Electronic Supplementary Information

Ionicity in acetate-based protic ionic liquids: evidences for both liquid and gaseous phase

Xiaofu Sun [a], Shuangyue Liu [b], Asim Khan [c], Chuan Zhao [c], Chuanyu Yan [a] and Tiancheng Mu [a]*

[a] Department of Chemistry, Renmin University of China, Beijing 100872, P. R. China

[b] School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, P. R. China

[c] School of Chemistry, The University of New South Wales, NSW 2052, Australia

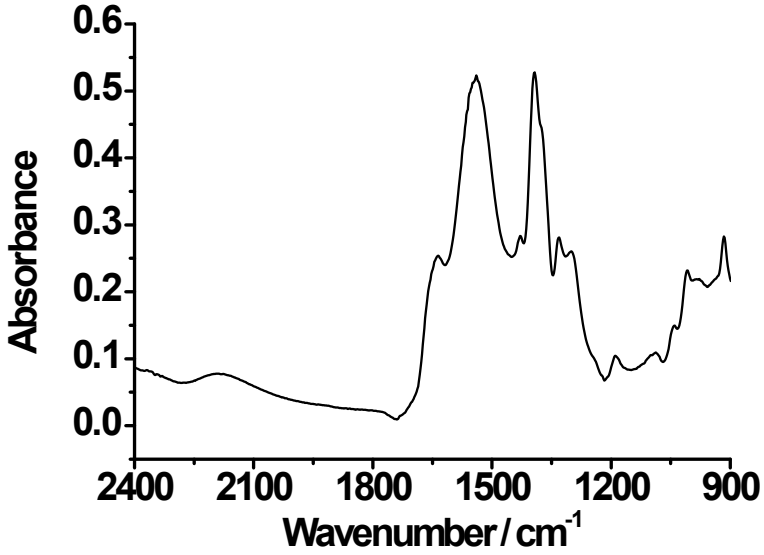


Fig. S1 The ATR-IR spectra of pure [DEA]OAc at the room temperature.

Table S1 The assignment of the vibrational mode of three kinds of PILs.

PILs	Bonds	Assignments	IR spectrum (cm^{-1})	DFT calculations (cm^{-1})
[DEA]OAc	N-H	δ	--	1661.3
		ν(s), ν(as)	3284, 3361	3409.3, 3456.7
	C-N-C	δ	--	389.4
		ν(s)	821	840.5
		ν(as)	911, 1007	898.6, 1005.0
	O-C-O	δ	--	616.1
		ω	1034	613.8, 1028.8
	C-O	ν	1333	1344.9
	C=O	ν	1631	1648.8
[BMOEA]OAc	N-H	δ	--	1441.5
		ν(s), ν(as)	3236, 3279	3408.1, 3455.0
	C-N-C	δ	--	244.2, 306.0, 508.7
		ν(s)	923, 1010	928.9, 1001.5
		ν(as)	954	955.5, 977.0
	O-C-O	δ	--	616.1
		ω	1048	613.8, 1028.8
	C-O	ν	1328	1344.9
	C=O	ν	1708	1648.8
[Pyrrol]OAc	N-H	δ	1821	1899.5
		ν(s), ν(as)	3169, 3247	3456.5, 3504.7
	C-N-C	δ	--	--
		ν(s)	932	822.3, 904.7
		ν(as)	979, 1014	893.8, 1007.9
	O-C-O	δ	--	616.1
		ω	--	613.8, 1028.8
	C-O	ν	1356	1344.9
	C=O	ν	1656	1648.8

Abbreviation: δ: symmetric bending vibration; ω: rocking vibration; ν(s): symmetric stretching; vibration; ν(as): asymmetric stretching vibration

Table S2 The assignment of the vibrational mode of base/acid Precursors.

