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Surface tension of alkanolamine solutions: An experimentally based review

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Abstract

Monoethanolamine solutions is one of several chemicals used for the absorption of acid gases since 1930. Physical and chemical properties of these amine solvents have also been studied by various research groups. One of the important thermodynamic data is surface tension, and in this paper, an evaluation onto techniques used to represent experimental surface tension data of MEA solutions were performed. Surface tension of aqueous MEA solutions were measured at temperatures between (303.15 and 338.15) K and compared with values from literature. Three different methods were used to correlate the experimental data. Analysis of suitability of these methods is presented in this paper and impact of the data deviation on engineering calculations will be discussed.

Keywords: surface tension, ethanolamine, modeling

1. Introduction

Chemical absorption of carbon dioxide (CO_2) using aqueous alkanolamine solutions such as ethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA) is the mature technology currently available for carbon capture and sequestration. Over the years, a number of new amines such as diethylethanolamine (DEEA) and

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N-methyl-1,3-diaminopropanone (MAPA) have also been suggested as potential candidates for CO_2 capture. In order to evaluate the effectiveness of a new solvent, a thorough investigation into physical and chemical properties must be conducted. Surface tension is one of the physical properties required when designing or simulating an absorption column for CO_2 absorption. It is well known that mass transfer performance of a column is proportionally related to the wetted surface area of column packings. An earlier investigation by Shi and Mersmann [1] demonstrated that the wetted surface area of packing in columns is affected by the surface tension. The dependency between wetted surface area of packing and surface tension has been incorporated onto several different mass transfer models such as that of Brunazzi and Paglianti [2], Onda et al. [3], Puranik and Vogelpohl [4], and Hanley et al. [5]. Therefore, accurate and reliable surface tension data are crucial as it will improve confidence in process simulations thus contribute towards cost reduction by reducing safety margins.

Surface tension experiments require precise temperature and pressure control, an instrument for drop or bubble formation and observation equipment. It is measured in force per unit length (N/m). It can be determined by various types of stalagmometer, tensiometer and goniometer utilizing different techniques such as Wilhelmy plate principle, the capillary-rise technique and the pendant/sessile drop method. In the Wilhelmy plate principle, the force due to wetting of a plate perpendicular to the liquid is measured, while in the capillary-rise technique, the height of the solution inside an immersed capillary is measured. In the pendant/sessile drop method, surface tension is measured from the geometry of a drop that could be hanging from a capillary tube or resting on a surface. Choosing a suitable technique for drop formation in the pendant/sessile drop method is fundamental.

Our search in literature showed that surface tension data of alkanolamines relevant for CO_2 capture are normally reported in two components; in the first part, surface tension of binary mixtures, in the absence of CO_2, are presented and a number of data are available. Recently, surface tension values for ternary mixtures have also been reported due to the current interest of mixing two alkanolamine solutions in order to achieve better absorption capacity [6]. The experimental data are then fitted using established methods such as the semi-empirical methods reported by Asprion [7], and Connors and Wright [8]. In the second component, surface tension of CO_2-loaded amine solutions are reported and the data are correlated using techniques available in the literature [9]. The number of different methods available makes it desirable for an investigation into the performance of these methods in determining surface tension of alkanolamines. In this present study, new surface tension data of MEA will be presented and compared with values from literature. Further analysis of these methods will be presented and impact of the data deviation on engineering calculations will be discussed. The outcome of this paper will help researchers to choose the best available technique for representing surface tension and throw light on deviations between values reported in the literature.

2. Experimental section

2.1. Materials

All chemicals used in this work were purchased from suppliers as shown in Table 1 and used without any purification. A Mettler Toledo balance (uncertainty 0.001 g) was used to weigh the required amount of MEA needed. Aqueous solutions of MEA were prepared using degassed deionized water (conductivity, 18.2 MΩ cm).

Table 1. Details of the chemicals used during experiments. N/A: Not available

Chemical	Purity (mass %)	Supplier
Ethanolamine (MEA)	≥ 99.5	Merck KGaA
Hydrochloric acid (HCl)	N/A	Merck KGaA
Sodium hydroxide (NaOH)	N/A	Merck KGaA
Barium chloride dehydrate ($BaCl_2.2H_2O$)	N/A	Merck KGaA

2.2. Surface tension experiments

Surface tension of aqueous MEA solutions was measured using a Rame-Hart Advanced Goniometer model 500 at different MEA concentrations and temperatures between (303.15 and 338.15) K. Once a bubble droplet is formed, a digitalized image is taken using a camera and the geometry size of the droplet is measured using DROPimage Advanced v2.4 software. Each surface tension value reported in this work was an average of 10 measurements with a maximum deviation of less than 2 mNm^{-1}. Further information on the technique used can be found in our earlier publications [9, 10]. As a precaution and quality control step, surface tensions of water were measured at temperatures of (303.15, 313.15 and 323.15) K. These data are then compared to values reported by Vazquez et al. [11], and shown in Table 2. As can be seen, the measured data in this work are comparable to the literature data suggesting the instrument reliability.

Table 2. Surface tension of water.

	γ/ mN.m^{-1}		
	303.15	313.15	323.15
This work	70.90	69.81	67.75
Vazquez et al. [11]	71.21	69.52	67.92

3. Results and discussion

Table 3 shows surface tension values of MEA measured in this work. As the mole fraction of MEA increases, surface tension decreases. When mole fraction of MEA increases, more molecules of MEA tend to concentrate at the solution-air interface resulting in smaller surface tension of MEA in comparison to water. A graphical representation of the surface tension changes against temperatures is shown in Fig. 1. As can be seen, surface tension decreases as temperature increases due to the fact that molecules at high temperature has high thermal motion, reducing the intermolecular attraction thus lowering the surface tension. The experimental data collected were also compared with available literature values from Vazquez et al. [11], and an average deviation of 1.06 mN.m^{-1} was calculated.

