Determination of the Dissociation Constants (pK_a) of Eight Amines of Importance in Carbon Capture: Computational Chemistry Calculations, and Artificial Neural Network Models

Venkata Sai Priyatham Varma Alluri, William (Hoang Chi Hieu) Nguyen and Amr Henni *

Clean Energy Technologies Research Institute (CETRi), Acid Gas Removal Laboratory (AGRL), Faculty of Engineering and Applied Science, University of Regina, Regina, SK S4S 0A2, Canada;
* Correspondence: amr.henni@uregina.ca

SUPPORTING INFORMATION

Table S1. The pH calibration values for the three buffer solutions at the experimental temperatures.

T/K	pH		
	Buffer 1 (4.00)	**Buffer 2 (7.00)**	**Buffer 3 (10.00)**
293.15	4.00 ± 0.01	7.02 ± 0.02	10.05 ± 0.02
298.15	4.00 ± 0.01	7.00 ± 0.02	10.00 ± 0.02
303.15	4.01 ± 0.01	6.99 ± 0.02	9.95 ± 0.02
308.15	4.02 ± 0.01	6.98 ± 0.02	9.91 ± 0.02
313.15	4.03 ± 0.02	6.98 ± 0.02	9.87 ± 0.03
323.15	4.06 ± 0.02	6.97 ± 002	9.81 ± 0.03

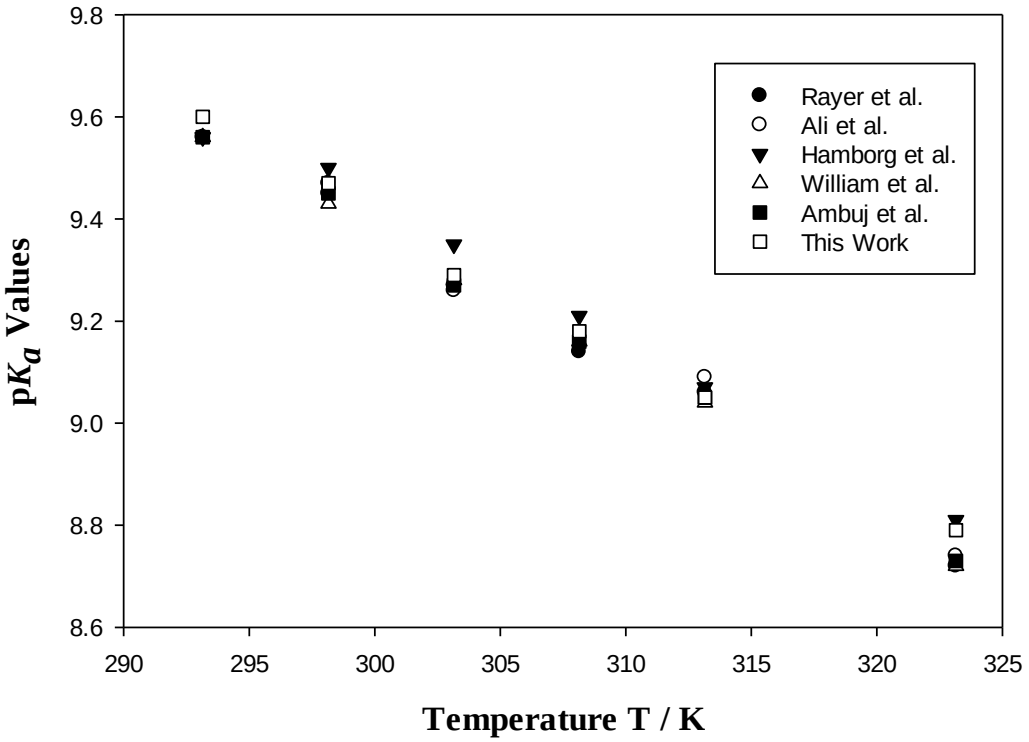

Figure S1. Dissociation constant of MEA at different temperatures: ●, Rayer et al. [14]; ○, Ali et al. [5]; ▼, Hamborg et al. [11]; Δ, Nguyen et al. [10]; ■, Ambuj et al. [9]; □, this work.

Demonstration of MEA pK_a calculation process

Initially, 50 mL of the aqueous MEA (0.010091 M) was added to the storing beaker.

In Table S2, [MEA] and [MEA+] stand for the concentrations of neutral and protonated MEA, respectively. The volume of the solution is the same for the two species; therefore, the ratio between the two will cancel out the volume. As a result, the ratio of the two

concentrations is equal to the ratio of the moles of the two components. In addition, HCl acid is assumed to completely react with the amine to generate the protonated amine. Therefore, the number of moles of protonated amine equals the number of added HCl.

Table S2. Recorded pH and calculated pK_a values of MEA before thermodynamic correction (TC) at 298.15 K.

[MEA]	Total Added HCl	[MEAH+]	pH	$\frac{[MEAH^+]}{[MEA]}$	Log($\frac{[MEAH^+]}{[MEA]}$)	pK_a^M
0.00050	0	0	10.77			
0.00045	0.5	0.00005	10.39	0.11	-0.95861	9.43
0.00040	1	0.0001	10.11	0.24719	-0.60697	9.50
0.00035	1.5	0.00015	9.9	0.42308	-0.37358	9.53
0.00030	2	0.0002	9.71	0.65672	-0.18262	9.53
0.00025	2.5	0.00025	9.54	0.98214	-0.00783	9.53
0.00020	3	0.0003	9.36	1.46667	0.16633	9.53
0.00015	3.5	0.00035	9.17	2.26471	0.35501	9.53
0.00010	4	0.0004	8.92	3.82609	0.58275	9.50
0.00005	4.5	0.00045	8.57	8.25	0.91645	9.49
0.00000	5	0.0005	7.32	110	2.04139	9.36

The remaining moles of neutral amine can be calculated by subtracting the number of moles of protonated amine from the initial values of the amine mole numbers.

