

Electronic Supplementary Information

The dissolution behavior of chitosan in acetate-based ionic liquids and their interactions: from experimental evidence to density functional theory analysis

Xiaofu Sun,^a Qingqing Tian,^b Zhimin Xue,^a Yuwei Zhang^a and Tiancheng Mu^{*a}

^a Department of Chemistry, Renmin University of China, Beijing 100872, China

^b School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China

Table S1 The acetate-based ILs employed in this study

No.	Name	Abbreviation	Structure
1	1-ethyl-3-methylimidazolium acetate	[Emim]OAc	
2	1-butyl-3-methylimidazolium acetate	[Bmim]OAc	
3	1-hexyl-3-methylimidazolium acetate	[Hmim]OAc	
4	1-octyl-3-methylimidazolium acetate	[Omim]OAc	
5	1-butyl-2,3-dimethylimidazolium acetate	[Bmmim]OAc	
6	tetra-ethyl-ammonium acetate	[TEA]OAc	
7	di-ethyl-ammonium acetate	[DEA]OAc	
8	bis-(2-methoxyethyl)-amine acetate	[BMOEA]OAc	
9	pyrrolidine acetate	[Pyrrol]OAc	

Table S2 The solution thermodynamic parameters of chitosan in the imidazolium-based ILs at different temperature. All the temperatures need to be converted into Kelvin temperature.

parameters	ILs	353 K	363 K	373 K	383 K	393 K	403 K
ΔG_s^θ (kJ/mol)	[Emim]OAc	31.04	31.05	30.57	30.87	31.11	31.56
	[Bmim]OAc	30.24	29.78	29.84	30.26	30.49	30.79
	[Hmim]OAc	31.28	31.30	31.02	31.00	31.36	31.60
	[Omim]OAc	36.55	36.36	36.47	35.66	33.50	33.12
ΔH_s^θ (kJ/mol)	[Emim]OAc	24.43	25.83	27.27	28.76	30.28	31.84
	[Bmim]OAc	21.60	22.84	24.11	25.42	26.77	28.15
	[Hmim]OAc	25.83	27.31	28.84	30.40	32.01	33.66
	[Omim]OAc	55.58	58.77	62.05	65.42	68.88	72.43
$T\Delta S_s^\theta$ (kJ/mol)	[Emim]OAc	-6.61	-5.22	-3.29	-2.12	-0.83	0.28
	[Bmim]OAc	-8.64	-6.94	-5.72	-4.83	-3.73	-2.64
	[Hmim]OAc	-5.45	-3.99	-2.18	-0.59	0.65	2.06
	[Omim]OAc	19.03	22.41	25.58	29.76	35.38	39.30

Table S3 Investigation of water content effect on chitosan solubilities of [Bmim]OAc.

Entry.	Ionic Liquid	Added water content/ppm	Solubility (gram per 100 g of the IL)				
			80°C	90°C	100°C	110°C	120 °C
1	[Bmim]OAc	0	4.4	6.5	8.5	9.7	11.9
2	[Bmim]OAc	530	4.0	6.4	8.4	9.8	12.0
3	[Bmim]OAc	1060	4.0	6.2	8.3	9.6	11.8
4	[Bmim]OAc	1590	3.7	5.8	8.0	9.3	11.6
5	[Bmim]OAc	2120	3.5	5.0	7.8	9.2	11.6
6	[Bmim]OAc	3200	3.2	4.5	7.7	9.1	11.4
7	[Bmim]OAc	5300	3.1	4.6	7.6	9.0	11.4
8	[Bmim]OAc	10540	2.6	4.1	6.8	7.8	10.0
9	[Bmim]OAc	50000	--	--	--	--	--
10	[Bmim]OAc	>50000	--	--	--	--	--

