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Vapor−Liquid Equilibrium for the Binary System of *N*,*N*-Dimethylaniline with 2-Amino-3-methylpyridine

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ABSTRACT: The isobaric vapor−liquid equilibrium (VLE) data of the binary system *N*,*N*-dimethylaniline + 2-amino-3-methylpyridine were collected at (5.158 and 8.041) kPa. The activity coefficients of the system were correlated with the Van Laar and UNIQUAC models. The results showed that the calculated values of the vapor phase mole fraction and boiling temperature by the two models agreed well with the experimental data. Furthermore, the activity coefficients at infinite dilution were also presented. The VLE data were shown to be thermodynamically consistent by both the Herington consistency and point consistency tests.

INTRODUCTION

Distillation operation has been extensively used for the separation of liquid mixtures. Accurate and complete vapor−liquid equilibrium data are essential for the development and the rational design of a distillation tower and other separation processes. Moreover, accurate vapor−liquid equilibrium (VLE) data are indispensable for developing and evaluating the activity coefficient model.

2-Amino-3-methylpyridine (boiling point, (221 to 222) °C) is a useful intermediate for manufacturing pharmaceuticals.[1−3] It is usually prepared by the Chichibabin reaction between 3-methylpyridine and sodium amide in *N*,*N*-dimethylaniline.[4−7] The yield of 2-amino-3-methylpyridine is more than 80 % by analyzing the composition of the reacted mixture, which contains some solvent and other byproducts. Therefore, the separation of 2-amino-3-methylpyridine from the binary mixture becomes an essential problem. Vacuum distillation could be used to solve this problem. Unfortunately, a literature survey revealed that VLE data are scarce for systems involving 2-amino-3-methylpyridine.

In this paper, VLE data for the binary system *N*,*N*-dimethylaniline (1) + 2-amino-3-methylpyridine (2) at two different pressures were reported, respectively. Furthermore, the phase equilibrium data were correlated by applying the Van Laar and UNIQUAC models for the Gibbs excess energy of the liquid mixture.

EXPERIMENTAL SECTION

Materials. The chemicals, *N*,*N*-dimethylaniline, benzene, and *n*-octane with purity 99.0 + mass %, were purchased from Lingfeng Chemical Reagent Company of Shanghai, and 2-amino-3-methylpyridine prepared in the laboratory was distilled prior to use. Its mass fraction purity, determined by gas chromatography equipped with a flame ionization detector (FID), was higher than 99.0 %.

VLE Measurement. The equipment and procedure for the measurement of low-pressure VLE are nearly the same as the ones described in the literature.[8,9] The apparatus mainly consists of a boiling chamber and a condenser. The total volume of the boiling chamber is about 400 cm^3. The temperature is measured with mercury thermometers with an uncertainty of ± 0.05 K. The pressure is determined using a U-tube mercury manometer with an uncertainty of ± 0.033 kPa. The thermometers and U-tube mercury manometer were calibrated before experimental measurements. For each experiment, about 120 mL of liquid mixture was placed in the vessel. An electrical heater supplied heat to evaporate the liquid steadily, and both liquid and vapor phases were kept at the same temperature for more than 1 h to ensure phase equilibrium. The equilibrium temperature and pressure were recorded. The vapor and liquid samples were then taken out separately from different positions of the apparatus for gas chromatography (GC) analysis. The analysis of compositions is given in the following section.

Method of Analysis. The compositions of vapor- and liquid-phase samples were analyzed by GC (GC-2000II) with an FID detector. The column used was 10 % SE30, 80/100 supelcoport, and 30 ft by 1/8 in. The optimum operation conditions of GC are as follows: injector temperature, 250 °C; column temperature, 210 °C; FID temperature, 210 °C; carrier gas, pure hydrogen gas with a flow rate of 30 $\text{mL}\cdot\text{min}^{-1}$; sample volume, 1.0 μL. For the binary system, the calibration curve was constructed prior to the experiment by the mole fraction and the peak area ratios of a set of standard solutions of known compositions. The uncertainties of mole fraction measurements for *N*,*N*-dimethylaniline were estimated to be 0.005 for two phases.

RESULTS AND DISCUSSION

Vapor−Liquid Equilibrium. The VLE data of the binary system benzene (1) + *n*-octane (2) were measured at 760 mmHg to check the apparatus and experimental procedure. The comparison of the experimental data with the literature data[10] for the $T-x-y$ diagram are shown in Figure 1, and the average absolute error in boiling temperature is 0.28 K. The experimental data agree well with the literature data, so the apparatus and experimental method are reliable and credible.

