Supporting Information

Kinetics of carbon dioxide absorption into water-lean potassium prolinate/ethylene glycol solutions

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■ Theoretical and Experimental section

The method of N_2O/CO_2 analogy was used to estimate CO_2 physical solubility into ProK/EG solutions, which can be expressed as follows [1,2]:

$$\frac{H_{CO_2-\text{solution}}}{H_{N_2O-\text{solution}}} = \frac{H_{CO_2-\text{solvent}}}{H_{N_2O-\text{solvent}}} \tag{S1}$$

where $H_{CO2\text{-solution}}$ and $H_{N2O\text{-solution}}$ are Henry's low constant of CO_2 and N_2O in ProK/EG solutions, kPa·m^3·kmol^{-1}, respectively. $H_{CO2\text{-solvent}}$ and $H_{N2O\text{-solvent}}$ are Henry's low constant of CO_2 and N_2O in water-lean EG solvent, kPa·m^3·kmol^{-1}, respectively. The effect of water in the ProK/EG solutions was considered.

The diffusion coefficients of CO_2 and ProK in ProK/EG solutions can be estimated using a modified Stokes-Einstein relation and the diffusion coefficient of ProK in EG was calculated using the Wilke-Chang equation [3-5]:

$$\frac{D_{\mathbf{CO_2,s}}}{D_{\mathbf{CO_2},\text{EG}}} = \frac{D_{\mathbf{ProK,s}}}{D_{\mathbf{ProK},\text{EG}}} = \left(\frac{\eta_{\text{EG}}}{\eta_{\mathbf{s}}}\right)^{0.6} \tag{S2}$$

$$D_{\mathbf{ProK,EG}} = 7.4\times10^{-8}\frac{\sqrt{\psi_{\mathbf{EG}}M_{\mathbf{EG}}}T}{\eta_{\mathbf{EG}}V_{\mathbf{ProK}}^{0.6}} \tag{S3}$$

where $D_{CO2,EG}$ and $D_{CO2,s}$ are the CO_2 diffusion coefficient in EG and ProK/EG solution respectively. $D_{ProK,\,s}$ and $D_{ProK,\,EG}$ were the diffusion coefficient of ProK in ProK/EG solutions and EG, respectively. η_{EG} and η_s are viscosity of EG and ProK/EG solution respectively. Solvent/solvent interaction constant (ψ_{EG}), relative molecular mass (M_{EG}) and molar volume (V_{ProK}) are 2.0, 62.07, 82.76 respectively [6,7]. The values of $D_{CO_2\text{-EG}}$ were obtained from the literature [8].

The overall kinetic rate constant, $k_{ov,}$ can be obtained from the observed rate constant k_{obs} ,

expressed by

$$k_{ov} = k_{obs} - k_{OH^-} C_{OH^-} \quad \text{(S4)}$$

$$\log_{10}(k_{OH^-}) = 13.635 - \frac{2895}{T} \quad \text{(S5)}$$

$$C_{OH^-} = \sqrt{K_w C_{PorK} / K_a} \quad \text{(S6)}$$

where k_{OH^-} is the rate constant for the CO_2 reaction with OH^- [9,10]. The hydroxyl ion concentration can be estimated from the relations given by [11]. The dissociation constants for water (K_w) and ProK (K_a for α-amine group) were taken from literature [13].

Physical solubility of N_2O and CO_2

Physical solubility of CO_2 cannot be directly measured, because ProK/EG solutions can react with CO_2. N_2O has similar molecular structure, electric structure, and volume to that of CO_2 and it is not reactive with ProK. In this study, N_2O was used to measure indirectly.

The physical solubility experiments were carried out in an apparatus, reported in our previous work [14].The apparatus mainly consists of a stainless steel vessel (V_v, 0.813L) for storing the N_2O gas, a stainless steel equilibrium cell (V_e, 1.335L) with a magnetic-drive stirrer and two temperature-controlled water baths (± 0.1 K). In each experiment, a known mass of solution (about 1.00 – 1.05 kilograms) was fed into the reactor and degassed by a vacuum pump (2XZ-1, Shanghai Shuang'e, China) at 293 K until the pressure of equilibrium cell dropped to under 1.0 kPa. Then, the solution was heated to the investigated temperature. The initial equilibrium pressure P_{ini} and temperature T_r of equilibrium cell were recorded by a pressure transducers (GS4200-USB, 0 – 3.5 bar absolute, ESI) and a Pt-100 temperature senor. It should be pointed out that the P_{ini} in the reactor is not referred to the saturated vapor pressure of solvents due to the presence of residual gases after degassing. The gas vessel was filled with the N_2O at controlled

