Solubilities of CO_2 and He in an ionic liquid containing poly(amidoamine) dendrimer Gen 0

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Supporting Information

Derivation of K_C for the case of only one primary amine reacting with CO_2

The reaction equilibrium constants (K_C) were calculated for [bmim][DCA] containing dendrimer in dry condition at 50°C, 80°C, 90°C, and 100°C. We assume here that the reaction of CO_2 takes place with only one of the four primary amines in the PAMAM dendrimer Gen 0 (the structure of the dendrimer molecule is shown in Figure 3) per equation (1):

$$CO_2 + 2\ R(NH_2)_4 \leftrightarrow R(NH_2)_3HNCOO^- + R(NH_2)_3NH_3^+ \quad (1)$$

For 20wt% dendrimer in [bmim][DCA] with a known mass (m) and volume of 0.01L (V_{IL}), the number of moles of dendrimer and [bmim][DCA] are respectively

$$n_{den} = \frac{0.2m}{517.0} \quad (2)$$

$$n_{IL} = \frac{0.8m}{205.26} \quad (3)$$

The number of moles of CO_2 absorbed in the IL containing dendrimer, n_2, was calculated from the experimental data. The Henry's law constants for CO_2 due to physical absorption in the IL containing dendrimer is calculated via the equation shown below

$$H_{CO2T} = H_{CO2}\frac{H_{HeT}}{H_{He}} = \frac{P_f}{x} \quad (4)$$

where H_{CO2T}: Henry's law constant of CO_2 due to physical absorption in the IL containing dendrimer

H_{CO2}: Henry's law constant of CO_2 in pure IL

H_{HeT}: Henry's law constant of He in the IL containing dendrimer

H_{He}: Henry's law constant of He in pure IL

x: mole fraction of CO_2

This approach is adopted since the physical solubility of CO_2 in the IL will be influenced by the presence of other electrolytes/compounds such as dendrimer. The effect of these compounds on the solubility of He will provide some guidance on the correction needed for CO_2 solubility. If N_2O was used instead of He, the correction may have been more accurate.[41,42] However, due to the radically different charge climate in an ionic liquid as opposed to water (for example), the effect is expected to be minor.

From equation (4), $$x = \frac{n}{n + n_{IL} + n_{den}} = \frac{P_f}{H_{CO2T}} \quad (5)$$

Therefore, $$n = \frac{x(n_{IL} + n_{den})}{1 - x} = \text{moles of free } CO_2 \text{ in solution} \quad (6)$$

Now, n_{CO2r}, the moles of CO_2 reacted with primary amines present in dendrimer, is equal to

$$n_{CO2,r} = n_2 - n \quad (7)$$

From equation (1), the reaction equilibrium constant, K_C, may be written as:

$$K_C = \frac{\dfrac{n_{R(NH2)_3\ HNCOO^-}}{V_{IL}} \dfrac{n_{R(NH2)_3\ NH_3^+}}{V_{IL}}}{\left(\dfrac{n_{CO_2|free}}{V_{IL}}\right)\left(\dfrac{n_{R(NH_2)_4}}{V_{IL}}\right)^2} \quad (8)$$

where we have assumed that only one primary amine group in any dendrimer molecule is reacting with CO_2 per equation (1). Obviously

$$n_{\mathrm{R(NH2)_3\ HNCOO^-}} = n_{CO2,r} = n_{\mathrm{R(NH2)_3\ NH_3^+}} \tag{9}$$

Also the unreacted dendrimer molecules, $n_{R(NH_2)_4}$ are related to

$$n_{R(NH_2)_4} = n_{den} - n_{CO_2,r} - n_{CO_2,r} = n_{den} - 2n_{CO_2,r} \tag{10}$$

Substituting relations (7), (9), and (10) in (8), we get

$$K_C = \frac{\left(n_{CO_2,r}\right)^2}{n\ \left(n_{den} - 2n_{CO_2,r}\right)^2} V_{IL} \tag{11}$$