The following steps are used to determine the thermodynamic corrections.

$\{MEAH^+\} = 10^{(pH - 14.004)} = 10^{(10.11 - 14.004)} = 1.276x10^{-4}$

$I_{initial} = \frac{[HCl]*[V_{HCl}]}{[V_{amine\ solution}+V_{HCl}]} + \{MEAH^+\} = \frac{0.1*1}{[50+1]} + 1.276x10^{-4} = 2.0884x10^{-3}$

$\gamma_{BH+} = \frac{1}{10^{(\frac{Az^2\sqrt{I_{initial}}}{1+Bk_i\sqrt{I_{initial}}})}} = \frac{1}{10^{(\frac{0.5092\sqrt{0.0020884}}{1+0.3286*4.5\sqrt{0.0020884}})}} = 0.95105$

The values of A and B are 0.5092 and 0.3286 x 10^8, as determined in the literature [16], at 298.15 K, while the value of k_i is 4.5 x 10^{-8}, as per the literature [17].

$[MEAH^+] = \frac{\{MEAH+\}}{\gamma BH+} = \frac{1.276x10^{-4}}{0.95105} = 1.3417x10^{-4}$

$I_{true} = \frac{[HCl]*[V_{HCl}]}{[V_{amine\ solution}+V_{HCl}]} + [MEAH^+] = \frac{0.1*1}{[50+1]} + 1.3417x10^{-4} = 2.09495x10^{-3}$

Thermodynamic Correction TC = $\frac{Az^2\sqrt{I_{true}}}{1+Bk_i\sqrt{I_{true}}} = \frac{0.5092\sqrt{0.00209495}}{1+0.3286*4.5\sqrt{0.00209495}} = 0.02$

$pK_a = pK_a^M - TC = 9.43 - 0.02 = 9.41$

By subtracting the thermodynamic correction from the dissociation constant before TC, the true values of the dissociation constant can be obtained. Table S3 shows the values of pK_a before and after the correction for MEA at 298.15 K.

Table S3. Detailed dissociation constant values before and after thermodynamic corrections (TC).

[MEA]	Total Added HCl (mL)	[MEAH+]	pH	$\frac{[MEAH^+]}{[MEA]}$	$\log(\frac{[MEAH^+]}{[MEA]})$	pK_a^M	Thermodynamic Correction	pK_a After TC
0.00050	0	0	10.77					
0.00045	0.5	0.00005	10.39	0.11	-0.95861	9.43	0.02	9.41
0.00040	1	0.0001	10.11	0.24719	-0.60697	9.50	0.02	9.48
0.00035	1.5	0.00015	9.9	0.42308	-0.37358	9.53	0.03	9.50
0.00030	2	0.0002	9.71	0.65672	-0.18262	9.53	0.03	9.50
0.00025	2.5	0.00025	9.54	0.98214	-0.00783	9.53	0.03	9.50
0.00020	3	0.0003	9.36	1.46667	0.16633	9.53	0.03	9.50
0.00015	3.5	0.00035	9.17	2.26471	0.35501	9.53	0.04	9.49
0.00010	4	0.0004	8.92	3.82609	0.58275	9.50	0.04	9.46
0.00005	4.5	0.00045	8.57	8.25	0.91645	9.49	0.04	9.45
5.9E-07	5	0.0005	4.12	848.3333	2.9286	7.05		

Table S4. Variations of the first pK_a of MEA and the eight amines studied with temperature (T/K).

Amine	Temperature T/K					
	293.15	**298.15**	**303.15**	**308.15**	**313.15**	**323.15**
3-(Diethylamino) propylamine (DEAPA)	10.58	10.44	10.3	10.15	10.03	9.83
1,3-Diaminopentane (EP)	10.56	10.38	10.23	10.07	9.92	9.7
3-Butoxypropylamine (BPA)	10.04	9.9	9.74	9.59	9.43	9.18
2-(Methylamino) ethanol (MAE)	9.91	9.84	9.7	9.54	9.4	9.22
Bis(2-methoxyethyl) amine (BMOA)	8.69	8.62	8.51	8.37	8.25	8.07
α-Methylbenzylamine	9.5	9.37	9.17	8.94	8.83	8.57
2-Aminoheptane (AH)	10.71	10.53	10.24	9.99	9.24	8.65
3-Amino-1-phenylbutane (APB)	10.42	10.19	9.98	9.79	9.61	9.34
MEA [This Study]	9.60	9.47	9.29	9.18	9.05	8.79
MEA [14]	9.56	9.45	9.27	9.14	9.06	8.72
MEA [15]		9.47	9.26		9.09	8.74
MEA [11]	9.56	9.50	9.35	9.21	9.07	8.81
MEA [10]	9.56	9.43	9.28	9.16	9.04	8.72
MEA [9]	9.56	9.45	9.27	9.16	9.05	8.73

Standard uncertainties: u(pK_a) = 0.03 and u(T) = 0.01K (0.95 level of confidence).

Table S5. Second dissociation constants for diamines at different temperatures.

Amine	Temperature T/K					
	293.15	298.15	303.15	308.15	313.15	323.15
3-(Diethylamino) Propylamine	8.42	8.24	8.06	7.91	7.73	7.52
1,3-Diaminopentane	8.36	8.17	8.06	7.86	7.69	7.4

Standard uncertainties: u(pK_a) = 0.02 and u(T) = 0.01K (0.95 level of confidence).

