

Supporting Information for:

Regulating phase separation behavior of DEEA-TETA biphasic solvent using sulfolane for energy-saving CO₂ capture

Lidong Wang^{1,2}, Shanshan Liu^{1,2}, Rujie Wang^{1,2*}, Qiangwei Li^{1,2}, Shihan Zhang³

1 Hebei Key Lab of Power Plant Flue Gas Multi-Pollutants Control, Department of Environmental Science and Engineering, North China Electric Power University, Baoding, 071003, PR China

2 MOE Key Laboratory of Resources and Environmental Systems Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing, 102206, PR China

3 College of Environment, Zhejiang University of Technology, Hangzhou, 310014

Summary: this file includes 10 Pages, 4 Figures, 2 Tables and 31 Equations

*Corresponding author. Tel.: +86 312 7525528.

E-mail address: rujiawang@gmail.com (R.J.W.)

Supporting Information

Apparatus and methodology for the mass transfer study, apparatus for measuring the latent heat of CO₂ desorption, ¹H NMR spectra and the calculation of concentration ratio $C_{\text{sulfolane}}/C_{\text{DEEA}}$, species distribution in upper and lower phases, kinetics of CO₂ absorption using the TETA-DEEA-sulfolane absorbent, and the possible reactions during CO₂ absorption.

Figure S1. The wet-wall column experimental apparatus

Figure S2. The detailed parameters of the wet-wall column

Figure S3. Apparatus for measuring the latent heat of CO₂ absorption

Figure S4. ¹H NMR spectra of DEEA-TETA-sulfolane: fresh, upper phase (CO₂ loading=0.516mol/L), lower phase (CO₂ loading=4.631mol/L)

Table S1. Quantitative species distribution in upper and lower phases

Table S2. Kinetics of CO₂ absorption using TETA-DEEA-sulfolane absorbent in a wet-wall column

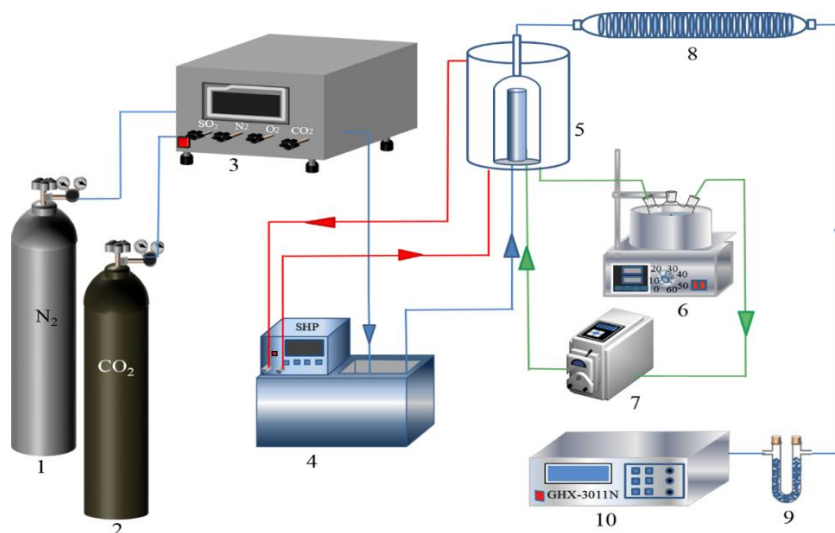


Figure S1. The wet-wall column experimental apparatus: 1. N₂ gas, 2. CO₂ gas, 3. gas distribution cabinet, 4. thermostat water bath (SHP), 5. WWC, 6. thermostat water bath magnetic stirrer, 7. peristaltic pump, 8. condensate tube, 9. drying tube, 10. infrared CO₂ analyzer (GHX-3011N).

