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Equilibrium Solubility of Carbon Dioxide in an Aqueous Mixture of *N*-Methyldiethanolamine and Diisopropanolamine: An Experimental and Modeling Study

Mehdi Vahidi, Ali T. Zoghi,* Behnoosh Moshtari, and Behrouz Nonahal

Research Institute of Petroleum Industry (R.I.P.I.), National Iranian Oil Company (N.I.O.C.), Tehran 14665-137, Iran

ABSTRACT: In the present work, the equilibrium solubility of carbon dioxide was measured for three different aqueous mixture of *N*-methyldiethanolamine (MDEA) and diisopropanolamine (DIPA). The sum of the mass fraction of MDEA and DIPA for each aqueous mixture was constant at 100 $w = 50$. The mass fraction of DIPA was chosen as 100 $w = (1, 3, \text{ and } 5)$ for the mixture, respectively. The experimental data were measured for the temperature range of (313.2 to 358.2) K and the equilibrium CO_2 partial pressure of (85 to 3984) kPa. To predict and correlate the equilibrium solubility behavior of carbon dioxide with an aqueous mixture of MDEA and DIPA, the Deshmukh–Mather model was used. The binary interaction parameters of the model were tuned by regression of experimental data. Having used the tuned parameters, the equilibrium behavior of CO_2 with relevant aqueous solution was estimated and compared with the equivalent experimental values. The average absolute deviation (AAD %) was obtained to be 13.2 % for all data points.

■ INTRODUCTION

The industrially practiced technology for removing acid gases such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2) is to use aqueous alkanolamine solution. Owing to some favorable properties such as low vapor pressure, low thermal degradation, and low corrosion rate, *N*-methyldiethanolamine is widely used in industry. Since MDEA is a tertiary amine, it does not react with CO_2 directly.¹ To overcome this weakness, a primary or secondary alkanolamine is added to aqueous MDEA solution.² Diisopropanolamine (DIPA) is a secondary alkanolamine which is widely used in gas sweetening industries. DIPA solutions are reported to be less corrosive than other alkanolamine solutions and have a greater selectivity for H_2S over CO_2 , and are also capable of removing COS without excessive degradation of the solution. DIPA is used in the ADIP, the Sulfinol, and the SCOT processes that are all licensed by Shell.³ Designing gas treating processes with alkanolamine-based aqueous solvents requires knowledge of the vapor–liquid equilibrium (VLE) of the CO_2 – H_2S –alkanolamine–water system.⁴

In the present work, the equilibrium carbon dioxide solubility is measured for different mixture ratios of DIPA and MDEA. In industrial gas sweetening plants, in a specific process condition and acid gas loading in a rich amine solution, the circulation rate of solvent has an approximate inverse relationship with concentration of amine solution. Moreover, the allowable industrial concentrations of the aqueous MDEA is between 100 $w = (40 \text{ and } 50)$. Having considered the above guidelines in the present work, the total concentration of aqueous mixture of MDEA and DIPA is selected at 100 $w = 50$. Then, the parameters of Deshmukh–Mather are correlated as function of temperature by regression of experimental data to the model.

■ EXPERIMENTAL SECTION

Materials. Carbon Dioxide with purity of 99.999 % was prepared by Roham Gas Company. Diisopropanolamine, DIPA, (CAS Registry No. 110-97-4) was supplied by Merck with a

nominal mass purity > 99 %. *N*-Methyldiethanolamine, MDEA (CAS Registry No. 105-59-9) was obtained from Aldrich with a nominal mass purity > 99 %. All chemicals were used without further purification. The aqueous mixtures were prepared using a calibrated electronic scale (Mettler model AE 200, Switzerland) with a precision of ± 0.01 mg.

Equipment and Experimental Method. A modified autoclave reactor was used for measuring CO_2 solubility. The experimental setup, experimental procedure, accuracy and the method of uncertainty calculation for the measured values were discussed in details in Zoghi et al.⁵ In Tables 1, 2, and 3, the measured values of equilibrium CO_2 loading for different mixture of aqueous DIPA + MDEA solutions were reported.

In these tables, P^* is the vapor pressure of the aqueous mixture of DIPA+MDEA, P_{CO_2} is the equilibrium pressure of carbon dioxide (the calculation procedure is given by Zoghi et al.⁵), α_{exp} is carbon dioxide loading (mole CO_2 /mole total amine) and finally for each experimental data point the uncertainty of CO_2 loading was calculated and reported.

