

Zn²⁺-Induced Vesicle Formation

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Zn²⁺-induced vesicle formation has been studied for the first time in aqueous mixtures of tetradecyldimethylamine oxide (C₁₄DMAO) and zinc 2,2-dihydroperfluorooctanoate [Zn(C₆F₁₃CH₂COO)₂]. The charged vesicle phase without any cosurfactants was prepared in the aqueous mixtures. The charged vesicle phase has interesting rheological properties. This ionically charged vesicle phase is not shielded by excess salts because of salt-free aqueous solutions. Such a vesicle phase is important for many applications where cosurfactant is not used. A cationic/anionic surfactant C₁₄DMAOH⁺ -OOCCH₂C₆F₁₃ system could be produced from C₁₄DMAO/Zn(C₆F₁₃CH₂COO)₂ mixtures because the zwitterionic surfactant C₁₄DMAO can be charged by the H⁺ released from H₂S to a cationic surfactant and Zn²⁺ is precipitated. After ZnS particles are removed from the cationic/anionic surfactant solutions, the finally mixed sample does not contain excess salts as do other studied cationic/anionic surfactant systems. The sample is a birefringent L α -phase and consists of unilamellar and multilamellar vesicles. The novel vesicle reproduction route should provide a new method to prepare nanoscale particles.

Vesicles in aqueous solutions are the fascinating supramolecular self-assemblies formed by amphiphiles in feasible experimental conditions, which is because vesicles represent the simple model systems for biological membranes¹ and recent developments in material sciences on the theme of “vesicle templating” are highlighted.² Vesicles have been first observed in biological systems that consisted of phospholipids such as lecithin. Vesicles from these compounds in aqueous solutions can be prepared by ultrasonication or extrusion of phospholipid dispersions.³ Now it is well-known that vesicles can form from different types of surfactant systems in aqueous solutions.⁴ In the physical sense, vesicles from the natural lipids such as egg phosphatidylcholine (PC)⁵ and synthetic amphiphiles such as dioctadecyldimethylammonium chloride (DODMAC)⁶ or tetradecyldimethylamine oxide (C₁₄DMAO)⁴ are thermodynamically unstable because the symmetric membrane is curved and the excess energy of each vesicle due to its curvature is $8\pi\kappa$, κ is the elastic bending modulus of the membrane.⁵ Vesicles are formed spontaneously only in the case of bilayers with very low values of κ .^{7,8} On the basis of the geometrical considerations, surfactants can form bilayer vesicles in aqueous solutions with packing parameters ($\rho = al/v$, where a is the interfacial area of a surfactant headgroup occupied and l and v are the length and the volume of the hydrophobic group, respectively) of $1/2 \leq \rho \leq 1$.⁹

Especially interesting, vesicles can be produced in the aqueous mixtures of single-chain cationic/anionic surfactants.^{10–13} Vesicle formation of cationic/anionic surfactants is because of the charge neutralization by ion-pairing coupled with the release of hydration water and screening. The charge neutralization leads to a

pronounced increase in the geometrical packing parameter (ρ), which values are higher than those of the individual surfactants.¹⁴ In cationic/anionic surfactant aqueous mixtures, vesicle phases are usually formed when one of the surfactants is present in a small excess. The precipitates are produced when the stoichiometry between the two surfactants is exactly 1.¹⁵ When the vesicles are produced from the cationic/anionic surfactant aqueous solutions, their ionic charge from the excess surfactant is shielded by the salt that is produced from the counterions of the two ionic surfactants. This is very important for the understanding of the macroscopic properties of the vesicle phases. Vesicles that are ionically charged and are not shielded by excess salt in solutions have been prepared, but cosurfactants are used in such vesicle phases.¹⁶ pH-induced charged vesicles without any cosurfactant in the spontaneous vesicle formation of C₁₄DMAO by the binding of an aromatic counterion have been reported recently.^{17,18} These charged vesicle phases have interesting rheological properties that are highly viscoelastic and yield stress values. Very recently, the self-assemblies of flat nanodiscs and unusual shapes such as regular hollow icosahedra in salt-free cationic/anionic surfactant solutions were studied by means of freeze-fracture transmission electron microscopy (FF-TEM) and small-angle neutron scattering (SANS) methods.^{19,20}

