Electronic Supplementary Information

Molecular Origin of High-Concentration Cellulose Dissolution in Organic Acid Media: A Combined Experimental and Computational Study

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Experimental and Computational Methods.

High-energy X-ray total scattering (HEXTS). HEXTS measurements were conducted at ambient temperature using a high-energy X-ray diffraction apparatus installed at SPring-8 (BL04B2 beamline, JASRI, Japan). Monochromatized 61.19 keV X-rays were obtained using a Si(220) monochromator. The observed X-ray scattering intensities were corrected for absorption, polarization, and incoherent scattering to determine coherent scattering intensities, $I_{coh}(q)$.[1-3] The experimental X-ray structure factor per stoichiometric volume, $S^{exp}(q)$, was obtained using the following equation:

$$S^{exp}(q) = \frac{\frac{I_{coh}(q)}{N} - \Sigma n_i f_i(q)^2}{\{\Sigma n_i f_i(q)\}^2} + 1 \qquad \text{(S1)},$$

where n_i and $f_i(q)$ correspond to the number and atomic scattering factor of atom i, respectively, and N is the total number of atoms in the stoichiometric volume. The radial distribution function, $G^{exp}(r)$ is obtained using the Fourier transform of the $S^{exp}(q)$ as follows:

$$G^{exp}(r) - 1 = \frac{1}{2\pi^2 r\rho_0}\int_0^{q_{max}} q\{S^{exp}(q) - 1\}\sin(qr)W(q)\mathrm{d}q \qquad \text{(S2)},$$

where ρ_0 is the number density of atoms, q_{max} is the maximum value of q (25 Å^{-1} in this study), and $W(q)$ corresponds to the Lorch window function.[4]

Table S1. Concentrations (weight percent and molarity), density (d) and refractive index (n_2) of CB/FA, CL/FA, CB/PA, and CL/PA solutions. c_{CB} and c_{CB}' denote the molarity of CB and the CB dimer–equivalent molarity of CL.

CB/FA solutions			
w_{CB} / wt%	c_{CB} / mol dm^{-3}	d / g cm^{-3}	n_2
0	0	1.211	1.368
20	0.614	1.261	1.397
30	0.872	1.293	1.406
40	1.090	1.306	1.417
50	1.284	1.318	1.422
CL/FA solutions			
w_{CL} / wt%	c_{CB}' / mol dm^{-3}	d / g cm^{-3}	n_2
5	0.179	1.219	1.378
10	0.346	1.235	1.384
15	0.500	1.243	1.391
20	0.644	1.252	1.396
25	0.780	1.264	1.401

CB/PA solutions			
w_{CB} / wt%	c_{CB} / mol dm^{-3}	d / g cm^{-3}	n_2
0	0	1.271	1.399
5	0.178	1.276	1.426
10	0.343	1.295	1.438
15	0.496	1.299	1.432
20	0.641	1.314	1.431
25	0.773	1.320	1.422
CL/PA solutions			
w_{CL} / wt%	c_{CB}' / mol dm^{-3}	d / g cm^{-3}	n_2
2	0.075	1.240	1.423
4	0.147	1.245	1.431
6	0.219	1.253	1.433
8	0.289	1.269	1.435
10	0.362	1.287	1.437

Table S2. Compositions (number of CB, FA, and PA) of the systems for MD simulations, and density (d) in 20 wt% CB/FA and 20 wt% CB/PA solutions.

Sample	CB(solvent)$_5$	FA	PA	d / g cm^{-3}	
				MD [a]	Exp.[b]
20 wt% CB/FA	139	4471	-	1.3583	1.261
20 wt% CB/PA	139	-	2007	1.3397	1.314

[a] Values obtained from the present MD simulations. [b] Experimental values.

