Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Ionicity of deep eutectic solvents by Walden plot and pulsed field gradient nuclear magnetic resonance (PFG-NMR)

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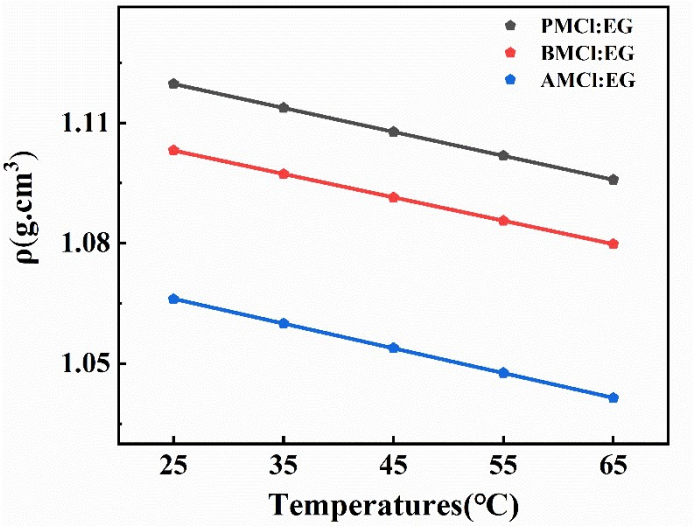


Figure S1. Density of the investigated DESs with different functional groups depending on temperature

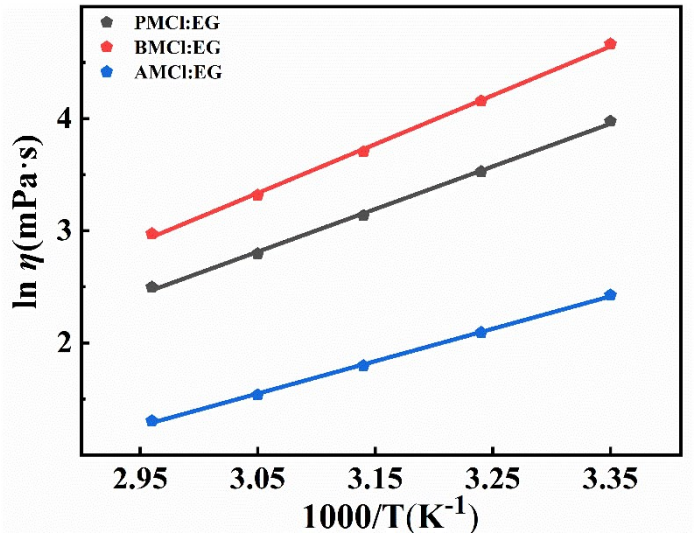


Figure S2. Viscosity of the investigated DESs with different functional groups depending on temperature

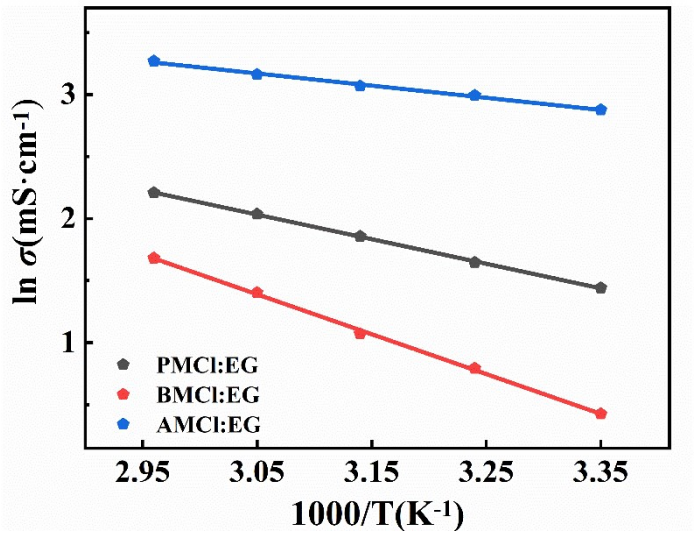
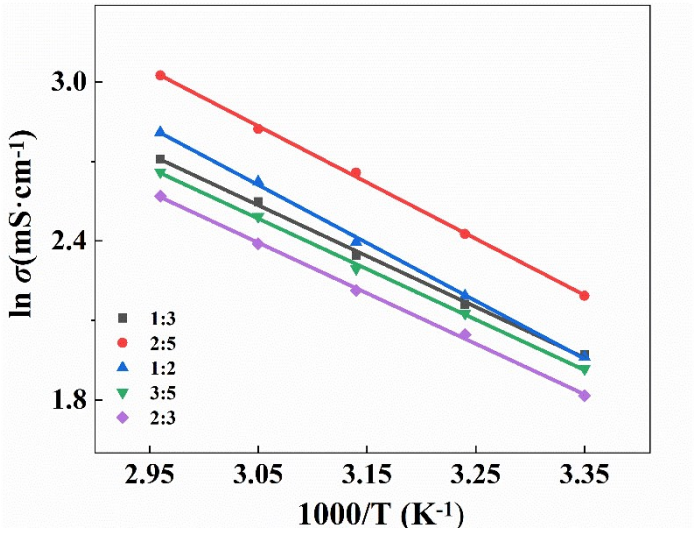


