Supplementary Information

Systematic comparison on extraction and adsorption of theophylline by new amino acid ester-based ionic liquids

Na Liu[a], Juan Teng[a], Alula Yohannes[b], Hang Song[a],* and Shun Yao[a],*

[a]School of Chemical Engineering, Sichuan University, Chengdu 650061, China

[b]College of Natural Science, Wolkite University, Wolkite, P. O. Box 07, Ethiopia

*Correspondence: pharmposter@163.com (H. Song); cusack@scu.edu.cn (S. Yao);

Fax &Tel.: +86-028-8540-5221

Journal: New Journal of Chemistry

11 pages, 2 Tables, 4 Figures, 2 References

Table of Contents

Preparation of amino acid ester ionic liquids

Four kinds of hydrophobic ionic liquids (see **Table S1**) based on amino acid esters were synthesized on the basis of previous method.[S1] Taking L-phenylalanine ethyl ester bis trifluoromethylsulfonimide ([$PheC_2$][Tf_2N]) for an example: firstly, 0.022 mol L-phenylalanine ethyl ester hydrochloride and 0.020 mol lithium bis trifluoromethyl sulfonimide were respectively dissolved in deionized water. Then the aqueous solution of lithium bis trifluoromethyl sulfonimide was added dropwisely into that of L-phenylalanine ethyl ester hydrochloride, and then the mixture was thoroughly stirred at 25°C for 12 h. After reaction, appropriate volume of ethyl acetate was added to the mixture to extract the lipid-soluble ionic liquid for several times. Then the ethyl acetate phase was washed with water until Cl^- was not detected by $AgNO_3$ aqueous solution. After the solvent removal, the product was further dried at 70°C for 72 h and kept at room temperature for use.

Similarly, L-phenylalanine methyl ester bis trifluoromethyl sulfonimide ([$PheC_1$][Tf_2N]), glycine benzyl ester bis trifluoromethyl sulfonimide ([$LeuC_2$][Tf_2N]), L-leucine ethyl ester bis trifluoromethyl sulfonimide ([GlyOBzl][Tf_2N]) were synthesized according to the above method. All the ILs were checked by Fourier transform infrared spectroscopy (FT-IR), LC/MS and HPLC-ELSD, and their purities were all above 96.3%.

Identification of prepared ionic liquids

Fig. S1 shows the FT-IR and MS spectra of four amino acid ester-based ionic liquids. From the bars at corresponding m/z position, it can be confirmed for the existence of four cations of $[PheC_2]^+$, $[PheC_1]^+$, $[LeuC_2]^+$ and $[GlyOBzl]^+$. **Table S2** summarizes important IR data of IL cations. Moreover, the strong bands below 1400 cm^{-1} are also contributed by the vibrations of the $[Tf_2N]^-$ anion for the four ILs.[S2] Among them, the band at 1060 cm^{-1} is mainly due to the asymmetric S-N-S stretching vibration; the dominating mode around 1210 cm^{-1} corresponds to the asymmetric stretching of $-CF_3$ group, which is strongly coupled to the symmetric SO_2 vibration. The features at 1330 and 1350 cm^{-1} are nearly pure asymmetric SO_2 stretching modes.

Table S1 Structure of four amino acid ester-based ionic liquids

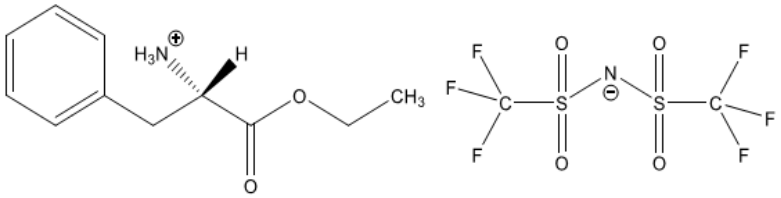
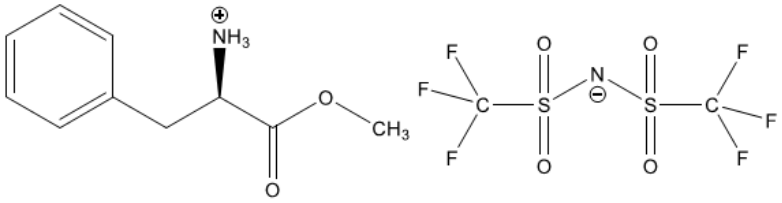
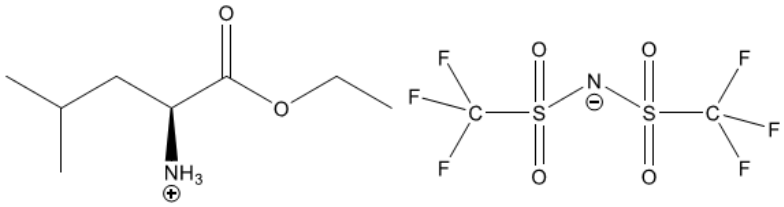
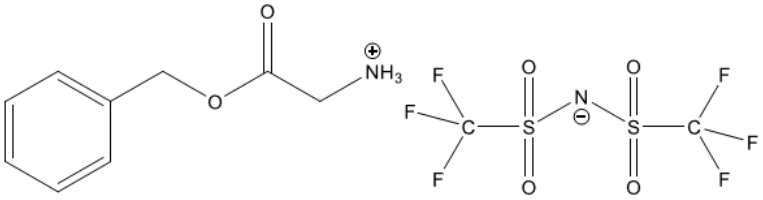
No.	IL name	IL structure
1	[PheC$_2$][Tf$_2$N]	
2	[PheC$_1$][Tf$_2$N]	
3	[LeuC$_2$][Tf$_2$N]	
4	[GlyOBzl][Tf$_2$N]	

