

## Supplementary Material

### Novel tributyl phosphate-based hydrophobic deep eutectic solvent: Application in simultaneous liquid-liquid microextraction of parabens and their metabolite in surface water samples

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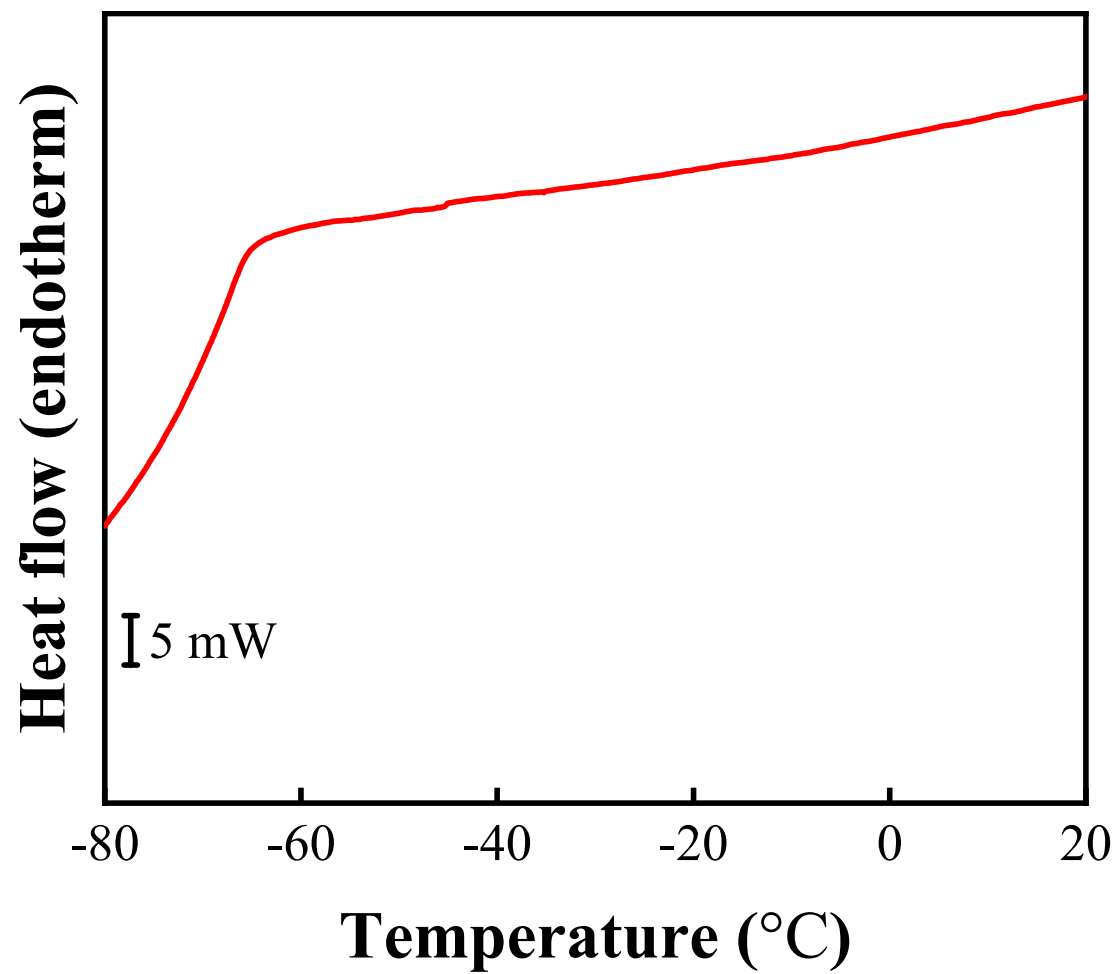
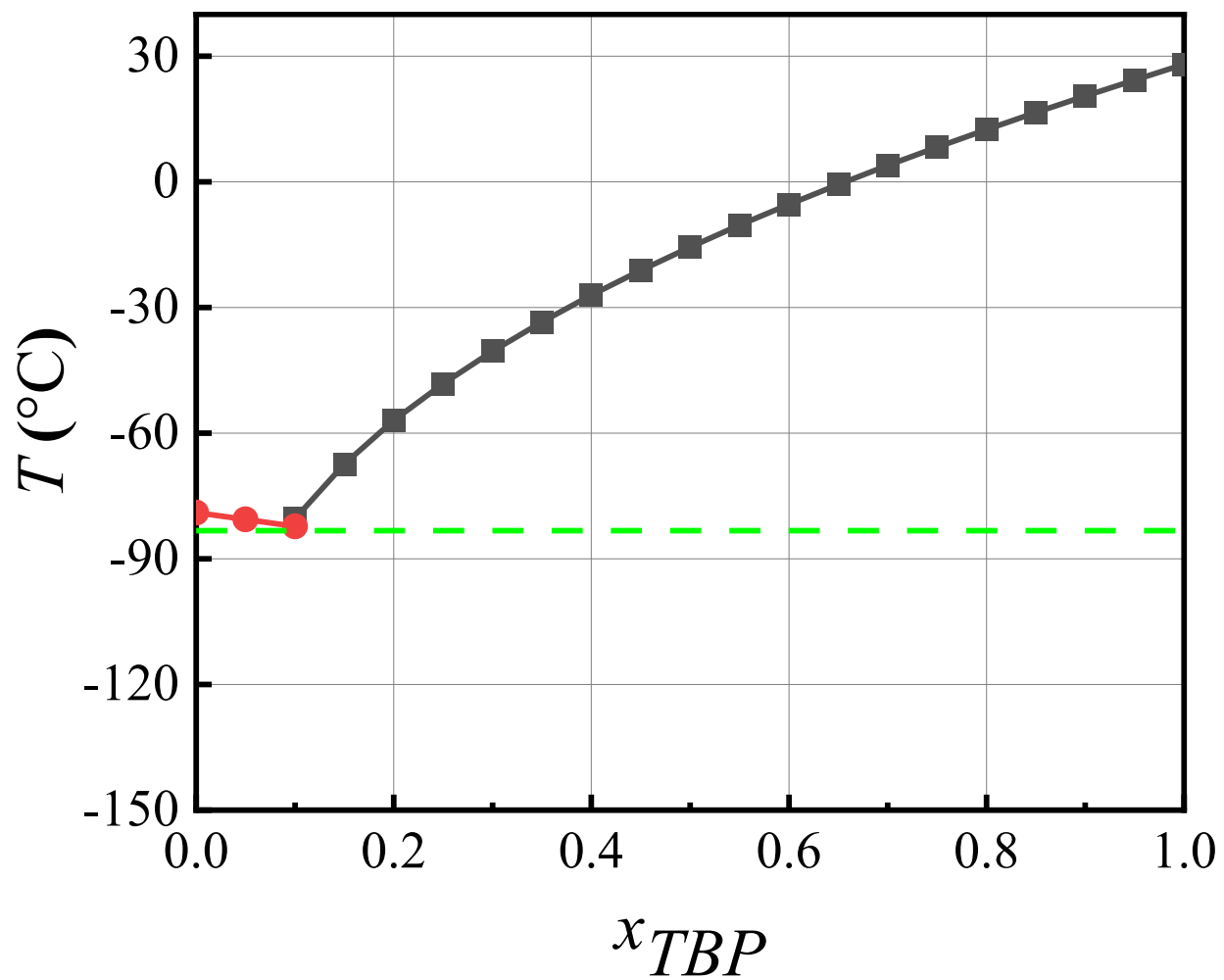
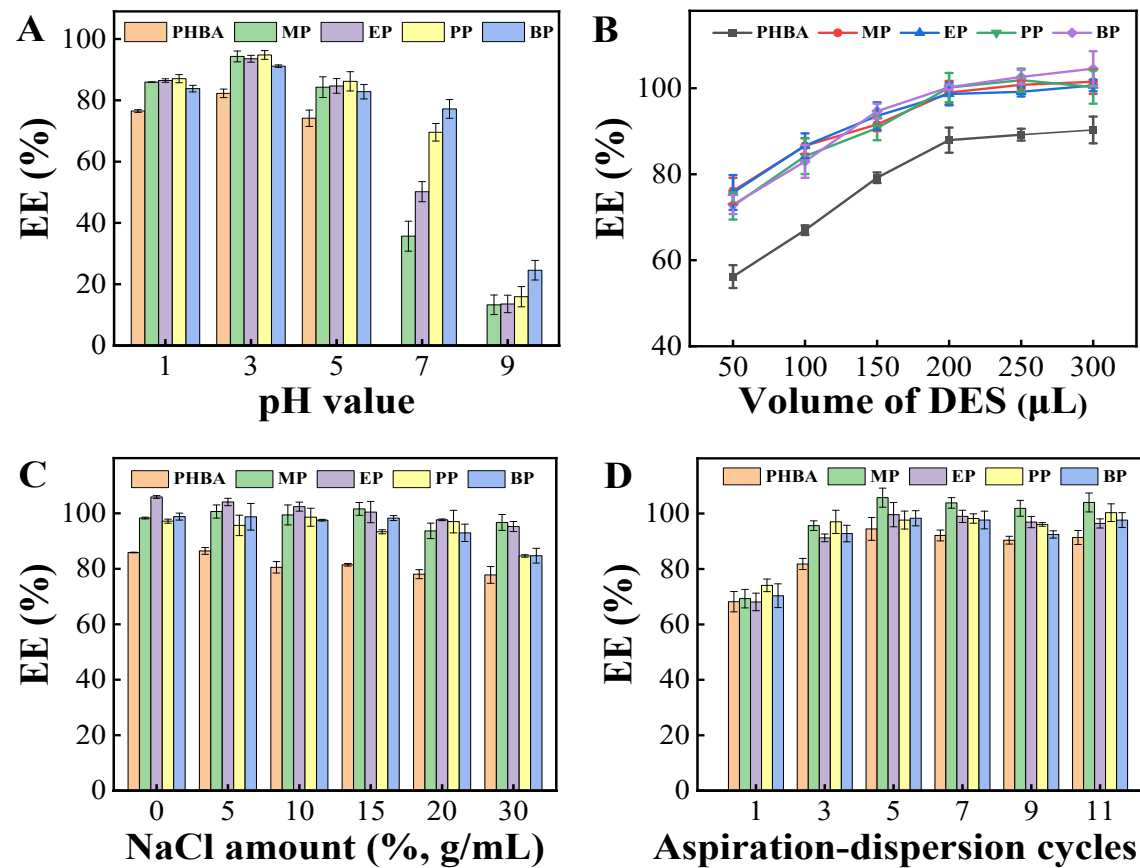


