

## Electronic Supporting Information *for* **Cryogenic wormlike micelles**

Hongyao Yin,<sup>a</sup> Yujun Feng,<sup>\*,a</sup> Peixun Li,<sup>b</sup> James Douch,<sup>b</sup> Yixiu Han<sup>c</sup> and Yongjun Mei<sup>c</sup>

<sup>a</sup> Polymer Research Institute, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, PR China. E-mail: yjfeng@scu.edu.cn; Tel: +86 28 85 40 80 37

<sup>b</sup> ISIS Neutron and Muon Source, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Didcot, OXON OX11 0QX, UK

<sup>c</sup> The Second Research Institute of Civil Aviation Administration of China (CAAC), Chengdu 610041, PR China

### **1. Experimental Section**

#### **Materials**

Erucyl dimethyl amidopropyl betaine (EDAB) was synthesized according to our previously-reported procedure.<sup>[1]</sup> Methanol (99.9%), ethylene glycol (EG, 99.5%), deuterated ethylene glycol (*d*<sub>6</sub>-EG, 99 atom% D) and deuterium oxide (99.9 atom% D) were purchased from J&K Scientific LTD., and were used as received. Pyrene (≥ 99.0%) was purchased from Sigma-Aldrich and used as obtained, without further purification. The commercial anti-icing fluid, P1, was obtained from Newave Aerochemical Co.,LTD (China). The deionized water (conductivity,  $\kappa = 7.9 \mu\text{S}\cdot\text{cm}^{-1}$ ) used throughout this study was obtained from an ultrapure water purification system (CDUPT-III type, Chengdu Ultrapure Technology Co., Ltd., China).

#### **Characterization**

*Rheology test.* Rheological properties were measured on a Physica MCR 302 (Anton Paar, Austria) rotational rheometer equipped with CC27 concentric cylinder geometry. The temperature is controlled via a Peltier temperature-control device with a solvent trap. Samples were equilibrated at set temperature for no less than 10 min before test. Both steady shear-rate viscosity measurements and dynamic frequency measurements were performed in the temperature range  $-20$  to  $20$  °C. The latter was conducted in the linear viscoelastic regime, which was previously determined from

dynamic stress-sweep measurements. In this work, the strain was fixed at 0.1% for all dynamic frequency measurements for comparison.

*Fluorescence spectra measurement.* Pyrene was used as a fluorescent probe to determine the local polarity in this work, which was first dissolved in methanol with 24 h sonication for complete solubilization. Then 0.1 mL pyrene solution was added into 10 mL EDAB EG/water solution or corresponding EG/water solvent. In this case, the pyrene concentration in all samples is  $2.4 \times 10^{-6}$  mol/L. Since only a small amount of methanol was introduced into the samples, the influence of methanol was ignored. Fluorescence spectra were recorded on a Hitachi F-7000 spectrometer at 20 and  $-20$  °C, respectively. The cell temperature was controlled by a circulating bath with ethylene glycol/water (v/v, 50/50) as the cycle liquid. Samples were equilibrated at set temperature for not less than 10 minutes prior to measurement. The ratio of the intensity of the first peak ( $I_1$ ) at 373 nm and the intensity of the third peak ( $I_3$ ) at 384 nm was taken as the polarity parameter.