Table 4b. CO_2 mole fractions in [bmim][DCA] at various feed pressures and temperatures

Temperature (^oC)	Pressure (bar)	CO_2 mole fraction	Pressure Ratio	Mole Fraction Ratio
50^oC	2.43	0.015	1.00	1.00
	3.75	0.024	1.54	1.56
	5.16	0.033	2.12	2.16
	6.51	0.042	2.68	2.74
	7.92	0.051	3.26	3.33
	9.23	0.060	3.80	3.92
	10.67	0.069	4.39	4.51
	12.08	0.078	4.97	5.12
	13.39	0.087	5.51	5.70
	14.77	0.097	6.08	6.35
80^oC	2.43	0.015	1.00	1.00
	3.75	0.024	1.70	1.73
	5.16	0.033	2.12	2.13
	6.51	0.042	2.68	2.66
	7.92	0.051	3.24	3.28
	9.23	0.060	3.81	3.84
	10.67	0.069	4.38	4.48
	12.08	0.078	4.97	5.05
	13.39	0.087	5.51	5.60
	14.77	0.097	6.07	6.21
90^oC	2.43	0.015	1.00	1.00
	3.75	0.024	1.52	1.52
	5.16	0.033	2.14	2.15
	6.51	0.042	2.72	2.74
	7.92	0.051	3.28	3.26
	9.23	0.060	3.85	3.86
	10.67	0.069	4.43	4.39
	12.08	0.078	5.01	4.95
	13.39	0.087	5.58	5.55
	14.77	0.097	6.15	5.92
100^oC	2.43	0.015	1.00	1.00
	3.75	0.024	1.63	1.63
	5.16	0.033	2.21	2.21
	6.51	0.042	2.80	2.82
	7.92	0.051	3.39	3.39
	9.23	0.060	4.00	4.05
	10.67	0.069	4.60	4.66
	12.08	0.078	5.17	5.23
	13.39	0.087	5.76	5.81
	14.77	0.097	6.32	6.42

Table 5b. Percent theoretical capacity of primary amines consumed under different pressures and its corresponding apparent equilibrium constants of primary amine reaction with CO_2 for 20 wt% dendrimer in [bmim][DCA] at different temperatures*

	P_{feed} (bar)	% Saturation (%)	K_C
50°C	2.43	10.56	6100 L/mol
	3.74	24.23	
	5.16	31.85	
	6.47	38.89	
	7.90	47.72	
	9.26	53.89	
	10.59	66.74	
	11.96	77.54	
	13.43	75.83	
	14.66	97.69	29972 L^4/mol^4
80°C	2.39	5.51	2804 L/mol
	3.76	9.03	
	5.14	12.88	
	6.53	16.61	
	7.77	18.83	
	9.27	22.85	
	10.67	27.42	
	12.14	32.13	
	13.39	34.83	
	14.83	42.08	
90°C	2.41	4.13	2227 L/mol
	3.87	6.88	
	5.17	9.78	
	6.58	13.28	
	7.93	15.47	
	9.38	19.62	
	10.68	23.08	
	12.07	27.51	
	13.38	29.10	
	14.77	34.36	
100°C	2.47	3.84	1790 L/mol
	3.76	5.73	
	5.16	8.20	
	6.52	10.06	
	7.91	12.65	
	9.27	15.06	
	10.61	17.99	
	11.99	20.52	
	13.43	22.52	
	14.47	26.96	

*Dry system

Table 6b. Percent theoretical capacity of primary amines consumed under different pressures and its corresponding apparent equilibrium constants of primary amine reaction with CO_2 for 30wt% dendrimer in [bmim][DCA] at different temperatures*

