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Vapor-liquid equilibria of water+monoethanolamine system

Sung Jin Park*, Hun Yong Shin*,[†], Byoung-Moo Min, Ara Cho**, and Jeon-Seop Lee****

*Department of Chemical Engineering, Seoul National University of Technology,
Gongreung 2-dong, Nowon-gu, Seoul 139-743, Korea
**Climate Change Technology Research Department, Korea Institute of Energy Research,
71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Korea
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Abstract−The accurate design of carbon dioxide separation processes by the absorption method requires knowledge of the vapor-liquid equilibrium of aqueous alkanolamine systems. MEA (monoethanolamine) is widely used for the separation of carbon dioxide by the chemical absorption process. The equilibrium apparatus was tested by comparing the measured VLE data for the methanol+ethanol system with the literature data. The isobaric vapor liquid equilibrium data were measured for the water+MEA binary system by using a modified Stage-Muller equilibrium still with circulation in both phases. The vapor liquid equilibrium data of water+MEA were measured in the pressure range from 50.0 to 70.0 kPa and temperature range from 355.2 to 430.3 K. The measured data were correlated with the UNIQUAC and NRTL activity coefficient models.

Key words: Vapor Liquid Equilibrium, Monoethanolamine, Water, Activity Coefficient, Thermodynamic Consistency

INTRODUCTION

The removal of carbon dioxide using chemical absorbents is of great interest, since global warming is primarily due to its excessive discharge. For the rational design of gas absorption units, the thermodynamics properties, such as the vapor-liquid equilibrium data of the absorbent solution, are required [1-4].

Among the different types of alkanolamines, monoethanolamine aqueous solution has been extensively used to prevent the discharge of carbon dioxide. Although many types of new absorption reactors have been applied in chemical plants and power plants to remove the carbon dioxide, the isobaric vapor-liquid equilibrium data of water+ethanolamine over the whole composition range have rarely been reported [5,6]. Touhara et al. reported the isothermal vapor-liquid equilibrium data of water+monoethanolamine at 298.15 and 308.15 K [5]. The volatility of monoethanolamine is quite low; thus experimental data at low pressure are required to meet the needs of the thermodynamic process design data for carbon dioxide removal processes. In this work, the isobaric vapor-liquid equilibrium data were measured at 50.0 and 70.0 kPa. The measured data were correlated with activity coefficient models such as UNIQUAC [7] and NRTL [8].

EXPERIMENTAL SESSION

1. Apparatus and Procedure

The equilibrium vessel was a modified Stage-Muller dynamic circulating still [9], equipped with a Cottrell circulation pump. The installed still is capable of handling pressures from 0.2 to 101.3 kPa and temperatures up to 433 K. A schematic diagram of the still used for the vapor-liquid equilibrium measurement is shown in Fig. 1. Vaporization is effected by means of an electrical immersion heater (1) made of quartz glass. The circulation of both phases with the simultaneous magnetic stirring of the reflowing circulation streams in the mixing cell (2) ensures the rapid adjustment of the equilib-

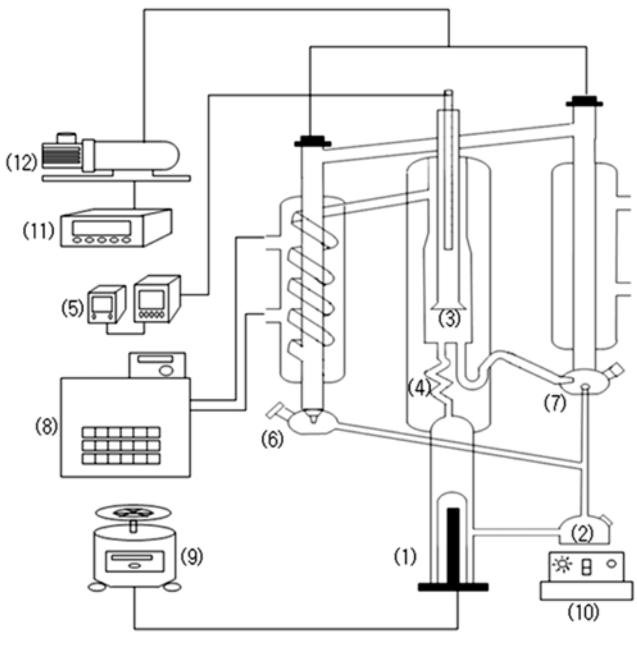

Fig. 1. Schematic diagram of VLE still.

