

VAPOUR-LIQUID EQUILIBRIUM OF CO₂ IN AQUEOUS SOLUTIONS OF N-METHYL-2-ETHANOLAMINE

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The equilibrium solubility of CO₂ into aqueous solution of sterically hindered *N*-methyl-2-ethanolamine or methyl amino ethanol (MAE) was investigated in the temperature range of 303.1–323.1 K and total CO₂ pressure in the range of 1–350 kPa. The *N*-methyl-2-ethanolamine aqueous solutions studied were 0.968, 1.574, 2.240 and 3.125 mol kg⁻¹ of solvent.

Keywords: solubility, carbon dioxide, *N*-methyl-2-ethanolamine, equilibrium

INTRODUCTION

The energy efficient CO₂ capture has become a global issue. For the rational design of gas treating processes through absorption, the equilibrium solubility of acid gases over alkanolamines of recent interest is extremely important besides the knowledge of mass transfer and kinetics. The rate studies conducted by Mimura et al. (1998) for the sterically hindered secondary alkanolamines like *N*-methyl-2-ethanolamine (MAE), ethylaminoethanol (EAE), butylamino ethanolamine (BAE) revealed that MAE showed a higher reaction rate towards CO₂ than the primary alkanolamine monoethanolamine (MEA) and higher than the secondary alkanolamines EAE and BAE. It might not be inappropriate here to mention that MAE has not yet been established as a potential solvent either to the gas treating industry or to the gas treating research community. A comprehensive summary of physical properties like molecular weight, boiling point, viscosity, refractive index etc., of MAE along with some other potential alkanolamine solvents like MEA, DEA and MDEA are presented in Table 1, to render a maiden perspective for MAE as a possible potential solvent for sour gas treating. The evaluation of physicochemical properties, transport properties, corrosion resistance, degradation resistance, and rate studies on MAE as a solvent has been the recent interest in gas treating research. Apart from the aforesaid properties, the determination of the CO₂/H₂S solubility in aqueous MAE solution deserves immense significance and according to our knowledge, no reference on vapour-liquid equilibrium (VLE) of CO₂ over MAE is available in the open literature until now. In view of this, the present investigation was taken up.

EXPERIMENTAL

Materials

MAE was supplied by E. Merck (Damstadt, Germany), Germany with a purity of >98%. Double distilled water, degassed by boiling was used for making the amine solutions. The specific amine concentration was determined by titration with standard HCl using methyl orange indicator. The relative uncertainty in the composition of the amine solution was estimated as ±0.007%. Carbon dioxide, obtained from Vadilal Chemicals Ltd. (Vadodara, Gujarat, India), has a certified mole fraction purity of 99.99%.

Apparatus and Procedure

The solubility of CO₂ in MAE aqueous solutions were measured in a stainless steel equilibrium cell. The temperature of the equilibrium cell and gas buffer was controlled within ±0.2 K of the desired level with the help of a circulator temperature controller (Polyscience (Niles, IL) model No: 9712). Pre-calibrated platinum sensors with a temperature indicator were used for measurement of temperatures in the equilibrium cell and gas buffer and the maximum uncertainty in temperature measurement is ±0.11 K.

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Table 1. Significant physical properties of MAE* along with MEA[†], DEA and TEA

	MEA	DEA	TEA	MAE
Chemical name	Monoethanolamine	Diethanolamine	Triethanolamine	N-methyl-2-ethanolamine
Molecular formula	C ₂ H ₇ NO	C ₄ H ₁₁ NO ₂	C ₆ H ₁₅ NO ₃	C ₃ H ₉ NO
Molecular weight	61.08	105.14	149.19	75.11
Specific gravity	1.017	1.092	1.126	0.94
Boiling point (°C)	170.4	268	335	152–162
Vapour pressure, mm Hg	<1	<0.01	<0.001	0.5
Abs. viscosity at 20°C, cp	24.1	380 at 30°C	921	13
Refractive index	1.4539	1.4747	1.4852	1.44
Solubility in water	Complete	Complete	Complete	Complete

*ARKEMA inc. datasheet.

[†]DOW datasheet.

VLE measurements were done at total pressures ranging from 1 to 350 kPa and in the temperature range of 303.1–323.1 K. A vacuum pump (INDVAC, Model-IV-50, Saurabh Engineers (Ahmedabad, India)), capable of creating 2 kPa abs was attached to the VLE cell and the buffer vessel, and used to evacuate both the VLE cell and the buffer vessel before the commencement of the experiment.

