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Deep eutectic solvents as novel extraction media for phenolic compounds from model oil

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Chemicals and Reagents

Choline chloride (99%) and *α*-naphthaleneacetic acid (99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Methyltriphenylphosphonium bromide (99%) and *p*-hydroxy benzoic acid (99%) were obtained from energy chemical (Shanghai, China). Phenol (99%)、*β*-naphthol (99%)、aniline (99%)、*p*-toluidine (99%) and *α*-naphthylamine (99%) were bought from Xilong Chemical (Guangdong, China). Urea (99%) and *p*-cresol (99%) were obtained from Shanghai Hushi Chemical (Shanghai, China). Ethylene glycol (99%)、glycerol (99%)、benzoic acid (99%) and toluene (99%) were purchased from Rionlon (Tianjin, China). Biphenyl (99%) was obtained from Alfa Aesar (Lancaster, UK). Safflower oil was bought from Tianshanhua (Xinjiang, China).

Instrument

The HPLC equipment used was a Shimadzu-GL LC-15C system including two high-pressure pumps, a SPD-15C UV/vis detector and a CTO-15C column oven. For all compounds of interest, the UV/vis detector was set at 254-nm wavelength. A Shimadzu-GL WondaSil C18-WR column (4.6×150 mm, particle size 5 μm) was used as the analytical column.

Synthesis

Preparation of DESs. The syntheses of DESs were conducted as described elsewhere.[1-3] Briefly, DESs were obtained by simply mixing the halide salts together (HS) and hydrogen bond donors (HBD) at a proper molar ratio with magnetic agitation at 80~100 °C until clear and colorless liquid formed. Table S1 lists the freezing points and the viscosities (25 °C) of studied DESs.

Table S1 DESs used in this work and their physical chemical data.*

Abbreviations	HS	HBD	HS/HBD Ratio	Tf/℃	Viscosities/cP
DES-1	ChCl	Ethylene glycol	1:3	-66	19
DES-2	ChCl	Glycerol	1:3	-40	330
DES-3	ChCl	Urea	1:2	12	750
DES-4	MTPPhBr	Ethylene glycol	1:3	-46	128

*The freezing points and viscosities (25 °C) were obtained from the reference.[4,5]

Preparation of IL. [BMIm]Cl was prepared as following: equimolar (0.2 mmol) 1-methylimidazole and 1-chlorobutane was mixed in a flask fitted and heated at 70 °C for 48 h. The desired product was washed with diethyl ether, and then dried under vacuum. [BMIm]BF_4 was prepared by metathesis with sodium tetrafluoroborate in acetone. The precipitates were filtered, the filtrate was concentrated on a rotary evaporator, and the resulting residue was dried under vacuum.

Chromatographic conditions

The HPLC-grade methanol and Millipore water were used as components of the mobile phase. All samples were directly dissolved in hexane as the sample solvent (10 μg/L). In this work, toluene and chloroform were also used as the sample solvents. The mobile phase was a mixture of methanol and water (65/35, v/v) and the flow-rate was 1.0 mL/min. Column temperature was fixed at 30 °C and the injection volume was 10 μL except for the program on effect of DES's volume. The retention time of the mixture of three phenols (phenol, *p*-cresol, *β*-naphthol) was in the range of 2.5~5 min. The retention time of the mixture of three anilines (aniline, *p*-toluidine, *α*-naphthylamine) was in the range of 2~4.5 min. The retention time of toluene was 12.9 min and biphenyl's was 33.5 min. The response of DESs ranged between 1.4 min and 2.2 min. The retention time of the mixture of three benzoic acids (benzoic acid, *p*-hydroxy benzoic acid, *α*-naphthaleneacetic acid) was in the range of 2.8~41.6 min with the mobile phase of 20 mmol/L NH$_4$Ac (pH 4.0) and methanol (60/40, v/v).

