Dissociation and aggregation behaviors of starch in choline amino acid ionic liquid solvents: the anion structure effect

1. The structure information of normal corn starch

The ATR-FTIR spectrum of normal corn starch is shown in Fig.S1. Starch exhibits a strong, broad absorption peak around 3200 cm^{-1}, which corresponds to the stretching vibration peak of the -OH group. A medium-intensity absorption peak at 2924 cm^{-1} is associated with the antisymmetric stretching vibration of the $-CH_2$ group in starch. The absorption peak around 1636 cm^{-1} corresponds to water absorption in the amorphous region of starch. The peak around 1342 cm^{-1} is attributed to the bending vibration of the C-OH bond and the twisting vibration of the $-CH_2$ group in starch. The absorption peak near 1003 cm^{-1} can be assigned to the stretching vibration of the C-O bond and the bending vibration of the C-OH group. These vibrational peak features of normal corn starch are consistent with those from previous studies of starch samples derived from both standard normal and waxy corn [1]. Additionally, the ATR-FTIR spectrum shows no apparent impurity peaks, indicating the high purity of the starch.

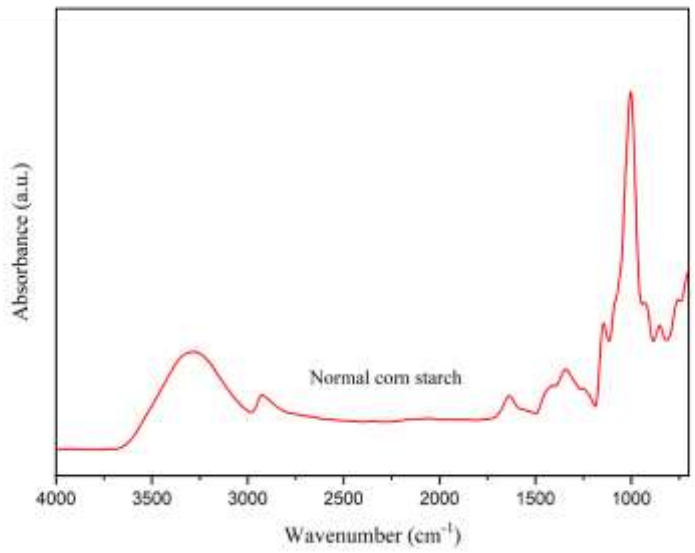

Fig.S1 The ATR-FTIR spectrum of normal corn starch.

2. The structure information of choline lysine ([Cho][Lys]) and choline aspartic acid ([Cho][Asp]) ionic liquid (IL)

2.1 ATR-FTIR spectra

By comparing the infrared spectral peaks of Lys/Asp and [Cho][Cl] with those of [Cho][Lys] and [Cho][Asp] ILs, the vibration modes of the -NH_2, -OH, -CH_3, -CH_2, -N-$(CH_3)_3$, -COOH, and -COO^- groups in the [Cho][Lys] and [Cho][Asp] ILs were identified in the ATR-FTIR spectra (Fig.S2). Thus, the basic structural framework of [Cho][Lys]/[Cho][Asp] ILs was established.