1. Heater	7. Liquid sampler
2. Mixing cell	8. Chiller
3. Equilibrium chamber	9. Autotransformer
4. Cottrell pump	10. Stirrer
5. Thermometer	11. Pressure controller
6. Vapor sampler	12. Vacuum pump

[†] To whom correspondence should be addressed.
E-mail: hyshin@snut.ac.kr

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rium. Before entering the equilibrium chamber (3), the vapor-liquid mixture passes through a lengthened contact path (4) which guarantees and intimate phase exchange. The samples of vapor and liquid were taken from (6) and (7) simultaneously. The pressure of the system was measured and controlled to within 0.2 kPa by using a pressure controller (EYELA, model NVC-2100). The equilibrium temperature was measured with a digital thermometer [Automics, model M5W-DI-XX]. The uncertainty of the measured temperature was ±0.01 K.

The sample compositions were determined from a standard curve of the refractive index versus mole fraction that was constructed by measuring the refractive index of a standard MEA aqueous solution at 23 °C. The refractive index measurements were performed with an Abbe Refractometer (2T) of ATAGO. The maximum error in the composition measurements is observed at the lowest MEA mole fraction and the uncertainty of the phase composition was estimated to be ±0.001 in mole fractions.

2. Materials

Water (HPLC grade) was purchased from J.T. BARKER Co. and MEA (min 99.0%) from JUNSEI Chemical. All chemicals were used without further purification.

RESULTS AND DISCUSSION

1. Fundamental Equation

The isobaric vapor-liquid equilibrium data were measured for the water+monoethanolamine system at 50.0 and 70.0 kPa. The activity coefficients, γ_i, of the liquid phase at low pressure were calculated from the following equation.

$$y_iP=x_i\gamma_iP_i^{sat} \tag{1}$$

where x_i and y_i are the liquid and vapor phase mole fractions of component i, respectively, P is the total pressure and P_i^{sat} is the vapor pressure of the pure component i. The vapor pressures of the pure components were obtained by using the KDB (Korean Data Bank) [10] calculation equation. The vapor pressure equation of the KDB is given by the following Eq. (2) and the coefficients of the vapor pressure equation are given in Table 1.

$$\ln(P_i^{sat})=A\ln(T)+B/T+C+DT^2 \tag{2}$$

2. Vapor-Liquid Equilibrium Data

The experimental apparatus was tested by measuring the vapor-liquid equilibrium of methanol+ethanol at 101.3 kPa. The VLE data for methanol+ethanol at 101.3 kPa are listed in Table 2. The experimental data are also compared with the literature data in Fig. 2. The measured data for the methanol+ethanol system at 101.3 kPa agree well with those of Kurihara et al. [11].

The VLE data for the water (1)+monoethanolamine (2) system at 50.0 and 70.0 kPa are reported in Tables 3 and 4, respectively, along with the activity coefficients calculated using Eq. (1).

The experimental data were tested for thermodynamic consistency. The area test method for isobaric data was described by Heringon [12]. For the water (1)+monoethanolamine (2) system, the plots of $\ln(\gamma_1/\gamma_2)$ vs. x_1 at 50.0 kPa and 70.0 kPa are shown in Figs. 3 and 4, respectively. The results are summarized in Table 5. Since D-J<10 for the two sets of isobaric data, the data can be considered to be thermodynamically consistent according to Herington's rule.

Table 2. Isobaric vapor-liquid equilibrium data for methanol (1)+ ethanol (2) system at 101.3 kPa

T	x_1	y_1
349.1	0.135	0.205
348.7	0.162	0.245
347.8	0.233	0.340
346.2	0.335	0.464
345.6	0.375	0.509
344.4	0.458	0.595
343.2	0.549	0.681
342.4	0.607	0.731
340.5	0.753	0.844
340.2	0.783	0.865
339.4	0.844	0.907

