

Supporting Information

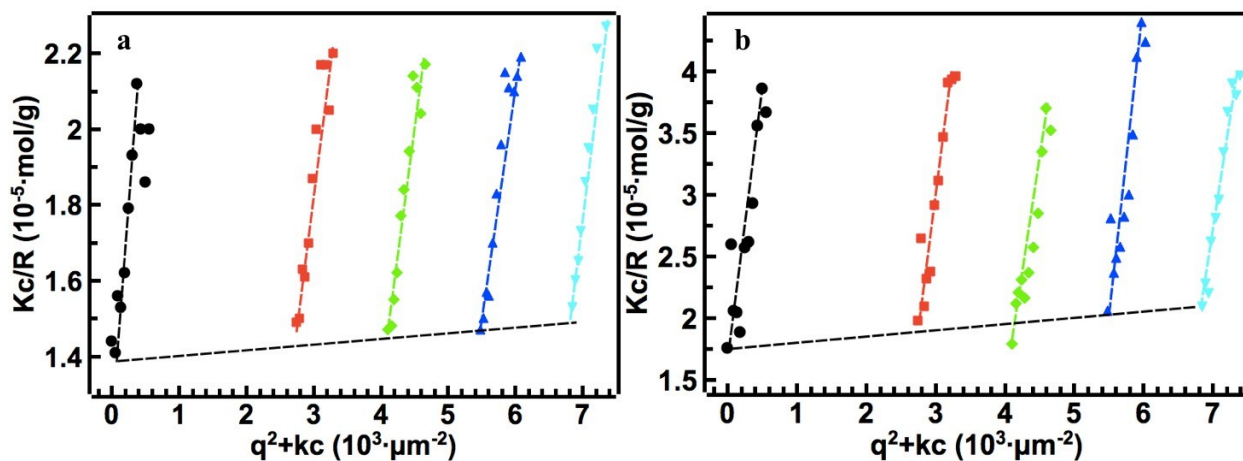


Figure S1 Zimm plots of cellulose solution dissolved in NaOH (a) and LiOH (b) aqueous solutions.

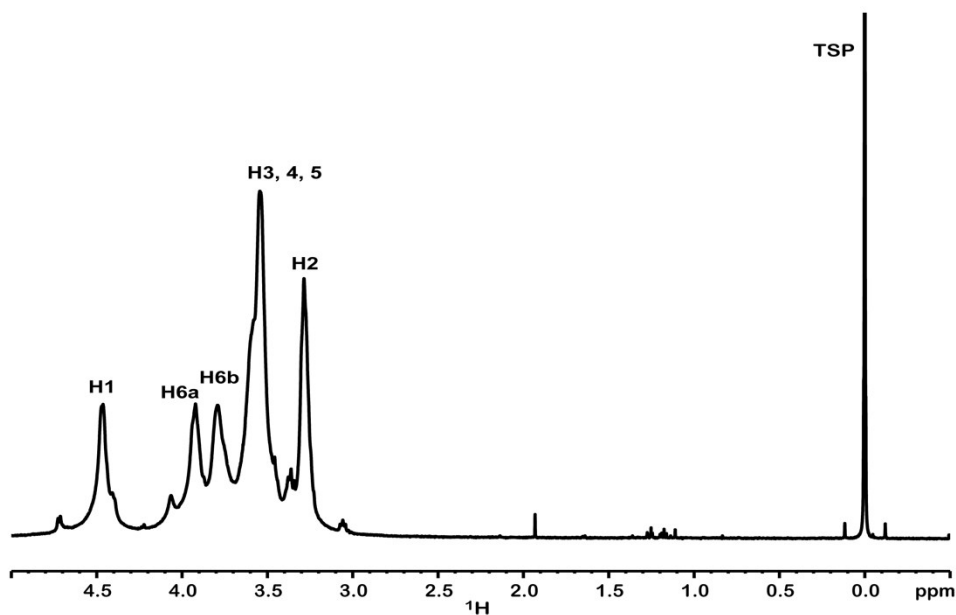


Figure S2 ^1H NMR spectrum of 2 wt% cellulose in NaOH solution, with the peak of TSP was calibrated to 0 ppm as reference.