In the present communication, we report, for the first time, to our knowledge, the preparation of a charged surfactant vesicle phase without any cosurfactants and the ionic charges are not shielded because of the salt-free solutions. The charged vesicle phase was induced by the heavy metal ion, Zn²⁺. We observed the phase behavior of 100 mM C₁₄DMAO and increasing amounts of Zn(C₆F₁₃CH₂COO)₂ in aqueous solutions. The birefringent L α -phase with unilamellar and multilamellar vesicles is demonstrated by FF-TEM. Nanoscale semiconductor ZnS particles via a flow of H₂S gas at room temperature into the

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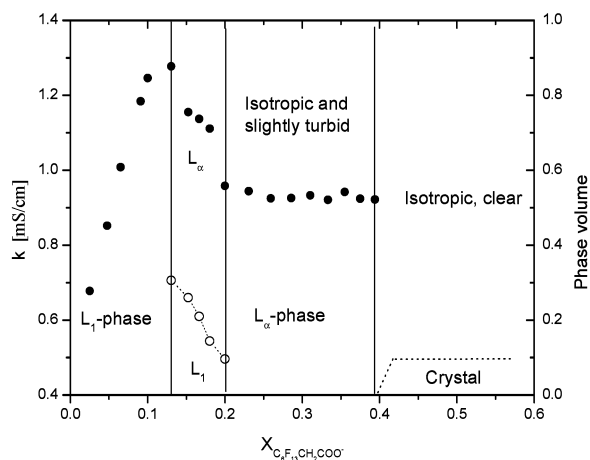


Figure 1. Phase diagram and conductivity data (●) of 100 mM C_{14} DMAO solution with increasing $Zn(C_6F_{13}CH_2COO)_2$ mole fraction at 25 °C.

vesicle phase are prepared in the birefringent $L\alpha$ -phase solutions of C_{14} DMAO and $Zn(C_6F_{13}CH_2COO)_2$. Vesicle formation could be the result of complexation between Zn^{2+} and the amine oxide group of C_{14} DMAO. When H_2S gas is injected into the vesicle phase, Zn^{2+} is precipitated by H_2S to form nanoscale semiconductor ZnS particles.²¹ The zwitterionic surfactant C_{14} DMAO is charged by the H^+ released by H_2S to a cationic surfactant and then to the combination of the cationic/anionic surfactant system $C_{14}DMAOH^+ -OOCCH_2C_6F_{13}$. The cationic/anionic surfactant system after removing ZnS particles is therefore positively charged but without excess salt in solutions. The finally birefringent cationic/anionic surfactant $L\alpha$ -phase solutions consist of unilamellar and multilamellar vesicles.²¹ The vesicle phase of the C_{14} DMAO and $Zn(C_6F_{13}CH_2COO)_2$ aqueous mixtures and the cationic/anionic $C_{14}DMAOH^+ -OOCCH_2C_6F_{13}$ system with unilamellar and multilamellar vesicles construct a novel and attractively circulative vesicle formation. Two purposes of the present study are (1) to prepare the charged vesicle phase without any cosurfactants and this ionically charged vesicle phase is not shielded by excess salts in aqueous solutions and (2) to attempt to provide a new method for preparing nanoscale semiconductor ZnS particles by the vesicle template.

Phase Behavior of C_{14} DMAO/ $Zn(C_6F_{13}CH_2COO)_2$ /H₂O System and Conductivity Data

C_{14} DMAO (100 mM) is a low viscosity L_1 -phase solution; the sequence of the phase is shown in Figure 1 which is mixing 100 mM C_{14} DMAO solution with increasing $Zn(C_6F_{13}CH_2COO)_2$ concentrations up to 75 mM. The solubility of $Zn(C_6F_{13}CH_2COO)_2$ in water at room temperature is low. When $Zn(C_6F_{13}CH_2COO)_2$ was mixed with 100 mM C_{14} DMAO solution, the Krafft temperature of $Zn(C_6F_{13}CH_2COO)_2$ is reduced. The samples were prepared at 75 °C under stirring and then thermostated at 25 °C. The samples are thermodynamically stable up to a mole fraction $x_{C_6F_{13}CH_2COO^-} = 0.395$. From $x_{C_6F_{13}CH_2COO^-} = 0-0.13$, one can note a single transparent solution, which is the L_1 -phase. Between $x_{C_6F_{13}CH_2COO^-} = 0.13$ and almost 0.20, we observe macroscopic phase separation into a birefringent $L\alpha$ -phase at the top of the L_1 -phase and an isotropic L_1 -phase at the bottom. The volumes of the birefringent $L\alpha$ -phase in the two-phase $L_1/L\alpha$ region increase with the mole fraction of $x_{C_6F_{13}CH_2COO^-}$. After the two-phase region, from $x_{C_6F_{13}CH_2COO^-} = 0.20$ to 0.395, one observes a single transparent birefringent $L\alpha$ -phase that is very stable, slightly turbid, and