■ THERMODYNAMIC MODELING

Aqueous solutions of alkanolamines absorb carbon dioxide via chemical reactions. Since the alkanolamines are weak bases, the equilibrium reactions taking place cause more complexity of modeling in such equilibrium systems. Moreover, the thermodynamic modeling mixture of alkanolamine adds further complexity to thermodynamic modeling.⁵ The liquid phase reactions are as follows:

Dissociation of water:



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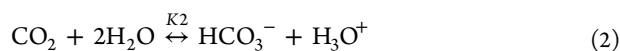
Table 1. The Experimental Solubility Data for CO₂ in Aqueous Solutions of MDEA (100 w = 49) and DIPA (100 w = 1)

T = 313.2 ± 0.1 K		T = 328.2 ± 0.1 K		T = 343.2 ± 0.1 K		T = 358.2 ± 0.1 K	
P _{solution} [*] = 6.3 ± 1 kPa		P _{solution} [*] = 13.8 ± 1 kPa		P _{solution} [*] = 27.2 ± 1 kPa		P _{solution} [*] = 51.1 ± 1 kPa	
P _{CO₂} /kPa	α _{exp}	P _{CO₂} /kPa	α _{exp}	P _{CO₂} /kPa	α _{exp}	P _{CO₂} /kPa	α _{exp}
158 ± 16	0.589 ± 0.005	109 ± 16	0.452 ± 0.005	232 ± 19	0.433 ± 0.006	499 ± 45	0.404 ± 0.006
185 ± 16	0.644 ± 0.005	166 ± 16	0.534 ± 0.005	245 ± 19	0.435 ± 0.005	600 ± 45	0.441 ± 0.005
227 ± 16	0.705 ± 0.005	171 ± 16	0.556 ± 0.005	330 ± 19	0.498 ± 0.005	712 ± 45	0.466 ± 0.005
248 ± 16	0.709 ± 0.005	240 ± 16	0.609 ± 0.005	366 ± 19	0.508 ± 0.005	867 ± 45	0.531 ± 0.005
432 ± 16	0.817 ± 0.005	302 ± 16	0.673 ± 0.006	400 ± 19	0.538 ± 0.005	985 ± 45	0.557 ± 0.004
630 ± 16	0.857 ± 0.005	393 ± 16	0.725 ± 0.005	500 ± 19	0.576 ± 0.006	1269 ± 45	0.615 ± 0.006
888 ± 16	0.894 ± 0.006	455 ± 16	0.738 ± 0.005	655 ± 19	0.636 ± 0.005	1456 ± 45	0.641 ± 0.005
1096 ± 16	0.907 ± 0.005	610 ± 16	0.777 ± 0.005	789 ± 19	0.674 ± 0.005	1955 ± 45	0.696 ± 0.005
1234 ± 16	0.924 ± 0.006	930 ± 16	0.822 ± 0.006	855 ± 19	0.686 ± 0.005	2104 ± 45	0.712 ± 0.005
1567 ± 16	0.942 ± 0.006	1150 ± 16	0.850 ± 0.006	1222 ± 19	0.751 ± 0.005	2334 ± 45	0.731 ± 0.005
1718 ± 16	0.939 ± 0.006	1378 ± 16	0.886 ± 0.006	1331 ± 19	0.772 ± 0.005	2507 ± 45	0.748 ± 0.005
1856 ± 16	0.953 ± 0.006	1888 ± 16	0.903 ± 0.006	1543 ± 19	0.790 ± 0.005	2765 ± 45	0.760 ± 0.005
2134 ± 16	0.962 ± 0.006	1903 ± 16	0.903 ± 0.006	1769 ± 19	0.813 ± 0.004	3120 ± 45	0.783 ± 0.005
2322 ± 16	0.965 ± 0.006	1996 ± 16	0.916 ± 0.006	1868 ± 19	0.825 ± 0.004	3201 ± 45	0.784 ± 0.005
2589 ± 16	0.972 ± 0.006	2330 ± 16	0.926 ± 0.006	2334 ± 19	0.856 ± 0.004	3410 ± 45	0.794 ± 0.005
3034 ± 16	0.987 ± 0.006	2594 ± 16	0.927 ± 0.006	2474 ± 19	0.859 ± 0.004	3718 ± 45	0.802 ± 0.005

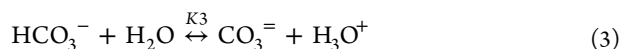
Table 2. The Experimental Solubility Data for CO₂ in Aqueous Solutions of MDEA (100 w = 47) and DIPA (100 w = 3)

