Viscosity, Refractive Index, Surface Tension, and Thermal Decomposition of Aqueous *N*-Methyldiethanolamine Solutions from (298.15 to 338.15) K

Ayyaz Muhammad,* Mohamed I. Abdul Mutalib, Cecilia D. Wilfred, Thanabalan Murugesan, and Amir Shafeeq

Chemical Engineering Department, Universiti Teknologi Petronas, Tronoh-31750, Perak, Malaysia

In this work, physical properties such as dynamic viscosity at (298.15 to 338.15) K, surface tension, and refractive index at temperatures (303.15 to 333.15) K of pure and aqueous *N*-methyldiethanolamine (MDEA) solutions (with mass fraction of MDEA of 0.3228 and 0.4880) were measured at atmospheric pressure and correlated. A thermogravimetric analyzer (TGA) was used to study the thermal stability of solvents in the presence of nitrogen (20 mL·min^{-1}), at a heating rate of 10 °C·min^{-1}.

Introduction

Aqueous solutions of alkanolamine such as monoethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP), and *N*-methyldiethanolamine (MDEA) are of great interest as chemical absorbents for the removal of carbon dioxide and hydrogen sulfide from sour natural gas. The distinctive properties of MDEA, such as high resistance to thermal and chemical degradation, low solution vapor pressure with minimum solvent loss during regeneration, and low enthalpy of absorption leading to lower energy requirements for regeneration, have contributed to its preferential use for the removal of carbon dioxide. The physical properties of solvents are essential for the design and development of gas absorption units. The physical properties can be used to derive other properties.[1,2] Physical properties of process solvents greatly affect the liquid−film mass transfer coefficients and are important for mass transfer rate modeling of absorbers and regenerators.[3] An extensive literature review for the determination of physical properties of pure and aqueous MDEA solutions has been summarized in Table 1.

The physical properties such as viscosity, refractive index, and surface tension of pure and aqueous MDEA solutions of mass fractions 0.3228 and 0.4880 have been measured. The thermal stability of pure and aqueous MDEA solutions has also been determined using thermogravimetric analysis.

Experimental

Materials. MDEA (CAS no. 105-59-9) was supplied by Merck with a stated purity of 99.5 % (determined by GC area) and used without further purification. The binary mixtures of MDEA were prepared gravimetrically with a precision of ± 0.0001 g, using an analytical balance (Mettler Toledo model AS120S). The possible error in the mole fraction calculations was estimated to be around ± 0.0001. All the measurements for each sample were performed in duplicate, and the values are reported as an average.

Apparatus and Procedures. The kinematic viscosity of pure and aqueous MDEA solutions was measured at temperatures (298.15 to 338.15) K, using four calibrated Ubbelohde viscometers (sizes 1, 1C, 1B, and 2). Viscometers were immersed in a thermostatic bath (Tamson, TVB445) with a built-in circulation stirrer for uniform temperature distribution. The bath temperature was regulated with a Pt-100 temperature probe to within ± 0.01 K. The viscometers containing samples were immersed in a thermostatic bath and allowed to equilibrate to the set point temperature for at least 15 min. Later, the efflux time of samples was measured manually with a digital stopwatch having an accuracy of 0.01 s. The kinematic viscosity was obtained by multiplying efflux time in seconds with the respective viscometer constant using the following equation

$$v = Ct \tag{1}$$

where v is the kinematic viscosity in centistokes (cSt); C is the viscometer constant in cSt·s^{-1}, and t is the efflux time in seconds (s). The dynamic viscosity of the samples studied here was calculated by multiplying the kinematic viscosity values with their corresponding density values. The maximum estimated error in calculating dynamic viscosity was within ± 0.03 mPa·s, after including the uncertainty of both the density and kinematic viscosity values.

The refractive indices of water, pure MDEA, and mixtures of (MDEA + water) were determined, using a programmable digital refractometer (RX-5000 alpha, Atago) with a measuring accuracy of ± 4·10^{-5}. The apparatus was calibrated by measuring the refractive index of Millipore quality water before each series of measurements and checked for pure liquids with known refractive indices. All the measurements were performed at temperatures (303.15 to 333.15) K with a temperature control accuracy of ± 0.05 °C. The surface tension of pure MDEA and mixtures of (MDEA + water) was measured using a spinning drop video tensiometer (SVT 20, dataphysics instruments GmbH) within the precision of ± 0.02 mN·m^{-1}. All the readings were taken at temperatures of (303.15 to 333.15) K with an accuracy of ± 0.03 °C. Thermal stability of MDEA and (MDEA + water) was investigated using a thermogravimetric analyzer (TGA, Perkin-Elmer, Pyris V-3.81) at temperatures (30 to 300) °C. The effect of temperature on the decomposition of samples was studied at a heating rate of 10 °C·min^{-1} with a temperature accuracy better than ± 3 °C, using a platinum pan under a nitrogen atmosphere supplied at the rate of 20 mL·min^{-1}.