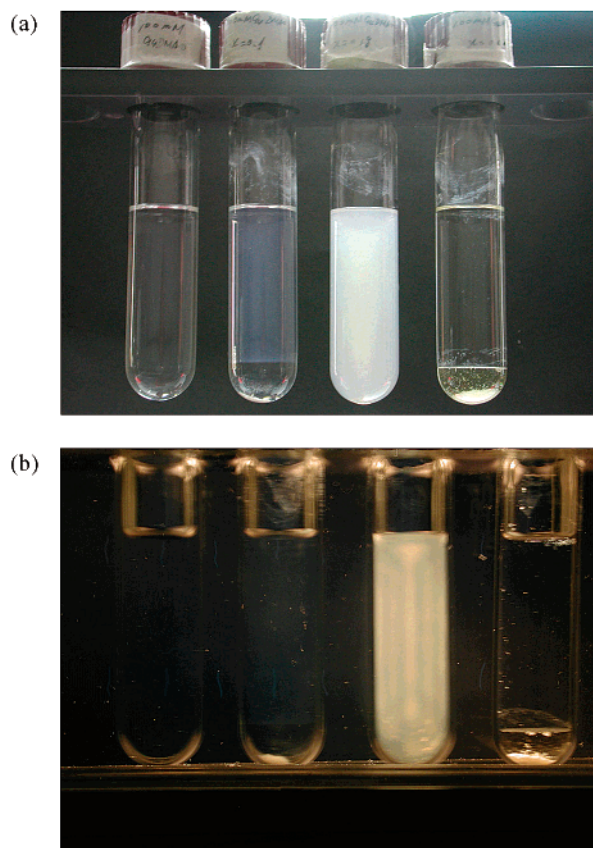


Figure 2. Phase behavior of the system 100 mM C_{14} DMAO and increasing amounts of $Zn(C_6F_{13}CH_2COO)_2$ at 25 °C without polarizers (a) and with polarizers (b). From left to right: $x_{C_6F_{13}CH_2COO^-} = 0.05$ (L_1 -phase), $x_{C_6F_{13}CH_2COO^-} = 0.16$ (two-phase $L_1/L\alpha$ -phase), $x_{C_6F_{13}CH_2COO^-} = 0.31$ (birefringent $L\alpha$ -phase), and $x_{C_6F_{13}CH_2COO^-} = 0.50$ (two-phase crystal/ L_1 -region).

bluish. The samples with the mole fractions $x_{C_6F_{13}CH_2COO^-} > 0.395$ again separate into a two-phase $L_1/L_{crystal}$ region. The upper phase is an isotropic L_1 -phase, and there are $Zn(C_6F_{13}CH_2COO)_2$ crystals at the bottom. The phase behavior of 100 mM C_{14} DMAO and increasing amounts of $Zn(C_6F_{13}CH_2COO)_2$ at 25 °C with or without polarizers are demonstrated in Figure 2; one can see that the third sample is birefringent.

The conductivity data of the mixed aqueous solutions are included in Figure 1. The different phase boundaries could be determined by the conductivity data. The conductivities increase more or less linearly with the $Zn(C_6F_{13}CH_2COO)_2$ mole fractions in the L_1 -phase up to $x_{C_6F_{13}CH_2COO^-} = 0.13$ and then show a sharp break at the phase boundary where the two-phase region is reached. In the two-phase region, the conductivities measured under stirring the samples decreases with $Zn(C_6F_{13}CH_2COO)_2$ mole fractions. When the $L\alpha$ -phase is reached, the conductivities decrease to a minimum even though more $Zn(C_6F_{13}CH_2COO)_2$ is added and have about constant conductivity, 0.95 mS/cm. The phase behavior and the conductivity change in the C_{14} DMAO/ $Zn(C_6F_{13}CH_2COO)_2$ /H₂O system are similar to those of the C_{14} DMAO/ $C_6F_{13}CH_2COOH$ /H₂O system.²²