Figure S3. Conductivity of the investigated DESs with different functional groups depending on temperature



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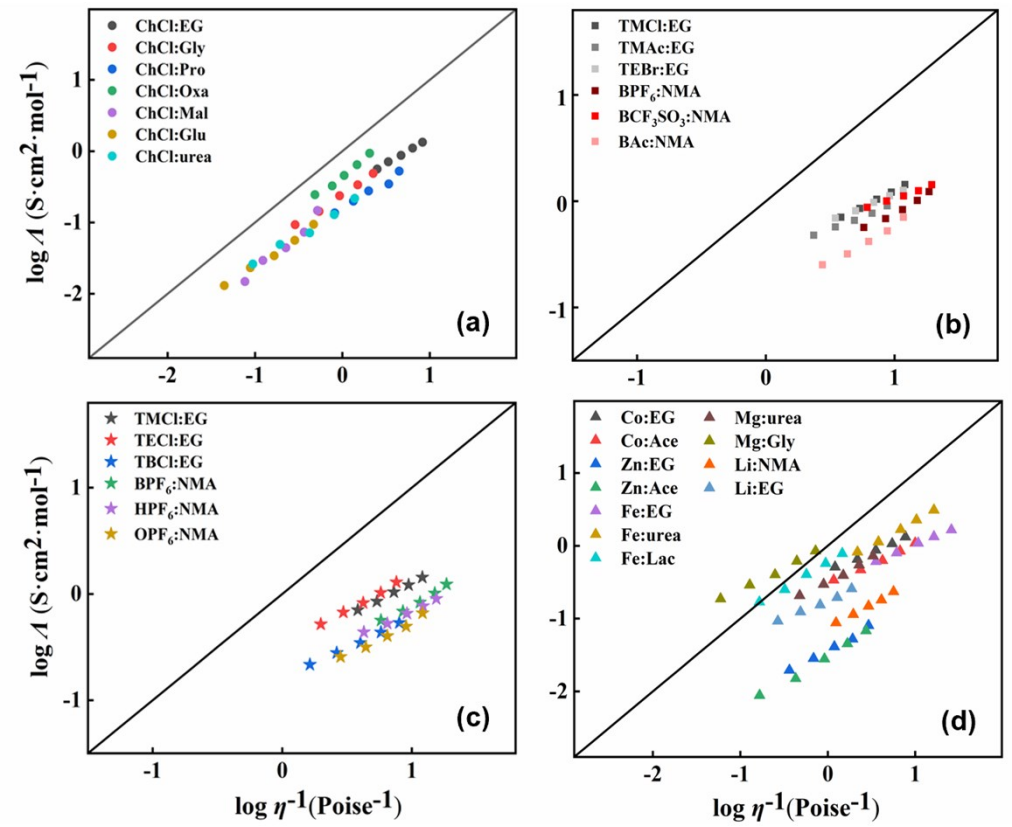

Figure S5. Ionicity of the investigated DESs depending on temperature (a) ChCl-based (b) with different alkyl chain lengths and (c) different anions (d) metal-based.