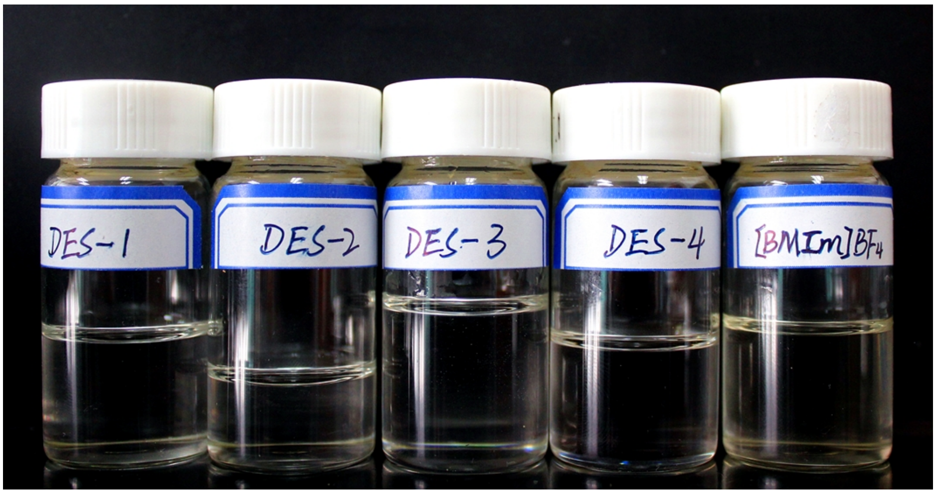


Fig. S1. The pictures of four DESs and [BMIm]BF$_4$ used in this work.

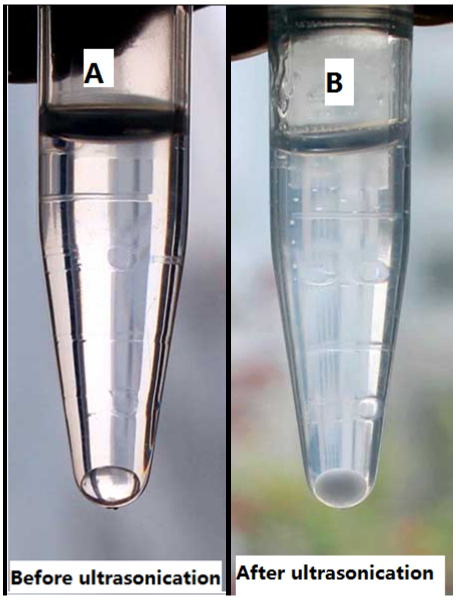


Fig. S2. The picture of the state of DES droplet (10 μL) in the sample solvent (10 μg/L phenolic compounds dissolved in hexane) before ultrasonication (A) and after ultrasonication (B).

Results

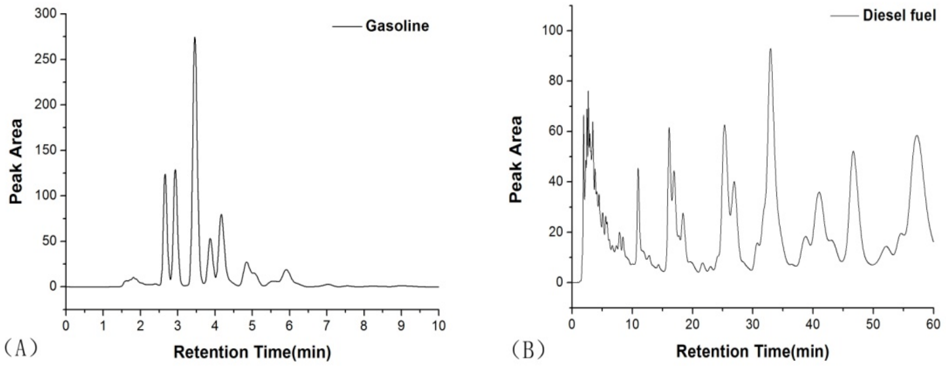
Table S2. Enrichment factor, linearity, and reproducibility for extraction of the selected phenols by the proposed direct-immersion LPME method [a]