Table S2 FI-IR spectra analysis of four amino acid ester-based ionic liquids

IL No.	Group type	Wavenumber (cm^{-1})	Vibration type	Group type	Wavenumber (cm^{-1})	Vibration type
1	-OH	3585	$\nu_{(O-H)}$	$-CH_3$	1472, 1382	$\delta_{as(C-H)}, \delta_{s(C-H)}$
	$-CH_3$	2970	$\nu_{(C-H)}$	C-O	1210, 1080	$\nu_{as,s(C-O)}$
	C=O	1725	$\nu_{(C-O)}$	C-N	1018	$\nu_{(C-N)}$
	C=C	1585, 1495	$\nu_{(C=C)}$	=CH	750, 692	$\delta_{(C-H)}$
2	-OH	3587	$\nu_{(O-H)}$	$-CH_3$	1464, 1385	$\delta_{as(C-H)}, \delta_{s(C-H)}$
	$-CH_3$	2940	$\nu_{(C-H)}$	C-O	1222, 1085	$\nu_{as,s(C-O)}$
	C=O	1715	$\nu_{(C-O)}$	C-N	1020	$\nu_{(C-N)}$
	C=C	1590, 1495	$\nu_{(C=C)}$	=CH	730, 681	$\delta_{(C-H)}$
3	-OH	3490	$\nu_{(O-H)}$	$-CH_3$	1480, 1385	$\delta_{as(C-H)}, \delta_{s(C-H)}$
	$-CH_3$	2980	$\nu_{(C-H)}$	C-O	1210, 1078	$\nu_{as,s(C-O)}$
	C=O	1725	$\nu_{(C=O)}$	C-N	1015	$\nu_{(C-N)}$
4	-OH	3589	$\nu_{(O-H)}$	$-CH_3$	1477, 1389	$\delta_{as(C-H)}, \delta_{s(C-H)}$
	$-CH_3$	2988	$\nu_{(C-H)}$	C-O	1180, 1084	$\nu_{as,s(C-O)}$
	C=O	1734	$\nu_{(C=O)}$	C-N	1014	$\nu_{(C-N)}$
	C=C	1567, 1493	$\nu_{(C=C)}$	=CH	750, 692	$\delta_{(C-H)}$

