**Density and viscosity measurements of (piperazine + water) and (piperazine + 2-dimethylaminoethanol + water) at high pressures**.

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**Abstract**

The purpose of this paper is broadening the understanding of amine solution behaviour through the experimental measurements of density (up to 140 MPa) and viscosity (up to 100 MPa) in a temperature range from (293.15 to 393.15) K. The two selected blends are Piperazine (PZ) + Water (10% amine weight concentration) and Piperazine (PZ) + 2-Dimethylaminoethanol (DMAE) + Water (10% and 30% amine weight concentration, respectively). Densities were measured using a vibrating tube densimeter (Anton Paar DMA HPM) with an expanded uncertainty ($k = 2$) less than 0.7 kg·m$^{-3}$. Viscosities were obtained using a falling body viscometer which was calibrated with water and dodecane. The viscosity expanded uncertainty ($k = 2$) ranges from 2.5% for the highest viscosity to 3.2% for the

lowest one. Experimental data were fitted to modified Tamman-Tait equation for densities and modified VFT model for viscosities, obtaining good results for both equations.

## 1. Introduction

In the next decades, the use of fossil fuels will continue leading the world energy consumption, representing more than 81% of the total energy employed. Energy sector accounts two-thirds of total greenhouse gas emissions (GHG) and 80% of $CO_2$. These GHG emissions include carbon dioxide, methane, $NO_X$, $SO_X$, etc. Electricity, heat generation and transportation are the main contributors of the worldwide $CO_2$ emissions which depend heavily on coal, oil and natural gas. Because of that, it is necessary to make an extra effort to reduce these emissions and mitigate climate change and energy sector must be included (IEA, 2017) [1].

Nowadays, there are many technological solutions developed to isolate carbon dioxide from exhaust gases. Post-combustion technology is one of the most suitable and mature technological process to remove $CO_2$ from the main combustion gas streams, with the advantage that, this technology can be easily installed on the pre-existing power plants [2]. The $CO_2$ separation from flue gas is based on chemical absorption with amine-based solvents. That process has been extensively studied in terms of cost and energy consumption, regarding as the most effective technology for $CO_2$ capture [3].

The use of piperazine (PZ) at low concentration shows a high potential as a solvent for $CO_2$ capture when it is mixed with conventional solvents (MDEA, AMP, etc) due of its $CO_2$ loading capacity and high reaction rate. Theoretically, PZ is able to absorb two moles of $CO_2$ for each mole of amine and the rate constant of PZ has been found one order higher than conventional alkanolamines such as MEA [4].

Blends of primary and tertiary amines or secondary and tertiary amines offer enhanced absorption capacity, higher absorption rates and reduced the required regeneration energy. As a result of the use of these mixtures and the lack of literature data, the knowledge of thermodynamic and thermophysical properties, as density, viscosity, heat capacity or surface tension, are essential to design the gas treating units.

The main objective of this work is to report new experimental data of densities and viscosities at wide pressure and temperature ranges. Also, this paper extends the information of thermodynamic properties of amines mixtures previously published concerning aqueous solutions of one amine and water: monoethanolamine (MEA) and n-methyldiethanolamine (MDEA) [5]; diethanolamine (DEA), triethanolamine (TEA) and 2-dimethylaminoethanol (DMAE) [6]. This new research is focused on two mixtures, the aqueous solution of PZ ($w_{pz}$ = 10%) and, a ternary aqueous mixture made up of PZ + DMAE ($w_{pz}$ = 10%; $w_{DMAE}$ = 30%) Densities were measured up to 140 MPa at temperatures between 293.15 K to 393.15 K (in steps of 20 K), whereas viscosities were obtained up to 100 MPa at the same temperature range as densities. Both properties were fitted as a function of temperature and pressure using empirical equations.

## 2. Experimental

### 2.1. Materials

The chemicals were purchased from Sigma-Aldrich with the highest purity available. Their characteristics are summarized in Table 1. Purities were specified by the supplier and no further purification was carried out. Liquid mixtures were prepared by weighting in a high precision balance with a standard uncertainty ($k$ = 1) in mass fractions less than $1 \cdot 10^{-4}$ (neglecting water content of amines).

Table 1. Material description.

| Compound | CAS-NO. | Source | Mass fraction purity[a] | Mass water content (%) | Purification method |
|---|---|---|---|---|---|
| Piperazine (PZ) | 110-85-0 | Sigma-Aldrich | $\geq 0.99$ | $< 0.1^b$ | None |
| DMAE | 108-01-0 | Sigma-Aldrich | $\geq 0.995$ | $< 0.1^b$ | None |
| Water | 7732-18-5 | Sigma-Aldrich | conductivity $\leq 2 \cdot 10^{-6}$ ohm$^{-1} \cdot$cm$^{-1}$ | | None |
| Dodecane | 112-40-3 | Sigma-Aldrich | $\geq 0.99$ | $\leq 0.01^a$ | None |

[a] Stated by the supplier by gas chromatography

[b] Measured by Karl Fisher titration (Mitsubishi CA-200)


