Kinetics Study of the Esterification Reaction of Diethylene Glycol Monobutyl Ether with Acetic Acid Catalyzed by Heteropolyanion-Based Ionic Liquids

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Supporting Information

Six heteropolyanion-based ionic liquids (HPA-ILs) composed of $PW_{12}O_{40}^{3-}$ anion and different cations were prepared in this work. ^{1}H NMR (Bruker DPX-400) spectrum of these HPA-ILs were recorded. FT-IR spectra for samples in KBr disks were recorded on Thermo Nicolet 870. Thermograimetric and differential scanning calorimetry (TG-DSC) curves were obtained on a TA Q600 thermal analyzer. Samples were heated from room temperature to 800 ℃ at a heating rate of 10 ℃/min under flowing nitrogen. Elemental analysis (C, H, N) was performed on a CHN elemental analyzer (vario EL).

$[Mim]_3PW_{12}O_{40}$: ^{1}H NMR (400 MHz, DMSO) δ 9.00 (s, 1H), 7.63 (s, 1H), 7.56 (s, 1H), 3.92 (s, 3H).

$[Et_3NH]_3PW_{12}O_{40}$: ^{1}H NMR (400 MHz, DMSO) δ 8.86 (s, 2H), 3.19-3.03 (m, 6H), 1.19 (t, *J* = 7.3 Hz, 9H).

$[Bmim]_3PW_{12}O_{40}$: ^{1}H NMR (400 MHz, DMSO) δ 9.10 (s, 1H), 7.75 (dd, *J* = 14.6, 13.0 Hz, 2H), 4.17 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.83 – 1.72 (m, 2H), 1.26 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

$[N_{2224}]_3PW_{12}O_{40}$: ^{1}H NMR (400 MHz, DMSO) δ 3.24 (q, *J* = 7.2 Hz, 6H), 3.15-3.08 (m, 2H), 1.57 (dt, *J* = 15.9, 7.8 Hz, 2H), 1.34 (dd, *J* = 14.8, 7.4 Hz, 2H), 1.18 (ddd, *J* = 7.2, 5.6, 1.6 Hz, 9H), 0.95 (t, *J* = 7.3 Hz, 3H).

$[BSmim]_3PW_{12}O_{40}$: ^{1}H NMR (400 MHz, DMSO) δ 9.13 (s, 2H), 7.74 (dt, *J* = 27.0, 1.7 Hz, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 3.86 (s, 3H), 2.54-2.43 (m, 2H), 1.95 – 1.79 (m, 2H), 1.54 (d, *J* = 7.3 Hz, 2H).

$[BSEt_3N]_3PW_{12}O_{40}$: ^{1}H NMR (400 MHz, DMSO) δ 3.37 (t, *J* = 6.4 Hz, 2H), 3.21 (q, *J* = 7.2 Hz, 6H), 2.54 (d, *J* = 7.6 Hz, 2H), 1.61 (dd, *J* = 8.6, 5.0 Hz, 2H), 1.46 (dt, *J* = 13.7, 6.7 Hz, 2H), 1.23-1.06 (m, 9H).

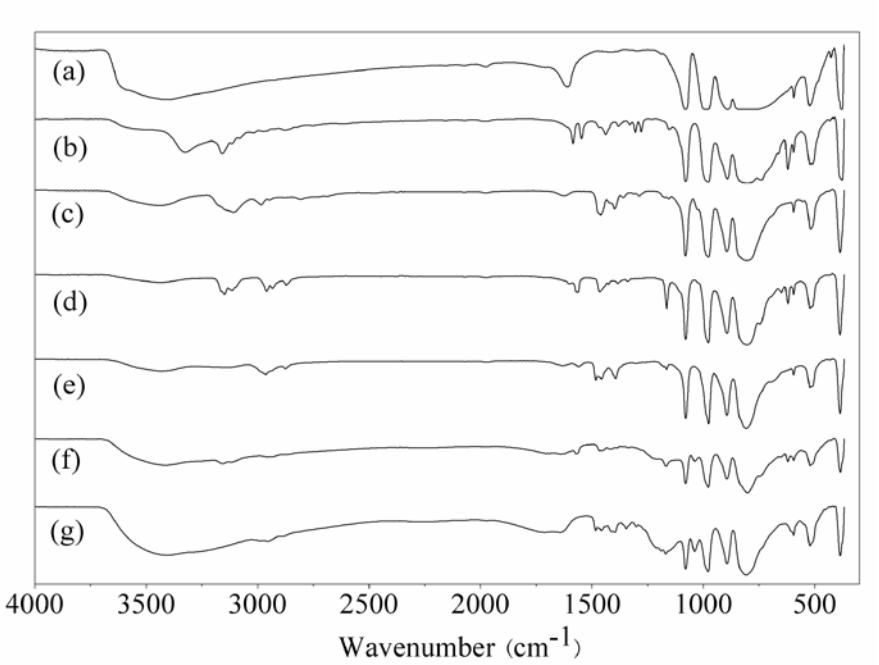

Fig. S1. FT-IR spectra of (a) $H_3PW_{12}O_{40}$, (b) $[Mim]_3PW_{12}O_{40}$, (c) $[Et_3NH]_3PW_{12}O_{40}$, (d) $[Bmim]_3PW_{12}O_{40}$, (e) $[N_{2224}]_3PW_{12}O_{40}$, (f) $[BSmim]_3PW_{12}O_{40}$, (g) $[BSEt_3N]_3PW_{12}O_{40}$.

