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

Electronic Supplementary Information

Rational design of efficient deep eutectic solvents for HCl absorption through their competitive H-bonding interaction

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Figures and Tables

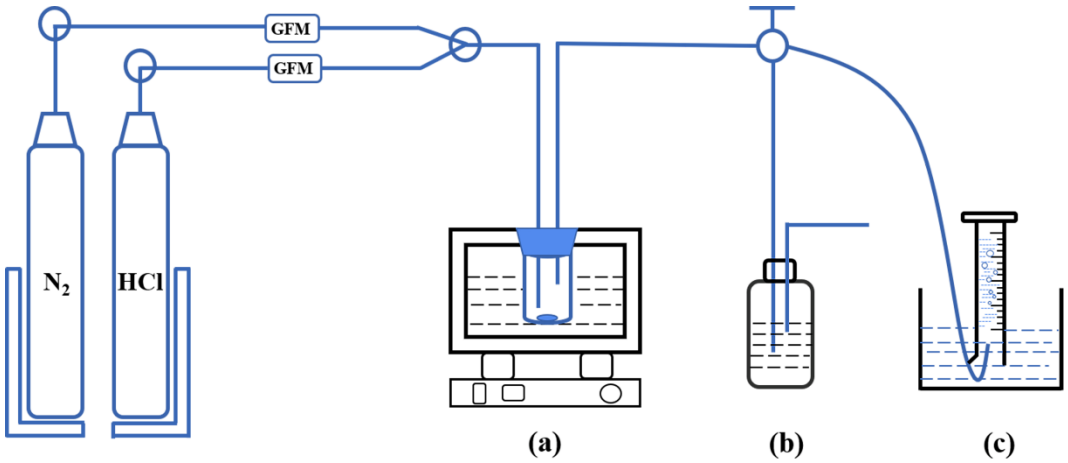
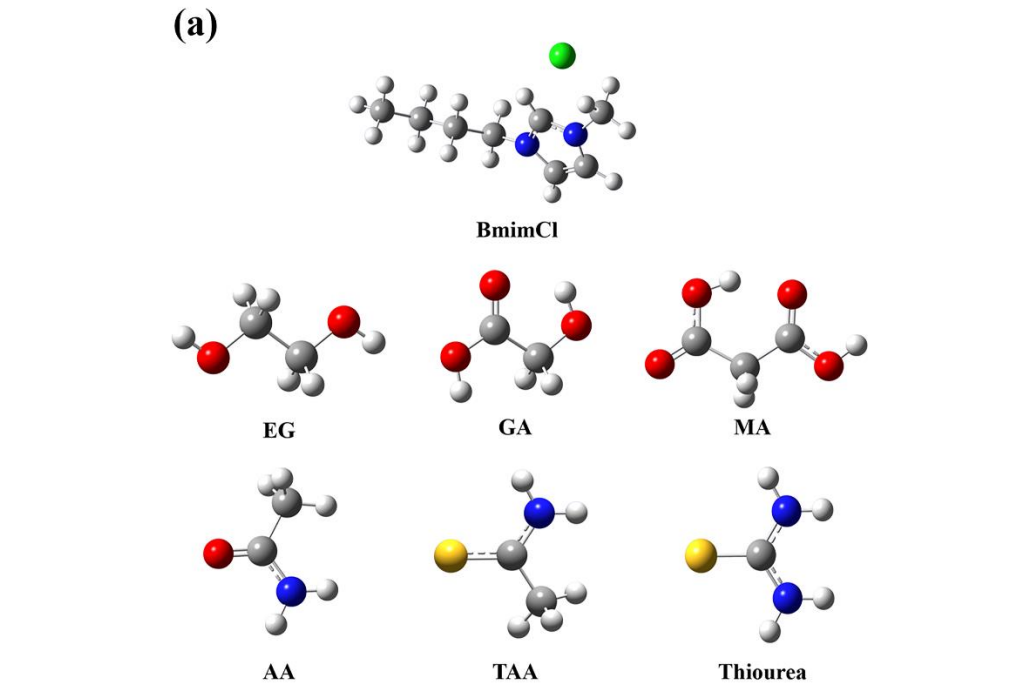


Fig. S1. Experimental apparatus for HCl solubility measurement

(a): absorption vessel; (b): exhaust gas treatment device; (c): gas collect device

The HCl absorption and DES regeneration were carried out in a glass tube with inner diameter of 15 mm, being immersed in a thermostatic water bath at set temperature. For absorption, about 1 g of DES solvent was added to the tube, to which HCl-bearing gas was bubbled at 60 mL·min^{-1}. The absorbed amount of HCl at specified time was determined by weighing the absorption tube with an electronic balance (Sartorius BS 224S, uncertainty of 0.1 mg).