After evacuation, the buffer vessel was isolated from the VLE cell and was allowed to receive 1.5–2.5 times of the desired maximum CO₂ total pressure from pure CO₂ gas cylinder. Pressure transducers in the range of 0–1,724 and 0–689 kPa (PMP450 FUTEK- Pressure sensor, 10 Thomas Irvine, CA) were attached to the buffer vessel and the equilibrium cell, respectively. The maximum combined uncertainty ($k=2$) in the pressure measurements can reach up to $\pm 0.3\%$ and $\pm 0.4\%$ of the maximum transducers' readings attached to the buffer vessel and the equilibrium cell, respectively. The VLE cell was equipped with a liquid phase stirrer (SPINOT-Magnetic Stirrer cum Hot Plate (Chennai, India)). Freshly prepared mixed alkanolamines solution (25 mL) (using degassed double distilled water) of the desired concentration was quickly transferred into the cell with the help of attached burette, and the cell was fully sealed.

A vacuum was initially present in the VLE cell so that the liquid existed under its own vapour pressure. This solution vapour pressure (p_v) was measured. The CO₂ gas from the buffer was then allowed to enter the equilibrium cell and after the requisite amount of gas transfer, the buffer vessel was disconnected from the VLE cell. The liquid phase stirrer was kept on with the commencement of absorption. The amount of CO₂, hence, the number of moles of CO₂ being transferred from the buffer vessel was calculated using the difference in pressure transducer readings attached to it. The attainment of equilibrium in the VLE cell was assumed when there was no change in total pressure of the

VLE cell for at least 1 h, while the temperature was maintained constant at its desired level. It took about 1 h to reach equilibrium for each run. The pressure indicator attached to the cell at equilibrium was an indication of the total equilibrium pressure. The equilibrium partial pressures of CO₂, which has been reported by the present study, was derived by subtracting the solvent vapour pressure at that temperature from the total pressure measurement. The number of moles of CO₂ absorbed by the aqueous alkanolamine solvents in the VLE cell was calculated by the difference in number of moles of CO₂ being transferred from the buffer vessel and the number of moles of CO₂ present in the gas phase of the VLE cell at its equilibrium partial pressure by taking into account the compressibility factors of the gas. The method of calculation adopted regarding the number of moles of CO₂ absorbed in the liquid phase; was described by Park and Sandall (2001). The estimated uncertainty in the number of moles of CO₂ being absorbed in the equilibrated liquid phase was ± 0.02 . At that equilibrium pressure, the CO₂ loading has been expressed as the number of moles of CO₂ absorbed per mole of alkanolamine (MAE).

RESULTS AND DISCUSSION

To validate the present experimental set-up, several VLE measurements were done in aqueous solutions of DEA as well as in (DEA + AMP) blend at 313.1 K and checked with the experimental results available in the open literature (Seo and Hong, 1996; Kundu, 2004). Table 2 presents some representative results of validation with an average absolute deviation percentage (AAD %) of 6.2 and 12.8 in predicting equilibrium CO₂ partial pressure over aqueous DEA, and (DEA + AMP) blend, respectively. In Table 2, the CO₂ loading (α) has been expressed as moles of

Table 2. Comparison among CO₂ solubility in aqueous solutions of DEA & (DEA + AMP) generated in this work and literature value at 313.1 K

DEA = 30 wt %				DEA + AMP = 6 wt % + 24 wt%			
Loading (α_{CO_2})	P_{CO_2} /kPa	P_{CO_2} /kPa ^a	AAD %	Loading (α_{CO_2})	P_{CO_2} /kPa	P_{CO_2} /kPa ^b	AAD %
0.39	2.2	1.8	6.2	0.372	2.0	1.61	12.8
0.51	14.5	15.0		0.614	12.7	15.3	
0.59	56.0	56.4		0.686	30.1	32.0	
0.64	85.3	87.5		0.774	85.2	89.5	

$$\text{AAD\%} = \left[\sum_{n=1}^n (p_{\text{cal}} - p_{\text{exp}}) / p_{\text{exp}} \right] / n \times 100$$

^a Kundu (2004).^b Seo and Hong (1996).

Table 3. Solubility ($\alpha_{\text{CO}_2}/(\text{mol CO}_2 \text{ mol}^{-1} \text{ MAE})$) of CO_2 in 0.968, 1.574, 2.240, and 3.125 mol kg^{-1} aqueous *N*-methyl-2 ethanolamine solutions in the temperature range $T = 303.1\text{--}323.1$ K

