

Dissociation constants of eight amines: Experimental measurements and modeling

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Keywords

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In this study, the dissociation constants of the eight amines, namely, N-(2-aminoethyl)-1,3-propanediamine, 2-methylpentamethylene diamine, N, n-dimethyldipropylene-triamine, 3,3'-Diamino-n-methyldipropylamine, Bis[2-(n, n-dimethylamino) ethyl]ether, 2-[2-(Dimethylamino) ethoxy] Ethanol, 2-(dibutylamino) Ethanol and N-propylethanolamine were determined from 298.15 K to 313.15 K. Using the van't Hoff equation, thermodynamic properties such as the standard state changes of enthalpy, entropy and Gibbs free energy were calculated. Using computational chemistry calculations, the amino group protonated first was predicted. Furthermore, computer free group contribution methods such as the original Perrin-Dempsey-Serjeant (PDS), the modified PDS and the Qian-Sun-Sun-Gao (QSSG) model were used to estimate the dissociation constants of the studied amines. In these methods, the QSSG provided the most accurate results as the database used in this method was updated with additional the functional groups as well as information about group positions. Finally, an artificial neural network was used to predict the pKa values.

1 | INTRODUCTION

Consuming petroleum products, coal and natural gas for human activities releases carbon dioxide (CO_2) into the atmosphere which is considered one of the reasons for global warming.¹ Among the CO_2 capture technologies, the aqueous amine solutions have been commonly used as the amine solution can react quickly with CO_2 , with lower costs than ionic liquids or solid sorbents. Mixtures of aqueous amine solutions are commercially used to capture CO_2 in steel production, cement and thermal power plants. The reaction mechanisms between CO_2 and amine solutions are different for different types of amines.² The study of the protonation between CO_2 and amines is important to explain the reaction mechanisms.³

The dissociation constants ($\text{p}K_a$) of many alkanolamines were measured by Perrin⁴ while additional alkanolamines and cyclic amine dissociation constants were reported by Tomizaki et al.⁵ and Chowdhury et al.⁶ The relationship between the dissociation constants and the reaction kinetics were reported by Versteeg et al.⁷ and Sharma.⁸ Nguyen and Henni⁹ reported the $\text{p}K_a$ of four polyamines namely 1,4-Bis(3-aminopropyl) piperazine, 1,3-Bis(aminomethyl) cyclohexane, Tris(2-aminoethyl) amine, and 1-Amino-4-methyl piperazine while Kumar et al.¹⁰ reported the values for 2-(Butylamino)ethanol, m-Xylylenediamine, 3-Picolylamine, Isopentylamine, and 4-(Aminoethyl)-piperidine. Furthermore, the amines' chemical and biological behaviors are determined by dissociation constants.⁹⁻¹²

The methods used to measure the dissociation constants include ultraviolet spectro-photometry, conductimetric titration, potentiometric titration and magnetic resonance.¹³ In these techniques, the potentiometric titration method is commonly used as the method is simple and convenient in the pH range between 2 to 11.¹³⁻¹⁵ Consequently, this method was used to determine the dissociation constants of Methyl-diethanolamine (MDEA), N-(2-aminoethyl)-1,3-propanediamine (n-2AOE13PDA), 2-Methylpentamethylene diamine (2-MPMDA), N, n-dimethyldipropylenetriamine (DMPAPA), 3,3'-Diamino-n-methyldipropylamine (DAOMDPA), Bis[2-(n,n-dimethylamino)ethyl]ether (2DMAOEE), 2-[2-(Dimethylamino)ethoxy]ethanol (DMAOEOE), 2-(Dibutylamino)ethanol (DBEA) and N-propylethanolamine (PEA) in the temperature range of 298.15 K to 313.15 K with 5 K increment. Measurement for Methyl-diethanolamine (MDEA) was done for validation purposes. The compound structures, suppliers, and purities are listed in Table S1 in the Supporting Information section.

As observed in Table S1, the nine amines studied included three triamines, two diamines and four monoamines. The monoamines include three tertiary amines which theoretically have lower heat of reaction with CO_2 than primary and secondary amines; however, the reaction rate is slower than with primary and secondary amines. Instead of measuring the kinetic between the amines with CO_2 , a difficult task, dissociation constants of these amines can be more easily be determined. Furthermore, the thermodynamic properties from the study can be used for solubility modeling. The rest of the amines in the study are polyamines which can absorb more CO_2 than monoamines. Therefore, it is important to measure their dissociation constants to ensure the reaction rate between the amines and CO_2 is of interest to the industry.

2 | CHEMICALS AND APPARATUS

All the nine amines of Methyl-diethanolamine (MDEA) ([?]99% in mass purity), N-(2-aminoethyl)-1,3-Propanediamine (n-2AOE13PDA) (97% in mass purity), 2-Methyl-pentamethylene diamine (2-MPMDA) (99% in mass purity), N,n-dimethyldipropylenetriamine (DMPAPA) (99% in mass purity), 3,3'-Diamino-n-methyldipropylamine (DAOMDPA) (96% in mass purity), Bis[2-(n,n-dimethylamino)ethyl]ether (2DMAOEE) (97% mass purity), 2-[2-Dimethylamino)ethoxy]ethanol (DMAOEOE) (98% mass purity), 2-(Dibutylamino)ethanol (DBEA) (99% mass purity) and N-propylethanolamine (PEA) (98% mass purity) were purchased from Sigma Aldrich Canada.

A Denver Instrument pH meter model 270 was used to measure the pH values of the amine solutions for the different temperatures at each titration step. The pH meter was calibrated with three pH buffer solutions purchased from VWR International. Buffer solutions at pH of 10.00, 7.00 and 4.00 were used. The uncertainties reported by the manufacturer for the buffer solutions were 0.02, 0.01 and 0.01 for pHs of 10.00, 7.00 and 4.00, respectively. The calibration information of the meter is reported in Table S2 in the SI section.