## 2.2. Apparatus and procedure

A vibrating tube densimeter (Anton Paar DMAHPM), that is able to measure density in the range of (0 - 3000) kg·m$^{-3}$ with a resolution of $10^{-2}$ kg·m$^{-3}$, was used for the density measurements. The apparatus is fully automated using the Agilent VEE Pro software for controlling the system and acquiring data. The technique was calibrated with water and vacuum from 283.15 K to 353.15 K. In the case of the 373.15 K and 393.15 K isotherms, the apparatus was calibrated using as reference decane and vacuum, being the procedure previously described in [7]. The uncertainty calculations were performed following "The guide to the expression of uncertainty in measurement JCGM100: 2008" [8] whose procedure was deeply explained in [7], obtaining an expanded uncertainty ($k = 2$) less than 0.7 kg·m$^{-3}$. Viscosities were measured using a falling body viscometer whose operation is based on the fall time measurement of a body through a vertical tube containing the fluid to be measured. Although the cell was developed by Groupe de Haute Pression, Laboratoire des Fluides Complexes of the University of Pau [9], it was implemented in our laboratory and  the experimental setup was entirely developed by our research group as it is described in [5,6,10]. This equipment works in wide pressure (0.1 to 140) MPa and temperature (253.15 to 523.15) K ranges.

This technique also requires a calibration procedure, described in [11, 12], which is based on the use of known viscosity reference fluids under $(p,T)$ conditions in which the viscosity is sought. For this work, the calibration was performed at $p = (0.1$ to $100)$ MPa and $T = (293.15$ to $393.15)$ K using fluids which were extensively studied in the pressure and temperature ranges such as water [13] and dodecane [10,14].

Uncertainty budget was also calculated according to the procedure JCGM 100:2008 [8], and all the details can be found in previous works [6,10]. Uncertainty was evaluated at the limits of the viscosity calibration range for all the studied mixtures: the lowest viscosity was 0.260 mPa·s for water at $T = 393.15$ K and $p = 5$ MPa, and the highest viscosity was 7.591 mPa·s for aqueous DMAE solution ($w = 0.4$) at $T = 293.15$ K and $p = 60$ MPa [6]. A normal distribution was considered with a coverage factor $k = 2$ (confidence level of 95.45%), obtaining a relative expanded uncertainty which varies from 2.5% to 3.2% for the highest and lowest viscosities, respectively.

Stabinger SVM3000 viscometer was used in order to double-check the viscosities obtained from the falling body viscometer at atmospheric pressure. The principle of measurement is based on the different velocity from a high speed rotating outer tube and the free buoyant inner rotor with a built-in magnet which is immersed in the fluid sample. When the system reaches the equilibrium (constant rotating velocity at the tube and the floating rotor), then viscosity is calculated form the floating rotor speed. Uncertainty was calculated according to the procedure JCGM 100:2008 [8], obtaining a relative expanded uncertainty (k=2) better than 2%.


## 3. Results and discussion

Density measurements of one binary system {PZ (1) + H$_2$O (2)} (with $w_1 = 0.1$ due to low solubility of PZ in water [15]) and, one ternary system {PZ (1) + DMAE (2) + H$_2$O (3)}, with

$w_1 = 0.1$ and $w_2 = 0.3$, were carried out at pressures from 0.1 MPa to 140 MPa and at six temperatures between 293.15 K and 393.15 K. The experimental values are reported in Tables 2 and 3, respectively.

Table 2. Experimental densities, $\rho$, for PZ (1) + $H_2O$ (2) mixture ($w_1 = 0.1001$)[a] at different conditions of temperature, $T$, and pressure, $p$. [b]

| | $\rho$/ kg·m$^{-3}$ | | | | | |
|---|---|---|---|---|---|---|
| | $T$/ K | | | | | |
| $p$/ MPa | 293.15 | 313.15 | 333.15 | 353.15 | 373.15 | 393.15 |
| 0.1 | 1004.7 | 998.0 | 988.2 | 977.8 | 963.9 | 948.3 |
| 0.5 | 1004.8 | 998.2 | 988.4 | 977.9 | 964.1 | 948.7 |
| 1 | 1005.0 | 998.4 | 988.6 | 978.1 | 964.4 | 948.9 |
| 2 | 1005.5 | 998.8 | 989.1 | 978.6 | 965.0 | 949.5 |
| 5 | 1006.7 | 1000.0 | 990.3 | 979.9 | 966.4 | 951.0 |
| 10 | 1008.8 | 1002.0 | 992.4 | 982.2 | 968.7 | 953.6 |
| 15 | 1010.8 | 1004.0 | 994.4 | 984.3 | 971.0 | 956.0 |
| 20 | 1012.8 | 1005.9 | 996.4 | 986.5 | 973.4 | 958.5 |
| 30 | 1016.9 | 1009.9 | 1000.4 | 990.8 | 977.9 | 963.2 |
| 40 | 1020.8 | 1013.8 | 1004.4 | 994.8 | 982.2 | 967.8 |
| 50 | 1024.5 | 1017.5 | 1008.1 | 998.9 | 986.2 | 972.2 |
| 60 | 1028.3 | 1021.3 | 1011.9 | 1002.9 | 990.3 | 976.6 |
| 70 | 1032.1 | 1024.9 | 1015.7 | 1006.7 | 994.4 | 981.0 |
| 80 | 1035.5 | 1028.4 | 1019.2 | 1010.5 | 998.3 | 984.8 |
| 90 | 1039.2 | 1031.8 | 1022.7 | 1014.0 | 1002.2 | 988.9 |

| 100 | 1042.7 | 1035.4 | 1026.3 | 1017.7 | 1005.9 | 992.9 |
| 110 | 1045.9 | 1038.7 | 1029.7 | 1021.3 | 1009.5 | 996.7 |
| 120 | 1049.4 | 1042.0 | 1033.3 | 1024.7 | 1013.1 | 1000.4 |
| 130 | 1052.8 | 1045.3 | 1036.5 | 1028.2 | 1016.6 | 1004.0 |
| 140 | 1055.9 | 1048.5 | 1039.9 | 1031.5 | 1020.0 | 1007.8 |

[a] $w_i$: mass fraction of component i.