T = 313.2 ± 0.1 K		T = 328.2 ± 0.1 K		T = 343.2 ± 0.1 K		T = 358.2 ± 0.1 K	
P _{solution} [*] = 6.1 ± 1 kPa		P _{solution} [*] = 13.6 ± 1 kPa		P _{solution} [*] = 27.0 ± 1 kPa		P _{solution} [*] = 48.7 ± 1 kPa	
P _{CO₂} /kPa	α _{exp}	P _{CO₂} /kPa	α _{exp}	P _{CO₂} /kPa	α _{exp}	P _{CO₂} /kPa	α _{exp}
85 ± 16	0.614 ± 0.005	118 ± 16	0.486 ± 0.004	131 ± 19	0.326 ± 0.004	276 ± 45	0.279 ± 0.005
151 ± 16	0.723 ± 0.004	203 ± 16	0.598 ± 0.005	207 ± 19	0.407 ± 0.004	324 ± 45	0.322 ± 0.005
296 ± 16	0.822 ± 0.004	335 ± 16	0.699 ± 0.005	275 ± 19	0.466 ± 0.004	453 ± 45	0.376 ± 0.005
346 ± 16	0.835 ± 0.005	445 ± 16	0.747 ± 0.004	647 ± 19	0.659 ± 0.005	690 ± 45	0.474 ± 0.004
544 ± 16	0.876 ± 0.005	575 ± 16	0.785 ± 0.005	745 ± 19	0.686 ± 0.004	903 ± 45	0.532 ± 0.004
617 ± 16	0.883 ± 0.005	778 ± 16	0.819 ± 0.005	976 ± 19	0.733 ± 0.005	1133 ± 45	0.595 ± 0.004
737 ± 16	0.901 ± 0.005	953 ± 16	0.839 ± 0.005	1125 ± 19	0.749 ± 0.005	1367 ± 45	0.628 ± 0.005
937 ± 16	0.918 ± 0.005	1023 ± 16	0.851 ± 0.005	1351 ± 19	0.789 ± 0.005	1593 ± 45	0.668 ± 0.005
1103 ± 16	0.933 ± 0.006	1242 ± 16	0.880 ± 0.005	1490 ± 19	0.791 ± 0.005	1763 ± 45	0.685 ± 0.005
1229 ± 16	0.949 ± 0.005	1426 ± 16	0.889 ± 0.005	1711 ± 19	0.821 ± 0.005	1980 ± 45	0.713 ± 0.004
1346 ± 16	0.950 ± 0.005	1573 ± 16	0.906 ± 0.005	1834 ± 19	0.824 ± 0.005	2135 ± 45	0.729 ± 0.005
1494 ± 16	0.962 ± 0.005	1845 ± 16	0.920 ± 0.005	2055 ± 19	0.847 ± 0.005	2440 ± 45	0.752 ± 0.005
1735 ± 16	0.973 ± 0.006	2030 ± 16	0.932 ± 0.005	2365 ± 19	0.866 ± 0.005	2750 ± 45	0.788 ± 0.005
2011 ± 16	0.980 ± 0.006	2489 ± 16	0.959 ± 0.005	2876 ± 19	0.901 ± 0.005	3043 ± 45	0.815 ± 0.005
2436 ± 16	1.009 ± 0.006	2890 ± 16	0.981 ± 0.005	3246 ± 19	0.925 ± 0.005	3147 ± 45	0.820 ± 0.005
2871 ± 16	1.032 ± 0.006	3256 ± 16	0.997 ± 0.005	3750 ± 19	0.946 ± 0.005	3389 ± 45	0.839 ± 0.005

Dissociation of CO₂:



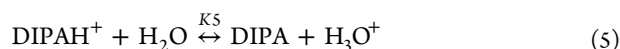
Dissociation of bicarbonate ion:



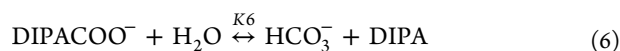
Dissociation of protonated MDEA:



Dissociation of protonated DIPA:



Formation of carbamate:



In the aqueous phase, as a result of the equilibrium reactions 1 to 6, the following possible ionic and molecular species are formed: MDEA, MDEAH⁺, DIPA, DIPAH⁺, DIPACOO⁻, CO₂, HCO₃⁻, CO₃²⁻, H₂O, H₃O⁺, and OH⁻.

Besides, the equivalent chemical equilibrium constants are expressed as follows:

$$K_j = \prod_i a_i^{\nu_{ij}} \quad (7)$$

where the subscript *j* is the reaction number, *a_i* is the activity of the *i*th species and *ν_{ij}* is the stoichiometric coefficient of component *i* in reaction *j*. Activity is defined by eq 8.

$$a_i = \gamma_i^{(m)} m_i \quad (8)$$

where *m_i* and *γ_i^(m)* indicate the molality of component *i* (excluding water) in the solution and its activity coefficient, respectively. The governing mass balance equations are as follows:

Table 3. The Experimental Solubility Data for CO₂ in Aqueous Solutions of MDEA (100 w = 45) and DIPA (100 w = 5)

