

Measurement and thermodynamic modeling of the phase equilibrium of aqueous *N*-methyldiethanolamine solutions

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Abstract

Isobaric vapor–liquid equilibrium (VLE) measurements at 40.0, 53.3 and 66.7 kPa (300, 400 and 500 mmHg) of aqueous *N*-methyldiethanolamine (MDEA) solutions were performed using a modified ebulliometer. The concentration of MDEA in the liquid phase ranged from about 0.06 to 0.93 in mole fraction and the temperatures from about 76 to 186 °C. The data measured in this work, along with other experimental data taken from the literature, are used for the improvement of the thermodynamic modeling of the water/MDEA binary system.

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1. Introduction

The purification of the natural gas, as well as the sweetening of gas streams in petroleum refining, petrochemical plants, coal gasification and hydrogen production is of major importance for both energy and environmental purposes. The dominant technique for these processes is the absorption of acid gases, primarily CO₂ and H₂S, into aqueous solutions of alkanolamines. Although monoethanolamine (MEA) and diethanolamine (DEA) were used almost exclusively for many decades, they are nowadays being replaced by other more efficient systems. Recent innovations using tertiary amines, such as methyldiethanolamine (MDEA), and blended amines have gained ground in the last years because they can selectively absorb hydrogen sulphide in the presence of carbon dioxide and because of their low vapor pressure, high capacity and low heat of reaction with CO₂ and H₂S [1].

Vapor–liquid equilibrium (VLE) of the acid gas/MDEA/water system is a key factor for the design of gas treating processes. The proper thermodynamic modeling of the water/MDEA binary system is necessary. To this purpose

accurate phase equilibrium data for a wide range of temperatures, pressures and amine concentrations are required.

Literature reported experimental phase equilibrium data for the binary aqueous MDEA mixture consist of total pressure [2,3] and freezing point [4] data, which cover the pressure range from 1.3 to 539.9 kPa, the temperature range from –13 to 160 °C and the MDEA concentration range up to 70 wt.% (0.261 mole fraction).

The first objective of this study is to provide new experimental isobaric VLE measurements of aqueous MDEA solutions, which extend the range of available experimental phase equilibrium data both in temperature and MDEA concentration. Specifically, the temperature range is extended up to about 186 °C and the MDEA concentration range up to 98.9 wt.% (0.933 mole fraction).

Thermodynamic modeling of the water/MDEA binary has been mainly presented with the NRTL activity coefficient model [5]. Chang et al. [4] regressed total pressure and freezing point depression data to fit temperature dependent NRTL parameters, while Posey [3] and Posey and Rochelle [6] utilized total pressure, freezing point depression and heat of mixing data.

The second objective of this study is the thermodynamic modeling of the MDEA/water binary mixture. To this purpose the UNIQUAC activity coefficient model [7] is used.

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2. Experimental

2.1. Materials

MDEA (99+% purity) was purchased from ACROS Organics and water (HPLC grade) was purchased from LAB-SCAN Ltd and they were used as received.

2.2. Experimental procedure

The experimental VLE measurements were performed in a modified Swietoslawski ebulliometer, which is described in details by Rogalski and Malanowski [8]. A schematic diagram of the apparatus is shown in Fig. 1. About 60 ml liquid was initially placed gravimetrically in the ebulliometer. The pressure controller was set and the liquid was heated

