Measuring the Density and Viscosity of Carbonated Aqueous 35 wt% Methyldiethanolamine Solution

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ABSTRACT: The density and viscosity of carbonated aqueous 35wt% methyldiethanolamine solution were experimentally measured accompanied with the solubility of CO$_2$ at temperatures from (303.15 to 363.15) K and pressures up to 0.8 MPa using the new setup developed in our laboratory. It was observed that both density and viscosity of mixtures decrease by increasing temperature and increase by increasing acid gas solubility (loading) in solution. Acid gas loading has an intense effect on the viscosity of solutions than on their density. The modified Seth now correlation was used to predict the density and viscosity of all solutions studied in this work.

KEYWORDS: Gas solubility; Chemical absorption; Transport property; Methyldiethanolamine; Density; Viscosity.

INTRODUCTION

Knowledge on the physical thermal and non-thermal properties of gas-loaded physical and chemical solvents such as density, viscosity, surface tension, enthalpy, heat capacity, thermal conductivity and thermal diffusivity are necessary for the design of acid gas treatment equipment and subsequent measuring operation, interpreting other physicochemical properties, and also, are very important in solvent regeneration at reduction stage.

An enormously growing number of experimental results for thermophysical properties of pure solvents as well as those of their mixtures with other solvents have been reported in the literature. However, data regarding acid gas absorbed in physical and chemical solvents are scarce. To the best of our knowledge, there is no information available in the open literature about the density and viscosity of gas-loaded solvents except for (i) liquid sulfolane loaded by CO$_2$ and H$_2$S [1] reported by our research group (ii) CO$_2$/Methanol system as a physical solvents [2] (iii) density and viscosity of MDEA, DEA, MEA and their mixture loaded by CO$_2$ reported by Weiland et al. research group [3] and (iv) density of CO$_2$ loaded solution of DIPA reported by Dell’ Era et al. [4]. It is worth noting that loaded aqueous alkanol amine solutions reported by Weiland et al. were prepared via quenching and separating method in which solutions were partially carbonated.

In this work, we focus on the measurement of density and viscosity of 35 mass% methyl diethanolamine (MDEA) loaded with CO$_2$ using a setup developed in our laboratory without any quenching procedure.
All experimental trials are carried out on stand situation at temperatures range from 303.15 to 363.15 K and all experimental trials are carried out on stand situation at temperatures ranging from (303.15 to 363.15) K and pressures up to 0.8 MPa. Gas loading was systematically measured by gravimetric method. Finally, the experimental density and viscosity data were correlated using a modified Setchenow equation [5-8].

EXPERIMENTAL SECTION

Materials
Carbon dioxide (c.p. grade 99.95% min) were obtained from Roham Gas Company. N-Methyldiethanoleamine [CAS registry number 105-59-9] was purchased from Sigma-Aldrich with purity >99% and used without further purification. Water used as solvent was distilled and deionized, which was degassed in an ultrasonic bath (FUNGILAB, model UA10MFD) at a temperature and wave frequency of 343K and 50 kHz, respectively for about 1 hour prior to use. All solutions were prepared by measurement of the mass of the solutes and solvent on a calibrated balance (Mettler model AE 200) with an uncertainty ± 0.0001 g and measuring the volume of the solution by a standard volumetric flask up to 100 mL.

Apparatus and Procedure
The solubility, as well as density and viscosity measurements, were carried out in a newly developed experimental setup. The details of the experimental method for the measurement of gas solubility, density and viscosity have been presented previously [1] and only a short description will be provided here.

The experimental setup having shown in Fig. 1, comprised of four separate apparatus, each one considered to perform a specific task: (a) the main Equilibrium Cell (EC), (b) a Gas Injection System (GIS), (c) a Vibrating Tube Densimeter (VTD), and (d) a Falling weight Viscometer (FV).