Table S6. Coefficients of determination (R^2) of the linear regression for Figures 1 and 2.

Amines	R^2	
	pK_{a1}	pK_{a2}
3-(Diethylamino) Propylamine	0.9965	0.9934
1,3-Diaminopentane	0.9960	0.9967
3-Butoxypropylamine	0.9990	
2-(methylamino) Ethanol	0.9886	
Bis(2-methoxyethyl) Amine	0.9922	
α-Methylbenzylamine	0.9899	
2-Aminoheptane	0.9577	
3-Amino-1-PhenylButane	0.9939	

Table S7. Based and shift values for PDS and QSSR methods.

		Perrin-Dempsey-Serjeant [16]	Sumon et al. [17]	QSSG et al. [18]
Based Value	Primary Amino	10.77	10.60	10.60
	Secondary Amino	11.15	11.10	10.80
	Tertiary Amino	10.5	10.60	10.60
pK_a Shift (ΔpK_a)	CH_3 on Tertiary Amino	-0.2	-0.2	-0.2
	CH_3 on Primary/Secondary Amino	-0.2	-0.2	0
	β NH_2	-0.8	-0.9	-0.9
	β OH	-1.1	-1.0	-1.0
	β OR	-1.2	-1.4	-1.3
	β NHR/NR_2	-0.9	-1.0	-0.8/-1.0
	γ Group	0.4*β group	0.4*β group	0.6*β group
	δ Group	0.4*γ group	0.4*γ group	0.6* γ group

ε Group	0	0	0.6* γ group
Ring Effect	0.2	0	0.2
Two Equivalent N sites	0.3	0.3	0.3
β – $CH(CH_3)_2$	-	-	-0.3
β – $C(CH_3)3$	-	-	-0.45
Solvent Effects $(CH_2CH_2OH)_2$	-	-	0.3
Solvent Effects $(CH_2CH_2OH)3$	-	-	0.6
Steric Effects of Cyclic Tertiary Amine	-	-	-0.5
Intramolecular H Bonding	-	-	0.2

Table S8. Gibbs free energy of proton on gas phase at the various temperatures.

Temperature /K	$G^0_{gas}(H^+)$ kcal·mol^{-1}
293.15	-25.77
298.15	-26.30
303.15	-26.84
308.15	-27.38
313.15	-27.91
323.15	-29.00

Table S9. List of chemicals and collected data for ANN model.

Chemicals	Abbreviation	CAS Number	Temperature K	Data Points	Reference
Methyldiethanolamine	MDEA	105-59-9	298.15 - 313.15	32	[26,27]
Monoethanolamine	MEA	141-43-5	298.15-323.15	45	[28–31]
1-amino-2-propanol	MIPA	78-96-6	298.15 - 313.15	24	[12,32]
Dimethylpropanolamine	DMPA	3179-63-3	298.15 - 313.15	24	[14,33]
2-(Methylamino)ethanol	MAE	109-83-1	298.15 - 313.15	24	[34,35]
2-amino-2-methyl-1-propanol	AMP	124-68-5	298.15 - 313.15	24	[35–37]
Diethanolamine	DEA	111-42-2	298.15 - 313.15	32	[38–41]
Triethanolamine	TEA	102-71-6	298.15 - 313.15	24	[42–44]
3-amino-1-propanol	3AP	105-87-6	298.15 - 313.15	24	[45,46]
N, N-Dimethylethanolamine	DMEA	108-01-0	298.15 - 313.15	16	[47–49]
Ethyldiethanolamine	EDEA	139-87-7	298.15	8	[14,49]
2-(Ethylamino)ethanol	EMEA	110-73-6	298.15	8	[14,50,51]
Diethylethanolamine	DEEA	100-37-8	298.15	8	[14,30,52]
Butylamine	BA	109-73-9	298.15	8	[53–55]
Tert-butylamine	tert-BA	75-64-9	298.15	8	[56,57]
3-(Dimethylamino)-1-Propylamine	DMAPA	109-55-7	298.15	8	[33,58,59]
N-(2-Aminoehtyl)-1,3-Propanediamine	n-2AOE13PDA	13531-52-7	298.15-313.15	28	[60]
Bis[2-(N,N-Dimethylamino)ethyl]ether	2DMAOEE	3033-62-3	298.15-313.15	28	[60]
N, N-Dimethyldipropylenetriamine	e(MDAPAPA)	10563-29-8	298.15-313.15	28	[60]
3,3'-Diamino-N-methyldipropylamine	DAOMDPA	105-83-9	298.15-313.15	28	[60]
2-[2-(Dimethylamino)ethoxy]ethanol	DMAOEOE	1704-62-7	298.15-313.15	28	[60]
2-(Dibutylamino)ethanol	DBEA	102-81-8	298.15-313.15	28	[60]

N-Propylethanolamine	PEA	16369-21-4	298.15-313.15	28	[60]
3-(Dimethylamino) propylamine		104-78-9	298.15-323.15	45	This Work
1,3-Diaminopentane		589-37-7	298.15-323.15	45	
3-Butoxypropylamine		16499-88-0	298.15-323.15	45	
2-(Methylamino)ethanol		109-83-1	298.15-323.16	45	
Bis(2-methoxyethyl)amine		111-95-5	298.15-323.16	45	
α-Methylbenzylamine		618-36-0	298.15-323.16	45	
2-Aminoheptane		123-82-0	298.15-323.16	45	
3-Amino-1-phenulbutane		22374-89-6	298.15-323.16	45	

Table S10. Density (g·cm^{-3}) of MEA and the studied amines.