FF-TEM Micrographs of the Birefringent $L\alpha$ -Phase

The birefringent $L\alpha$ -phase in the C_{14} DMAO/ $Zn(C_6F_{13}CH_2COO)_2$ /H₂O system consists of unilamellar and multilamellar vesicles, which are demonstrated in Figure 3 by means of FF-TEM experiments. The features of the vesicles are apparent: (i) Both unilamellar and multilamellar vesicles coexist. (ii)

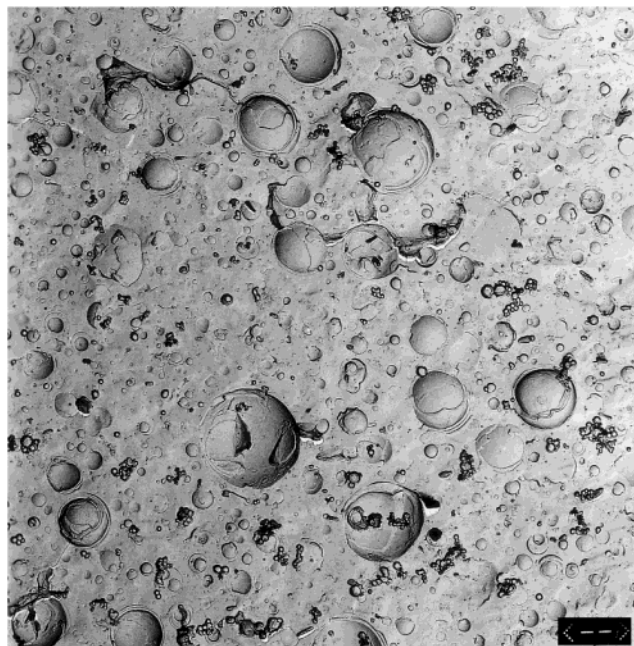


Figure 3. Unilamellar and multilamellar vesicles induced by Zn^{2+} between C_{14}DMAO and $\text{Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2$. Bar corresponds to $2.33 \mu\text{m}$.

Both unilamellar and multilamellar vesicles have rather poly-dispersed size distributions. The unilamellar vesicles have diameters ranging from about 40 nm to more than 500 nm, and the multilamellar vesicles have diameters ranging from about 500 nm to $3.0 \mu\text{m}$. (iii) The large unilamellar vesicles are relatively rarely present. (iv) In the multilamellar vesicles, the interlamellar spacing between two adjacent bilayers is about 40–60 nm.

The Zn^{2+} -induced vesicle formation in the aqueous mixtures of C_{14}DMAO and $\text{Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2$ is very interesting. The vesicle may be the result of the complexation between Zn^{2+} and the amine oxide group of C_{14}DMAO . The vesicle phase is ionically charged by Zn^{2+} , but the ionic charges are not shielded because of the salt-free aqueous solutions. The complexation could be primarily demonstrated from the slightly blue and viscoelastic solutions when C_{14}DMAO solutions are mixed with $\text{Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2$. To further examine the essential role of Zn^{2+} in the vesicle formation of $\text{C}_{14}\text{DMAO}/\text{Zn}(\text{OOCCH}_2\text{C}_6\text{F}_{13})_2/\text{H}_2\text{O}$, three samples were prepared: (a) 100 mM $\text{C}_{14}\text{DMAO}/22 \text{ mM Zn}(\text{OOCCH}_2\text{C}_6\text{F}_{13})_2/\text{H}_2\text{O}$, (b) 100 mM $\text{C}_{14}\text{DMAO}/44 \text{ mM C}_6\text{F}_{13}\text{CH}_2\text{COOK}/\text{H}_2\text{O}$, and (c) 100 mM $\text{C}_{14}\text{DMAO}/44 \text{ mM C}_6\text{F}_{13}\text{CH}_2\text{COOK}/22 \text{ mM ZnCl}_2/\text{H}_2\text{O}$. The three samples contain the same mole fraction of $x_{\text{C}_6\text{F}_{13}\text{CH}_2\text{COO}^-} (=0.31)$. However, (a) the sample is a $\text{L}\alpha$ -phase with birefringence from which the ionic charges of the vesicle phases are not shielded, (b) in the aqueous mixtures of 100 mM $\text{C}_{14}\text{DMAO}/44 \text{ mM C}_6\text{F}_{13}\text{CH}_2\text{COOK}/\text{H}_2\text{O}$ we only obtain a clear, isotropic, and low viscosity L_1 -phase, and (c) the sample is the $\text{L}\alpha$ -phase with birefringence from which the ionic charges of the vesicle phases are shielded because of the salt, KCl, in the solution. The phase behavior of the three samples demonstrates the Zn^{2+} -induced vesicle formation in the aqueous mixtures of C_{14}DMAO and $\text{Zn}(\text{OOCCH}_2\text{C}_6\text{F}_{13})_2$. Two samples of 100 mM $\text{C}_{14}\text{DMAO}/22 \text{ mM Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2/\text{H}_2\text{O}$ ($x_{\text{C}_6\text{F}_{13}\text{CH}_2\text{COO}^-} = 0.31$) and 100 mM $\text{C}_{14}\text{DMAO}/44 \text{ mM C}_6\text{F}_{13}\text{CH}_2\text{COOK}/\text{H}_2\text{O}$ ($x_{\text{C}_6\text{F}_{13}\text{CH}_2\text{COO}^-} = 0.31$) are shown in Figure 4 with or without polarizers. The two samples contain the same mole fraction of $x_{\text{C}_6\text{F}_{13}\text{CH}_2\text{COO}^-}$ but have completely different properties. One can see that the