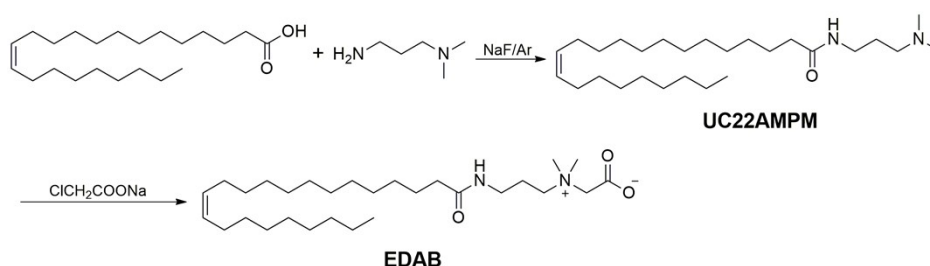
*SANS experiment.* SANS measurements were conducted on the LOQ instrument at ISIS pulsed neutron source (ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, STFC, Didcot, Oxfordshire). The neutron scattering pattern of the samples were collected on a two-dimensional detector placed at 4.1 m from the sample giving scattering vector  $q$  range from 0.009 to  $0.29 \text{ \AA}^{-1}$ , using the time-of-flight technique with neutrons of wavelength 2.2–10 Å. The samples were prepared in EG/D<sub>2</sub>O to optimize the contrast with EDAB. They were placed in clean disc-shaped quartz cells (Hellma) with 2 mm path length and the measurements were performed in the temperature range from  $-20$  to 20 °C, controlled by a water bath with an accuracy of 0.1 °C. Raw data were corrected for detector efficiency, transmission, scattering from the empty cell, and corresponding background (the identical solvent but without EDAB) using Mantid data reduction software. The data were then converted to the differential scattering cross-sections (in absolute units of  $\text{cm}^{-1}$ ) by calibration of the beamline using a polymer standard of well known cross-section.

*Cryo-TEM observation.* The specimens for cryo-TEM observation were prepared in a controlled environment to vitrify the solutions. The temperature of the chamber was regulated between 25 and 28 °C, and the relative humidity was kept close to saturation to prevent evaporation during the preparation. All the samples of bulk solutions were put in set temperatures at least 30 min, then 2  $\mu\text{L}$  of solution was taken out to place on a carbon-coated holey film supported by a copper grid, and

gently blotted with filter paper to obtain a thin liquid film (20–400 nm) on the grid. Next, the grid was quenched rapidly into a cryogen reservoir containing liquid ethane at  $-180\text{ }^{\circ}\text{C}$  and transferred into liquid nitrogen ( $-196\text{ }^{\circ}\text{C}$ ) for storage. Then the vitrified specimen stored in liquid nitrogen was transferred into a Tecnai F20 cryo-microscope using a Gatan 626 cryo-holder and its workstation. The acceleration voltage was set to 200 kV, and the working temperature was kept below  $-170\text{ }^{\circ}\text{C}$ . The images were recorded digitally with a charge-coupled device camera (Eagle) under low-dose conditions with an under-focus of approximately  $2\text{ }\mu\text{m}$ .

*Freezing temperature test.* The freezing temperature of the samples were measured according to the engine coolant freezing temperature determination method (SH/T0090-91) of China on a XY-117 freezing point, turbidity point and crystal point detector (Dalian Xinyi Automation Instrument Co., LTD.). Each sample was measured twice, and the average value was taken as the final freezing point when the difference between each measured value and the average value is no more than  $0.3\text{ }^{\circ}\text{C}$ .

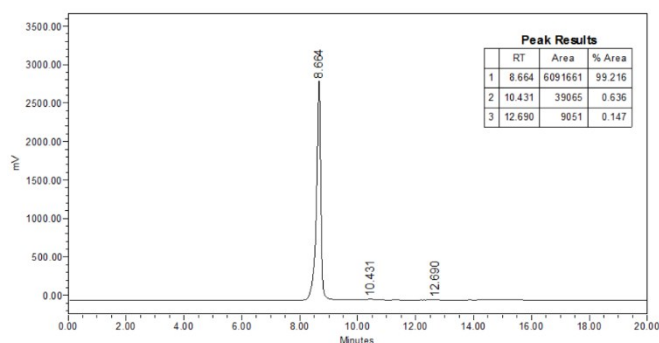
### Preparation and characterization of EDAB



EDAB was prepared in a two step process. In the first step, working under argon atmosphere, a mixture of erucic acid (20.3 g, 60 mmol), *N,N*-dimethyl propanediamine (9.2 g, 90 mmol) and NaF (0.5 g) was vigorously stirred at  $160\text{ }^{\circ}\text{C}$  for 12 h. During this period, the by-product  $\text{H}_2\text{O}$  was continuously absorbed by  $\text{Al}_2\text{O}_3$  placed in a solvent still-head distillation apparatus. After the completion of the reaction, the mixture was cooled and added to cold acetone-water cosolvent (v/v, 15:1) to precipitate the crude product which was collected and washed repeatedly with the same solvent to afford pure intermediate UC22AMPM (21.7 g, yield 85.6%).

