



Thermodynamic Modeling of Vapor-Liquid Equilibrium of Aqueous N-methyldiethanolamine Solution Using N-NRTL-NRF model

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Abstract

One of the chemical solvents which are widely used in the oil, gas, and chemical industries is The N-methyldiethanolamine (MDEA). The blending of MDEA with water especially uses in the natural gas sweetening and power plant flue gas treatment for the absorption of carbon dioxide and hydrogen sulfide. In this work the nonelectrolyte NRTL nonrandom factor (N-NRTL-NRF) model that is one of the local composition activity coefficient models is used to correlate the vapor-liquid equilibrium (VLE) of the binary aqueous MDEA solution at the various condition. Also, to check the power of the model for prediction of the other properties of this aqueous mixture, the excess enthalpy of this system at 298.15 K, 101.3 kPa, and whole range of composition is predicted. The results show that the N-NRTL-NRF model can describe the vapor-liquid equilibrium of binary aqueous MDEA solution very well and in following predict the excess enthalpy excellently. The vapor-liquid equilibrium and excess enthalpy are two major properties for industrial applications such as for the design of the process equipment.

Keywords: N-methyldiethanolamine, N-NRTL-NRF, Aqueous MDEA solution, Vapor-liquid equilibrium, Excess enthalpy.

Introduction

The main technology for the removal of acid gases such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S) from natural gas or other flow gases, such as power plants, is absorption with alkanolamines. Acid gases are removed from commercial hydrocarbon streams due to Industrial, environmental and economic reasons [1,2]. Although traditional alkanolamines such as monoethanolamine (MEA) or diethanolamine (DEA) were used almost exclusively for many decades, however, 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 sulfide in the presence of carbon dioxide and because of their low vapor pressure, high capacity and low heat of reaction with CO₂ and H₂S [3]. The best-known example of such mixed solvents is the mixture of sulfolane (tetrahydrothiophene dioxide) and the aqueous solution of MDEA as used in the sulfinol process or blend of Piperazine and the aqueous solution of MDEA as used in activated MDEA process.



Vapor-liquid equilibria (VLE) are fundamental properties, and a knowledge of them is essential for the designing, simulating and operating of many chemical processes [4,5]. For the synthesis, design, and optimization of separation processes, thermodynamic models can be applied. For the development of these methods, reliable knowledge of the phase equilibrium behavior is required, and consequently, a systematic extension of the existing database is desirable [2].

Despite the great uses of aqueous MDEA solutions in the different industries, the data on the VLE of this system is very rare. Literature reported experimental phase equilibrium data for the binary aqueous MDEA mixture to consist of isobaric [3,6], isothermal [1,7], freezing point [8], and other [7,8] methods. The isobaric T and x measurements for the aqueous MDEA mixture solutions were performed by Voutsas et al. [3] at (40.0, 53.3, and 66.7) kPa and by Barreau et al. [6] at (30, 50, 70, 90, and 101.33) kPa. As a different measurement method, Kim et al. [7] were determined isothermal VLE data of binary and ternary mixture of aqueous MDEA at (40, 60, 80, and 100) °C. In this method also, Dell'Era et al. [1] report the VLE of the systems of water + MDEA at several temperatures with a static total pressure apparatus. Additionally, Xu et al. [9] reported total pressure data depending on temperature for aqueous MDEA solutions of different concentrations, w) (0.10 to 0.70). The authors calculated vapor-phase composition based on the Gibbs-Duhem equation.

In the field of modeling using an activity coefficient model, Voutsas et al. [3], used the NRTL model and UNIQUAC activity coefficient model to correlate the experimental data. Also, Barreau et al. [6] and Dell'Era et al. [1] applied the NRTL model to representing the VLE behavior of the binary aqueous MDEA system. The NRTL and NRTL models are used by Kim et al. [7].

An accurate estimation of the phase behavior of aqueous MDEA systems over a wide range of operating conditions is vital if this binary mixture is to be used as a solvent in industrial applications. On the other hand, experimental works are time-consuming, expensive, and in some cases dangerous. Therefore, in this work, we attempt to correlate the VLE data of the aqueous MDEA binary systems using the new activity coefficient model namely nonelectrolyte NRTL nonrandom factor (N-NRTL-NRF) and then the excess enthalpy of this system is predicted without using additional adjusting parameters.

Vapor-Liquid equilibrium modeling

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

$$P = \sum x_i \gamma_i P_i^{sat} \quad (1)$$

where , x_i, γ_i, P_i^{sat} are the mole fraction, activity coefficient, and saturated vapor pressure of components in the system. In this work, we are used the Nonelectrolyte NRTL-NRF model [10] to drive the activity coefficients of different components present in the equilibrated liquid phase.