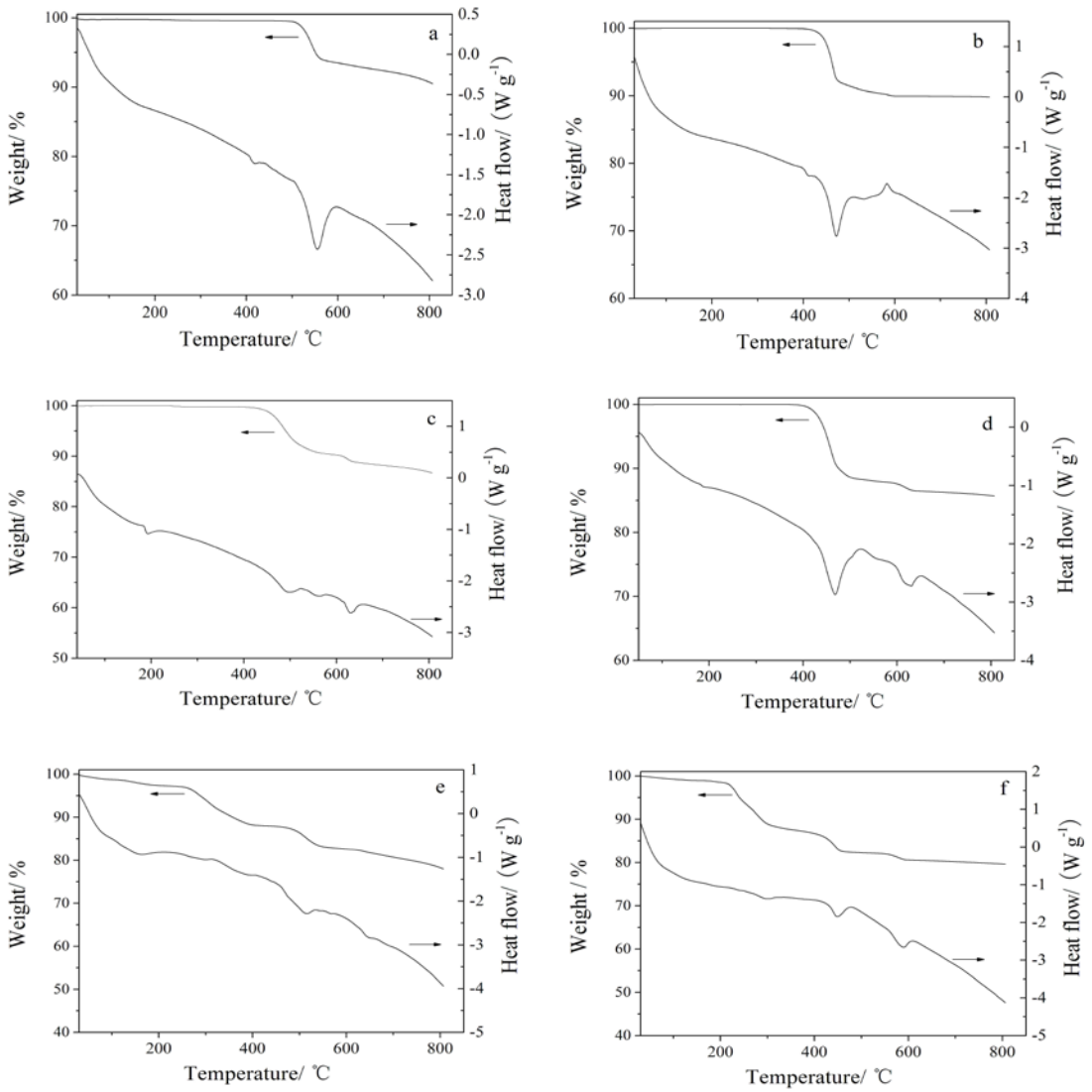

Figure S2. TG-DSC curves of (a) $[Mim]_3PW_{12}O_{40}$, (b) $[Et_3NH]_3PW_{12}O_{40}$, (c) $[Bmim]_3PW_{12}O_{40}$, (d) $[N_{2224}]_3PW_{12}O_{40}$, (e) $[BSmim]_3PW_{12}O_{40}$, (f) $[BSEt_3N]_3PW_{12}O_{40}$

Table S1. Elemental analysis (C, H, N) of catalysts

Catalyst	Element	Measured value,%	Calculated value,%
$[Mim]_3PW_{12}O_{40}$	C	4.27	4.60
	H	0.60	0.67
	N	2.43	2.69
$[Et_3NH]_3PW_{12}O_{40}$	C	7.12	6.78
	H	1.36	1.51
	N	1.19	1.32
$[Bmim]_3PW_{12}O_{40}$	C	9.08	8.74
	H	1.45	1.37
	N	2.68	2.55
$[N_{2224}]PW_{12}O_{40}$	C	11.08	10.74
	H	2.41	2.15
	N	1.41	1.25
$[BSmim]_3PW_{12}O_{40}$	C	8.45	8.14
	H	1.36	1.28
	N	2.52	2.38
$[BSEt_3N]_3PW_{12}O_{40}$	C	9.66	10.02
	H	1.85	2.00
	N	1.07	1.17