Supplementary Information

Thermal Properties and Cold Crystallization Kinetics of

Deep Eutectic Solvent Confined in Nanopores

Xue Lan¹, Xin Wang², Weihong Du^{1*}, Tiancheng Mu^{1*}, Xiao Zheng Lan^{2*}

¹Department of Chemistry, Renmin University of China, Beijing 100872, China

²College of Chemistry and Material Science, Shandong Agricultural University, Tai'an 271018, Shandong, China

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1. Experimental

1.1 Chemicals and Materials

Choline chloride and urea were purchased from Aladdin Reagents Co. (China) with purities of higher than 99 wt.%. Both compounds were used as received.

The controlled pore glasses (Millipore, USA) were commercial products. Before use, the CPG powder was leached with concentrated nitric acid, which is a method recommended by the supplier. The treatment was reported to have negligible influence on the mean pore diameter and pore size distribution.¹ The specifications of the CPGs are listed in Table 1, as provided by the manufacturer.

Porous matrix	Mean pore	Specific pore	Specific surface area
	diameter (nm)	(cm ³ g ⁻¹)	$(m^2 g^{-1})$
CPG3000	300	1.08	10
CPG1000	107.6	1.59	31
CPG500	46.4	1.31	64

Table 1 Mean pore sizes, specific pore volumes and specific surface areas of the CPGs§.

[§] The information for CPGs is provided by the manufacturer.

1.2 Preparation

Choline chloride and urea were heated respectively under vacuum at about 60 °C for several hours, to remove any possible water in them. Under a high purity nitrogen atmosphere, the two components of a total mass of about 1 gram with a molar ratio of 1:2 (choline chloride to urea) were weighed into a glass bottle with a small Teflon-covered magnetic stirrer inside. After sealed tightly under a silicon rubber gasket, the mixture was heated and stirred at about 60 °C.² A colorless solution was obtained in a short time and the stirring was kept for 3 h. After then, the DES reline was cooled down at room temperature.

1.3 TG, DSC and XRD measurements

The absorption of reline into the CPGs was completed at 60 °C through capillary action. Briefly, the CPG powder was heated under vacuum at a temperature of 150 °C

for at least 3 hours to remove water or any other organic materials. Afterward, the CPG powder with a mass of 30 mg or so was weighed together with reline in a given mass ratio inside a glass tube in a nitrogen atmosphere. The glass tube was sealed tightly with a silicon rubber plug and put in an electric oven operated at 60 °C for 3 h. During this period, the glass tube was shaken and overturned every 20 min to mix the CPG powder and the reline melt thoroughly. In these samples, the reline had a volume of 80–90 % of the total pore volume of the CPG in the glass tube. The actual mass ratio of the reline to CPG powder was estimated by thermogravimetric (TG) analysis with a DTG 60A instrument (Shimazu, Japan), scanned at a rate of 10 °C min⁻¹ in a nitrogen atmosphere (50 ml min⁻¹).

Thermal behavior of reline in bulk and in the pores of the CPGs was scanned using a DSC Q10 instrument (TA Instruments, USA) purged with a nitrogen gas at a flow rate of 20 ml min⁻¹. The sample was transferred to an aluminum pan, aligned a lid with the pan in a nitrogen atmosphere. Then the pan and the lid were taken out of the nitrogen gas, crimped quickly, and put in the DSC sample cell. The mass of the bulk reline was about 0.50 mg, while the sample of the CPGs loaded with reline was 3 to 5 mg. In a typical procedure, the sample was cooled down to -70 °C at a rate of about 5 °C min⁻¹, and then heated up to 60 °C at a rate of 1, 3, 5, and 10 °C min⁻¹ respectively. The temperature and enthalpy scale during the heating process were calibrated using adamantane, water, and high purity indium. The hot-stage microscope (Zeiss Axio Scope A1Pol) was used to observe the formation and melting of the crystals on cooling and heating.

The variable temperature X-ray diffraction measurements were performed with a Smartlab diffractometer, Rigaku, Japan. The diffractometer utilized a Cu K α (0.154 nm) radiation source. The diffraction patterns were collected in the 2θ range of 5–40° with a step size of 0.02°. Before measurement, the samples were cooled down to -50 °C at a rate of about 2 °C min⁻¹, and then heated up at approximately the same rate. After equilibrated for 10 min at each given temperature, the diffraction patterns were recorded.

