Supporting Information

Extraction of ionic liquids from aqueous solutions by humic acid: an environmentally benign, inexpensive and simple procedure

Huiyong Wang, Jianji Wang*, and Maohong Fan

1. The materials and apparatus

1-methylimidazole (99%) was from Shanghai Chem. Co.; 1-bromobutane (99%), 1-bromohexane (99%), 1-bromooctane (99%), 1-bromodecane (99%) and 1-bromododecane (99%) were purchased from Alfa Aeser. 2-Nitrophenyloctyl ether (*o*-NPOE) was from Fluka and used without further purification. Dibutylphthalate (DBP), tetrahydrofuran (THF) and poly(vinylchloride) (PVC) of high molecular mass were obtained from Shanghai Chem. Co. Aldrich humic acid (tech., lot. S15539-384) with 35.1% dissolved organic carbon was used as received.

The stock solution of humic acid was prepared by dissolving the solid sample in deionized water, which was then filtered through a 0.22μm membrane. The buffer solutions at pH 5, 7 and 10 were prepared by acetate (0.5740g CH_3CO_2Na + 0.2700g CH_3COOH per liter), phosphate (1.0230g Na_2HPO_4 + 0.6190g NaH_2PO_4 per liter) and carbonate (0.6831g Na_2CO_3 + 0.5041g $NaHCO_3$ per liter), respectively.

The potentials were recorded by an Orion 920A+ ion-meter, and a Br^- selective electrode (Orion) was used as a reference electrode.

2. The synthesis of [C$_n$mim]Br (n=4, 6, 8, 10, 12)

[C$_n$mim]Br (n= 4, 6, 8, 10, 12) were prepared and purified by the procedure described in the literature.[1] Briefly, the reactions of 1-methylimidazole with excess 1-bromoalkane were performed in 1,1,1-trichloroethane under reflux at ca. 343 K for 48 h. The products [C$_4$mim]Br and [C$_{12}$mim]Br were recrystallized three times from ethyl acetate and ethyl acetate/ acetonitrile (3:2 by volume), respectively, to remove any unreacted reagents. [C$_6$mim]Br, [C$_8$mim]Br and [C$_{10}$mim]Br were washed with

1,1,1-trichloroethane. The residual solvents were removed by heating at 343 K under vacuum. Then, the samples were dried under vacuum at 343 K for 2-3 days in the presence of P_2O_5. The ^{1}H NMR spectra of these ionic liquids were determined by a Bruck AV-400 spectrometer, and they were found to be in good agreement with those reported in literature.[2, 3] The water content in the ionic liquids was determined by Karl-Fisher titration. It was found that less than 0.02 wt% of water were still remained in [$C_n$mim]Br (n= 4, 6, 8, 10, 12).

3. The preparation of ion selective electrodes

Ion selective electrodes for the cations of [$C_n$mim]Br (n= 4, 6, 8, 10, 12) were prepared by the procedure described in the literature.[4] In brief, electrode membrane was prepared by dissolving 3.0mg of [$C_n$mim]Br, 100mg of PVC and 200mg of 2-nitrophenyloctyl ether in 5mL of THF. The solution was poured into a glass ring with a diameter of 18 mm, which was fixed tightly on a glass plate. The solvent THF was allowed to evaporate at room temperature for two days, and the resulting membrane with about 0.4 mm thickness was cut into small disks. A disk with diameter of 10 mm was removed carefully from the glass plate and incorporated into an electrode body ISE containing 1×10^{-2}M [$C_n$mim]Br and 1×10^{-2}M KBr as an internal filling solution. The electrodes prepared were preconditioned by soaking in a solution containing 1×10^{-2}M [$C_n$mim]Br in water with constant stirring. When not in use, the electrodes were immersed in the same solution.

4. The general procedure for the calibration of the ion selective electrodes

The ion selective electrode was calibrated at a given pH by titrating, while stirring, adequate small volumes of the ILs standard solution into a 25mL solution at constant pH to cover the ILs concentration range from 1×10^{-7} to 1×10^{-3}M. The obtained electrode potentials (E) were plotted against logarithm of the ILs concentrations, and the calibration parameters were computed by fitting the experimental data to the equation:[4]

$$E = E^0 + S \log (A + C_{IL}) \qquad (1)$$

where E^0 is the standard potential of the cell, C_{IL} is the free concentration of [$C_n$mim]Br in water, S and A are the slope and the detection limit of the electrode, respectively. The slope of the electrodes is in the range from 54.9 ± 0.5 to 59.1 ± 0.3 mV, the linear range is from 2.1×10^{-3} to 3.8×10^{-6} M, and the detection limit of the electrode is 1×10^{-6} M.