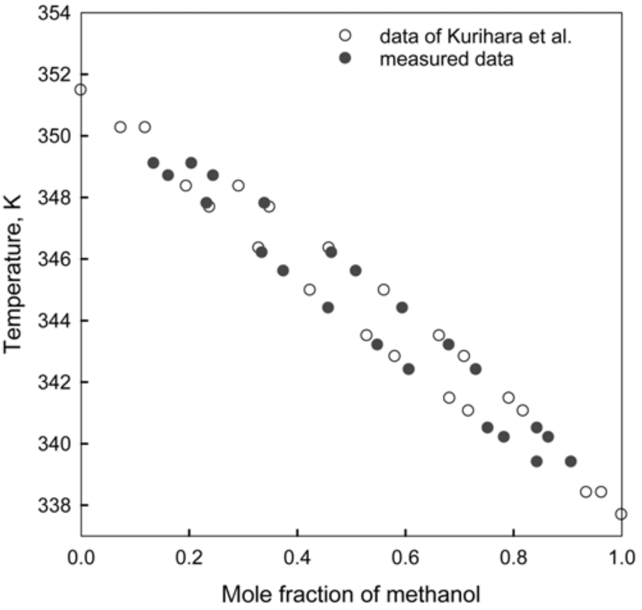

Fig. 2. Vapor-liquid equilibrium of methanol+ethanol at 101.3 kPa.

3. Correlation

The VLE relations for the binary system were correlated by using the NRTL equation [8].

$$\ln\gamma_1=x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2+\frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})}\right] \tag{3}$$

Table 1. Coefficients of KDB vapor pressure equation

	A	B	C	D
Water	−7.342973E+00	−7.276391E+03	6.702455E+01	4.161914E-06
Monoethanolamine	−2.135425E+01	−1.336048E+04	1.622910E+02	1.316681E-05

Table 3. Isobaric vapor-liquid equilibrium data for water (1)+monoethanolamine (2) system at 50.0 kPa

T	x_1	y_1	γ_1	γ_2
420.8	0.012	0.073	0.679	1.002
416.5	0.038	0.214	0.709	1.019
413.2	0.055	0.295	0.741	1.052
410.0	0.084	0.412	0.742	1.022
406.2	0.109	0.501	0.777	1.032
403.1	0.135	0.572	0.785	1.030
401.1	0.166	0.636	0.755	0.985
397.2	0.185	0.679	0.814	1.043
392.5	0.233	0.758	0.836	1.018
389.2	0.256	0.788	0.879	1.060
381.2	0.344	0.869	0.941	1.062
376.2	0.418	0.909	0.963	1.051
372.3	0.481	0.932	0.985	1.063
367.2	0.601	0.965	0.983	0.917
363.3	0.686	0.979	1.011	0.854
360.2	0.805	0.991	0.982	0.693
355.2	0.970	0.999	1.000	0.657

Table 4. Isobaric vapor-liquid equilibrium data for water (1)+monoethanolamine (2) system at 70.0 kPa

T	x_1	y_1	γ_1	γ_2
430.3	0.021	0.113	0.655	0.973
425.7	0.063	0.293	0.639	0.949
423.0	0.087	0.380	0.645	0.939
419.5	0.122	0.483	0.642	0.922
415.4	0.155	0.564	0.661	0.939
407.6	0.236	0.710	0.683	0.928
403.6	0.286	0.780	0.697	0.881
401.1	0.317	0.816	0.709	0.851
394.7	0.405	0.875	0.725	0.864
391.9	0.450	0.902	0.735	0.826
387.2	0.508	0.936	0.786	0.739
381.2	0.632	0.969	0.800	0.627
379.5	0.650	0.971	0.826	0.668
376.3	0.705	0.982	0.860	0.571
371.5	0.792	0.991	0.916	0.511
366.5	0.931	0.998	0.943	0.439

$$\tau_{12}=\frac{g_{12}-g_{22}}{RT} \text{ and } \tau_{21}=\frac{g_{21}-g_{11}}{RT} \tag{4}$$

$$G_{12}=\exp(-\alpha_{12}\tau_{12}) \text{ and } G_{21}=\exp(-\alpha_{12}\tau_{21}) \tag{5}$$

where Δg_{12} and Δg_{21} are parameters adjusted by the experimental data. The interaction coefficient, α, was set to a constant value of 0.3. Also, the VLE data were correlated with the UNIQUAC model. The activity coefficient component, 1, of the binary system was given by,

$$\ln\gamma_1=\ln\frac{\Phi_1^*}{x_1}+\frac{z}{2}q_1\ln\frac{\theta_1}{\Phi_1^*}+\Phi_2^*\left(l_1-\frac{r_1}{r_2}l_2\right)-q_1'\ln(\theta_1'+\theta_2'\tau_{21})$$
$$+\theta_2' q_1'\left(\frac{\tau_{21}}{\theta_1'+\theta_2'\tau_{21}}-\frac{\tau_{12}}{\theta_2'+\theta_1'\tau_{12}}\right) \tag{6}$$