The EC was equipped with a magnetically driven mechanical stirrer to accelerate equilibrium state and a Side glass Window (SW) to allow one to monitor both the liquid level and the foaming of the solution in the EC. The EC was double wall jacketed to facilitate the circulation of water from Water Recirculation Bath (WRB) to control the temperature of the solution in the cell. The temperature of EC was monitored using a Lutron model TM-917 digital thermometer with a 0.01 K resolution using a PT-100 sensor inserted into the thermowell of the EC (not shown in Fig. 1). The pressure of the system was measured using a Keller model PA-33X pressure transmitter sensor (P2) in the range of (0 to 4) MPa with an uncertainty of ±0.01% of full scale.

The Gas Injection System (GIS) consists of a gas container (GR) with constant known volume equipped with a Keller model PA-33X pressure transmitter sensor (P1) in the range of 0 to 4 MPa with an uncertainty of ±0.01% of full scale. The GIS, which is connected to the EC through V3 valve, is directly fed from gas cylinders through V1 valve.

To measure the solubility of gases in the liquid solvent, known quantities of gaseous solute and degassed solvent are brought into contact at a constant temperature inside the measurement system (EC + VTD + FV) of known volume. On reaching thermodynamic equilibrium, the pressure above the liquid solution, which is measured by the P2 pressure transmitter, is constant and directly related to the solubility of the gas in the liquid. The quantity of solute present in the liquid solution is calculated by the difference between two pVT measurements: first on the introduction of the gas from the container GR of known volume into the measurement system (EC + VTD + FV) containing the solvent and secondly after reaching thermodynamic equilibrium, i.e. when autoclave pressure, \( p \), remains fixed and no longer changes with time. Using the procedure adopted by Park & Sandall [9] and Hosseini Jenab et al. [10]:

\[
\frac{V_{ag}}{RT_a} = \frac{P_i}{Z_i} - \frac{P_f}{Z_f}
\]

Where \( V_{ag} \) denotes the volume of the gas container, \( Z_i \) and \( Z_f \) are the compressibility factors corresponding to the initial and final pressures, \( P_i \) and \( P_f \), respectively, in the gas container before and after transferring gas, and \( T_a \) is the ambient temperature, which is equal to that in the gas container. Compressibility factors were calculated using NIST [11]. Equilibration between liquid and vapor phases inside the cell were normally achieved within about 2h after the beginning of stirring and the partial pressure of gas at equilibrium in the equilibrium cell \( p_{ag}^{e} \), was calculated as follow:

\[
p_{ag}^{e} = P_T - P_{VP}
\]

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Fig. 1: Experimental setup for the simultaneous measurement of gas loading, density, and viscosity; V1–V6: valves; P1, P2: pressure transmitter sensors; EC: main liquid tank; SW: side glass window; GIS: gas injection system; VTD: Anton-Paar vibrating–tube densimeter; IM: interface module of densimeter; EU: evaluation unit of densimeter; CP: high-pressure centrifuge pump; FV: viscometer tube; S1, S2: magnetic sensors; TM: electronic time registration device; WRB: water recirculation bath; GR: constant volume gas container; WCP: water circulation path.

Where $P_T$ and $P_{vp}$ denote the total pressure and vapor pressure of the solution. A key issue is the determination of the vapor pressure of the mixture solution since this value must be subtracted from the total pressure to obtain the partial acid gas pressure.

The moles of remaining acid gas in the gas phase, $n_{ag}^e$, was determined from:

$$n_{ag}^e = \frac{V_g \rho_{ag}^e}{Z_{ag} RT} = V_g \rho_{ag}$$

(3)

Where $V_g$ is the gas phase volume, $T$ is the equilibrium temperature of the cell, and $Z_{ag}$ and $\rho_{ag}$ are the compressibility factor and density of the acid gas at $P_{ag}^e$ and $T$, respectively. The quantity of gas in the liquid phase was then determined from:

$$n_{ag}^l = n_{ag} - n_{ag}^e$$

(4)

The molality and loading of charged gas in the liquid phase is defined as:

$$m_{ag} = \frac{n_{ag}^l \text{ (mole)}}{w_{\text{Solvent}} \text{ (g)}} \times 1000$$

(5)

$$\alpha_{ag} = \frac{n_{ag}^l \text{ (mole)}}{\sum w_i \text{ (g)}}$$

(6)

$W_i$ is the weight of comprised amines in a fresh solvent in g, and $M_i$ is the molar mass of pure solvent in g/mol.