Chemicals	Temperature /K				
	298.15	**303.15**	**308.15**	**313.15**	**323.15**
Monoethanolamine [61]	1.01260	1.01063	1.00670	1.00040	0.99861
Monoethanolamine [62]		1.00874		1.00077	0.99275
Monoethanolamine [this work]	1.01259	1.09712	1.00681	1.00061	0.99683
3-(Diethylamino) Propylamine	0.82318	0.8189	0.81463	0.81036	0.80179
1,3-Diaminopentane	0.8571	0.85285	0.84859	0.84433	0.83576
3-Butoxypropylamine	0.84626	0.84188	0.83749	0.8331	0.82426
2-(methylamino) Ethanol	0.93651	0.93263	0.92872	0.92479	0.91687
Bis(2-methoxyethyl) Amine	0.91113	0.90664	0.90214	0.89762	0.88857
α-Methylbenzylamine	0.95294	0.94864	0.94432	0.93999	0.93128
2-Aminoheptane	0.76062	0.75643	0.75221	0.74797	0.73946
3-Amino-1-PhenylButane	0.92301	0.91898	0.91501	0.91104	0.90305

Table S11. Dynamic viscosity (cP) of MEA and the studied amines.

Chemicals	Temperature (K)				
	298.15	**303.15**	**308.15**	**313.15**	**323.15**
Monoethanolamine [63]	18.924	15.151		10.006	6.962
Monoethanolamine [62]		14.956		9.839	6.902
Monoethanolamine [this work]	18.919	15.135	12.85	9.993	6.921
3-(Diethylamino) Propylamine	1.12	1.01	0.928	0.851	0.726
1,3-Diaminopentane	1.9	1.69	1.52	1.28	1.06
3-Butoxypropylamine	1.5	1.31	1.19	1.09	0.924
2-(methylamino) Ethanol	10.63	8.57	7.06	6.06	4.34
Bis(2-methoxyethyl) Amine	1.15	1.07	0.994	0.922	0.783
α-Methylbenzylamine	1.89	1.69	1.44	1.311	1.09
2-Aminoheptane	0.821	0.752	0.699	0.646	0.563
3-Amino-1-PhenylButane	2.66	2.35	2.1	1.88	1.55

Table S12. Refractive index of MEA and the studied amines.

Chemical	Temperature (K)				
	298.15	**303.15**	**308.15**	**313.15**	**323.15**
Monoethanolamine [62]		1.44880		1.44490	1.44170
Monoethanolamine [this work]	1.45350	1.45190	1.45050	1.44460	1.43980
3-(Diethylamino) Propylamine	1.43999	1.43787	1.43567	1.43335	1.42868
1,3-Diaminopentane	1.45042	1.44808	1.44572	1.44344	1.43876
3-Butoxypropylamine	1.42474	1.42247	1.42018	1.41789	1.41322
2-(methylamino) Ethanol	1.43701	1.43513	1.43303	1.43099	1.42719
Bis(2-methoxyethyl) Amine	1.41821	1.41605	1.41394	1.41176	1.40739
α-Methylbenzylamine	1.52412	1.52151	1.51917	1.51659	1.51161
2-Aminoheptane	1.41633	1.41407	1.41175	1.40930	1.40430
3-Amino-1-PhenylButane	1.51126	1.50865	1.50668	1.50483	1.50003
Water	1.33220	1.33170	1.33150	1.33040	1.32880
Water [64]	1.33230	1.33180	1.33120	1.33050	1.32890

Table S13. Sound velocity ($m \cdot s^{-1}$) of MEA and the studied amines.

Chemical	Temperature (K)				
	298.15	**303.15**	**308.15**	**313.15**	**323.15**
Monoethanolamine [61]	1724.13	1733.24	1742.59	1751.28	1760.21
Monoethanolamine [this work]	1718.27	1702.06	1686.19	1670.45	1638.65
3-(Diethylamino) Propylamine	1343.68	1333.49	1320.88	1305.47	1277.5
1,3-Diaminopentane	1491.65	1472.99	1453.88	1435.04	1395.53
3-Butoxypropylamine	1331.75	1317.35	1302.46	1288.15	1257.7
2-(methylamino) Ethanol	1469.59	1455.97	1440.54	1425.15	1396.37
Bis(2-methoxyethyl) Amine	1273.78	1259.39	1244.3	1234.62	1202.62
α-Methylbenzylamine	1482.89	1473.81	1461.42	1446.26	1411.66
2-Aminoheptane	1277.4	1271.53	1257.26	1240.32	1199.32
3-Amino-1-PhenylButane	1555.62	1538.69	1520.93	1502.51	1465.26

