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VAPOR-LIQUID EQUILIBRIUM DATA FOR BINARY SYSTEM OF [2-METHOXYETHANOL + H2O] AT 100 KPA

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ABSTRACT

Isobaric vapor-liquid equilibrium (VLE) data for binary system of [2-Methoxyethanol + H_2O] was measured which using CE-1 equilibrium cell at 100 kPa. The thermodynamic consistency of the experimental data was tested with the Herington method and passed. Then the experimental data were correlated using the nonrandom two-liquid (NRTL) and Wilson activity coefficient models, and the more precise interaction parameters were obtained.

KEYWORDS

Vapor-liquid equilibrium, thermodynamic consistency, Herington method, activity coefficient.

1. INTRODUCTION

2-Methoxyethanol (ethylene glycol monomethyl ether, ME) is a water-miscible solvent used extensively in the chemical industry [1]. It is converted by alcohol dehydrogenase into methoxyacetic acid which is the substance which causes the harmful effects [2]. At the same time, 2-Methoxyethanol is the most important byproduct in morpholine production progress and there is often a certain amount of water in the process. Considered all of those aspects, the VLE data of [2-Methoxyethanol + H_2O] system is required to serve as basis for the separation.

However, there is no VLE data of [2-Methoxyethanol + H_2O] has been found from the NIST Thermodynamics Research Center at 100 kPa. Therefore, isobaric vapor-liquid equilibrium data of the binary system at 100 kPa is considered in this study. The VLE data passed the thermodynamic consistency tests with the Herington test [3]. Then the experimental data were correlated using the nonrandom two-liquid (NRTL) and Wilson activity coefficient models, and the results of root mean square deviations (RMSD) show that the experimental values are reliable.

2. EXPERIMENTAL SECTION

2.1 Experimental reagents

2-Methoxyethanol was commercially obtained and used before distillation treatment, and the information of the two chemicals is listed in Table 1. All samples analysis was completed by gas chromatography (GC, GC9800, Shang Hai Ke Chuang Chromatographic Instrument Co. Ltd.). No appreciable peak of impurity was detected. The purification methods were distillation to remove impurities with high boiling point.

2.2 Sample analysis

All samples which include the liquid phase and vapor condensate analysis by Gas chromatography (GC). Thermal Conductivity Detector (TCD) was used with a packed column which using Chromosorb as supporter. Continuous-flow hydrogen at a constant flow rate of 30 mL/min was used as the carrier gas. The temperature of vaporizer and detector were 413.1 and 393.1 K, respectively. Each sample is tested three times at least. The standard uncertainty of compositions is 0.005 in mole fraction the two repeated measurements.

2.3 Apparatus and procedure

The VLE data were carried out by a CE-1 equilibrium still. The disadvantage of the still is that a higher amount of the reagents must be used, while its advantage is that the data obtained from CE-1 equilibrium still on several binary system shown very good agreement with previous literature showed that the apparatus used in measuring the saturated vapor pressure data was reliable.

Table 1: Materials Description at 99 kPa[a]

Variables	CASRN	source	intial purity[b]	final purity[b]	Analysis
2-Methoxyethanol	109-86-4	Energy Chemical	0.991	0.999	GC[c]
H_2O	7732-18-5	Ultra-pure water system	1	-	GC

[a]Standard uncertainties u(P) = 0.5 kPa. [b]Mole fraction. [c]Gas chromatography.

The CE-1 still structure is displayed in Figure 1. The apparatus contains liquid-phase sampling port, vapor-phase sampling port, equilibrium chamber, heating bar, and condenser. Both the vapor and the liquid phase were continuously circulating to ensure the equilibrium could be established in the equilibrium process. In each experiment, equilibrium between the vapor and the liquid phases was assumed when the temperature remained constant for 60 min at least.

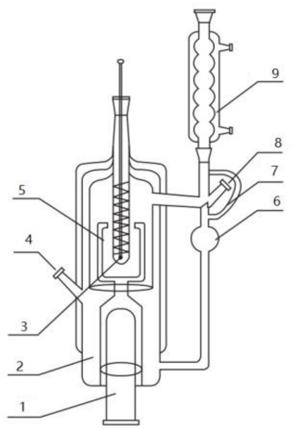

Figure 1l: CE-1 still: (1) heater; (2) boiling chamber; (3) equilibrium temperature thermometer; (4) liquid phase sample valve; (5) balancing chamber; (6) mixing chamber; (7) equalizing pipe; (8) vapor condensate sampling valve; (9) cooler.