As mentioned above the amount of dissolved gas is calculated from the amount of gas charged to the cell by subtracting a correction for the amount of gas that is still present in the vapor phase. That correction is calculated...
assuming that the volume of the vapor phase is the difference between the cell volume and the volume of the unloaded solvent (which is known from the preparation of the solvent). However, that procedure neglects a volume change (mostly a volume expansion) when a gas is dissolved in a liquid.

In this case, Eq (3) may be corrected as (7).

\[ n_{ag}^s = \rho_{ag} \cdot \left( V_{auto} - \frac{m_{ag} \cdot W_{Solvent}}{1000} + W_{Solvent} \right) \rho_{charged solution} \]  

where \( m_{ag} \) is the molality of acid gas obtained from iteration technique or as an approximate estimation obtained from molality calculated with Eqs. (3) through (6). \( \tau \rho_{charged solution} \) is the charged solution density measured on the stand (without quenching method) using the procedure described in the following section.

**Density measurement**

Measurement of the density of fresh as well as acid-gas saturated liquid solutions prepared in equilibrium cell, EC, at each specified temperature, \( T \) and pressure, \( p \) was carried out by the Vibrating Tube Densimeter (VTD). The VTD was an Anton-Paar model DMA HPM, equipped with a liquid jacket by the supplier, the temperature of which was thermostatted through circulation of water from the external water recirculation bath, WCP. The DMA HPM density measuring cell is a U-shaped Hastelloy C-276 tube electronically excited to vibrate at its characteristic frequency, which in turn depends on the density of the sample.

The DMA HPM is connected to the interface module (IM), which generates and measures the period of oscillation and is also responsible for the temperature measurement. The IM is in turn connected to an mPDS 2000 V3 evaluation unit (EU), which converts the measured raw data (oscillation period, temperature and pressure) to the density of the sample through the appropriate calibration equations. The VTD density measuring device was calibrated by using distilled deionized water, pure methanol, pure sulfolane and nitrogen gas in the temperature range (298.15–363.15) K and from atmospheric pressures up to about 7.0 MPa employing Eq. (8) as suggested by the supplier:

\[ \rho = \sum_{i,j,k} a_{ijk} \cdot \tau^i \cdot T^j \cdot p^k \]  

where \( a_{ijk}, \tau, T, \) and \( p \) stand for apparatus constant, period of oscillation, temperature, and absolute pressure, respectively, with \( i = 0, 2, 4, j = 0, 1, 2, \) and \( k = 0, 1, 2. \)

**Viscosity measurement**

The viscosity of pure as well as gas saturated liquid solutions was measured by the falling weight viscometer (FV). FV, which was a cylindrical steel tube with 85 cm length and 6.8 mm inner diameter, was equipped with a liquid jacket to be thermostatted by an external Water Recirculation Bath (WRB). The FV was mounted vertically and consisted of a cylindrical sinker of 6.4 mm outer diameter and 20.4 mm length, with hemispherical ends and a density of 2880.3 kg/m\(^3\). The sinker was an iron magnetic bar coated with Teflon PTFE to prevent corrosion of the bar and the resultant contamination of the solution during measurement. A working equation of the functional form suggested by Daugé et al. [12] was used to measure the viscosity of acid gas-loaded solutions:

\[ \eta(T,p) = K_a(T) + K_b(T) \cdot (\rho_s - \rho) \cdot \tau \]
importantly (2) starting the measurement of the viscosity of the mixtures, i.e. the drag force, which is produced as a result of the operation of the high-speed centrifuge pump and lifts the sinker up the vertical cylinder without the need for any additional external/internal apparatus. By closing V4 valve, the drag force ceases and the sinker falls through the liquid down from the top to the base of the vertical tube. By passing through the two S1 and S2 sensors, the falling time is registered and the viscosity is calculated by using Eq. (9). The speed of the centrifuge pump was adjusted in such a way that a laminar flow regime of the liquid always prevailed in the FV vertical cylinder. A laminar flow ensured a uniform liquid phase without any bubble formation during the falling of the sinker in the cylinder.

