COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Vesicle formation induced by metal ions from micelle-forming sodium hexadecylimino diacetate in dilute aqueous solution

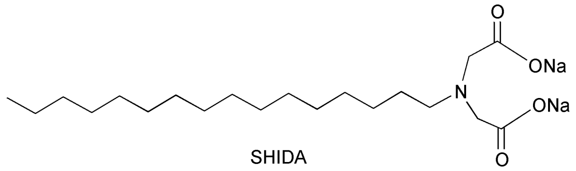
Xuzhong Luo, Sanxie Wu and Yingqiu Liang*

Lab of Mesoscopic Materials Science and State Key Lab of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China. E-mail: yqliang@nju.edu.cn

Received (in Cambridge, UK) 26th November 2001, Accepted 24th January 2002
First published as an Advance Article on the web 7th February 2002

In dilute aqueous solution, micelle-forming sodium hexadecylimino diacetate assembles into vesicles induced by Cu(II), Co(II) and Ni(II) ions.

Syntheses of amphiphilic molecules that can self-organize into vesicular structure are pursued in many laboratories because of their importance in various fields of chemistry and biochemistry. In recent years, synthetic amphiphiles that can self-organize into vesicles in dilute aqueous solution have been reported with different chemical structures and composition of headgroups and hydrophobic tail(s).[1–8] Several recent reports reveal that vesicle-forming synthetic double-tail amphiphiles can self-assemble into columns of stacked lipid bilayers by metal ion recognition.[9,10] 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, azobezene *etc.*)[11,12] or with a hyperextended hydrocarbon chain[13] and the mixed ‘ion-pair single-tail hydrocarbon amphiphiles’[2,14] can form vesicles in dilute aqueous solution. To our knowledge, reports concerning vesicle formation induced by metal ions in dilute aqueous solution from a simple micelle-forming amphiphile with a common hydrocarbon chain and possessing no rigid segment are relatively few.[1] Herein, we show that in dilute aqueous solution, sodium hexadecylimino diacetate (SHIDA) assembles into vesicles induced by Cu(II), Co(II) and Ni(II) ions.


SHIDA

SHIDA used here were prepared in our laboratory.† SHIDA forms micelles in water with a critical micelle concentration of 1.0 × 10^{-3} M. Copper sulfate, cobalt chloride and nickel sulfate used here were of analytical grade. In order to study the influence of adding metal ions on the aggregation behavior, 10^{-2} M dispersions A [2SHIDA·$CuSO_4$], B [2SHIDA·$CoCl_2$] and C [2SHIDA·$NiSO_4$] were prepared by dispersing SHIDA in aqueous solution of $CuSO_4$ (5 × 10^{-3} M), $CoCl_2$ (5 × 10^{-3} M) and $NiSO_4$ (5 × 10^{-3} M), respectively, under sonication. The dispersions were investigated by transmission electron microscopy (JEOL Model JEM-200CX), differential scanning calorimetry (SETA-RAM MODEL Micro-DSC) and UV–VIS spectrometry (Shimadzu UV3100) and their cast films[9,15] were studied by small-angle X-ray diffraction (Rigaku Model D/Max-RA). The results are summarized in Table 1.

Typical transmission electron micrographs reveal that all the dispersions display vesicular morphologies and typical transmission electron micrographs of the dispersions are shown in Fig. 1. The XRD patterns (shown in Fig. 2) of the corresponding cast films from the dispersions all exhibit periodic peaks, demonstrating a well-ordered structure. The long spacings (*D*) of the aggregates (shown in Table 1) obtained by small-angle X-ray diffraction experiments are all slightly larger than the evaluated monomolecular length by CPK modelling. On heating, all the dispersions exhibit the gel-to-liquid crystal phase transition (T_c transition) at relatively high temperatures (shown in Table 1). It is known that the T_c transition is an intrinsic physicochemical property of bilayer membranes, and the relatively high phase transition temperature implies a tight packing model of the hydrocarbon chain (interdigitated packing model).[15] According to the TEM, XRD and DSC results, it can be deduced that in dispersions A, B and C the amphiphiles assemble into bilayer membranes showing interdigitated packing.

