Electronic Supplementary Information

Title: Dicarboxylic Acid Salts as Task-Specific Ionic Liquids for Reversible Absorption of SO₂ with Low Enthalpy Change

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1. Experimental section

1.1 Materials

Triethylamine ($(C_2H_5)_3N$), n-butyl bromide (C_4H_9Br), silver oxide (Ag_2O), and ethanol, obtained commercially from Sinopharm Chemical Reagent Co., Ltd., (Nanjing, China), were of analytical grade and used without further purification. All dicarboxylic acids of analytical grade were purchased from Nanjing Chem. Co. (Nanjing, China) and used as received.

1.2 General procedure for the synthesis of [N₂₂₂₄][dicarboxylate] ionic liquids

A three-step procedure was used to prepare acid salt ionic liquids (ASILs): the halide precursor was synthesized in the first step, followed by the anion exchange and neutralization (see Scheme S1).



Scheme S1. Synthesis route and chemical structure of [N₂₂₂₄][dicarboxylate] ILs.

Triethylbutylammonium bromide ($[N_{2224}][Br]$) was prepared via the alkylation of (C_2H_5)₃N (70.0 g) with C_4H_9Br (95.0 g) in ethanol (200 ml) under reflux and vigorous stirring for 12 h. The solvent and unreacted reactants were removed by rotary evaporation, $[N_{2224}][Br]$ (160 g) as white solid was obtained after being dried at 60 °C under vacuum (≈ 0.1 kPa) for 24 h.

In the anion exchange reaction, Ag_2O was added in portions into $[N_{2224}][Br]$ solution with mole ratio (Ag_2O to $[N_{2224}][Br]$) of 1:1, and stirred without air and light at room temperature for 6 h. After filtration, the $[OH^-]$ concentration of the resulting solution was determined from the titration with standard HCl solution.

Then, the triethylbutylammonium hydroxide ($[N_{2224}][OH]$) solution reacted with a slight excess of dicarboxylic acids via neutralization at room temperature for 2 h. Water was evaporated to generate a residual solution that contained the required ionic liquid. After further dried at 60 °C under vacuum (≈ 0.1 kPa), the residue was extracted with diethyl ether for several times to remove the unreacted acids. The crude product was dissolved in the mixed solvent of dichloromethane with 2 vol % methanol, and the solution was passed through a column filled with neutral silica. After the removal of the solvent by evaporation, the product was dried in vacuum (≈ 0.1 kPa) at 80 °C for at least 5 days before being used for analytical instruments.

1.3 Characterization of ASILs and measurement of physical properties

All samples were dried in a vacuum oven at 0.1 kPa and 80°C for at least 5 days to remove volatile impurities before the determination of the physico-chemical properties and absorption experiments. The concentrations of [Br] anion residual in all samples were measured using the Mohr titration, and the impurities were found to be less than 0.02%. The structure of ASILs was confirmed by the ¹H NMR spectra (BRUKER DPX 300) and elemental analysis (Elementar Vario MICRO).

The mass fraction of water in the samples were measured using Karl Fisher Coulometric Titration (Brinkmann Metrohm 787 KF Titrino) to be less than 0.05% for all the dried samples. The determination of physico-chemical parameters was performed on analytical instruments such as Different Scanning Calorimetry (Perkin-Elmer Diamond DSC), Thermogravimetric Analysis (Perkin-Elmer TG/DTA, 2010), Viscometer (HAAKE Rheostress 600), and Densimeter (DMA 5000 density meter). The glass transition temperature (T_g) and melting temperature (T_m) were recorded in the temperature range of -100 to 0 °C and 20 to 500 °C under N₂ atmosphere, at a scan rate of 10 °C /min under N₂ in the temperature range of 20 to 500 °C.

2 Characterization of ASILs prepared in this work (¹H NMR spectra and elemental analysis)

 $[\mathbf{N}_{2224}][\mathbf{dimalonate}]: {}^{1}\text{H NMR (300 MHz, DMSO, 25 °C, TMS): } \delta=0.93 (t, J=7.2 \text{ Hz}, 3\text{H}, C\underline{H}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{C}), 1.16 (t, J=7.2 \text{ Hz}, 9\text{H}, C\underline{H}_{3}\text{CH}_{2}\text{N}), 1.24-1.39 (m, 2\text{H}, C\underline{H}_{3}\text{C}\underline{H}_{2}\text{C}\underline{H}_{2}\text{C}\underline{H}_{2}\text{C}), 1.48-1.62 (m, 2\text{H}, C\underline{H}_{3}\text{C}\underline{H}_{2}\text{C}\underline{H}_{2}\text{N}), 2.68 (s, 2\text{H}, \text{HOOCC}\underline{H}_{2}\text{COO}), 3.12 (t, J=8.55 \text{ Hz}, 2\text{H}, C\underline{H}_{3}\text{C}\underline{H}_{2}\text{C}\underline{H}_{2}\text{N}), 3.18-3.30 (q, 6\text{H}, C\underline{H}_{3}\text{C}\underline{H}_{2}\text{N}). Elemental analysis (%) Calc. for C_{13}H_{27}\text{NO}_{4}: C 59.53, H 10.21, N 5.23; Found: C 59.74, H 10.41, N 5.36.$