$T = 313.2 \pm 0.1 \text{ K}$		$T = 328.2 \pm 0.1 \text{ K}$		$T = 343.2 \pm 0.1 \text{ K}$		$T = 358.2 \pm 0.1 \text{ K}$	
$P_{\text{solution}}^* = 6.6 \pm 1 \text{ kPa}$		$P_{\text{solution}}^* = 14.1 \pm 1 \text{ kPa}$		$P_{\text{solution}}^* = 28.1 \pm 1 \text{ kPa}$		$P_{\text{solution}}^* = 51.2 \pm 1 \text{ kPa}$	
$P_{\text{CO}_2}/\text{kPa}$	α_{exp}	$P_{\text{CO}_2}/\text{kPa}$	α_{exp}	$P_{\text{CO}_2}/\text{kPa}$	α_{exp}	$P_{\text{CO}_2}/\text{kPa}$	α_{exp}
145 ± 16	0.663 ± 0.004	126 ± 16	0.421 ± 0.004	112 ± 19	0.192 ± 0.004	245 ± 45	0.230 ± 0.004
174 ± 16	0.695 ± 0.004	136 ± 16	0.440 ± 0.004	176 ± 19	0.345 ± 0.004	327 ± 45	0.308 ± 0.004
262 ± 16	0.773 ± 0.004	186 ± 16	0.533 ± 0.004	210 ± 19	0.397 ± 0.004	495 ± 45	0.396 ± 0.004
334 ± 16	0.815 ± 0.004	242 ± 16	0.592 ± 0.004	265 ± 19	0.459 ± 0.004	604 ± 45	0.452 ± 0.004
430 ± 16	0.841 ± 0.004	345 ± 16	0.672 ± 0.004	345 ± 19	0.521 ± 0.004	831 ± 45	0.519 ± 0.004
543 ± 16	0.880 ± 0.004	489 ± 16	0.742 ± 0.004	473 ± 19	0.587 ± 0.004	1024 ± 45	0.587 ± 0.004
684 ± 16	0.898 ± 0.004	712 ± 16	0.804 ± 0.004	648 ± 19	0.647 ± 0.004	1312 ± 45	0.639 ± 0.004
1109 ± 16	0.953 ± 0.004	1012 ± 16	0.855 ± 0.004	852 ± 19	0.696 ± 0.004	1632 ± 45	0.689 ± 0.004
1296 ± 16	0.969 ± 0.004	1442 ± 16	0.911 ± 0.004	1086 ± 19	0.738 ± 0.004	1999 ± 45	0.733 ± 0.004
1614 ± 16	0.994 ± 0.004	1636 ± 16	0.930 ± 0.004	1407 ± 19	0.784 ± 0.004	2520 ± 45	0.779 ± 0.004
1952 ± 16	1.025 ± 0.004	1957 ± 16	0.954 ± 0.004	1916 ± 19	0.842 ± 0.004	2725 ± 45	0.795 ± 0.004
2288 ± 16	1.035 ± 0.004	2306 ± 16	0.986 ± 0.004	2108 ± 19	0.861 ± 0.004	2934 ± 45	0.817 ± 0.004
2622 ± 16	1.045 ± 0.004	2648 ± 16	0.997 ± 0.004	2428 ± 19	0.891 ± 0.004	3047 ± 45	0.825 ± 0.004
2932 ± 16	1.055 ± 0.004	2998 ± 16	1.008 ± 0.004	2782 ± 19	0.922 ± 0.004	3418 ± 45	0.858 ± 0.004
3019 ± 16	1.063 ± 0.004	3322 ± 16	1.019 ± 0.004	3123 ± 19	0.950 ± 0.004	3742 ± 45	0.875 ± 0.004
3599 ± 16	1.066 ± 0.004	3671 ± 16	1.029 ± 0.004	3474 ± 19	0.978 ± 0.004	3984 ± 45	0.884 ± 0.004

MDEA mass balance in the liquid phase:

$$m_{\text{MDEA},t} = m_{\text{MDEA}} + m_{\text{MDEAH}^+} \quad (9)$$

DIPA mass balance in the liquid phase:

$$m_{\text{DIPA},t} = m_{\text{DIPA}} + m_{\text{DIPAH}^+} + m_{\text{DIPACOO}^-} \quad (10)$$

CO₂ mass balance in the liquid phase:

$$m_{\text{CO}_2,t} = \alpha \times (m_{\text{MDEA},t} + m_{\text{DIPA},t}) \\ = m_{\text{CO}_2} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} + m_{\text{DIPACOO}^-} \quad (11)$$

In eq 11, α is CO₂ loading (mol CO₂ to moles of (MDEA + DIPA)).

The electroneutrality equation is

$$m_{\text{H}_3\text{O}^+} + m_{\text{MDEAH}^+} + m_{\text{DIPAH}^+} \\ = m_{\text{OH}^-} + m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{DIPACOO}^-} \quad (12)$$

To determine the equilibrium concentration of ionic and molecular species in the liquid phase eqs 1–6 and 9–12 should be solved simultaneously. These equations form a system of nonlinear equations for which the Smith and Missen⁶ method was applied.

VLE Modeling. The nonlinear mass balance equations described in the previous section should be solved simultaneously with thermodynamic vapor–liquid equilibrium (VLE) conditions for the volatile species. Owing to low vapor pressure of DIPA and MDEA, the presence of these species were ignored in the vapor phase.⁷ As a result, CO₂ and water were considered in the vapor phase.