Precursors	Bonds	Assignments	IR spectrum (cm^{-1})
DEA	N-H	δ	1455
		ν(s), ν(as)	3280
	C-N-C	δ	--
		ν(s)	1040
		ν(as)	1132
BMOEA	N-H	δ	1455
		ν(s), ν(as)	3242
	C-N-C	δ	--
		ν(s)	1094
		ν(as)	1198
Pyrrol	N-H	δ	1379
		ν(s), ν(as)	3259
	C-N-C	δ	--
		ν(s)	976
		ν(as)	1077
HAc	O-C-O	δ	--
		ω	1053
	C-O	ν	1226
	C=O	ν	1711

Abbreviation: δ: symmetric bending vibration; ω: rocking vibration; ν(s): symmetric

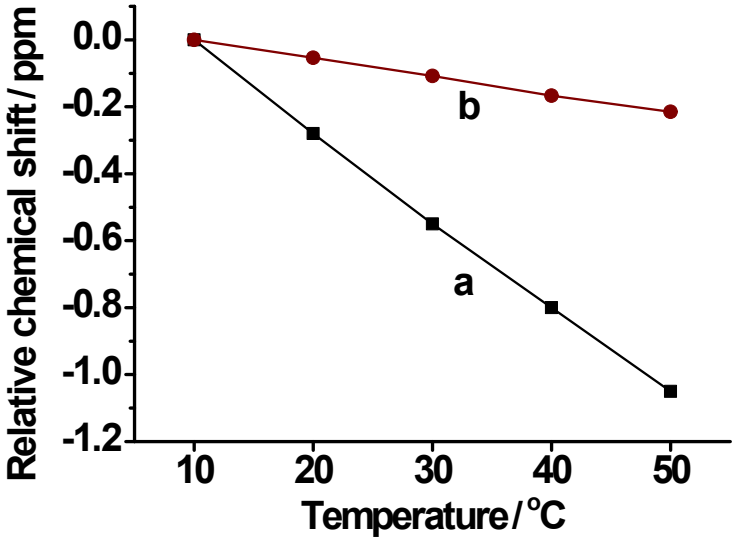
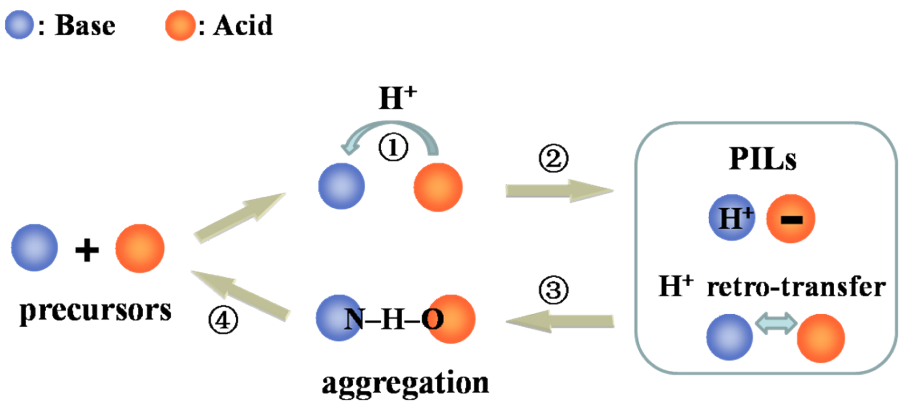


Fig. S2 The relative ^{15}N NMR chemical shift against the values at 10 °C for [BMOEA]OAc (a) and [Pyrrol]OAc (b) .



① Proton transfer from acid to base

② PILs formation

③ Proton retro-transfer and ions aggregation formation

④ H-bonds breaking and precursors formation

Scheme S1 The situation and the main forces involved in the liquid phase of PILs.

