



## Assembly of Aminopropyltetrasiloxane Cu<sup>2+</sup>-Induced in Aqueous Solution

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A Cu<sup>2+</sup>-induced vesicle phase was prepared from a mixture of 3-aminopropyltetrasiloxane and CuCl<sub>2</sub> or Cu(NO<sub>3</sub>)<sub>2</sub> in aqueous solutions. Cu<sup>2+</sup> coordinated with 3-aminopropyltetrasiloxane resulting in the formation of molecular bilayers, because Cu<sup>2+</sup> can firmly bind to the amino groups of 3-aminopropyltetrasiloxane which reduced the area of the head-group. In this system, no counter ions in aqueous solution exist because of the Cu<sup>2+</sup>-ligand coordination and the bilayer membranes are not shielded by salts. The vesicles were determined by transmission electron microscopy images and dynamic light scattering measurements.

**Key Words:** Copper(II), Aminopropyltetrasiloxane, Vesicle.

### INTRODUCTION

Vesicles are one of a large variety of structures from amphiphiles self-assemble<sup>1,2</sup>. Vesicles are particularly interesting because they provide simple models for biological membranes. Spontaneous vesicle formation can be observed in natural surfactant (phospholipid) solutions<sup>3</sup>. Therefore, the construction of vesicular phases by surfactants in aqueous solution has been studied extensively. For example, catanionic vesicles can be obtained by mixing cationic and anionic surfactants<sup>4,5</sup>. However these cationic-anionic surfactant systems often precipitate in aqueous solution due to partial shielding of charges, especially when the mixture involves equal proportions of each component. This significantly limits the creation of such vesicles and the applications for which they can be used.

So design of novel surfactants which can form vesicle is, therefore, extremely interesting and important for further studies of vesicle structure. As for common single-tail hydrocarbon amphiphiles, it has been known that they usually form micelles in dilute aqueous solution other than vesicles. Those incorporating large rigid segments within the chain (*e.g.* biphenyl, azobenzene, fullerene *etc.*)<sup>6,7</sup> or with a hyperextended hydrocarbon chain<sup>8</sup> and the mixed ion-pair single-tail hydrocarbon amphiphiles<sup>9,10</sup> can form vesicles in dilute aqueous solution spontaneously. Recently, a variety of well defined siloxane based amphiphiles have been synthesized and their self-aggregation was investigated<sup>11-14</sup>. The intense hydrophobic effect developed by siloxane chains results in the formation vesicles.

To date, double-chain dialkyldimethyl-aminonium surfactants<sup>15</sup> and diesterquats<sup>16</sup> can form vesicle. Recently single gemini surfactants<sup>17,18</sup> and bola surfactants<sup>19</sup> have been reported to form vesicles spontaneously. Further more, metal-ligand complexations have been used as new non covalent interactions in the engineering of supramolecular assemblies. Metal-ligand interaction used in the formation of supramolecular links in traditional surfactant systems were investigated recently by Hoffmann *et al.*<sup>20</sup>. They reported salt-free M<sup>2+</sup> (Zn<sup>2+</sup>, Ba<sup>2+</sup> and Ca<sup>2+</sup>)-coordination complex vesicles in aqueous solutions<sup>20-22</sup>. A spontaneous phase transition from micelles to vesicles has been observed in presence of the Cu<sup>2+</sup>, Co<sup>2+</sup> or Ni<sup>2+</sup> in dilute aqueous solution of sodium hexadecyliminodiacetate<sup>23</sup>.

In the present work, we report a new vesicle-phase system constructing by 3-aminopropyltetrasiloxane [(Me<sub>3</sub>SiO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>] and Cu<sup>2+</sup>. Vesicle phases form because of the introduction of Cu<sup>2+</sup>. As comparison, we mixed 3-aminopropyltetrasiloxane with KCl in aqueous solution and no vesicle phase was found.

