

Electronic supplementary information

Using dialkyl amide via forming hydrophobic deep eutectic solvents to separate citric acid from fermentation broth

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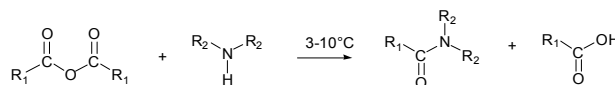


Fig. S1 The synthesis route of alkylamide as HBA

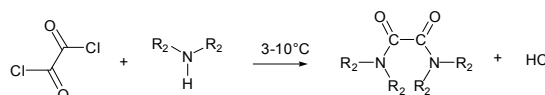


Fig. S2 The synthesis route of n-C₁₈H₃₆N₂O₂

Table S1 Chemical structures of the BHBA studied in this work as well as the abbreviation and respective molar mass, M (g·mol⁻¹)

Entry	Molecular formula	M	R ₁	R ₂
1	i-C ₁₈ H ₃₇ NO	283	methyl	Isooctyl
2	n-C ₁₈ H ₃₇ NO	283	methyl	1-octyl
3	n-C ₁₄ H ₂₉ NO	227	methyl	1-hexyl
4	n-C ₁₀ H ₂₁ NO	171	methyl	1-butyl
5	n-C ₁₅ H ₃₁ NO	241	ethyl	1-butyl
6	i-C ₁₂ H ₂₅ NO	199	1-propyl	Isobutyl
7	n-C ₁₂ H ₂₅ NO	199	1-propyl	1-butyl
8	i-C ₁₆ H ₃₃ NO	255	1-propyl	Isohexyl
9	n-C ₁₆ H ₃₃ NO	255	1-propyl	1-hexyl
10	n-C ₁₈ H ₃₆ N ₂ O ₂	312		1-butyl

Entry 1-9 are synthesized according to Fig. S1, and the route of n-C₁₈H₃₆N₂O₂ is shown in Fig. S2.

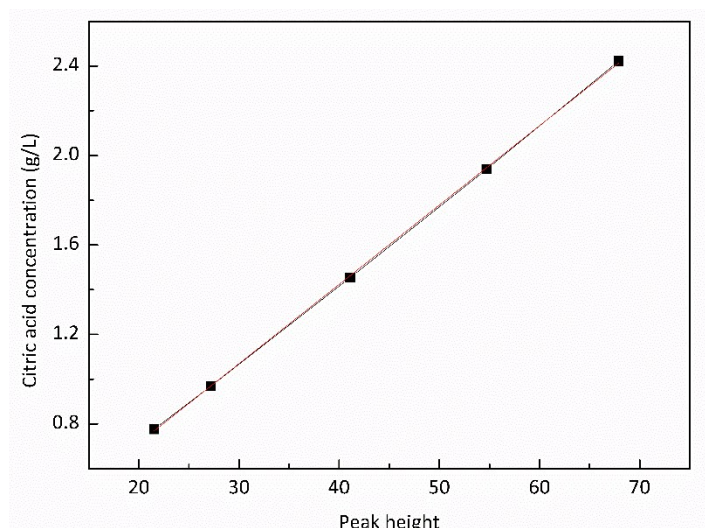


Fig. S3 Determination of citric acid standard curve by HPLC

The BHBA was mixed with water in a mass ratio of about 1: 1 (1 gram BHBA with 1 gram water), respectively. The BHBA contents leaching to the water were measured by GC-MS after mixing with water. As is shown in table S2, the peak height h_0 of the known concentration of BHBA was determined by GC-MS, W_1 and h_1 represented the concentration and the peak height of BHBA in the water-rich phase after mixing the BHBA with water.

