Viscosity Of Aqueous Solutions Of N-Methyldiethanolamine + Monoethanolamine (MDEA+MEA)

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Abstract: The blended amine viscosities of N-Methyldiethanolamine and monoethanolamine (MDEA+MEA) are measured for temperature range from 293.15 to 413.15 K. The total amine strength in the solution is maintained at 0.2, 0.3 and 0.4 mass basis. Temperature range 293.15 to 303.15 K is performed with cooling system to achieve the lower stable temperatures during the experiment. Operating pressure is maintained at 1 bar for temperature range 293.15 to 353.15 K and 4.5 bar for higher temperatures. Measured viscosity data is compared with available literature data as well as with modeled data by Grunberg and Nissan model. Earlier viscosity values are available up to 353.15 K for some blended amine concentrations. Therefore, this study is given highly importance for gas absorption process while developing regression models for reacting systems in gas separation. The average absolute deviation between measured viscosity values and viscosity calculated by regression model is around 2.1%. Therefore, measured blended amine viscosities are in good agreement with the predicted viscosity by regression model which is given by Grunberg and Nissan equation.

Index Terms: Amines, Dynamic viscosity, Methyldiethanolamine, Monoethanolamine, Temperature effect

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1 INTRODUCTION

The various types of amines such as Monoethanolamine (MEA), Diethanolamine (DEA), N-Methyldiethanolamine (MDEA) have been used for gas treating systems in a wide variety of applications [1]. However, single amine for gas treating is economically unfavorable due to high energy demand. Therefore, searching of alternative solvents is an important factor to continue the process. In that case, blended amines (mixture of primary and tertiary or secondary and tertiary) will play a vital role in gas absorption and desorption process. The tertiary amine, which has higher equilibrium capacity, together with primary or secondary amines which has higher reaction rate will bring the considerable effect. The physical properties of those amines and blended amines are important to understand the complete process. However, lack of physical property data such as viscosity of blended amines forced us to continue this research. The viscosity data of blended amines has been reported in several literatures such as (MEA+MDEA+H2O) [2, 3, 4], DEA+MDEA+H2O [5, 6, 7, 8]. All most reported data in above literatures are available for the viscosities of blended amines over the temperature range (303 to 353) K. Bishnu et.al 2003 [9] has been performed the density and viscosity measurements for temperature range (293 to 323) K to complete the gap with previous works. Hence, in this work the viscosity measurements of blended amines have done in the temperature range, T= (293 to 413) K to complete the range with high temperature. Viscosities of pure and aqueous solutions of MDEA, MEA and DEA has been already completed and reported in the previous paper [10]. In this paper, we are reporting the viscosity of blended amine systems. The viscosity of (MDEA+MEA+H2O) are measured over the temperature range (293- 413) K. The total amine concentration (mass basis) is maintained at 20%, 30% and 40% separately. The mass ratio, r, is defined as r = Mamine/M amine+water = 0.2, 0.3 and 0.4 for this study.

2 EXPERIMENTAL SECTION

The MEA was purchased from Merck KGaA and the MDEA from Merck Schuchardt OHG. The purity of the amines is 99.5% and 98% (mass basis) respectively for MEA and MDEA. The Amine solutions were prepared with degassed distilled water. Amine solutions are prepared to get total concentration of amine mixture as 20%, 30% and 40% mass basis. There are several mass fraction variations followed to develop the measuring samples. The mixture after adding amines and distilled water, is well stirred to get uniformity of the solution. Dynamic viscosity was measured using MCR 101 Anton Paar double-gap rheometer. The viscometer was calibrated against the petroleum distillate and mineral oil calibration fluid which is purchased from Paragon Scientific Ltd. The calibration factor was decided according to the experimental value and given literature value. The low-temperature measurements (293.15 – 303.15) K were achieved by applying cooling system Physica VT2 connected together with the rheometer setup. Without further purification, all these amines were used for experimental studies. The temperature range from 313.15 – 413.15 K is measured without cooling system. Two different pressure values are used for the measuring process in order to avoid the water vaporization at high temperatures. First part of the process (293.15 – 353.15) K was completed with pressure 1.01 bar and the second part of the process (363.15 – 413.15) K is completed with the 4.5 bar pressure.

3 RESULTS AND DISCUSSION

Viscosities of MDEA+MEA+H2O tertiary mixture are experimentally calculated for mass ratio 0.2, 0.3 and 0.4 of total amine weight base concentrations. The experimental viscosity values are tabulated in Table 1, 2 and 3 for r = 0.2, 0.3 and 0.4 concentration respectively.