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* Corresponding author. Tel.: +60175203418. Fax: +6053654090. E-mail: atozmoon@yahoo.com.

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Table 1. Literature Review for the Determination of Physical Properties of Pure and Aqueous MDEA Solutions at Atmospheric Pressure

year	composition	T/K	ref	apparatus
		Viscosity		
1989	pure & $w = (0.1, 0.2, 0.3, 0.4, 0.5)$	(288.15 to 333.15)	3	Cannon-Fenske routine viscometer
1992	pure	(293.1 to 424.1)	4	Cannon-Ubbelohde capillary viscometers
1994	pure & $w = (0.0079$ to $0.8989)$	(298.15 to 353.15)	5	Schott Gerate type viscometers
1994	$w = (0.1, 0.2, 0.3, 0.4, 0.5)$	(303.15 to 333.15)	6	Cannon-Fenske routine viscometers
1995	$w = 0.5$	(283.15 to 333.15)	7	Cannon-Fenske viscometers
2000	pure	(298.15 to 343.15)	9	Ubbelohde and Cannon-Ubbelohde viscometers
2003	$w = 0.3$	(293.15 to 323.15)	10	Ostwald viscometer
2004	$w = (0.06$ to $0.74)$	(313.15 to 363.15)	11	Cannon-Fenske viscosimeters
2006	pure & $w = (0.3, 0.5)$	(313.15 to 333.15)	12	Cannon-Fenske viscosimeters
		Surface Tension		
1998	pure & $w = (0.008$ to $0.5)$	(298.15 to 323.15)	8	Traube stalagmometer and a Prolabo tensiometer
2007	pure & $w = (0.1, 0.2, 0.3, 0.4, 0.5)$	(313.15, 333.15)	13	pendant drop method using a FTA200 contact angle system
		Viscosity and Surface Tension		
1994	$w = (0.1, 0.2, 0.3, 0.4, 0.5)$	(293.15 to 373.15)	2	Cannon Fenske and Ubbelohde viscometers, Rosano surface tensiometer

Table 2. Physical Properties of Water, MDEA, and MDEA + Water

T	MDEA		MDEA + water	
(K)	present work	lit.	$w_{MDEA} = 0.3228$	$w_{MDEA} = 0.4880$
		η/(mPa·s)		
298.15	77.85	77.190[9]	3.48	9.25
308.15	43.90	44.14[3]	2.26	6.14
318.15	27.44		1.82	4.37
328.15	17.89		1.34	3.46
338.15	12.34	11.88[4][a]	1.17	2.81
100AAD	0.03		3.16	0.47
		n_D		
303.15	1.46532		1.37748	1.40298
313.15	1.46074		1.37604	1.39971
318.15	1.45892		1.37467	1.39629
323.15	1.45708		1.37305	1.39254
333.15	1.45287		1.37134	1.38821
100AAD	0.68		8.20	7.86
		σ/mN·m^{-1}		
303.15	38.74	38.10[8]	53.16	47.56
313.15	37.48	37.31[8] 37.29[13]	52.38	46.92
323.15	36.82	36.88[8]	51.42	45.58
333.15	35.31	35.58[13]	50.67	44.83
100AAD	0.002	0.02[8]	0.02	0.02

[a] At 338.1 K.

Table 3. Fitting Parameters of Equations 2 to 4 to Correlate Physical Properties of MDEA and Aqueous MDEA Solutions and Standard Deviations (SD) Using Equation 5

	A_0	A_1	A_2	SD
		MDEA		
η/mPa·s	−4.939	2032	-	0.0166
n_D	1.676	−0.001	$9 \cdot 10^{-7}$	0.001
σ/m·N·m^{-1}	2.797	10903	-	0.2
		$w = 0.3228$		
η/mPa·s	−3.466	1186	-	0.0271
n_D	1.353	-	$-9 \cdot 10^{-7}$	0.1128
σ/m·N·m^{-1}	25.43	8416	-	0.0564
		$w = 0.4880$		
η/mPa·s	−3.458	1312	-	0.0208
n_D	1.272	0.001	$-3 \cdot 10^{-6}$	0.1098
σ/m·N·m^{-1}	16.19	9543	-	0.1709