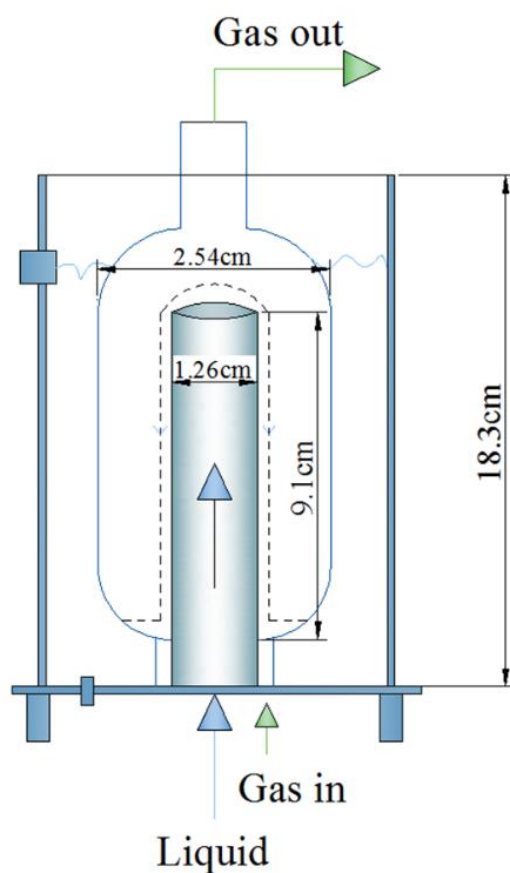


Figure S2. The detailed parameters of the wet-wall column

Calculation on kinetics of CO₂ absorption

According to previous study^{1 2}, the relationships among gas film mass transfer resistance ($1/k_g$), liquid film mass transfer resistance ($1/k_L$), and total mass transfer resistance ($1/K_G$) were determined as follows:

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k_L} = \frac{1}{k_g} + \frac{H}{Ek_L^0} \quad (S1)$$

where k_g , k_L , and K_G represent the gas film mass transfer coefficient, liquid film mass transfer coefficient, and total mass transfer coefficient, respectively ($\text{mol}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$); The total mass transfer resistance K_G was obtained through the slope of flux in relation to the logarithmic mean pressure, which is expressed described as follows:

$$K_G = \frac{Flux}{P_{CO_2} - P_{CO_2}^*} = \frac{dFlux}{dP_{CO_2}} \quad (S2)$$

$$Flux = \frac{(C_{CO_2,in} \% - C_{CO_2,out} \%) V_g}{22.4F} \quad (S3)$$

where $P_{CO_2}^*$ is the equilibrium partial pressure of CO₂ (Pa); P_{CO_2} is the operating partial pressure of CO₂ in the WWC (Pa); and $Flux$ is the gas absorption rate, which was estimated using Eq.(S3). F is the gas–liquid contact area of the WWC. P_{CO_2} was estimated using the logarithmic mean as follows:

$$P_{CO_2} = \frac{P_{CO_2,in} - P_{CO_2,out}}{\ln(P_{CO_2,in} / P_{CO_2,out})} \quad (S4)$$

The equilibrium partial pressure, $P_{CO_2}^*$, was calculated at $Flux = 0$. The gas film mass transfer coefficient (k_g) in the WWC was estimated as follows³⁻⁸:

$$\frac{RTk_g h}{D_{CO_2}} = Sh = 1.075 \left(Re Sc \frac{d}{h} \right)^{0.85} \quad (S5)$$

where Sh is the Sherwood number, Re is the Reynolds number, Sc is the Schmidt

number, d is the hydraulic diameter (cm), h is the height of the WWC (cm), and D_{CO_2} is the diffusion coefficient (cm^2/s).

Regeneration Energy consumption estimation:

$$Q_{\text{reg}} = Q_{\text{rxn}} + Q_{\text{sens}} + Q_{\text{latent}} \quad (\text{S6})$$

$$Q_{\text{rxn}} = -m_{\text{am}} \int_{\text{lean}}^{\text{rich}} \Delta H_{\text{rxn}}(\alpha) d\alpha \quad (\text{S7})$$

$$Q_{\text{sens}} = m_{\text{am}} (c_{\text{am}} + r_w c_w + \alpha_{\text{lean}} c_{\text{CO}_2}) \Delta T \quad (\text{S8})$$

$$Q_{\text{latent}} = m_w \lambda \quad (\text{S9})$$

$$m_w = MP_w(T_{\text{top}}) / p_{\text{CO}_2}^*(T_{\text{top}}, \alpha_{\text{top}}) \quad (\text{S10})$$

In these equations, m_{am} is defined as the molar amount of amines in the circulating solvent per ton of CO_2 product (mol/t CO_2); ΔH_{rxn} is the reaction enthalpy (kJ/mol); α and α_{lean} represent the CO_2 loading of the absorbent and lean solutions, respectively (mol/mol); c_{am} , c_w and c_{CO_2} are the heat capacity of the amines, water, and CO_2 per ton of CO_2 product, respectively ($\text{kJ}/(\text{mol} \cdot \text{K})$); r_w is the molar ratio of water to amine in the fresh solvent; m_w is the molar amount of water vapor in the outlet gas steam per ton of CO_2 product (mol); λ is the latent heat of water (kJ/mol); M is the molar amount per ton of CO_2 (mol); P_w is the partial pressure of water vapor (kPa); and $P_{\text{CO}_2}^*$ is the partial pressure of CO_2 .