RESULTS AND DISCUSSION

As reported in our previous paper [1] the accuracy and reliability of the experimental data produced by the apparatus developed in this work was checked through comparison of the measured solubility, density and viscosity of pure sulfolane, pure methanol and the (CO$_2$ + methanol) binary mixture with the available experimental data reported in the literature [2,13]. The Sih et al. [2] and Chien-Ming et al. [13] methods are in principle similar to the method used in our work. The maximum percent deviation of the density values reported by Sih et al. [2] from this work is less than 0.50%. The maximum percent deviation of the viscosity values reported by Sih et al. [2] from this work is less than 1.0 % with the average deviation of 0.39 %. The two sets of solubility measurements are also in quite good agreement with each other. This is also the case for the solubility and density data from (298 to 313) K reported by Chiehming et al. [13].

The pT$x$ solubility data obtained using our setup for (CO$_2$ + methanol) binary mixture are also consistent with the corresponding values reported by Weber et al. [15] at 298 K (AAD% = 3.7% and MAD% = 6.0%), with those reported by Ohgaki & Katayama [15] at T = (298 and 313) K (AAD% = 4.8% and MAD% = 6.8%), and also with those reported by Xia et al. [16] at 313.75 K (AAD% = 7.2% and MAD% = 8.4%).

Experimental solubility of CO$_2$, fresh and loaded density and viscosity accompany with their uncertainty are reported in Table 1. Temperature and pressure dependency of CO$_2$ solubility, graphically have been shown in Fig. 2. Dependency of density and viscosity on gas loading has been shown schematically in Figs. 3 and 4, respectively. As may be seen from Figs. 3 and 4, both density and viscosity increase with loading. This result is exactly opposite of that arisen from the solubility of CO$_2$ and H$_2$S in physical solvents such as sulfolane and methanol [1] in which density and viscosity both reduce with increasing of gas loading. In physical solution, dissolved gases lie within free spaces of solvent, which causes an increase in the degree of volume expansion of the liquid phase and thereby reduction in liquid phase density and viscosity. The increased viscosity of fluids with increasing density is consistent with Enskog theory [17]. The viscosity of CO$_2$ and pure solvents increase with pressure, but the viscosity of physical solvent with CO$_2$-loaded decreases with pressure at low loading and after going through a minimum, it rises [2,18]. In CO$_2$-loaded physical solvents, an increase in system pressure results in an enrichment of liquid phase with CO$_2$ and a competing effect of viscosity reduction with dissolved CO$_2$ and viscosity enhancement with increasing pressure leads to a cross-over effect on viscosity [18]. In the case of electrolyte systems such as MDEA/H$_2$O/CO$_2$, it seems that ionic strength of solution results to higher attractive interaction and whereby it brings about volume compression [19-21].

DENSITY AND VISCOSITY MODELING

The experimental density and viscosity of solution are correlated using modified Setchenow type equation which is recently used for correlating of density, viscosity and surface tension of binary and ternary solutions [3-6]. The working equation is represented by Eq. (10):

$$\ln \left( \frac{P}{P_r} \right) = \sum_{j=1}^{2} k_j \alpha^j$$

(10)