(a)
BmimCl
EG
GA
MA
AA
TAA
Thiourea
(b)
2.25 Å
2.14 Å
BmimCl-EG
1.93 Å
2.34 Å
BmimCl-GA
1.89 Å
2.68 Å
2.24 Å
BmimCl-MA
2.23 Å
2.68 Å
BmimCl-AA
2.4 Å
2.18 Å
BmimCl-TAA
2.14
2.15
2.75
BmimCl-Thiourea

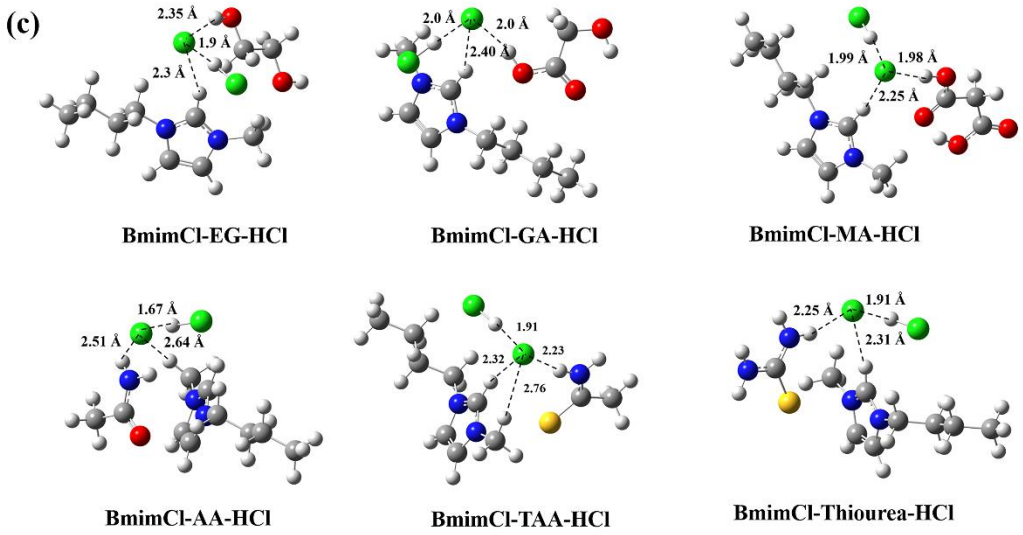


Fig. S2. Optimized structure of components in the system;

(a) HBA/HBD; (b) DES; (c) DES-HCl； S-yellow, N-blue, O-red, C-gray, H-white, Cl-green.

