

VAPOR-LIQUID EQUILIBRIA FOR THE BINARY MONOETHANOLAMINE+WATER AND MONOETHANOLAMINE+ETHANOL SYSTEMS

Sung-Bum Park and Huen Lee[†]

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
373-1 Kusung-dong, Yusung-gu, Taejon 305-701, South Korea
(Received 27 January 1997 • accepted 11 March 1997)

Abstract – Isobaric vapor-liquid equilibrium data for monoethanolamine (MEA)+water and monoethanolamine (MEA)+ethanol were measured in an equilibrium cell circulating both the vapor and liquid phases. The measurements of the boiling temperatures and corresponding equilibrium compositions for two binary mixtures were carried out at the atmospheric pressure. The results were checked for thermodynamic consistency by the point test method. The activity coefficients for nonideality of the liquid phase were calculated by using the Wilson, NRTL, and UNIQUAC equations. The fugacity coefficients for nonideality of the vapor phase were calculated from the virial equation of state with the second virial coefficient. The experimental data were verified to be thermodynamically consistent and showed a good agreement with the calculated values.

Key words: Vapor-Liquid Equilibrium, Monoethanolamine, Ethanol, Water

INTRODUCTION

Measurements of vapor-liquid equilibrium (VLE) data play an important role in the design and operation of the chemical processes. The development and extension of the prediction methods such as ASOG and UNIFAC require reliable experimental data of typical binary systems. Monoethanolamine (MEA) is a commonly used chemical for the removal of acidic gases such as CO₂, H₂S, and COS. The information on the boiling temperature of MEA mixed with water and alcohol can be helpful in the design of absorption process.

In this work, the VLE data at the atmospheric pressure for the simple binary systems of MEA+water and MEA+ethanol were measured to offer the basic information on the system including MEA. A thermodynamic consistency test [Fredenslund et al., 1977] was carried out to check the reliability of the experimental data. Also, the correlations by the activity coefficients models such as Wilson [1964], NRTL [1968], and UNIQUAC [1975] equations were carried out to show a good agreement with the experimental data.

EXPERIMENTAL

The VLE experiments were carried out by using the equilibrium apparatus circulating both vapor and liquid phases. The detailed description of the apparatus and experimental procedure were presented in our previous study [Lee et al., 1992]. The compositions of vapor and liquid phases were determined by gas chromatography on HP5890 series II apparatus with a thermal conductivity detector and HP3396 series II integrator. Capillary column (HP-1) coated with crosslinked methyl silicone gum, 25 m long, 0.2 mm in inner diameter, and 0.33 μm in film thickness was used for separation. The oven, injector, and

detector temperature were 363.12, 393.12, and 473.12 K, respectively. Helium was used for carrier gas, and split ratio was 150:1. The capillary column used in these conditions showed a good separation for both systems. The calibration curves for analyzing the compositions of vapor and liquid samples were prepared by the area normalization method. The accuracies in the calibrations were within ±0.005 mole fractions for two systems. The temperature in the equilibrium cell was measured with an accuracy of ΔT=±0.1 K.

MEA was purchased by Sigma-Aldrich Chemical Co. with a minimum purity of 99 mol % and ethanol by the same company with a purity of 99.8 mol %. Distilled water was prepared and used for experiments. Since any significant impurities were not found by gas chromatography, all of above reagents were used without further purification. The boiling points of the pure compounds at the atmospheric pressure were presented in Table 1.

RESULTS AND DISCUSSION

The experimental VLE data were presented in Table 2.

At vapor and liquid equilibrium at pressure P and temperature T,

$$f_i^V = f_i^L \quad (1)$$

where f_i^V and f_i^L are fugacities of vapor and liquid phases of component i. Eq. (1) can be rewritten as the following equation.

Table 1. Boiling points (T_b) of compounds and constants for Antoine Equation^a

Compounds	T_b /K (K)	A	B	C
Ethanol	351.1	7.7483	1375.5	204.66
Water	373.1	7.9203	1638.5	225.14
MEA	443.3	7.8709	1819.8	194.62

$$^a \log_{10}[P(\text{mmHg})] = A - B/[T(^{\circ}\text{C}) + C]$$

[†]To whom all correspondence should be addressed.

$$y_i \phi_i P = x_i \gamma_i P_i^s \phi_i^s \exp\left[\frac{V_i^L(P - P_i^s)}{RT}\right] \quad (2)$$

where x_i and y_i are the mole fraction of component i in liquid and vapor phases, respectively, γ_i is its activity coefficient depending on the used excess Gibbs free energy models. ϕ_i and ϕ_i^s denote its fugacity coefficients in the gas phase and at saturation, respectively, P_i^s is its saturated vapor pressure, and V_i^L is its liquid molar volume. The fugacity coefficients were calculated from the virial equation of state using the second virial coefficient estimated by Hayden and O'Connell's method [1975]. The vapor pressures of pure compounds were calculated from