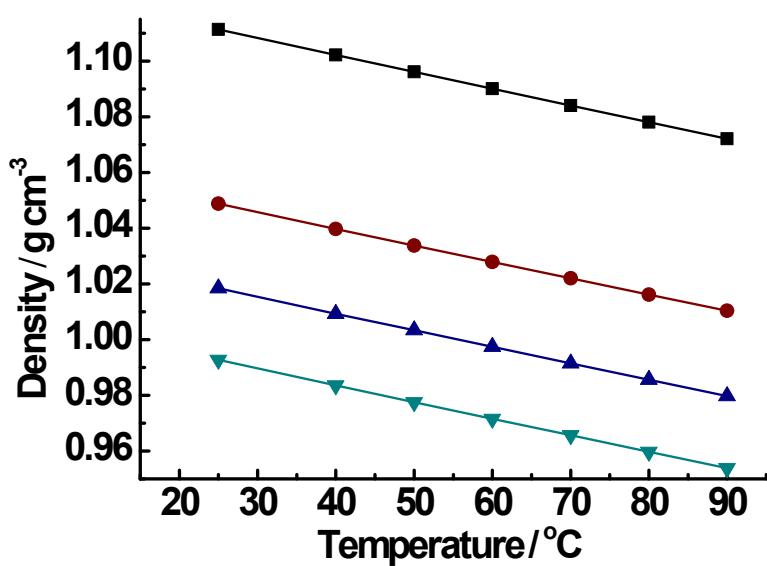


Fig. S1 Density of imidazolium-based ILs as a function of temperature. (From the top to bottom: [Emim]OAc, [Bmim]OAc, [Hmim]OAc and [Omim]OAc.)