[b] Standard uncertainties ($k=1$): $u(T) = 0.01$ K; $u_r(p) = 0.0001$; $u(w) = 0.0001$ and $u(\rho) = 0.35$ kg·m$^{-3}$.

Table 3. Experimental densities, $\rho$, for PZ (1) + DMAE (2) + H$_2$O (3) mixture ($w_1 = 0.1002$; $w_2 = 0.2996$)[a] at different conditions of temperature, $T$, and pressure, $p$.[a]

| | $\rho$/ kg·m$^{-3}$ | | | | | |
|---|---|---|---|---|---|---|
| | $T$/ K | | | | | |
| $p$/ MPa | 293.15 | 313.15 | 333.15 | 353.15 | 373.15 | 393.15 |
| 0.1 | 998.6 | 984.8 | 969.7 | 953.6 | 935.9 | 916.8 |
| 0.5 | 998.6 | 985.0 | 970.0 | 953.8 | 936.1 | 917.2 |
| 1 | 998.8 | 985.1 | 970.2 | 954.0 | 936.4 | 917.4 |
| 2 | 999.2 | 985.5 | 970.6 | 954.4 | 936.9 | 918.0 |
| 5 | 1000.3 | 986.7 | 971.8 | 955.8 | 938.4 | 919.7 |
| 10 | 1002.0 | 988.6 | 973.9 | 958.1 | 941.0 | 922.6 |
| 15 | 1003.8 | 990.5 | 976.0 | 960.4 | 943.4 | 925.3 |
| 20 | 1005.5 | 992.3 | 978.0 | 962.6 | 945.9 | 928.0 |
| 30 | 1008.9 | 996.0 | 981.9 | 966.9 | 950.6 | 933.2 |
| 40 | 1012.4 | 999.7 | 985.9 | 971.0 | 955.1 | 938.1 |
| 50 | 1015.5 | 1003.0 | 989.5 | 975.0 | 959.3 | 942.7 |
| 60 | 1018.8 | 1006.5 | 993.1 | 979.0 | 963.5 | 947.4 |

| | | | | | | |
|------|--------|--------|--------|--------|--------|--------|
| 70 | 1022.0 | 1009.7 | 996.6 | 982.6 | 967.6 | 951.9 |
| 80 | 1024.9 | 1013.0 | 1000.1 | 986.3 | 971.7 | 956.1 |
| 90 | 1028.0 | 1016.0 | 1003.3 | 989.9 | 975.5 | 960.2 |
| 100 | 1031.0 | 1019.3 | 1006.7 | 993.4 | 979.1 | 964.3 |
| 110 | 1033.8 | 1022.3 | 1009.8 | 996.9 | 982.9 | 968.2 |
| 120 | 1036.7 | 1025.3 | 1013.2 | 1000.2 | 986.4 | 972.0 |
| 130 | 1039.4 | 1028.2 | 1016.2 | 1003.5 | 989.9 | 975.7 |
| 140 | 1042.1 | 1031.1 | 1019.2 | 1006.8 | 993.2 | 979.4 |

[a] $w_i$: mass fraction of component i.

[b] Standard uncertainties ($k=1$): $u(T) = 0.01$ K; $u_r(p) = 0.0001$; $u(w) = 0.0001$ and $u(\rho) = 0.35$ kg·m$^{-3}$.

As expected, density increases with pressure and decreases with temperature for both systems. The increase of density due to an increase of pressure (from 0.1 MPa to 140 MPa), is similar in both systems. In the case of the aqueous solution of PZ, this effect varies from 5.1% to 6.3%, increasing with temperature, and quite similar behaviour is observed in the ternary system ranging from 4.4% to 6.8%. at 293.15 K and 393.15 K, respectively.

In addition, density decreases when temperature is raised from 293.15 K to 393.15 K. For the aqueous solution of PZ, that reduction in density ranges from 5.6% to 4.6% at 0.1 MPa and 140 MPa respectively, in the aforementioned temperature range. This behaviour is greater for the ternary system, decresing density between 8.2% and 6.0% in the same ranges of temperature and pressure and, being the effect higher at lower pressures.

The experimental data were correlated using a modified Tammann–Tait equation (Eq. (3)) for each composition:

$$\rho(T,p)=\frac{A_0 + A_1T + A_2T^2}{1 - C\ln\left(\dfrac{B_0 + B_1T + B_2T^2 + p}{B_0 + B_1T + B_2T^2 + 0.1MPa}\right)} \quad (3)$$

The fitting results are shown in Table 4, which contains the adjustable parameters and the

standard deviation of the adjustment ($\sigma$).