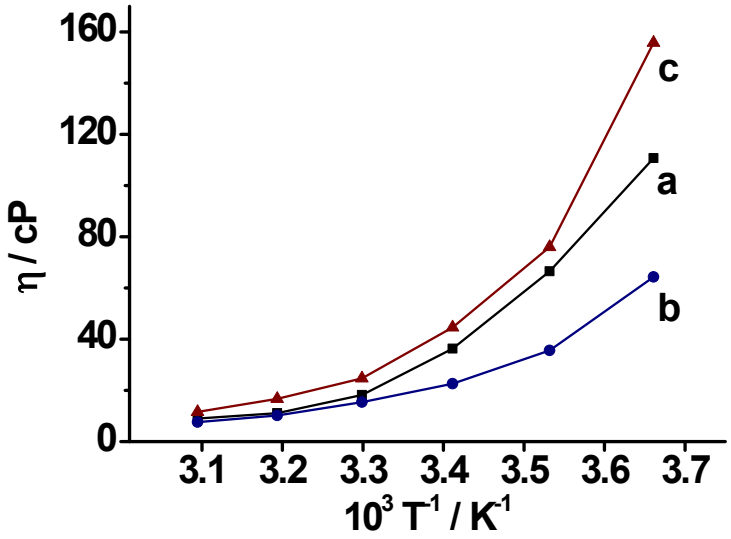


Fig. S3 Temperature dependence of viscosities for the present acetate-based PILs, including [DEA]OAc (a), [BMOEA]OAc (b) and [Pyrrol]OAc (c).

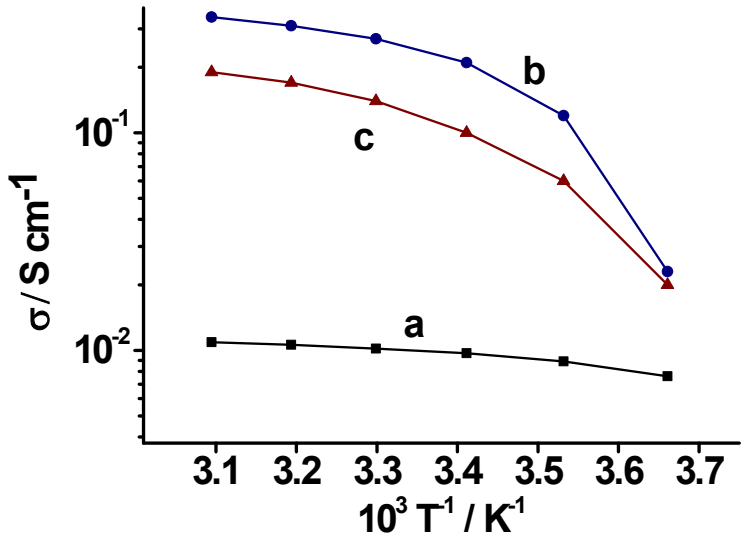


Fig. S4 Temperature dependence of ionic conductivities for the present acetate-based PILs, including [DEA]OAc (a), [BMOEA]OAc (b) and [Pyrrol]OAc (c).