Table 2. Isobaric VLE data (Liquid Phase Mole Fraction x_i , Vapor Phase Mole Fraction y_i , and Temperature T) at the atmospheric pressure

T (K)	x_1	y_1	T (K)	x_1	y_1
water (1)+MEA (2)					
443.3	0.0000	0.0000	443.3	0.0000	0.0000
440.1	0.0194	0.1126	437.4	0.0142	0.1712
437.4	0.0377	0.2050	432.6	0.0296	0.3154
435.1	0.0488	0.2560	421.8	0.0629	0.5332
433.0	0.0624	0.3135	418.6	0.0735	0.5850
430.0	0.0889	0.4105	412.3	0.0967	0.6720
420.6	0.1551	0.5903	409.4	0.1135	0.7215
418.5	0.1754	0.6411	401.4	0.1552	0.8088
415.2	0.2076	0.6855	397.5	0.1801	0.8353
408.5	0.2785	0.7749	388.1	0.2474	0.8981
404.4	0.3228	0.8279	385.1	0.2815	0.9085
397.3	0.4157	0.8830	377.9	0.3642	0.9411
392.8	0.4948	0.9211	372.6	0.4482	0.9617
385.5	0.6529	0.9577	369.6	0.4916	0.9796
382.0	0.7483	0.9743	366.7	0.5459	0.9753
378.5	0.8370	0.9814	363.8	0.6367	0.9883
374.3	0.9652	0.9966	358.5	0.7769	0.9943
373.1	1.0000	1.0000	356.2	0.8442	0.9964
			354.1	0.9017	0.9985
			351.1	1.0000	1.0000

Table 3. Parameters and Root Mean Square Deviations of the Wilson, NRTL, and UNIQUAC Activity Models

Model	Parameters ^a	ΔT_{rms}	Δy_{rms}
Water (1)+MEA (2)			
Wilson	$\Delta\lambda_{12}=1201.6$ $\Delta\lambda_{21}= 1021.9$	0.48	0.004
NRTL	$\Delta g_{12}= 2306.8$ $\Delta g_{21}=1884.8$ $\alpha=0.3$	0.90	0.008
UNIQUAC	$\Delta\mu_{12}=2106.3$ $\Delta\mu_{21}= 2151.6$	0.89	0.007
Ethanol (1)+MEA (2)			
Wilson	$\Delta\lambda_{12}=914.45$ $\Delta\lambda_{21}= 458.98$	0.47	0.004
NRTL	$\Delta g_{12}= 1898.8$ $\Delta g_{21}=2599.6$ $\alpha=0.3$	0.65	0.009
UNIQUAC	$\Delta\mu_{12}= 1322.8$ $\Delta\mu_{21}=1877.2$	0.61	0.004

^aAll energy parameters are expressed in Jmol⁻¹

Antoine's equation with coefficients in Table 1. These coefficients were determined from the correlations of vapor pressure with temperature [Reid et al., 1988]. By regressing the vapor pressures calculated from the reference correlations to the form of Antoine equation, Antoine constants in Table 1 were obtained. Molar volumes in the liquid phase were calculated from the Yen and Woods's correlation [1966]. The models used for liquid phase activity coefficients were the Wilson, NRTL, and UNIQUAC equations. Table 3 lists the model parameters fitted for each systems with the root mean squared deviations in y and T .

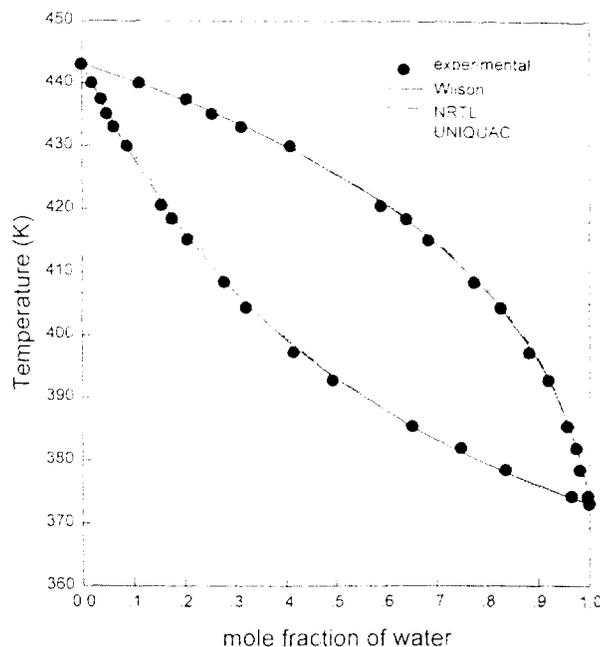


Fig. 1. VLE data for water (1)+MEA (2) at the atmospheric pressure.