Table 4. Fitting parameters of Eq. (3) and standard deviations $\sigma$ for the density measurements

| | PZ (1) + H$_2$O (2) | PZ (1) + DMAE (2) + H$_2$O (3) |
|---|---|---|
| | ($w_1 = 0.1001$)[a] | ($w_1 = 0.1002$; $w_2 = 0.2996$)[a] |
| $A_0$/ kg·m$^{-3}$ | 867.144 | 1049.507 |
| $A_1$/ kg·m$^{-3}$·K$^{-1}$ | 1.2366 | 0.3031 |
| $A_2$/ kg·m$^{-3}$·K$^{-2}$ | -0.00262 | -0.00163 |
| $B_0$/ MPa | -161.649 | 667.514 |
| $B_1$/ MPa·K$^{-1}$ | 3.2407 | -1.3949 |
| $B_2$/ MPa·K$^{-2}$ | -0.00568 | 0.00031 |
| C | 0.12572 | 0.10469 |
| $\sigma$/ kg·m$^{-3}$ | 0.381 | 0.088 |

[a] $w_i$: mass fraction of component i.

Moreover, the experimental and calculated densities of both systems are plotted as function of

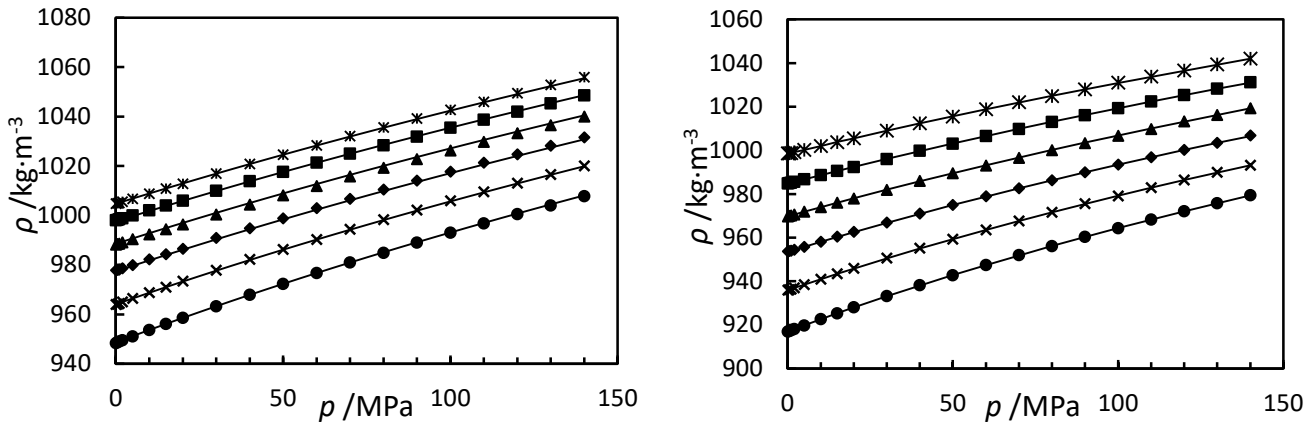pressure for the six measured isotherms in Fig. 1.

Figure 1. Experimental density of the system PZ (1) + $H_2O$ (2) (left graph) and the system PZ (1) + DMAE (2) + $H_2O$ (3) (right graph) as function of pressure and at different temperatures: (✳) 293.15 K; (■) 313.15 K; (▲) 333.15 K; (♦) 353.15 K; (×) 373.15 K; (●) 393.15 K. Lines represent the calculated values using modified Tammann-Tait equation with the parameters given in Table 4.

Experimental densities were also compared with literature data available at the same conditions (temperature, pressure and composition) but unfortunately, only data at atmospheric pressure are in existence.

For aqueous PZ solutions, Rizwan et al. [15] measured at $w_1 = 0.1$ and $T = (303.15, 308.15, 313.15, 318.15, 323.15, 328.15$ and $333.15)$ K, Ayyaz et al. [16] at $w_1 = 0.1035$ and $T = (303.15, 313.15, 318.15, 323.15$ and $333.15)$ K, Stec et al. [17] at $w_1 = 0.1$ and $T = (293.15, 298.15, 303.15, 313.15, 323.15$ and $333.15)$ K, Murshid et al. [18] at $w_1 = 0.1035$ and $T = (298.15, 303.15, 308.15, 313.15, 318.15, 323.15, 328.15$ and $333.15)$ K. Finally, Moioli et al. [19] have been developed a correlation to predict density and viscosity at atmospheric pressure as function of temperature and composition for the aqueous solution of PZ. The authors stated that the deviation of the correlation is less than 5%, being our experimental data better than 0.45%. In the case of the ternary system (PZ (1) + DMAE (2) + $H_2O$ (3)) only Patzschke et al. [20] reported experimental data at atmospheric pressure with a concentration