The equipment and experimental procedures were validated by determining the pK_a of Methyldiethanolamine (MDEA) and compared with the works in the literature.¹⁴⁻¹⁶ Table S3 is the validation comparison of MDEA in this study with data published in the literature. Note that the pH meter memory could only store three values around 10.00, 7.00 and 4.00, and therefore the reading would not very accurate if the pH values were much lower than 4.00 or higher than 10.0. pH values were therefore reported within 1.5 pH unit around the calibration values would be considered accurate enough for the study. Dissociation constants with pH values over 11.5 or under 2.5 were not be reported in the study.

Hydrochloric acid (HCl) was purchased from VWR International with a concentration of 0.100 M (± 0.002 M). The cylinder gas of nitrogen (N_2) with 99.99% purity was purchased from Praxair for flushing the space on the top of the amine solution to replace CO_2 and O_2 gases in the atmosphere. A water bath was used to control the experimental temperature by pumping water through a glass beaker that stores the amine. The uncertainty of the temperature was 0.01K. The aqueous amine solutions were mixed with the concentration of 0.01000 M (± 0.00002 M) for at least 10 minutes before starting the experiments.

Initially, 50 mL of the solutions were filled into the storing beaker with a stirring magnetic bar (30 rpm) until vapour-liquid equilibrium was reached. The beaker was always closed to avoid oxidization and vaporization. The initial pH values of each solution were recorded. For each step in the titration process, 0.5 mL of hydrochloric acid was added to the aqueous solutions while stirred at a moderate speed. After 20 to 30 seconds, the pH values were recorded when values became stable.

3 | CALCULATION OF DISSOCIATION CONSTANTS (pK_a)

As mentioned, the potentiometric titration method was used in this study for determining the dissociation constants of MDEA and the other amines. The suggested protonated mechanism of MDEA is reported in Equation 1. Equation 2 is used for calculating the dissociation constants before any thermodynamic correction.⁹



$$pK_a^M = pH + \log \left(\frac{MDEA^+}{MDEA} \right) \quad (2)$$

The details of calculating the dissociation constants as well as the thermodynamic corrections are in the Supporting Information section with the values of A and B taken from the literature.¹⁷ In Equation 3, the ionic strength (I) is a function of the molecular concentration of ionization species (C_i) in the solution and the valency of species (z_i). In Equation 4, the ionic strength is used to determine the extended Debye-Huckel activity coefficient (γ) and k_i is an adjustable parameter. This parameter depends on the ion size and its value was reported in the literature¹⁸ while Equation 5 is used to determine the true protonated amine concentration.

$$I = 0.5 \sum C_i z_i^2 \quad (3)$$

$$\gamma_i = 10^{-\frac{A z_i^2 \sqrt{I}}{1 + B k_i \sqrt{I}}} \quad (4)$$

$$[MDEAH^+] = \frac{\{MDEAH^+\}}{\gamma_i} \quad (5)$$

For the first dissociation constant values, the value of ionic strength (I) can be simply determined as in the example of MDEA reported in the SI section. However, the ionic strength (I) for the second dissociation constant can be calculated by the method of Albert et al.¹³ as reported in detail in the SI section of the literature.⁹

4 | RESULTS OF pK_a AND DISCUSSIONS

Table S4 in the SI section is an example of the recorded pH values and the calculation steps for the pK_a of MDEA at 298.15K. In particular, the first column is the number of moles of neutral MDEA which remained in the solution after adding the hydrochloric acid. The second column is the total volume of the acid added. The third column represents the moles of the protonated amine which are assumed as the same as the moles of added HCl. The pH column is the recorded stable pH value at each step. The last three columns are the dissociation constant values before the thermodynamic correction, the value of the thermodynamic correction and the dissociation constant values after thermodynamic correction, respectively. Equation 6 represents the relationship between the three quantities:

$$pK_a = pK_a^M - TC \quad (6)$$

The measurements of pK_a values of MDEA in the temperature range varying from 298.15K to 313.15K are summarized and compared with literature data¹⁴⁻¹⁶ in Figure S1 and Table S3. The values of this study and literature are in excellent agreement. The dissociation constants of the eight studied amines in addition to MDEA and monoethanolamine (MEA)⁹ in the same temperature range were determined. In the eight amines studied, three amines (DMAOEOE, DBEA and PEA) are monoamines while two (2DMAOEE and 2-MPMDA) were diamines. Final the remaining three amines (2AOE13PDA, DMAPAPA and DAOMDPA) were triamines. The first, second and third dissociation constants of the amines were reported in Tables 1 to 3 and Figures 1 to 3, respectively.

Table 1 pK_{a1} values for the eight studied amines, MDEA and MEA at various temperatures ^a

Amine	Abbreviation Name
N-(2-aminoethyl)-1,3-propanediamine	n-2AOE13PDA
2-Methylpentamethylene diamine	2-MPMDA
N, n-dimethyldipropylenetriamine	DMAPAPA
3,3'-Diamino-n-methyldipropylamine	DAOMDPA
Bis[2-(n,n-dimethylamino)ethyl]ether	2DMAOEE
2-[2-(Dimethylamino)ethoxy]ethanol	DMAOEOE
2-(Dibutylamino)ethanol	DBEA
N-propylethanolamine	PEA
Methyldiethanolamine ^{This Study}	MDEA
Monoethanolamine ⁹	MEA
^a Standard uncertainties: $u(pK_a) = 0.02$ and $u(T) = 0.01K$ (0.95 level of confidence). ^a Standard uncertainties: $u(pK_a) = 0$	

Figure 1 The relationship between the pK_{a1} with the inverse temperature of the studied amines, MDEA^{this study} and MEA.⁹: MDEA; : DMAOEOE; V: MEA; : 2DMAOEE; *: PEA; *: DBEA; *: n-2AOE13PDA; V: DMAPAPA; Δ: DAOMDPA; *: 2-MPMDA