temperature T_v and the initial pressure P_1 was recorded by a pressure senor (PX409-050AUSBH, Omega Engineering Inc.). Then, the N_2O gas in the vessel was injected into equilibrium cell and the pressure decreased down to P_2. The total amount of N_2O gas entered into the equilibrium cell can be calculated. After about three hours, the VLE can be reached at each temperature T_r. The total pressure P_{tot} in equilibrium cell was obtained. The physical solubility of N_2O can be calculated as follows:

$$P_{N_2O} = P_{tot} - P_{ini} = H_{N_2O} \times C_{N_2O} \tag{S7}$$

$$C_{N_2O} = \left(\frac{V_V}{RT_V} \left(\frac{P_1}{z_1} - \frac{P_2}{z_2} \right) - \frac{(P_{eq} - P_s)(V_R - V_S)}{z_{eq} RT_R} \right) \Big/ V_s \tag{S8}$$

where V_V , V_R and V_s are the volumes of the vessel, the reactor and the solvent, respectively. In these experiments, the effect of the loaded N_2O on the volume of solution can be neglected due to the very low concentration of N_2O in the liquid phase. z_1 , z_2 and z_{eq} are the compressibility factors of gas at different conditions, respectively, which were calculated using the Peng-Robinson equation of state using the critical temperature of 309.57 K, critical pressure of 7245 kPa, and acentric factor of 0.143 [15].

For the determination of CO_2 physical solubility in water-lean EG, the similar method and operation procedure was applied. The compressibility factors of CO_2 gas are calculated by the Peng-Robinson equation of state using the critical temperature of 304.21 K, critical pressure of 7383 kPa, and acentric factor of 0.2236 [15].

The results of CO_2 solubility in pure EG and water-lean EG with 3.1 and 6.4 mass% water are presented in Table S1. Physical solubility of N_2O and CO_2 was correlated as a function of temperature and water content. Parameters in the empirical equations are shown in Table S2.

Physical mass transfer coefficient

The liquid-side mass transfer behavior in the stirred cell reactor is usually expressed by the correlation of Sherwood number, *Sh*, Reynolds number, *Re*, and Schmidt number, *Sc*, as follows [16, 17]:

$$\mathrm{Re} = \frac{n_S d_S^2 \rho}{\eta} \tag{S9}$$

$$Sc = \frac{\eta}{\rho D_{\mathrm{CO_2}}} \tag{S10}$$

$$Sh = \frac{k_{\mathrm{L}} d_{\mathrm{S}}}{\mathrm{D}_{\mathrm{CO_2}}} \tag{S11}$$

$$Sh = aRe^b Sc^c \tag{S12}$$

where ρ and η are the density and viscosity of solution, respectively; n_s is stirrer speed; d_s is stirrer length; D_{CO2} is the CO_2 diffusion coefficient in solution; k_L is the liquid-side physical mass transfer coefficient. a,b and c are the parameters to be fitted from experimental results. The experimental results are listed in Table S3.

Kinetic measurement of CO_2 absorption using aqueous ProK

To validate the experimental apparatus and method, the reaction kinetic of CO_2 absorption into aqueous ProK solution at 303 K was measured in the stirred cell reactor and compared with the data in open literature [10, 18]. The results are given in Table S4 and Fig.S1. The experimental data agree well with the reported data in the experimental condition investigated.

The observed CO_2 molar flows at different CO_2 partial pressures for the solutions at temperatures from 283.2 to 313.2 K and ProK concentrations from 0.5 to 2.0 M have been listed in Tables S5–8. A representative plot of P_{CO2} vs Q_{CO2} for ProK(1)/water(2)/EG(3) solution with 2.0 M (m_1=2.393 mol/kg) ProK at 303.2 K is shown in Fig.S2.