of $w_1 = 0.10$ / $w_2 = 0.30$ and $T = (298.15, 303.15, 313.15, 323.15, 333.15, 343.15$ and $353.15)$ K. The results of the comparison with the available literature are shown in Fig. 2, where the relative deviations of density are plotted as a function of the experimental density.
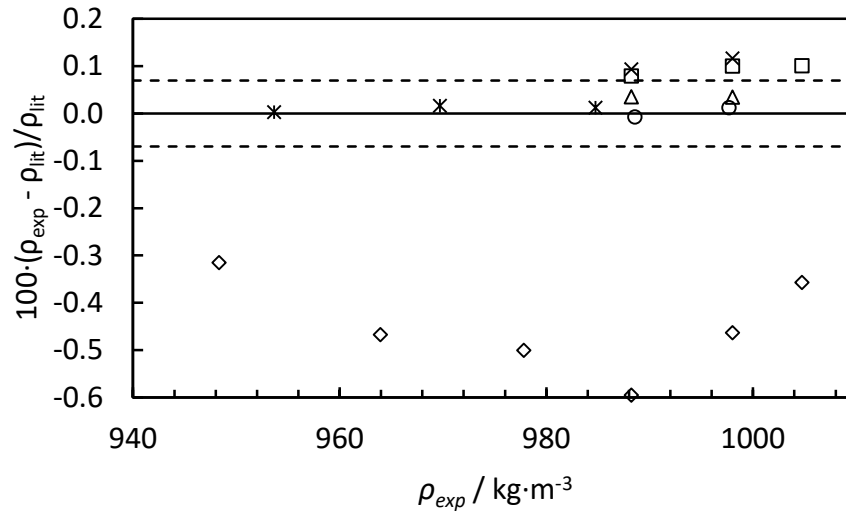


Figure 2. Relative deviations of density measurements ($\rho_{exp}$) at 0.1 MPa in comparison with literature values ($\rho_{lit}$): (○) Rizwan et al. [15], (Δ) Ayyaz et al. [16], (□) Stec et al. [17], (×) Murshid et al [18] and (◊) Moioli et al. [19] for PZ aqueous solutions. For the system PZ-DMAE, (✳) Patzschke et al. [20]. Dotted lines represent the relative expanded uncertainty of our measurements.

Average absolute deviations for PZ-water mixtures are 0.01% from Rizwan et al. [15]. In the case of Ayyaz et al. [16], the composition of the mixture is not the same ($w_{pz} = 10.35\%$) showing an absolute deviation of 0.04%. Same case happens with Murshid et al. [18] ($w_{pz} = 10.35\%$), showing an absolute deviation of 0.1%. Stec et al. [17] present an average absolute deviation of 0.1%. Moioli et al. [19] correlation presents an average absolute deviation of 0.45% for a maximum deviation of 5%, showing a good agreement with our experimental

data. Finally, Patzschke et al [20] shows an average absolute deviation of 0.01% for the ternary mixture.

Other authors have measured the aqueous solution of PZ, but their experimental measurements are at 0.1 MPa and at different compositions, for example: Freeman et al. [21] measured at higher concentrations, Arunkumar et al [22] measured at lower concentrations than ours and Derks et al. [23] performed measurements at lower and higher concentrations of PZ. When density is plotted as a function of mass fraction of amine at different temperatures, our experimental data show a coherent tendency, increasing the density of the solution for greater PZ mass fraction.

Finally, density behaviour is compared taking into account the effect of adding a second amine to the mixture. The addition of DMAE to the PZ aqueous solution decreases the density of the mixture being this effect higher at higher temperatures, for example, at 0.1 MPa, the decrease is 0.6% at 293.15 K and 3.3% at 393.15 K, and, at 140 MPa, the decrease is 1.3% and 2.8%, respectively. As can be seen, this effect increases with pressure at 293.15 K but decreases with pressure at 393.15 K being nearly constant at the isotherms in between. Analyzing the effect of adding PZ to the aqueous solution of DMAE (30%w) [6], density is slightly increased between 0.8% at 293.15 K and 0.2% at 393.15 K (at 0.1 MPa) and between 0.6% at 293.15 K and 0.2% at 393.15 K (at 140 MPa), concluding that the effect is not significantly affected by pressure.

In addition, viscosity measurements were carried out for the same mixtures and compositions: {PZ (1) +water (2)} and {PZ (1) + DMAE (2) +water (3)}. Both systems were measured up to 100 MPa and at six isotherms $T = (293.15, 313.15, 333.15, 353.15, 393.15)$ K, using the falling body viscometer technique. The results of the measurements are listed in Tables 5 and 6.

Table 5. Experimental viscosities, $\eta$, for PZ (1) + $H_2O$ (2) mixture ($w_1 = 0.1001$)[a] at different conditions of temperature, $T$, and pressure, $p$.[b]