### EXPERIMENTAL

3-Aminopropyltetrasiloxane was synthesized according to method of Zhang *et al.*<sup>24</sup>. Double distilled was used for the analysis and for the measurements.

**Dispersion preparation:** Dispersions were prepared according to the described method: A mixture of 2 mmol of (Me<sub>3</sub>SiO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> 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 ( $[\text{Cu}((\text{Me}_3\text{SiO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]\text{Cl}_2$ ) was prepared by mixing dispersion A and 10 mmol/L  $\text{CuCl}_2$  aqueous solution with equal volume and sonicated for 2 h. The 5 mmol/L dispersion C ( $[\text{Cu}((\text{Me}_3\text{SiO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2](\text{NO}_3)_2$ ) was prepared by means of the same method as dispersion B.

**Dynamic light scattering measurement:** The size measurements were recorded by means of dynamic light scattering method on a Brookhaven Zeta plus particle size analysis rig at a scattering angle of  $90^\circ$  with a wavelength of 675 nm. The samples were equilibrated and run at  $25^\circ\text{C}$ . The obtained scattering data were fitted using an intensity-weighted cumulative analysis to estimate the diffusion coefficient. For spherical particles, the hydrodynamic diameter  $d(h)$  were obtained from diffusion coefficient by using the Stokes-Einstein relation  $d(h) = kT/(3\pi\eta D)$  where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature and  $\eta$  is the viscosity of the solution.

**Transmission electron microscopy:** The structures of dispersions were observed by transmission electron microscopy using a JEM-1011 electron microscope (JEOL, JAPAN) at an acceleration voltage of 100 kV. A droplet of dispersion solution was placed onto a 400-mesh copper grid coated with a thin film of carbon. The grid was tapped with filter paper to remove excess liquid. When solvent evaporated at room temperature under atmospheric pressure for 24 h, the grids were negatively stained by 1.5 wt % phosphor-tungstic acid.

## RESULTS AND DISCUSSION

**Dispersion studies:** The dispersion of 3-aminopropyltetrasiloxane was a white uniform emulsion. The tremendous difference was observed after the addition of copper salt., while the dispersion  $[\text{Cu}((\text{Me}_3\text{SiO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]\text{Cl}_2$  showed a sky blue emulsion,  $[\text{Cu}((\text{Me}_3\text{SiO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2](\text{NO}_3)_2$  is light blue as shown in Fig. 1. The suspension turned from absolutely white transparent to sky-blue or light blue translucent, indicating that the dimensions of the resulting species should be within nanoscale and there exists interaction between  $(\text{Me}_3\text{SiO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  and  $\text{Cu}^{2+}$  ion.

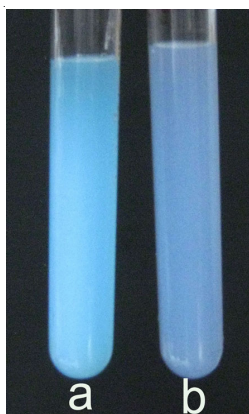


Fig. 1. Picture of dispersion B (1a) and C (1b)

**TEM studies:** TEM techniques were used to further visualize the structure of the large aggregates. Transmission electron micrographs of dispersion were shown in Fig. 2a and 2b. It can be seen that dispersions B and C exhibit vesicles

typical morphologies. The diameter of the vesicles was 400 nm in dispersion B. However, the vesicles have rather poly-disperse size distribution in dispersion C. Its diameters of the vesicles range greatly from around 150 nm to 300 nm. Obviously the type of ion has important effect on its diameters of vesicles.

