

## Transformation of Structure and Properties of Vesicles Induced by Transition Metal Ions

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**Abstract:** This paper proved that octodecyl propylenediamine could form vesicles in pure water and aqueous solution of  $\text{CuCl}_2$  or  $\text{Cu}(\text{NO}_3)_2$ . The structure and morphology of vesicles were different when the copper (II) salt was added to the solution. The results showed that both the counterions and the ligands had strong influence on the configuration of coordinated structures and packing model in bilayer membrane of vesicles.

**Keywords:** Octodecyl propylenediamine, copper (II) ions, vesicle, bilayer membrane, counterions, coordinated structure.

Vesicles have long been a scientific curiosity due to their structural resemblance to primitive biological cells. Synthetic amphiphiles with different chemical structures and composition of headgroups and hydrophobic tails that can self-organize into vesicles in dilute aqueous solutions have been reported<sup>1</sup>. In recent years, self-assembly structures induced and controlled by metal ions have become a topic of increasing interest. It has been found that the counterions have a strong influence on the organized structure of  $\text{Cu}^{2+}$ -coordinated bilayer membranes formed by monoalkylethylenediamine amphiphiles<sup>2</sup>. Unfortunately, the influence of amphiphilic ligands on the organized structure has not been reported. It is known that the replacement of ethylenediamine group by propylenediamine in the ligand results in a considerable decrease of stability of chelate, which means that selective binding to metal ions happens. It is interesting to understand how the counterions and ligands affect the configuration of coordinated structures and packing model in bilayer membrane of vesicles. In this work, the amphiphile octodecyl propylenediamine ( $\text{C}_{18}\text{H}_{37}\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) has been chosen to study the effects of ligands and counterions on membrane structure and properties.

### Experimental

Octodecyl propylenediamine ( $\text{C}_{18}\text{H}_{37}\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) was obtained from Jiangsu Feixiang Chemical Co., LTD., and recrystallized three times from methanol *prior to* use.  $\text{CuCl}_2$  and  $\text{Cu}(\text{NO}_3)_2$  were of analytical grade and used as received. Water was distilled

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twice.

The 0.02 mol/L dispersion A was prepared by mixing  $C_{18}H_{37}NHCH_2CH_2CH_2NH_2$  and water. The 0.005 mol/L dispersion B ( $[Cu(C_{18}H_{37}NHCH_2CH_2CH_2NH_2)_2]Cl_2$ ) was prepared by mixing dispersion A and 0.01 mol/L  $CuCl_2$  aqueous solution with equal volume. The 0.005 mol/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.

Surface tension was measured by the Wilhelmy vertical plate method using a Krüss model K100 processor tensiometer. The electronic spectra were measured with a PGENERAL model Tu-1901 UV-Vis spectrophotometer. The morphological structures of the dispersions were observed with a Hitachi H-8100 transmission electron microscope, using the negative staining method. A Malvern ZetaSizer model Nano ZS was employed to characterize the size of vesicles by means of dynamic light scattering. The XRD patterns of cast films were measured on Bruker D8 Advance X-ray Diffractometer. The DSC measurements were performed on Netzsch DSC 200PC.

## Results and Discussion

Significant reduction in surface tension of water is one of the important properties of amphiphiles<sup>3</sup>. It has been observed that the surface tension of dispersion A, B and C sharply decreased with the increase of concentration and reached a plateau, indicating that aggregations have formed in all the dispersions. The fundamental surface physicochemical properties of these dispersions are shown in **Table 1**. Compared with dispersion B and C, dispersion A has higher critical aggregation concentration (cac) and lower surface tension at cac ( $\gamma_{cac}$ ). Packing parameter concept proposed by Israelachvili told us that the geometric constraints of surfactant molecule play a critical role in defining its supramolecular properties<sup>4</sup>. It has been established that when the value of packing parameter (P) is in the range of 0.5-1, the self-aggregate structure could be vesicles or bilayers<sup>4</sup>. The value of P is calculated as 0.62, 0.74 and 0.64 for dispersion A, B and C, respectively, which means that the vesicles or bilayers would be preferred. Transition electron micrographs showed that vesicular structures have formed, and the size of these vesicles ranges from several ten to several hundred nm, which was further confirmed by dynamic light scattering technique.

