they were dispersed in Cu^{2+}-containing solutions, stable bilayer membranes could also form, however, these structures were quite different from that in pure water. It has been found that the membrane structure and properties are strongly dependent on the counterions. In $CuCl_2$ dispersions, the amphiphiles adopted a compressed tetrahedral coordinated configuration and a tilted tail-to-tail chain-packing model in bilayer membranes, while for $Cu(NO_3)_2$ dispersions, a square plane coordinated configuration and a interdigitated chain-packing model were adopted [17]. In the present work, the amphiphiles of octodecyl propylenediamine ($C_{18}H_{37}NHCH_2CH_2CH_2NH_2$) has been chosen to study the effects of ligand and counterions on the membrane structure and properties. It is known that the replacement of ethylenediamine group by propylenediamine one in the ligand would result to a considerable decreasing in the stability of chelate, which means that selective binding to metal ions would appear. It is interesting to understand how the conuterions and ligands to affect the configuration of coordinated structures and packing model in bilayer membranes.

2. Materials and methods

2.1. Materials

Octodecyl propylenediamine ($C_{18}H_{37}NHCH_2CH_2CH_2NH_2$) was obtained commercially, and recrystallized three times from methanol prior to use. $CuCl_2$ and $Cu(NO_3)_2$ were of analytical grade and were used as received. Double-distilled water, which was prepared more than 24 h in advance, was used in the preparation of the dispersions.

2.2. Methods

2.2.1. Dispersion preparation

Dispersions were prepared by means of the described method [17]. A mixture of 2 mmol of $C_{18}H_{37}NHCH_2CH_2CH_2NH_2$ and 100 mL of doubly distilled water were sonicated until fully dissolved, then 20 mmol/L stable white emulsion dispersion A was obtained. The 5 mmol/L dispersion B ($[Cu(C_{18}H_{37}NHCH_2CH_2CH_2NH_2)_2]Cl_2$) was prepared by mixing dispersion A and 10 mmol/L $CuCl_2$ aqueous solution with equal volume, and sonicated for 2 h. The 5 mmol/L dispersion C ($[Cu(C_{18}H_{37}NHCH_2CH_2CH_2NH_2)_2](NO_3)_2$) was prepared by means of the same method as dispersion B.

2.2.2. Surface tension measurements

The surface tension was measured by the Wilhelmy vertical plate method using a Krűss model K100 processor tensionmeter at 30 °C, which was thermostated using a Thermo Haake DC 30. The concentration of solution was changed by a Metrohm 765 dosimat.

2.2.3. UV–vis spectral measurements

The dispersion A, B and C were used to measure the electronic spectra with a PGENERAL model Tu-1901 UV–vis spectrophotometer, pure water was used as reference.

2.2.4. Transmission electron microscopic measurements

The morphological structures of the dispersions were observed with a Hitachi H-8100 transmission electron microscope by the negative staining method. One drop of the dispersion was placed on a Cu grid coated with conductive polymer film. After one minute the excess fluid was drained off with filter paper and a drop of the negative stain added. After one minute the residue of 2 wt% aqueous uranyl acetate was removed with filter paper and grid immediately placed in the electron microscope.

2.2.5. Size measurements

The size of dispersion A, B and C was recorded by means of dynamic light scattering method on a Malvern ZetaSizer model Nano ZS. The equipment can measure particles from 0.6 nm to 6 μm with a detector at position 173° to measure the intensity of the scattered light.

2.2.6. Small-angle XRD measurements

The cast films were prepared by spreading a few drops of the dispersions on glasses. After the water has been fully evaporated in air, the glasses were continuously dried in vacuum for 3 days. The obtained cast films were kept in a saturated water atmosphere for 2 days at room temperature. The XRD patterns of cast films were measured on BRUKER D8 advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å).

2.2.7. DSC measurements

Twenty microlitres sample and 20 μL doubly distilled water were sealed into aluminic pan, respectively. The DSC measurements were performed on NETZSCH DSC 200PC, and the DSC thermograms were scanned at a heating rate of 3 °C min^{-1}.

3. Results and discussion

3.1. Surface tension measurements

Significant reduction in surface tension of water is one of the important properties of amphiphiles [1]. Surface tension measurements have been introduced into our experiments. The surface tension (γ) versus logarithm of concentrations ($\log C$) curves of dispersion A, B and C are shown in Fig. 1. It can be seen that the surface tension sharply decreases with the concentration increasing, and reaches a plateau after critical aggregation concentration (cac). This proves that self-aggregations formed in dispersions. The values of cac and surface tension at cac (γ_{cac}) of these dispersions can be determined from the inflection points in the γ–$\log C$ curves. The adsorption of surfactants (Γ) is calculated according to Gibbs adsorption equation $\Gamma = -d\gamma/RT\, d\ln C$ for dispersion A, and $\Gamma = -d\gamma/3T\, d\ln C$ for dispersion B and C [1]. For calculating the saturation adsorption (Γ_{max}), the slopes of the straight parts of γ–$\log C$ curves are taken for the $d\gamma/d\ln C$ values in Gibbs equation. Then the minimum area per surfactant molecule (A_{min}) is obtained from the saturation adsorption by $A_{min} = 1/N_A\Gamma_{max}$ [1]. The values of cac, γ_{cac}, Γ_{max} and A_{min} are shown in Table 1. Compared with dispersion B and C, metal ion-free dispersion A shows higher cac and lower γ_{cac}. As we all