| | $\eta$/ mPa·s | | | | | |
|---|---|---|---|---|---|---|
| | $T$/K | | | | | |
| $p$/ MPa | 293.15 | 313.15 | 333.15 | 353.15 | 373.15 | 393.15 |
| 0.1 | 1.6075 | 0.9677 | 0.6556 | 0.4758 | | |
| 5 | 1.6026 | 0.9692 | 0.6551 | 0.4771 | 0.3711 | 0.3028 |
| 10 | 1.6075 | 0.9711 | 0.6571 | 0.4813 | 0.3724 | 0.3045 |
| 15 | 1.6056 | 0.9727 | 0.6587 | 0.4833 | 0.3748 | 0.3069 |
| 20 | 1.6032 | 0.9749 | 0.6618 | 0.4857 | 0.3772 | 0.3090 |
| 25 | 1.6061 | 0.9783 | 0.6642 | 0.4882 | 0.3790 | 0.3115 |
| 30 | 1.6015 | 0.9798 | 0.6672 | 0.4898 | 0.3806 | 0.3128 |
| 40 | 1.6038 | 0.9840 | 0.6716 | 0.4950 | 0.3859 | 0.3170 |
| 60 | 1.6023 | 0.9938 | 0.6821 | 0.5042 | 0.3935 | 0.3246 |
| 80 | 1.6085 | 1.0047 | 0.6923 | 0.5131 | 0.4013 | 0.3319 |
| 100 | 1.6151 | 1.0135 | 0.7007 | 0.5228 | 0.4103 | 0.3381 |

[a] $w_i$: mass fraction of component i.

[b] Standard uncertainties ($k$=1): $u(T) = 0.01$ K; $u_r(p) = 0.0001$; $u(w) = 0.0001$ and $u_r(\eta) = 0.016$

Table 6. Experimental viscosities, $\eta$, for PZ (1) + DMAE (2) + $H_2O$ (3) mixture ($w_1 = 0.1002$; $w_2 = 0.2996$)[a] at different conditions of temperature, $T$, and pressure, $p$.[b]

| | $\eta$/ mPa·s | | | | |
|---|---|---|---|---|---|
| | $T$/ K | | | | |
| $p$/ MPa | 313.15 | 333.15 | 353.15 | 373.15 | 393.15 |

| | | | | | |
|---|---|---|---|---|---|
| 0.1 | 3.533 | 1.904 | 1.180 | | |
| 5 | 3.574 | 1.922 | 1.194 | 0.807 | 0.573 |
| 10 | 3.624 | 1.952 | 1.215 | 0.815 | 0.583 |
| 15 | 3.663 | 1.978 | 1.229 | 0.826 | 0.591 |
| 20 | 3.741 | 2.004 | 1.246 | 0.839 | 0.602 |
| 25 | 3.784 | 2.038 | 1.260 | 0.851 | 0.610 |
| 30 | 3.847 | 2.059 | 1.277 | 0.863 | 0.618 |
| 40 | 3.939 | 2.114 | 1.313 | 0.887 | 0.637 |
| 60 | 4.114 | 2.216 | 1.376 | 0.935 | 0.669 |
| 80 | 4.354 | 2.319 | 1.442 | 0.981 | 0.704 |
| 100 | 4.572 | 2.426 | 1.503 | 1.023 | 0.738 |

[a] $w_i$: mass fraction of component i.

[b] Standard uncertainties (k=1): $u(T) = 0.01$ K; $u_r(p) = 0.0001$; $u(w) = 0.0001$ and $u_r(\eta) = 0.016$

Viscosity of the mixtures decreases when temperature is increased, or pressure is decreased, as can be seen in Fig. 3 where the experimental viscosity data of both systems are plotted as function of pressure for the six measured isotherms. For PZ-water system, the viscosity is decreased by 80 % when the temperature is increased from 293.15 K to 393.15 K and, in contrast, the increase of viscosity ranges from 0.5% to 12%, being larger at higher temperatures, when pressure is increased from (0.1 to 100) MPa. In contrast, the behaviour of the ternary system (PZ-DMAE-water) is more uniform, viscosity is reduced by 84% when temperature is increased from 313.15 K to 393.15 K at all pressures) and it is increased by 29% when pressure is raised from 0.1 to 100 MPa at all temperatures.
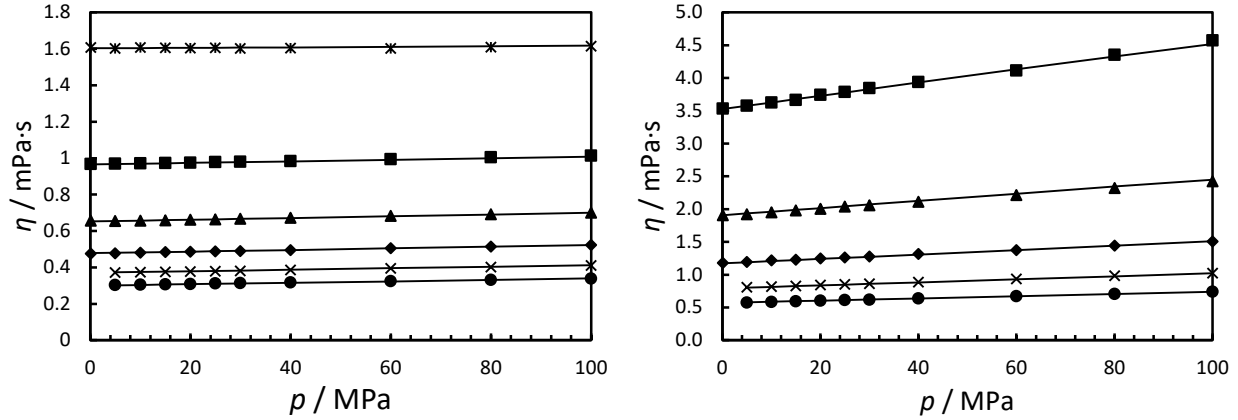
Figure 3. Experimental viscosity of the system PZ (1) + H$_2$O (2) (left graph) and the system PZ (1) + DMAE (2) + H$_2$O (3) (right graph starting at 313.15 K) as function of pressure and at different temperatures: (✶) 293.15 K; (■) 313.15 K; (▲) 333.15 K; (♦) 353.15 K; (×) 373.15 K; (●) 393.15 K. Lines represent the calculated values using modified VFT model with the parameters given in table 7.