The tremendous difference was observed after the addition of copper (II) salt. The dispersion A was a white uniform emulsion, while the dispersion B showed a cyan emulsion, and dispersion C showed a sky blue emulsion. Comparison of dispersion A and dispersion B showed two obvious bands at 336 nm and 659 nm in UV-Vis spectra, while the bands of dispersion C showed at 335 nm and 627 nm. The representative results are summarized in **Table 2**. From the color and electron spectra, it can be concluded that complexes of octodecyl propylenediamine and  $Cu^{2+}$  have formed in dispersion B and C. It has been established that complexes of  $CuN_4$  with a square-coplanar structure showed d-d transition energies in the range of  $(18-20)\times 10^3\text{ cm}^{-1}$ , while the range for tetrahedral structure is  $(12-16)\times 10^3\text{ cm}^{-1}$ <sup>2,5</sup>. Based on the electron transition, it can be thought that the  $Cu^{2+}$ -coordinated headgroups adopt tetrahedral structures in dispersion B and C, which probably slightly compressed due to asymmetric

**Table 1** The surface physicochemical properties of dispersion A, B and C

Dispersion	cac (mol L <sup>-1</sup> )	$\gamma_{\text{cac}}$ (mN m <sup>-1</sup> )	G <sub>max</sub> ( $\mu\text{mol m}^{-2}$ )	A <sub>min</sub> (nm <sup>2</sup> )	P
A	2.14×10 <sup>-4</sup>	24.69	4.86	0.34	0.62
B	3.08×10 <sup>-5</sup>	31.60	2.94	0.57	0.74
C	5.19×10 <sup>-5</sup>	32.20	2.43	0.66	0.64

**Table 2** The solution physicochemical properties of dispersion A, B and C

Dispersion	Solution appearance	UV-Vis (nm)	XRD (D <sub>n</sub> nm)	DSC (T <sub>c</sub> °C)	
A	White emulsion	200	—	5.74	77.7
B	Cyan emulsion	336	659	3.49	82.2
C	Blue emulsion	335	627	3.37	92.4

derivatives of propylenediamine, and the degree of tetrahedral structure compressed is quite different in these two systems due to the difference of counter ions. However, our finding is quite different from complexes  $[\text{Cu}(\text{C}_{18}\text{H}_{37}\text{NHC}_2\text{H}_4\text{NH}_2)_2]\text{X}_2$ , where the complex adopts compressed tetrahedral structures when  $\text{X}=\text{Cl}$  and square-coplanar ones when  $\text{X}=\text{NO}_3$ <sup>2</sup>. It means that even only one more  $-\text{CH}_2-$  group existed in the headgroups of amphiphiles, the influence of counter ions on complexes structures become weaker. It showed that the coordinated structures were not only influenced by counter ions, but by the ligands as well.

UV-Vis spectral measurement showed that one molecule of copper (II) coordinate with two molecules of octodecyl propylenediamine, and the two tails in the complexes took approximately diagonal positions because of the compressed tetrahedral structure. It is well known that double chained amphiphiles have lower value of cac than that of single chained ones<sup>3</sup>, which has also been observed in our surface tension measurements.

The small angle X-ray diffraction measurement was used to determine the long spacing (D<sub>n</sub>) of the aggregates<sup>2</sup>. The XRD patterns of the corresponding cast film from dispersion A, B and C exhibited periodic peaks, which demonstrated the well ordered structures. The molecular length of the corresponding amphiphile octodecyl propylenediamine is estimated to be 2.84 nm by the CPK molecular model. In the case of dispersion A, the long spacing of bilayer was approximately twice the evaluated monomolecular length, showing that the amphiphilic molecules probably assume the erective tail-to-tail chain packing model (H-like model) in bilayer membranes<sup>6</sup>. The gel-to-liquid crystal phase transition is one of the intrinsic physicochemical properties of bilayer membranes, and the relatively high phase transition temperature implied a tight packing model of the hydrocarbon chain<sup>2,6</sup>. DSC curve of each dispersion showed endothermic peaks, from which the phase transition temperatures can be obtained. The results are showed in **Table 2**. DSC measurements revealed that the dispersion B and C have higher T<sub>c</sub>, which means that the molecular packing models in the bilayer membranes become tighter after the Cu<sup>2+</sup>-coordinated amphiphiles formed. It has shown that the interdigitated-type bilayer membranes displayed high T<sub>c</sub> values<sup>2</sup>. XRD results that dispersion B and C have thinner bilayer membranes than dispersion A, so it can be inferred that for dispersion B and C, the Cu<sup>2+</sup>-coordinated amphiphiles adopted

the interdigitated chain packing model of aliphatic chains in the bilayer membranes. Considering the higher  $T_c$  and lower  $D_n$ , the inserted degree of dispersion C was larger than that of dispersion B.

In conclusion, the amphiphile octodecyl propylenediamine could form vesicles in pure water and aqueous solution of  $\text{CuCl}_2$  or  $\text{Cu}(\text{NO}_3)_2$ . The properties of solution and surface were changed when amphiphiles octodecyl propylenediamine were cooperated with  $\text{Cu}^{2+}$ . The results showed that both the counterions and the amphiphilic ligands had strong influence on the configuration of coordinated structures and packing model in bilayer membrane of vesicles. By altering the counterions and the types of amphiphilic ligands, the structure and properties of vesicle induced by transition metal ions could be modulated.

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