5. Procedure for the determination of the extraction percent of the ILs

The extraction percent of the ILs by HA is defined as the ratio of the associated and the total mole number of the ILs in solution. The extraction experiments were carried out by employing the HA titration protocol in the presence of ILs. After each addition, a maximum of 15 min was needed to reach equilibrium, and the equilibration criterion was ≤0.1 mV/min. The recorded electrode potential is a measure of the equilibrium monomer ILs concentration in solution. The mole number of free ILs in solution was calculated from the equilibrium monomer concentration and the known total solution volume. The mole number of the ILs associated to HA was calculated by subtracting the mole number of free ILs from that initially added to the solution. Thus, extraction percent of the ILs can be calculated by

$$R = (n_i - n_f)/ n_i \qquad (2)$$

where n_i and n_f are the initial and final mole number of ILs in aqueous solution, respectively.

6. Determination of the binding constants and binding Gibbs energies of the ILs to HA in water

The binding constants and binding Gibbs energies of [$C_n$mim]Br (n = 4, 6, 8, 10, 12) to HA is determined by measuring pyrene fluorescence in solutions. Steady-state fluorescence measurements were performed by using a Cary Eclipse fluorophotometer (Varian, America) at 298 ± 1 K. The concentration of pyrene was always remained constant at 5×10^{-7} molL^{-1}. Both excitation and emission band slits were fixed at 5 nm. The excitation and emission wavelength was selected at 335 and 373 nm, respectively. Concentration of HA was in the range of 1 to 19 mgL^{-1} for a

3

given IL concentration.

It has been reported that pyrene is less emissive when it was bound to HA.[5] This behavior is clearly demonstrated in Figure S1, which shows that the emission intensity of pyrene is a function of HA concentrations in aqueous solutions without IL. Similar behavior was also observed in aqueous ILs solutions. Therefore, fluorescence experiments were performed at a chosen pyrene concentration of 5×10^{-7} molL^{-1}, but varied HA concentrations in any given aqueous IL solution.
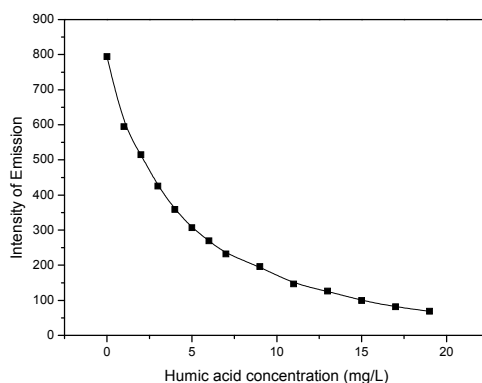

Fig. S1 Emission intensity of pyrene as a function of HA concentrations in aqueous solutions at pH 7.
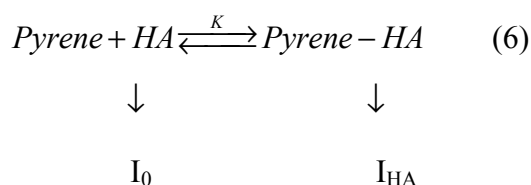
Interestingly, it was found that the intensity of pyrene can be fitted to the following equations：

$$I = \frac{I_0 + I_{HA}KC_{HA}}{1 + KC_{HA}} \qquad (3)$$

$$K = K_{\max}\frac{e^t}{1+e^t} \qquad (4)$$

$$t = \frac{C_{HA} - h}{j} \qquad (5)$$

This suggests that pyrene is partially bound to HA in the presence of ILs, as shown in equation (6):[5]

$$Pyrene + HA \underset{}{\overset{K}{\rightleftharpoons}} Pyrene - HA \qquad (6)$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$I_0 \qquad\qquad\qquad I_{HA}$$

4

where I_0 denotes the emission intensity of the free pyrene, I_{HA} stands for the emission intensity of the bound pyrene, C_{HA} is the concentration of HA in solutions, and K represents the constant of the binding between pyrene and HA. In eq (4), K_{max} is the maximum value of K. In eq (5), h is the value of C_{HA} at $K=(1/2) K_{max}$, and j is an adjustable parameter.[6] Equation (3) represents the average value of I_0 and I_{HA}. According to equations (4) and (5), there is a sigmoidal relationship between K and C_{HA}, which indicates that the binding of pyrene to HA is anti-cooperative due to sigmoidal dependence of K on concentration.[7]

