

상압하에서 MEA + Water, MEA + Ethanol 계의 기액상평형

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Vapor-Liquid Equilibrium at 101.3kPa for Monoethanolamine + Water and
Monoethanolamine + Ethanol

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Introduction

Measurements of vapor-liquid equilibrium (VLE) data play an important role in design of the chemical processes. Hence, lots of VLE data have been measured to offer the basic information for the systems of interest. Monoethanolamine (MEA) is used for the removal of acidic gases, such as CO₂, H₂S and so on, and can be used as an anti-crystallization additive for absorption heat pump. In this work, VLE data at 101.3kPa for the systems of MEA + water and MEA + ethanol were measured to check a tendency of the typical systems including MEA. Besides, the correlations between the experimental data and activity coefficients models such as Wilson, NRTL, UNIQUAC equations were carried out.

Theory

For vapor-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 . Equation (1) can be rewritten as the following equation.

$$y_i \phi_i^V P = x_i \gamma_i P_i^s \phi_i^s \exp[V_i^L (P - P_i^s) / RT] \quad (2)$$

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 Gibb's free energy models. ϕ_i^V 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. The vapor pressures of pure compounds were calculated from Antoine's equation with coefficients in Table 1. These coefficients were determined from the correlations of vapor pressure with temperature in reference[7]. By regressing the vapor pressures calculated from the reference correlations, Antoine constants in Table 1 were obtained. The differences between the two calculated vapor pressures were less than 1%. Molar volumes in the liquid phase were calculated from the Yen and Woods's correlation. The models used for the liquid phase activity coefficients were the Wilson, NRTL, and UNIQUAC equation. Table 2 lists the model parameters fitted for each systems with the root mean squared deviation in y and T . Parameters in Table 2 were estimated using maximum likelihood principle based on the following assumptions.

First, experimental errors are small. Second, experimental errors are independent of one another, both within a given data point and from point to point. Third, the fitting equation is able to represent the true values with deviations of an order less than the order of the experimental errors. Fourth, experimental errors display a normal distribution with zero mean from the true values.

Experimental Section

MEA was supported by Aldrich with purities 99+% and ethanol by MERCK with purities 99.8+%. 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 101.3kPa appear in Table 1. Experiments were carried out by using the VLE equilibrium apparatus circulating both vapor and liquid phases. Its schematic diagram is presented in Fig.1. 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, 25m long, 0.2mm in inner diameter, and 0.33 μ m in film thickness was used for separation. Oven temperature, injector temperature, and detector temperature was 363.12, 393.12, and 473.12K, respectively. Helium was used for carrier gas, and split ratio was 150:1. Capillary column used in these conditions showed a good separation for both systems. Calibrations were carried out to convert the percentages of the peak area to the weight fractions of MEA. Accuracies in the calibrations were ± 0.005 mole fraction for both cases. Temperature was measured at an accuracy of $\Delta T = \pm 0.1$ K.

Results and Discussion

Figure 2 and 3 show the comparisons between the experimental data and the predicted values by Wilson, NRTL, UNIQUAC equations for each systems. Thermodynamic consistency tests were applied to the experimental data by using the point test of Fredenslund et. al and the area test of Herington. In point test, mean deviations in 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 when the order of Legendre polynomial was 5. In area test suggested by Herington, D-J should be less than 10 for thermodynamic consistency. Since the values of J are larger than those of D for both systems, thermodynamic consistency of the experimental data was confirmed.

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Table 1. Boiling Points (T_b) of compounds and Constants for Antoine Equation^a

compounds	T_b (K)	A	B	C
ethanol	351.1	7.7483	1375.3	204.66
water	373.1	7.9203	1638.5	225.14
MEA	343.1	7.8709	1819.8	194.62

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

Table 2. 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

^a All energy parameters are expressed in Jmol^{-1}

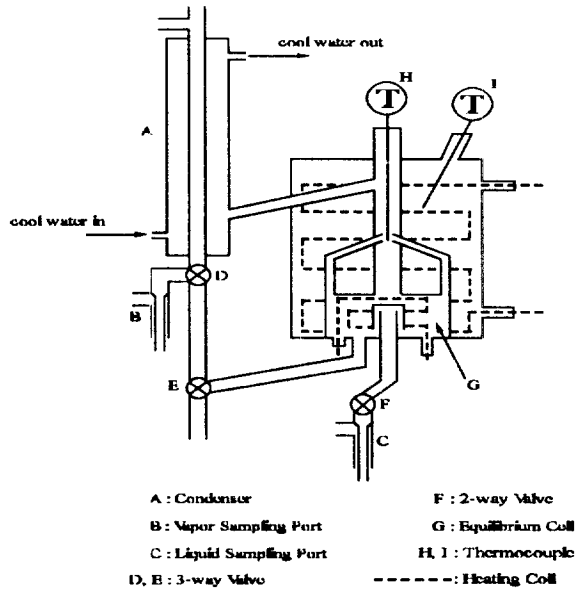


Fig.1 Apparatus for vapor-liquid equilibria

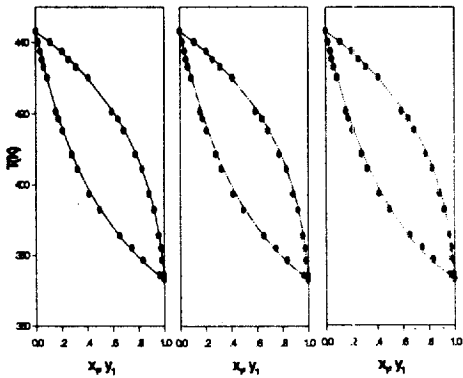


Fig.2 T-xy diagram for MEA + Water system.
 (—)Wilson, (---)NRTL, (.....)UNIQUAC
 x_1 and y_1 denote the liquid and vapor mole fraction of water respectively.

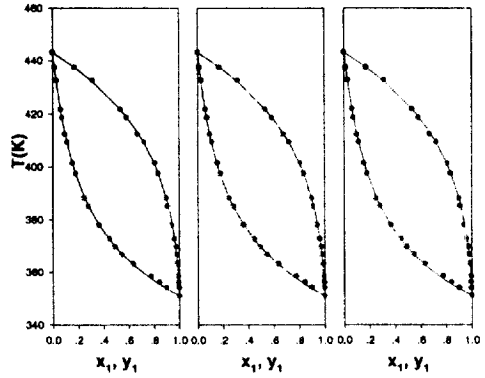


Fig.3 T-xy diagram for MEA + Ethanol system.
 (—)Wilson, (---)NRTL, (.....)UNIQUAC
 x_1 and y_1 denote the liquid and vapor mole fraction of ethanol respectively.