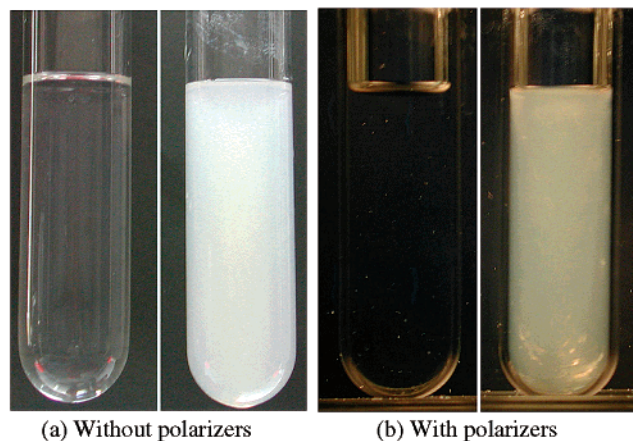


Figure 4. L_1 -phase formed by 100 mM C_{14}DMAO and 44 mM $\text{C}_6\text{F}_{13}\text{CH}_2\text{COOK}$ (left) and birefringent $\text{L}\alpha$ -phase (right) formed by 100 mM C_{14}DMAO and 22 mM $\text{Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2$. The two samples have the same mole fraction of $x_{\text{C}_6\text{F}_{13}\text{CH}_2\text{COO}^-} = 0.31$.

solution of C_{14}DMAO and $\text{Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2$ is the $\text{L}\alpha$ -phase with birefringence and in the aqueous mixtures of $\text{C}_{14}\text{DMAO}/\text{C}_6\text{F}_{13}\text{CH}_2\text{COOK}$ we only obtain only a clear, isotropic, and low viscosity or viscous L_1 -phase.

The ionically charged vesicle phase induced by Zn^{2+} is not shielded by the excess salt because of the salt-free aqueous solutions. The vesicle has been prepared without introducing any amount of cosurfactant. Such a vesicle phase is important for many applications where cosurfactant is not used.^{4,16} When H_2S gas is injected into the vesicle phase, Zn^{2+} is precipitated by H_2S to form nanoscale semiconductor ZnS particles, which has primarily been demonstrated by TEM experiments.²¹ The final solution after removing ZnS particles is the birefringent $\text{L}\alpha$ -phase with unilamellar and multilamellar vesicles, but the components are cationic/anionic surfactants because the zwitterionic surfactant C_{14}DMAO is charged by the H^+ released from H_2S to a cationic surfactant and then to the combination of the cationic/anionic surfactant system of $\text{C}_{14}\text{DMAOH}^+-\text{OOCCH}_2\text{C}_6\text{F}_{13}$. The circulative vesicle formation during the preparation of the nanoscale semiconductor ZnS particles by vesicle reproduction is completely novel and attractive.²¹

Rheological Properties of the L_1 -Phase and the Birefringent $\text{L}\alpha$ -Phase