	P_{feed} (bar)	% Saturation (%)	K_C
50°C	2.41	9.29	6659 L/mol
	3.75	13.18	
	5.16	19.22	
	6.47	25.06	
	7.90	32.37	
	9.26	39.53	
	10.59	47.15	
	11.96	55.09	
	13.43	64.05	
	14.66	69.58	10329 L^4/mol^4
80°C	2.43	4.49	3061 L/mol
	3.62	6.77	
	5.16	10.43	
	6.47	13.08	
	7.90	16.75	
	9.26	20.17	
	10.59	23.02	
	11.96	26.47	
	13.43	31.19	
	14.96	33.84	
90°C	2.43	3.93	2431 L/mol
	3.71	6.00	
	5.16	8.58	
	6.47	10.61	
	7.90	14.08	
	9.26	17.09	
	10.59	19.47	
	11.96	23.00	
	13.43	26.18	
	14.86	28.06	
100°C	2.43	2.98	1954 L/mol
	3.72	4.82	
	5.16	6.72	
	6.47	8.49	
	7.90	10.63	
	9.26	13.00	
	10.59	14.39	
	11.96	16.46	
	13.43	19.78	
	14.66	21.93	

*Dry system

Table 7. Solubilities of pure CO_2 and pure He in 20 wt% dendrimer in [bmim][DCA] at different feed pressures and temperatures

Temperature (^oC)	Feed pressure (bar)	CO_2 mole fraction	He mole fraction
50^oC	2.40	0.038	0.0015
	3.75	0.059	0.0024
	5.16	0.081	0.0032
	6.47	0.101	0.0044
	7.90	0.125	0.0049
	9.26	0.143	0.0059
	10.59	0.169	0.0066
	11.96	0.191	0.0075
	13.43	0.208	0.0084
	14.65	0.231	0.0092
80^oC	2.39	0.023	0.0022
	3.75	0.036	0.0033
	5.14	0.050	0.0045
	6.53	0.064	0.0058
	7.77	0.074	0.0070
	9.26	0.088	0.0083
	10.67	0.103	0.0095
	12.13	0.118	0.0109
	13.39	0.126	0.0121
	14.83	0.145	0.0132
90^oC	2.41	0.020	0.0027
	3.87	0.032	0.0042
	5.16	0.044	0.0057
	6.58	0.057	0.0071
	7.93	0.066	0.0086
	9.37	0.080	0.0101
	10.68	0.092	0.0116
	12.07	0.106	0.0132
	13.38	0.114	0.0147
	14.76	0.128	0.0160
100^oC	2.46	0.019	0.0034
	3.75	0.028	0.0051
	5.15	0.039	0.0071
	6.51	0.048	0.0090
	7.90	0.059	0.0110
	9.26	0.070	0.0131
	10.60	0.079	0.0148
	11.98	0.091	0.0167
	13.43	0.100	0.0186
	14.46	0.111	0.0199

Table 8. Solubilities of pure CO_2 and pure He in 20 wt% dendrimer in [bmim][DCA] with moisture at different feed pressures and temperatures

Temperature (^oC)	Feed pressure (bar)	CO_2 mole fraction	He mole fraction
50^oC	2.47	0.046	0.0015
	3.74	0.071	0.0023
	5.16	0.102	0.0031
	6.46	0.121	0.0038
	7.90	0.148	0.0047
	9.26	0.169	0.0055
	10.69	0.205	0.0064
	11.96	0.227	0.0073
	13.43	0.247	0.0080
	14.66	0.263	0.0088
80^oC	2.41	0.029	0.0020
	3.69	0.041	0.0030
	5.16	0.057	0.0043
	6.72	0.069	0.0052
	7.90	0.081	0.0064
	9.26	0.091	0.0075
	10.59	0.108	0.0086
	11.96	0.125	0.0097
	13.43	0.141	0.0107
	14.66	0.151	0.0119
90^oC	2.41	0.023	0.0023
	3.66	0.031	0.0034
	5.16	0.051	0.0048
	6.47	0.057	0.0061
	7.90	0.069	0.0074
	9.26	0.079	0.0086
	10.59	0.089	0.0099
	11.96	0.105	0.0112
	13.43	0.120	0.0124
	14.66	0.126	0.0138
100^oC	2.41	0.020	0.0027
	3.78	0.033	0.0040
	5.16	0.043	0.0054
	6.41	0.054	0.0068
	7.90	0.065	0.0084
	9.26	0.078	0.0096
	10.59	0.084	0.0109
	11.96	0.096	0.0126
	13.43	0.107	0.0138
	14.66	0.115	0.0153