Table 2 The pK_{a2} values for the five studied amines at various temperatures (K)^a

Amine	Abbreviation Name
N-(2-aminoethyl)-1,3-propanediamine	n-2AOE13PDA
2-Methylpentamethylene diamine	2-MPMDA
N,n-dimethyldipropylenetriamine	DMAPAPA
3,3'-Diamino-n-methyldipropylamine	DAOMDPA
Bis[2-(n,n-dimethylamino)ethyl]ether	2DMAOEE
^a Standard uncertainties: $u(pK_a) = 0.02$ and $u(T) = 0.01K$ (0.95 level of confidence) ^a Standard uncertainties: $u(pK_a) = 0$	

Figure 2 The relationship between the pK_{a2} with the inverse temperature of the studied amines. : 2DMAOEE, *: n-2AOE13PDA; V: DMAPAPA; *: 2-MPMDA; Δ : DAOMDPA

Table 3 pK_{a3} values for the three studied amines at various temperatures (K)^a

Amine	Abbreviation Name
N-(2-aminoethyl)-1,3-propanediamine	n-2AOE13PDA
N, n-dimethyldipropylenetriamine	DMAPAPA
3,3'-Diamino-n-methyldipropylamine	DAOMDPA
^a Standard uncertainties: $u(pK_a) = 0.02$ and $u(T) = 0.01K$ (0.95 level of confidence). ^a Standard uncertainties: $u(pK_a) =$	

The ranking of all amines in terms of the values of the three pK_a s is presented in Table 4. It clearly shows that all the studied amines have a higher pK_a than MEA. 2-MPMDA, with two primary amino groups, has the highest pK_{a1} and the second pK_{a2} . It should be an amine of great interest in carbon capture operations. DAOMDPA, with two primary and a tertiary amino group, also has a high pK_a value. The coefficient of determination (R^2) of the linear regression for the Figure 1, 2, and 3 are presented in Table S5.

Table 4 pK_a ranking at 298 K for all amines

Full Name	Abbreviation Name	Abbreviation Name	Abbreviation Name	Molecular Structure	Pka_1 Ranking	Pka_2 Ranking	Pka_3 Ranking
Methyldiethanolamine	MDEA	MDEA	MDEA		8		
N-(2-aminoethyl)-1,3-propanediamine	n-2AOE13PDA				4	4	3
2-Methylpen-tamethyl-ene diamine	2-MPMDA				1	2	
N, n-dimethyldipropyl-enetriamine	DMAPAPA	DMAPAPA			3	3	1
3,3'-Diamino-n-methyldipropylamine	DAOMDPA				2	1	2
Bis[2-(n-n-dimethyl-amino)ethyl]ether	2DMAOEE				7	5	
2-[2-(Dimethylamino)ethoxy]ethanol	DMAOEOE				10		
2-(Dibutylamino)-ethanol	DBEA				5		
N-propylethanolamine	PEA				6		

Full Name	Abbreviation Name	Abbreviation Name	Abbreviation Name	Molecular Structure	Pka ₁ Ranking	Pka ₂ Ranking	Pka ₃ Ranking
Monoethanolamine	MEA				9		

Figure 3 The relationship between the pK_{a3} with the inverse temperature of the studied amines. *: n-2AOE13PDA; V: DMAPAPA; *: DAOMDPA

All amines were ranked in terms of pKa

Equation 7 is the van't Hoff equation and is used for determining the standard state entropy change (ΔS^0 , kJ·mol⁻¹·K⁻¹) and enthalpy change (ΔH^0 , kJ·mol⁻¹). In the equation, the slope and intercept of the plots in Figures 1 to 3 represent $-\frac{\Delta H^0}{R}$ and $\frac{\Delta S^0}{R}$, respectively with R being the Universal gas constant (8.3145x10⁻³kJ·mol⁻¹·K⁻¹). Furthermore, the standard state Gibbs free energy change (ΔG^0 , kJ·mol⁻¹) of the reaction can be calculated using Equation 8. The values of ΔH^0 , ΔS^0 and ΔG^0 for the studied amines are summarized in Tables 5 to 10.

$$\ln(K_a) = -\ln(10^{pK_a}) = \frac{S^0}{R} + \frac{-H^0}{RT} \quad (7)$$

$$G^0 = R.T.\ln(10^{pK_a}) \quad (8)$$

Table 5 Standard state enthalpy and entropy changes of the first pK_a of the eight studied amines

Amine	ΔH^0 (xΘ·μoλ ⁻¹)	$\Delta \Sigma^0$ (xΘ·μoλ ⁻¹ ·K ⁻¹)
N-(2-aminoethyl)-1,3-propanediamine	38.21	-6.84E-02
2-Methylpentamethylene diamine	61.84	4.12E-03
N, n-dimethyldipropylenetriamine	46.10	-4.42E-02
3,3'-Diamino-n-methyldipropylamine	44.74	-4.99E-02
Bis[2-(n, n-dimethylamino)ethyl]ether	27.23	-9.22E-02
2-[2-(Dimethylamino)ethoxy]ethanol	37.15	-4.88E-02
2-(Dibutylamino)ethanol	48.95	-2.48E-02
N-propylethanolamine	48.26	-2.63E-02

Table 6 The Gibbs free energy change of the protonated reaction (ΔG^0 / kJ·mol⁻¹) for the first pK_a of the studied amines at different temperatures

Amine	T(K)	T(K)	T(K)	T(K)
	298.15	303.15	308.15	313.15
N-(2-aminoethyl)-1,3-propanediamine	58.50	59.08	59.23	59.59
2-Methylpentamethylene diamine	60.62	60.59	60.58	60.55
N, n-dimethyldipropylenetriamine	59.25	59.48	59.76	59.89
3,3'-Diamino-n-methyldipropylamine	59.65	59.83	59.99	60.43
Bis[2-(n, n-dimethylamino)ethyl]ether	54.79	55.07	55.57	56.17
2-[2-(Dimethylamino)ethoxy]ethanol	51.65	52.00	52.21	52.39
2-(Dibutylamino)ethanol	56.33	56.41	56.69	56.65
N-propylethanolamine	56.11	56.18	56.40	56.47