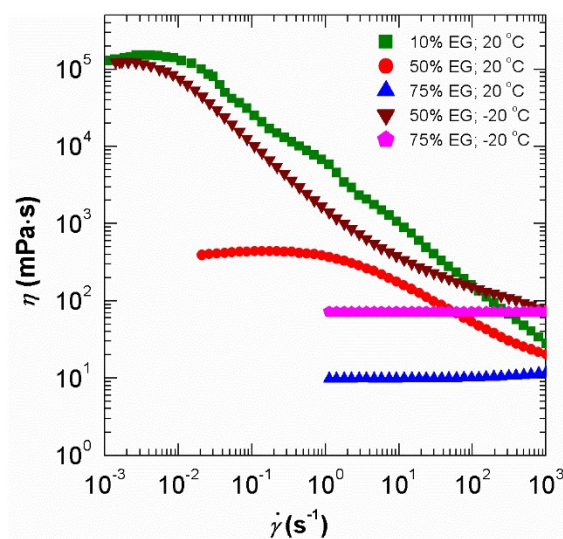
In the second step, UC22AMPM (21.1 g, 50 mmol), sodium chloroacetate (7.3 g, 62.7 mmol), tetrabutylammonium chloride (0.5 g), and 150 mL ethanol-water cosolvent (v/v, 6:1) were added to a 250-mL round-bottom flask. The mixture was refluxed with vigorous stirring for 12 h, then the

solvent was removed by evaporation. The resulted mixture was added to cold ethyl acetate to precipitate the crude product which was collected and washed repeatedly with cold ethyl acetate until no UC22AMPM was found by thin-layer chromatography. Afterward, the crude product was dissolved in ethanol and filtered to removal the side product NaCl. The filtrate was concentrated and added to cold ethyl acetate. The precipitate was collected and dried at room temperature in a vacuum oven to afford the final product as a white solid (17.3 g, yield 72.0%).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ),  $\delta/\text{ppm}$ : 0.86 (t, 3H,  $\text{CH}_3$ ), 1.20-1.40 (m, 28H,  $\text{CH}_2$ ), 1.60 (m, 2H,  $\text{CH}_2$ ), 2.00 (m, 6H,  $\text{CH}_2$ ), 2.20 (t, 2H,  $\text{NHCOCH}_2$ ), 3.30 (t, 8H,  $\text{NCH}_2$ ,  $\text{NCH}_3$ ), 3.70 (t, 2H,  $\text{NHCH}_2$ ), 3.90 (s, 2H,  $\text{NCH}_2\text{CO}$ ), 5.35 (m, 2H,  $\text{C}=\text{CH}$ ). ESI HRMS: Calc., 481.44 ( $\text{M} + \text{H}^+$ ); Found:  $m/z = 481.69$ . High-performance liquid chromatography test (Figure S1) shows the purity of the final EDAB is 99.22%.