Viscosity data were correlated using the modified VFT model, Eq(4), which was successfully used by other authors [24].

$$\eta(T, p) = \exp[a + b.p + (c + d.p + e.p^2)/(T - f)] \qquad (4)$$

The fitting of the experimental data was performed applying the least-squares method contained in the MATLAB software [25].

The results, such as the values of the parameters and the standard deviation of the adjustment, are given in Table 7. It can be seen that the standard deviations obtained, 0.0033 mPa·s for both mixtures, are less than the viscosity uncertainties, which indicates that the model is appropriate for this kind of mixtures.

Table 7. Fitting parameters of Eq. (4) and standard deviations σ for the viscosity measurements.

| | PZ (1) + H$_2$O (2) | PZ (1) + DMAE (2) + H$_2$O (3) |
|---|---|---|

|  | $(w_1 = 0.1001)^a$ | $(w_1 = 0.1002; w_2 = 0.2996)^a$ |
|---|---|---|
| a | -3.4835 | -3.9933 |
| b/ $MPa^{-1}$ | 0.002759 | 0.002723 |
| c/ K | 538.12 | 792.62 |
| d/ $K \cdot MPa^{-1}$ | -0.36527 | 0.02447 |
| e/ $K \cdot MPa^{-2}$ | 1.8406E-05 | -0.000607 |
| f/ K | 157.11 | 162.26 |
| $\sigma$/ $mPa \cdot s$ | 0.0033 | 0.0033 |

[a] $w_i$: mass fraction of component i.

In order to check the reliability of viscosity data, viscosities were also measured at atmospheric pressure using a Stabinger SVM 3000 viscometer that is available in our laboratory. The results of the comparison are summarized in Table 8 and plotted in Fig.4, showing that these deviations are in agreement with the uncertainties of the measurements.

Table 8. Viscosity comparison between falling body viscometer $(\eta_{FB})^a$ and Stabinger SVM 3000 viscometer $(\eta_{SV})^b$ at $p = 0.1$ MPa.

| $T$/K | $\eta_{FB}$/mPa·s | $\eta_{SV}$/mPa·s | $\Delta\eta/\eta_{SV}$(%) | $\eta_{FB}$/mPa·s | $\eta_{SV}$/mPa·s | $\Delta\eta/\eta_{SV}$(%) |
|---|---|---|---|---|---|---|
|  | PZ (1) + $H_2O$ (2) | | | PZ (1) + DMAE (2) + $H_2O$ (3) | | |
|  | $(w_1 = 0.1001)^c$ | | | $(w_1 = 0.1002; w_2 = 0.2996)^c$ | | |
| 313.15 | 0.968 | 0.988 | -2.0 | 3.533 | 3.620 | -2.5 |
| 333.15 | 0.656 | 0.656 | 0.0 | 1.904 | 1.912 | -0.4 |
| 353.15 | 0.476 | 0.486 | -2.2 | 1.180 | 1.184 | -0.3 |

[a] Standard uncertainties ($k$ =1): $u(T) = 0.01$ K; $u_r(p) = 0.0001$; $u(w) = 0.0001$; $u_r(\eta) = 0.016$

[b] Standard uncertainties ($k$ =1): $u(T) = 0.02$ K; $u_r(p) = 0.005$; $u(w) = 0.0001$; $u_r(\eta) = 0.010$
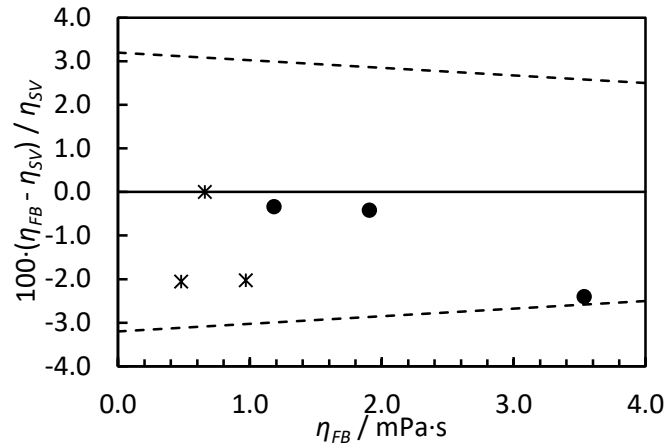
$w_i$: mass fraction of component i.



Figure 4. Relative viscosity deviation between falling body viscometer ($\eta_{FB}$) and Stabinger SVM 3000 viscometer ($\eta_{SV}$) for the mixtures: (✷) PZ + water; (●) PZ + DMAE + water. Discontinuous lines represent the relative expanded uncertainty of our measurements.