Table S3. Coordination numbers $N(r)$ of O_H atoms of solvent molecules around O_X atoms of the CB(solvent)$_5$ molecules, obtained from MD simulations for 20 wt% CB/FA and CB/PA systems. The $N(r)$ was calculated by the integration of the corresponding $g_{OX\text{-}OH}(r)$ up to r = 3.0 Å, shown in Figure 11.

O (solute)−O (solvent)	CB/FA system	CB/PA system
O_1−O_H	0.99	0.83
O_2−O_H	0.51	0.30
O_3−O_H	0.86	0.49
O_4−O_H	-	0.27
Total	2.36	1.89

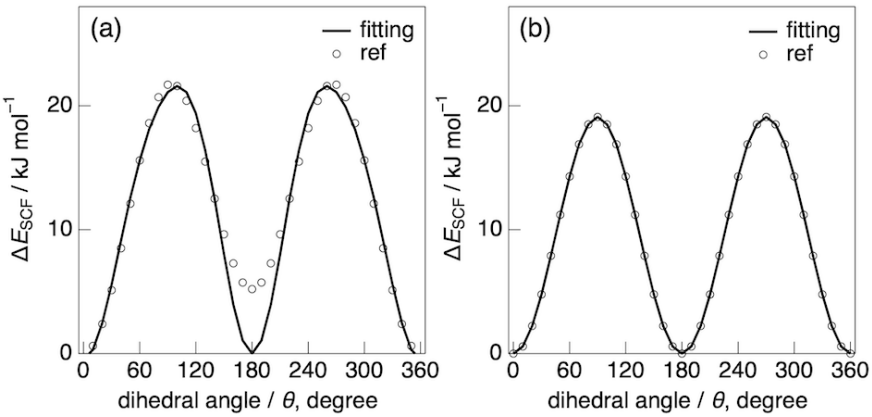

Figure S1. Torsion potential energy surface as a function of the (a) H–C–O–H and (b) O=C–O–H dihedral angle of FA molecule from ref 5 (open circles). The solid line shows the fitting result for the data using the following equation to determine the parameters V_n (n = 1, 2, 3, and 4). The resulting V_n values are: V_1 = -0.5468 kJ mol^{-1}, V_2 = 5.2941 kJ mol^{-1}, V_3 = 0.6960 kJ mol^{-1}, and V_4 = 0.5412 kJ mol^{-1} for H–C–O–H; V_1 = 0 kJ mol^{-1} , V_2 = 4.565 kJ mol^{-1}, V_3 = 0 kJ mol^{-1}, and V_4 = 0 kJ mol^{-1} for O=C–O–H.

$$E(\phi) = \frac{V_1}{2}[1+\cos(\phi+f1)] + \frac{V_2}{2}[1-\cos(2\phi+f2)] + \frac{V_3}{2}[1+\cos(3\phi+f3)] + \frac{V_4}{2}[1-\cos(4\phi+f4)] \quad \text{(S3)}.$$