Table 7 Standard state of enthalpy and entropy changes of the second pK_a of the studied amines

Amine	ΔH^0 ($\times \Theta \cdot \mu\text{ol}^{-1}$)	$\Delta \Sigma^0$ ($\times \Theta \cdot \mu\text{ol}^{-1} \cdot \text{K}^{-1}$)
N-(2-aminoethyl)-1,3-propanediamine	55.32	1.79E-02
2-Methylpentamethylene diamine	61.45	3.23E-02
N, n-dimethyldipropylenetriamine	46.10	-1.51E-02
3,3'-Diamino-n-methyldipropylamine	43.60	-2.86E-02
Bis[2-(n,n-dimethylamino)ethyl]ether	25.39	-6.62E-02

Table 8 The Gibbs free energy change of the protonated reaction (ΔG^0 / $\text{kJ} \cdot \text{mol}^{-1}$) for the second pK_a of the studied amines at different temperatures

Amine	T(K)	T(K)	T(K)	T(K)
	298.15	303.15	308.15	313.15
N-(2-aminoethyl)-1,3-propanediamine	49.89	49.97	49.97	49.58
2-Methylpentamethylene diamine	51.77	51.77	51.50	51.32
N, n-dimethyldipropylenetriamine	50.57	50.66	50.79	50.78
3,3'-Diamino-n-methyldipropylamine	52.11	52.35	52.38	52.57
Bis[2-(n,n-dimethylamino)ethyl]ether	45.09	45.56	45.66	46.16

Table 9 Standard state enthalpy and entropy changes for the third pK_a of the three amines

Amine	ΔH^0 ($\times \Theta \cdot \mu\text{ol}^{-1}$)	$\Delta \Sigma^0$ ($\times \Theta \cdot \mu\text{ol}^{-1} \cdot \text{K}^{-1}$)
N-(2-aminoethyl)-1,3-propanediamine	38.23	2.52E-02
N,n-dimethyldipropylenetriamine	43.56	1.61E-02
3,3'-Diamino-n-methyldipropylamine	20.71	-5.17E-02

Table 10 Gibbs free energy change of the protonated reaction (ΔG^0 / $\text{kJ} \cdot \text{mol}^{-1}$) for the third pK_a of the three studied amines at different temperatures

Amine	T(K)	T(K)	T(K)	T(K)
	298.15	303.15	308.15	313.15
N-(2-aminoethyl)-1,3-propanediamine	30.71	30.53	30.56	30.27
N, n-dimethyldipropylenetriamine	38.70	38.71	38.70	38.43
3,3'-Diamino-n-methyldipropylamine	36.07	36.45	36.63	36.87

5 | PREDICTING THE ORDER OF PROTONATION

As observed by considering the molecular structures of the compounds, two of the amines are diamines while the three of them are triamines. The structure of Bis[2-(n,n-dimethylamino)ethyl]ether is symmetrical while the other structures were not symmetrical with the presence of primary, secondary and tertiary amino groups. Therefore, it is important to study the order of protonation to better understand the reaction mechanism of the amines. In this study, the amine structures were optimized by commercial computational chemistry software [Gaussian (09 Revision B.01 SMP)] with different models and basis sets. These molecular structures were built using GaussView version 5.0.9. Water was used as a solvent with a polarizable continuum model (PCM). After structural optimization, the energy (E) of different protonated amine scenarios could be used for predicting the protonation locations. Equation 9 was used to calculate the difference in energy levels. The main chain of the organic compounds is the longest chain with additional groups attached to the chain,

and are called functional groups. In the equation, $E_{\text{Primary Protonated}^*}$ is that of the amino group which is closer to the functional group. In the case of n-2AOE13PDA, the primary* group is the one close to the secondary amino group because its structure is straight. Table 11 shows the different energy levels for the scenarios.

$$\Delta E(\text{kJ}\cdot\text{mol}^{-1}) = E_{\text{Secondary/Tertiary/Primary Protonated}^*} - E_{\text{Primary Protonated}} \quad (9)$$

Table 11 Differences in energies between the different protonated positions

$\Delta E/\text{kJ}\cdot\text{mol}^{-1}$	Model/Basis Set	n-2AOE13PDA	n-2AOE13PDA	2-MPMDA	2-MPMDA
$E_{\text{Primary}^*} - E_{\text{Primary}}$	HF/6-311G+(d,p)	3.93	8.81	8.81	
	DFT/B3LYP/3-21G	9.84	5.99	5.99	
	DFT/B3LYP/6-311+(d,p)	4.09	1.02	1.02	
	MP2/6-311G+(d,p)	3.92	1.93	1.93	
$E_{\text{Secondary}} - E_{\text{Primary}}$	HF/6-311G+(d,p)	-7.99			-11.51
	DFT/B3LYP/3-21G	-0.13			-0.60
	DFT/B3LYP/6-311+(d,p)	-6.56			-9.58
	MP2/6-311G+(d,p)	-4.77			-7.39
$E_{\text{Tertiary}} - E_{\text{Primary}}$	HF/6-311G+(d,p)				16.93
	DFT/B3LYP/3-21G				4.19
	DFT/B3LYP/6-311+(d,p)				12.13
	MP2/6-311G+(d,p)				13.11