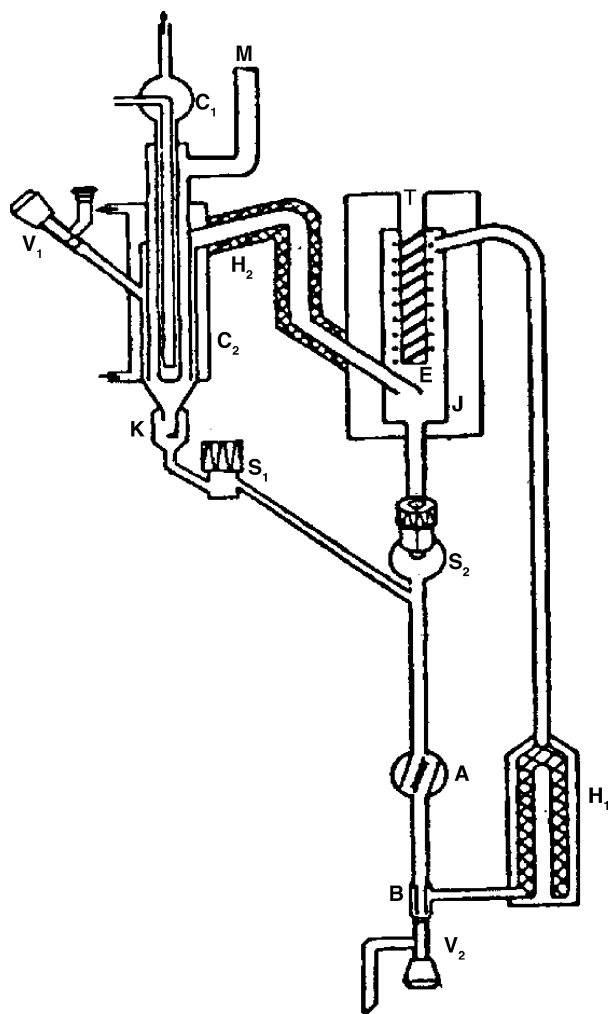


Fig. 1. Schematic diagram of the ebulliometer used in this work. A, B: mixing devices; C_1 , C_2 : condensers; E: equilibrium chamber; H_1 , H_2 : heaters; J: vacuum jacket; K: drop counter; M: to the manostat (pressure controller); S_1 : device for withdrawal of vapor condensate; S_2 : device for withdrawal of liquid sample; V_1 : valve for introducing samples; V_2 : valve for removing liquid from the ebulliometer.

Table 1
Boiling points of pure water

Pressure (kPa)	Temperature ($^{\circ}\text{C}$)		Literature references
	This work	Literature	
39.99	75.9	75.85/75.84	[9,10]
53.30	83.0	82.93/82.93	[9,10]
66.66	88.7	88.65/88.66	[9,10]

by heater H_1 and partially evaporated. Equilibrium is established inside the ebulliometer chamber. The equilibrium vapor is condensed by C_1 and C_2 , it is then dropped by K and it is mixed with the equilibrium liquid by means of flow turbulence. Finally, they go up to the reboiler again and complete the normal circulation of vapor and liquid in the still. Samples of the liquid were taken from S_2 by means of gas-tight syringe for analysis. The pressure of the system was controlled within ± 0.13 kPa (1 mmHg) using a pressure controller (Druck DPI 530) connected with a vacuum pump and the equilibrium temperature was measured with an accuracy of ± 0.1 K using a thermometer calibrated with the ISOCAL-6 VENUS^{PLUS} 2140 calibrator of temperature sensors.

Liquid compositions were determined using the standard curve of refractive index versus mole fraction of the binary mixture at 25°C . The measurements were made with an Abbe Refractometer (1T/4T) of ATAGO. The maximum deviation in the composition measurements were observed at the highest MDEA concentrations and it is 0.007 mole fraction, which corresponds also to the maximum error 0.77%.

When the temperature and the refractive index of the liquid samples have been stabilized, it is considered that equilibrium has been attained.

2.3. Experimental results

The experimental apparatus was tested by measuring the boiling points of pure water. The results are listed in Table 1

Table 2
Experimental isobaric VLE data for the water/MDEA binary at 40.0, 53.3 and 66.7 kPa

40.0 kPa		53.3 kPa		66.7 kPa	
x_{MDEA}	T (K)	x_{MDEA}	T (K)	x_{MDEA}	T (K)
0.062	350.2	0.064	357.2	0.067	362.8
0.098	350.8	0.101	358.0	0.106	363.8
0.143	352.2	0.153	359.2	0.158	364.8
0.262	355.8	0.265	362.9	0.266	368.4
0.342	359.0	0.351	366.6	0.357	372.3
0.558	370.1	0.583	379.6	0.461	378.3
0.797	394.7	0.747	397.1	0.595	388.4
0.933	437.7	0.860	419.7	0.728	403.6
		0.933	449.2	0.854	429.9
				0.919	458.7

and they are in excellent agreement with those reported by NIST [9] and DIPPR [10].

Isobaric T - x measurements for the water/MDEA binary were performed at 40.0, 53.3 and 66.7 kPa (300, 400 and 500 mmHg) and they are presented in Table 2.

3. Thermodynamic modeling

In this work the UNIQUAC activity coefficient model is utilized in order to model the phase equilibria of the water/MDEA binary. The database used to this purpose consists of: (a) the isobaric T - x data measured in this work; (b) the total pressure reported by Xu et al. [2]; (c) the freezing point depression data of Chang et al. [4]; and (d) the heats of mixing data of aqueous MDEA solutions of Posey [3]. Although the freezing points of water/MDEA mixtures are below 0 °C and, consequently, outside the range of acid gas absorption in commercial applications, their combination with the other types of thermodynamic data constitutes a database that cover a wide range of temperatures, pressures and concentrations, and, therefore, may lead to a reliable thermodynamic modeling of the water/MDEA binary.