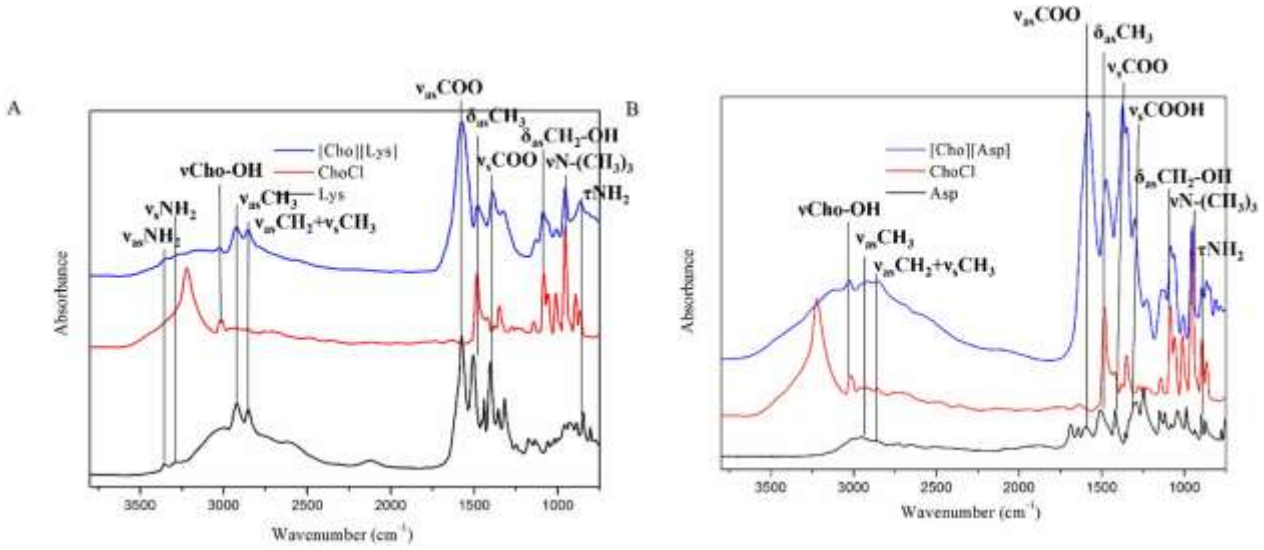

Fig.S2 The ATR-FTIR spectra of lysine (Lys), aspartic acid (Asp), choline chlorine ([Cho][Cl]), [Cho][Lys] and [Cho][Asp] ILs. ν_a: asymmetrical stretching vibration; ν_s: symmetrical stretching vibration; δ_{as}: asymmetrical deformation vibration; τ: twisting vibration.

2.2 NMR spectra

The 1H NMR spectra (Fig.S3) of [Cho][Lys] and [Cho][Asp] ILs were obtained using an AVANCE III HD 600 NMR spectrometer (Bruker Corporation Inc., Karlsruhe, Germany), with their structural information presented as follows:

[Cho][Lys]: ^{1}H NMR (600 MHz): δ (ppm) 1.31-1.20 (m, 2H, $CH_2CH_2CH_2CH_2NH_2$), 1.41 (t, J = 10.3 Hz, 2H, $CH_2CH_2CH_2CH_2NH_2$), 1.59-1.46 (m, 2H, $CH_2CH_2CH_2CH_2NH_2$), 2.61 (t, J = 7.2 Hz, 2H, $CH_2CH_2CH_2CH_2NH_2$), 3.12 (s, 10H, $(CH_3)_3N$, $CHNH_2$), 3.48-3.39 (m, 2H, CH_2CH_2OH), 4.02 -3.91 (m, 2H, CH_2CH_2N)

[Cho][Asp]: ^{1}H NMR (600 MHz): δ (ppm) 2.61 (dd, J = 17.2 and 8.8 Hz, 1H, C*H*$_2$COOH), 2.76 (dd, J = 17.2 and 3.7 Hz, 1H, C*H*$_2$COOH), 3.17 (s, 9H, *(CH*$_3$*)*$_3$N), 3.52-3.46 (m, 2H, CH$_2$*CH*$_2$OH), 3.83 (dd, J = 8.8 and 3.7 Hz, 1H, *CH*NH$_2$), 4.07-4.00 (m, 2H, CH$_2$*CH*$_2$N)