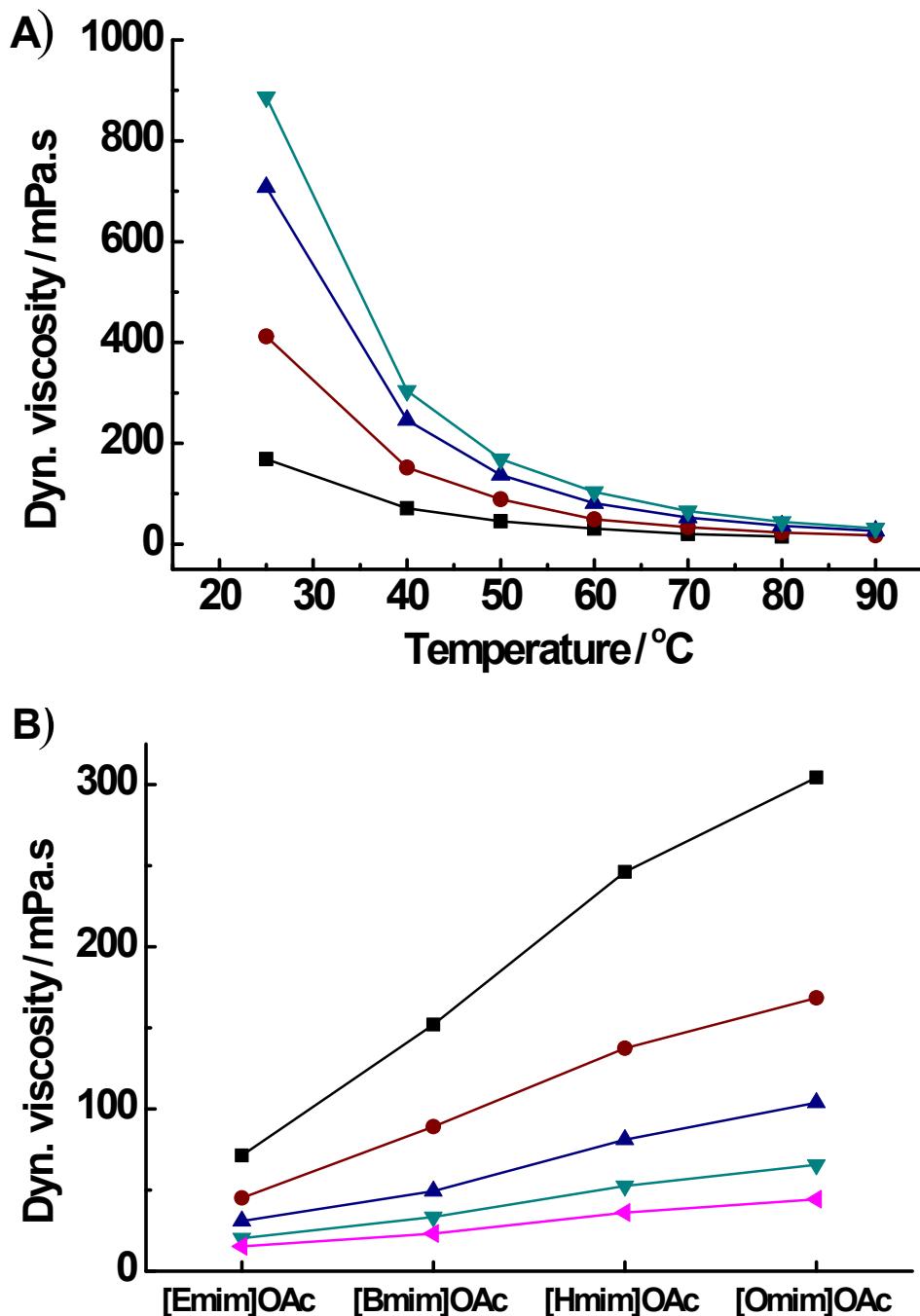


Fig. S2 Viscosity measurements of imidazolium-based ILs A) at a function of temperature (from top to bottom: [Omim]OAc, [Hmim]OAc, [Bmim]OAc and [Emim]OAc); B) with different side-chains in cations (from top to bottom: 40 °C, 50 °C, 60 °C, 70 °C and 80 °C).

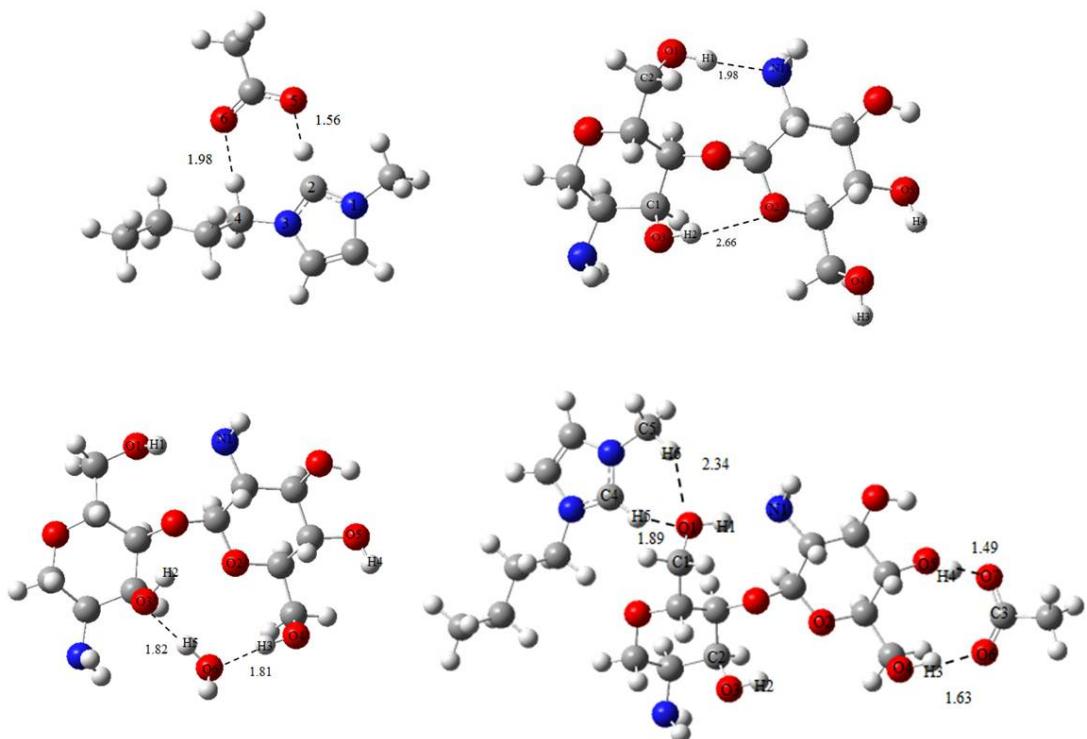


Fig. S3 The optimized structures and geometrical parameters for various species in [Bmim]OAc, chitobiose, chitobiose/H₂O and chitobiose/[Bmim]OAc at B3LYP/6-31G(d,p).