The ionically charged vesicle phases that are not shielded by excess salts in solutions have interesting rheological properties. These phases are highly viscoelastic and have yield stress values. The rheological properties of the mixed surfactant solutions of C_{14}DMAO and $\text{Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2$ are completely different from those of the $\text{C}_{14}\text{DMAO}/\text{C}_6\text{F}_{13}\text{CH}_2\text{COOK}$ mixtures, even though the mole fractions of $x_{\text{C}_6\text{F}_{13}\text{CH}_2\text{COO}^-}$ are same in the two systems. However, the rheological properties of the solutions in the two systems behave somewhat similarly in the presence of excess salt added in solution. We measured the rheological properties of the L_1 -phase and $\text{L}\alpha$ -phase in the $\text{C}_{14}\text{DMAO}/\text{Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2$ system. In the L_1 -phase region of the mixed $\text{C}_{14}\text{DMAO}/\text{Zn}(\text{C}_6\text{F}_{13}\text{CH}_2\text{COO})_2$ solutions, one observes that the zero-shear viscosities and the relaxation times of the mixed solutions strongly increase with increasing mole fractions of $x_{\text{C}_6\text{F}_{13}\text{CH}_2\text{COO}^-}$. A typical rheogram of a sample with $x_{\text{C}_6\text{F}_{13}\text{CH}_2\text{COO}^-} = 0.10$ is shown in Figure 5. This sample is slightly viscous solution and behaves like Maxwell fluids.

In contrast to the viscous solutions of the L_1 -phase, which behave like Maxwell fluids, the solutions of the $\text{L}\alpha$ -phase are

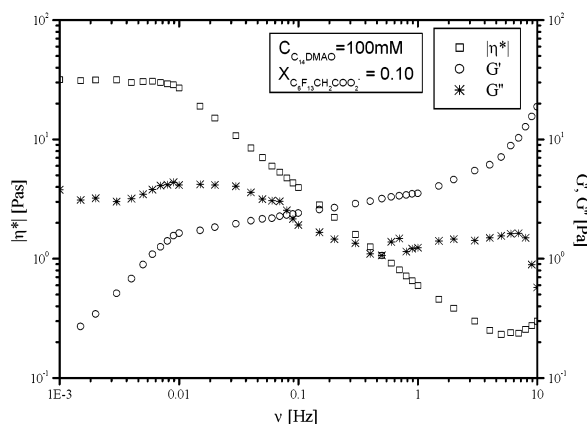


Figure 5. Rheogram of a mixed solution of 100 mM C_{14} DMAO and 5.5 mM $Zn(C_6F_{13}CH_2COO)_2$ ($x_{C_6F_{13}CH_2COO^-} = 0.10$) at 25 °C.

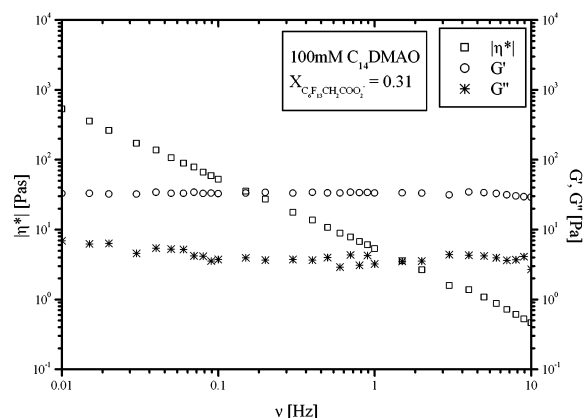


Figure 6. Rheogram of the oscillatory shear for one sample of the $L\alpha$ -phase with 100 mM C_{14} DMAO and 22 mM $Zn(C_6F_{13}CH_2COO)_2$ ($x_{C_6F_{13}CH_2COO^-} = 0.31$) at 25 °C.

highly viscoelastic and birefringent. The $L\alpha$ -phase solutions have yield values and behave, therefore, like Bingham fluids. A typical rheogram of one such $L\alpha$ -phase sample with $x_{C_6F_{13}CH_2COO^-} = 0.31$ is shown in Figure 6. The rheograms of the $L\alpha$ -phase solutions have typical properties consisting of multilamellar vesicles that behave in the same way as other charged multilamellar vesicle phases with different compositions.^{4,10,21} Both moduli are frequency independent, and the storage modulus ($G' = 33$ Pa) is about 1 order of magnitude higher than the loss modulus ($G'' = 3.5$ Pa).