The phase equilibrium relationship used for the isobaric VLE and the total pressure data is the following:

$$P = \sum x_i \gamma_i P_i^s \quad (1)$$

In Eq. (1) x_i is the mole fraction of component i , γ_i is its activity coefficient and P_i^s its vapor pressure. Due to the low pressures involved (up to 1 atm) it is assumed that fugacity coefficients and the Poynting correction term are equal to unity.

Vapor pressures for water were taken from DIPPR [10], while for MDEA from the following Clausius–Clapeyron type expression [3]:

$$\ln P^s = 26.13691 - \frac{7588.516}{T} \quad (2)$$

where P^s in Pa and T in K. Eq. (2) has been derived by fitting experimental vapor pressure data in the range of 413–513 K [11]. MDEA vapor pressures calculated by Eq. (2) are in satisfactory agreement with the ones calculated by a similar equation proposed by Xu et al. [2] that was developed by fitting data in the range of 323–383 K.

The freezing point depression data have been converted to water activity coefficients using the following expression [4]:

$$\gamma_w = \frac{\exp(-0.018\Delta T_f/1.86)}{x_w} \quad (3)$$

where γ_w is the water activity coefficient, x_w is the water mole fraction and ΔT_f is the freezing point depression.

The objective function that was minimized for the regression of the experimental data is the following:

$$F = \sum_{i=1}^{NP} \left(100 \frac{T_i^{\text{exp}} - T_i^{\text{calc}}}{T_i^{\text{exp}}} \right)^2 + \sum_{j=1}^{NP} \left(100 \frac{P_j^{\text{exp}} - P_j^{\text{calc}}}{P_j^{\text{exp}}} \right)^2 + \sum_{k=1}^{NP} \left(100 \frac{\gamma_{w,k}^{\text{exp}} - \gamma_{w,k}^{\text{calc}}}{\gamma_{w,k}^{\text{exp}}} \right)^2 + \sum_{l=1}^{NP} \left(100 \frac{H_l^{\text{E,exp}} - H_l^{\text{E,calc}}}{H_l^{\text{E,exp}}} \right)^2 \quad (4)$$

The first term in Eq. (4) corresponds to the three sets of isobaric T - x data measured in this work, the second to the total pressure data of Xu et al., the third to the water activity coefficient data derived from Eq. (3) using the freezing point depression measurements of Chang et al. and the last to the heats of mixing data of Posey. NP is the number of points in each case.

The following quadratic temperature dependent UNIQUAC molecular interaction parameters were obtained:

$$\frac{\Delta u_{\text{water-MDEA}}}{R} = -1678.2 + 10.794T - 0.0169T^2 \quad \text{and} \quad \frac{\Delta u_{\text{MDEA-water}}}{R} = 705.6 - 6.229T + 0.0111T^2 \quad (5)$$

where $\Delta u/R$ is in K and R is the gas constant. The van der Waals volume and area parameters of water are: $r = 0.92$ and $q = 1.4$, respectively, while the corresponding ones of MDEA are: $r = 4.9441$ and $q = 4.268$.

The average absolute errors obtained with the UNIQUAC model using the parameters of Eq. (5) are: (a) in the bubble point temperatures 0.69%, (b) in the total pressure data 2%, (c) in water activity coefficients derived from the freezing point data 0.25%, and (d) in the heats of mixing 3.3%. The corresponding errors of the NRTL model with the parameters proposed by Posey [3,6] are: 2.3, 1.9, 0.38 and 4.9%.

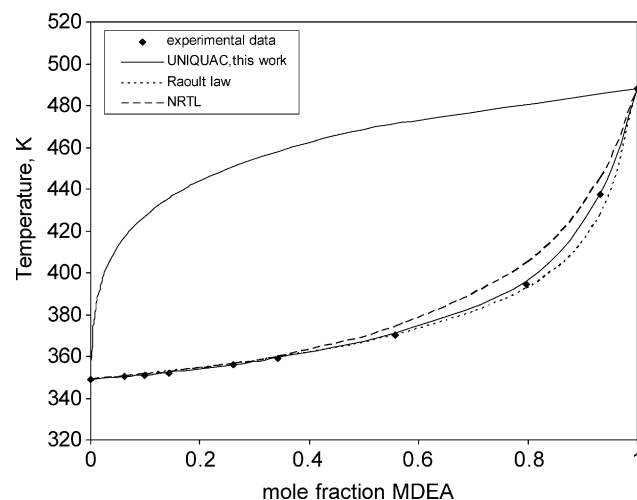


Fig. 2. T - x - y diagram of the water/MDEA system at 40.0 kPa.