The free Gibbs energy of the N-NRTL-NRF model as a nonelectrolyte local composition model is expressed as:

$$\frac{g^E}{RT} = \sum_i \sum_j x_i x_j \lambda_{ji} (\Gamma_{ji} - 1) \quad (2)$$

By using the above equation, the activity coefficient of species i in system was obtained as following equation:

$$\ln \gamma_i = \sum_j x_j \lambda_{ji} \Gamma_{ji} + \sum_j x_j \Gamma_{ij} \left(\lambda_{ij} - \sum_r x_r \lambda_{rj} \Gamma_{rj} \right) - \sum_l x_l \left(\lambda_{il} + \lambda_{li} - \sum_k x_k \lambda_{kl} \right) \quad (3)$$



Γ_{ij} is nonrandom factor and defined by expression:

$$\Gamma_{ij} = \frac{\beta_{ij}}{\sum_{k=1}^N x_k \beta_{kj}} \quad (4)$$

$$\beta_{ij} = \exp\left(-\alpha_{ij} \frac{g_{ij} - g_{jj}}{RT}\right) = \exp(-\alpha_{ij} \lambda_{ij}) \quad (5)$$

$$\beta_{ij} \neq \beta_{ji}, \beta_{ii} = \beta_{jj} = 1 \quad (6)$$

where g_{ij} , α_{ij} and Γ_{ij} are the Gibbs interaction energy, nonrandomness and non-random factor, respectively, between species i and j . The parameter λ_{ij} is the binary adjustable energy parameter of the N-NRTL-NRF model. Also, N is the number of components in the solution.

Results and Discussion

The activity coefficient model, N-NRTL-NRF, was used to correlate the phase equilibria of the Aqueous MDEA binary system. The model parameters were fitted to the experimental VLE data in the wide range of temperatures, pressures, and mole fraction.

As shown in Eq. (1), in this work, due to the low pressures involved the fugacity coefficients and the Poynting correction term was taken equal to unity. The objective function (OF) that was minimized for the regression of the experimental data is the following:

$$OF = \frac{100}{N} \times \sum \left| \frac{P^{\text{exp}} - P^{\text{cal}}}{P^{\text{exp}}} \right| \quad (7)$$

where N is the number of experimental points.

Considering the value of 0.1 for the nonrandomness parameter in the N-NRTL-NRF model, the following interaction parameters were obtained:

$$\lambda_{\text{Water-MDEA}} = 5.2661 - \frac{2466.9}{T} \quad (8)$$

$$\lambda_{\text{MDEA-Water}} = 32.9417 - \frac{1132.7}{T} \quad (9)$$

Table 1 presents the percent of absolute average relative deviation (AARD%) in the bubble point obtained with the N-NRTL-NRF model.

Table 1. The percent of absolute average relative deviation (AARD%) for correlation of the VLE data for the binary aqueous MDEA systems at various conditions using N-NRTL-NRF.

System	Temperature(K)	Pressure(kPa)	Mole fraction (MDEA)	N	Ref.	AARD%
1	353.1	31.97-47.19	0-0.3063	13	[7]	0.59
2	373.16	94-99.88	0.0113-0.0753	5	[7]	0.19
3	373.15	64.18-99.8	0.012-0.3573	6	[7]	2.09
4	333.1	13.38-19.88	0-0.2902	10	[7]	1.90
5	357.91	48.9-57.9	0.0314-0.1693	6	[1]	2.90
6	333.8	0.2-18.2	0.15-1.0	15	[1]	11.92
7	356.9	12.2-46.6	0.1699-0.7636	8	[1]	4.67
Total	333.1-373.16	0.2-99.88	0-1	63		4.75



As given the deviation as AARD% in table 1 and are shown in Figs. 1-3, the model gives very good results, especially in high temperatures and pressures.