In order to understand the mechanism of the formation of vesicles of SHIDA in dilute $CuSO_4$, $CoCl_2$ and $NiSO_4$ solution dispersions of SHIDA in dilute Na_2SO_4 and KCl solutions were

Table 1 TEM and DSC results on the morphology and phase transition temperature of amphiphilic aggregates in aqueous dispersions A, B and C, along with small-angle XRD results of their cast films

Sample	Solution appearance	Morphology (TEM)	T_c/°C (DSC) (ΔH^a/kJ mol^{-1})	Evaluated molecular length/nm (CPK)	Long space/nm (XRD)
A	Blue emulsion	Vesicle	55 (39.9)	2.7	3.22
B	Purple emulsion	Vesicle	60 (47.0)	2.7	3.07
C	White emulsion	Vesicle	73 (51.6)	2.7	3.21

[a] kJ per mol SHIDA

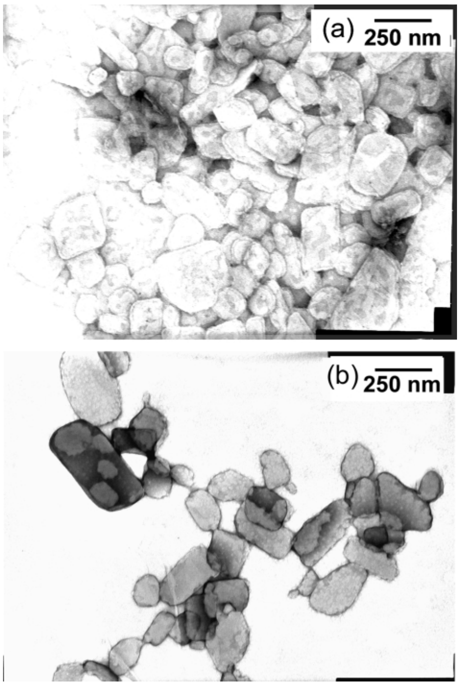


Fig. 1 Transmission electron micrographs of aqueous samples from dispersions B (a) and C (b) (post-stained with 2 mass% uranyl acetate).

DOI: 10.1039/b110797f

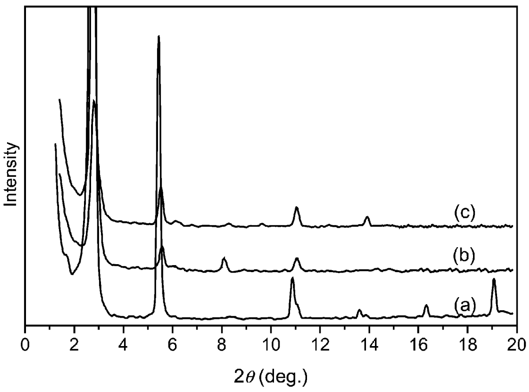


Fig. 2 XRD patterns of the cast films from dispersions A (a), B (b) and C (c).

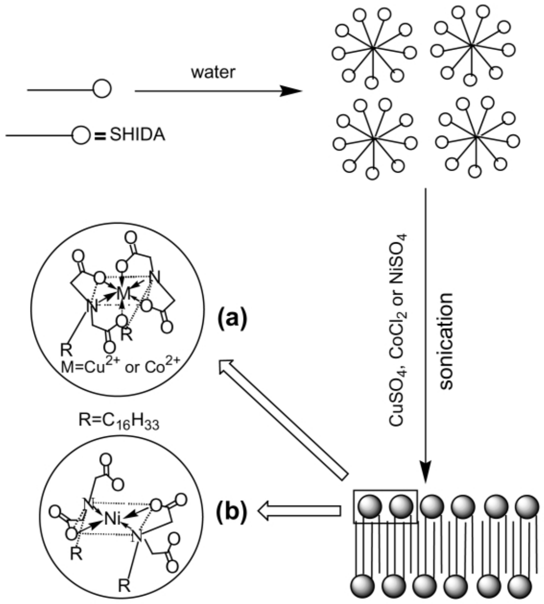


Fig. 3 Schematic representation of micelle formation from SHIDA in aqueous solution and bilayer formation upon coordination of Cu(II), Co(II) and Ni(II) ions to SHIDA. (a) The proposed coordination model of SHIDA with Cu(II) and Co(II) ions; (b) the proposed coordination model of SHIDA with Ni(II) ions. The relative headgroup size between micelle and vesicle is not drawn to scale.