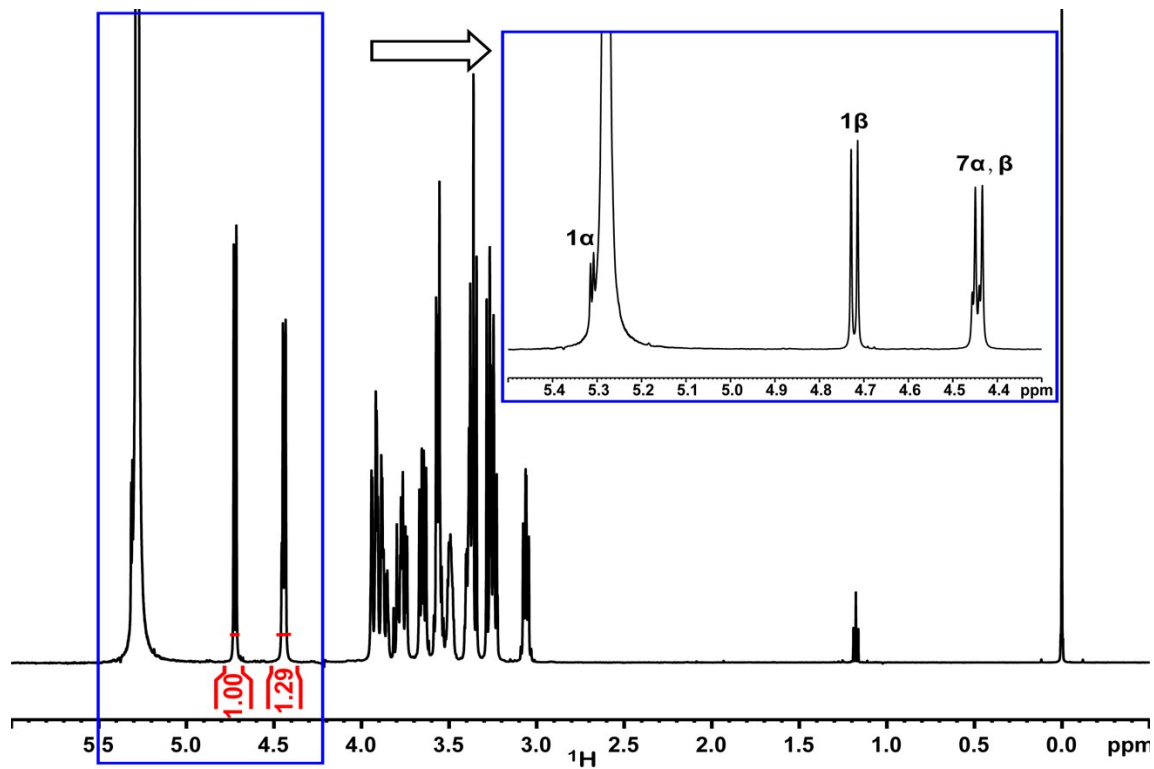


Figure S3 ^1H NMR spectrum and the integrals and assignment of anomeric hydrogens of cellobiose in NaOH solution, with the peak of TSP was calibrated to 0 ppm as reference.

Table S1 Experimental results of $M_{w,app}$, A_2 , and $M_{w,agg}$ of cellulose solution dissolved in NaOH and LiOH aqueous solution.

	A_{sin}/A_{agg}	$M_{w,app}(\times 10^{-4})$ (g/mol)	$A_2(\times 10^7)$ (mol·dm ³ ·g ⁻²)	$M_{w,agg}(\times 10^{-4})$ (g/mol)
NaOH	0.5688	6.933	3.348	27.26
LiOH	0.5296	5.670	15.46	10.73

Table S2 Diffusion coefficients($D \cdot 10^{10}(\text{m}^2/\text{s})$) of H_2O , Li^+ , Na^+ and cellulose in the solution of LiOH and NaOH with variable content of cellulose. Every set of experiments was repeated three times.

Cellulose (%)	LiOH-Cellulose- H_2O				NaOH-Cellulose- H_2O			
	0	0.5	1.0	2.0	0	0.5	1.0	2.0
	Li^+				Na^+			
1	2.363	2.234	2.176	2.089	3.611	3.590	3.518	3.420
2	2.361	2.232	2.178	2.097	3.610	3.580	3.515	3.413
3	2.356	2.233	2.176	2.091	3.613	3.581	3.497	3.389
Mean	2.360	2.233	2.177	2.092	3.611	3.584	3.510	3.407
Std. error	0.004	0.001	0.001	0.004	0.002	0.006	0.011	0.016
	Cellulose							
1	-	0.144	0.110	0.091	-	0.129	0.106	0.107
2	-	0.136	0.103	0.085	-	0.119	0.102	0.100
3	-	0.129	0.096	0.081	-	0.110	0.095	0.095
Mean	-	0.136	0.103	0.086	-	0.119	0.101	0.101
Std. error	-	0.007	0.007	0.005	-	0.009	0.006	0.006
	H_2O							
1	5.951	5.791	5.699	5.573	6.581	6.580	6.428	6.234
2	5.944	5.809	5.697	5.591	6.580	6.553	6.426	6.283
3	5.959	5.795	5.703	5.567	6.560	6.560	6.432	6.271
Mean	5.951	5.798	5.700	5.577	6.574	6.564	6.429	6.263
Std. error	0.008	0.009	0.003	0.012	0.012	0.014	0.003	0.026

Table S3 Fraction of free and bound cations in the solution of different concentration of cellulose.