Based on Table 11, for n-2AOE13PDA and 2-MPMDA amines, the difference in energies were all positive. It means that the electronic energies of the primary protonated amines were lower than the alternative positions which were at the nitrogen closer to the functional groups. For n-2AOE13PDA and DMAPAPA amines, the difference in energies were all negative. Therefore, the electronic energy of the secondary protonated of the amines was lower than at the primary position. Similarly, for DMAPAPA and DAOMDPA amines, the different energies were positive; therefore, for the tertiary protonated structures, the electronic energies were higher than the primary positions. As a result, the secondary amino groups were probably responsible for the first pK_a of n-2AOE13PDA and DMAPAPA amines while the primary amino which were away from functional groups were responsible for the first pK_a of 2-MPMDA and DAOMDPA amines. As mentioned in the literature,¹⁹ the secondary amino group was protonated before the primary amino group which was in turn protonated before the tertiary amino group. The computational study was in good agreement with the literature.¹⁹

6 | ESTIMATING THE FIRST DISSOCIATION CONSTANT VALUES WITH PERRIN – DEMPSREY – SERJEANT (PDS) METHODS

The PDS method¹⁹ is also called a pencil and paper method which estimates the first dissociation constant values at 298.15K of chemical compounds based on group contributions. The method simply collects pK_{a1} values at 298.15K and divides the compounds into multiple functional groups. The dissociation constant of the main amino groups (primary, secondary and tertiary amines) and the constant shift ($[?]pK_a$) of each functional group will be calculated by minimizing the difference between the experimental and estimated values. Therefore, the method will be more accurate if more data is available in the database. To improve the accuracy of the method, Sumon et al.²⁰ collected more experimental data and reoptimized the constants and the constant shifts. Furthermore, Qian et al.²¹ added more data as well as contribution groups to improve the accuracy further. Qian's method is referred to as the QSSG method while Sumon's method is simply called the modified PDS method in this work. The suggested constant values of the three methods were summarized in Table S6. For applying the methods to determine the value of the first dissociation constants at 298.15 K, n-2AOE13PDA amine was chosen as an example for demonstration purposes. For the original PDS method, the secondary amino has a value of 11.15 and with the two primary amino groups at γ and

δ positions. Therefore, the final value was determined as $11.15 - 0.8.0.4 - 0.4.0.4.0.8 = 10.70$, compared to the experimental value of 10.25. The modeling results are presented in Table 12.

Table 12 Estimation of the first pK_a of the studied amines by using original PDS, Sumon’s and Qian’s methods at 298.15 K

Solvent	$pK_{a,PDS}^{19}$	$pK_{a, Sumon}^{20}$	$pK_{a,QSSG}^{21}$	$pK_a^{Exp.}$
N-(2-aminoethyl)-1,3-propanediamine	10.70	10.60	9.94	10.25
2-Methylpentamethylene diamine	10.77	10.60	10.60	10.62
N, n-Dimethyldipropylenetriamine	11.15	11.10	10.39	10.38
3,3’-Diamino-n-methyldipropylamine	11.07	10.90	10.68	10.45
Bis[2-(n,n-dimethylamino)ethyl]ether	9.92	9.94	9.72	9.60
2-[2-(Dimethylamino)ethoxy]ethanol	9.62	9.64	9.42	9.05
2-(Dibutylamino)ethanol	10.06	10.10	10.00	9.87
N-propylethanolamine	10.71	10.70	10.20	9.83

As observed in Table 12, Qian’s method provided the closest values to the experimental values for the studied amines. The original and modified PDS methods have somewhat larger errors than the QSSG method. Note that its database was updated with more functional groups as well as additional positions for the functional groups.

7 | ARTIFICIAL NEURAL NETWORK (ANN) APPLICATION IN PREDICTING THE DISSOCIATION CONSTANTS FOR AMINES

Although the dissociation constant values of amines can be experimentally measured, it is costly to purchase these chemicals, in addition to the cost for disposal of chemical waste and time used to generate the data. Furthermore, researchers are mostly interested in obtaining dissociation constants of new compounds which have not been synthesized yet. It is important to estimate the constant values in advance to save chemical costs and experimental efforts. Therefore, many studies have attempted and focused on improving pK_a prediction accuracy.

In all prediction methods, computational chemistry is a common method for the development of pK_a estimation. Khalili et al.¹² predicted the pK_a values of 17 amines using the Gaussian software with 0.68 pK_a unit of accuracy. Later, Sumon et al.²⁰ improved Khalili’s method (KHE method) to reduce the accuracy to 0.28 pK_a unit. However, the computational chemistry method can be challenging to predict the dissociation constants for large molecule amines which consume longer time and computer memory for optimizing the structures.

Besides computational chemistry and quantitative structure-property relationship (QSPR) methods, artificial neural networks (ANN) can be applied to predict the dissociation constant values. In short, ANN is inspired by the human brain and aims to process information in a soft modeling way without forming a complicated mathematical model.²² Therefore, one of the advantages of ANN, compared to QSPR is its flexibility and ability to recognize the nonlinear relationship in complicated systems without prior knowledge of an existing model; as a result, ANN has become more popular in solving scientific as well as engineering problems.^{23,24} Habibi-Yangjeh et al.²⁴ have combined both ANN and QSPR to successfully estimate the dissociation constant values of different benzoic acids and phenol at 298.15K. The final squared correlation coefficients (R^2) for training, validation and prediction were 0.9926, 0.9943 and 0.9939, respectively. However, the work was limited to a prediction at 298.15K. This work will focus on estimating the pK_a of amines for CO₂ capture at various temperatures by applying ANN.