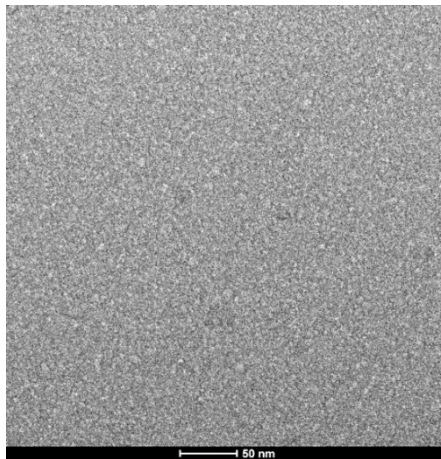


**Fig. S1** HPLC result of EDAB.

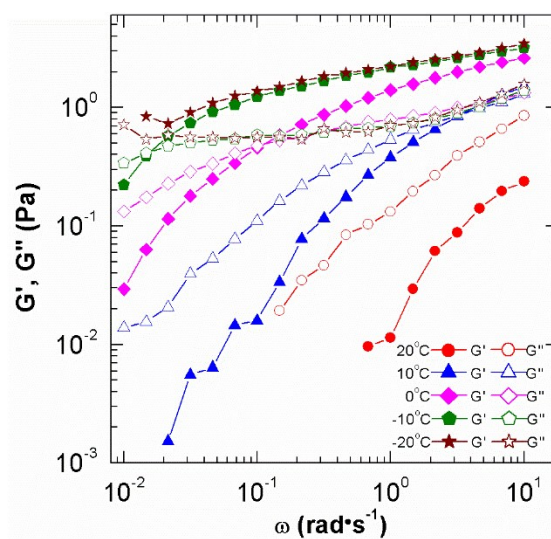
## 2. Additional results



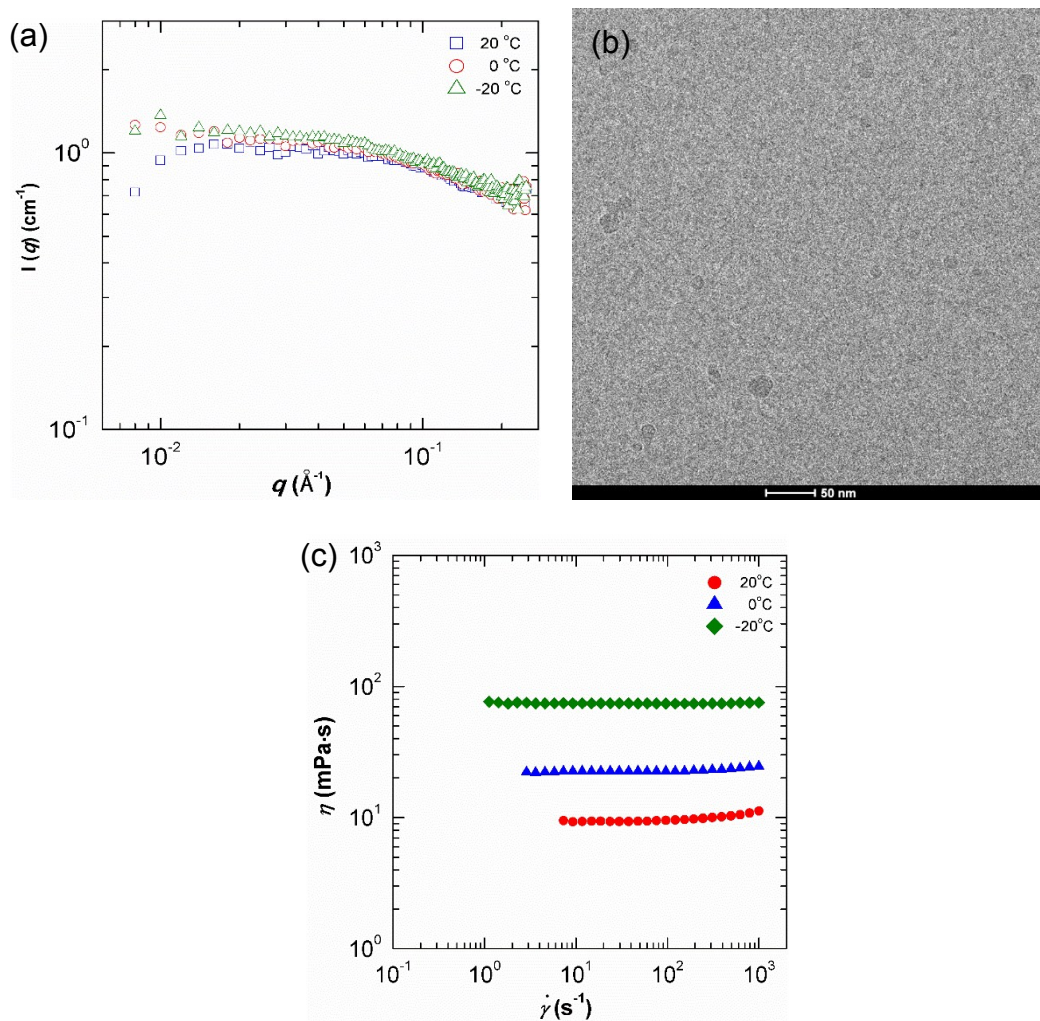
**Fig. S2** Steady rheology of 30 mM EDAB EG/D<sub>2</sub>O solutions. By comparison with the results from corresponding H<sub>2</sub>O-containing solutions, it is clear that the replacement of H<sub>2</sub>O with D<sub>2</sub>O does not affect the rheological behavior.