The schematic for determining $P_{\text{CO}_2}^*$ of the CO_2 -loaded phase-splitting solvent is illustrated in Fig. S3. The total pressure (P_{total}) was measured by a 50-ml high-pressure reactor at different CO_2 loadings (0.25–0.48 mol/mol) and temperatures (110 and 120 $^\circ\text{C}$). The partial pressure of water vapor was calculated according to Raoult's law and $P_{\text{CO}_2}^*$ was obtained by subtracting P_w from P_{total} . Accordingly, m_w was calculated

using Equation S10 and the corresponding Q_{latent} was obtained using Equation S9.

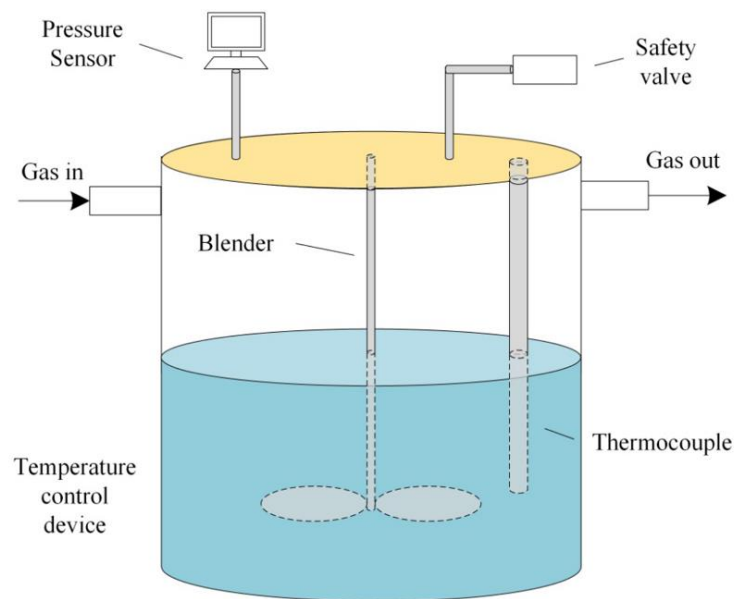


Figure S3. Apparatus for measuring the latent heat of CO₂ desorption

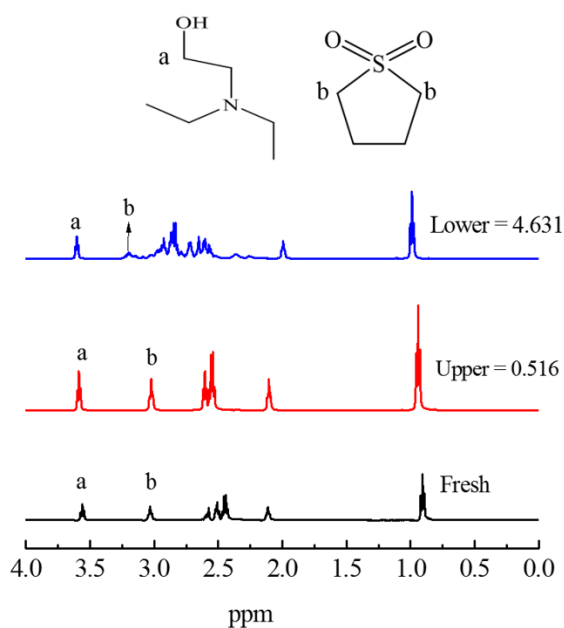


Figure S4. ¹H NMR spectra of DEEA-TETA-sulfolane: fresh, upper phase (CO₂ loading=0.516mol/L), lower phase (CO₂ loading=4.631mol/L).

The calculation of concentration ratio $C_{\text{sulfolane}}/C_{\text{DEEA}}$ from ¹H NMR spectra:

$$C_{\text{sulfolane}} / C_{\text{DEEA}} = S_b / 2S_a \quad (\text{S11})$$

where S_a and S_b represent the integral areas of group a and group b, respectively.