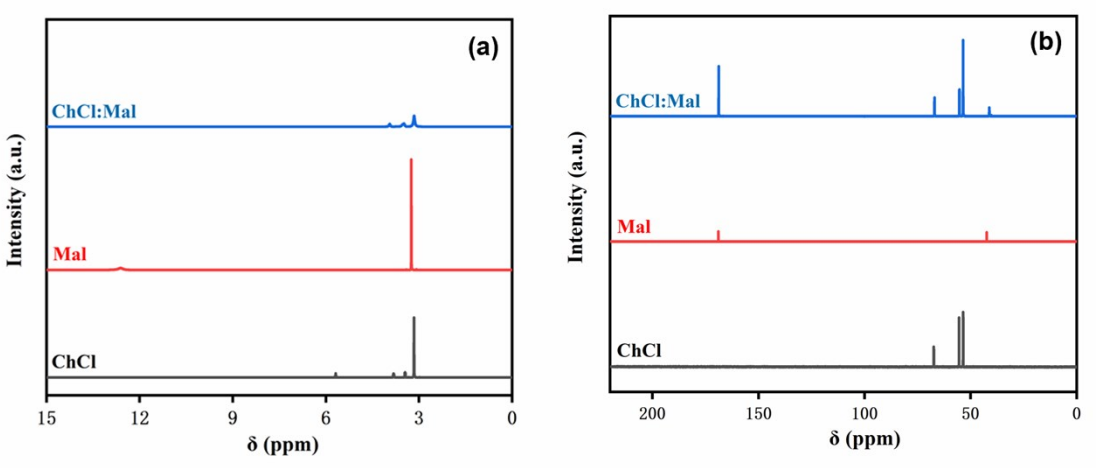

Figure S6. ^{1}H NMR and ^{13}C NMR spectra of pure ChCl, malonic acid and corresponding DES.

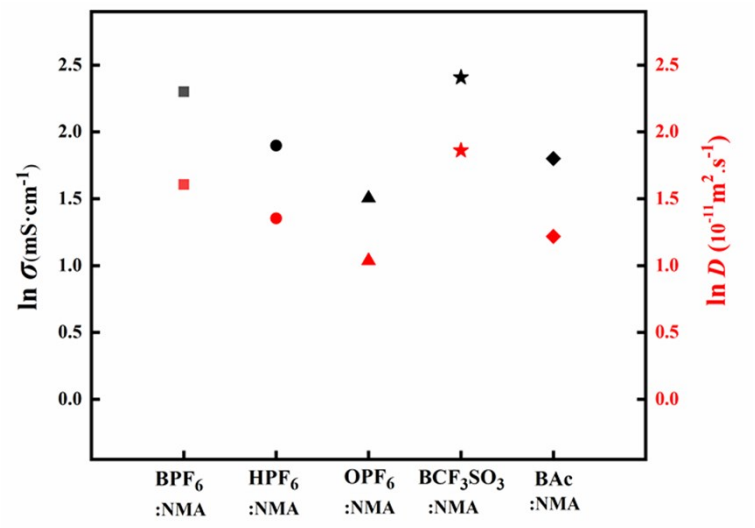

Figure S7. Relationship between diffusion coefficient and conductivity at room temperature.

2. Supplementary Tables

Table S1. General formula for the classification of DESs.

type	general formula	terms
Ⅰ	Cat^+X^- $zMCl_x$	M= Zn, Sn, Fe, Al
Ⅱ	Cat^+X^- $zMCl_x{\cdot}yH_2O$	M= Cr, Co, Cu, Fe, Mg
Ⅲ	Cat^+X^- zRZ	Z= $CONH_2$, COOH, OH
Ⅳ	$MCl_x + RZ = MCl_{x-1}^+{\cdot}RZ + MCl_{x+1}^-$	M= Al, Zn, Fe

Table S2. Melting points of pure components and corresponding DESs

DES	melting point (°C)		
	HBA	HBD	DES
BPF_6:NMA	7	28	-11
HPF_6:NMA	-74	28	-86
OPF_6:NMA	-70	28	-88
BCF_3SO_3:NMA	16	28	-11
BAc:NMA	-20	28	-83
LiTFSI:NMA	234	28	-72

Table S3. Ionicity of each investigated DES depending on temperature.