Table 4. Thermal Decomposition Values of Pure and Aqueous MDEA Solutions

	MDEA	$w_{MDEA} = 0.3228$	$w_{MDEA} = 0.4880$
T_{start}/°C	58	30	31
T_{onset}/°C	169	64 and162	62 and173
T_f/°C	231	252	267

Results and Discussion

A literature review [2–13] for the determination of physical properties such as viscosity and surface tension of pure and aqueous MDEA solutions (summarized in Table 1) reveals that the experimental data for the viscosity of pure and aqueous MDEA solutions are widely scattered and limited to specific temperatures and compositions. Moreover, the experimental data for surface tension of pure and aqueous MDEA solutions are also scarce. In processes like gas−liquid absorption, surface tension of the liquid phase greatly affects the hydrodynamics and mass transfer rates. Due to these reasons, in the present work, new experimental data for viscosity and surface tension of the said system have been proposed. In Table 2, viscosity, refractive index, and surface tension values of pure and aqueous MDEA solutions with compositions (32.28 and 48.80) mass % at atmospheric pressure have been presented. The average absolute percentage deviation values of all the measured properties are also presented in Table 2. The viscosities of pure MDEA are found to be in good agreement with the reported values of Al-Ghawas et al. (1989) and DiGuillo et al. (1992) as shown in Table 2. With an increase in temperature, an overall decrease in all the measured system properties was observed. For a given temperature, the surface tension of binary mixtures of MDEA and water decreased with an increase in MDEA concentration. However, an increase in viscosity and refractive index values was observed with an increase in MDEA concentration. The influence of temperature on refractive index of MDEA and (MDEA + water) was found to be linear and correlated by eq 2, whereas the dependence of viscosity and surface tension on temperature was nonlinear and correlated by eqs 3 and 4, respectively.

$$n_D = A_0 + A_1 T + A_2 T^2 \qquad (2)$$

$$\log \eta = A_0 + A_1/T \qquad (3)$$

$$\sigma = A_0 + A_1/T \qquad (4)$$

and

$$SD = \left[\sum_{i}^{n_{dat}} (Z_{exptl} - Z_{calcd})^2 / n_{dat} \right]^{1/2} \qquad (5)$$

where A_0, A_1, and A_2 are fitting parameters; n_{dat} is the number of experimental data points; and Z_{exptl} and Z_{calcd} are experimental and calculated values. The fitting parameters were estimated using a method of least squares and presented in Table 3 along with the standard deviations (SD) calculated using eq 5.

Thermal stabilities of pure and aqueous MDEA solutions of (32.28 and 48.80) mass % were evaluated using thermogravi-