1.4 Data 3 It should be noted that samples exhibited decreasing melting temperatures or enthalpies during repeated heating and cooling. Considering reline is sensitive to thermal history unexpectedly, corresponding parameters mostly obtained from the first DSC scans are presented, thereby ensuring the original properties. Data from parallel experiments are also used to calculate standard deviation. Enthalpies are normalized to the mass of reline present, *i.e.*, the mass of the confined samples multiplied by the percent of reline.

2. Characteristics and methods

2.1 Hot-stage microscopy

To ascertain the peaks on DSC curves, hot-stage microscopy was employed.³ Microscope images can provide visible information of phase transition. Upon heating, many thin needle- or short rod-like colorless crystals emerged from the supercooled liquid at -45 °C and completed at -35 °C. This corresponds to the same temperature range where the exothermic behavior occurred, showing on the DSC curve. Therefore, this exothermic peak can be ascribed to cold-crystallization. In the following heating process, part of the crystals melted as close to -13 °C and all the crystals disappeared at 10 °C, corresponding to the tiny endothermic peak and the sharp one on the DSC curve, respectively.

2.2 Excess reline outside the pores

Small peaks above 0 °C are observed on DSC curves and signify that the residue of reline outside the pores melts in this range. Since areas of these peaks are all less than 5% of those of the corresponding crystallization peaks, combined with the loading ratios determined by TG analysis, we suppose that reline outside the pores is essentially negligible.

2.3 Gibbs-Thomson equation

The Gibbs-Thomson equation is generally used to describe the decrease of melting temperature and enthalpies of nanosized particles,

$$\Delta T_{\rm m} = T_{\rm m,bulk} - T_{\rm m,r} = 2\sigma_{\rm sl}T_{\rm m,bulk}/r\rho_{\rm s}\Delta H_{\rm m,bulk}$$
$$\Delta H_{\rm m,r} = \Delta H_{\rm m,bulk} - 2\sigma_{\rm sl}/r\rho_{\rm s}$$

where $\Delta T_{\rm m}$ represents the difference of melting temperatures, $T_{\rm m,bulk}$ is the bulk melting temperature, $T_{\rm m,r}$ is the melting temperature of particles with radius r, $\sigma_{\rm sl}$ is the interface energy of solid-liquid interface, $\rho_{\rm s}$ is the solid phase density of the bulk material, $\Delta H_{\rm m,bulk}$ is the bulk heat of fusion, $\Delta H_{\rm m,r}$ is the enthalpy of melting of nanoparticles with radius r.

2.4 Kissinger equation

The Kissinger method is a suitable approach for determining kinetic parameters by thermal analysis, especially in heating experiments.⁴ As usually used for polymer, ⁵

Kissinger method is expected to clarify cold-crystallization kinetics of both bulk and confined reline. This method is based upon a series of experiments in which samples are heated at several heating rates while exothermic peak temperatures are recorded. After logarithmization, Kissinger equation is described as:^{4,5}

$$ln\frac{\beta_i}{T_{p,i}^2} = ln\frac{AR}{E_a} - \frac{E_a}{RT_{p,i}}$$

where E_a , generally estimated from the slope of $\ln(\beta_i/T_{p,i}^2)$ vs. $T_{p,i}^{-1}$ plot, is the effective activation energy; A, pre-exponential factor; β , heating rate; T_p , exothermic peak temperature of the corresponding DSC curve; R, ideal gas constant, and *i* for β_i and $T_{p,i}$ represents the *i*-th test of several DSC scans. T_p values are practically independent of baseline choice which is crucial to other ways (such as the isoconversional treatment⁶), endowing this method with a more robust alternative.

3. Kinetics analysis



Fig. S1. Representative DSC curves for the crystallization of reline (a) in the bulk, and confined in (b) the CPG (300 nm, (c) CPG (100 nm), and (d) CPG (50 nm) at the heating rates of 1, 3, 5, and $10 \,^{\circ}$ C min⁻¹ respectively, as recorded during the heating processes.

4. References

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