Where $P_r$ and $P$ stand for the thermo-physical property of the mixture and reference substance, respectively; for example, $P_r$ represents the density / viscosity of the (CO$_2$ + alkanol amine solution) mixture and $P$ is the density / viscosity of uncharged alkanol amine solution at the same temperature as the mixture. The $k_j$’s are temperature dependent parameters, which are known as the Setchenow coefficients, and $\alpha$ is the concentration of CO$_2$ dissolved in the liquid phase.
Table 1: Experimental solubility, density, and viscosity for (CO\textsubscript{2} - 35 mass\% MDEA) system.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P\textsubscript{CO\textsubscript{2}} (bar)</th>
<th>α (mol CO\textsubscript{2}/mol MDEA)</th>
<th>±δα</th>
<th>ρ (g/cm\textsuperscript{3})</th>
<th>η (mPa.s)</th>
<th>±δη</th>
</tr>
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<tbody>
<tr>
<td>303.15</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td>1.0232</td>
<td>3.209</td>
<td>±0.073</td>
</tr>
<tr>
<td></td>
<td>0.057</td>
<td>0.188</td>
<td>±0.003</td>
<td>1.0432</td>
<td>3.392</td>
<td>±0.036</td>
</tr>
<tr>
<td></td>
<td>0.173</td>
<td>0.392</td>
<td>±0.004</td>
<td>1.0600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.111</td>
<td>0.298</td>
<td>±0.003</td>
<td>1.0555</td>
<td>3.619</td>
<td>±0.056</td>
</tr>
<tr>
<td></td>
<td>0.278</td>
<td>0.532</td>
<td>±0.005</td>
<td>1.0777</td>
<td>3.668</td>
<td>±0.048</td>
</tr>
<tr>
<td></td>
<td>0.497</td>
<td>0.660</td>
<td>±0.005</td>
<td>1.0863</td>
<td>3.813</td>
<td>±0.075</td>
</tr>
<tr>
<td></td>
<td>0.738</td>
<td>0.814</td>
<td>±0.005</td>
<td>1.1037</td>
<td>4.077</td>
<td>±0.065</td>
</tr>
<tr>
<td>323.15</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td>1.0125</td>
<td>1.826</td>
<td>±0.027</td>
</tr>
<tr>
<td></td>
<td>0.095</td>
<td>0.187</td>
<td>±0.004</td>
<td>1.0326</td>
<td>1.986</td>
<td>±0.056</td>
</tr>
<tr>
<td></td>
<td>0.516</td>
<td>0.529</td>
<td>±0.005</td>
<td>1.0608</td>
<td>2.141</td>
<td>±0.04</td>
</tr>
<tr>
<td></td>
<td>0.812</td>
<td>0.654</td>
<td>±0.005</td>
<td>1.0710</td>
<td>2.192</td>
<td>±0.032</td>
</tr>
<tr>
<td>343.15</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td>0.9989</td>
<td>1.067</td>
<td>±0.052</td>
</tr>
<tr>
<td></td>
<td>0.152</td>
<td>0.186</td>
<td>±0.004</td>
<td>1.0189</td>
<td>1.274</td>
<td>±0.047</td>
</tr>
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<td></td>
<td>1.088</td>
<td>0.512</td>
<td>±0.004</td>
<td>1.0492</td>
<td>1.294</td>
<td>±0.016</td>
</tr>
<tr>
<td></td>
<td>1.999</td>
<td>0.627</td>
<td>±0.005</td>
<td>1.0595</td>
<td>1.367</td>
<td>±0.03</td>
</tr>
<tr>
<td></td>
<td>3.665</td>
<td>0.758</td>
<td>±0.006</td>
<td>1.0672</td>
<td>1.348</td>
<td>±0.04</td>
</tr>
<tr>
<td>363.15</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td>0.9823</td>
<td>0.594</td>
<td>±0.075</td>
</tr>
<tr>
<td></td>
<td>0.540</td>
<td>0.178</td>
<td>±0.004</td>
<td>1.0016</td>
<td>0.806</td>
<td>±0.035</td>
</tr>
<tr>
<td></td>
<td>2.923</td>
<td>0.474</td>
<td>±0.004</td>
<td>1.0284</td>
<td>0.793</td>
<td>±0.056</td>
</tr>
<tr>
<td></td>
<td>5.156</td>
<td>0.561</td>
<td>±0.005</td>
<td>1.0375</td>
<td>0.867</td>
<td>±0.06</td>
</tr>
<tr>
<td></td>
<td>5.292</td>
<td>0.571</td>
<td>±0.004</td>
<td>1.0365</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.019</td>
<td>0.682</td>
<td>±0.005</td>
<td>1.0430</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
at the specified temperature and pressure. The final working equation for correlation of density and viscosity are:

\[
\ln \left( \frac{\rho_s}{\rho_r} \right) = \left( k_{0,0,p} + k_{0,1,p} \cdot T \right) \cdot \alpha + \left( k_{1,0,p} + k_{1,1,p} \cdot T \right) \cdot \alpha^2
\]  

(11)

\[
\ln \left( \frac{\eta_s}{\eta_r} \right) = \left( k_{0,0,\eta} + k_{0,1,\eta} \cdot T \right) \cdot \alpha + \left( k_{1,0,\eta} + k_{1,1,\eta} \cdot T \right) \cdot \alpha^2
\]  

(12)

The average of relative deviations, ARD %, defined by Eq. (13) and maximum of relative deviations, MRD %, defined by Eq. (14) for a number of N experimental points are reported.

\[
\text{ARD} \% = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{P_{i}^{\text{cal}} - P_{i}^{\exp}}{P_{i}^{\exp}} \right)
\]  

(13)

\[
\text{MRD} \% = \text{Maximum} \left( \frac{P_{i}^{\text{cal}} - P_{i}^{\exp}}{P_{i}^{\exp}} \cdot 100 \right)
\]  

(14)

\(P_{i}^{\text{cal}}\) and \(P_{i}^{\exp}\) in Eqs (13) and (14) stand for the calculated and experimental value of the physical property of interest, respectively. It can be observed that modified Seth now equation is able to describe the temperature and loading variation of the density and viscosity of the three systems studied in this work both qualitatively and quantitatively. The average and maximum percent deviations of the correlated values from experimental ones are also reported in Table 2.

**CONCLUSIONS**

The physical equilibrium and transport properties, i.e. gas loaded density and viscosity of MDEA solutions which are in use in the natural gas sweetening processes, were measured in this work. The experimental setup developed in our laboratory is able to measure simultaneously the density and viscosity with the solubility of acid gases in both physical and chemical solvents. The reliability of the experimental data generated by the setup was assessed through comparison of the measured solubility, density and viscosity of pure sulfolane, pure methanol and the (CO\(_2\) + methanol)
Table 2: Numerical values of the parameters of the modified Setchenow equation for correlation of density and viscosity.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{0,0}$</td>
<td>0.08954</td>
</tr>
<tr>
<td>$k_{0,1}$</td>
<td>6.6898x10^{-5}</td>
</tr>
<tr>
<td>$k_{1,0}$</td>
<td>0.00127</td>
</tr>
<tr>
<td>$k_{1,1}$</td>
<td>-0.00010</td>
</tr>
<tr>
<td>$k_{0,0}$</td>
<td>-4.2673</td>
</tr>
<tr>
<td>$k_{0,1}$</td>
<td>0.0148</td>
</tr>
<tr>
<td>$k_{1,0}$</td>
<td>5.6312</td>
</tr>
<tr>
<td>$k_{1,1}$</td>
<td>-0.0183</td>
</tr>
<tr>
<td>ARD% ($\rho$)</td>
<td>0.11%</td>
</tr>
<tr>
<td>MRD% ($\rho$)</td>
<td>0.55%</td>
</tr>
<tr>
<td>ARD% ($\eta$)</td>
<td>1.71%</td>
</tr>
<tr>
<td>MRD% ($\eta$)</td>
<td>7.96%</td>
</tr>
</tbody>
</table>

binary mixture with the available experimental data reported in the literature [2]. The Modified Setchenow equation was used to correlate the experimental physical properties of multicomponent solutions.

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