J. Chem. Thermodynamics 97 (2016) 282–289

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Densities of unloaded and CO_2-loaded 3-dimethylamino-1-propanol at temperatures (293.15 to 343.15) K

Zulkifli Idris [a], Jia Chen [a], Dag A. Eimer [a,b,*]

[a] Faculty of Technology, University College of Southeast Norway, Kjølnes Ring 56, Porsgrunn 3918, Norway
[b] Tel-Tek, Kjølnes Ring 30, Porsgrunn 3918, Norway

ARTICLE INFO

Article history:
Received 6 November 2015
Received in revised form 3 February 2016
Accepted 4 February 2016
Available online 10 February 2016

Keywords:
Density
Excess volume
Modeling
CO_2 loadings
Alkanolamine
3-Dimethylamino-1-propanol

ABSTRACT

This article reports experimental density values of aqueous 3-dimethylamino-1-propanol (3DMA1P) solutions over the entire range of 3DMA1P mass fractions and temperatures of (293.15 to 343.15) K. Based on the experimental results, corresponding values of thermal expansion and excess molar volume of 3DMA1P solutions were established. A second order Redlich–Kister polynomial equation satisfactorily correlates excess molar volumes against mole fractions of 3DMA1P solutions, and regression of these parameters as a function of temperature is demonstrated. Densities of carbonated 3DMA1P solutions were also measured at three 3DMA1P mass fractions of 0.20, 0.30 and 0.50, at different CO_2-loadings up to 0.8 mol CO_2/mol 3DMA1P, and temperatures. These data were modeled. A comparison between experimental and calculated values are discussed.

1. Introduction

Aqueous alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA) are utilized in the removal of acid gases such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S) [1]. New candidates are also being identified and characterized [2,3]. Tertiary amines such as MDEA offer a lower regeneration energy requirement and a higher theoretical capture capacity in comparison to other classes of amines. However, the absorption rates of tertiary amines are lower than primary and secondary amines. Chowdhury *et al.* [3] studied and identified several potentially relevant tertiary amine absorbents. Comprehensive and accurate measurements of the physical properties of these absorbents are required before they can be used in CO_2 related industrial processes. Physical and chemical data of these amines are needed for engineering design and calculations. As an example, density and viscosity data are used in the mass transfer modeling of absorbers and regenerators, sizing of pumps and pipelines, and in the design of heat exchangers [4]. These experimental data are also used for calculating pressure drop in a column and/or dimensioning column diameter [5].

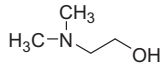
The focus of this study is 3-dimethylamino-1-propanol (3DMA1P), and a schematic diagram of the molecule is shown in figure 1. A previous study suggested that 3DMA1P has a higher rate of reaction with CO_2 than conventional MDEA [6]. Several studies on heat of absorption, kinetics, limit of CO_2 solubility, absorption equilibria, density and viscosity of 3DMA1P have been performed and reported in the literature [6–11]. The present work was performed to extend the range of available experimental density data. We present densities of unloaded and CO_2-loaded aqueous 3DMA1P solutions over a wide range of mass fractions and temperatures of (293.15 to 343.15) K. Accurate representation of the experimental data is desirable. In this work we have utilized the Redlich–Kister equation to correlate densities of unloaded aqueous 3DMA1P solutions [12], and the method of Weiland to fit densities of CO_2-loaded solutions [13].

2. Materials and methods

The chemicals used in this work are listed in table 1. These chemicals were of analytical grade and were used as received without any purification, except for degassing. An analytical balance with standard uncertainty of 1×10^{-6} kg from Mettler Toledo was used to weigh required chemicals. Aqueous solutions of 3DMA1P were prepared by mixing pure degassed 3DMA1P with degassed Milli-Q water (resistivity 18.2 MΩ·cm). As explained in our previous publication [14], an acid-base titration method was used to confirm the

* Corresponding author at: Faculty of Technology, University College of Southeast Norway, Kjølnes Ring 56, Porsgrunn 3918, Norway. Tel.: +47 3557 4000.
E-mail address: Dag.A.Eimer@tel-tek.no (D.A. Eimer).

http://dx.doi.org/10.1016/j.jct.2016.02.007
0021-9614/



3-dimethylamino-1-propanol (3DMA1P)

FIGURE 1. The structure of 3-dimethylamino-1-propanol (3DMA1P) studied in this work.

TABLE 1
Chemicals description.

Chemical name	Mole fraction purity[a]	Source	Purification
3-Dimethylamino-1-propanol (3DMA1P)	⩾0.99	Alfa Aesar	No
Carbon dioxide (CO_2)	0.9999	AGA Norge AS	No

[a] As stated by the supplier.

concentrations of gravimetrically prepared 3DMA1P solutions. We observed negligible difference between mass fractions calculated from routine sample preparation and titration.