On the basis of the infinite dilution reference state, the vapor liquid equilibria for carbon dioxide is defined as follows:

$$\phi_{\text{CO}_2} \gamma_{\text{CO}_2} P = \gamma_{\text{CO}_2}^* x_{\text{CO}_2} H_{\text{CO}_2}^\infty \exp\left(\frac{v_{\text{CO}_2}^\infty (P - P_W^0)}{RT}\right) \quad (13)$$

The fugacity of carbon dioxide in the vapor phase is presented by the left-hand side of eq 13, where γ_{CO_2} , ϕ_{CO_2} , and P are the mole fraction, the fugacity coefficient, and the total pressure, respectively. The fugacity of carbon dioxide in the liquid

phase is presented by the right-hand side of eq 13. The partial molar volume of carbon dioxide at infinite dilution in water and the Henry's law constant (mole fraction scale) are expressed by $v_{\text{CO}_2}^\infty$ and $H_{\text{CO}_2}^\infty$, respectively.

To estimate the Henry's law constant for the solubility of carbon dioxide in water and the molar volume of carbon dioxide at infinite dilution, the correlations proposed by Chen et al.⁸ and the general corresponding state equation introduced by Brelvi et al.⁷ are used, respectively.

The mole fraction in the liquid phase, activity coefficient (mole fraction scale), temperature, and vapor pressure of water are presented by x_{CO_2} , $\gamma_{\text{CO}_2}^*$, T , and P_W^0 , respectively.

The VLE for water is given by

$$\phi_W \gamma_W P = \gamma_W^* x_W P_W^0 \phi_W^0 \exp\left(\frac{v_W (P - P_W^0)}{RT}\right) \quad (14)$$

In eq 15, the subscript W denotes water, ϕ_W^0 is the fugacity coefficient of water at its vapor pressure and γ_W is the water activity coefficient (mole fraction scale).

The fugacity coefficients of all volatile components in the vapor phase are estimated by the mPR EoS.¹⁰

Liquid Phase Non-ideality: Since the alkanolamine solutions are categorized as weak electrolyte solutions and react partially with acid gases in liquid phase, the molecular and ionic species are produced simultaneously in the liquid phase. To model the equilibrium phase behavior of such solutions, the thermodynamic models could be classified in three categories: (a) empirical models, (b) the models based on excess Gibbs free energy ($\gamma-\phi$), (c) the models based on equation of state ($\phi-\phi$). Details of all categories were discussed by Zoghi et al.,¹¹ each type of the mentioned models have some advantages and disadvantages. In this work, the Deshmakh–Mather¹² model is applied to correlate the solubility of carbon dioxide in an aqueous mixture of MDEA and DIPA because of its benefit of high relative speed of calculation rather than other G^E models.¹³ According to this model the activity coefficient of all molecular and ionic species in liquid phase are calculated by eq 15. On the basis of the assumptions of the model, the

Table 4. The Constants of eq 17 Describing the Temperature Dependence of the Equilibrium Constants in Reactions 1 to 6 and Henry's Law Constant for the Solubility of CO₂ (Molality Scale)

reaction no.	K_{eq}	C_1	C_2	C_3	C_4	T/K	ref
1	K_{water}	140.932	-13445.90	-22.4773	0.0	273.15 to 498.15	14
2	K_{CO_2}	235.482	-12092.10	-36.7816	0.0	273.15 to 498.15	14
3	$K_{HCO_3^-}$	220.670	-12431.70	-35.4819	0.0	273.15 to 498.15	14
4	$K_{MDEA\ H^+}$	-73.244	-1116.5	10.06	0.0	293.15 to 333.15	15
5	$K_{DIPA\ H^+}$	-9.279	-4214.076	0.0	0.0099612	293.15 to 333.15	16
6	$K_{DIPACOO^-}$	1.655469	-2057.437	0.0	0.0	313.15 to 368.15	16
	H_{CO_2}	155.1699	-8477.711	-21.9574	0.00578	273.15 to 413.15	8

activity coefficient of water is assumed to be approximately equal to its mole fraction.

$$\ln \gamma_i = -\frac{Az_i^2\sqrt{I}}{1+B\sqrt{I}} + 2 \sum_{j \neq W} \beta_{ij}m_j \quad (15)$$

where A is a function of the density and dielectric of the solvent. The equation proposed by Chen et al.⁸ is used to estimate this parameter. B is considered as a constant value equal to 1.2.^{12,14} I is the ionic strength of the solution that is given by eq 16. The specific binary interaction parameter between components i and j and the molar mass of component i are presented by β_{ij} and m_i , respectively.

$$I = \frac{1}{2} \sum_{i=\text{for ionic species}} m_i z_i^2 \quad (16)$$

where z_i is the ionic charge of component i . In eq 15, the contribution of electrostatic effect of the solvent on the solute species at infinite dilution is presented by the first term. The net effect of various short-range forces between the i and j species are accounted by the second term. β_{ij} is usually considered an empirical interaction parameter.