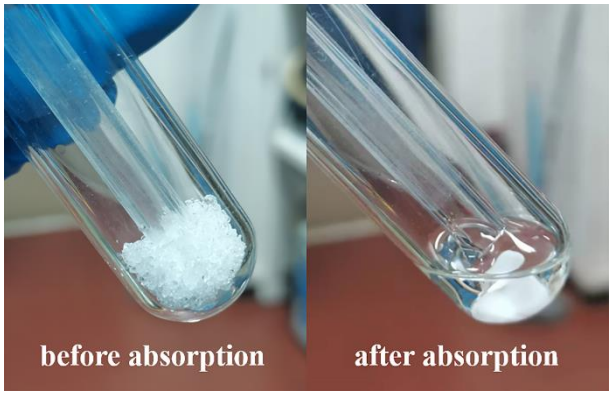


Fig. S3. The picture of phase change before and after HCl absorption by BmimCl

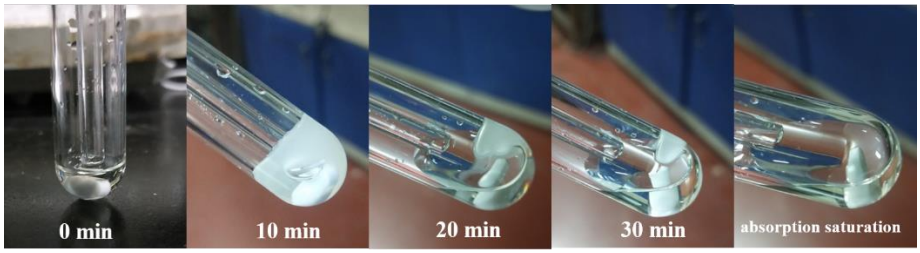


Fig. S4. The picture of BmimCl-Thiourea (1:1) during HCl absorption

Fig. S5. The phase change of BmimCl-TAA (1:1) in absorption process of HCl gas

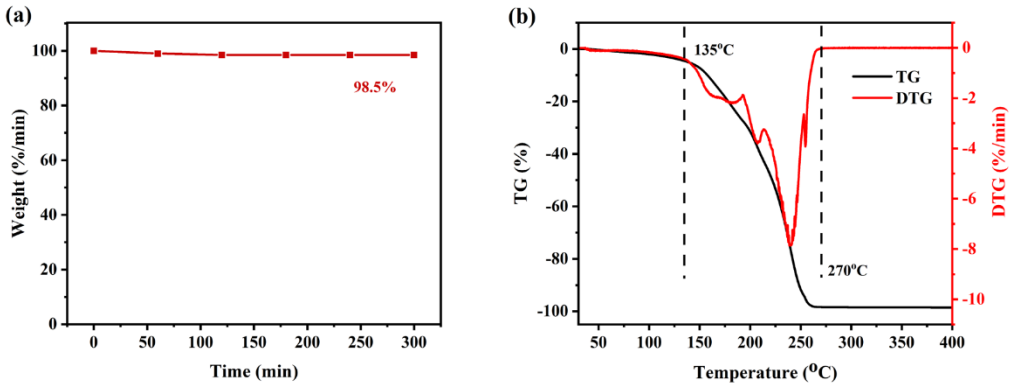


Fig. S6. (a) Thermal stability of BmimCl-TAA (1:1) at 373.15 K; (b) Thermogravimetric diagram of BmimCl-TAA (1:1)

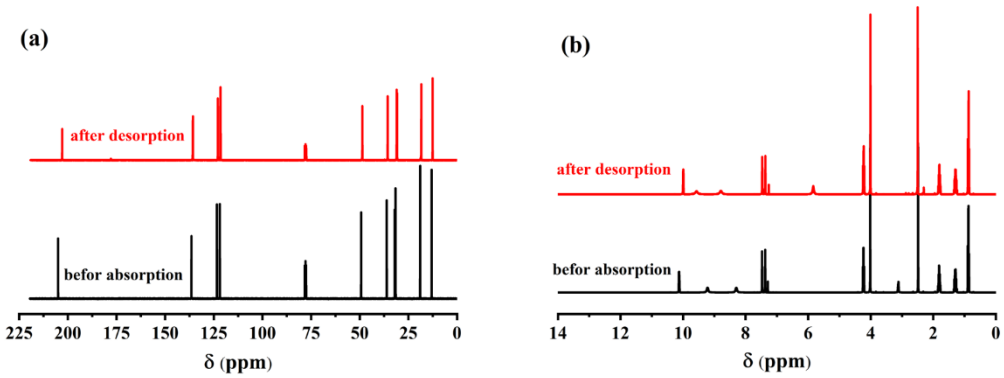


Fig. S7. NMR spectra of the BmimCl-TAA (1:1) before and after regeneration.

(a) ^{13}C NMR; (b) ^{1}H NMR

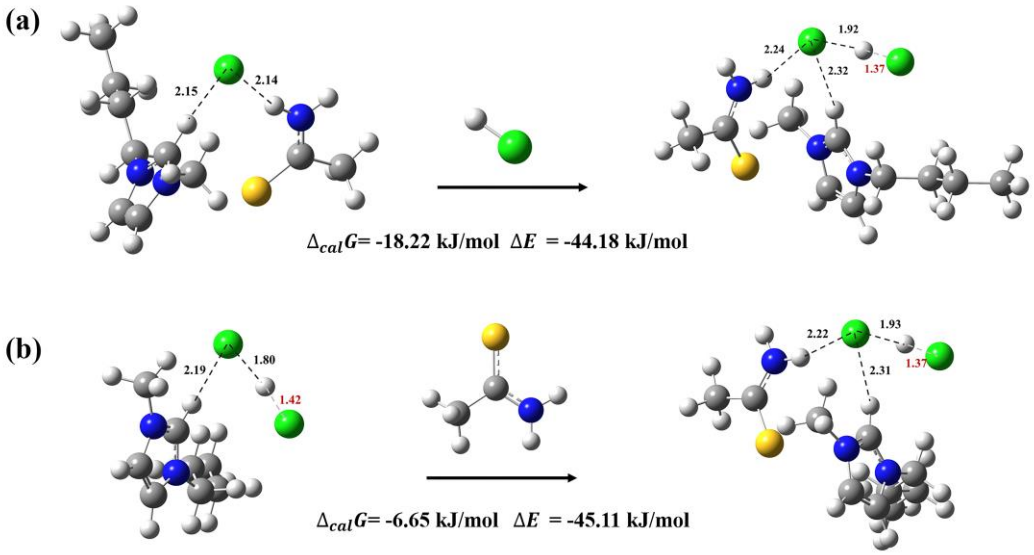


Fig. S8. Optimized configurations and Gibbs free energies for BmimCl-TAA+ HCl and BmimCl-HCl +TAA; S-yellow, N-blue, C-gray, H-white, Cl-green.