 $[N_{2224}][disuccinate]: {}^{1}H NMR (300 MHz, DMSO, 25 {}^{\circ}C, TMS): \delta=0.92 (t, J=7.35 Hz, 3H; CH_{3}CH_{2}CH_{2}CH_{2}N), 1.15 (t, J=7.2 Hz, 9H; CH_{3}CH_{2}N), 1.24-1.38 (m, 2H; CH_{3}CH_{2}CH_{2}CH_{2}N), 1.49-1.62 (m, 2H; CH_{3}CH_{2}CH_{2}N), 2.23 (s, 4H; OOCCH_{2}CH_{2}COO), 3.12 (t, J=8.4 Hz, 2H; CH_{3}CH_{2}CH_{2}N), 3.20-3.28 (q, 6H; CH_{3}CH_{2}N). Elemental analysis (%) Calc. for C_{14}H_{29}NO_{4}: C 61.22, H 10.74, N 5.31; Found: C 61.06, H 10.61, N 5.09.$

 $[N_{2224}][diglutarate]: {}^{1}HNMR (300 MHz, DMSO, 25 °C, TMS): \delta=0.93 (t, J=6.6 Hz, 3H; CH_{3}CH_{2}CH_{2}CH_{2}N)$, 1.15 (t, J=7.65 Hz, 9H; CH_{3}CH_{2}N), 1.21-1.39 (m, 2H;

 $CH_3CH_2CH_2CH_2N$), 1.48-1.61 (m, 2H; CH₃CH₂CH₂CH₂N), 3.10 (t, J=8.7 Hz, 2H: CH₃CH₂CH₂CH₂N), 3.15-3.29 (q, 6H; CH₃CH₂N), 6.40 (s, 2H; OOCCH=CHCOO). Elemental analysis (%) Calc. for C₁₅H₃₁NO₄: C 62.25, H 10.80, N 4.84; Found: C 62.10, H 11.04, N 4.74. $[N_{2224}]$ [dimaleate]: ¹H NMR (300 MHz, DMSO, 25 °C, TMS): $\delta = 0.91$ (t, J = 7.86 Hz, 3H: $CH_3CH_2CH_2CH_2N$), 1.15 (t, J = 6.75 Hz, 9H; CH₃CH₂N), 1.22-1.37 (m, 2H; $CH_3CH_2CH_2CH_2N$), 1.48-1.62 (m, 2H; $CH_3CH_2CH_2N$), 3.12 (t, J = 8.55 Hz, 2H; CH₃CH₂CH₂CH₂N), 3.17-3.31 (q, 6H; CH₃CH₂N), 6.06 (s, 2H; OOCCH=CHCOO). Elemental analysis (%) Calc. for C₁₄H₂₇NO₄: C 61.76, H 10.03, N 5.09; Found: C 61.51, H 9.96, N 5.12. $[N_{2224}]$ [diphthalate]: ¹H NMR (300 MHz, DMSO, 25 °C, TMS): δ =0.86 (t, J=7.2 Hz, 3H, CH₃CH₂CH₂CH₂CH₂N), 1.13 (t, J=7.05 Hz, 9H, CH₃CH₂N), 1.21-1.35 (m, 2H, CH₃CH₂CH₂CH₂N), 1.45-1.59 (m, 2H, CH₃CH₂CH₂CH₂N), 3.19 (t, J=8.7 Hz, 2H, $CH_3CH_2CH_2CH_2N$, 3.14-3.28 (q, 6H, CH_3CH_2N), 7.48-7.57 (q, 2H, α -ph-<u>H</u>), 8.09-8.19 (q, 2H, β -ph-H). Elemental analysis (%) Calc. for C₁₈H₂₉NO₄: C 66.96, H 9.18, N 4.56; Found: C 66.84, H 9.04, N 4.33.