Most researchers have combined ANN and QSPR for estimating pK_a ; however, one of the challenges is to convert the chemical structures of the compounds to numerical information which are readable in ANN. In general, the researchers need to generate the descriptors by constructing and optimizing the molecular

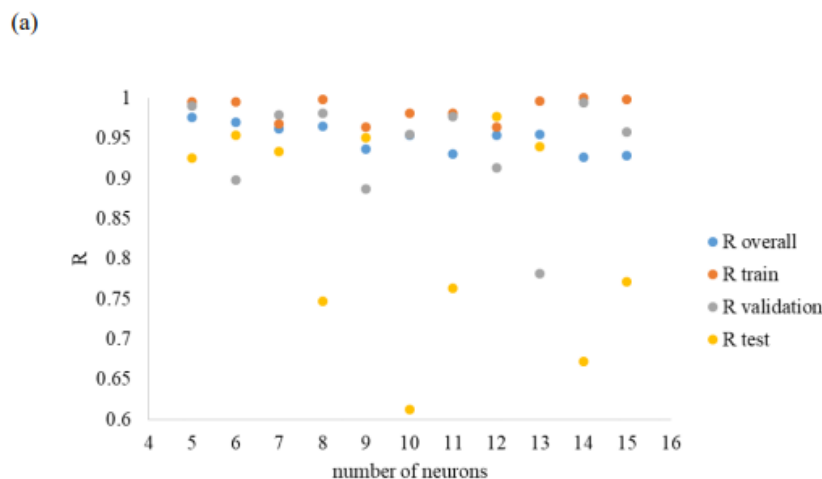
models using a software such as HyperChem or MOPAC.²⁴ The descriptor process would consume much time and efforts. Furthermore, the ANN and QSPR combined model can only work at 298.15K.

For this work, 568 data points of 25 sets of amines which are relevant to CO₂ capture were collected. The list of amines is provided in Table S7. The collected data were divided into three categories: (a) molecular weight, critical temperature and pressure as input data to identify the compounds; (b) temperature dependent properties such as density, viscosity, surface tension and refractive index to correlate the dissociation constant values; and (c) pK_a values as output data. Table S8 reports the densities (g[?]mL⁻¹) of the eight studied amines at the various temperatures while Table S9 lists the measured dynamic viscosities (mPa.s) of the amines. Lastly, Table S10 and S11 report the refractive indices and surface tension (mN/m) of the amines, respectively.

For inputs, the critical properties (T_c and P_c) were used to identify the specific amines while the temperature dependent properties (density, dynamic viscosity, surface tension and refractive index) were chosen as variables of the ANN model. For the entire model, a default data set was applied for training, validating and testing. In particular, a random 70% of data was chosen for training the model while 15% of the data set was selected for validation and the remaining 15% for testing the model.

Optimization of ANN plays an important role in network training which include optimization of the hidden layer numbers and the number of neurons in each hidden layer. Theoretically, there are no methods for determining the optimal number of hidden layers and neuron numbers. As a result, the program was executed with one layer and several neurons varying from 5 to 15 firstly to compare their performance. Figure 4 shows the performance comparison in terms of R and mean squared error (MSE). Based on the Figure 4, the single hidden layer with number neurons of 5 had the best performance with $R_{\text{overall}} = 0.97598$, $MSE_{\text{train}} = 0.0062$, $MSE_{\text{val}} = 0.0094$ and $MSE_{\text{test}} = 0.0244$.

To improve the model, the ANN model with two hidden layers has been executed with five neurons for the first hidden layer while the second layer's number of neurons varied from 4 to 15. Figure 5 shows the best performance when seven neurons were used in the second hidden layer with $R_{\text{overall}} = 0.99424$, $MSE_{\text{train}} = 2.2 \times 10^{-5}$, $MSE_{\text{val}} = 0.0094$ and $MSE_{\text{test}} = 0.0078$.



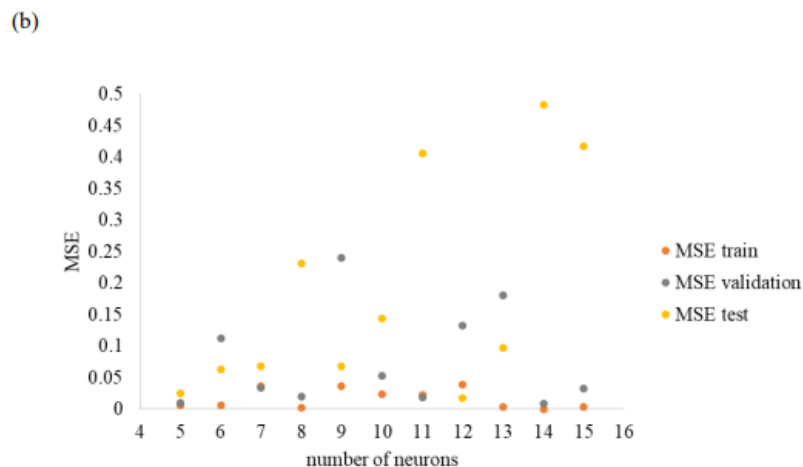


Figure 4 Performance of ANN model with a single hidden layer with variable neuron number. (a) R; (b) MSE