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TABLE 1

VISCOSITY OF MDEA+MEA AMINE MIXTURE WHERE r = 0.2.

T/K	Composition of the sample (MDEA/MEA)%			
	20/0	15/5	5/15	0/20
	ŋ/mPa·s			
293.15	2.264	2.180	2.064	2.002
298.15	1.921	1.868	1.784	1.700
303.15	1.695	1.631	1.534	1.496
313.15	1.320	1.263	1.206	1.163
323.15	1.062	1.016	0.976	0.942
333.15	0.862	0.830	0.808	0.772
343.15	0.716	0.705	0.678	0.665
353.15	0.602	0.595	0.588	0.583
363.15	0.532	0.523	0.480	0.398
373.15	0.476	0.464	0.432	0.362
383.15	0.426	0.406	0.386	0.329
393.15	0.396	0.368	0.320	0.286
403.15	0.362	0.324	0.294	0.246
413.15	0.34	0.294	0.264	0.201

TABLE 2

VISCOSITY OF MDEA+MEA AMINE MIXTURE WHEN r = 0.3.

T/K	Composition of the sample (MDEA/MEA)%							
	30/0	28.5/1.5	25/5	20/10	15/15	10/20	5/25	0/30
	ŋ/mPa·s							
293.15	3.53	3.52	3.50	3.44	3.25	3.06	3.07	2.97
298.15	2.99	2.95	2.92	2.90	2.74	2.59	2.53	2.46
303.15	2.54	2.52	2.50	2.47	2.36	2.22	2.18	2.13
313.15	1.89	1.86	1.83	1.80	1.79	1.68	1.67	1.64
323.15	1.45	1.42	1.40	1.37	1.32	1.29	1.26	1.23
333.15	1.14	1.12	1.08	1.04	1.02	1.00	0.97	0.95
343.15	0.93	0.90	0.87	0.84	0.81	0.80	0.79	0.77
353.15	0.77	0.75	0.74	0.73	0.71	0.69	0.66	0.64
363.15	0.64	0.62	0.59	0.55	0.54	0.48	0.46	0.41
373.15	0.58	0.56	0.52	0.50	0.47	0.44	0.41	0.39
383.15	0.53	0.50	0.48	0.46	0.42	0.40	0.38	0.36
393.15	0.47	0.44	0.42	0.40	0.38	0.36	0.32	0.30
403.15	0.42	0.40	0.36	0.35	0.32	0.31	0.29	0.28
413.15	0.38	0.37	0.32	0.31	0.30	0.28	0.26	0.24

TABLE 3

VISCOSITY OF MDEA+MEA AMINE MIXTURE WHEN r = 0.4.

T/K	Composition of the sample (MDEA/MEA)%								
	40/0	35/5	30/10	25/15	20/20	15/25	10/30	5/35	0/40
	ŋ/mPa·s								
293.15	6.35	6.01	5.85	5.34	5.21	5.03	4.84	4.73	4.64
298.15	5.25	5.02	4.89	4.47	4.31	4.27	3.92	3.86	3.76
303.15	4.34	4.19	4.09	3.77	3.69	3.63	3.37	3.32	3.27
313.15	3.14	3.04	3.00	2.71	2.57	2.49	2.44	2.35	2.30
323.15	2.36	2.29	2.25	2.05	2.01	1.96	1.86	1.82	1.78
333.15	1.82	1.79	1.74	1.61	1.53	1.45	1.43	1.41	1.39
343.15	1.48	1.42	1.39	1.27	1.23	1.19	1.18	1.16	1.15
353.15	1.19	1.15	1.16	1.03	1.01	0.98	0.96	0.95	0.94
363.15	0.97	0.95	0.93	0.90	0.88	0.86	0.85	0.85	0.84
373.15	0.92	0.90	0.88	0.86	0.85	0.82	0.80	0.80	0.78
383.15	0.81	0.76	0.73	0.72	0.70	0.68	0.64	0.62	0.60
393.15	0.72	0.69	0.66	0.64	0.63	0.60	0.58	0.58	0.57
403.15	0.58	0.66	0.62	0.60	0.58	0.54	0.52	0.50	0.50
413.15	0.46	0.45	0.43	0.42	0.40	0.38	0.34	0.32	0.30

The pure amine viscosities of MDEA, MEA, and Water are given in Table IV [10].