Cellulose (%)	P _f (Na ⁺) (%)	P _f (Li ⁺) (%)	P _b (Na ⁺) (%)	P _b (Li ⁺) (%)
0.5	99.35	97.12	0.65	2.88
1	99.37	96.30	0.63	3.70
2	99.01	94.61	0.99	5.39

Experimental notes

‡ Cellulose (DP=180) (From Alfa Aesar and the purity of 98+%) was dissolved in 1.75M NaOH (LiOH) aqueous solution at 0°C with stirring for 2 minutes. The dynamic and static light scattering experiments were made with a commercial light scattering spectrometer (ALV/SP-125,ALV, Germany) equipped with an ALV-5000/Ecorrelator and a He-Ne laser (at 632.8nm). For a polymer mixture of individual chains and multi-chainaggregates, the area ratio of these two modes (A_{sin}/A_{agg}) could be expressed by:

$$\frac{A_{sin}}{A_{agg}} = \frac{M_{w,sin}X_{sin}}{M_{w,agg}X_{agg}} \quad (4)$$

where X_{sin} and X_{agg} are the weight fractions of individual chains and multi-chain aggregates, respectively and their sum equals to 1. In the static light scattering,

$$M_{w,app} = M_{w,sin}X_{sin} + M_{w,agg}X_{agg} \quad (5)$$

On the basis of equations (4) and (5) we could obtain the $M_{w,agg}$, which reflected the dissolving capacity of the solvent on cellulose.

^7Li and ^{23}Na NMR spectra of the solution were recorded on a Bruker AVANCE III 500 NMR spectrometer with BBO probe at 273 K. The pulse program developed in literature¹ was used to quantitatively investigate the interaction of ions (Li^+ and Na^+) with macromolecule (cellulose) in the solution. Diffusion coefficients were extracted from nonlinear least squares of the integrated resonance intensity as a function of the gradient amplitude. Every set of experiments was repeated three times to access the reliable standard error and coefficient of variation. The resonance intensity of these integrals, I , and the diffusion coefficient, D , are related according to the following equation:

$$I = I_0 \exp \left[-D \left(\Delta - \frac{1}{3}\delta - \frac{1}{2}\tau \right) g^2 \gamma^2 \delta^2 \right] \quad (6)$$

Where I is the resonance intensity measure with pulse sequence, I_0 is the intensity of the resonance in the absence of a gradient pulse, D is the self-diffusion coefficient, Δ is the diffusion delay time, which defines the diffusional time scale, γ is the gyromagnetic ratio. The parameters δ and g are the duration and strength of the gradient pulses, respectively. In addition, τ is the delay between the positive and negative gradient pulse. Because the γ for ^{23}Na and ^7Li is small, in order to get enough attenuation of signal intensity, Δ and δ equal 30 ms, 12 ms (for mass fraction of cellulose 0%, 0.5%, 1%) or 14 ms (for mass fraction of

cellulose 2 %) for ^{23}Na NMR experiments and 80 ms, 7.6 ms (for mass fraction of cellulose 0%, 0.5%, 1%) or 8 ms (for mass fraction of cellulose 2 %) for ^7Li NMR experiments, respectively. For ^{23}Na NMR experiments, 128 transients were acquired into 4 K data points over a spectral width of 2645.5 Hz, with a recycle delay of 0.78 s, and 6 ms or 7 ms (half of δ) SMSQ10.100-shaped gradients with strength in the range 1.083 - 53.073 G/cm in steps of 3.466 G/cm were used. For ^7Li NMR experiments, 8 transients were acquired into 8 K data points over a spectral width of 1943 Hz, with a recycle delay of 3.1 s, and 3.8 ms or 4 ms (half of δ) SMSQ10.100-shaped gradients with strength in the range 1.083 - 53.073 G/cm in steps of 3.466 G/cm were used.

To obtain the diffusion coefficients for water and cellulose, ^1H PFG-SE NMR experiments were also carried out. In ^1H NMR experiments for water diffusion coefficient, 8 transients were acquired into 16 K data points over a spectral width of 5000 Hz, with a recycle delay of 6.6 s and a diffusion time of 40 ms, and 1.3 ms (SMSQ10.100-shaped gradients with strength in the range 1.083 - 53.073 G/cm in steps of 3.466 G/cm were used. In ^1H NMR experiments for diffusion coefficient of cellulose, 32 transients were acquired into 16 K data points over a spectral width of 5000 Hz, with a recycle delay of 6.6 s and a diffusion time of 200 ms, and 4.0 ms (SMSQ10.100-shaped gradients with strength in the range 1.083 - 53.073 G/cm in steps of 3.466 G/cm were used.

Reference

1D. H. Wu, A. D. Chen and C. S. Johnson, *J. Magn. Reson. A*, 1995, **115**, 260–264.