3. RESULTS AND DISCUSSION

3.1 Vapor-liquid equilibrium model

An activity coefficient model is used to calculate the activity coefficient, expresses the equilibrium relationship between vapor and liquid phase [4]:

$$y_i\varphi_i^v p = x_i\gamma_i\varphi_i^s p_i^s \exp\left(\frac{v_i^l(p-p_i^s)}{RT}\right) \quad (1)$$

where p is the total pressure, T is the temperature, R is the universal gas constant, x_i and y_i are the mole fractions of component i in the liquid phase and vapor phase, respectively, φ_i^v is the fugacity coefficient of component i in the vapor mixture, φ_i^s is the fugacity coefficient in the saturate state, p_i^s is the saturated vapor pressure, v_i^l is the liquid molar volume of pure component *i*. The Poynting factor $\exp\left(\frac{v_i^l(p-p_i^s)}{RT}\right)$ in eq 1 is close to unity at 100 kPa. The vapor phase is usually treated ideality when under atmosphere pressure. The liquid phase fugacity is assumed to be 1, so eq 1 can be simplified as

$$y_i p = x_i\gamma_i p_i^s \quad (2)$$

The vapor pressure of the pure components is obtained from Antoine equation, which is shown in eq 3:

$$\ln p_i^s = A - \frac{B}{T+C} \quad (3)$$

where T/K is the temperature and p_i^s(kPa) is the standard vapor pressure of pure component *i*. The coefficients A, B and C are the Antoine constant, which were displayed in Table 2.

Table 2: Antoine equation coefficients *A*, *B* and *C* for the chemicals [5]

component	*A*	*B*	*C*	*T*(K) range
2-Methoxyethanol	14.696	3256.01	-74.169	346-416
H_2O	7.96681	1668.21	228	333-423

3.2 VLE data

This binary system experimental data, activity coefficients and the relative volatilities for [2-Methoxyethanol + H_2O] at 100 kPa are listed in Table 3.

Table 3: Isobaric VLE data for temperature *T*, liquid phase mole fraction *x*, vapor phase mole fraction *y*, activity coefficient *γ*, and relative volatilities for the system

T	x_1	y_1	γ_1	γ_2	12
397.2	0	0	-	1.000	-
394.5	0.039	0.118	1.460	0.999	3.297
392	0.078	0.216	1.447	1.001	3.257
390.9	0.098	0.259	1.430	1.002	3.217
388.9	0.137	0.336	1.415	1.002	3.188
387	0.176	0.402	1.403	1.006	3.147
384.6	0.235	0.485	1.371	1.010	3.066
382.5	0.294	0.554	1.343	1.017	2.983
380.2	0.373	0.628	1.299	1.033	2.838
378.3	0.451	0.687	1.253	1.061	2.672
376.4	0.549	0.748	1.197	1.112	2.438
375.2	0.627	0.788	1.152	1.178	2.211
374.1	0.725	0.833	1.095	1.309	1.892
373.2	0.843	0.887	1.035	1.603	1.462
372.9	0.902	0.92	1.015	1.837	1.249
372.7	0.941	0.947	1.008	2.036	1.120
372.7	0.98	0.98	1.001	2.266	1
372.7	1	1	1.001	-	-

The relative volatilities can be obtained with eq 4 [6, 7]:

$$\alpha_{12} = \frac{y_1/x_1}{(1-y_1)/(1-x_1)} \quad (4)$$

where α_{12} is the relative volatility and x_1 and y_1 are the liquid and vapor mole fractions, respectively.

3.3 Thermodynamic consistency test of binary system

Thermodynamic consistency of the experimental data was verified by the Herington test. The Herington test is an area test which is used to examine the VLE data, and it is expressed as eq 5 and eq 6:

$$D = \frac{\left|\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1\right|}{\int_0^1 \left|\ln\left(\frac{\gamma_1}{\gamma_2}\right)\right| dx_1} \quad (5)$$

$$J = 150 \times \frac{T_{max} - T_{min}}{T_{min}} \quad (6)$$

In which $D - J$ must be less than 10. T_{max} (K) and T_{min} (K) are the highest and the lowest boiling points in the system, respectively. The result is shown in Figure 2:

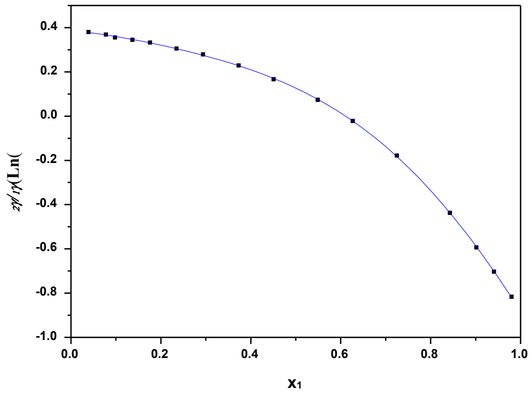

Figure 2: Diagram of $\ln(\gamma_1/\gamma_2)$ to x_1 for this binary system (D = 0.798, J = 9.860, $|D - J|$ = 9.062 < 10)

which all satisfy the consistent criteria, illustrating that the experimental VLE data of the [2-Methoxyethanol + H_2O] binary system can be considered as thermodynamically consistent at 100 kPa.