Furthermore, our experimental data were compared with the scarce literature data at atmospheric pressure, selecting those data measured at the same conditions of composition and temperature as our data [15,16,18-20]. Viscosities of the {PZ (1) + $H_2O$ (2)} mixture were measured at the same conditions as densities [15,16,18]. Moioli et al. [19] developed a correlation to predict the viscosities of the mixtures PZ-water as function of temperature and composition. Finally, in the case of the aqueous solution of PZ-DMAE ($w_1 = 0.10$ / $w_2 = 0.30$), only Patzschke et al [20] reported experimental data at atmospheric pressure. Relative viscosity deviations are plotted in Fig. 5.

Average absolute deviations between our measurements and those reported in the literature are 2.8% in comparison with Rizwan et al. [14]; 8.1% with Ayyaz et al. [15], 6.6% with Murshid et al [17]. As mentioned with the density, Ayyaz and Murshid measured the system PZ-water with a total mass fraction of PZ of 10.35% which also contributes to the

discrepancies of viscosities. The correlation proposed by Moioli et al. [18] gives an average

absolute deviation of 3.6% for a maximum correlation deviation of 5%, showing a good

agreement with our experimental data. Finally, Patzschke et al [19] shows an average absolute

deviation of 1.6% for the ternary mixture. There are other viscosity measurements in the

literature for the systems studied in this paper, but they were measured at different

compositions and it is not possible to compare the data. As can be seen, there are deviations

higher than the uncertainty of the measurements for the binary system, but there are also

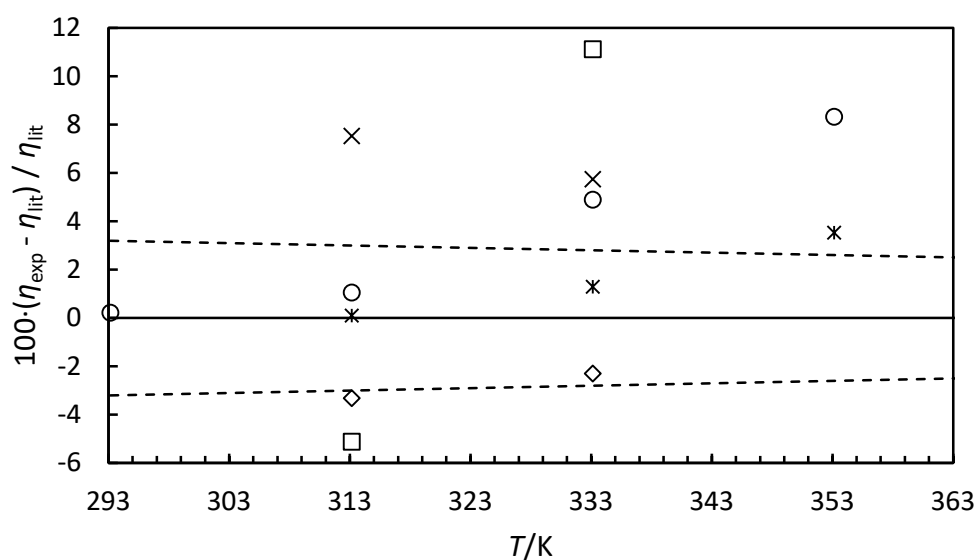significant discrepancies between the literature values.



Figure 5. Relative viscosity deviation at 0.1 MPa between our experimental data ($\eta_{exp}$) and

literature values ($\eta_{lit}$): (◊) Rizwan et al. [14], (□) Ayyaz et al. [15], (×) Murshid et al [17] and

(○) Moioli et al. [16] for PZ + water mixtures. For the ternary system PZ-DMAE-water, (✶)

Patzschke et al [19]. Dotted lines represent the relative expanded uncertainty of our

measurements.

Finally, it is interesting to comment the behaviour of the ternary system in comparison with

the binaries (amine +water). First of all, viscosities of ternary solution are higher than

viscosities of aqueous PZ solution or aqueous DMAE solution [6] at the same temperature and pressure. The increase ranges from 89%, at 393.15K and 5 MPa, up to 351% at 313.15 K and 100 MPa when the ternary system is compared with the aqueous solution of PZ (10%w) and the increase varies from 32%, at 393.15K and 5 MPa, up to 89% at 313.15 K and 100 MPa when the ternary system is compared with the aqueous solution of DMAE (30%w). Therefore, the highest increase is always at the lowest temperature (313.15 K), in addition, the effect of pressure, at this temperature, is also noticeable, the growth of the viscosity for the ternary system at $p = 0.1$ MPa is 265% and 73% in comparison with the binaries PZ and DMAE, respectively.

## 4. Conclusions

Density and viscosity measurements of a binary and ternary amine of aqueous solutions (PZ (1) + $H_2O$ (2) and PZ (1) + DMAE (2) + $H_2O$ (3)) were measured at amine mass fractions $w_1$=10% for the binary system and $w_1 = 10\%$ / $w_2 = 30\%$ for the ternary mixture, in a wide range of temperatures and pressures. A modified Tamman-Tait equation fits quite well the density as a function of pressure and temperature for a given composition.

In addition, viscosities of those mixtures were measured in the same range of temperature and up to 100 MPa. The experimental data were successfully correlated using a modified VFT model.

There are no data for these systems at high pressures but these measurements have proven the important effect of pressure, increasing density and viscosity up to 12% and 29%, respectively.

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