Based on the K_{max} values, the values of ΔG_{max} were computed by the equation:

$$\Delta G_{max} = -RT \ln K_{max} \quad (7)$$

These values represent the binding ability of pyrene to HA relative to the aqueous IL solutions in which free pyrene molecules are present. Obviously, the ΔG_{max} values obtained in this way cannot be directly compared because of the differences in ILs used and variation in their concentrations. Thus, the ΔG_{max} values should be adjusted with the difference of Gibbs energy of pyrene in solutions due to the presence of ILs. Assuming that S and S_0 are the solubility of pyrene in aqueous solutions with and without IL, the change of Gibbs energy, ΔG, can be correlated with the activity coefficient and solubility of pyrene by

$$\Delta G = RT \ln \gamma_{py} = RT \ln \frac{S_0}{S} \quad (8)$$

Then, the corrected Gibbs energy, ΔG_{max}^{corr}, can be obtained from the following equation:

$$\Delta G_{max}^{corr} = \Delta G_{max} - RT \ln \frac{S_0}{S} \quad (9)$$

Because there are two kinds of HA, free HA and HA bound to ILs, in solution at the same time. They have different ability to bind pyrene, in the sense that the corrected Gibbs energy of binding of pyrene to HA will be different for each kind of HA. The observed Gibbs energy could be the average values of these Gibbs energies given by the following equation:

$$\Delta G_{\text{max}}^{corr} = \frac{(\Delta G_{\text{max}}^{corr})_{HA} + K_{HA}^{IL}(\Delta G_{\text{max}}^{corr})_{HA}^{IL} C_{IL}}{1 + K_{HA}^{IL} C_{IL}} \quad (10)$$

in this equation, $(\Delta G_{\text{max}}^{corr})_{HA}^{IL}$ and $(\Delta G_{\text{max}}^{corr})_{HA}$ are the binding Gibbs energy of pyrene to HA with and without IL, respectively, C_{IL} is the concentration of ILs in solutions, and K_{HA}^{IL} is the binding constant of the ILs to HA.

Figure S2 shows the variation of the corrected maximum Gibbs energy $\Delta G^{corr}{}_{max}$ for the binding of pyrene to HA with the [C$_8$mim]Br concentrations at pH 7. Similar trends have been observed for other ILs at other pHs. The values of K_{HA}^{IL} could be obtained by using nonlinear least-square regression, and then used to calculate the binding Gibbs energy of the ILs to HA by

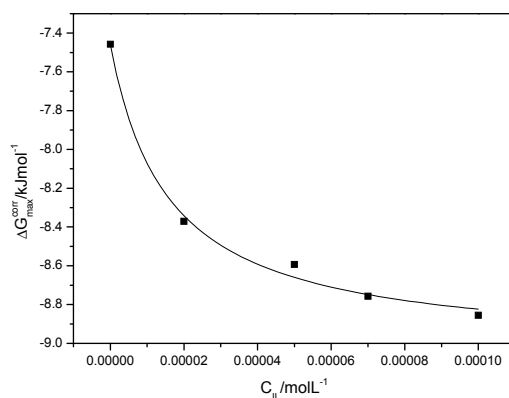$$\Delta G_{HA}^{IL} = -RT \ln K_{HA}^{IL} \quad (11)$$

Fig. S2 Variation of the corrected maximum Gibbs energy $\Delta G^{corr}{}_{max}$ for the binding of pyrene to HA against the [C$_8$mim]Br concentrations at pH 7.
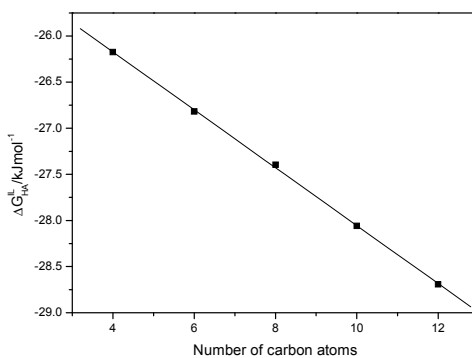
Fig. S3 The binding Gibbs energies of the ILs to HA in aqueous solutions at pH 7 versus carbon atoms number in the alkyl chain of the ILs.

Reference

1 P. D. María, *Angew. Chem. Int. Ed.,* 2008, **47**, 6960.

2 J. Dupont, C. S. Consort, P. A. Z. Suarez, and R. F. Souza, *Org. Synth*., 1999, **79**, 236.

3 J. D. Holbrey, and K. R. Seddon, *J. Chem. Soc. Dalton Trans*., 1999, 2133.

4 J. A. Ortuño, M. Cuartero, M. S. García, and M. I. Albero, *Electrochim. Acta*, 2010, **55**, 5598.

5 E. Grueso, and F. Sanchez, *J. Phys. Chem. B,* 2008, **112**, 698.

6 P. López-Cornejo, P. Pérez, F. García, R. De la Vega, and F. Sánchez, *J. Am. Chem. Soc*., 2002, **124**, 5154.

7 G. G. Hammes, *Thermodynamics and Kinetics for the Biological Sciences*; Wiley-Interscience: New York, 2000; p 124.