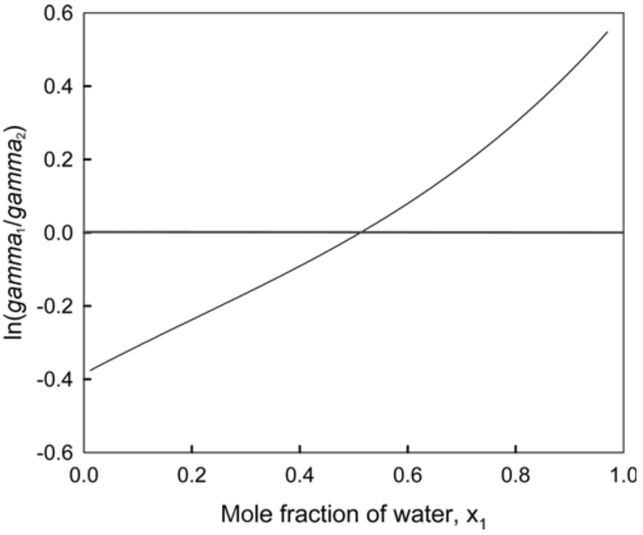

Fig. 3. Thermodynamic consistency test of water+MEA system at 50.0 kPa.

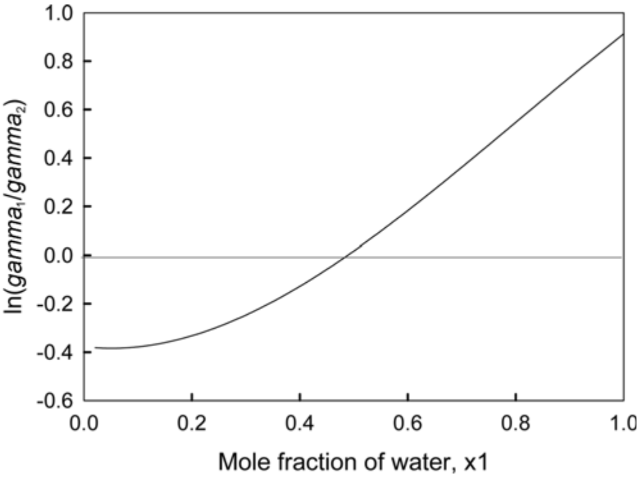

Fig. 4. Thermodynamic consistency test of water+MEA system at 70.0 kPa.

Table 5. Thermodynamic consistency test for experimental data of water (1)+monoethanolamine (2)

Pressure	D	J
50.0	12.48	27.70
70.0	28.22	26.11

Criterion of consistency D-J<10

$$D=100\left|\int_0^1\log(\gamma_1/\gamma_2)dx_1\right|/\int_0^1\left|\log(\gamma_1/\gamma_2)\right|dx_1$$

$$J=150(T_{max}-T_{min})/T_{min}$$

where,

$$\tau_{12}=\exp\left(-\frac{\Delta u_{12}}{RT}\right)=\exp\left(-\frac{a_{12}}{RT}\right) \tag{7}$$

$$\tau_{12}=\exp\left(-\frac{\Delta u_{21}}{RT}\right)=\exp\left(-\frac{a_{21}}{RT}\right) \tag{8}$$

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

$$\mathrm{OF}=\frac{1}{\mathrm{N}}\sum_{i}^{N}\left|\mathrm{T}_i^{exp}-\mathrm{T}_i^{cal}\right|+\frac{1}{\mathrm{N}}\sum_{i}^{N}\left|(\mathrm{y}_i^{exp}-\mathrm{y}_i^{cal})\right|\times 100 \tag{9}$$

where N is the number of experimental data points.