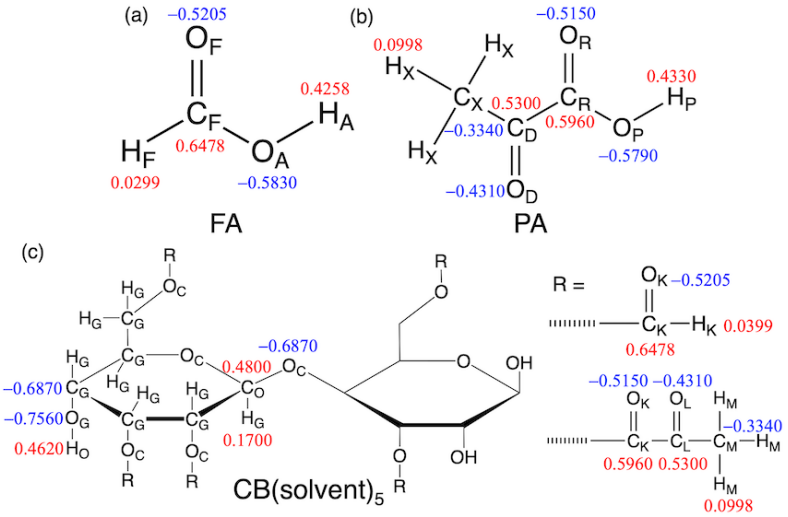

Figure S2. The partial charges of (a) FA, (b)PA and (c) CB(solvent)$_5$ were calculated based on the ChelpG method [MP2/cc-pVTZ(-f)//HF/6-31G(d)]. R is a substituent derived from an OH group, which is modified in the reactive solvent (FA or PA). In a formic acid system, the OH group is formylated, and the resulting R corresponds to a formyl group. In a pyruvic acid system, it is esterified, and R corresponds to an ester group.

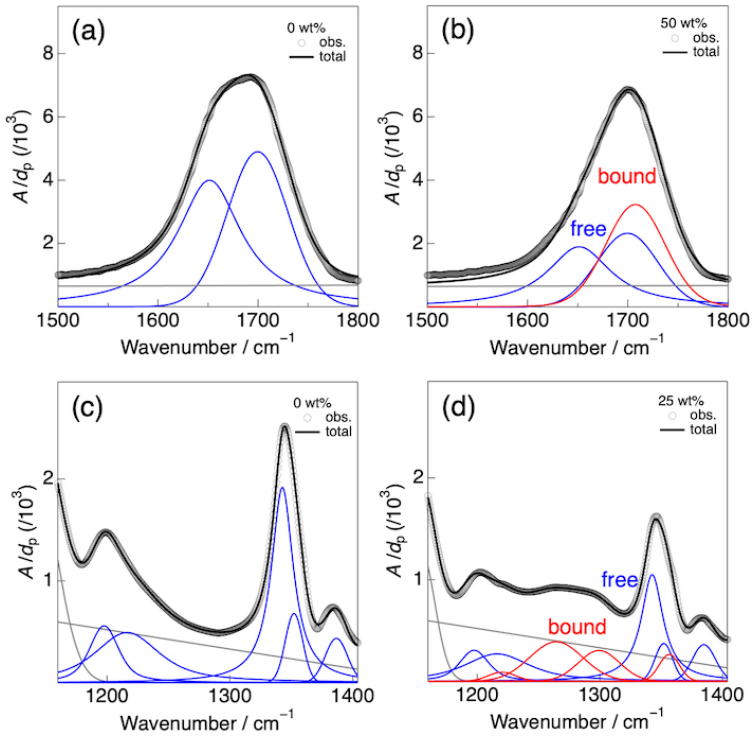

Figure S3. Full peak deconvolution into individual peaks for (a) neat FA and (b) 50 wt% CB/FA solution, (c) neat PA, and (d) 25 wt% CB/PA solution.

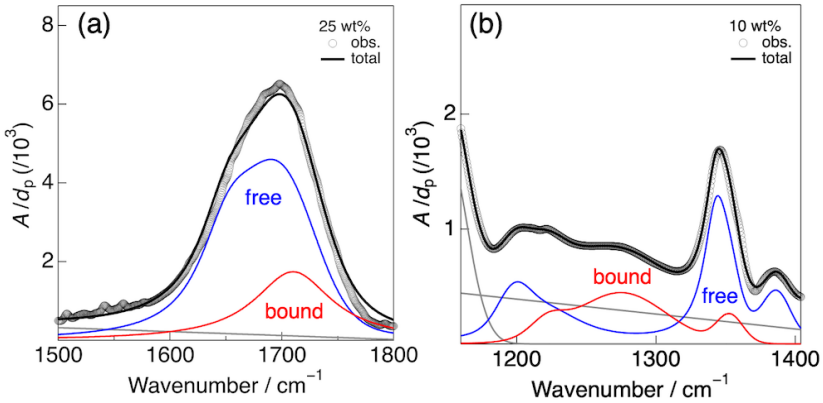

Figure S4. Typical peak deconvolution results for (a) 25 wt% CL/FA and (b) 10 wt% CL/PA solutions.