HENRY'S LAW AND EQUILIBRIUM CONSTANTS

Usually the Henry's law and the equilibrium reaction constants are considered as a function of temperature. The general dependency of these constants to temperature is given by eq 17:

$$\ln(K \text{ or } H) = C_1 + C_2/T + C_3 \ln T + C_4T \quad (17)$$

The corresponding coefficients for reactions 1 to 6 are summarized in Table 4. The molality scale values of the coefficients are given in this table. In this work, the desired correction for changing to mole fraction scale has been carried out for VLE calculation.

DATA REGRESSION

In this work, both experimental data for the present work and the data reported by Jenab et al.¹⁷ were used to extend the range of application of the model.

The data regressions were carried out in the temperature range from (313.2 to 358.2) K. To perform data regression, the β_{ij} in eq 15 were assumed as adjustable variables.

To tune the β_{ij} , the objective function (OF) that is given by eq 18 is minimized.

$$OF = \sum_{i=1}^n \frac{|P_{CO_2}^{calc} - P_{CO_2}^{exp}|}{P_{CO_2}^{exp}} \quad (18)$$

In eq 18, n is the number of data points on each isotherm, and the superscripts calc and exp refer to the calculated and experimental values, respectively.

In this work, to minimize the objective function, an algorithm is used based on the Davidon–Fletcher–Powell optimization method.¹⁸

Since there are 11 molecular and ionic species existing in the liquid phase and because of application of the Deshmukh–Mather model, the number of possible interaction parameters is found to be 121 in this system. There are some constraints that help to reduce the number of adjustable parameters. In this step, it has been tried to reduce the number of adjustable parameters. In addition, some assumptions have been made to reduce the number of adjustable parameters. All binary interaction parameters are considered to be symmetrical, that is, $\beta_{ij} = \beta_{ji}$. Also self-interactions of molecular and ions and all like-charged interactions are ignored.

Moreover, for those ionic species that are present in low concentration such as H^+ , OH^- , CO_3^{2-} and $DIPA\ H^+$, all interactions of ionic and molecular species are discarded. As a result, there are only 19 parameters that are left to be adjusted. To further reduce the number of adjustable parameters, a sensitivity analysis was carried out. The results of the analysis declare that there are only a few parameters that affect the improvement of the model precision. Finally, our analyses showed that there only four interaction parameters that were needed to be adjusted. First, these interaction parameters were tuned at each temperature separately and then were correlated as a function of temperature based on eq 19. The relevant coefficient of all binary interaction parameters are given in Table (5).

Table 5. The Coefficients from eq 19 for the Binary Interaction Parameters (β_{ij}) in the MDEA–DIPA–CO₂–H₂O Solution

binary interaction	a_1	a_2	a_3
$\beta_{(MDEA^+, HCO_3^-)}$	$-1.173 \cdot 10^{-05}$	$7.777 \cdot 10^{-03}$	-1.297
$\beta_{(MDEA^+, MDEA)}$	$6.696 \cdot 10^{-07}$	$-4.434 \cdot 10^{-04}$	$7.731 \cdot 10^{-02}$
$\beta_{(CO_2, HCO_3^-)}$	$-1.674 \cdot 10^{-06}$	$1.121 \cdot 10^{-03}$	$-1.898 \cdot 10^{-01}$
$\beta_{(HCO_3^-, MDEA)}$	$2.517 \cdot 10^{-07}$	$-1.627 \cdot 10^{-04}$	$2.980 \cdot 10^{-02}$

$$\beta_{ij} = a_1 T^2 + a_2 T + a_3 \quad (19)$$

In Figures 1, 2, and 3 the modeling results are shown. The obtained AAD % which is given by eq 20, for solubility of carbon dioxide in aqueous solutions of (MDEA (100 w = 49)+DIPA (100 w = 1)), (MDEA (100 w = 47)+DIPA (100 w = 3)) and (MDEA (100 w = 45)+DIPA (100 w = 5)) are 16.77 %, 8.08 %, and 14.29 %, respectively.

$$AAD\% = \frac{1}{n} \sum_{i=1}^n \frac{|P_i^{exp} - P_i^{calc}|}{P_i^{exp}} 100 \quad (20)$$

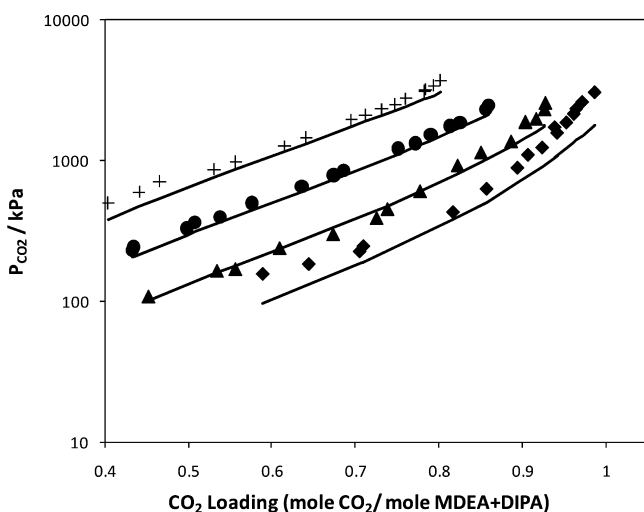


Figure 1. Comparison of calculated and experimental partial pressure of CO_2 as a function of CO_2 loading for aqueous MDEA (100 w = 49) + DIPA (100 w = 1) solution at various temperatures (\diamond , T = 313.2 K; \blacktriangle , T = 328.2 K; \bullet , T = 343.2 K; $+$, T = 358.2 K; the prediction of the model (solid line)).