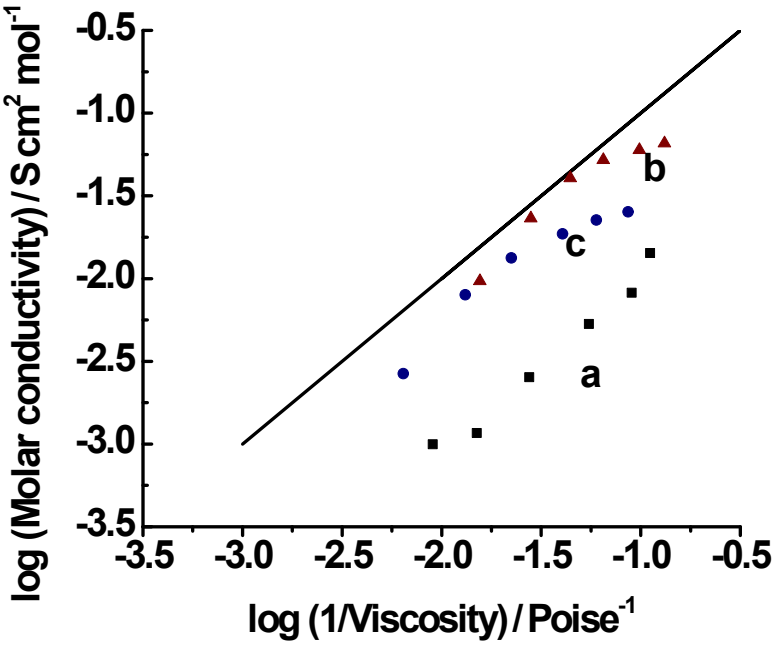


Fig. S5 Walden plot of log (Molar conductivity) against log (1/Viscosity) as a measure of ionicity for the present acetate-based PILs, including [DEA]OAc (a), [BMOEA]OAc (b) and [Pyrrol]OAc (c). Solid line represents the ideal line for completely dissociated 0.01 mol/L KCl aqueous solution.

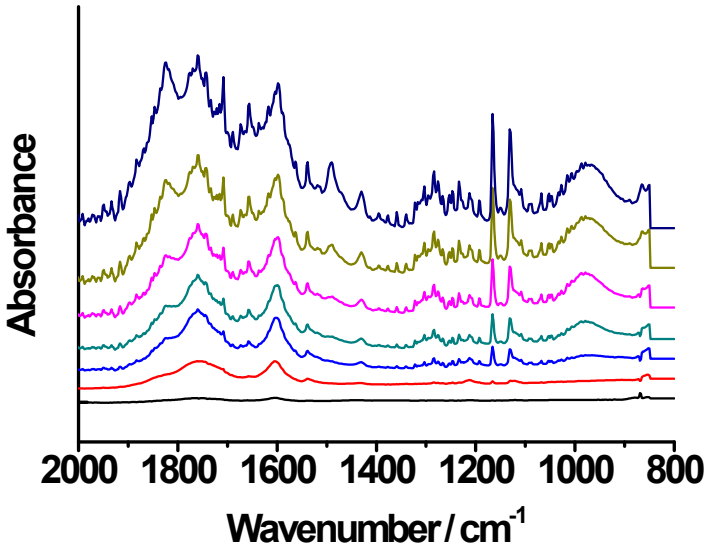


Fig. S6 The *in situ* gas FT-IR spectra of [DEA]OAc at different temperature (from bottom to top: 40 °C, 80 °C, 120 °C, 140 °C, 160 °C, 200 °C and 250 °C).

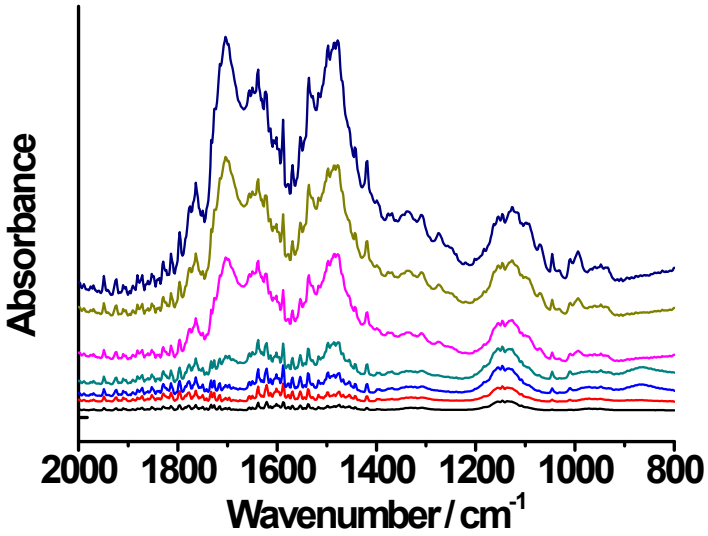


Fig. S7 The *in situ* gas FT-IR spectra of [Pyrrol]OAc at different temperature (from bottom to top: 40 °C, 80 °C, 120 °C, 140 °C, 160 °C, 200 °C and 250 °C).