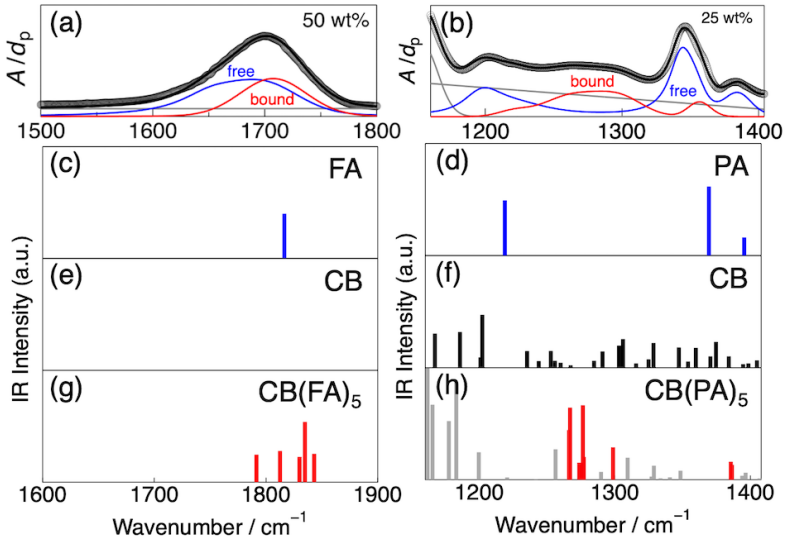

Figure S5. Typical peak deconvolution results for (a) 50 wt% CB/FA and (b) 25 wt% CB/PA solutions, and the theoretical IR bands for (c) FA, (d) PA, (e, f) CB, (g) $CB(FA)_5$, and (h) $CB(PA)_5$ molecules.

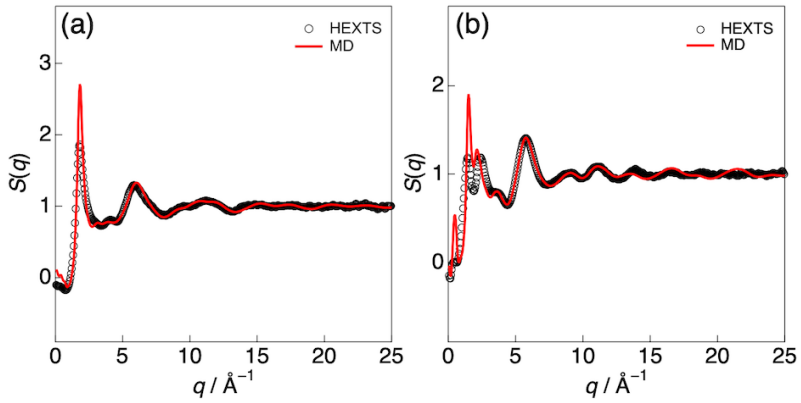

Figure S6. The X-ray structure factor $S(q)$ obtained from HEXTS experiments (open circles) and MD simulations (solid line) obtained for (a) 20 wt% CB/FA and (b) 20 wt% CB/PA solutions.