3.4 Data regression

The experimental data of binary systems were fitted with the NRTL and Wilson models based on Aspen Plus. The maximum likelihood objective function was used in the regression calculation. In this function, errors of T and y were considered. The function is shown as follows:

$$Q = \sum_{i=1}^{N} \left[\left(\frac{T_i^{exp} - T_i^{est}}{\sigma_T} \right)^2 + \left(\frac{p_i^{exp} - p_i^{est}}{\sigma_p} \right)^2 + \left(\frac{x_i^{exp} - x_i^{est}}{\sigma_x} \right)^2 + \left(\frac{y_i^{exp} - y_i^{est}}{\sigma_y} \right)^2 \right] \quad (7)$$

where σ is the standard deviation of the indicated data, N is the number of experimental points, T is the equilibrium temperature, x_i and y_i are the liquid mole fraction and vapor mole fraction of the light component, respectively, superscripts *exp* and *est* are the abbreviation of experiment and estimate, respectively, and Q is the objective function to be minimized by data regression.

Table 4: Correlation parameters and root mean square deviation for the binary system

System	Models	Correlation parameters[a]				RMSD	
		a_{ij}[b]	a_{ji}[c]	b_{ij}	b_{ji}	□$_{yl}$[d]	□$_T$[e]
Methoxyethanol + H_2O	NRTL	0	0	639.746	-243.491	0.000033	0.139
	Wilson	0	0	133.4757	-527.618	0.00137	0.237

[a]a and b parameters of the NRTL or Wilson model. bSubscripts ij represents the pair interaction. cSubscripts ji represents the pair interaction. [d]$\sigma_{yl} = (\sum(y_{l,i}^{est} - y_{l,i}^{exp})^2/\mathrm{n})^{0.5}$.[e] $\sigma_T = (\sum(T_i^{est} - T_i^{exp})^2/\mathrm{n})^{0.5}$. [f]The value of □$_{ij}$ was fixed at 0.3 for the binary system as these systems belong to type I according to the definition [8].

The binary interaction parameters and the RMSD for the binary system at 100 kPa are shown in Table 4. It can be observed that the RMSD of vapor phase composition is no more than 0.002, and the RMSD of the temperature is no more than 0.237. The calculated results of the vapor phase composition and temperature by two models tend to be the same, which show reasonably good agreement with the experimental values.

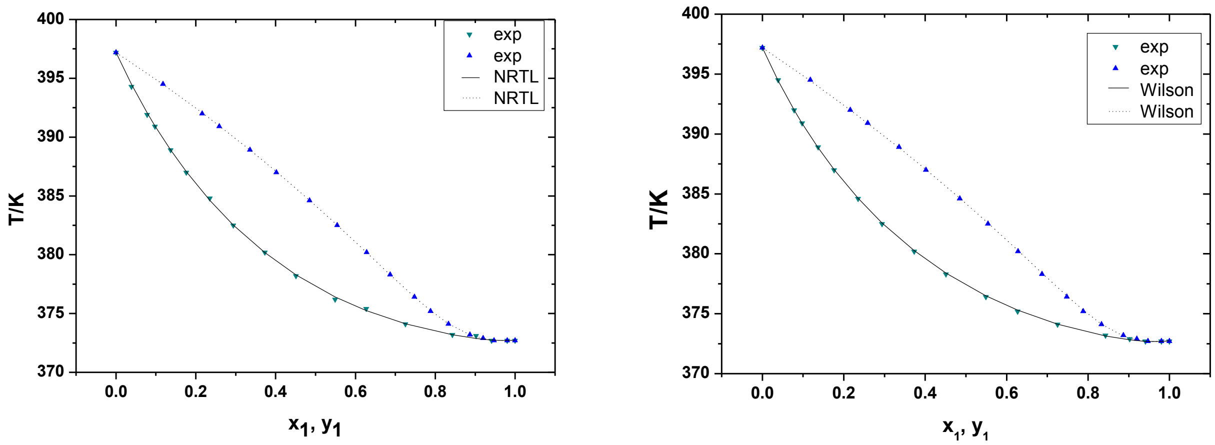

Figure 3: Combined plots for [2-Methoxyethanol + H_2O] system at 100 kPa.

The plots of three models for the system of [2-Methoxyethanol + H_2O] system are shown separately in Figures 3 and the combined plots of three models for the two systems are also shown below in, to make the comparison more clearly. All tables and figures indicate that the correlated values agree well with VLE data.

4. CONCLUSION

New isobaric VLE values of binary system [2-Methoxyethanol + H_2O] were measured at 100 kPa, and all experimental data passed the thermodynamic consistency test with Herington test. The VLE data were regressed, and the corresponding binary interaction parameters were correlated by the NRTL and Wilson models, which agreed well with the experimental data. The experimental result for the binary system [2-Methoxyethanol + H_2O] expanded the VLE database, providing data support for further study.

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