Table S2 The solubility of BHBA in Water

Entry	HBAs	h_0	W_0 mg/g	h_1	W_1 mg/g
1	n-C ₁₀ H ₂₁ NO	27247360	3.625	1976843	0.263
2	n-C ₁₄ H ₂₉ NO	31534526	3.513	2315943	0.258
3	n-C ₁₈ H ₃₇ NO	48782312	3.423	3463073	0.243
4	i-C ₁₈ H ₃₇ NO	46389563	3.265	3310495	0.233
5	n-C ₁₂ H ₂₅ NO	30537554	3.831	1634162	0.204
6	i-C ₁₂ H ₂₅ NO	30678368	3.683	1674274	0.201
7	n-C ₁₅ H ₃₁ NO	32462674	3.452	1720935	0.183
8	n-C ₁₆ H ₃₃ NO	41563946	3.272	2146793	0.169
9	i-C ₁₆ H ₃₃ NO	43689457	3.531	1831220	0.148
10	C ₁₈ H ₃₆ N ₂ O ₂	39562485	3.296	996264	0.083

Table S3 Hydrophobic DES Based on Alkylamide as a BHBA with Citric Acid as a HBD as well as the respective molar ratio [n: n], the equilibrium constant and van der Waals volume of HBAs at room temperature

Entry	BHBA	HBD	n	K_{ex}	V^a	V_x^b
1	i-C ₁₈ H ₃₇ NO	Citric acid	1.2	0.2996	434.92	276.03
2	n-C ₁₈ H ₃₇ NO	Citric acid	1.2	0.4123	437.09	276.03
3	n-C ₁₄ H ₂₉ NO	Citric acid	2.4	1.5553	346.87	219.67
4	n-C ₁₀ H ₂₁ NO	Citric acid	2.8	3.1424	243.63	163.31
5	n-C ₁₅ H ₃₁ NO	Citric acid	1.1	0.1849	368.90	233.76
6	i-C ₁₆ H ₃₃ NO	Citric acid	1.1	0.0969	388.97	247.85
7	n-C ₁₆ H ₃₃ NO	Citric acid	1.1	0.1380	390.91	247.85
8	i-C ₁₂ H ₂₅ NO	Citric acid	1.1	0.2599	299.87	191.49
9	n-C ₁₂ H ₂₅ NO	Citric acid	1.2	0.3592	300.75	191.49
10	n-C ₁₈ H ₃₆ N ₂ O ₂	Citric acid	1.0	0.0386	448.85	287.58

^a V is the van der Waals volume of HBAs at room temperature, ^b V_x is McGowan volume of HBAs, the unit is $\text{cm}^3\text{mol}^{-1}$.

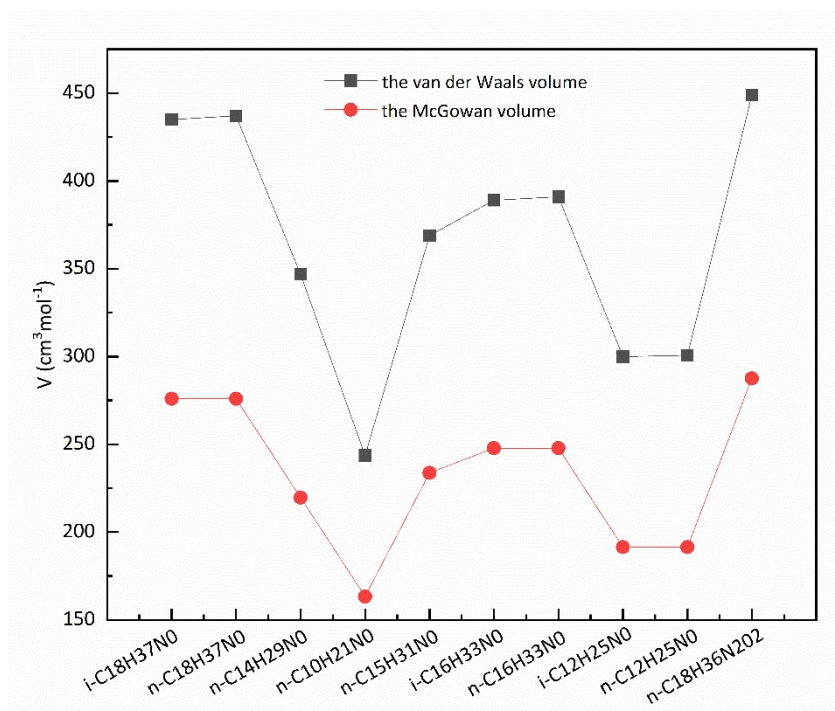
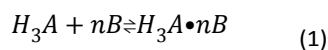