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Table S1

Experimental solubility of CO_2 in the mixture of EG (1) + water (2) at temperatures T[a].

w_2 / %	T / K	ρ [c] / kg·m^{-3}	m_{CO2} [d] / mol.kg^{-1}	P_{tot} / kPa	P_{CO2} / kPa	H_{CO2} / Pa.m^3.mol^{-1}
0	293.2	1114	0.0508	130.02	127.39	2246
	303.2	1106	0.0483	146.86	143.97	2699
	313.2	1099	0.0285	100.33	99.17	3158
	323.2	1092	0.0273	110.87	109.13	3642
	333.2	1085	0.0351	159.89	158.10	4164
3.1	293.2	1111	0.0295	81.37	79.08	2413
	303.2	1104	0.0496	159.10	156.71	2849
	313.2	1097	0.0265	99.68	98.07	3375
	323.2	1090	0.0253	108.65	106.78	3877
	333.2	1082	0.0243	117.48	115.07	4382
6.4	293.2	1109	0.0274	78.98	77.26	2540
	303.2	1102	0.0260	89.00	87.07	3044
	313.2	1095	0.0244	97.98	94.85	3550
	323.2	1087	0.0234	107.29	103.37	4058
	333.2	1080	0.0226	116.55	111.42	4558

[a] The standard uncertainties u are u (T) = 0.2 K, u (w_{H2O}) = 0.001, u (m_1) = 0.005 mol·kg^{-1}, u (m_{CO2}) = 0.0002 mol·kg^{-1}, u (P_{tot}) = 0.25 kPa, u (P_{CO2}) = 0.25 kPa, u_r (H) = 0.03.

[b] w_2 is the mass fraction of water in EG solution.

[c] ρ is the density of CO_2-free solution for the system water + EG. The density measurement was under the pressure of 101.3 ± 0.5 kPa and the standard uncertainties u are u (T) = 0.02 K, u (ρ)=1 kg·m^{-3}.

[d] m_{CO2} is the molality of CO_2 in water + EG solutions.

[e] The initial equilibrium pressure in the reactor is not equal to the saturated vapor pressure of the corresponding solvent at the same temperature due to the presence of residual gases after degassing.

Table S2

Parameters in empirical equations for Henry's law constant of N_2O and CO_2 into water-lean EG solutions.[a]

Gas	k_1	k_2	k_3	R^2	AAD,%[b]
N_2O [c]	316992 ± 39158	192134 ± 16441	-1217 ± 26.8	0.9960	0.83
CO_2	554114 ± 49518	311529 ± 19828	-1439 ± 20.0	0.9975	0.77

[a] Empirical equation for Henry's law constant of N_2O and CO_2 : $H_{gas-\mathrm{EG/water}} = (k_1 \times w_2 + k_2) \times \exp(\frac{k_3}{T/K})$, w_2 is the mass fraction of water in EG.

[b] Average absolute deviation: $\mathrm{AAD},\% = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{H_i^{\exp} - H_i^{\mathrm{mod}}}{H_i^{\exp}}\right| \times 100$

[c] Henry's constant of N_2O in water-lean EG solutions was obtained from literature [14].

Table S3

Experimental results for liquid-film mass transfer coefficient at the speed of the stirrer n_s = 2.67 s^{-1}. [a]

T	P_{CO2}	$N_{CO2} \times 10^3$	$D_{CO2\text{-}EG}$ [b] $\times 10^{10}$	$Sh \times 10^{-3}$	$Re \times 10^{-3}$	$Sc \times 10^{-4}$
K	kPa	$mol.s^{-1}.m^{-2}$	$m^2.s^{-1}$			
275.1	89.7	0.96	1.09	12.720	0.472	32.985
278.2	89.9	0.97	1.25	11.867	0.537	25.117
283.2	89.3	0.98	1.57	10.615	0.658	16.385
288.3	89.9	1.03	1.95	9.743	0.803	10.759
293.2	89.8	1.08	2.40	9.016	0.967	7.281
298.2	89.3	1.10	2.94	8.251	1.161	4.952
303.2	90.0	1.12	3.58	7.431	1.385	3.411
308.3	89.8	1.14	4.34	6.776	1.648	2.361
313.0	69.8	0.92	5.16	6.328	1.924	1.699
313.3	89.3	1.22	5.22	6.541	1.943	1.665
318.3	89.6	1.16	6.24	5.563	2.280	1.187
323.1	89.6	1.19	7.37	5.196	2.645	0.866
328.1	89.2	1.20	8.73	4.738	3.073	0.630
332.8	88.8	1.19	10.18	4.324	3.523	0.471

[a] The standard uncertainties u are u (T) = 0.2 K, u (P_{CO2}) = 0.25 kPa, u (N_{CO2}) = 0.022 $mmol \cdot s^{-1} \cdot m^{-2}$, u (n_s) = 0.02 s^{-1}.