The viscosity variation of blended amines is analyzed with following figures. As an example, r = 0.2 of blended amine viscosities also compared with available literatures. Literature values are taken from the Li and Lie [3]. However, they have performed experiments for temperature range 303.15-353.15 K only. Fig. 1 represents the comparison of viscosities for mass ratio 0.2. According to the figures, it can be seen that viscosity of blended amine is decreasing with the increase of the temperature. The measurement values are in good agreement with available literature data.

TABLE 4

PURE AMINE AND WATER VISCOSITY WATER VISCOSITY VARIATION WITH TEMPERATURE [10].

T/K	MEA	MDEA	H2O
	ŋ/mPa·s		
293.15	24.085	103.67	1.051
298.15	18.924	77.32	0.900
303.15	15.151	57.50	0.843
313.15	10.006	34.622	0.665
323.15	6.962	22.402	0.557
333.15	5.037	15.276	0.478
343.15	3.775	9.965	0.414
353.15	2.919	7.146	0.360
363.15	2.334	5.818	0.315
373.15	1.914	4.385	0.281
383.15	1.586	3.362	0.254
393.15	1.324	2.656	0.232
403.15	1.105	2.122	0.210
413.15	0.934	1.696	0.190

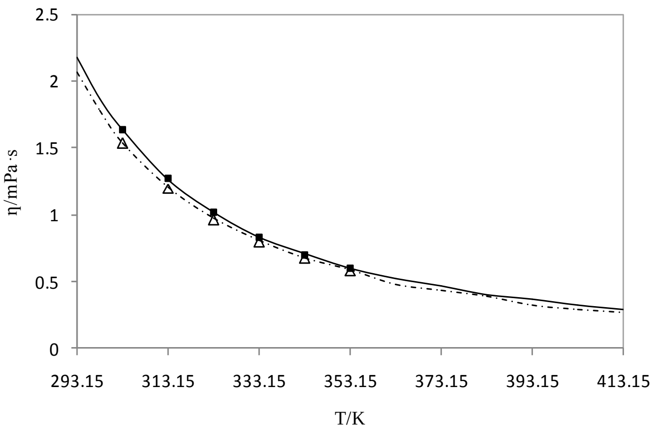

Fig. 1.*Viscosity of MDEA/MEA blends for 15/5% and 5/15%. Lines are experimental data; Symbols refer to the literature data [3]: ■, 15/5%; ∆, 5/15%.*

Similarly, MDEA+MEA blend of 28.5+1.5% and 25+5% for complete temperature is considered. At the same time, literature data is plotted in the same figure (Fig. 2 and 3) for available temperature range. Literature values of 28.5/1.5% are taken from the Bishnu et. al [9]. However, they have performed experiments for temperature from 293.15 to 323.15 K only.

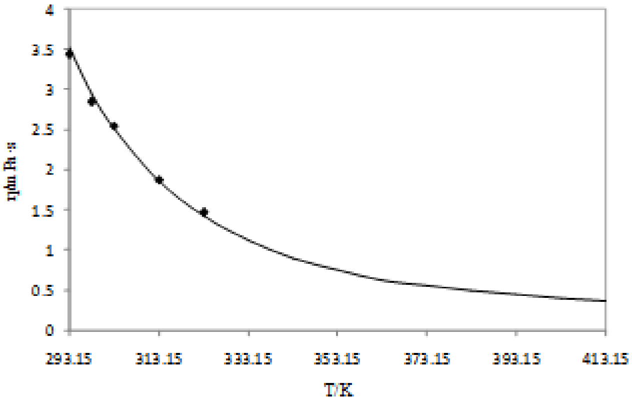

Fig. 2.*Viscosity of MDEA/MEA blends for 28.5/1.5%. Lines are experimental data and symbols refer to the literature data [9].*

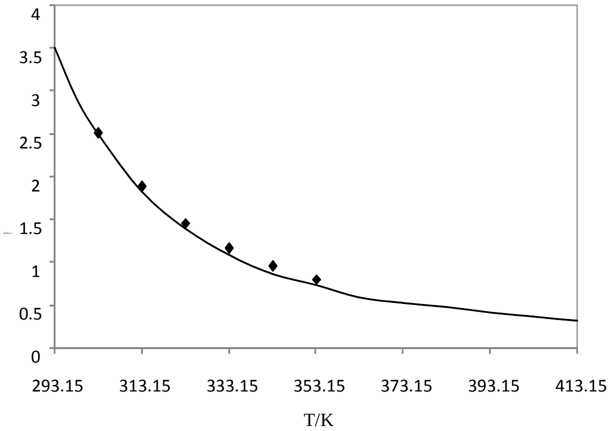

Fig. 3.*Viscosity of MDEA/MEA blends for 25/5%. Lines are experimental data (25/5%) and symbols refer to the literature data (24/6%) [3].*