Fig. S4 The van der Waals volume and McGowan volume of HBAs

The slope method is used to derive the reaction coefficient and equilibrium constant of the process. H_3A stands for citric acid and B stands for HBAs using isostearyl alcohol as a diluent. It is assumed that the diluent has no interaction with the HBD and the BHBA. The process of forming hydrophobic deep eutectic solvents is as follows:



When the process reaches equilibrium, the equilibrium constant is

$$K_{ex} = \frac{[H_3A \cdot nB]}{[H_3A][B]^n} \quad (2)$$

The distribution ratio during the HDESs formation process is described by

$$D = \frac{[H_3A \cdot nB]}{[H_3A]} \quad (3)$$

From (2) and (3), Eq. (4) was arrived:

$$D = K_{ex}[B]^n \quad (4)$$

logarithm on both sides of the equation the following equation was derived:

$$\ln D = \ln K_{ex} + n \ln [B] \quad (5)$$

The equilibrium constant that forms the DESs can be calculated from Fig. S4

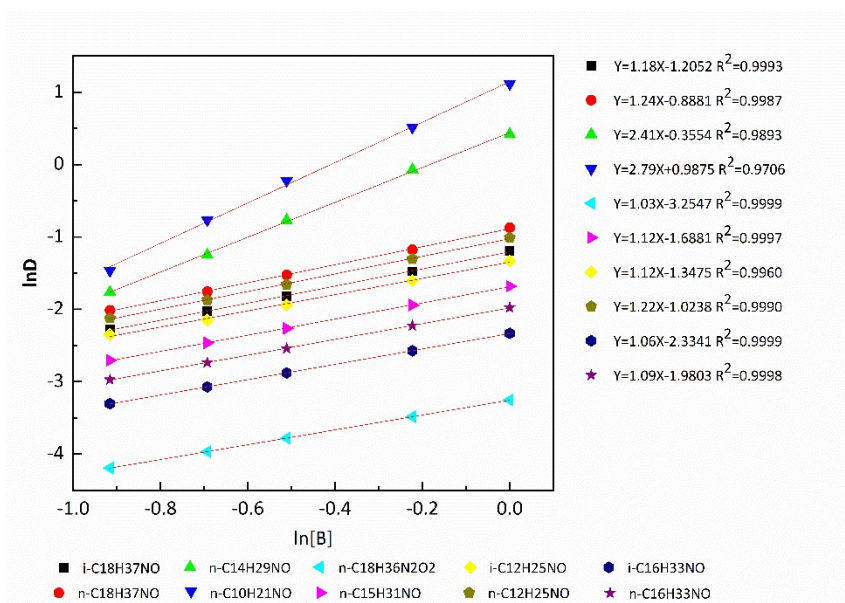


Fig. S5 The relationship between lnB and lnD

Table S4 The distribution ratio of citric acid in hydrophobic DESs and fermentation broth at different temperatures

T	iC ₁₈ H ₃₇ NO	nC ₁₈ H ₃₇ NO	nC ₁₄ H ₂₉ NO	nC ₁₀ H ₂₁ NO	nC ₁₈ H ₃₆ N ₂ O ₂	nC ₁₅ H ₃₁ NO	iC ₁₂ H ₂₅ NO	nC ₁₂ H ₂₅ NO	iC ₁₆ H ₃₃ NO	nC ₁₆ H ₃₃ NO
25	0.3591	0.5179	1.9797	3.5579	0.0884	0.2557	0.3344	0.4449	0.1502	0.2262
30	0.3029	0.4178	1.5202	3.0552	0.0386	0.1861	0.2647	0.3641	0.0972	0.1387
35	0.2346	0.3410	1.2789	2.4746	0.0263	0.1302	0.2026	0.2953	0.0523	0.0884
40	0.1792	0.2710	1.0816	2.0358	0.0145	0.0906	0.1489	0.2262	0.0296	0.0487
45	0.1448	0.2070	0.8779	1.7670	0.0077	0.0533	0.0981	0.1712	0.0158	0.0322

Conditions: mass ratio of BHBA to feed is 1:1, and the contact time is 20 min, the concentration of citric acid feed is 12 wt%.