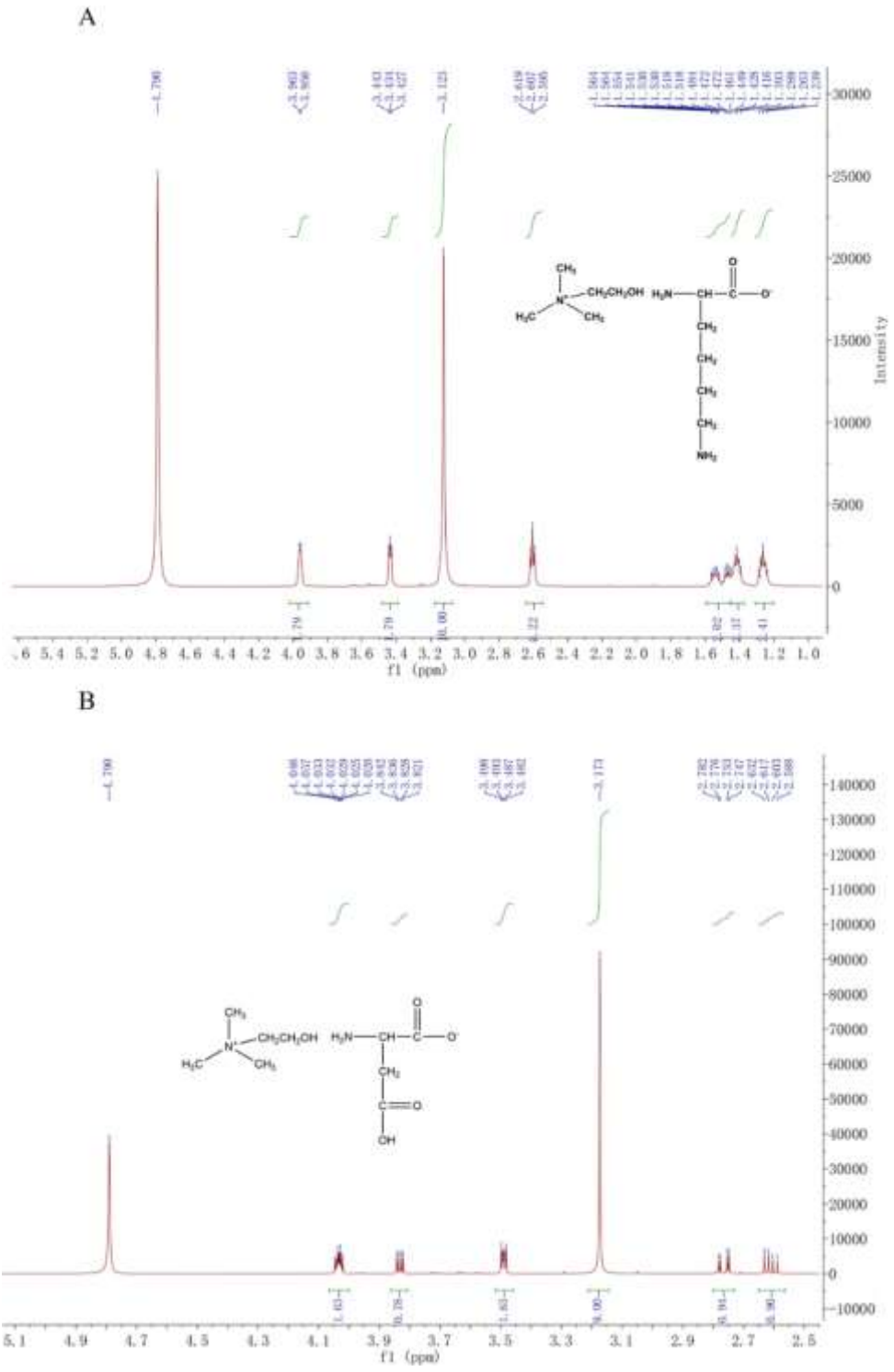

Fig.S3 1H NMR spectra of [Cho][Lys] (A) and [Cho][Asp] ILs (B).

3. The insolubility of starch in pure [Cho][Lys] and [Cho][Asp] IL

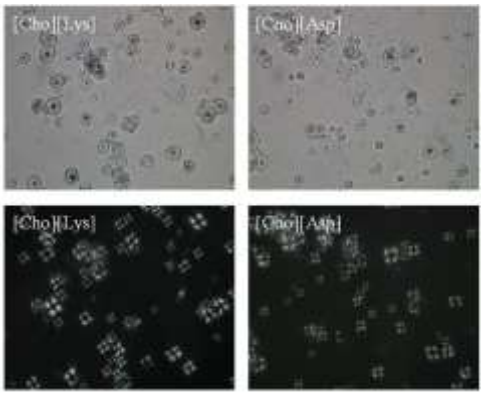

Fig.S4 The dissolution situation of starch granules in pure [Cho][Lys] and [Cho][Asp] at 100 °C for 20 min (micrographs: grey vision and polarized light micrographs: black vision).