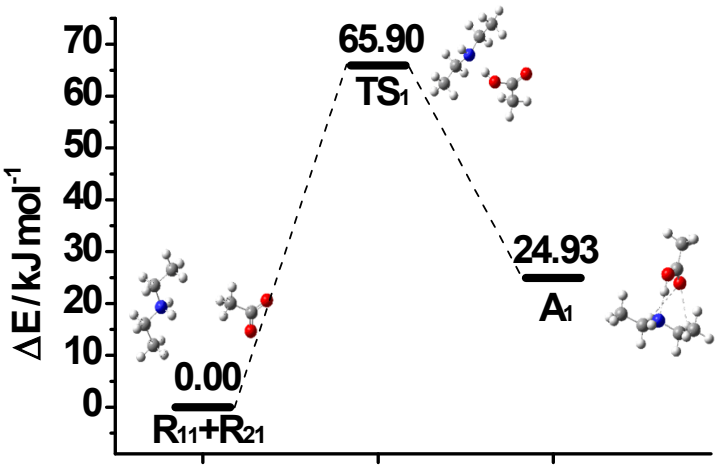


Fig. S8 The potential energy surface profile of [DEA]OAc.

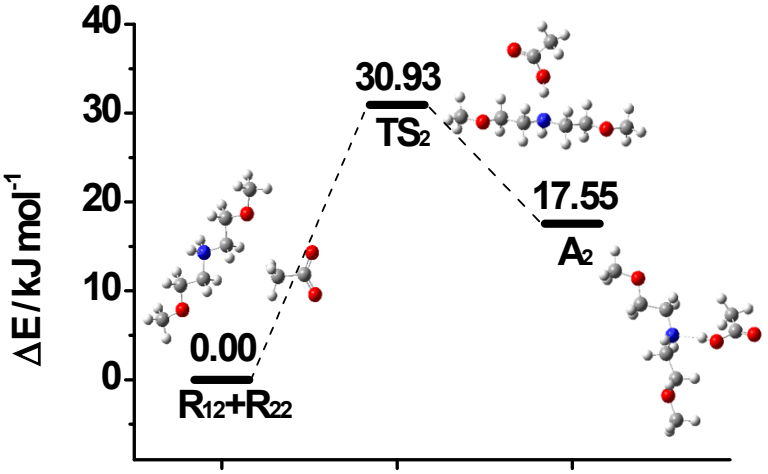


Fig. S9 The potential energy surface profile of [BMOEA]OAc.

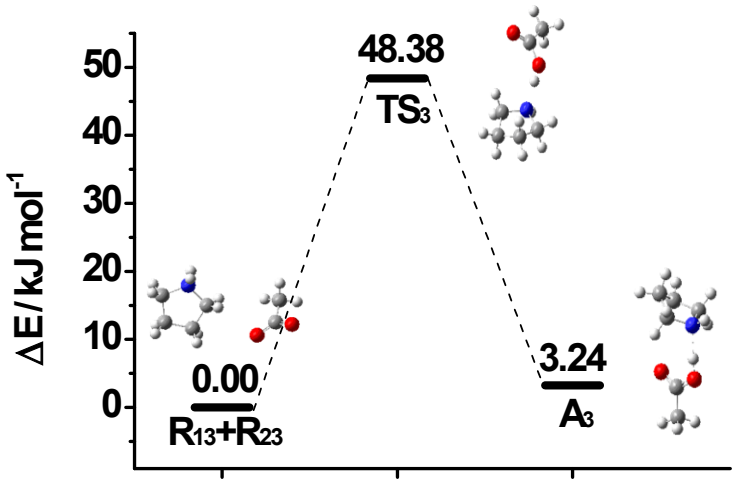


Fig. S10 The potential energy surface profile of [Pyrrol]OAc.