Analyte	**EF**	**R^2**	**RSD** (%,n=5)	**LOD** (μg/L)
Phenol	137	0.9373	10.6	0.025
p-Cresol	92	0.9899	6.7	0.05
β-Naphthol	98	0.9798	8.3	0.05

[a] Condition: extractant: 10 μL of DES-1; sample solution volume: 1 mL; concentration of analytes: 10 μg/L; extraction time: 3 min.

The extraction effect of DES for real oils

Three real oils including gasoline, diesel fuel, and kerosene were selected as real sample solvents.



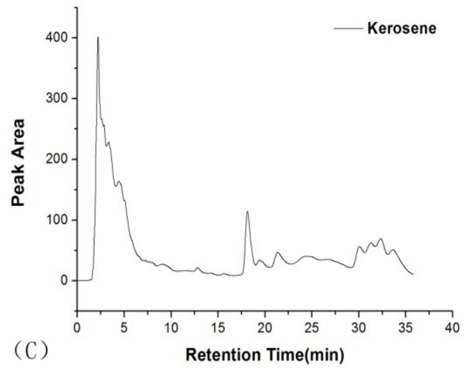


Fig. S3. The extraction chromatogram (HPLC) of DES for gasoline (A), diesel fuel (B) and kerosene, sample concentration: 10 μg/L, extraction time: 3 min, DES volume: 10 μL for DES-1, in ultrasonic wave-assisted condition.

Regeneration of DES

In order to regenerate the DES, we added some experiments. 1 mL DES-1 was added to the sample solution (100 mL) for the extraction of three phenols (10 μg/L) in the optimized conditions, and then DES-1 was separated and evaporated using the Rotary evaporator at 36 °C for 30 min to remove the volatile compounds and solvents. The regenerated DES-1 looks like brand new DES-1 (clear and colorless liquid). As the following Fig. A shown, the regenerated DES-1 was successfully obtained as checked by HPLC. From the Fig. B, the regenerated DES-1 has the same activity as the brand new DES-1 for the extraction of three phenols.

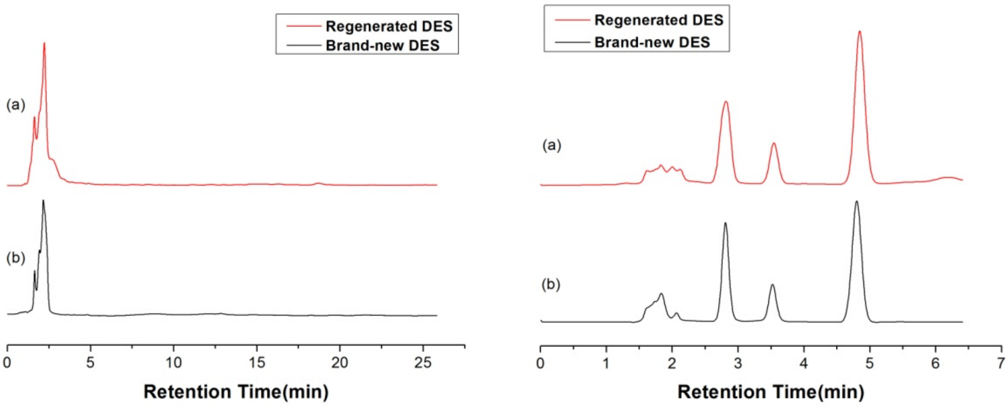


Fig. S4. Left figure: Chromatogram of regenerated DES-1 (a) and brand new DES-1

(b) injected directly to HPLC; Right figure: Chromatogram of phenolic compounds after extracted by regenerated DES-1 (a) and brand new DES-1 (b).

References

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