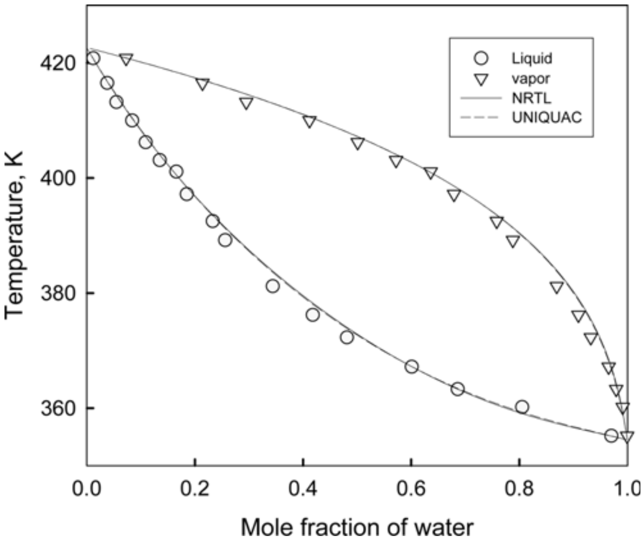

Fig. 5. Vapor liquid equilibrium of water+monoethanolamine system at 50.0 kPa.

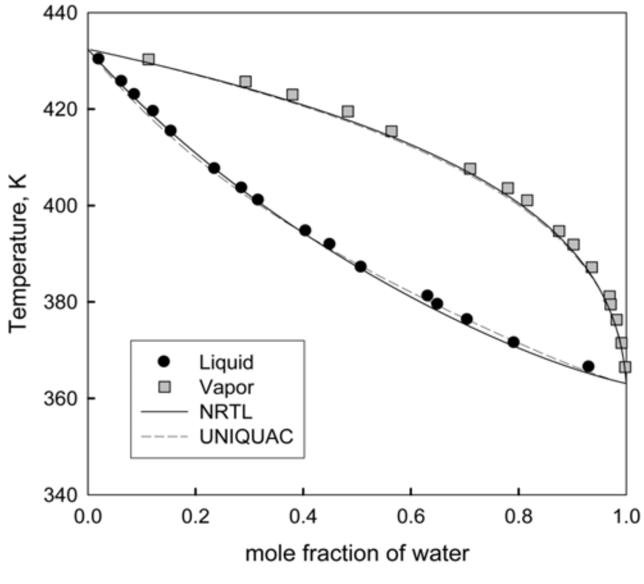

Fig. 6. Vapor liquid equilibrium of water+monoethanolamine system at 70.0 kPa.

The calculated data at 50.0 kPa and 70.0 kPa were plotted and compared with the experimental data in Figs. 5 and 6, respectively.

Table 6 presents the average absolute errors in the bubble point temperatures and the deviation in the dew point composition obtained with the NRTL and UNIQUAC models. The calculated results of both models agree well with the experimental data within an absolute average error deviation of 1% vapor mole fraction. The experimental data were tested for thermodynamic consistency by the method of Van Ness et al. [13]. The Δy_1 values of the water (1)+monoethanolamine (2) system were below 0.01 at both 50.0 kPa and 70.0 kPa. The present VLE data satisfied the thermodynamic consistency rule of Van Ness ($\Delta y_1<0.01$) [13].

CONCLUSIONS

The isobaric VLE data were measured for the water+monoethanolamine binary system at 50.0 and 70.0 kPa with a new dynamic circulating still. The NRTL and UNIQUAC activity coefficient models were used for the correlation of the experimental data. The results of the two models were found to be comparable and in very good agreement with the experimental data.

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Table 6. Parameters and absolute deviations between calculated and experimental temperatures, ΔT, and vapor phase mole fractions, Δy_1, of NRTL and UNIQUAC models for experimental water (1)+ethanolamine (2) system

P (kPa)	NRTL parameters				UNIQUAC parameters			
	Δg_{12} (J/mol)	Δg_{21} (J/mol)	ΔT	Δy	a_{12} (J/mol)	a_{21} (J/mol)	ΔT	Δy
50.0	9627.2	−5369.1	0.965	0.0036	−1632.2	272.59	0.934	0.0030
70.0	5061.5	−5172.8	0.794	0.0100	532.96	−2519.72	0.887	0.0065

$\Delta \mathrm{T}=\frac{1}{\mathrm{N}}|\mathrm{T}-\mathrm{T}^{exp}|,\ \Delta \mathrm{y}=\frac{1}{\mathrm{N}}|\mathrm{y}-\mathrm{y}^{exp}|$