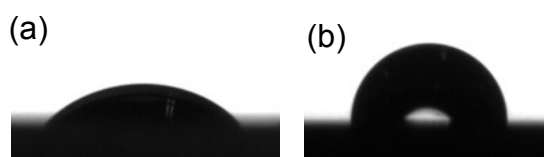
**Fig. S3** Cryo-TEM micrograph of 30 mM EDAB solution with 100% EG at 20 °C. Only spherical micelles are observed.



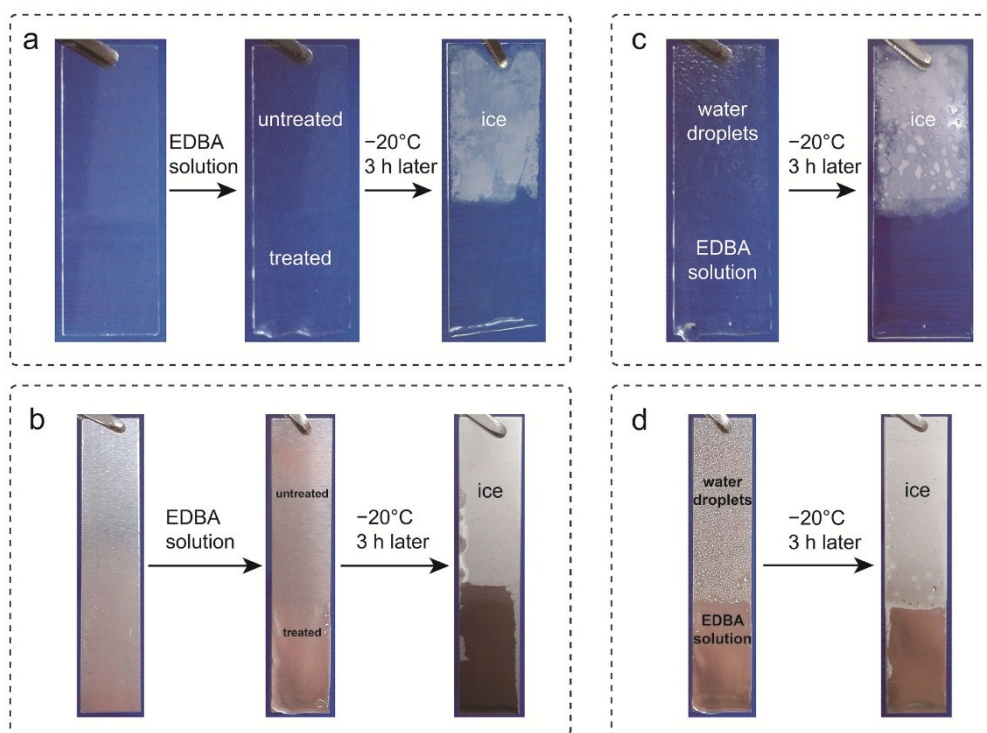
**Fig. S4** Dynamical rheology of 30 mM EDAB solution with 50% EG from -20 to 20 °C.



**Fig. S5** Characterization of 30 mM EDAB with 75% EG. (a) SANS spectra at 20, 0 and  $-20$  °C. (b) Cryo-TEM microimage at  $-20$  °C. (c) Steady rheology at 20, 0 and  $-20$  °C.



**Fig. S6** Water contact angle measurement performed on glass (a) and aluminum (b) substrates. While the contact angle of the glass substrate is  $41.5^\circ$ , showing hydrophilic character, the corresponding value of the aluminum is  $98.5^\circ$ , exhibiting hydrophobic character.



**Fig. S7** Images of (a) glass and (b) aluminum substrates with half of the surface were treated with 50 mM EDAB EG/water (50/50, v/v) and then were placed in a cold environment under  $-20\text{ }^{\circ}\text{C}$  and 35% relative humidity for 3 h. Images of the corresponding (c) glass and (d) aluminum substrates sprayed with water droplets and incubated in the same environment for 3 h.

## Reference

- [1] Y. Wang, Y. Zhang, X. Liu, J. Wang, L. Wei, Y. Feng, *J. Surfactants Deterg.* **2014**, *17*, 295.