Supplementary Information

Selective removal of acetylenes from olefin mixtures through specific physicochemical interactions of ionic liquids with acetylenes

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Solubility measurement

Solubility measurements were carried out based on the isochoric saturation method. A stainless steel-made solubility test apparatus consisting of an equilibrium cell (EC) and a gas reservoir (GR) was constructed in an oven as illustrated in Fig. S-1. The apparatus was equipped with a pressure transducer, P1 for measuring pressures close to atmospheric pressure (OMEGA Engineering PX309-030AI, 0 to 207 kPa, accuracy 0.25% full scale). Volume of the EC was measured by filling it with distilled water at room temperature. The solubility test unit was placed in an isothermal oven and the inside temperature was carefully controlled with an accuracy of ± 0.1 K.
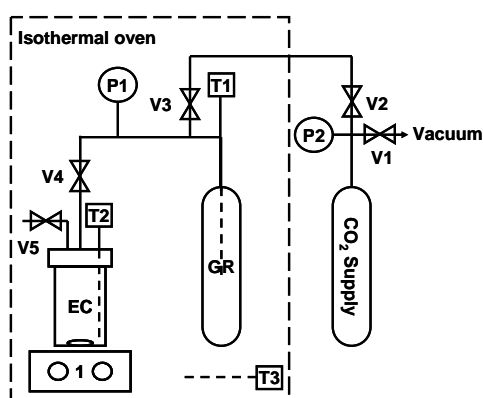

Fig. S-1 Schematic diagram of the apparatus for GAS solubility test: Equilibrium cell, (EC); gas reservoir, (GR); valves, (V1-5); thermocouples, (T1-3); pressure transducers, (P1); magnetic stirrer, (1).

In a typical experiment, a known quantity of a IL was loaded into the EC and degassed under vacuum at 343 K at least for 2 h prior to each test. At a specified oven temperature, the valve (V4) connecting EC and GR was closed to separate these vessels. Gas was fed from the gas supply cylinder to the GR through V2 and V3, and the amount of gas at equilibrium was

calculated from the *pVT* relation. Gas was then brought into contact with the absorbent in the EC by opening V4 and the absorbent was then stirred vigorously to facilitate the gas absorption. After the absorption reached equilibrium, the amount of dissolved gas was calculated from a difference between the initial gas concentration in the GR and the concentration in the gaseous phase.

The moles of dissolved gas in a IL (n_2^{liq}) can be obtained from Eq. (1) on the assumption that the gaseous phase consists of only pure gas due to the negligible vapor pressure of IL,

$$n_2^{\text{liq}} = \frac{p_{\text{ini}}V_{\text{GR}}}{[Z_2(p_{\text{ini}},T_{\text{ini}})RT_{\text{ini}}]} - \frac{p_{\text{eq}}(V_{\text{tot}} - V_{\text{liq}})}{[Z_2(p_{\text{eq}},T_{\text{eq}})RT_{\text{eq}}]} \tag{1}$$

where p_{ini} and T_{ini} are the initial pressure and temperature in the first *pVT* determination (in the GR), and p_{eq} and T_{eq} are the pressure and the temperature at equilibrium, respectively. V_{tot} is the total volume of the entire solubility apparatus, V_{liq} is volume of the absorbent which is assumed to be constant over the entire range of pressure, and Z_2 is the compressibility factor for the pure component 2, the solute (gas).

The solubility of gas expressed in a mole fraction (x_2) and in a mole ratio ( ) was calculated according to Eq. (2) and Eq. (3), respectively.

$$x_2 = \frac{n_2^{\text{liq}}}{n_1^{\text{liq}} + n_2^{\text{liq}}} \tag{2}$$

$$\alpha = \frac{n_2^{\text{liq}}}{n_1^{\text{liq}}} \tag{3}$$

At a very low solute concentration in an absorbent, the solubility can be expressed in terms of Henry's law coefficient as Eq. (4)

$$H_{2.1}(p,T) \approx \frac{\phi_2(p,T)p}{x_2}. \tag{4}$$

Based on the solubility data, Henry's law coefficient was obtained from the slope of an isotherm linear fit of fugacity versus mole fraction.

