Supporting Information for

Experimental and Theoretical Studies on Efficient Carbon Dioxide Capture using Novel Bis(3-aminopropyl)amine (APA) Activated Aqueous 2-Amino-2-methyl-1-propanol (AMP) Solutions

Bisweswar Das, Binay Deogam and Bishnupada Mandal *

Department of Chemical Engineering, Indian Institute of Technology Guwahati,

Guwahati - 781039, Assam, India.

*Corresponding author. Telephone: 91-361-2582256 (O)/2584256 (R). Fax: 91-361-2582291. Email: bpmandal@iitg.ernet.in

Table S1: Reaction scheme for the reactions of CO_2 into novel (AMP+APA+H_2O) systems

Type of Reaction	Reactions	No.
Base-catalysed hydration reaction	$CO_2 + AMP + H_2O \xleftrightarrow{K_a, k_{2a}} AMPH^+ + HCO_3^-$	1
Monocarbamate formation by APA/H_2O	$CO_2 + APA + H_2O \xleftrightarrow{K_b, k_{2b}} APACOO^- + H_3O^+$	**2**
Monocarbamate formation by AMP/APA	$CO_2 + APA + AMP \xleftrightarrow{K_c, k_{2c}} APACOO^- + AMPH^+$	**3**
Dicarbamate formation by APA/H_2O	$CO_2 + APACOO^- + H_2O \xleftrightarrow{K_d, k_{2d}} APA(COO^-)_2 + H_3O^+$	**4**
Dicarbamate formation by AMP/APACOO$^-$	$CO_2 + APACOO^- + AMP \xleftrightarrow{K_e, k_{2e}} APA(COO^-)_2 + AMPH^+$	**5**
Bicarbonate formation by direct reaction of CO_2 with H_2O	$CO_2 + 2H_2O \xleftrightarrow{K_f, k_{2f}} HCO_3^- + H_3O^+$	**6**
Formation of carbonate:	$HCO_3^- + H_2O \xleftrightarrow{K_g} CO_3^- + H_3O^+$	**7**
Protonation of APA	$APA + H_3O^+ \xleftrightarrow{K_h} APAH^+ + H_2O$	**8**
Protonation of monocarbamate formed	$APACOO^- + H_3O^+ \xleftrightarrow{K_i} H^+APACOO^- + H_2O$	**9**
Protonation of AMP	$AMP + H_3O^+ \xleftrightarrow{K_j} AMPH^+ + H_2O$	**10**
Dissociation of the water molecule	$2H_2O \xleftrightarrow{K_m} H_3O^+ + OH^-$	**11**

Where, the equilibrium constants and second-order forward rate coefficients for reactions x, y are represented as $K_{x(x=a,....m)}$ and $k_{2y(y=a,...f)}$, respectively.

In the reaction (2) the rate constant, k_{2b}, can be viewed as the global rate constant for zwitterion formation and deprotonation reactions. The reaction (4) indicates the APA-dicarbamate formation, where k_{2d} denotes global rate coefficient. The reaction (3) show the AMP catalyzed APA-carbamate formation and reaction (5) shows APA-dicarbamate production with AMP and APA carbamate.

Table S2. Density ρ and Viscosity η for APA (1) + AMP (2) + H_2O (3) at Different Molar Concentration m and Temperature T at a pressure of 0.1 MPa[a]

m_1/m_2	ρ/kgm^{-3}					
kmol·m^3	298K	303K	308K	313K	318K	323K
0/3	994.97	992.54	989.40	986.50	983.20	979.70
0.1/2.9	995.90	993.58	990.69	987.81	984.00	981.00
0.3/2.7	997.30	994.87	991.71	988.91	985.20	982.20
0.5/2.5	998.86	995.88	992.90	989.63	986.40	982.90
0.7/2.3	1000.30	996.90	994.20	991.30	987.70	983.80
0.9/2.1	1001.70	998.50	995.50	992.30	989.00	984.90
1.1/1.9	1003.20	1000.10	996.90	993.60	990.30	986.30

m_1/m_2	η/mPas					
kmol·m^3	298K	303K	308K	313K	318K	323K
0/3	3.55	2.80	2.32	1.95	1.62	1.40
0.1/2.9	3.71	2.95	2.42	2.04	1.75	1.50
0.3/2.7	3.85	3.05	2.56	2.16	1.85	1.60
0.5/2.5	4.05	3.29	2.72	2.29	1.98	1.72
0.7/2.3	4.31	3.54	2.94	2.48	2.13	1.85
0.9/2.1	4.57	3.79	3.16	2.68	2.28	1.98
1.1/1.9	4.84	4.05	3.38	2.89	2.43	2.13