Table 3. Surface tension of aqueous MEA.

| Mass fraction of MEA	γ/ mN.m^{-1}						
Temperature, T/ K	0.3	0.4	0.5	0.6	0.8	0.9.	1.0
303.15	59.61	57.94	56.52	55.20	53.40	50.60	48.10
308.15	58.81	57.13	55.71	54.39	52.89	50.10	47.41
313.15	58.00	56.32	54.90	53.58	52.40	49.60	46.70
318.15	57.20	55.51	54.09	52.77	51.62	48.90	46.25
323.15	56.39	54.70	53.28	51.96	51.10	48.40	45.60
328.15	55.59	53.89	52.48	51.15	50.35	47.70	45.09
333.15	54.78	53.08	51.67	50.35	49.60	47.00	44.60
338.15	53.98	52.27	50.86	49.54	49.08	46.50	43.93
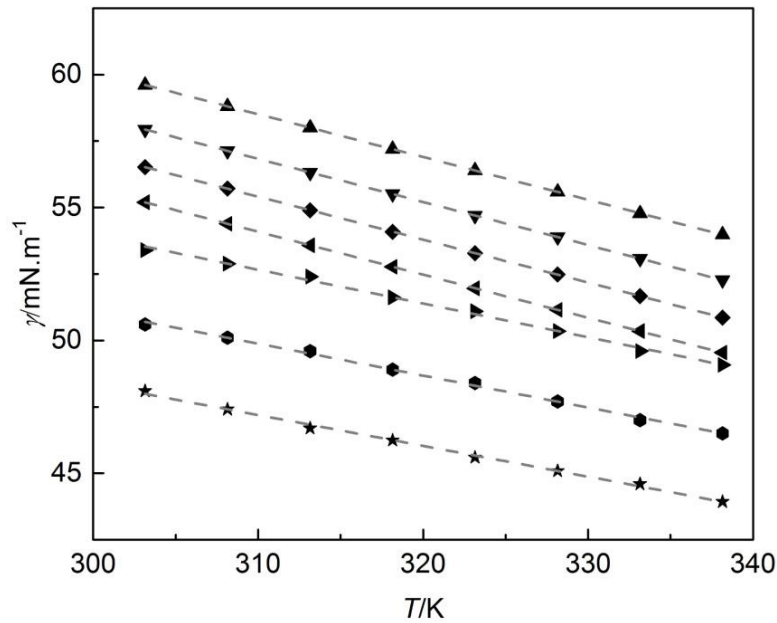
Fig. 1. Surface tension of aqueous MEA against temperature. Experiments were performed at different mass fractions: ▲: 0.3, ▼: 0.4, ◆: 0.5, ◀: 0.6, ▶: 0.8, ⬠: 0.9 and ★: 1.0. Dashed lines show linear correlation between surface tension and temperature.

Three different correlations were used to correlate the surface tension data of this work: surface tension against temperature, Asprion [7], and Connors and Wright [8] methods. As evident from Fig. 1, it can be postulated that surface tension of MEA has a linear relationship with temperature and as such, equation 1 was used to correlate the experimental data,

$$\gamma_m = A.T + B \tag{1}$$

where *A* and *B* corresponds to the slope and intercept on the *y*-axis. The values of *A* and *B* are tabulated in Table 4.

Table 4. Parameters *A* and *B* based on equation 1.

Mass fraction of MEA	*A*	*B*
0.3	-0.161	108.404
0.4	-0.162	107.050
0.5	-0.162	105.520
0.6	-0.162	104.221
0.8	-0.127	92.043
0.9	-0.120	87.078
1.0	-0.116	83.155

Corresponding equations from Asprion [7], and Connors and Wright [8] methods used to estimate surface tension of aqueous MEA solutions are shown below:

$$\gamma_m = \gamma_1 + \sum_{i \geq 2} \frac{S_i x_i}{1 + \sum_{j \geq 2}^i (S_j - 1) x_j} (\gamma_i - \gamma_1) \tag{2}$$

$$\gamma_m = \gamma_1 + \sum_{i \geq 2} \left(1 + \frac{a_i x_i}{(1 - b_i)\left(1 + \sum_{j \geq 2}^i \frac{b_j}{(1 - b_j)} x_j\right)} \right) x_i (\gamma_i - \gamma_1) \tag{3}$$

where S_i, a_i and b_i are adjustable parameters for system with binary components. In both cases, surface tension and mole fraction of MEA are represented with γ_m and x_m, respectively. The average absolute deviation values between experimental and correlation data are given in Table 5. As can be seen, the smallest deviation of 0.25 mN.m^{-1} was obtained from the method of Connors and Wright. However, the deviations from correlations against temperatures and Asprion method are also minimal suggesting that any of these methods can be applied for correlating surface tension of aqueous MEA solutions.

Table 5. Average absolute deviations (AAD) between experimental and correlation data.

Method	AAD/ mN.m^{-1}
Surface tension against temperature	0.42
Asprion	0.62
Connors and Wright	0.25

4. Conclusion

Surface tensions of aqueous MEA solutions have been measured at temperatures between (303.15 and 338.15) K at different MEA mass fractions. Values of the surface tension decrease at increasing temperatures and mass fractions of MEA. The experimental data were correlated against temperature, and methods of Asprion, and Connors and Wright. Average absolute deviations of (0.42, 0.62, and 0.25) mN.m^{-1} were calculated based on correlations against temperature, Asprion, and Connors and Wright methods, respectively. The small deviation values between experimental and correlated data suggest that any of these methods could be employed for representing surface tension of MEA solutions, with errors that would be negligible for engineering calculations.

Acknowledgements

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