Fig. S1 DSC profiles of TBP-M DES with the molar ratio of 1: 2 (heating rate: 10 °C/min; atmosphere: N<sub>2</sub>).



**Fig. S2** The ideal solid-liquid phase diagram of TBP-M DES; the red line, the liquidus line of TBP; the black line, the liquidus line of M.



**Fig. S3** Effect of solution pH (A), DES volume (B), ionic strength (C) and aspiration-dispersion cycles (D) on the extraction efficiency of PBs and PHBA (n=3). Conditions: Sample, 5 mL of spiked water working solution (100  $\mu\text{g/L}$ ); extraction temperature, room temperature; centrifugation, 1 min at 5000 rpm, other varying extraction conditions were illustrated in the figures.

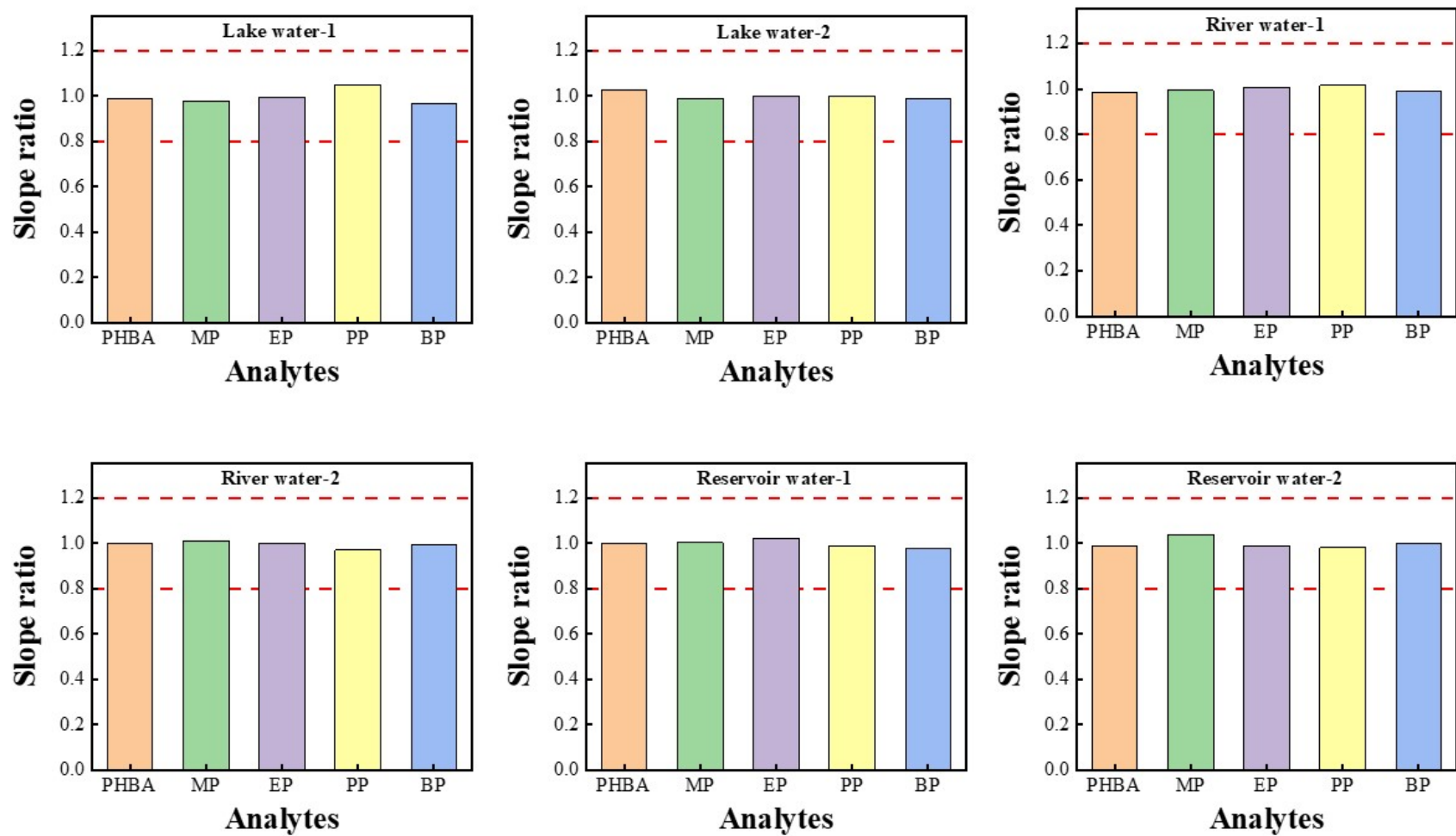
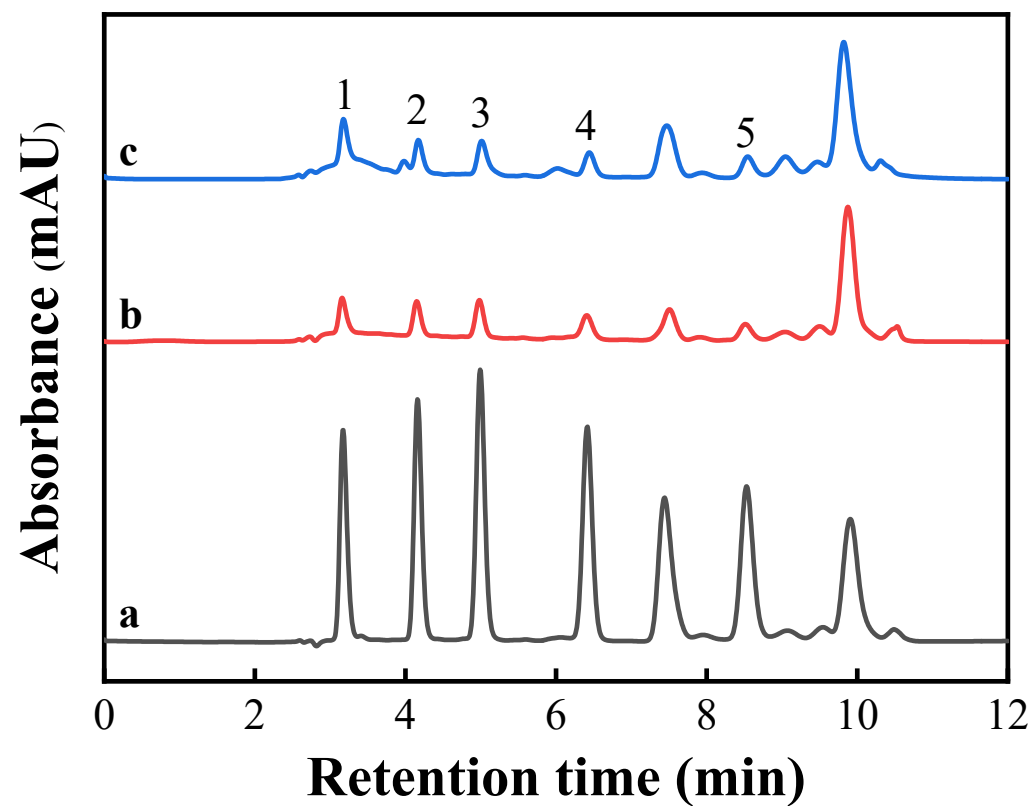
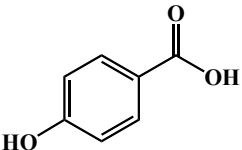
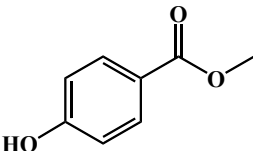
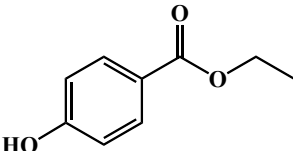
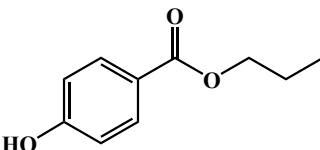
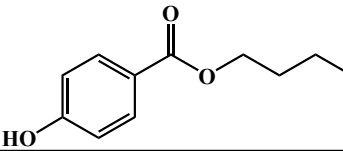