[b] These values were deduced from the literature [8].

Table S4

Overall reaction rate constant of CO_2 absorption into ProK/water solution compared with literature at 303 K.

C_{ProK} mol·L^{-1}	k_{obs} s^{-1}	Sources
0.50	11937	This work
1.00	26914	
1.50	47570	
2.00	72802	
0.49	10967	Paul et al., 2012 [10]
0.97	26632	
1.51	48289	
2.00	71940	
0.50	10791	Majchrowicz et al., 2014[18]
1.01	26424	
1.96	67645	

Table S5

Absorption rate of CO_2 into ProK(1)/water(2)/EG(3) solutions at ProK concentration m_1=0.480 mol/kg and temperatures T [a].

P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}
283.2 K		293.2 K		303.2 K		313.2 K	
0.87	0.52	0.92	0.76	0.87	0.85	0.49	0.61
1.09	0.69	1.21	1.04	1.13	1.18	0.66	0.84
1.40	0.93	1.61	1.41	1.51	1.62	0.93	1.17
1.83	1.25	2.13	1.87	2.00	2.16	1.29	1.62
2.37	1.60	2.88	2.44	2.75	2.81	1.79	2.15
3.13	2.08	3.85	3.11	3.70	3.62	2.49	2.86
4.10	2.63	6.03	4.48	5.89	5.19	3.42	3.73
6.09	3.59	11.64	6.85	10.49	7.55	5.36	5.33
9.15	4.70					9.03	7.46
13.77	5.63						

[a] Standard uncertainties u are $u(C_{ProK})$= 0.002 mol·L^{-1}, u (T) = 0.2 K, $u(P_{CO2})$= 0.04 kPa, $u(N_{CO2})$= 0.022 mmol·s^{-1}·m^{-2}.

Table S6

Absorption rate of CO_2 into ProK(1)/water(2)/EG(3) solutions at ProK concentration m_1=1.027 mol/kg and temperatures T [a].

P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}
283.2 K		293.2 K		303.2 K		313.2 K	
1.03	1.03	1.01	1.30	0.92	1.42	0.70	1.30
1.31	1.37	1.32	1.82	1.21	1.99	0.93	1.73
1.70	1.80	1.75	2.47	1.63	2.70	1.25	2.32
2.20	2.33	2.39	3.35	2.24	3.68	1.67	3.06
2.92	3.01	3.26	4.41	3.06	4.93	2.30	4.09
3.86	3.85	5.10	6.51	4.89	7.31	3.15	5.38
5.80	5.42	8.89	10.10	8.17	11.31	4.95	7.91
9.68	8.15	14.85	14.71	14.12	16.74	8.22	11.66
15.75	11.35					13.10	16.70

[a] Standard uncertainties u are $u(C_{ProK})$= 0.002 mol·L^{-1}, u (T) = 0.2 K, $u(P_{CO2})$= 0.04 kPa, $u(N_{CO2})$= 0.022 mmol·s^{-1}·m^{-2}.

Table S7

Absorption rate of CO_2 into ProK(1)/water(2)/EG(3) solutions at ProK concentration m_1=1.654 mol/kg and temperatures T [a].

P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}
283.2 K		293.2 K		303.2 K		313.2 K	
0.81	0.99	0.59	1.01	0.66	1.39	0.56	1.42
1.01	1.25	0.75	1.30	0.85	1.86	0.78	2.04
1.30	1.61	0.99	1.72	1.18	2.49	1.08	2.90
1.69	2.09	1.32	2.31	1.52	3.32	1.56	4.14
2.19	2.70	1.76	3.05	2.10	4.49	2.23	5.81
2.89	3.50	2.35	4.07	2.91	5.99	3.74	9.28
3.82	4.51	3.24	5.36	4.57	9.12	6.94	15.72
5.71	6.46	5.01	7.96	8.18	15.01	12.27	25.27
9.62	10.03	8.74	12.84	13.78	22.98		
15.58	14.60	14.53	19.33				

[a] Standard uncertainties u are $u(C_{ProK})$= 0.002 mol·L^{-1}, u (T) = 0.2 K, $u(P_{CO2})$= 0.04 kPa, $u(N_{CO2})$= 0.022 mmol·s^{-1}·m^{-2}.