4. The physicochemical properties of [Cho][Lys]-water and [Cho][Asp]-water solvents

4.1 pH values

Table S1 pH values of [Cho][AA]-water solvents with different water/IL (w:IL) ratios.

Ratios	$pH_{[Cho][Lys]}$	$pH_{[Cho][Asp]}$
w:IL-10:0	6.28 ± 0.01^{g}	6.28 ± 0.01^{g}
w:IL-9:1	11.42 ± 0.01^{f}	7.40 ± 0.02^{f}
w:IL-7:3	11.66 ± 0.03^{e}	7.53 ± 0.04^{e}
w:IL-5:5	11.86 ± 0.01^{d}	8.09 ± 0.01^{d}
w:IL-4:6	12.03 ± 0.04^{c}	8.26 ± 0.03^{c}
w:IL-2:8	12.41 ± 0.06^{b}	9.28 ± 0.05^{b}

4.2 Apparent viscosity

From Fig.S5 and Table S2, it can be seen that the viscosity of [Cho][Asp]-water mixture at the same ratio was much higher than that of [Cho][Lys]-water mixture. Also, the viscosities of [Cho][Lys]-water and [Cho][Asp]-water solvents decreased significantly with continually water addition or with elevated temperature.

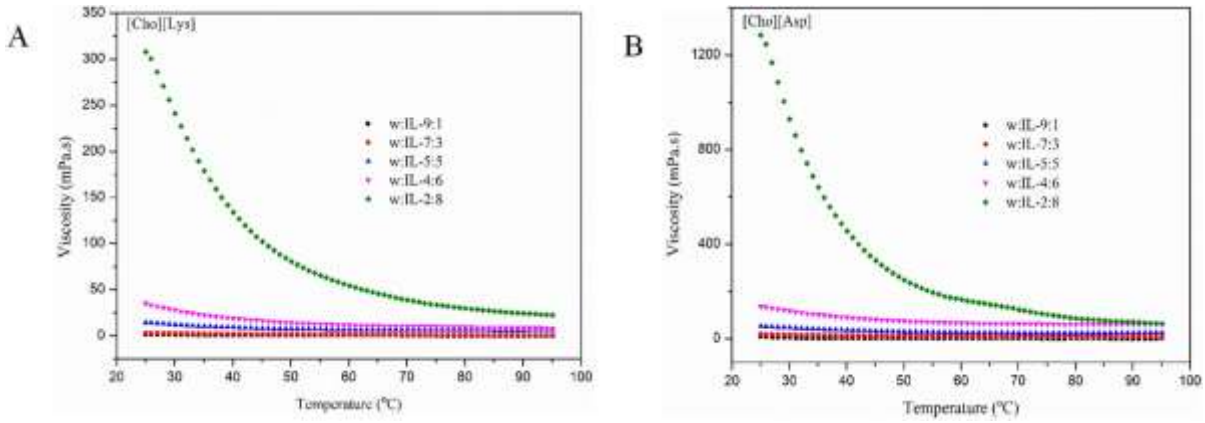

Fig.S5 The effect of temperature on the viscosities of [Cho][Lys]-water (A) and [Cho][Asp]-water (B) solvents.

Table S2 The viscosity values (mPa.s) of [Cho][Lys]-water and [Cho][Asp]-water solvents at 28 ℃.