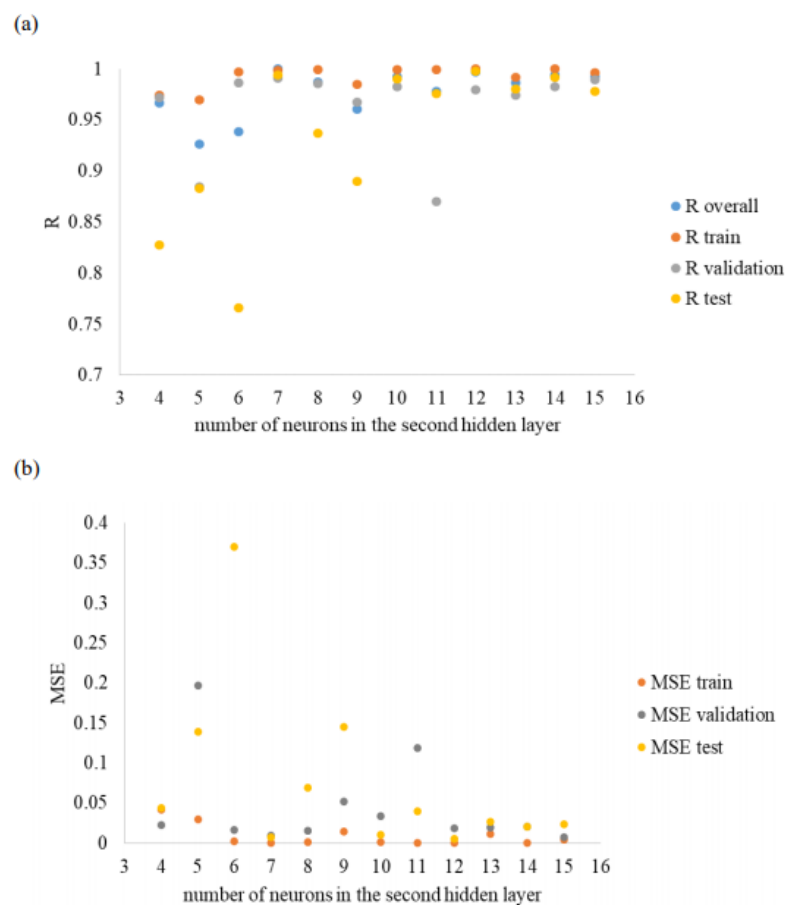


Figure 5 Performance of ANN model with a variable number of neurons in the second hidden layer. (a) R; (b) MSE

The final architectural diagram of the selected ANN model is shown in Figure 6 with 8 inputs, five neurons for the first hidden layer and 7 for the second. The improvement in performance of the ANN model during the training, validating and testing processes is illustrated in Figure 7. At the epoch 19th, the best validation performance was reached while the training performance still improved after epoch 19th.

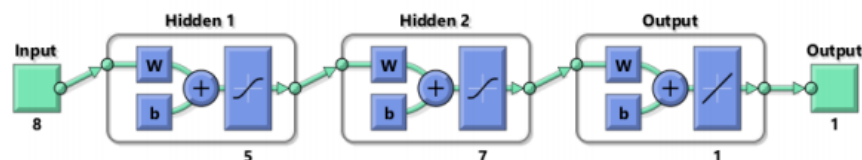


Figure 6 The architectural diagram of the ANN model for predicting pK_a values

Figure 7 ANN performance improvement diagram

Figure 8 shows the plot of outputs with respect to the targets for the training, validation and testing processes. The line is an ideal trendline in which the ANN predicted values should equal the experimental values. R_{overall} was found to be 0.99424 (Figure 8), as a result, the ANN predicted values were in good agreement with the experimental data.

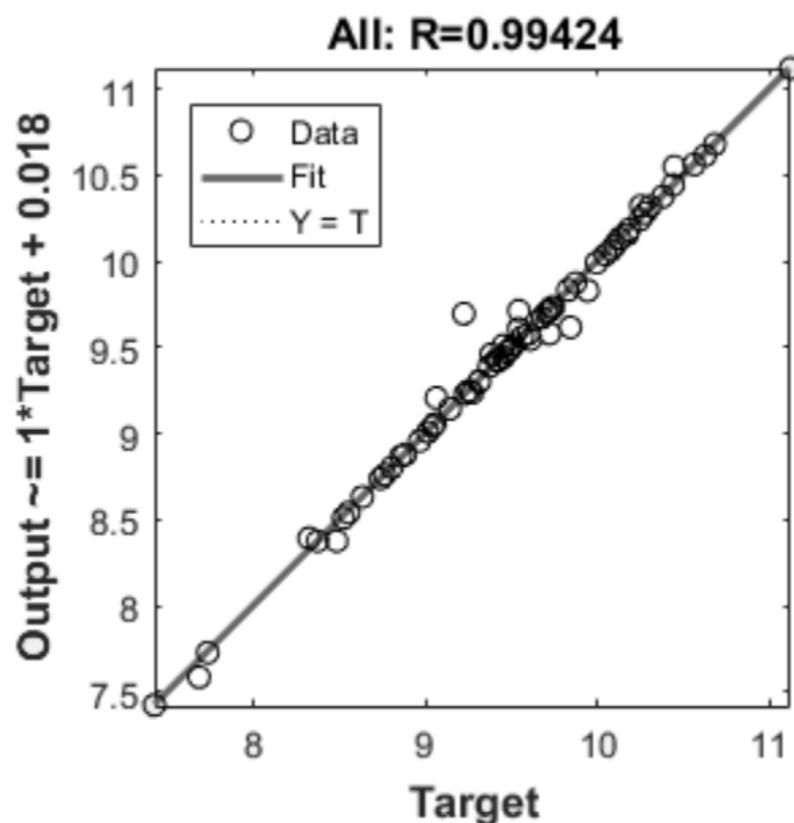


Figure 8 Regression plots for the estimated and experimental pK_a values for 71 data points

The developed ANN model did an excellent job in the prediction of dissociation constants, however, the

method is limited by the large number of properties to be used as input parameters limitation to be found in the literature or measured experimentally. The ANN model can be more useful and flexible if it was possible to use fewer input data. In this study, the ANN model was also tested by reducing the number of input data. The molecular weight, critical temperature and pressure were maintained as inputs in the new model as they identified the studied compound, in addition to the temperature as the dissociation constants values were temperature-dependent. As for the four physical parameters left, the ANN model was tested by removing them one by one, then two and three at the time. The performance of the ANN models based on R_{overall} , $\text{MSE}_{\text{train}}$, MSE_{val} and MSE_{test} were summarized in Table 13. It was found that the performance of the model deteriorated slightly by removing some input information, compared to the original model. However, the ANN model while leaving only the surface tension and refractive index data had a very good performance and is now called the new ANN model. Although the new ANN model had a slightly lower performance than the full model, the estimated $\text{p}K_a$ values were still in good agreement with the experimental values but the model allowed for more flexibility in its application.

As observed in Figure 9, the best validation performance was reached at epoch 76 and became unchanged with the increase in the number of epochs. Figure 9 shows the regression between the estimated and experimental values of the new ANN model. Regression plots for the estimated and experimental $\text{p}K_a$ values for 71 data points for the new ANN model are presented in Figure 10.