inspected and no vesicle formation was observed. A previous study[16] reveals that 2 mol of iminodiacetate can coordinate 1 mol of Cu(II), Co(II) and Ni(II) ions, respectively, to form stable coordination compounds, while Na(I) and K(I) ions can not. Therefore, it is reasonable to deduce that the coordination between the iminodiacetate group of SHIDA and metal ion (Cu(II), Co(II) or Ni(II)) stimulates the aggregation of the amphiphiles into vesicles. Israelachvili and coworkers[17] proposed a shape-structure or packing parameter concept, which predicts micelle formation for single-chain surfactants and bilayers for double-chain surfactants. In dispersions A, B and C, SHIDA coordinates with Cu(II), Co(II) and Ni(II) ions to form double-tailed surfactants with a coordinated headgroup, which may self-assemble into vesicles. The bilayer formation of SHIDA in dilute $CuSO_4$, $CoCl_2$ and $NiSO_4$ solution and the proposed coordinated models[16] of the headgroup are illustrated in Fig. 3. For Cu(II) and Co(II) ions, the coordinated headgroups lead to octahedral coordination with the two tails in the complexes located at diagonal positions of a parallelogram (Fig. 3(a)); while for Ni(II) ion, a parallelogram (four coordinate) coordination model is adopted with the two tails in the complexes also located at diagonal positions (Fig. 3(b)).

In conclusion, we have shown that in dilute aqueous solution, SHIDA, a amphiphile which forms micelles in dilute aqueous solution, assembles into vesicles induced by Cu (II), Co(II) and Ni(II) ions.

This work was financially supported by the National Natural Science Foundation of China (NSFC, NO. 20073019).

Notes and references

† 1-Bromohexadecane reacts with diethyl iminodiacetate in THF and Et_3N to give diethyl hexadecylimino diacetate. Sodium hexadecylimino diacetate was obtained by hydrolyzing diethyl hexadecylimino diacetate in 1 M NaOH solution. Satisfactory ^{1}H NMR, IR and elemental analysis were obtained for the final product after recrystallization.

1 J. S. Martinez, G. P. Zhang, P. D. Holt, H.-T. Jung, C. J. Carrano, M. G. Haygood and A. Butler, *Science*, 2000, **287**, 1245.
2 B. zu Putlitz, H. P. Hentz, K. Landfester and M. Antonietti, *Langmuir*, 2000, **16**, 3003.
3 P. Bandyopadhyay and P. K. Bharadwaj, *Langmuir*, 1998, **14**, 7537.
4 S. Bhattacharya and S. De, *Chem. Commun.*, 1997, 2287.
5 N. Kimizuka, T. wakiyama, H. Miyauchi, T. Yoshimi, M. Tokuhiro and T. Kunitake, *J. Am. Chem. Soc.*, 1996, **118**, 5808.
6 P. Ghosh, T. K. Khan and P. K. Bharadwaj, *Chem. Commun.*, 1996, 189.
7 T. Shimizu, M. Masuda and M. Shibakami, *Chem. Lett.*, 1997, 267.
8 A. P. H. Schenning, B. de Bruin, M. C. Feiters and R. J. M. Nolte, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1662.
9 T. A. Waggoner, J. A. Last, P. G. Kotula and D. Y. Sasaki, *J. Am. Chem. Soc.*, 2001, **123**, 496.
10 E. C. Constable, W. Meier, C. Nardin and S. Mundwiler, *Chem. Commun.*, 1999, 1483.
11 T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami and K. Takarabe, *J. Am. Chem. Soc.*, 1993, **115**, 3840.
12 T. Kunitake, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 709.
13 F. M. Menger and Y. Yamasaki, *J. Am. Chem. Soc.*, 1993, **115**, 3840.
14 H. Fukuda, K. Kawata and H. Okuda, *J. Am. Chem. Soc.*, 1990, **112**, 1635.
15 T. Kunitake, N. Kimizuka, N. Higashi and N. Nakashima, *J. Am. Chem. Soc.*, 1984, **106**, 1978; C. Li, X. Lu, X. Luo and Y. Liang, *Chem. Commun.*, 2001, 1440.
16 S. Chaberek Jr. and A. E. Martell, *J. Am. Chem. Soc.*, 1952, **74**, 5052.
17 J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1525.