[a]Standard uncertainties u are $u(T)$ = 0.25 K, $u(m)$ = 0.001 kmol·m^3 and $u(p)$ = 0.2 kPa. The combined expanded uncertainty for density measurement $U_c(\rho)$ = 3.97 kg·m^{-3} and for viscosity measurement $U_c(\eta)$ =0.058 mPa·s(95% level of confidence, k = 2). Solvent = water.

Table S3. Excess molar volume, (V^E), thermal expansion coefficient (α), viscosity deviation ($\Delta\eta$) of ternary blend X_1 APA (1) + X_2 AMP (2) + (1-X_1- X_2) H_2O (3) system at different temperature and molar concentration (*m*) (X_1, X_2= mole fraction)[a]

APA (1) + AMP (2) + H_2O (3)					
m_1/m_2 kmol·m³	X_1	X_2	V^E (cm³ mol⁻¹)	$\alpha \times 10^3$ (K⁻¹)	$\Delta\eta$ (mPa s)
T=298 K					
0/3	0.0000	0.0691	-0.3904	0.6161	-6.4297
0.1/2.9	0.0023	0.0671	-0.4219	0.6089	-6.0244
0.3/2.7	0.0070	0.0630	-0.4751	0.6149	-5.3815
0.5/2.5	0.0118	0.0589	-0.5336	0.6379	-4.6793
0.7/2.3	0.0166	0.0547	-0.5893	0.6455	-3.9039
0.9/2.1	0.0216	0.0504	-0.6461	0.6600	-3.1169
1.1/1.9	0.0266	0.0460	-0.7053	0.6676	-2.3068
T=303 K					
0/3	0.0000	0.0691	-0.3876	0.6176	-4.8607
0.1/2.9	0.0023	0.0671	-0.4220	0.6103	-4.5277
0.3/2.7	0.0070	0.0630	-0.4733	0.6164	-4.0524
0.5/2.5	0.0118	0.0589	-0.5196	0.6398	-3.4378
0.7/2.3	0.0166	0.0547	-0.5658	0.6477	-2.8032
0.9/2.1	0.0216	0.0504	-0.6280	0.6621	-2.1600
1.1/1.9	0.0266	0.0460	-0.6901	0.6696	-1.4970
T=308 K					
0/3	0.0000	0.0691	-0.3717	0.6196	-3.2603
0.1/2.9	0.0023	0.0671	-0.4123	0.6121	-3.0338
0.3/2.7	0.0070	0.0630	-0.4578	0.6183	-2.6342
0.5/2.5	0.0118	0.0589	-0.5088	0.6418	-2.2152
0.7/2.3	0.0166	0.0547	-0.5624	0.6495	-1.7291
0.9/2.1	0.0216	0.0504	-0.6179	0.6641	-1.2373
1.1/1.9	0.0266	0.0460	-0.6758	0.6718	-0.7385
T=313 K					
0/3	0.0000	0.0691	-0.3647	0.6214	-1.9140
0.1/2.9	0.0023	0.0671	-0.4062	0.6139	-1.7416
0.3/2.7	0.0070	0.0630	-0.4541	0.6201	-1.4526
0.5/2.5	0.0118	0.0589	-0.4945	0.6439	-1.1540
0.7/2.3	0.0166	0.0547	-0.5575	0.6514	-0.7907
0.9/2.1	0.0216	0.0504	-0.6064	0.6662	-0.4138
1.1/1.9	0.0266	0.0460	-0.6625	0.6740	-0.0222
T=318 K					
0/3	0.0000	0.0691	-0.3524	0.6235	-1.2080
0.1/2.9	0.0023	0.0671	-0.3821	0.6163	-1.0241
0.3/2.7	0.0070	0.0630	-0.4328	0.6224	-0.8136
0.5/2.5	0.0118	0.0589	-0.4852	0.6460	-0.5734
0.7/2.3	0.0166	0.0547	-0.5399	0.6537	-0.3100
0.9/2.1	0.0216	0.0504	-0.5966	0.6685	-0.0444
1.1/1.9	0.0266	0.0460	-0.6532	0.6763	0.2245
T=323 K					
0/3	0.0000	0.0691	-0.3379	0.6257	-0.7933
0.1/2.9	0.0023	0.0671	-0.3799	0.6181	-0.6539