Ratios	η [Cho][Lys]	η [Cho][Asp]
w:IL-9:1	1.46±0.02^{e}	8.78±0.09^{e}
w:IL-7:3	3.24±0.03^{d}	19.27±2.01^{d}
w:IL-5:5	14.43±1.13^{c}	53.09±5.19^{c}
w:IL-4:6	35.15±1.68^{b}	136.35±11.12^{b}
w:IL-2:8	307.99±15.68^{a}	1283.80±39.01^{a}

5. Molecular characteristics of dissolved starches

The weight average molecular mass (M_w), dispersity (M_w/M_n) and mean square radius of gyration (R_g) of dissolved starches after heating at 100 °C for 20 min were measured and analyzed by a gel permeation chromatography system coupled with a multiangle light scattering detector (632.8 nm, DAWN HELEOS, Wyatt Technology, Santa Barbara, CA, USA) and a refractive index detector (Optilab rex, Wyatt Technology) according to the method of our previous study [2]. Here the molecular features of starch treated with high concentration [Cho][AA] solvents were chosen to understand the degradation effect of [Cho][AA] on starch (Fig.S6). And the M_w, M_w/M_n, and R_g values of dissolved starches are shown in Table S3. Compared with water, the M_w values of dissolved starches decreased slightly in [Cho][Asp]-water solvents, and this decrease grew with increasing [Cho][Asp]

concentration. All these molecular features suggest that starch could be moderately depolymerized during heating in [Cho][Asp]-water solvents. While due to the strong basicity of [Cho][Lys] (Table S1), the degradation degrees of starches were more prominent in [Cho][Lys]-water solvents.

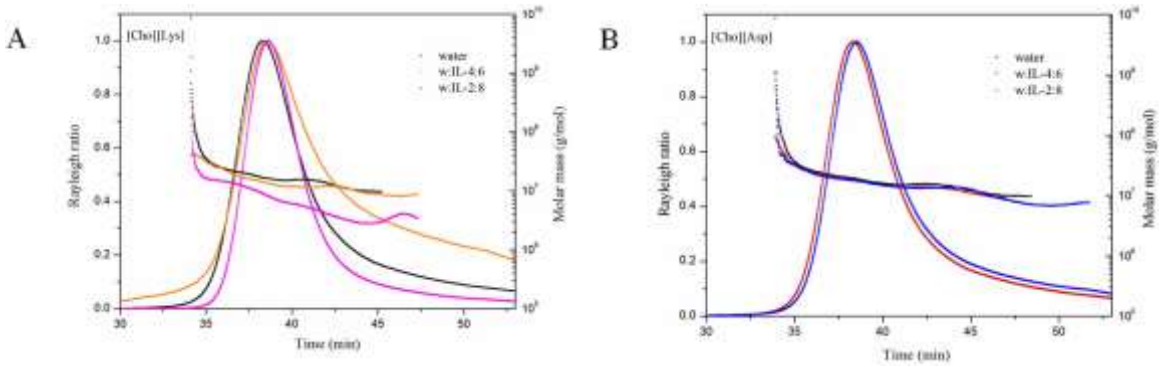

Fig.S6 Molecular characterizations of starches after being heated in [Cho][Lys]-water (A) and [Cho][Asp]-water solvents (B) for 20 min.

Table S3 Weight average molecular mass (M_w), dispersity (M_w/M_n), and mean square radius of gyration (R_g) of dissolved starches.

Solvents	M_w (g/mol)	*Mw/Mn*	R_g (nm)
water	1.790×10^7 (0.9%)	1.135 (1%)	106.4 (0.7%)
[Cho][Lys]			
w:IL-4:6	1.189×10^7 (2%)	1.098 (2%)	161.1 (0.6%)
w:IL-2:8	8.299×10^6 (0.6%)	1.415 (1%)	74.7 (0.9%)
[Cho][Asp]			
w:IL-4:6	1.706×10^7 (0.9%)	1.113 (1%)	105.4 (0.7%)
w:IL-2:8	1.276×10^7 (0.8%)	1.158 (2%)	113.3 (0.6%)

References:

1. P. Rubens, J. Snauwaert, K. Heremans and R. Stute, In situ observation of pressure-induced gelation of starches studied with FTIR in the diamond anvil cell, *Carbohydrate Polymers*, 1999, **39**, 231-235.
2. J. Chen, X. Zeng and L. Chen, Regulation nature of water-choline amino acid ionic liquid mixtures on the disaggregation behavior of starch, *Carbohydrate Polymers*, 2021, **272**, 118474.