Table S1 Effect of properties of DESs on saturated and reversible solubility of HCl

DESs HBA : HBD =1:1	Interaction energy between different pairs [a] ΔE (kJ·mol^{-1}) HBA-HBD	DES-HCl	HBD-HCl	Absorption enthalpy of HCl [a] $\Delta_{cat}H$ (kJ·mol^{-1})	Absorption capacity of HCl (mol·mol^{-1})(g·g^{-1}) [b]		Reversible absorption of HCl (mol·mol^{-1}) [c]	Free volume [d] (cm^3·mol^{-1})	(cm^3·g^{-1})	pH [e]	Regeneration efficiency of DESs (%) [f]
BmimCl-HCl	--	-62.11	--	-68.91	2.11	0.45	1.65	54.04	0.319	6.91	78%
BmimCl-EG	-46.68	-47.04	-27.42	-53.07	1.35	0.417	1.30	37.26	0.315	5.89	96%
BmimCl-GA	-94.96	-36.47	-14.78	-38.84	1.16	0.339	1.03	35.37	0.282	2.91	89%
BmimCl-MA	-87.77	-32.02	-19.56	-36.90	1.08	0.284	0.97	36.37	0.261	2.45	90%
BmimCl-AA	-30.27	-56.33	-28.86	-63.29	1.48	0.461	1.26	36.96	0.316	5.01	85%
BmimCl-TAA	-62.80	-44.18	-20.79	-49.91	1.81	0.529	1.76	39.80	0.319	6.43	97%
BmimCl-Thiourea	-51.24	-61.66	-26.13	-69.03	1.54	0.454	1.16	36.30	0.290	6.99	75%

[a] Calculated values based on B3LYP/6-31++G (d, p) method.

[b] The absorption was carried out at 303.15 K and 101.3 kPa.

[c] The desorption amount of HCl via 1 h N_2 purge at 160 mL·min^{-1} and 343.15 K.

[d] Calculation values based on eqn 2 and eqn 3.

[e] The solution pH for their 1mol·L^{-1} aqueous solution

[f] As calculated by eqn 4.

Table S2 Densities and viscosities of BmimCl-DESs at 298.15 K

parameters	BmimCl-EG 1:1	BmimCl-GA 1:1	BmimCl-MA 1:1	BmimCl-AA 1:1	BmimCl-TAA 1:1	BmimCl-Thiourea 1:1
η (mPa·s)	128.33	261.18	547.22	587.60	881.67	5483.33
ρ (g·cm^{-3})	1.08211	1.14646	1.18698	1.07257	1.08871	1.14698

Table S3 The regression parameters for HCl absorption isothermal data with PCAM model

Tampreture (K)	K	H(bar)	n	R^2
303.15	121.06	6.11	1.65	0.996
313.15	55.17	6.68	1.5	0.993
323.15	27.39	8.60	1.51	0.996
333.15	18	9.20	1.41	0.992

Table S4 Changes of thermodynamic parameters and interatomic distance during HCl absorption

Interaction pair	Interaction energy of different pairs ΔE (kJ·mol^{-1})	Absorption enthalpy of HCl $\Delta_{cal}H$ (kJ·mol^{-1})	Gibbs Free Energy of HCl $\Delta_{cal}G$ (kJ·mol^{-1})	*d* (Å)			
				$d_{\text{Bmim-Cl}}$	$d_{\text{Cl-TAA}}$	$d_{\text{Cl-HCl}}$	$d_{\text{H-Cl}}$
BmimCl	--	--	--	2.63	--	--	--
BmimCl-HCl	-62.11	-68.91	-33.29	2.19	--	1.8	1.42
DES (BmimCl-TAA)	-62.80	-64.98	-22.23	2.15	2.14	--	1.29
DES-1HCl (Cl)	-44.18	-49.91	-18.23	2.32	2.23	1.91	1.37
DES-1HCl (S)	-27.81	-33.67	-2.61	2.16	2.09	2.12	1.34
DES-2HCl (Cl)	-72.18	-82.96	-18.24	2.41	2.3	2.03	1.34
DES-2HCl (Cl+S)	-72.08	-83.00	-12.41	2.38	2.23	1.91	1.38
DES-3HCl (2Cl+S)	-97.10	-111.18	-18.44	2.38	2.25	2.04	1.33
DES-3HCl (Cl)	-95.06	-107.78	-14.52	2.38	2.37	2.13	1.32
DES-4HCl (3Cl+S)	-121.04	-139.63	-6.43	2.42	2.42	2.16	1.32
DES-4HCl (Cl)	-112.64	127.78	-3.39	2.5	2.45	2.2	1.31
DES-5HCl (3Cl+2S)	-135.09	-156.50	6.96	2.42	2.32	2.16	1.32