By using a mass flow meter (SmartTrak 100 from Sierra Instruments), the CO_2 gas was administered at a rate of 0.15 $dm^3 \cdot min^{-1}$ into aqueous 3DMA1P solutions to prepare carbonated 3DMA1P solutions. The resulting aqueous CO_2-loaded 3DMA1P solutions were then subjected to titration analyses in order to determine the accurate content of CO_2 in 3DMA1P solutions using previously published methods [15,16]. Based on this work, we found that the CO_2-loaded solutions remain stable for a period of one week if stored carefully in a fridge: titration of samples from day one and day seven gave identical value. Similar observation was also reported earlier by Zhang *et al.* [17]. In order to document the possible change in densities over time during our measurements, density checks for the CO_2-loaded solution at 0.50 3DMA1P mass fraction at $T = (293.15, 323.15$ and $343.15)$ K were performed. Densities of CO_2-loaded 3DMA1P solution at these selected temperatures are shown in table S2 and a graphical representation is shown in figure S1. There is no change in the density for measurements at temperatures lower than 323.15 K, whereas at 343.15 K a minimal change, smaller than our standard uncertainty, was recorded after 1.5 h. This indicates that 3DMA1P solutions were sufficiently stable during the period of measurements.

An Anton Paar DMA 4500 density meter was used to measure densities of MilliQ water, unloaded and CO_2-loaded 3DMA1P solutions. Density checks with water at a temperature of 293.15 K were performed before and after each series of measurements, as suggested by the manufacturer. The density data of water at different temperatures were also compared with the reference data from Bettin and Spieweck [18]. Details of the water density are tabulated in the table S1 of Supplementary Information. The calibration was accepted if the difference between experiment and reference data was lower than 0.05 $kg \cdot m^{-3}$. An average experimental standard deviation of 0.03 $kg \cdot m^{-3}$ was calculated suggesting that our instrument is functioning properly. It is worth mentioning that each set of experiments in this work was repeated three times and the reported data are the average values from those measurements.

3. Assessment of experimental uncertainties

Several uncertainty factors can influence the measured densities and these factors are discussed in this section. The uncertainty analysis is based on the error propagation principle as explained in the Guide to the Expression of Uncertainty in Measurement (GUM) [19]. Whilst performing uncertainty calculations, we assumed that all uncertainty factors are independent from each other.

According to the manufacturer, the density meter has two sources of uncertainties. The given temperature and instrument standard uncertainties are $T = 0.03$ K and 0.05 $kg \cdot m^{-3}$, respectively. In the case of aqueous 3DMA1P solutions, considered uncertainty factors were temperature and mass fraction of 3DMA1P. We calculated a value of 0.84 $kg \cdot m^{-3} \cdot K^{-1}$ for the change of densities against temperatures based on the experimental data. Since the purity of the 3DMA1P used in this work is ⩾0.99, we rate the standard uncertainty of its mass fraction to be 0.01. Considering the change of densities against mass fractions of 3DMA1P, an uncertainty value of 2.42 $kg \cdot m^{-3}$ is quoted. The combined standard uncertainty can be calculated using a root-sum of squares formula of the factors and the value obtained was 2.42 $kg \cdot m^{-3}$ (at 68% confidence level, $k = 1$).

The combined standard uncertainty for CO_2-loaded 3DMA1P solutions is 3.66 $kg \cdot m^{-3}$, at 68% confidence level, upon consideration of factors discussed earlier and the contribution from error in CO_2-loading values. In the process of determining the uncertainty values, the possible changes in pressure during period of experiments were not considered as experiments were performed at atmospheric pressure and the pressure changes are negligible in relation to liquid densities.

Average absolute deviation (AAD) was calculated according to equation (1). In this case, N, ρ_i^E and ρ_i^C denote the number of data points available, density values obtained from the experimental work and calculated from the model, respectively.

$$\mathrm{AAD}\ (\mathrm{kg \cdot m^{-3}}) = \frac{1}{N}\sum_{i=1}^{N}|\rho_i^E - \rho_i^C|. \quad (1)$$

4. Results and discussion

For easy reading, the results and discussion section is divided into two subsections. The first subsection discusses the densities of aqueous 3DMA1P solutions, and the second subsection presents the densities of CO_2-loaded aqueous 3DMA1P solutions.

4.1. Densities of H_2O (1) and 3DMA1P (2) solutions

Densities of aqueous 3DMA1P solutions ρ, were measured at different mass fractions of 3DMA1P w_2, ranging from 0.10 to 1.00 at temperatures of (293.15 to 343.15) K. These values alongside calculated excess molar volumes V_m^E, are tabulated in table 2. In order to investigate the reliability of our measurements, a comparison between our experimental data and literature values was performed, and a graphical representation is illustrated in figure 2. It is evident from the figure that there is a small but systematic deviation between our data and literature values. The calculated average absolute deviations between our data and those of Chowdhury *et al.* [10] and Narayanaswamy *et al.* [6] are (3.33 and 2.78) $kg \cdot m^{-3}$, respectively. In addition, densities of binary 3DMA1P solutions at 3DMA1P mass fraction of 0.80 were also compared to the values reported by Chowdhury *et al.* [10]. Details of the binary density data are listed in table S3 of the Supplementary Information, and a graphical representation is presented in figure 3. An average absolute deviation value of 0.41 $kg \cdot m^{-3}$ was calculated between our data and those of Chowdhury *et al.* [10] at 0.80 mass fraction. Upon consideration of our experimental uncertainty, we concluded that these deviations are within experimental uncertainty and that our measurements are reliable.

Figure 4 shows plots of densities of 3DMA1P solutions at different mass fractions against temperatures. A general observation of the plots indicate that densities decrease with increasing temperatures, as expected and the relation is linear in the range considered. Furthermore, at a constant temperature, an increase in the