m_{MAE} (mol kg^{-1})	$T = 303.1$ K		$T = 313.1$ K		$T = 323.1$ K	
	P_{CO_2} (kPa)	α_{CO_2}	P_{CO_2} (kPa)	α_{CO_2}	P_{CO_2}	α_{CO_2}
0.968	5.1	0.708	4.0	0.566	5.1	0.554
	7.2	0.748	35.2	0.835	25.9	0.753
	23.1	0.854	95.1	0.937	80.3	0.894
	50.85	0.946	167.7	1.020	152.8	0.955
	85.1	0.986	238.5	1.070	238.6	1.032
	177.9	1.09	334.9	1.110		
	242.7	1.134				
1.574	352.8	1.162				
	0.9	0.345	3.0	0.527	2.0	0.416
	5.1	0.647	41.1	0.778	24.1	0.687
	44.3	0.857	105.3	0.895	86.3	0.848
	93.75	0.935	171.8	0.955	167.5	0.924
	181.9	1.018	246.9	0.982	276.8	0.992
2.240	322.5	1.10	342.2	1.060	353.3	1.043
	3.2	0.534	1.0	0.436	4.0	0.474
	35.1	0.770	18.1	0.685	48.1	0.722
	85.45	0.879	75.3	0.826	132.3	0.818
	161.3	0.934	169.1	0.921	203.8	0.891
	249.8	0.989	258.7	0.971	264.5	0.930
3.125	351.9	1.023	344.6	1.010	355.9	0.965
	1.0	0.366	1.0	0.429	3.0	0.422
	17.1	0.678	24.1	0.667	27.1	0.637
	87.4	0.846	72.6	0.774	94.8	0.753
	159.2	0.902	153.1	0.865	148.5	0.806
	247.7	0.963	242.8	0.914	239.7	0.865
	341.3	0.988	341.1	0.967	332.8	0.915

α_{CO_2} = loading of CO_2 = moles of CO_2 /moles of MAE. m_{MAE} = moles of *N*-methyl-2-ethanolamine/kg of solvent.

CO_2 /mole of alkanolamine. The CO_2 solubility in (0.968, 1.574, 2.240 and 3.125 mol kg^{-1})/(6.76, 10.52, 14.27 and 18.78 by wt percentage) aqueous *N*-methyl-2-ethanolamine solutions in the temperature range of 303.1–323.1 K are presented in Table 3, where the CO_2 loading has been expressed as the number of moles

of CO_2 absorbed per mole of alkanolamine. It is evident from Table 3 that at a fixed temperature, an increase in total MAE concentration (mol kg^{-1}) leads to a decrease in solution CO_2 loading capacity. Table 3 also reveals that at a constant amine concentration and CO_2 partial pressure, an increase in temperature leads to a decrease in solution CO_2 loading capacity. Figure 1 shows the comparison in solubility for the MAE concentrations studied at 313 K. Figure 1 also compares the CO_2 solubility of MAE with that of MEA (2.94 mol kg^{-1} /15.3 by wt percentage) and DEA (3.817 mol kg^{-1} /30 by wt percentage) in the same pressure range at 313 K. It has been a significant observation that MAE, in the total pressure range of 1–350 kPa possesses comparatively higher CO_2 loading than alkanolamines like diethanolamine (DEA)/MEA. Solubility data of MEA and DEA were adapted from (Lee et al., 1974; Seo and Hong, 1996).

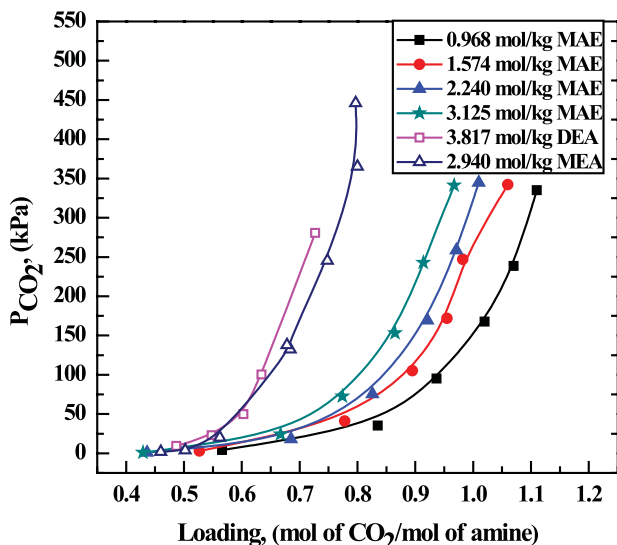


Figure 1. Comparison of the solubility of CO_2 in aqueous solutions of MAE, DEA and MEA of different concentration at 313 K. (Lines are polynomial fit).

CONCLUSIONS

The present study was taken up to explore the applicability of *N*-methyl-2-ethanolamine as an important component in the new alkanolamine blends to be proposed for acid gas absorption. These are the very first published CO_2 solubility data in MAE aqueous solutions. The appreciable CO_2 loading over low to moderately high range of CO_2 partial pressure seems to be encouraging. The determination of the properties like corrosion resistance, viscosity (pump-ability) and rate of degradation are equally important to be considered in conjunction with solubility and rate studies for MAE, which will ensure its acceptability as a potential solvent in industrial practice.

NOMENCLATURE

- P_{CO_2} total equilibrium pressure of CO_2 (kPa)
 α_{CO_2} liquid phase loading of CO_2 ($\text{mol CO}_2 \text{ mol}^{-1}$ amine)
 m_{CO_2} molality of CO_2 ($\text{mol CO}_2 \text{ kg}^{-1}$ solvent)
 m_{MAE} molality of amine (mol MAE kg^{-1} solvent)

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