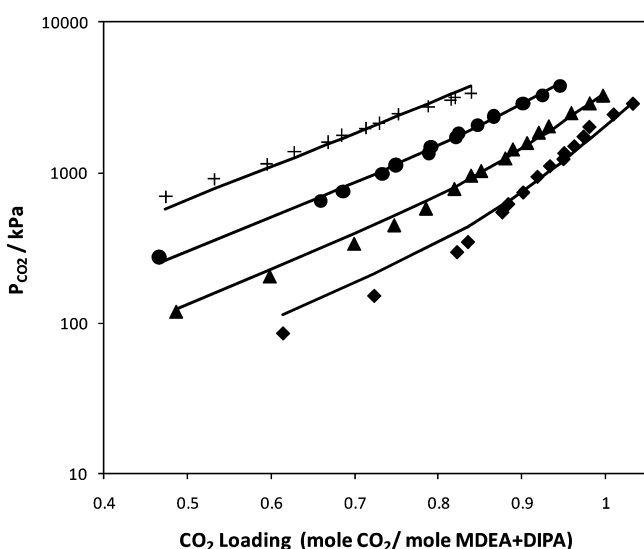


Figure 2. Comparison of calculated and experimental partial pressure of CO_2 as a function of CO_2 loading for aqueous MDEA (100 w = 47) + DIPA (100 w = 3) solution at various temperatures (\diamond , T = 313.2 K; \blacktriangle , T = 328.2 K; \bullet , T = 343.2 K; $+$, T = 358.2 K; the prediction of the model (solid line)).

In Figure 4, the ratio of $P_{\text{calc}}/P_{\text{exp}}$ against loading is shown. As seen for the aqueous solution of MDEA (100 w = 49) + DIPA (100 w = 1), the entire range of CO_2 loading is less than 1, for the aqueous solution of MDEA (100 w = 47) + DIPA (100 w = 3), this ratio is around 1, and for the aqueous solution of MDEA (100 w = 45) + DIPA (100 w = 5) in high loading, this ratio is more than 1 based on the tuned model prediction. In Figure 5, calculated pressure by tuned model versus experimental pressure is shown. As seen, a good agreement between calculated pressure and experimental data is observed.

RESULTS AND DISCUSSION

By using the Henry's law and equilibrium constants and tuned β_{ij} parameters from Table 5, the equilibrium partial pressures of

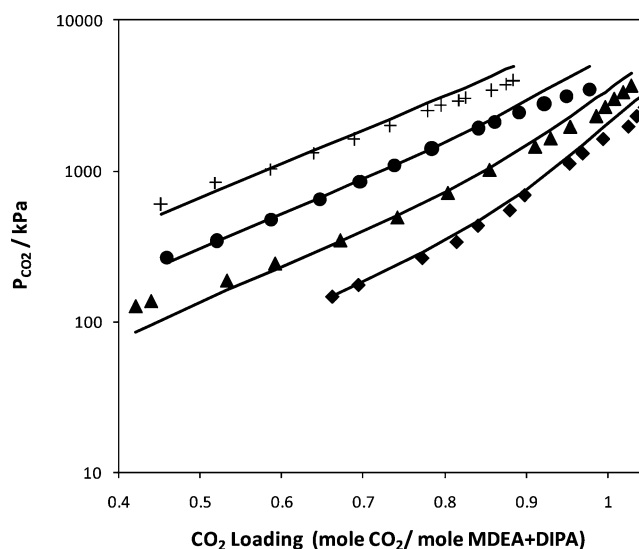


Figure 3. Comparison of calculated and experimental partial pressure of CO_2 as a function of CO_2 loading for aqueous MDEA (100 w = 45) + DIPA (100 w = 5) solution at various temperatures (\diamond , T = 313.2 K; \blacktriangle , T = 328.2 K; \bullet , T = 343.2 K; $+$, T = 358.2 K; the prediction of the model (solid line)).