The rheological properties of one sample from 100 mM C_{14} DMAO and 22 mM $Zn(C_6F_{13}CH_2COO)_2$ ($x_{C_6F_{13}CH_2COO^-} = 0.31$) solution but the Zn^{2+} was precipitated by H_2S and ZnS was removed by centrifugation is shown in Figure 7. When H_2S gas is injected into the vesicle phase, Zn^{2+} could be precipitated by H_2S to form nanoscale semiconductor ZnS particles.²¹ The zwitterionic C_{14} DMAO is charged by the H^+ released by H_2S to a cationic $C_{14}DMAOH^+$ and then to the combination of the cationic/anionic $C_{14}DMAOH^+ - OOCCH_2C_6F_{13}$ surfactant system. The cationic/anionic surfactant system with $C_{14}DMAOH^+ - OOCCH_2C_6F_{13}$ is therefore without excess salt and thus behaves as the other studied cationic/anionic surfactant systems.^{4,10,21} The final sample is the birefringent $L\alpha$ -phase. The birefringent $L\alpha$ -phase consists of novel unilamellar and multilamellar vesicles.²¹

In comparison with Figure 6, the rheological properties are completely the same. The sample in Figure 7 has the same mole fractions of $C_6F_{13}CH_2COO^-$ as in Figure 6. However, the system

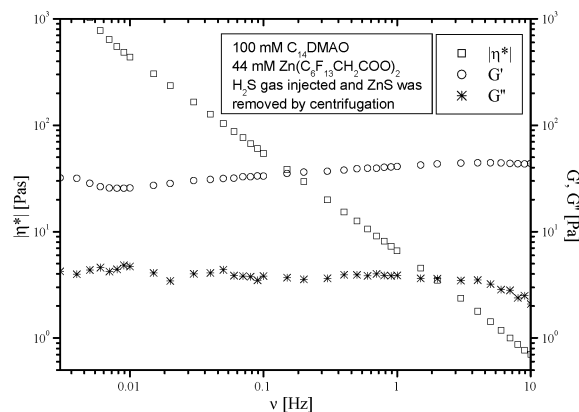


Figure 7. Rheogram of the oscillatory shear for one sample from 100 mM C_{14} DMAO/22 mM $Zn(C_6F_{13}CH_2COO)_2$ ($x_{C_6F_{13}CH_2COO^-} = 0.31$) solution, from which Zn^{2+} was precipitated by H_2S and ZnS was removed by centrifugation at 25 °C.

in Figure 7 is a cationic/anionic surfactant solution and the static electric interaction plays an important role in the vesicle formation. The cationic/anionic surfactant solution, which is similar to that in the C_{14} DMAO/ $C_6F_{13}CH_2COOH$ system, is a birefringent $L\alpha$ -phase,²² where the perfluoro-fatty acid protonates the zwitterionic surfactant because pK_a of the perfluoro-fatty acid is smaller than that of C_{14} DMAO, and a cationic surfactant is formed that recombines with the anionic perfluoro-surfactant formed by releasing protons. The rheogram of the cationic/anionic surfactant $L\alpha$ -phase solution shows typical properties consisting of multilamellar vesicles that behave in the same way as the charged multilamellar vesicles in Figure 6. Both moduli are frequency independent, and the storage modulus ($G' = 36$ Pa) is about 1 order of magnitude higher than the loss modulus ($G'' = 3.7$ Pa).

Conclusions

Zn^{2+} -induced vesicle formation in the mixed surfactant aqueous solutions of C_{14} DMAO and $Zn(C_6F_{13}CH_2COO)_2$ was studied. It is believed to be the first time, to our knowledge, that vesicle formation induced by heavy-metal ions has been observed in single-chain zwitterionic and ionic surfactant mixed aqueous solutions.

The vesicle phase reported in this communication has three properties: (1) The charged vesicle phase without any cosurfactants was prepared in a single-chain zwitterionic and ionic surfactant aqueous mixture, and the charged vesicle phase has interesting rheological properties. (2) This ionically charged vesicle phase is not shielded by excess salts because of salt-free aqueous solutions. (3) The attractively circulative vesicle formation should provide a new approach to prepare nanoscale particles by means of vesicle reproduction.

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