The isobaric VLE measurements (T, x, y) of the binary system *N*,*N*-dimethylaniline (1) + 2-amino-3-methylpyridine (2) at (5.158

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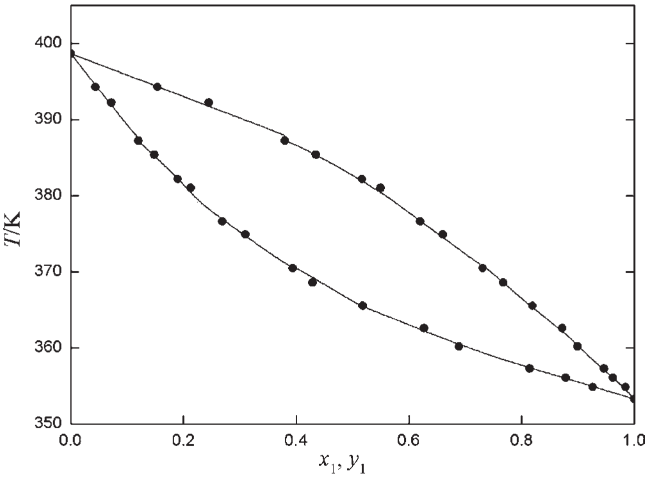

Figure 1. $T-x_1-y_1$ diagram of benzene (1) + *n*-octane (2) at 760 mmHg. —, literature data; ●, experimental data.

Table 1. Experimental VLE Data of the *N*,*N*-Dimethylaniline + 2-Amino-3-methylpyridine Binary Mixture at 5.158 kPa

no.	T/K	x_1	y_1	γ_1	γ_2
1	402.57	0.0000	0.0000		1.0000
2	399.15	0.0442	0.1724	1.4862	0.9984
3	397.30	0.0707	0.2552	1.4687	0.9994
4	394.48	0.1203	0.3726	1.3946	1.0038
5	391.60	0.1873	0.4886	1.3049	1.0045
6	388.93	0.2624	0.5873	1.2361	1.0060
7	386.21	0.3401	0.6721	1.2090	1.0104
8	384.35	0.4115	0.7231	1.1539	1.0423
9	382.32	0.4888	0.7737	1.1240	1.0779
10	380.27	0.5875	0.8234	1.0780	1.1485
11	378.15	0.7342	0.8868	1.0101	1.2645
12	376.15	0.8633	0.9390	0.9851	1.4601
13	373.70	1.0000	1.0000	1.0000	

Table 2. Experiment VLE Data of the *N*,*N*-Dimethylaniline + 2-Amino-3-methylpyridine Binary Mixture at 8.041 kPa

no.	T/K	x_1	y_1	γ_1	γ_2
1	413.74	0.0000	0.0000		1.0000
2	410.02	0.0515	0.1855	1.4735	0.9922
3	408.01	0.0834	0.2742	1.4386	0.9906
4	405.29	0.1311	0.3845	1.4074	0.9884
5	402.60	0.1768	0.4715	1.4039	0.9997
6	399.32	0.2445	0.5625	1.3583	1.0335
7	396.73	0.3208	0.6439	1.2993	1.0442
8	394.02	0.4115	0.7295	1.2662	1.0297
9	391.67	0.5089	0.7892	1.2061	1.0649
10	389.01	0.6795	0.8597	1.0863	1.2230
11	387.03	0.8123	0.9123	1.0384	1.4268
12	385.74	0.9445	0.9648	0.9917	2.0549
13	384.96	1.0000	1.0000	1.0000	

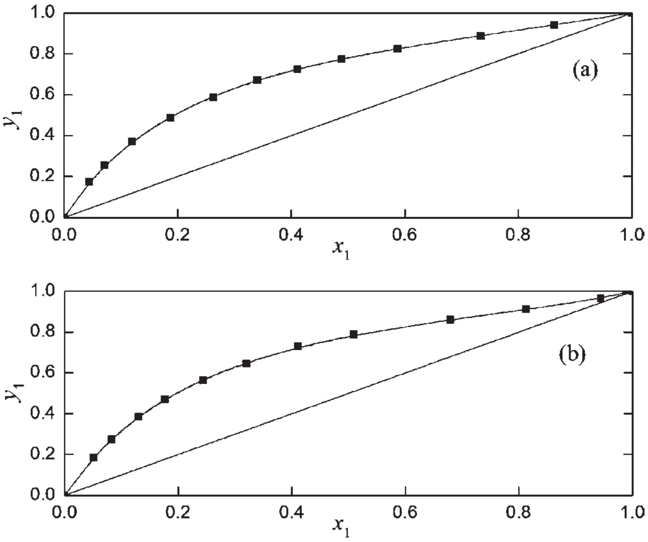

Figure 2. y_1-x_1 diagram for *N*,*N*-dimethylaniline (1) + 2-amino-3-methylpyridine (2) at P = pressure: (a) P = 5.158 kPa; (b) P = 8.041 kPa; ■, experimental values; - -, Van Laar model; —, UNIQUAC model.