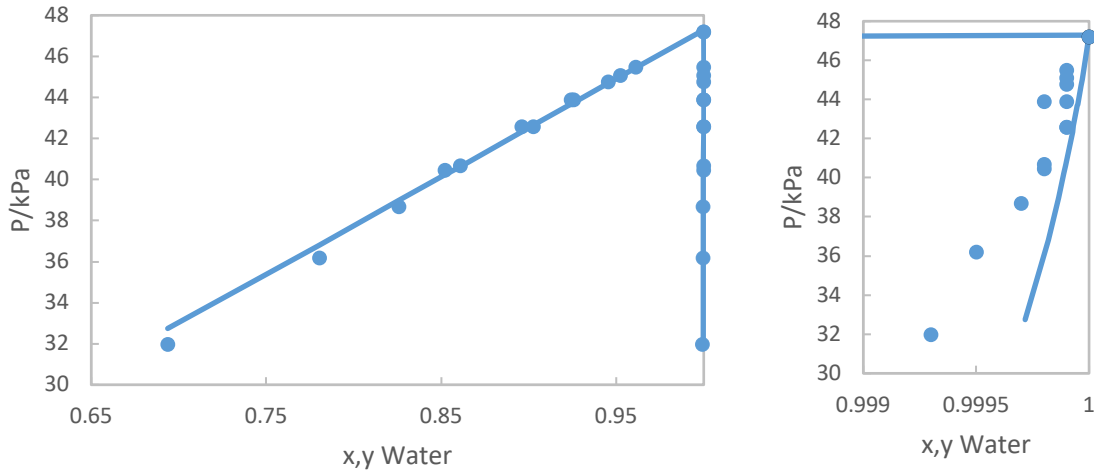


Fig. 1 Experimental and predicted P - x - y behavior of the aqueous MDEA mixture at $T=353.1$ (system 1): (●), experimental data; solid line, N-NRTL-NRF model.

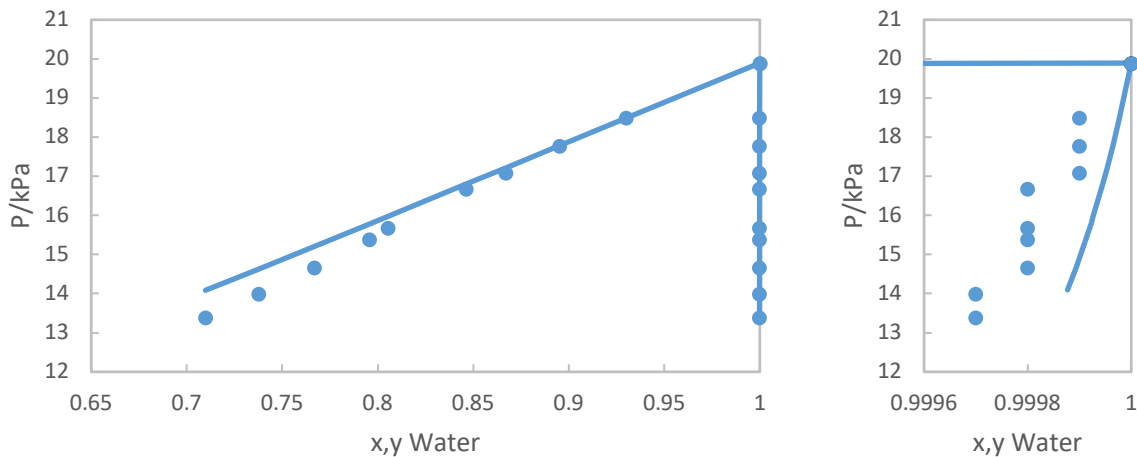


Fig. 2 Experimental and predicted P - x - y behavior of the aqueous MDEA mixture at $T=333.1$ (system 4): (●), experimental data; solid line, N-NRTL-NRF model.

In following, to explore the reliability of obtained parameters and to check the predictively of the present model the excess molar enthalpy of the water/MDEA systems are calculated using the following expression that is obtained from N-NRTL-NRF model for binary systems,

$$\frac{h^E}{RT} = x_1 x_2 \left\{ \lambda_{12} \left[(\Gamma_{12} - 1) + x_2 \ln \beta_{12} \left(\frac{\Gamma_{12}}{x_2 + x_1 \beta_{12}} \right) \right] + \lambda_{21} \left[(\Gamma_{21} - 1) + x_1 \ln \beta_{21} \left(\frac{\Gamma_{21}}{x_1 + x_2 \beta_{21}} \right) \right] \right\} \quad (10)$$

Using equation (10) the excess enthalpy of the binary aqueous MDEA solutions are calculated and compared with experimental data [4,5] and shown in Fig. 4. The %AARD in H^E obtained from N-NRTL-NRF is equal to 28.22%, which is good for this predictive property.



Finally, Fig. 5 shows the total pressure deviation of the present model versus the mole fraction of the water and temperature for all binary mixtures which are studied in present work. As one can see from Fig. 5, deviations decrease with increasing temperature and mole fraction of water, and the maximum deviations for the pressure and composition are observed at the temperature of 303.15 K and $x_{\text{water}}=0$, respectively. Also Fig. 5 demonstrates that most of the deviation points are above the zero line, which indicates the N-NRTL-NRF model slightly upper estimate the total pressure of the equilibrium systems.