Table S3 The theoretical FT-IR vibrational modes and corresponding bond length of [DEA]OAc.

Bonds	Assignments	Ionic state		Transition state		Molecular state	
		F (cm^{-1})	L (Å)	F (cm^{-1})	L (Å)	F (cm^{-1})	L (Å)
N-H	δ	1661.3	1.0247	1473.2	1.0188	1474.9	1.0185
	ν(s)	3409.3		--		--	
	ν(as)	3456.7		3473.2		3474.0	
C-N-C	δ	389.4	1.5190	421.7	1.4767	420.6	1.4751
	ν(s)	840.5		1048.3		1050.1	
	ν(as)	898.6		1121.3		1094.7	
		1005.0		1125.9		1120.0	
O-C-O	δ	616.1	1.2562	604.2	1.3555	626.1	1.3347
	ω	613.8	1.2554	589.7	1.2060	603.6	1.2154
		1028.8		1050.8		1066.7	
C-O	ν	1344.9		1238.0		1297.0	
C=O	ν	1648.8		1784.9		1764.6	

Abbreviation: δ: symmetric bending vibration; ω: rocking vibration; ν(s): symmetric stretching vibration; ν(as): asymmetric stretching vibration; F: Frequency; L: Bond length

Table S4 The theoretical FT-IR vibrational modes of and corresponding bond length [BMOEA]OAc

Bonds	Assignments	Ionic state		Transition state		Molecular state	
		F (cm^{-1})	L (Å)	F (cm^{-1})	L (Å)	F (cm^{-1})	L (Å)
N-H	δ	1441.5	1.0247	1488.3	1.0188	1053.6	1.0182
	ν(s)	3408.1		--		--	
	ν(as)	3455.0		3471.6		3479.6	
C-N-C	δ	244.2	1.5131	256.6	1.4729	242.4	1.4713
		306.0		324.2	1.4750	365.8	1.4737
		508.7		529.9		550.5	
	ν(s)	928.9		959.8		948.1	
		1001.5		1046.6		1011.3	
	ν(as)	955.5		1123.3		1133.3	
		977.0		1147.6		1150.5	
O-C-O	δ	616.1	1.2562	603.6	1.3580	618.8	1.3463
	ω	613.8	1.2554	590.4	1.2055	585.9	1.2048
		1028.8		1049.5		1058.9	
C-O	ν	1344.9		1234.8		1262.5	
C=O	ν	1648.8		1787.3		1819.1	

Abbreviation: δ: symmetric bending vibration; ω: rocking vibration; ν(s): symmetric stretching vibration; ν(as): asymmetric stretching vibration; F: Frequency; L: Bond length

Table S5 The theoretical FT-IR vibrational modes of and corresponding bond length [Pyrrol]OAc

Bonds	Assignments	Ionic state		Transition state		Molecular state	
		F (cm^{-1})	L (Å)	F (cm^{-1})	L (Å)	F (cm^{-1})	L (Å)
N-H	δ	1899.5	1.0210	1424.1	1.0132	1425.4	1.0133
	ν(s)	3456.5		--		--	
	ν(as)	3504.7		3544.9		3541.8	
C-N-C	δ	--	1.5352	--	1.4996	--	1.4950
	ν(s)	822.3		630.7	1.4931	655.7	1.4970
		904.7		893.0		892.7	
	ν(as)	893.8		924.4		917.8	
		1007.9		1075.1		1075.5	
O-C-O	δ	616.1	1.2562	603.7	1.3542	621.9	1.3323
	ω	613.8	1.2554	590.2	1.2063	604.6	1.2163
		1028.8		1051.0		1067.0	
C-O	ν	1344.9		1238.5		1302.6	
C=O	ν	1648.8		1783.4		1759.0	

Abbreviation: δ: symmetric bending vibration; ω: rocking vibration; ν(s): symmetric stretching vibration; ν(as): asymmetric stretching vibration; F: Frequency; L: Bond length