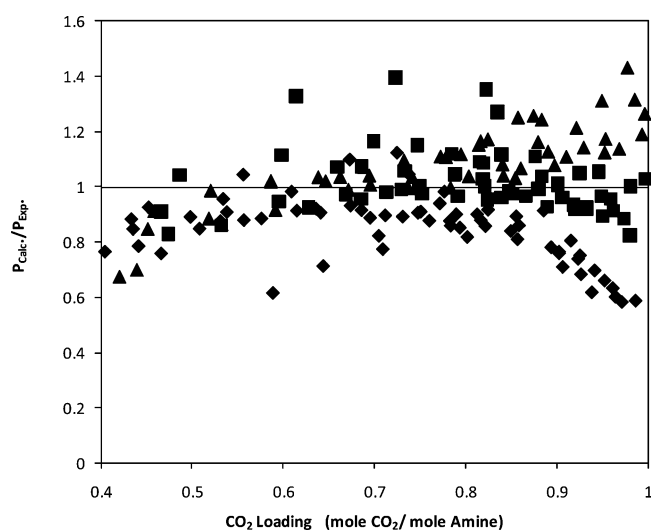


Figure 4. Ratio of calculated pressure to the experimental pressure for each data point against loading of CO_2 in the CO_2 –MDEA–DIPA– H_2O system (\diamond , MDEA (100 w = 49) + DIPA (100 w = 1); \blacksquare , MDEA (100 w = 47) + DIPA (100 w = 3); \blacktriangle , MDEA (100 w = 45) + DIPA (100 w = 5)).

carbon dioxide are estimated at different acid gas loadings and temperatures using the Deshmukh–Mather model. The results and the related graphs are shown in Figures 1–5. The maximum and minimum absolute relative deviations are 40.3 % and 0.2 %, respectively. Finally the value of AAD percentages is 13.2 for all experimental data points. As observed in Figures 1–5, the calculated carbon dioxide partial pressure by the tuned model and the experimental data show good agreement. On the basis of the tuned parameters of the Deshmukh–Mather model, the overall obtained AAD % for those experimental data reported by Jenab et al.¹⁷ is 33.1 %. In their work, the molar ratios of DIPA to MDEA were 2 to 1.36 and 2.5 to 0.86. Therefore, the DIPA concentration was dominant, while in the present work, the molar ratios of DIPA to MDEA are 0.078 to

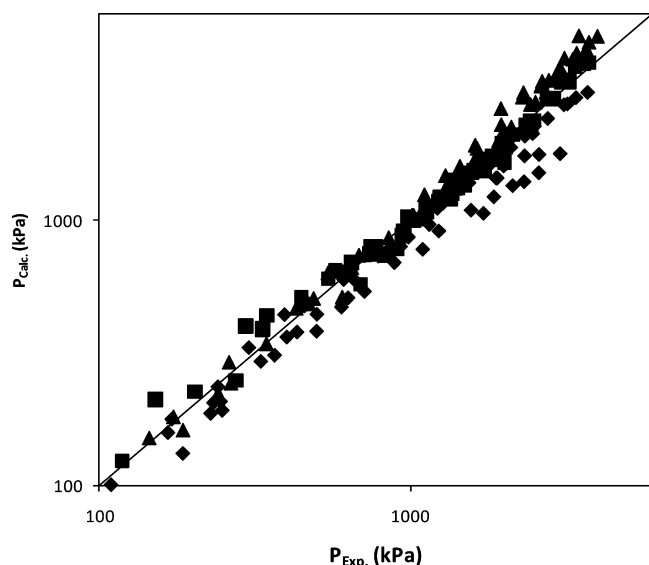


Figure 5. Calculated pressure against the experimental pressure for each data in the CO₂–MDEA–DIPA–H₂O system (◆, MDEA (100 w = 49) + DIPA (100 w = 1); ■, MDEA (100 w = 47) + DIPA (100 w = 3); ▲, MDEA (100 w = 45) + DIPA (100 w = 5)).

4.26, 0.23 to 4.09, and 0.39 to 3.91, respectively for DIPA 100 w = (1, 3 and 5). Owing to the lack of experimental data for the chemical equilibrium reaction constants of DIPA, the assumption of Lee¹⁶ is used. It seems that the dominant DIPA concentration could be the major responsible parameter that leads to high AAD % for the prediction of the experimental data of Jenab et al.¹⁷ by the tuned model.

CONCLUSIONS

New experimental VLE data for the solubility of CO₂ in different mixtures of aqueous solution of MDEA and DIPA were measured for four temperatures ranging from (313.2 to 358.2) K and pressures ranging between (85 to 3984) kPa. To further extend applicability of the model, both solubility data for present work and those obtained by Jenab et al.¹⁷ for the same temperature range were used to adjust the binary interaction parameters of the Deshmukh–Mather model. In all ranges of temperature, pressure and acid gas loading, the tuned model showed a good capability for predicting carbon dioxide solubility in aqueous solution of MDEA+DIPA for different mixtures.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zoghiat@ripi.ir; zoghiat@gmail.com. Tel.: (0098 21) 48252116. Fax: (0098 21) 44739782. Address: Gas Research Division, Research Institute of Petroleum Industry (R.I.P.I.), National Iranian Oil Company (N.I.O.C.), Tehran 14665-137, Iran

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Notes

The authors declare no competing financial interest.

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