Table S-1 Solubilities of acetylene and ethylene in various absorbents at 313 K and 0.1 MPa of the gas, acidity constants of acid and basicity constants of the corresponding conjugate base

Absorbent	MW (gr mol^{-1})	pK_a^{aq}	pK_b^{aq}	$H_{2.1}$ (MPa)	
				C_2H_2	C_2H_4
[BMIM][AcO]	198.26	4.76[a]	9.24	0.64	17.59
[BMIM][MeHPO$_3$]	234.23	2.05[b]	11.95	0.71	18.34
[BMIM][BF$_4$]	226.02	-0.44[c]	14.44	1.75	19.22
[BMIM][TFA]	252.23	0.00[c]	14.00	1.42	13.63
[BMIM][Me$_2$PO$_4$]	264.26	1.29[d]	12.71	0.49	13.42
DMF	73.09	-0.01[e]	14.01	2.01	18.34

[a] J. P. Guthrie, *Can. J. Chem.*, 1978, **56**, 2342.
[b] Cald. using ACD/Labs software V8.14 for Solaris (1994-2009 ACD/Labs).
[c] D. R. Macfarlane, J. M. Pringle, K. M. Johansson, S. A. Forsyth and M. Forsyth, *Chem. Commun.*, 2006, **1905**.
[d] W. D. Kumler and J. J. Eiler, *J. Am. Chem. Soc*. 1943, **65**, 2355.
[e] *N,N*-dimethylformamide in *Hazard Assessment Report*, Chemicals Evaluation and Research Institute (CERI), Japan, 2007, pp. 2.
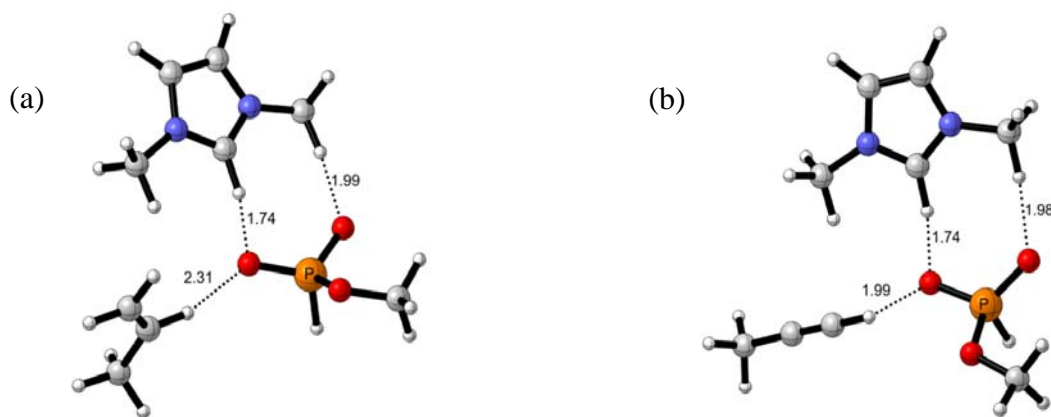

Fig. S-2 Optimized structures showing the interaction of [DMIM][MeHPO$_3$] with propyne and propylene: (a) [DMIM][MeHPO$_3$] + propyne (ΔH = -2.50 kcal/mol), (b) [DMIM][MeHPO$_3$] + propylene (ΔH = -0.03 kcal/mol).
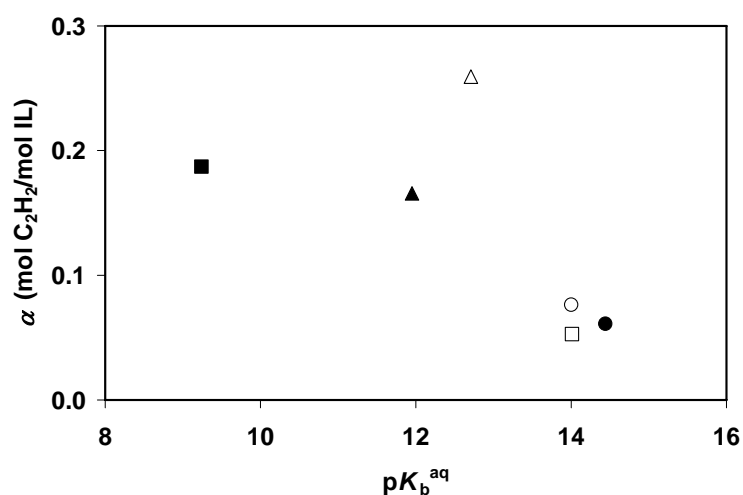

Fig. S-3 Correlation of pK_b^{aq} of anion and acetylene solubility in the corresponding IL at 313.15 K and at 0.1 MPa of acetylene. (■), [Acetate]$^-$; (△), [Me$_2$PO$_4$]$^-$; (▲), [MeHPO$_3$]$^-$; (○), [TFA]$^-$; (●), [BF$_4$]$^-$; (□), DMF.