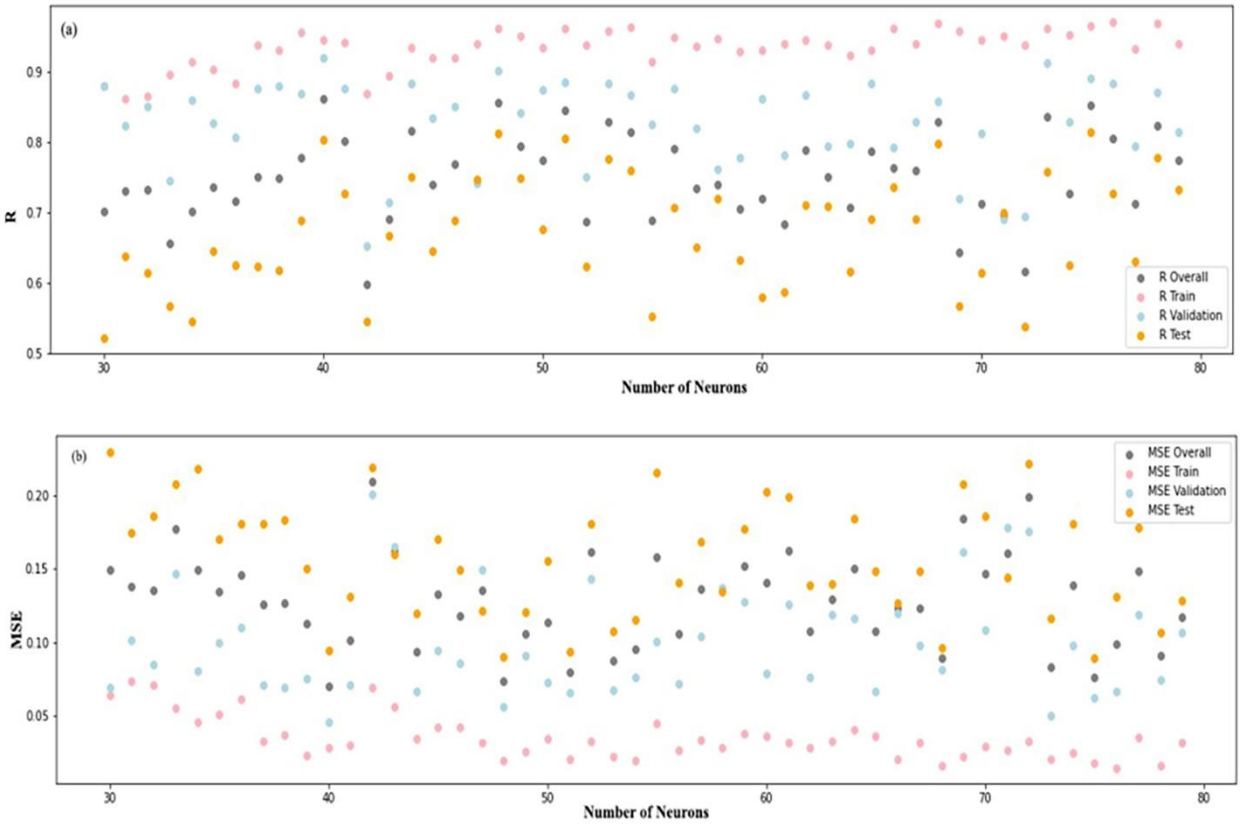

Figure S2. Performance of the ANN model with one hidden layer with the number of neurons from 30 to 80. (a) R; (b) MSE.

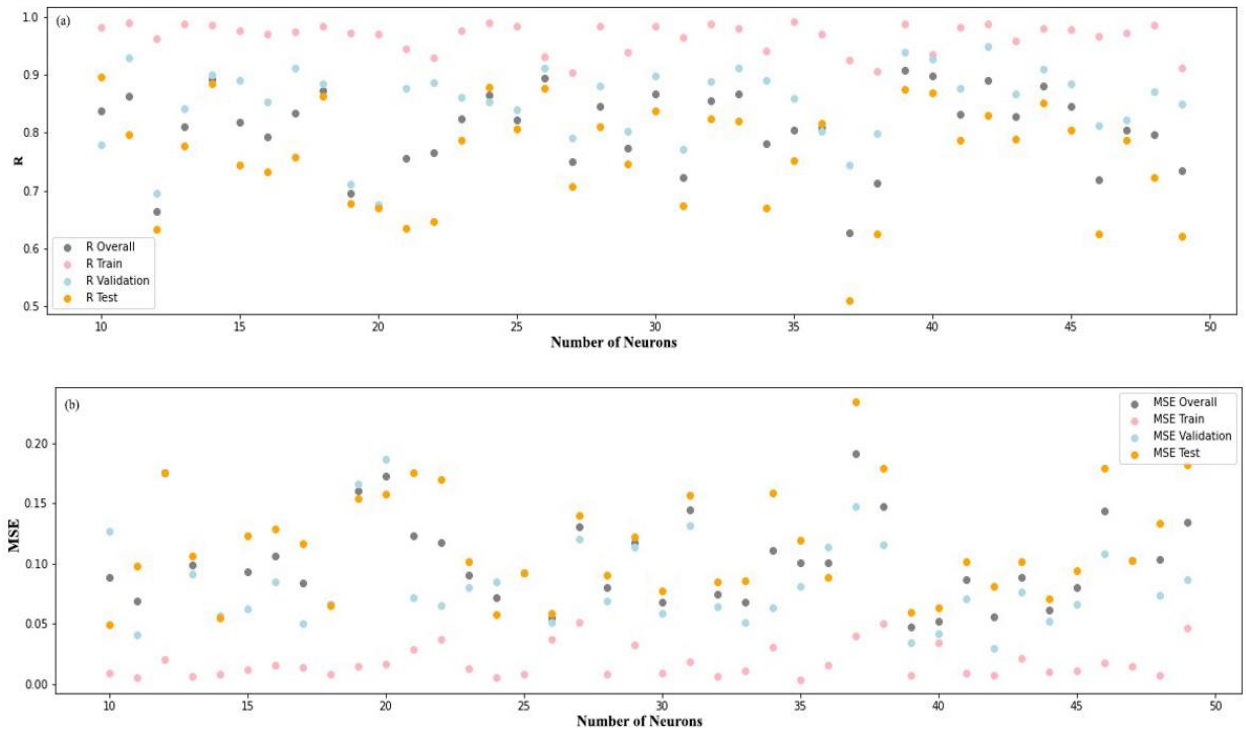

Figure S3. Performance of the ANN model with two hidden layers with the number of neurons on the second layer varying from 10 to 50. (a) R; (b) MSE.