Figure 9 The performance improvement of the new ANN model

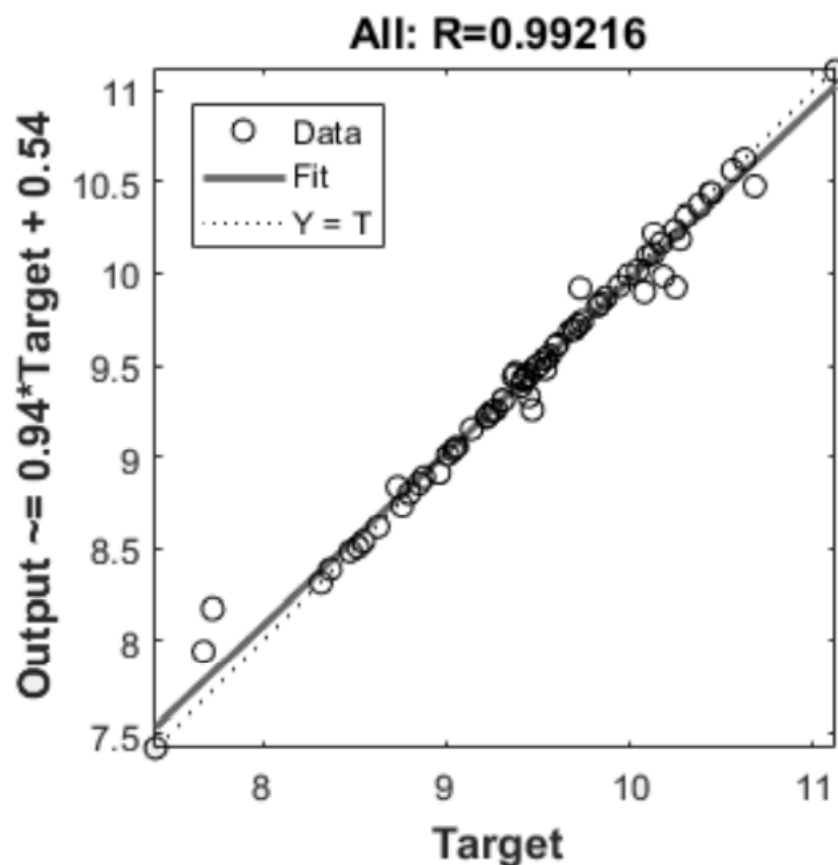


Figure 10 Regression plots for the estimated and experimental $\text{p}K_a$ values for 71 data points for the new ANN model

Table 13 Performance of ANN models

Input Physical Properties	R_{overall}	MSE_{train}	MSE_{test}	MSE_{val}
Without Density	0.99166	5.72E-04	0.0473	0.0024
Without Surface Tension	0.99072	5.94E-05	0.0517	0.0031
Without Viscosity	0.99332	3.49E-05	0.0538	0.0058
Without Refractive Index	0.98861	5.65E-04	0.0644	0.0013
Density & Viscosity	0.97433	4.96E-05	0.1914	0.0126
Density & Surface Tension	0.97124	1.05E-05	0.0958	0.0231
Density & Refractive Index	0.97976	1.39E-04	0.0479	0.0353
Viscosity & Surface Tension	0.97322	2.84E-04	0.0491	0.0019
Viscosity & Refractive Index	0.96911	1.57E-04	0.0772	0.0405
Surface Tension & Refractive Index	0.99216	4.40E-05	0.0203	0.0045
Density	0.91996	1.20E-03	0.1431	0.0041
Viscosity	0.92769	2.41E-02	0.3153	0.0448
Refractive Index	0.92286	6.91E-02	0.0605	0.1315
Surface Tension	0.91592	7.67E-02	0.1705	0.0334

8 | CONCLUSION

The first, second and third dissociation constants of eight amines of importance in carbon capture operations, namely, N-(2-aminoethyl)-1,3-propanediamine (n-2AOE13PDA), 2-Methyl-pentamethylene diamine (2-MPMDA); N, n-dimethyldipropylenetriamine (DMPAPA) and 3,3'-Diamino-n-methyldipropylamine (DAOMDPA), Bis[2-(n,n-dimethylamino)ethyl]ether (2DMAOEE), 2-[2-(Dimethylamino)ethoxy]ethanol (DMAOEOE), 2-(Dibutylamino)ethanol (DBEA) and N-propylethanolamine (PEA) were measured in a temperature range varying from 298.15 K to 313.15 K with 5 K increments. As expected, the dissociation constant values for all studied amines decreased with increasing temperature. The study shows that all amines studied have a higher pK_a than MEA. 2-MPMDA, with two primary amino groups, had the highest pK_{a1} and the second pK_{a2} . It should be an amine of great interest in carbon capture operations. DAOMDPA, with two primary and a tertiary amino group, also had a high pK_a value. A tertiary amine, Methyldiethanolamine pK_a values were the lowest. Using computational chemistry calculations, the first protonated positions for the studied amines were predicted and the results agreed well with the literature.

In terms of modelling, the first pK_a values of the studied amines at 298.15K were estimated using the original and modified PDS but also with the Qian-Sun-Sun-Gao (QSSG) method. This method provided the best estimation of pK_a values when compared to the experimental data.

Finally, an artificial neural network (ANN) was developed to predict the values of the dissociation constants for the temperature range studied in this work. The input data included the molecular weight, critical temperature, and pressure to identify the compounds as well as temperature as pK_a values are temperature-dependent. In addition, the density, dynamic viscosity, refractive index and surface tension were also used as inputs. The predicted values were in very good agreement with the experimental values. An optimum ANN architecture of 8-5-7-1 was selected, its predicted outputs were in a good agreement with targets, with a regression coefficient of 0.99424 and a mean squared error for training, validation and testing of 2.20E-05, 0.0094 and 0.0078, respectively.

The full ANN model was further simplified and optimized by only including the surface tension and the refractive index as inputs.

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Notes

The authors declare no competing financial interest.

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