Table S8

Absorption rate of CO_2 into ProK(1)/water(2)/EG(3) solutions at ProK concentration m_1=2.393 mol/kg and temperatures T [a].

P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}	P_{CO2} / kPa	$N_{CO2} \times 10^3$ /mol·s^{-1}·m^{-2}
283.2 K		293.2 K		303.2 K		313.2 K	
0.75	1.03	0.68	1.22	0.85	1.81	0.70	1.91
0.95	1.30	0.87	1.68	1.08	2.50	0.90	2.65
1.22	1.68	1.15	2.32	1.39	3.44	1.26	3.77
1.59	2.19	1.53	3.10	1.89	4.73	1.81	5.31
2.07	2.83	2.11	4.20	2.59	6.43	2.48	7.13
2.75	3.70	2.91	5.62	4.17	9.82	3.90	10.95
3.65	4.77	4.61	8.45	7.56	16.55	7.11	18.49
5.52	6.89	8.24	13.81	12.96	25.85	12.29	29.06
9.39	10.77	13.92	21.12				

[a] Standard uncertainties u are $u(C_{ProK})$= 0.002 mol·L^{-1}, u (T) = 0.2 K, $u(P_{CO2})$= 0.04 kPa, $u(N_{CO2})$= 0.022 mmol·s^{-1}·m^{-2}.

Figure S1

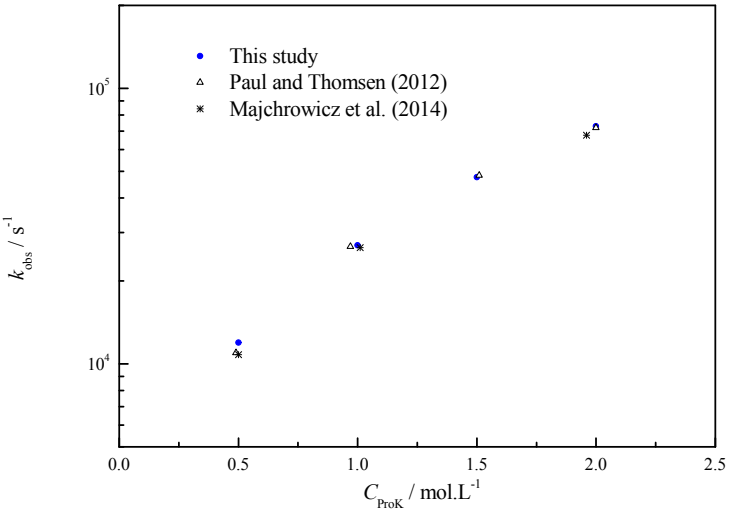

Fig.S1. Overall kinetic constant for aqueous ProK solutions compared with the literature data [10,18] at 303 K.

Figure S2

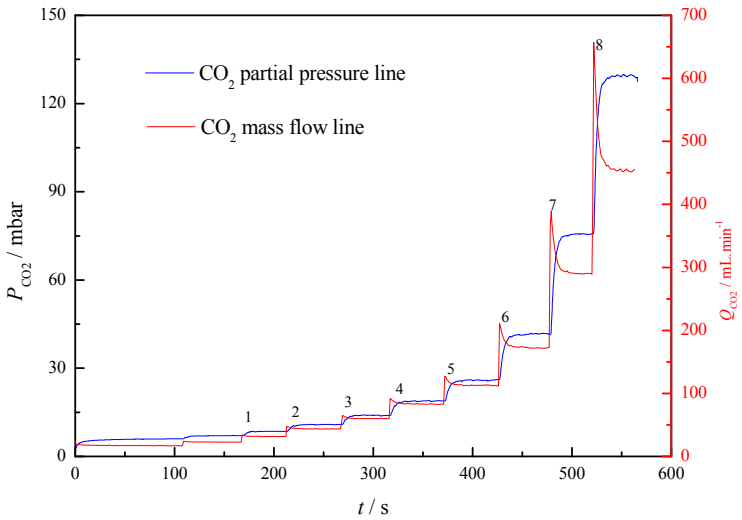

Fig.S2. Representative plot of P_{CO2} vs Q_{CO2} for ProK(1)/water(2)/EG(3) solution with 2.0 M (m_1=2.393 mol/kg) ProK at 303.2 K.