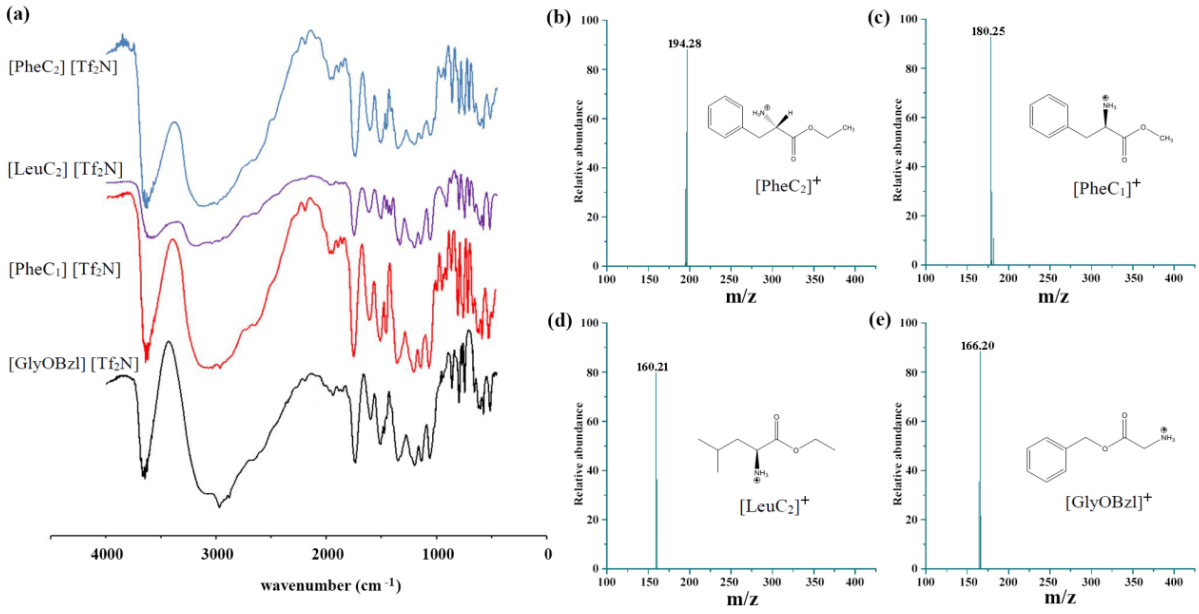


Fig.S1 FT-IR (a) and MS (b) spectra of four amino acid ester-based ILs.