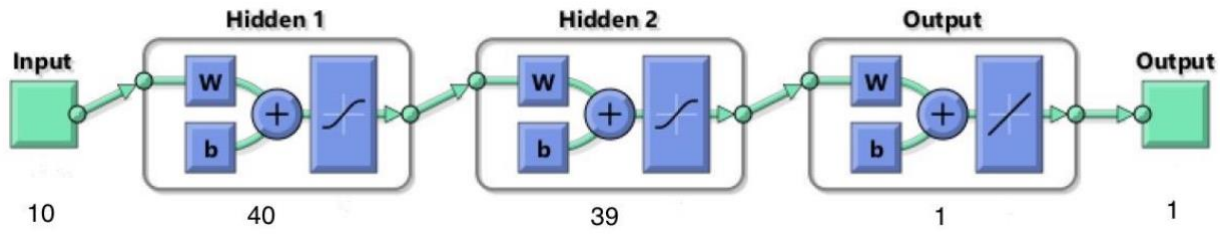

Figure S4. Completed ANN architectural diagram for estimating dissociation constants.

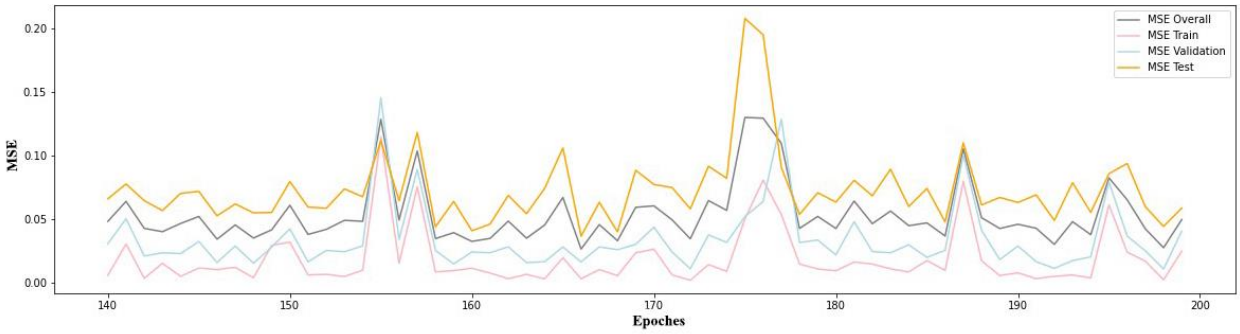

Figure S5. Performance of the ANN model with various numbers of epochs.

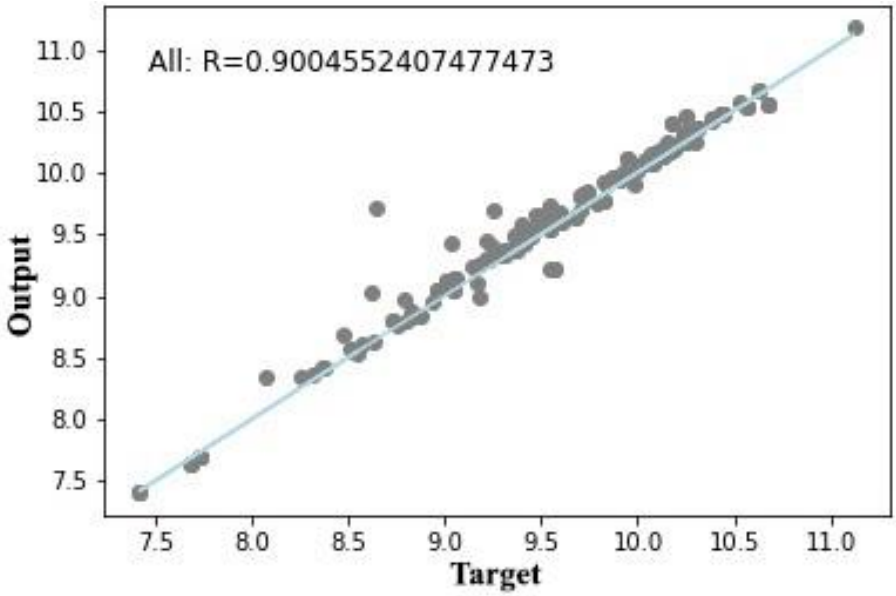

Figure S6. Parity plot for the output and target pK_a values.

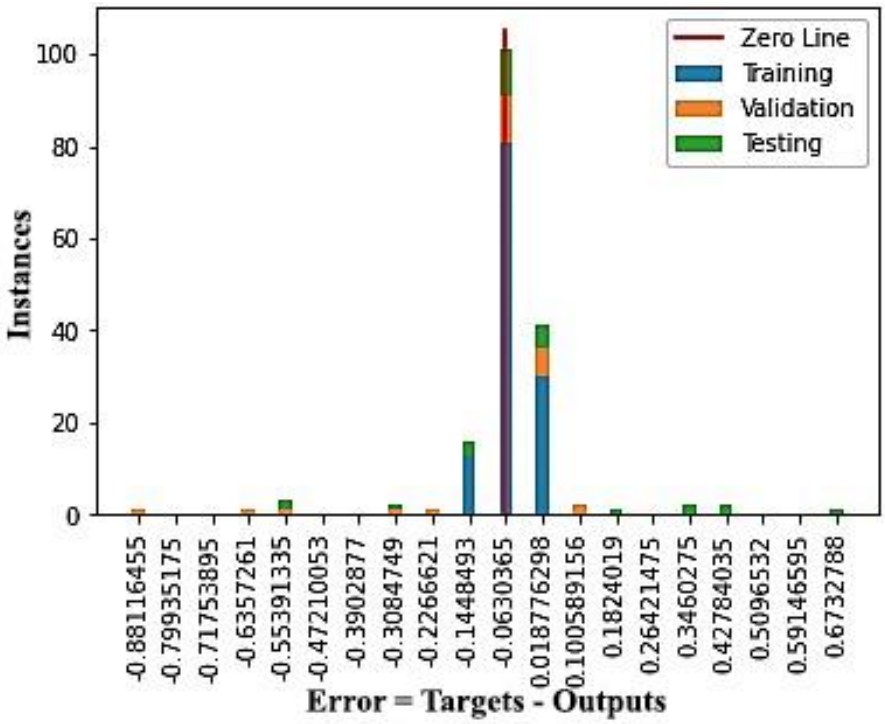

Figure S7. Error histogram of the ANN model.