 $[N_{2224}][difumarate]: {}^{1}H NMR (300 MHz, DMSO, 25 {}^{\circ}C, TMS): \delta=1.004(t, J=7.5Hz, 3H, CH_3), \delta=1.253(m, 2H, CH_2), \delta=1.357(m, 9H, CH_3), \delta=1.418(m, 2H, CH_2), \delta=1.648(m, 2H, CH_2), \delta=1.910(m, 2H, CH_2), \delta=2.440(t, 4H, J=6.6Hz, CH2-CH2), \delta=3.211(m, 2H, CH_2), \delta=3.401(m, 6H, CH_2).$ Elemental analysis (%) Calc. for $C_{14}H_{27}NO_4: C 61.24, H 9.76, N 5.21;$ Found: C 61.51, H 9.96, N 5.12.

3 Solubility of SO₂ in [N₂₂₂₄][disuccinate]

It was found from the experiments that 1g $[N_{2224}]$ [disuccinate] could absorb 0.177g SO₂ at 15.0 kPa within 2.5 h, but the absorption equilibrium was still not reached because of the high viscosity

(>3800 mPa·s). In order to reduce the viscosity and facilitate the mass transfer, ethylene glycol was chosen to be a diluting solvent of $[N_{2224}]$ [disuccinate] for the absorption because of its low volatility. The viscosity of the mixture (40 wt% $[N_{2224}]$ [disuccinate] and 60 wt% ethylene glycol) at 25°C was reduced to 49.7 mPa·s, much lower than other pure ASILs in this work (see Table 1). Not surprisingly, the time for reaching absorption equilibrium was observed to be within 5 min for the mixtures. Assuming that $[N_{2224}]$ [disuccinate] and the solvent formed an ideal solution, the solubility of SO₂ in pure $[N_{2224}]$ [disuccinate] could be calculated by subtracting the solubility of SO₂ in pure solvent from that in the $[N_{2224}]$ [disuccinate]-solvent mixture (see Figure S1).



Figure S1. Solubility of SO₂ in ILs and ethylene glycol at 40°C as a function of pressure. (\blacktriangle pure [N₂₂₂₄][disuccinate] (calculated from the mixture of IL and ethylene glycol); \blacksquare a mixture of 40 wt% [N₂₂₂₄][disuccinate] + 60 wt% ethylene glycol; \bigstar pure ethylene glycol.)

It is found that $[N_{2224}]$ [disuccinate] can absorb quite a large quantity of SO₂ even at very low partial pressure(ie., 0-5 kPa). In addition, the solubility of SO₂ in pure ethylene glycol as shown in

Figure 3 is almost linearly related to the partial pressure, obeying apparently the Henry's law. As is known to all, physical absorption depends on pressure greatly, which generally obeys the Henry's law. Therefore, when the pressure increases, the solubility of SO_2 also increases linearly. Obviously, Ethylene glycol traps SO_2 via physically absorption at the whole pressure range from 0 to 100 kPa.

4. Results of DFT calculations



Figure S2. The optimized structures of $[N_{2224}]$ [dimalonate]. The shown values mean the relative energies in kJ/mol.



Figure S3. The optimized structures of $[N_{2224}]$ [dimalonate]^{...}SO₂. The shown values mean the relative energies in kJ/mol.

5. ¹H NMR spectra of [N_{2224}][dimalonate] before and after SO₂ absorption



Figure S5. ¹H NMR spectra of SO₂-satured [N₂₂₂₄][dimalonate]

6. Calculating procedure for the equilibrium thermodynamic properties of SO₂ absorption in ASILs

In order to evaluate the energy releasing in SO₂ absorption process, absorption isotherms of SO₂ in $[N_{2224}]$ [dimalonate] and $[N_{2224}]$ [dimaleate] at various temperatures are measured to calculate the equilibrium thermodynamic properties (Henry's law constant H, and reaction equilibrium constant K° and molar reaction enthalpy ΔH) of SO₂ absorption in ASILs. Absorption isotherms are

shown in Figure S4 and S5, respectively.



Figure S6. Absorption isotherms of SO₂ in [N₂₂₂₄][dimalonate]. (■ 295.15 K; • 303.15 K; ▲ 308.15 K; ★313.15 K.)



Figure S7. Absorption isotherms of SO₂ in [N₂₂₂₄][dimaleate]. (■ 298.15 K; • 313.15 K; ▲ 333.15 K.)