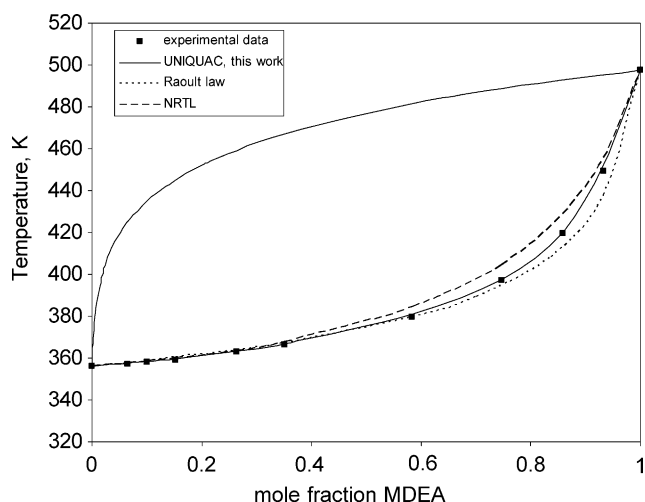


Fig. 3. T - x - y diagram of the water/MDEA system at 53.3 kPa.

Figs. 2–4 present a comparison between the experimental bubble point temperatures measured in this work and models' results. Improved results over the Raoult's law and the NRTL model of Posey [3,6] are obtained with the UNIQUAC model and the parameters determined in this work. The NRTL model with the parameters of Posey overestimates the system nonideality as the MDEA concentration increases.

UNIQUAC and NRTL models give very similar results for the total pressure data of Xu et al. [2] as shown in Fig. 5. Also, Fig. 6 presents a comparison between water activity coefficients derived from the freezing point depression measurements and the results of the UNIQUAC and the NRTL models. UNIQUAC gives better results than NRTL, which greatly overestimates the experimental data with decreasing water concentration. Finally, Figs. 7 and 8 presents a comparison between heat of mixing experimental data and the

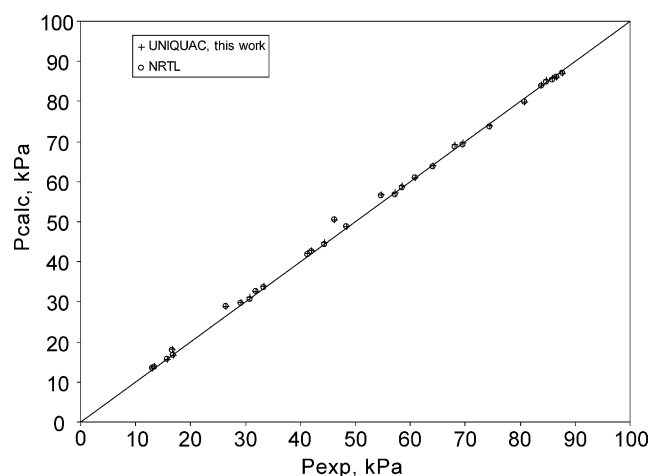


Fig. 5. Experimental vs. predicted total pressures for the water/MDEA system. Experimental data from Xu et al. [2].

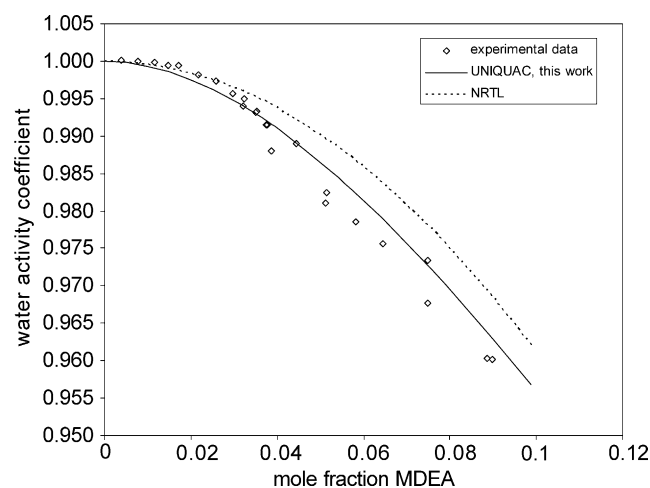


Fig. 6. Water activity coefficient predictions with the UNIQUAC and the NRTL models. Experimental water activity coefficients were obtained from the freezing point depression measurements of Chang et al. [4].