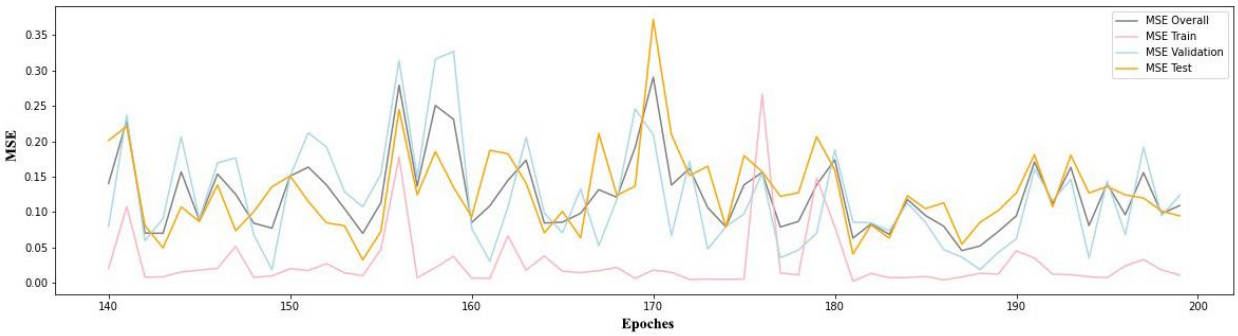

Figure S8. Performance of the reduced ANN model with various epochs.

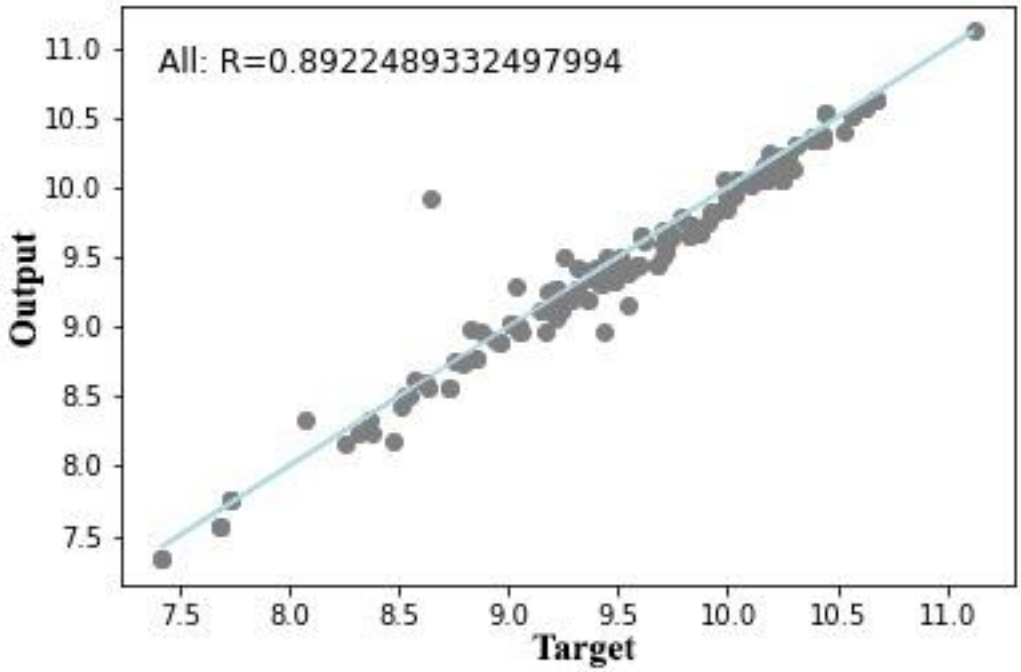

Figure S9. Parity plot between the estimated and experimental values of the reduced ANN model.