0.3/2.7	0.0070	0.0630	-0.4314	0.6243	-0.4730
0.5/2.5	0.0118	0.0589	-0.4723	0.6483	-0.2726
0.7/2.3	0.0166	0.0547	-0.5178	0.6563	-0.0597
0.9/2.1	0.0216	0.0504	-0.5701	0.6712	0.1549
1.1/1.9	0.0266	0.0460	-0.6298	0.6790	0.3918

Table S4. Values of Δ*H* and Δ*S* as a function of concentration from (298 to 323) K and ΔG against APA mole fraction at 298 K.

X_1	Δ*H*, (kJ mol^{-1})	*T*Δ*S*, (kJ mol^{-1})	Δ*G*, (kJ mol^{-1})
	APA (1) + AMP (2) + H_2O (3)		
0.0000	26.623	13.424	13.199
0.0023	27.718	14.402	13.316
0.0070	26.767	13.340	13.427
0.0118	26.350	12.778	13.572
0.0166	26.079	12.335	13.744
0.0216	25.810	11.901	13.909
0.0266	25.434	11.364	14.070

Table S5. Measured Henry's constant of N_2O (H_{N_2O}) and Estimated Henry's constant of CO_2 (H_{CO_2}) in APA (1) + AMP (2) + H_2O (3) at Temperatures *T* Using the N_2O Analogy as a Function of Molar Concentration (*m*) at a pressure of 0.1 MPa[a]

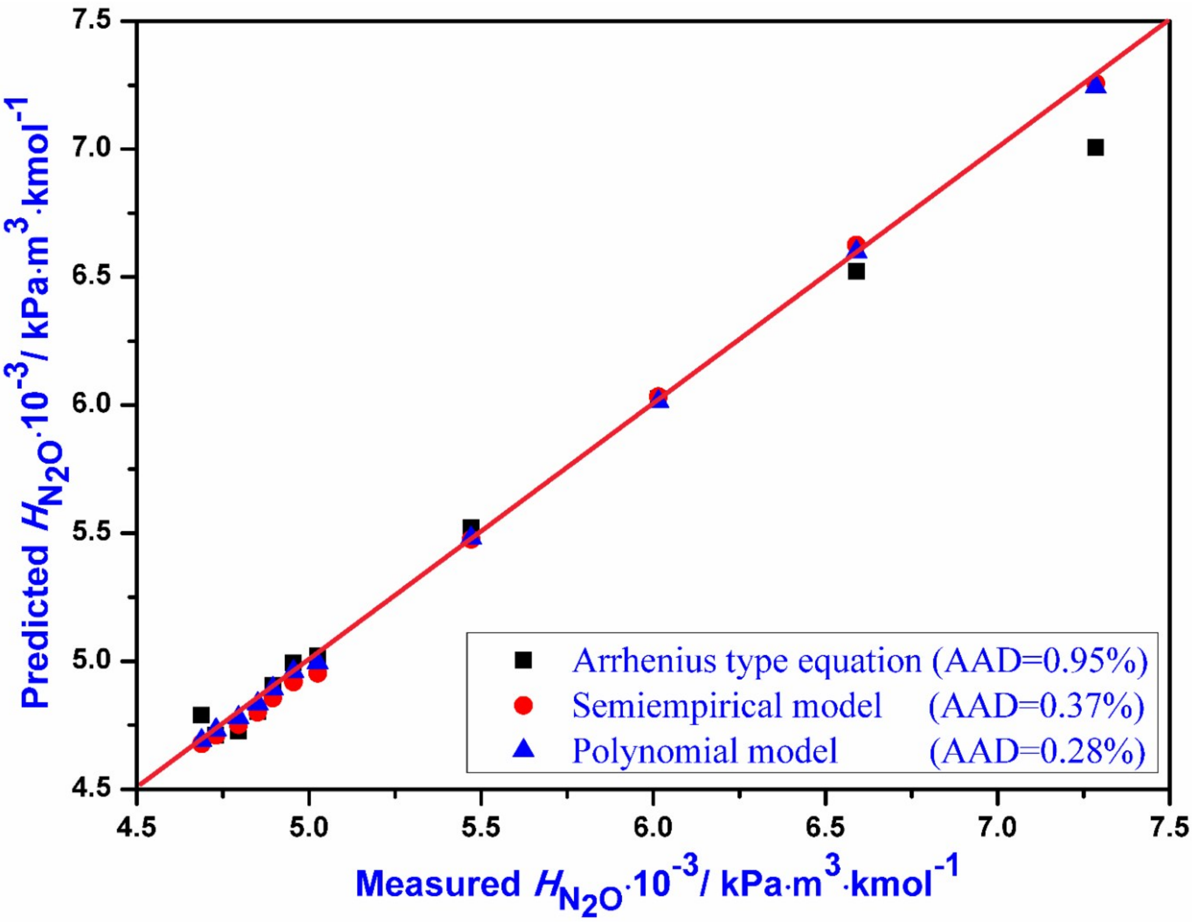
m_1/m_2	H_{N_2O} /kPa.m^3.kmol^{-1}						H_{CO_2} /kPa.m^3.kmol^{-1}					
kmol·m^3	298K	303K	308K	313K	318K	323K	298K	303K	308K	313K	318K	323K
0/3	5025	5471	6015	6590	7285	7924	3809	4140	4561	4751	5230	5626
0.1/2.9	4955	5405	5968	6550	7203	7875	3756	4090	4526	4722	5171	5591
0.3/2.7	4895	5341	5910	6487	7097	7807	3710	4041	4482	4677	5095	5543
0.5/2.5	4851	5285	5860	6405	7025	7721	3677	3999	4444	4618	5044	5482
0.7/2.3	4795	5225	5785	6345	6935	7605	3634	3953	4387	4575	4979	5400
0.9/2.1	4730	5165	5728	6310	6880	7555	3585	3908	4344	4549	4940	5364
1.1/1.9	4688	5135	5690	6272	6845	7521	3553	3885	4315	4522	4914	5340