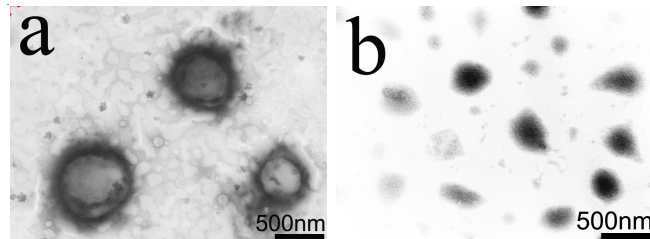


Fig. 2. Transmission electron micrographs of aggregates of dispersion B (1a) and C (1b)

**Size distribution:** Dynamic light scattering measurements were carried out to further investigate the size of dispersion from 3-aminopropyltetrasiloxane and  $\text{Cu}^{2+}$  ion. The size distribution of the dispersion B and C is shown in Fig. 3. As can be seen from Fig. 3, the distribution profile is one distribution peaks for B and two distribution peaks for C, which indicates a much wider size distribution. These diameters were larger than those obtained for a micelle, which generally ranged between 5 and 10 nm and suggest the formation of vesicles. In bimodal distributions the maximum corresponding to larger aggregates indicates that there is only a small population of these aggregates. The size of the structures seen in the TEM images does not exactly reflect the size distribution of the vesicles observed by DLS. Taking into account this swelling, the sizes of the aggregates observed by DLS were in agreement with those derived by TEM.

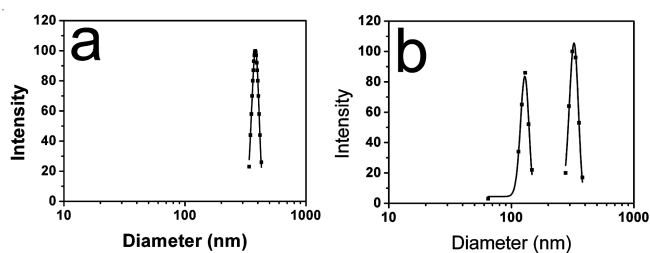


Fig. 3. Size distribution of dispersion B (upper) and C (down)

**Mechanism of aggregates:** To understand the mechanism of the vesicle formation of 3-aminopropyltetrasiloxane in dilute  $\text{Cu}^{2+}$  solution, in another experiment, we found that no vesicles could be obtained by dispersing 3-aminopropyltetrasiloxane (0.10 mmol) in 10 mL of an aqueous solution of KCl (5 mmol/L) under sonication. The geometries of single amphiphilic molecules are important factors dominating the aggregate morphology formed in aqueous solutions. Israelachvili and coworkers<sup>25</sup> proposed a geometric packing model. The allowed packing of amphiphilic molecules is governed by the packing parameter  $P = v/la$ . In this scheme, when  $P$  is greater than  $1/2$ , first highly curved bilayer vesicles and then flat bilayers form as  $f$  goes to 1. In the dispersion of 3-aminopropyltetrasiloxane in  $\text{CuCl}_2$  solution, a  $\text{Cu}^{2+}$  ion coordinates with

two 3-aminopropyltetrasiloxane molecules and thus they form pseudo-double-tailed surfactants with a coordinated head group, which are of a cuplike structure. The packing parameter  $f$  of the ion complex is between  $1/2$  and  $1$ , which meets the requirement for vesicle formation and may self-assemble into spherical vesicles in aqueous solution. The micelle formation in dilute KCl aqueous solution and bilayer formation of 3-aminopropyltetrasiloxane in dilute  $\text{CuCl}_2$  solution are illustrated in Fig. 4.

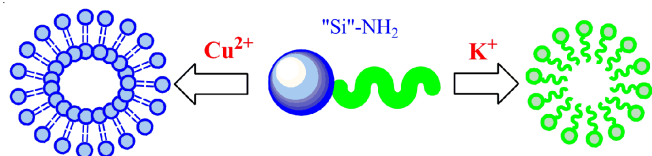


Fig. 4. Schematic representation of vesicle formation of 3-aminopropyltetrasiloxane induced by  $\text{Cu}^{2+}$  ion. The relative headgroup size between micelle and vesicle is not drawn to scale

### Conclusion

In conclusion, we have shown that 3-aminopropyltetrasiloxane, which only forms micelles in dilute KCl aqueous solution, assembles into vesicles induced by  $\text{Cu}^{2+}$  ion.

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