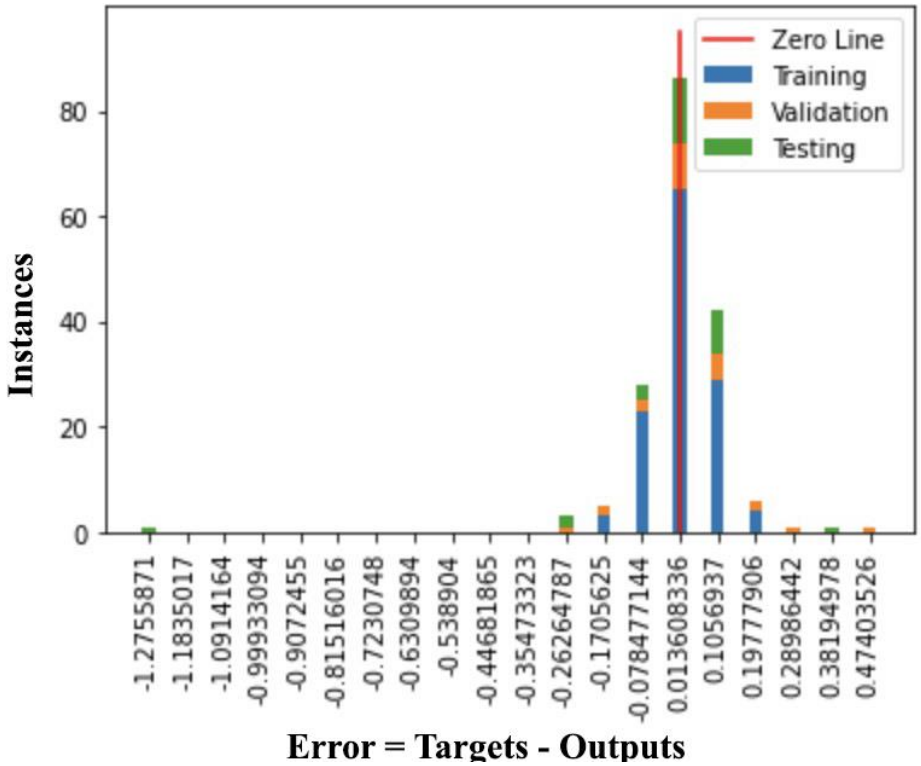

Figure S10. Error histogram of the reduced ANN model.

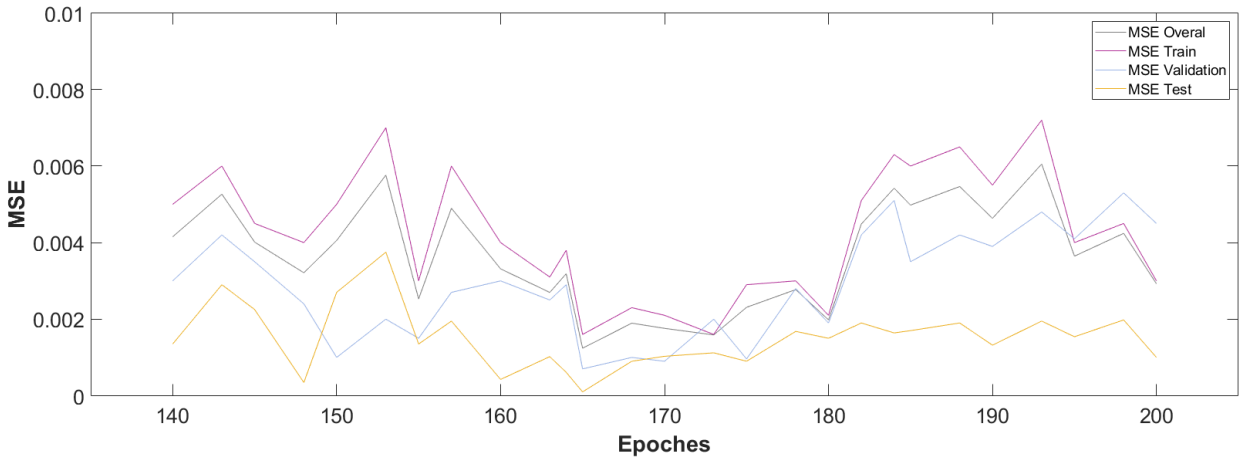

Figure S11. Performance of the simulated ANN model with various epochs.

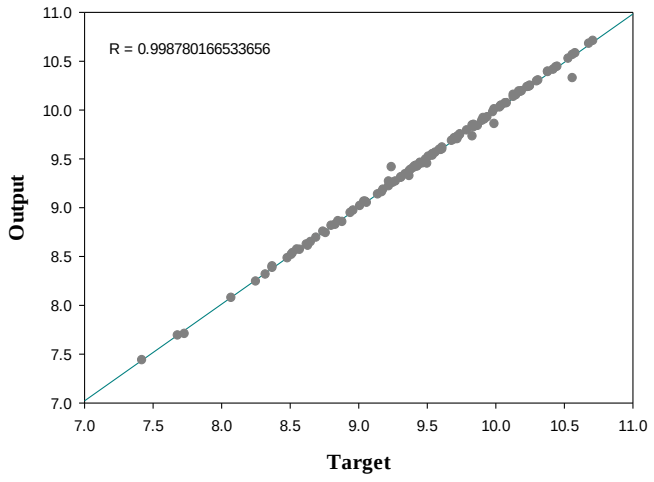

Figure S12. Parity plot between the estimated and experimental values of the simulated ANN model.

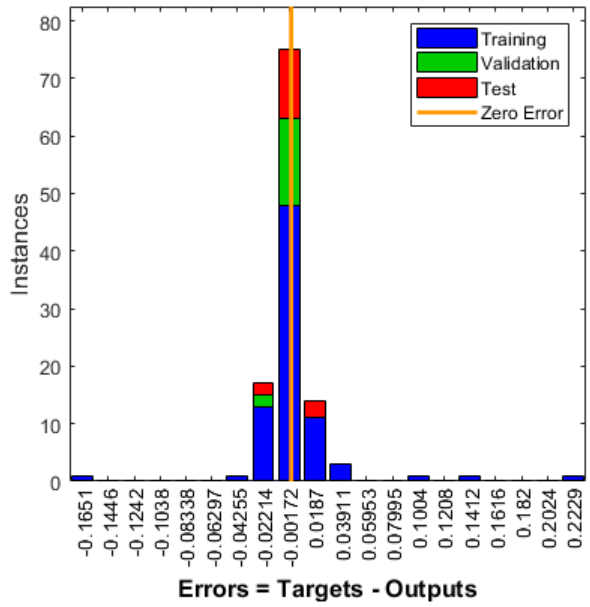

Figure S13. Error histogram of the simulated ANN model.