Based on the reaction mechanism proposed in the text, there are two aspects of SO_2 absorption in ASILs, physical and chemical absorption, which are simply expressed as Equations (S1) and (S2), respectively.

$$SO_2(g) \rightarrow SO_2(l)$$
 (S1)

$$SO_2(l) + IL(l) \rightarrow SO_2IL(l)$$
 (S2)

The overall reaction is expressed as Equation (S3):

$$SO_2(g) + IL(l) \rightarrow SO_2IL(l)$$
 (S3)

The Henry's law for SO₂ absorption in the liquid phase is defined in terms of molality and expressed as Equation (S4). P is the partial pressure of SO₂ in kPa, H is the Henry's law constant in kPa, and m_{SO_2} is the concentration of physically dissolved SO₂ in mol·kg⁻¹. The chemical reaction equilibrium of Equation (S2) is expressed as Equation (S5), where K_1° is the equilibrium constant,

 γ_{SO_2} , γ_{IL} and γ_{SO_2IL} are the activity coefficients of the physically dissolved SO₂, IL and SO₂-IL complex in the liquid phase, respectively. m_{IL} and m_{SO_2IL} are the concentrations of the IL and SO₂-IL complex after absorption equilibrium in mol·kg⁻¹ and m° is the standard molality (1mol·kg⁻¹). Similarly, the overall reaction equilibrium corresponding to Equation (S3) is expressed as Equation (S6), where K° is the equilibrium constant of the overall reaction and P° is the standard pressure (100kPa). Equation (S7) is the mass balance for the IL, where m_{IL_0} is the initial concentration of the IL and is a constant that can be calculated from Equation (S9). M_{IL} is the molar mass of the IL in g·mol⁻¹. The mass balance for SO₂ is expressed as Equation (S8), where m_{I_0} is the liquid phase.

$$P = H\gamma_{SO_2} \frac{m_{SO_2}}{m^{\circ}}$$
(S4)

$$K_{1}^{\circ} = \frac{\gamma_{SO_{2}IL}}{\gamma_{SO_{2}}} \frac{m_{SO_{2}IL}}{m^{\circ}}}{\gamma_{SO_{2}}} \frac{m_{SO_{2}}}{m^{\circ}} \cdot \gamma_{IL}} \frac{m_{IL}}{m^{\circ}}}{m^{\circ}}$$
(S5)

$$K^{\circ} = \frac{\gamma_{SO_2IL}}{\frac{P}{P^{\circ}} \cdot \gamma_{IL}} \frac{m_{SO_2IL}}{m^{\circ}}}{\frac{P}{p^{\circ}} \cdot \gamma_{IL}} \frac{m_{IL}}{m^{\circ}}}$$
(S6)

$$m_{IL_0} = m_{IL} + m_{SO_2IL}$$
(S7)

 $m_t = m_{SO_2} + m_{SO_2IL}$ (S8)

$$m_{H_0} = \frac{1}{M_{IL}} \cdot 10^3$$
(S9)

It is not easy to calculate the activity coefficients of the three species in the liquid phase of the reaction system. However, ideal diluted solution can be easily fulfilled and all the activity coefficients tend to be unity when the concentration of free SO_2 in the liquid is low. In fact, only the products of activity coefficients are required in the calculation of K_1° and K° as shown in

Equations (S5) and (S6). Therefore, it is reasonable to assume that the products of activity coefficients in Equations (S5) and (S6) are constant during the whole absorption process to avoid the calculation of activity coefficient. After simple deduction, the following equation is obtained to relate the total solubility of SO_2 in ILs to the partial pressure of SO_2 .

$$m_{t} = \left(\frac{m_{IL_{0}}}{P + \frac{H}{K_{1}^{\circ}}} + \frac{1}{H}\right)P$$
(S10)

Combining Equations (S4), (S5) and (S6) results in Equation (S11):

$$K^{\circ} = \frac{K_1^{\circ}}{H} P^{\circ}$$
(S11)

Correlating experimental solubility of SO₂ in ASILs using Equation (S10) (correlation coefficient $R^2>0.99$) results in the values of Henry's law constant and the reaction equilibrium constant of Equation (S2). The reaction equilibrium constant of the Equation (S3) could be obtained from Equation (S11). All the resulting values of H and K° are presented in Table S2. The molar reaction enthalpy of the Equation (S3) ΔH (heat of absorption process) is calculated using the van't Hoff equation (see Equation (S12)) by drawing a linear fit of $\ln K^\circ$ with $\frac{1}{T}$. Results of ΔH were also presented in Table S1.

$$\frac{\partial \ln K^{\circ}}{\partial T} = \frac{\Delta H}{RT^2}$$
(S12)

Table S1. Equilibrium thermodynamic properties of SO₂ in ASILs

ASILs	T(K)	H(kPa)	K°	riangle H (kJ/mol)
	295.15	15.0	37.4	
[N ₂₂₂₄][dimalonate]	303.15	18.4	36.4	-42.2
	308.15	25.3	18.2	

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	313.15	26.0	13.4	
	298.15	18.9	6.4	
[N ₂₂₂₄][dimaleate]	313.15	33.0	3.4	-29.9
	333.15	76.0	1.8	