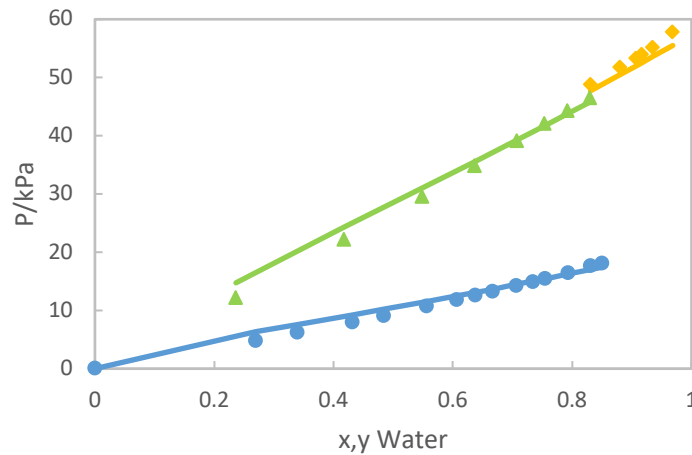


Fig. 3 Experimental and predicted P - x behavior of the aqueous MDEA mixture at various temperatures (system 5-7): (♦), experimental data at $T=357.9$; (▲), experimental data at $T=356.9$; (●), experimental data at $T=333.8$; solid line, N-NRTL-NRF model.

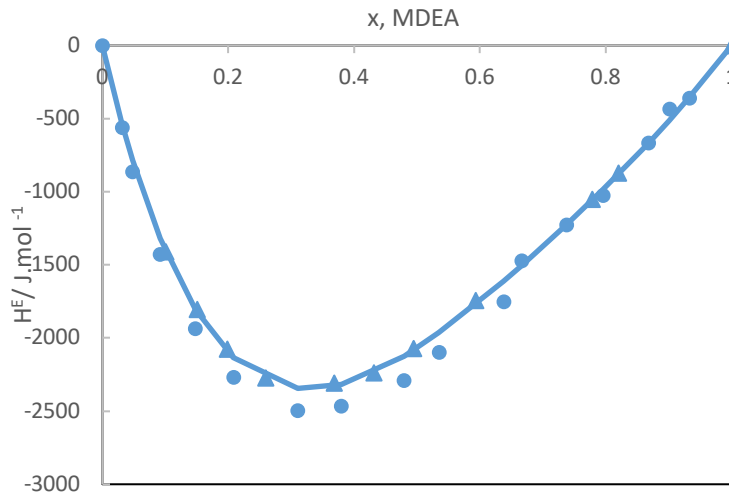


Fig. 4 Experimental and predicted excess enthalpy data for the aqueous MDEA mixture at 298.15 K and 101.3 kPa; (●) experimental data from maham et al. [4] ; (▲) experimental data from Mundhwa and Henni [5] ; solid line, N-NRTL-NRF model.

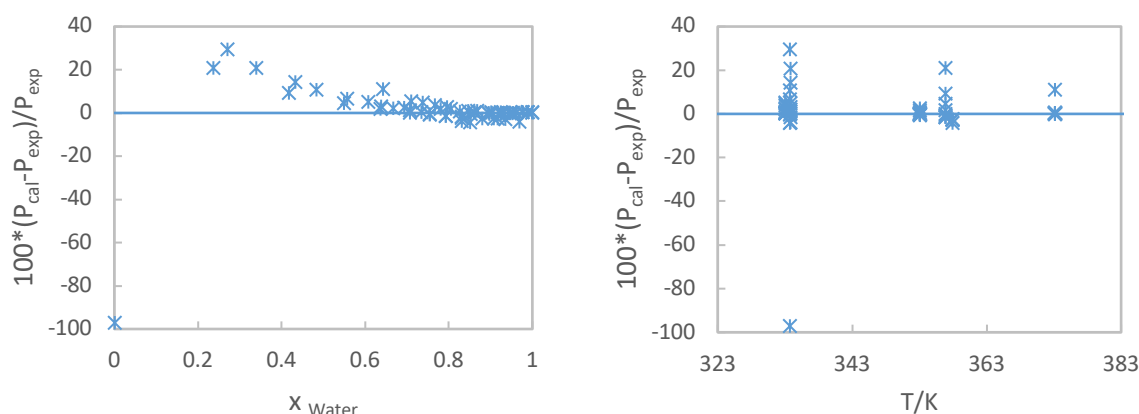


Fig. 5 Percent of relative deviation of the total pressure versus the mole fraction of water (left) and Temperature (right) for All aqueous MDEA binary system.

Conclusions

The vapor-liquid equilibrium of binary aqueous MDEA systems in a wide range of temperatures, pressures, and the whole range of concentration is modeled with a modified Antoine equation. For representing the activity in modified Raoult's equation the new activity model namely N-NRTL-NRF is applied. To check the predictability of the model, by using the parameters of the model that are obtained in the previous section the excess enthalpy of the system in different condition are calculated and compared with experiment. The results show that the modified Antoine equation with N-NRTL-NRF can describe the vapor-liquid equilibrium of water/ MDEA binary systems very well and can predict the other properties such as the excess enthalpy acceptable.

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