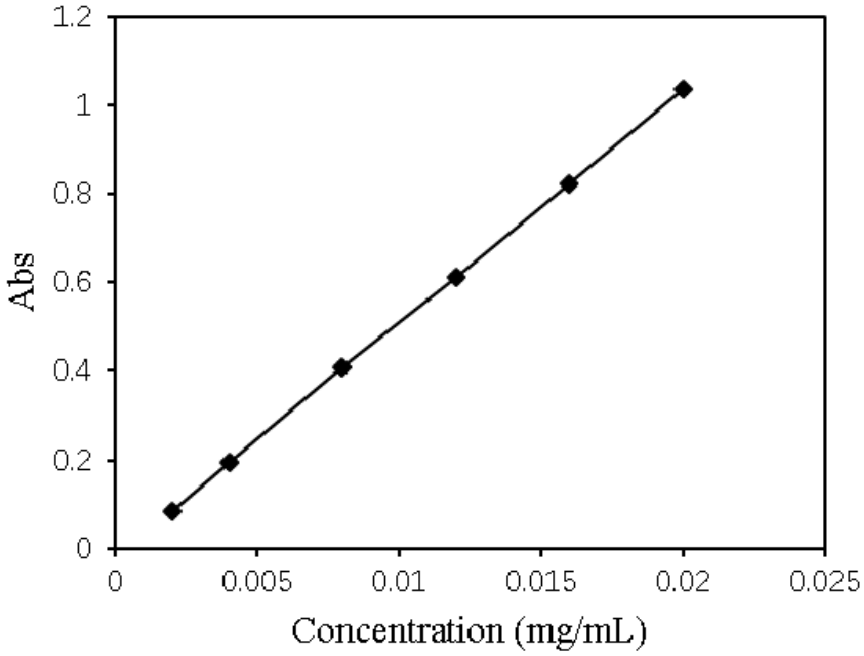


Fig. S2 The standard curve of theophylline for quantitation

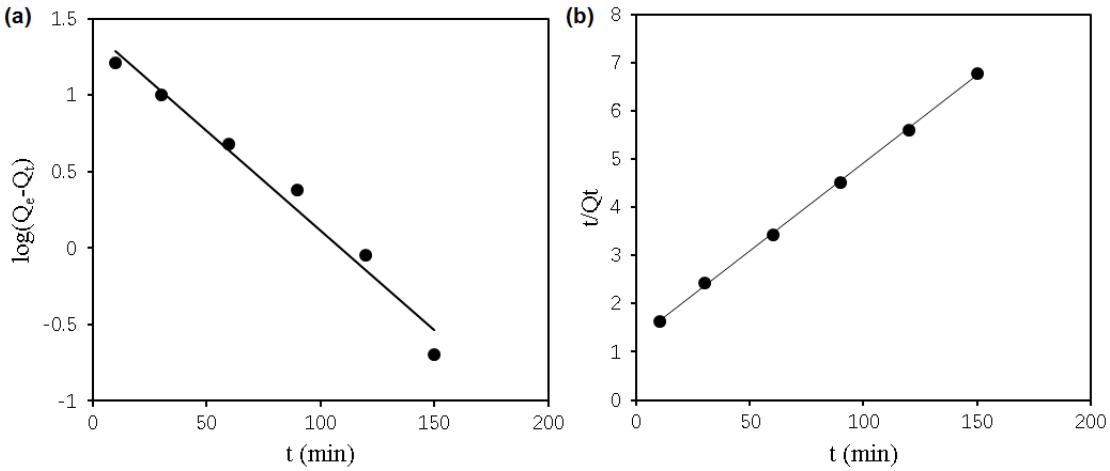


Fig. S3 The fitted plots of the pseudo-second-order (a) and pseudo-second-order (b) kinetic models for adsorption process

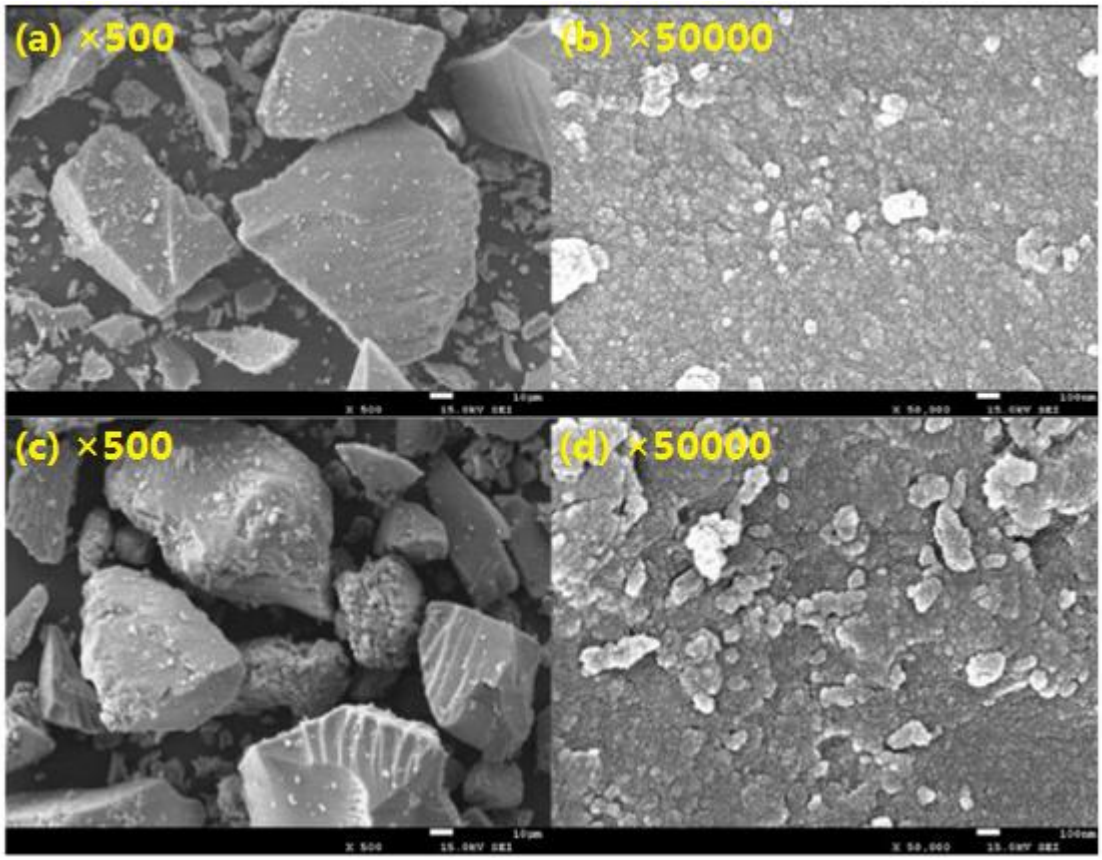


Fig. S4 The SEM photos of immobilized [PheC_2][Tf_2N] after adsorption (a, b) and desorption (c, d) of theophylline

Notes and references

S1. D. K. Bwambok, H. M Marwani, V. E. Fernand, S. O. Fakayode, M, Lowry, I. Negulescu, R. M. Strongin and I. M. Warner, *Chirality*, 2008, **20**, 151–158.

S2. M. Sobota, M. Schmid, M. Happel, M. Amende, F. Maier, H. P. Steinrück, Hans-Peter, N. Paape, P. Wasserscheid, M. Laurin, J. M. Gottfried and J. Libudaet, *Phys. Chem. Chem. Phys.,* 2010, **12**, 10610–10621.