DES	% Ionicity				
	25 °C	35 °C	45 °C	55 °C	65 °C
ChCl:EG	22.4	21.2	18.6	17.3	16.1
ChCl:Gly	32.2	26.4	25.3	22.5	21.6
ChCl:Pro	16.6	14.9	13.8	10.2	11.7
ChCl:Oxa	50.3	42.6	43.4	43.7	45.3
ChCl:Mal	19.3	23.9	19.5	20.0	28.4
ChCl:Glu	29.2	26.3	20.6	19.6	20.0
ChCl:urea	27.5	25.5	16.9	16.0	15.7
PMCl:EG	19.8	15.6	13.1	11.2	9.9
BMCl:EG	15.3	13.3	11.2	10.7	10.1
AMCl:EG	16.3	13.2	10.6	9.0	8.1
TMCl:EG	18.5	15.9	14.3	12.9	11.9
TECl:EG	26.2	22.7	19.6	17.8	17.0
TBCl:EG	13.2	10.6	8.6	7.5	6.7
BPF_6:NMA	10.4	8.3	7.4	6.8	6.6
HPF_6:NMA	10.2	8.2	7.2	6.3	5.8
OPF_6:NMA	9.1	7.2	6.2	5.5	5.5
TMAc:EG	20.3	16.5	13.5	11.5	10.3
TEBr:EG	19.9	16.2	14.1	12.3	10.8
BCF_3SO_3:NMA	14.3	11.6	9.5	8.2	7.4
BAc:NMA	9.1	7.4	6.6	6.0	6.0
Co:EG	42.2	30.0	24.6	19.6	17.1
Co:Ace	28.9	19.6	14.9	12.6	10.9
Zn:EG	5.4	4.1	3.5	2.7	2.8
Zn:Ace	5.3	3.5	3.0	2.7	2.5
Fe:EG	17.1	13.0	10.1	8.1	6.4
Fe:urea	37.5	29.8	24.5	21.9	18.9
Fe:Lac	102.1	77.8	70.9	60.5	53.4
Mg:urea	43.4	33.0	26.1	23.9	22.0
Mg:Gly	313.9	225.8	160.6	138.7	116.9
Li:NMA	7.0	5.8	5.1	4.4	4.1
Li:EG	34.4	25.4	18.9	15.3	13.7

Tables S4 and S5 below show the viscosity and conductivity data at different temperatures. For ChCl:malonic acid, η_0 and σ_0 data are from recent work (Gontrani et al., *ACS Sustainable Chem. Eng.*, 2019, 7, 12536), η_1 and σ_1 are measured by us.

As shown in Table S4, the viscosity data measured by us are larger than those of previous work. And then we strictly controlled the reaction temperature and water content of the solution, repeated the viscosity measurement experiment three times, and still got almost the same result. Our values are in good agreement with the density and viscosity data from *ACS Sustainable Chem. Eng.*, 2018, 6, 1039.

As shown in the ^{1}H NMR spectra and ^{13}C NMR spectra of the ChCl:malonic acid (Figure S6), there is no significant decarboxylation or other substances. The difference between this work and the above-mentioned literature value may be due to the measurement method.

For ChCl:Oxalic acid dehydrate, η_0 and σ_0 data are from recent work (*Phys. Chem. Chem. Phys.*, 2018, 20, 30120-30124), η_1 and σ_1 are measured by us. As shown in Table 2, the viscosity and conductivity data measured by us are very similar to the above-mentioned literature values.

Table S4. Viscosity and conductivity of ChCl:malonic acid (η_0 and σ_0 data are from Gontrani et al., *ACS Sustainable Chem. Eng.*, 2019, 7, 12536-12543, η_1 and σ_1 are measured by us.)

T °C	η_0 mPa·s	η_1 mPa·s	σ_0 mS·cm^{-1}	σ_1 mS·cm^{-1}
25	660.3	1257.4	0.33	0.23
35	353.7	648.1	0.57	0.44
45	189.4	360.8	0.97	0.68
55	101.5	205.9	1.66	1.13

Table S5. Viscosity and conductivity of ChCl:Oxalic acid dihydrate (η_0 and σ_0 data are from *Phys. Chem. Chem. Phys.*, 2018, 20, 30120-30124; η_1 and σ_1 are measured by us.)

T °C	η_0 mPa·s	η_1 mPa·s	σ_0 mS·cm^{-1}	σ_1 mS·cm^{-1}
25	82.9	95.02	5.60	5.31
35	52.8	62.31	8.11	7.82
45	43.6	42.27	11.46	10.57
55	23.3	29.39	15.86	14.80

65	16.1	19.86	21.53	20.76

Table S6. Diffusion coefficient of each component of the five DESs at room temperature.

DES	*D* (10^{-11} $m^2 \cdot s^{-1}$)		
	Cation	Anion	HBD
BPF_6:NMA	4.93	5.03	10.9
HPF_6:NMA	3.67	4.08	8.66
OPF_6:NMA	2.57	3.08	7.27
BCF_3SO_3:NMA	6.49	6.38	11.5
BAc:NMA	2.84	3.92	4.94