[a]Standard uncertainties *u* are *u*(*T*) = 0.25 K, *u*(*m*) = 0.001 kmol·m^3, u(p) = 0.2 kPa. The combined expanded uncertainty for solubility measurement U_c(H_{N_2O}) = 66.5 kPa·m^3·kmol^{-1} (95% level of confidence, k = 2). Solvent = water.

Table S6. Measured Diffusivity of N_2O (D_{N_2O}) and Estimated Diffusivity of CO_2 (D_{CO_2}) in APA (1) + AMP (2) + H_2O (3) at Temperature *T* Using the N_2O Analogy as a Function of Molar Concentration (*m*) at a pressure of 0.1 MPa[a]

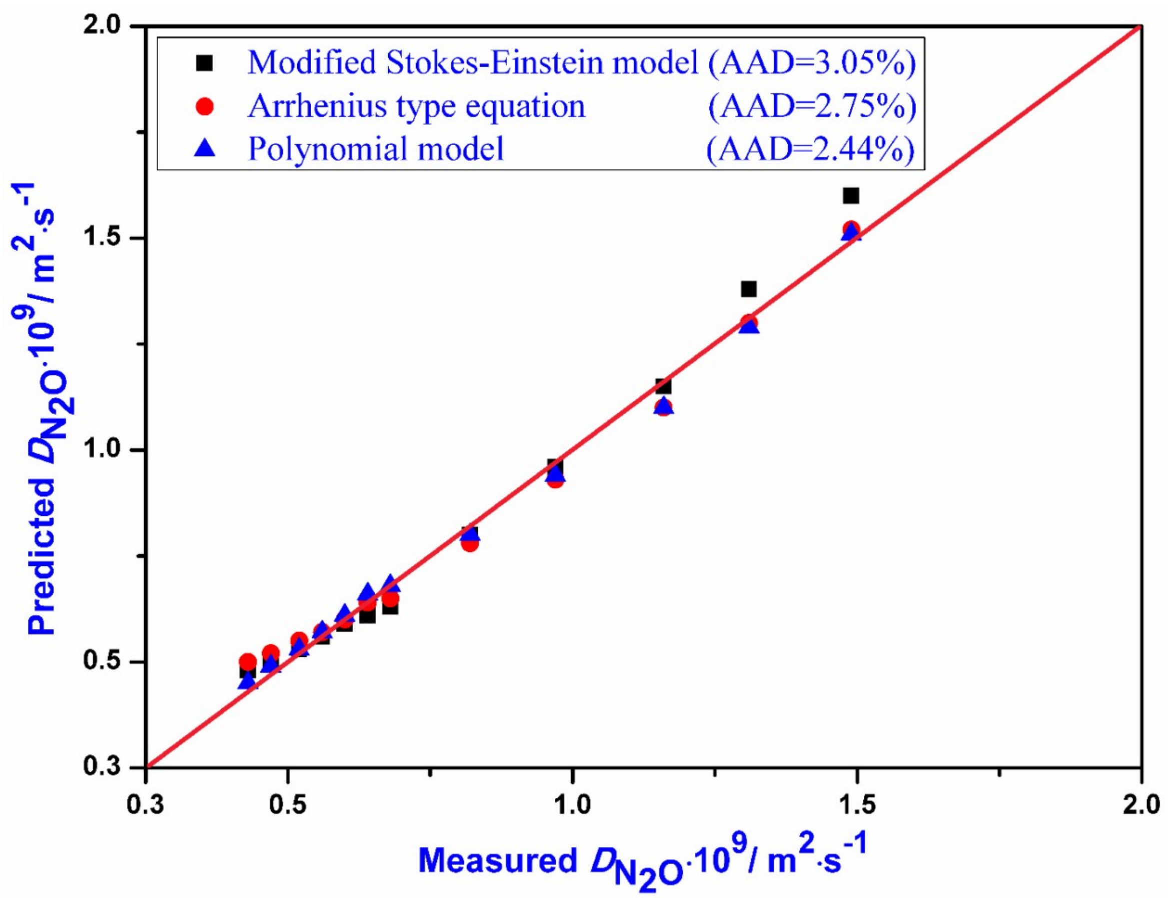
m_1/m_2	$D_{N_2O}\cdot10^9$ /m²s⁻¹						$D_{CO_2}\cdot10^9$ /m²s⁻¹					
kmol·m³	298K	303K	308K	313K	318K	323K	298K	303K	308K	313K	318K	323K
0/3	0.68	0.82	0.97	1.16	1.31	1.49	0.73	0.90	1.05	1.29	1.47	1.69
0.1/2.9	0.64	0.76	0.91	1.1	1.25	1.42	0.69	0.83	0.98	1.22	1.40	1.61
0.3/2.7	0.6	0.72	0.87	1.05	1.2	1.38	0.65	0.79	0.94	1.17	1.34	1.57
0.5/2.5	0.56	0.68	0.83	1	1.15	1.34	0.60	0.75	0.90	1.11	1.29	1.52