Fig. S4 Matrix effects of target PBs and PHBA in six different surface water samples.



**Fig. S5** Chromatograms of partial hydrolysate from the mixture of four PBs (initial concentration for each PB: 500  $\mu\text{g/L}$ ) (a), spiked blank lake water (spiked level: 20  $\mu\text{g/L}$ ) (b), b + 200  $\mu\text{g/L}$  phenol, bisphenol A and naphthalene as model coexistences (c) after AALLME. Peak identification: 1, PHBA; 2, MP; 3, EP; 4, PP; 5, BP.

**Table S1** Physiochemical properties of target PBs and PHBA in the present study.

Analyte	Abbreviation	Chemical formula	Structure	CAS number	Molecular weight	$pK_a^*$	$\log P^{**}$
p-Hydroxybenzoic acid	PHBA	$C_7H_6O_3$		99-96-7	138.12	$4.57 \pm 0.10$	$1.401 \pm 0.221$
Methylparaben	MP	$C_8H_8O_3$		99-76-3	152.15	$8.31 \pm 0.13$	$1.882 \pm 0.224$
Ethylparaben	EP	$C_9H_{10}O_3$		120-47-8	166.17	$8.31 \pm 0.13$	$2.391 \pm 0.224$
Propylparaben	PP	$C_{10}H_{12}O_3$		94-13-3	180.20	$8.23 \pm 0.15$	$2.901 \pm 0.224$
Buthylparaben	BP	$C_{11}H_{14}O_3$		94-26-8	194.23	$8.22 \pm 0.15$	$3.410 \pm 0.224$

\*  $K_a$ : acid dissociation constant, \*\* P: octanol-water partitioning coefficient. The data were obtained from SciFinder scholar database (25 °C).

**Table S2** Microbial toxicity of DES-4 by the 2-fold dilution method.

Compd	G+ bacteria	G- bacteria
	<i>S.a</i> <sup>a</sup>	<i>E.c</i> <sup>b</sup>
TBP	>128	>128
M	>128	>128
DES-4	>128	>128
VAN <sup>c</sup>	1	--- <sup>d</sup>
MEM <sup>e</sup>	---	0.0625

<sup>a</sup>S.a: *Staphylococcus aureus*, <sup>b</sup>E.c: *Escherichia coli*, <sup>c</sup>VAN: *Vancomycin*, <sup>d</sup>---: no microbial toxicity, <sup>e</sup>MEM: *Meropenem*.



**Table S3** Analytical parameters of the proposed method for the determination of PBs and PHBA.

Analyte	Linear range ( $\mu\text{g/L}$ )	$R^2$	LOD ( $\mu\text{g/L}$ )	LOQ ( $\mu\text{g/L}$ )	RSD (% , n=3)		Enrichment factor
					Intra-day	Inter-day	
PHBA	3-500	0.9983	0.8	2.4	3.3	7.6	22.6
MP	3-500	0.9995	0.6	2.1	1.9	4.8	23.0
EP	3-500	0.9990	0.7	2.2	4.0	5.1	24.5
PP	3-500	0.9993	0.5	1.8	2.6	6.3	24.1
BP	3-500	0.9989	0.9	2.9	3.0	5.5	23.9

**Table S4** Recoveries of spiked blank water sample and the spiked sample with coexistences.

Analyte	without coexistences		with coexistences	
	Recoveries (%)	RSD (%)	Recoveries (%)	RSD (%)
PHBA	94.0	2.8	93.3	0.7
MP	97.4	1.0	87.3	3.8
EP	95.7	3.2	96.5	1.6
PP	102	2.6	97.1	2.4
BP	97.0	4.5	93.9	3.0