As can be seen from both figures, viscosity of the blended amine is decreasing with the increase of temperature. According to the Fig. 3, literature data is given for 24/6% of MDEA/MEA mixture. However, experimental data is plotted for 25/5% of MDEA/MEA mixture. When the MEA composition in the blended amine is decreasing, viscosity of the blend is also decreasing. This is because of the viscosity of MEA is less compared to the MDEA viscosity. All the literature values are fallen above the experimental viscosity line in Figure3. There for experimental results are in good agreement with the literature data. However, there is a slight deviation between experimental data and regression data. The reason may be due to the practical errors or different amine conditions.

4 RESULTS VALIDATION

The experimental viscosity values in this study are compared with the Grunberg and Nissan model [9]. The Grunberg and Nissan model is suggested for calculating viscosity of the liquid mixtures. The Grunberg and Nissan equation has the following form (equation 1):

$$\ln \eta_m / mPa \cdot s = \sum x_i \ln \eta_i + \sum \sum x_i x_j G_{ij} \qquad (1)$$

Where η_m is the viscosity of the liquid mixture, η_i is the viscosity of the i^{th} pure fluid and mole fraction of the i^{th} component is given by the xi. Pure liquid viscosities are given in the Table 4. The component G_{ij} is given by temperature dependent equation which is assumed to follow the equation 2 which is given below.

$$G_{ij} = a + b(T/K) + c(T/K)^2 \qquad (2)$$

The parameter values for a, b and c is taken from the literatures and given in the Table 5 [9].

TABLE 5
CONSTANT VALUES FOR EQUATION 2, MEA (1) + MDEA (2) +H2O (3) [10].

Parameter - Gij	Constant values from equation (2)	MDEA+MEA+H2O
10^3 G_{12}	a	2061147.2
	b	-12381.298
	c	18.523985
10^3 G_{13}	a	-23598.380
	b	196.27770
	c	-0.3298253
10^3 G_{23}	a	126845.80
	b	-625.32640
	c	0.8442153

The calculated viscosity values using equation (1) and experimental viscosity values measured in this study are in good agreement. The average absolute deviation of the viscosity data is 2.1% for MDEA+MEA+H2O system. The parameter values used for the equation 1 was taken from the regression results developed by Bishnu et.al [9]. However, they have performed experiments for temperature range 293.15-323.15 K only. That may be the reason for deviation of the current study. The experimental viscosity values and the viscosity values calculated by the equation 1 are representing by Fig. 4-6 for 20%, 30% and 40% total amine concentration respectively.

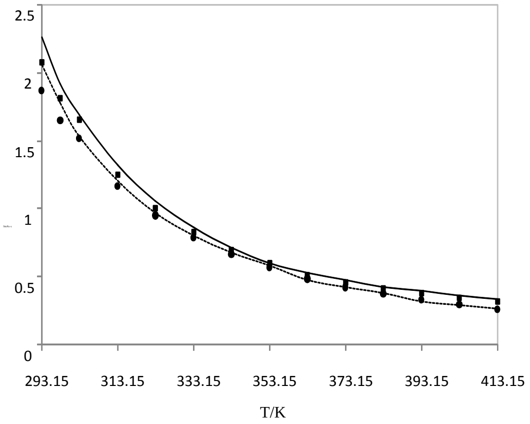

FIG. 4.*Experimental results vs. equation modeled results for MDEA+MEA+H2O mixture: Symbols refer to equation values: ■, 20/0%; ●, 5/15%. Lines are experimental data.*