Table 9. Solubilities of pure CO_2 and pure He in 30 wt% dendrimer in [bmim][DCA] at different feed pressures and temperatures

Temperature (^oC)	Feed pressure (bar)	CO_2 mole fraction	He mole fraction
50^oC	2.43	0.047	0.0015
	3.74	0.07	0.0024
	5.16	0.097	0.0033
	6.47	0.121	0.0041
	7.90	0.149	0.0050
	9.26	0.176	0.0060
	10.59	0.201	0.0068
	11.96	0.224	0.0076
	13.43	0.250	0.0086
	14.66	0.268	0.0091
80^oC	2.43	0.028	0.0021
	3.62	0.042	0.0034
	5.16	0.062	0.0046
	6.47	0.076	0.0058
	7.90	0.094	0.0070
	9.26	0.111	0.0083
	10.59	0.125	0.0094
	11.96	0.141	0.0108
	13.43	0.160	0.0125
	14.66	0.171	0.0131
90^oC	2.43	0.025	0.0025
	3.71	0.038	0.0039
	5.16	0.053	0.0054
	6.47	0.065	0.0069
	7.90	0.081	0.0083
	9.26	0.096	0.0098
	10.59	0.108	0.0111
	11.96	0.123	0.0126
	13.43	0.138	0.0146
	14.66	0.148	0.0153
100^oC	2.43	0.021	0.0031
	3.72	0.032	0.0048
	5.16	0.044	0.0065
	6.47	0.055	0.0082
	7.90	0.067	0.0102
	9.26	0.080	0.0117
	10.59	0.090	0.0138
	11.96	0.101	0.0156
	13.43	0.115	0.0177
	14.66	0.126	0.0187

Table 10. Solubilities of pure CO_2 and pure He in 30 wt% dendrimer in [bmim][DCA] with moisture at different feed pressures and temperatures

Temperature (^oC)	Feed pressure (bar)	CO_2 mole fraction	He mole fraction
50^oC	2.43	0.052	0.0014
	3.74	0.083	0.0023
	5.16	0.118	0.0030
	6.47	0.159	0.0037
	7.77	0.186	0.0046
	9.26	0.219	0.0054
	10.59	0.242	0.0062
	11.96	0.277	0.0070
	13.43	0.316	0.0078
	14.66	0.338	0.0086
80^oC	2.43	0.031	0.0019
	3.62	0.044	0.0029
	5.16	0.067	0.0041
	6.47	0.082	0.0050
	7.80	0.098	0.0062
	9.26	0.114	0.0071
	10.59	0.127	0.0082
	11.96	0.142	0.0093
	13.43	0.166	0.0108
	14.66	0.180	0.0115
90^oC	2.43	0.027	0.0022
	3.71	0.042	0.0034
	5.16	0.057	0.0048
	6.47	0.072	0.0059
	7.90	0.088	0.0073
	9.26	0.106	0.0085
	10.59	0.115	0.0098
	11.96	0.127	0.0110
	13.43	0.145	0.0126
	14.66	0.158	0.0137
100^oC	2.43	0.023	0.0025
	3.72	0.035	0.0038
	5.16	0.047	0.0053
	6.47	0.060	0.0068
	7.86	0.072	0.0081
	9.26	0.087	0.0093
	10.59	0.098	0.0107
	11.96	0.108	0.0121
	13.43	0.124	0.0142
	14.66	0.136	0.0149