Table S1. Quantitative species distribution in upper and lower phases

Category	Component	Loading (mol/l)	Volume (%)
Upper phase	DEEA	5.51	61
	sulfolane	2.89	
Lower phase	DEEA	1.64	39
	TETA	2.56	
	sulfolane	0.61	

Table S2. Kinetics of CO₂ absorption using TETA-DEEA-sulfolane absorbent in a wet-wall column

Loading	T	V_g	μ	ρ	D_{CO_2}	K_G	k_g	k_L	K_G/k_g	K_G/k_L
(mol/l)	(K)	(ml/s)	(cp)	(g/ml)	(cm ² /s)	(mol/cm ² . s.Pa)	(mol/cm ² . s.Pa)	(mol/cm ² . s.Pa)	(%)	(%)
1.23	303	16.67	13.10	1.07	3.93E-06	1.88E-11	1.21E-10	2.23E-11	15.58	84.42
1.23	318	16.67	7.98	1.07	5.67E-06	2.66E-11	1.21E-10	3.40E-11	21.87	78.13
1.23	333	16.67	4.50	1.07	7.93E-06	3.15E-11	1.22E-10	4.24E-11	25.80	74.20
1.23	348	16.67	3.37	1.07	1.09E-05	3.33E-11	1.22E-10	4.57E-11	27.17	72.83
0.00	333	8.33	4.20	1.02	8.24E-06	6.21E-11	6.80E-11	7.05E-10	91.20	8.80
0.00	333	16.67	4.20	1.02	8.24E-06	1.07E-10	1.23E-10	8.08E-10	86.83	13.17
0.00	333	25.00	4.20	1.02	8.24E-06	1.45E-10	1.73E-10	9.08E-10	83.98	16.02
0.00	333	33.33	4.20	1.02	8.24E-06	1.80E-10	2.21E-10	9.68E-10	81.41	18.59
0.54	333	8.33	4.32	1.06	8.11E-06	4.54E-11	6.80E-11	1.37E-10	66.87	33.13
0.54	333	16.67	4.32	1.06	8.11E-06	7.05E-11	1.22E-10	1.66E-10	57.63	42.37
0.54	333	25.00	4.32	1.06	8.11E-06	8.62E-11	1.73E-10	1.72E-10	49.93	50.07
0.54	333	33.33	4.32	1.06	8.11E-06	9.97E-11	2.20E-10	1.82E-10	45.22	54.78
1.23	333	8.33	4.50	1.07	7.93E-06	2.11E-11	6.77E-11	3.06E-11	31.15	68.85
1.23	333	16.67	4.50	1.07	7.93E-06	3.15E-11	1.22E-10	4.24E-11	25.80	74.20
1.23	333	25.00	4.50	1.07	7.93E-06	3.47E-11	1.72E-10	4.35E-11	20.16	79.84
1.23	333	33.33	4.50	1.07	7.93E-06	3.77E-11	2.20E-10	4.55E-11	17.16	82.84

The possible reactions during CO₂ absorption:

Dissociation of water:



Dissociation of carbonic acid:



Dissociation of HCO_3^- :



Dissociation of protonated TETA:



Dissociation of deprotonated TETA:



Dissociation of triprotonated TETA:



Dissociation of tetraprotonated TETA:



Formation of zwitterion:



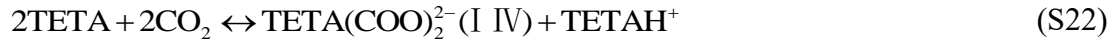
Formation of primary carbamate:



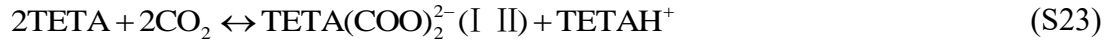
Formation of secondary carbamate:



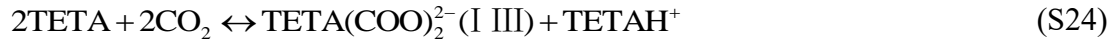
Formation of primary-primary dicarbamate:



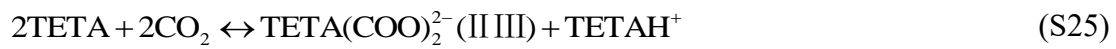
Formation of primary-secondary dicarbamate:



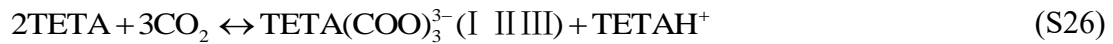
Formation of primary-secondary dicarbamate:



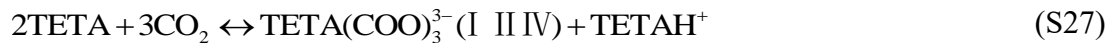
Formation of secondary-secondary dicarbamate:



Formation of primary-secondary-secondary tricarbamate:



Formation of primary-secondary-primary tricarbamate:



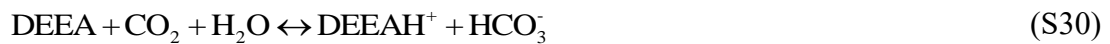
Formation of tetracarbamate:



Dissociation of carbamate:



Formation of bicarbonate:



Dissociation of protonated DEEA:



References

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