0.7/2.3	0.52	0.64	0.79	0.96	1.1	1.29	0.56	0.70	0.85	1.07	1.23	1.47
0.9/2.1	0.47	0.61	0.75	0.92	1.05	1.24	0.51	0.67	0.81	1.02	1.17	1.41
1.1/1.9	0.43	0.57	0.7	0.86	1	1.18	0.46	0.63	0.76	0.95	1.12	1.34

[a]Standard uncertainties *u* are *u*(*T*) = 0.25 K, *u*(*m*) = 0.001 kmol·m³and *u(p)* = 0.2 kPa. The combined expanded uncertainty for diffusivity measurement U_c(D_{N_2O}) = 19.3·10⁻¹² m²·s⁻¹(95% level of confidence, k = 2).Solvent = water.



7.5
7.0
6.5
6.0
5.5
5.0
4.5
Predicted $H_{N_2O}\cdot10^{-3}$/ kPa·m^3·kmol^{-1}
4.5
5.0
5.5
6.0
6.5
7.0
7.5
Measured $H_{N_2O}\cdot10^{-3}$/ kPa·m^3·kmol^{-1}
Arrhenius type equation (AAD=0.95%)
Semiempirical model (AAD=0.37%)
Polynomial model (AAD=0.28%)

Figure S1



Modified Stokes-Einstein model (AAD=3.05%)
Arrhenius type equation (AAD=2.75%)
Polynomial model (AAD=2.44%)
Predicted $D_{N_2O} \cdot 10^9 / m^2 \cdot s^{-1}$
Measured $D_{N_2O} \cdot 10^9 / m^2 \cdot s^{-1}$
2.0
1.5
1.0
0.5
0.3

Figure S2