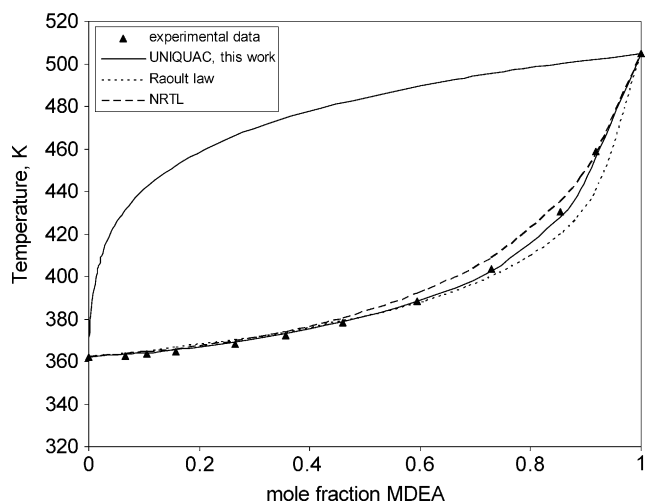


Fig. 4. T - x - y diagram of the water/MDEA system at 66.7 kPa.

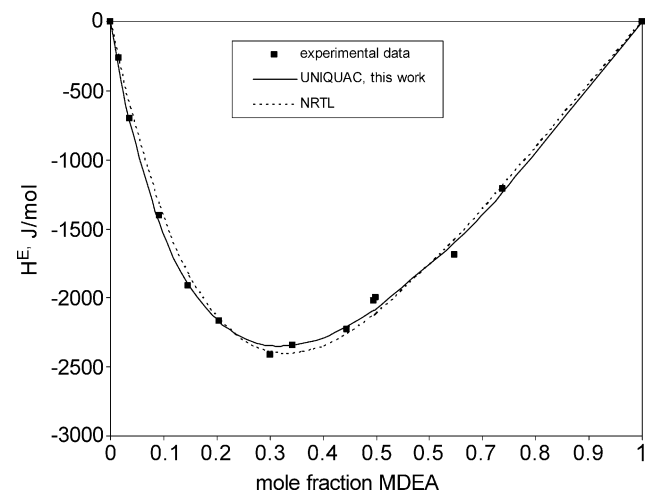


Fig. 7. Heats of mixing of aqueous MDEA solutions at 25 °C. Experimental data from Posey [3].

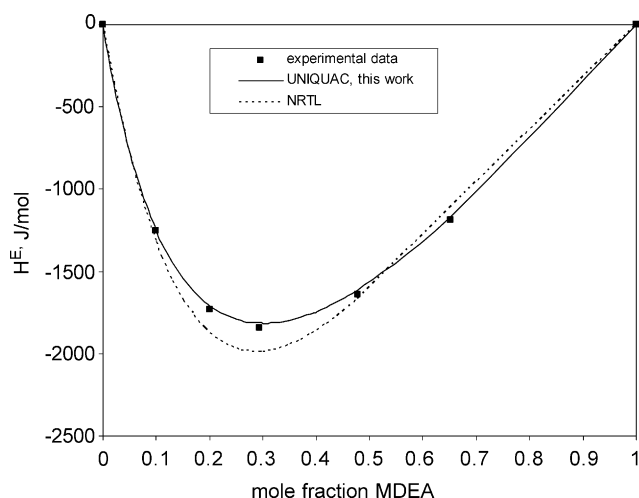


Fig. 8. Heats of mixing of aqueous MDEA solutions at 70 °C. Experimental data from Posey [3].

results obtained with the UNIQUAC and the NRTL models. Comparable results are obtained by the two models at 25 °C, while UNIQUAC gives better results than NRTL at 70 °C.

4. Conclusions

Isobaric VLE data at 40.0, 53.3 and 66.7 kPa (300, 400 and 500 mmHg) of aqueous *N*-methyldiethanolamine solutions, over a relatively wide range of temperatures and MDEA concentrations, have been measured. These data along with other thermodynamic experimental data taken from the literature were used for fitting UNIQUAC temperature dependent interaction parameters. The results of the model were found to be in all cases in good agreement with the experimental data.

List of symbols

H^E	excess enthalpy (J mol^{-1})
P	pressure (Pa)
P^s	vapor pressure (Pa)
q	van der Waals area parameter
r	van der Waals volume parameter
R	universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
T	temperature (K)
ΔT_f	freezing point depression (K)
$\Delta u/R$	interaction energy parameter (K)
x	liquid phase mole fraction

Greek letters

γ	activity coefficient
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