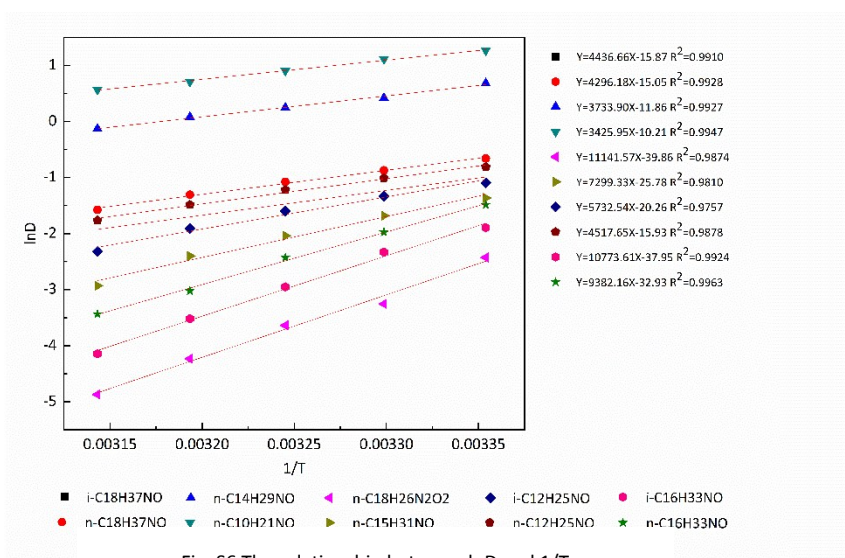


Fig. S6 The relationship between lnD and 1/T

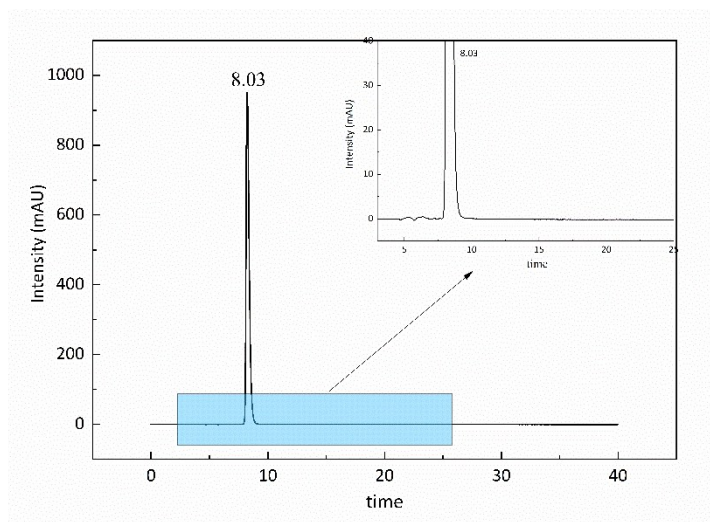


Fig. S7 The high-performance liquid chromatogram (HPLC) of the separated citric acid via forming hydrophobic DESs.