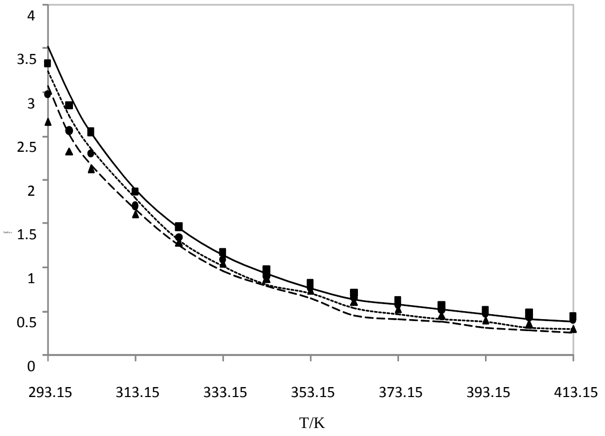

FIG. 5. *Experimental results vs. equation modeled results for MDEA+MEA+H2O mixture: Symbols refer to equation values: ■, 30/0%; ●, 15/15%; ▲, 5/25%. Lines are experimental data.*

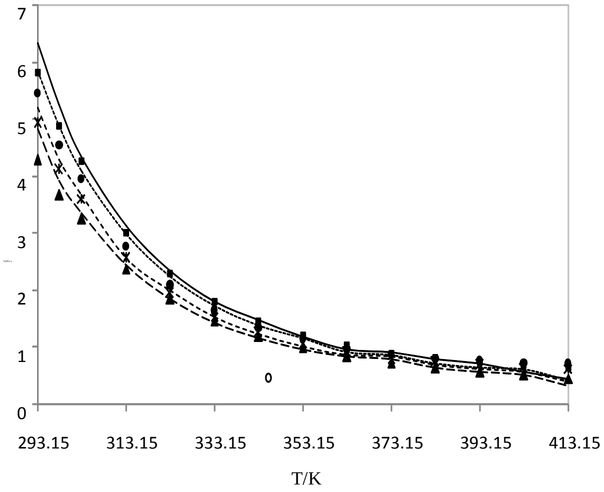

FIG. 6. *Experimental results vs. equation modeled results for MDEA+MEA+H2O mixture: Symbols refer to equation values: ■, 40/0%; ●, 30/10%; ⁎, 20/20%; ▲, 10/30%. Lines are experimental data.*

There are slight changes of experimental data trend after 353.15K temperature for every case. Reason for that may be use of high pressure after that temperature value. However, the fluctuation of the trend is negligible.

5 EXPERIMENTAL UNCERTAINTIES

The experimental uncertainties have to be discussed for better understandings. The uncertainty of the viscosity measurements of MEA+MDEA amine mixtures arises as a combination of the uncertainty of the temperature measurements and sample preparation uncertainties due to measuring instrument uncertainties. The temperature accuracy, U(T), which is related to rheometer temperature controller, is given as ±0.3K. The maximum viscosity gradient against the temperature, $\Delta\eta/\Delta T$, is calculated as 0.044 mPa·s·K-1. The corresponding uncertainty in ŋ, $(\Delta\eta/\Delta T).\Delta T$, is then estimated as ±0.0132 mPa·s. The uncertainties of the sample preparation were found by calculating the error values (difference between the expected value and measured value r) of the prepared sample. The ±0.004 of mass ratio uncertainty, U(r), is calculated with 0.06 mPa·s viscosity gradient $(\Delta\eta/\Delta r)$. The resulting uncertainty in the sample preparation is calculated as, $(\Delta\eta/\Delta r).\Delta r$, ±0.00024. The rheometer accuracy is given as ± 0.002 mPa·s. The overall uncertainty of ŋ, U(ŋ), is calculated by combining the partial uncertainties reported in this section with root sum of square method. The value is calculated as ±0.0134 mPa·s. The combined expanded uncertainty of the viscosity, Uc(ŋ), is calculated as ±0.0268 mPa·s (level of confidence 0.95). The combined expanded uncertainty, suggested by symbol Uc, is obtained by multiplying overall uncertainty, U(ŋ), by a coverage factor, suggested symbol k. Typically, k is assumed to be 2 with the level of confidence 0.95.

6 CONCLUSION

The viscosities of MDEA+MEA+H2O mixtures for different concentrations have been analyzed for temperature range from 293.15 to 413.15 K. High temperature data was measured by keeping high pressure of the measuring system. A decrease in the viscosity with increasing temperature were observed. Measured viscosities were compared with the available literature values as well as with viscosities calculated by Grunberg and Nissan equation. The experimental data is in good agreement with literature data as well as with the calculated data. The average absolute deviation between the experimental values and values predicted by equation is around 2.1%. The parameter values used in the equation is developed by using experimental data from 293.15 to 323.15K. Same parameters used for comparison with the present study even though this study was performed at temperature range 293.15 to 413.15K.

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