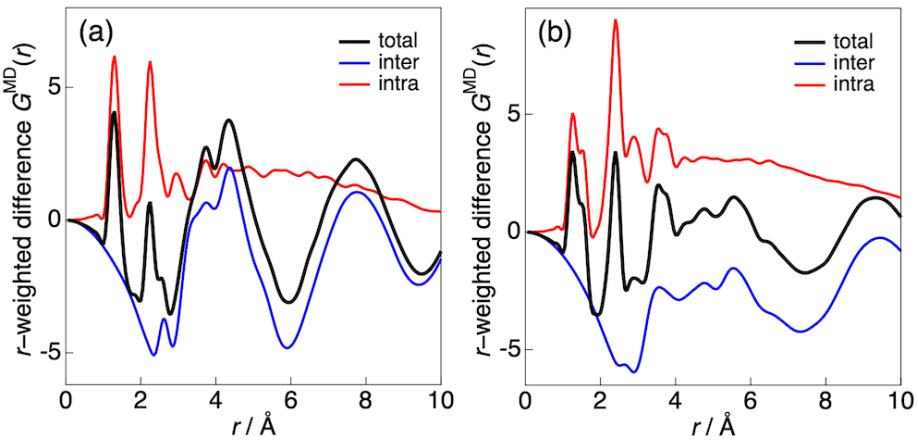

Figure S7. r^2-weighted partial $G^{MD}(r)$s for intramolecular [red; $G^{MD}_{intra}(r)$] and intermolecular [blue; $G^{MD}_{inter}(r)$] contributions, associated with the total profile [black; i.e., $G^{MD}_{total}(r) = G^{MD}_{intra}(r) + G^{MD}_{inter}(r)$], for (a) 20 wt% CB/FA and (b) 20 wt% CB/PA solutions.

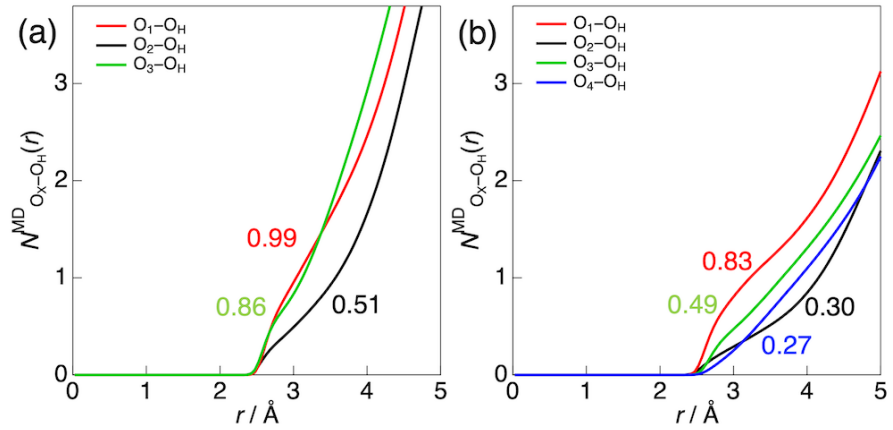

Figure S8. Coordination numbers $N(r)$ obtained by integrating the radial distribution functions $g_{OX–OH}(r)$ for CB(solvent)$_5$ in (a) formic acid (FA) and (b) pyruvic acid (PA) systems. The curves represent the cumulative numbers of solvent O_H atoms around each oxygen site (O_1–O_4) in the chemically modified CB unit as a function of distance r. The coordination numbers at r = 3.0 Å, corresponding to the number of hydrogen bonds per oxygen site, are indicated in the figure and summarized in Table S3.

References

1. S. Sakai, *KEK Report 90-16*, National Laboratory for High Energy Physics, Tsukuba, Japan, 1990.

2. D. T. Cromer, *J. Chem. Phys.*, 1969, **50**, 4857-4859.
3. J. H. Hubbell, Wm. J. Veigele, E. A. Briggs, R. T. Brown, D. T. Cromer and R. J. Howerton, *J. Phys. Chem. Ref. Data*, 1975, **4**, 471-538.
4. K. Hirosawa, K. Fujii, K. Hashimoto and M. Shibayama, *Macromolecules*, 2017, **50**, 6509-6517.
5. N. Dawass, J. Langeveld, M. Ramdin, E. Perez-Gallent, A. A. Villanueva, E. J. M. Giling, J. Langerak, L. J. P. van den Broeke, T. J. H. Vlugt and O. A. Moultos, *J. Phys. Chem. B*, 2022, **126**, 3572-3584.