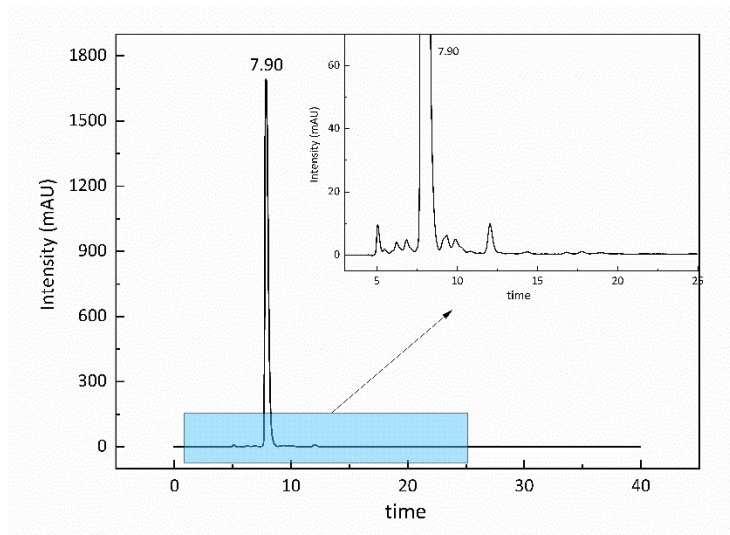


Fig. S7 The high-performance liquid chromatogram (HPLC) of the separated citric acid using TOA

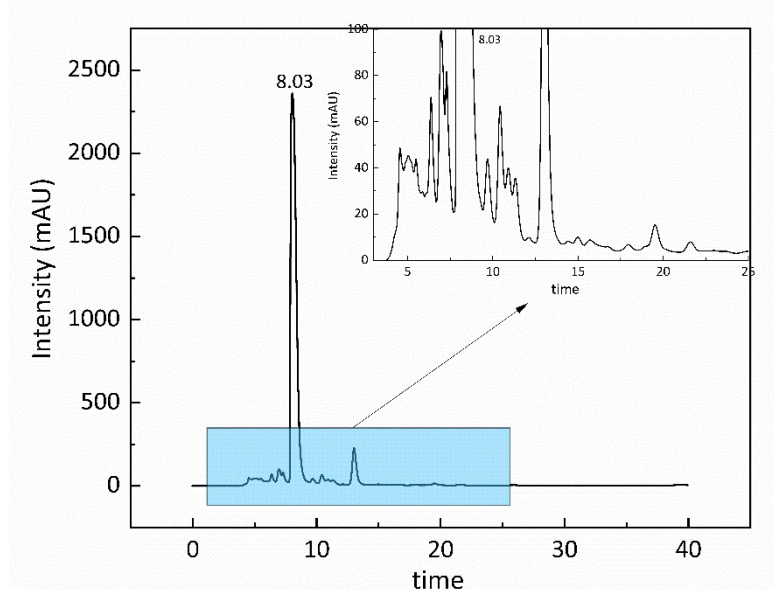


Fig. S8 The high-performance liquid chromatogram (HPLC) of the citric acid fermentation broth

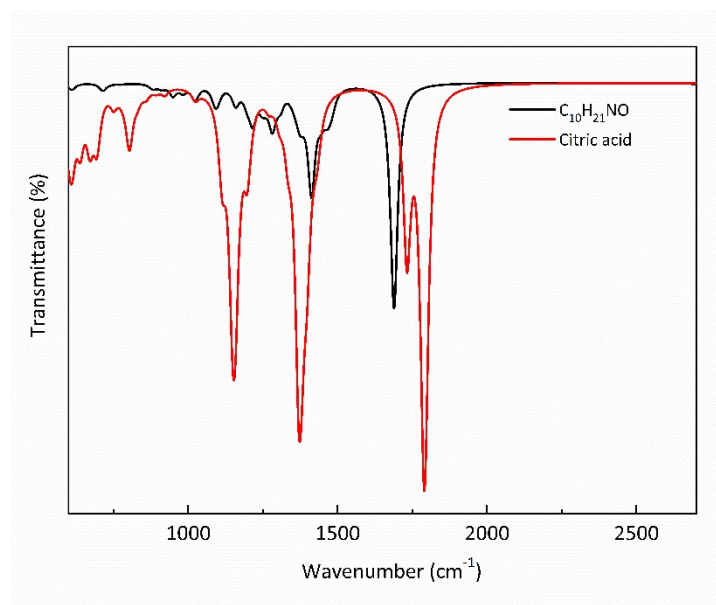


Fig. S9 The theoretical infrared spectra of $C_{10}H_{21}NO$ and citric acid