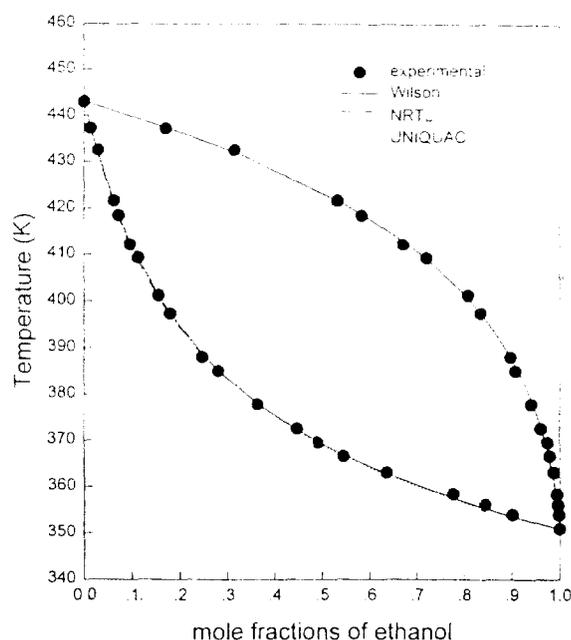


Fig. 2. VLE data for ethanol (1)+MEA (2) at the atmospheric pressure.

Parameters in Table 3 were estimated using maximum likelihood principle [Kemeny et al., 1978]. Figs. 1 and 2 show the comparisons between the experimental data and predicted values. A thermodynamic consistency test was applied to the experimental data by using the point test of Fredenslund et al [1977]. In the point test of Fredenslund, the mean deviations between the experimental and calculated values of the vapor phase mole fractions should be less than 0.01 to satisfy the thermodynamic consistency. The results of this test were 0.0094 for MEA+water system, and 0.0086 for MEA+ethanol system, which confirmed the thermodynamic consistency of the experimental data.

CONCLUSION

The experimental boiling temperatures and corresponding equilibrium compositions at the atmospheric pressure for the binary MEA+water and MEA+ethanol systems were measured in an equilibrium cell circulating both liquid and vapor phases. The experimental data satisfied thermodynamic consistency tests and the calculated values by Wilson, NRTL, and UNIQUAC equations showed a good agreement with the experimental results. The calculated values by Wilson equation showed slightly better agreement with the experimental data when compared with other equations.

NOMENCLATURE

- f_i^g : fugacity of vapor phase of component i
 f_i^l : fugacity of liquid phase of component i
 x_i : mole fraction of component i in the liquid phase
 y_i : mole fraction of component i in the vapor phase
 γ_i : activity coefficient of component i

- ϕ_i : fugacity coefficient of component i in the gas phase
 ϕ_i^s : fugacity coefficient of component i at saturation
 P_i^s : saturated vapor pressure of component i
 V_i^l : liquid molar volume of component i

REFERENCES

- Abrams, D. S. and Prausnitz, J. M., "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems", *AIChE J.*, **21**, 116 (1975).
 Fredenslund, A. G., Gmehling, J. and Rasmussen, P., "Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method", Elsevier, Amsterdam, 1977.
 Hayden, J. G. and O'Connell, J. P., "A Generalized Method for Predicting Second Virial Coefficients", *Ind. Eng. Chem. Process Des. Dev.*, **14**, 209 (1975).
 Kemeny, S. and Manczinger, J., "Treatment of Binary Vapor-Liquid Equilibrium Data", *Chem. Eng. Sci.*, **33**, 71 (1978).
 Lee, H. S., Yoon, J. H. and Lee, H., "VLE for the Systems Water-Ethylene Glycol, Methanol-Ethylene Glycol and Pentanol-Ethylene Glycol", *HWAHAK KONGKAK*, **30**(5), 553 (1992).
 Renon, H. and Prausnitz, J. M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", *AIChE J.*, **14**, 135 (1968).
 Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids", 4th ed., McGraw-Hill, New York, 1988.
 Wilson, G. M., "Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing", *J. Am. Chem. Soc.*, **86**, 127 (1964).
 Yen, L. C. and Woods, S. S., "A Generalized Equation for Computer Calculation of Liquid Densities", *AIChE J.*, **12**, 95 (1966).