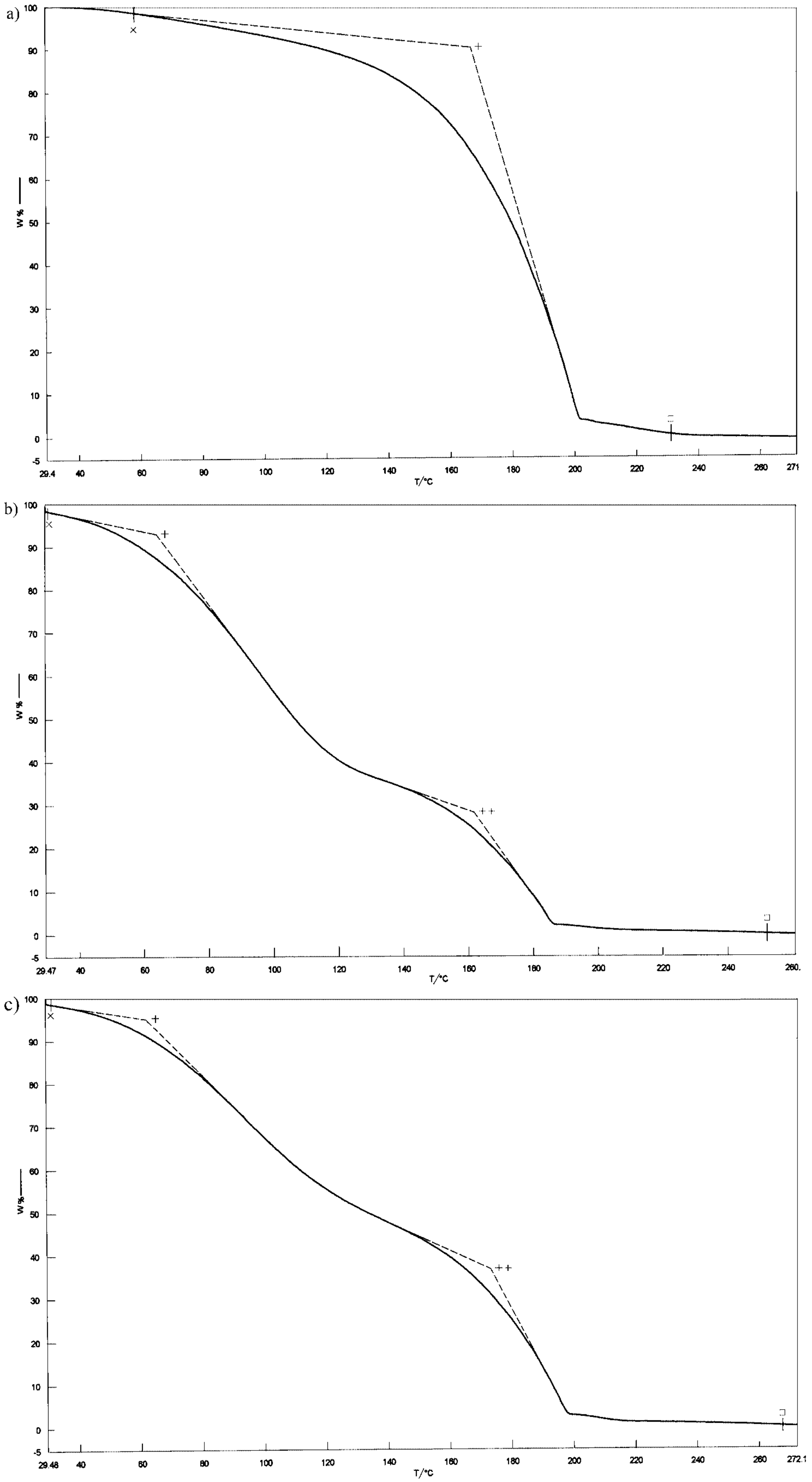

Figure 1. Plots for thermal decomposition as weight percent loss (W %) vs temperature (T/°C) of pure MDEA (a). ×, T_{start} (start decomposition temperature) = 58.295 °C at 98.4606 (W %); +, T_{onset} {intersection of baseline weight and the tangent of weight vs temperature curve (- - - -)} = 166.851 °C at 89.9677 (W %); □, T_{f} (final decomposition temperature) = 231.170 °C at 0.0968 (W %). Of MDEA + water at w = 0.3228 (b). ×, T_{start} = 29.460 °C at 98.4966 (W %); +, 1st T_{onset} = 63.89 °C at 92.9528 (W %); ++, 2nd T_{onset} = 161.640 °C at 28.1363 (W %); □, T_{f} = 251.917 °C at 0.0969 (W %). At w = 0.4880 (c). ×, T_{start} = 31.388 °C at 98.4788 (W %); +, 1st T_{onset} = 62.025 °C at 94.8941 (W %); ++, 2nd T_{onset} = 173.113 °C at 36.5520 (W %); □, T_{f} = 267.442 °C at 0.0972 (W %) at a heating rate of 10 °C·min^{-1}.

metric analysis. The values for thermal decomposition of all samples are shown in Table 4, in terms of T_{start} (start temperature for decomposition), T_{onset} (obtained at the point of 1.5 % degradation by the intersection of baseline weight and the tangent of weight vs temperature curve), and T_{f} (final decomposition temperature at 1 % sample weight). Figure 1 shows the decomposition of pure MDEA (a) and aqueous MDEA, $w = 0.3228$ (b) and $w = 0.4880$ (c), as percentage weight loss with increase in temperature. The binary mixtures of MDEA + water have shown low temperature values at the start of decomposition as compared to pure MDEA as expected. The onset temperature and two-step degradation of aqueous MDEA solutions indicate that initially free water molecules were decomposed (i.e., (64 and 62) °C) followed by degradation of MDEA molecules in the second step (i.e., (162 and 173) °C). Final decomposition temperature (T_{f}) of aqueous MDEA solutions was found to be higher than pure MDEA which could be due to the strong hydrogen bonding interactions.

Conclusion

Physical properties such as viscosity, refractive index, and surface tension of pure and binary mixtures of (MDEA + water) have been measured at a wide temperature range, and a satisfactory agreement was obtained with the available literature values. A decrease in all the measured physical properties was observed with the increase in temperature as expected. Thermal stability of pure and aqueous MDEA solutions has also been investigated using thermogravimetric analysis.

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