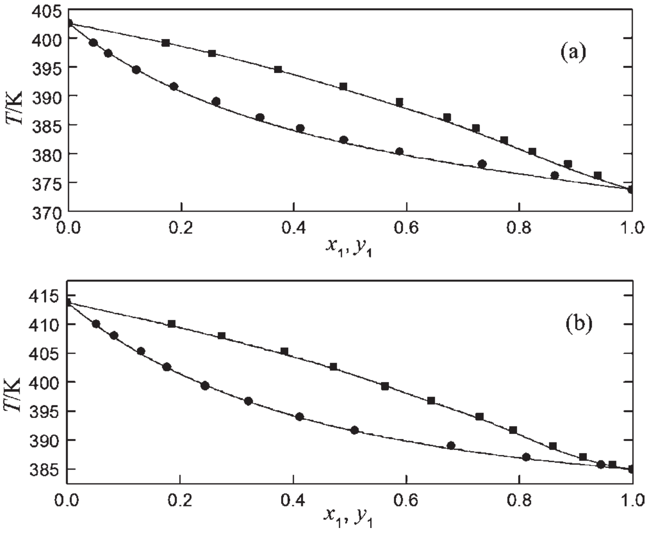

Figure 3. $T-x_1-y_1$ diagram of *N*,*N*-dimethylaniline (1) + 2-amino-3-methylpyridine (2) at P = pressure: (a) P = 5.158 kPa; (b) P = 8.041 kPa; ●, x_1 measured; ■, y_1 measured; - -, Van Laar model; —, UNIQUAC model.

and 8.041) kPa, together with the calculated activity coefficients, γ_i, are presented in Tables 1 and 2 and also plotted in Figures 2 to 4. The vapor phase is treated as an ideal gas mixture since the pressure is so low that the pressure effect on the phase equilibrium is neglected. The activity coefficients in the liquid phase can be calculated by eq 1.[9]

$$y_iP = x_i\gamma_iP_i^s \qquad i = 1, 2 \tag{1}$$

where x_i and y_i are the liquid and vapor phase mole fraction of species i; P is the total pressure; and P_i^s is the saturation vapor pressure of pure liquid i at system temperature T, which can be obtained from the Antoine equation. The Antoine equation constants of *N*,*N*-dimethylaniline[11] and 2-amino-3-methylpyridine[12] are gathered in Table 3.

Consistency Tests of Experimental Data. The activity coefficients should satisfy the Gibbs–Duhem equation.[13] A set of experimental data, generally, exhibit systematic or random errors and fail to represent the true behavior of a mixture. Therefore, the

Table 3. Molecular Structure and Antoine Parameters Used in the Present Work

	N,N-dimethylaniline	2-amino-3-methylpyridine
r	5.1093	4.2629
q	3.908	3.551
	$Y = A_i - B_i/(T/K + C_i)$	
Antoine coefficients	$Y = \log(P_i^{\text{sat}}/\text{bar})$	$Y = \ln(P_i^{\text{sat}}/\text{KPa})$
A_i	4.83	14.8098
B_i	2117.236	4213.632
C_i	−27.606	−82.163

Table 4. Regression Results of the UNIQUAC and Van Laar Model

	N,N-dimethylaniline (1) + 2-amino-3-methylpyridine (2)	
parameter	P/kPa = 5.158	P/kPa = 8.041
	UNIQUAC	
$\Delta u_{12}/(\text{J}\cdot\text{mol}^{-1})$	1511.96	2928.42
$\Delta u_{21}/(\text{J}\cdot\text{mol}^{-1})$	−913.41	−1645.63
γ_1^∞	1.5108	1.5311
γ_2^∞	1.7538	2.4825
AAD(γ_1), %	2.56	1.51
AAD(γ_2), %	1.20	1.72
AAD(y_1), %	0.67	0.61
AAD(T), %	0.13	0.08
	Van Laar	
A_{12}	0.4061	0.4107
A_{21}	0.5323	0.8935
γ_1^∞	1.5010	1.5079
γ_2^∞	1.7028	2.4437
AAD(γ_1), %	2.31	0.94
AAD(γ_2), %	1.24	1.86
AAD(y_1), %	0.66	0.47
AAD(T), %	0.11	0.07

thermodynamic consistency must be checked to confirm whether the experimental VLE data are consistent with the Gibbs−Duhem equation.

The Herington consistency test[14] based on the Gibbs−Duhem theorem is an empirical method, and it is usually employed to verify the experimental data. The expressions of the Herington thermodynamic consistency test are as follows

$$\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \tag{2}$$

$$D = 100\left|\frac{S_+ - S_-}{S_+ + S_-}\right| = 100\,\frac{\left|\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2}\, dx_1\right|}{\int_{x_1=0}^{x_1=1} \left|\frac{\gamma_1}{\gamma_2}\right| dx_1} \tag{3}$$

$$J = 150\,\frac{T_{\max} - T_{\min}}{T_{\min}} \tag{4}$$

where S_+ and S_- are the area of the region above the horizontal coordinate axis and that under the horizontal coordinate axis, respectively, and $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperature in the studied system. Equation 2 does not usually equal zero exactly because of experimental errors; therefore, Herington presented a criterion to confirm the thermodynamic consistency of the experimental data: $D < J$ or $D - J < 10$.

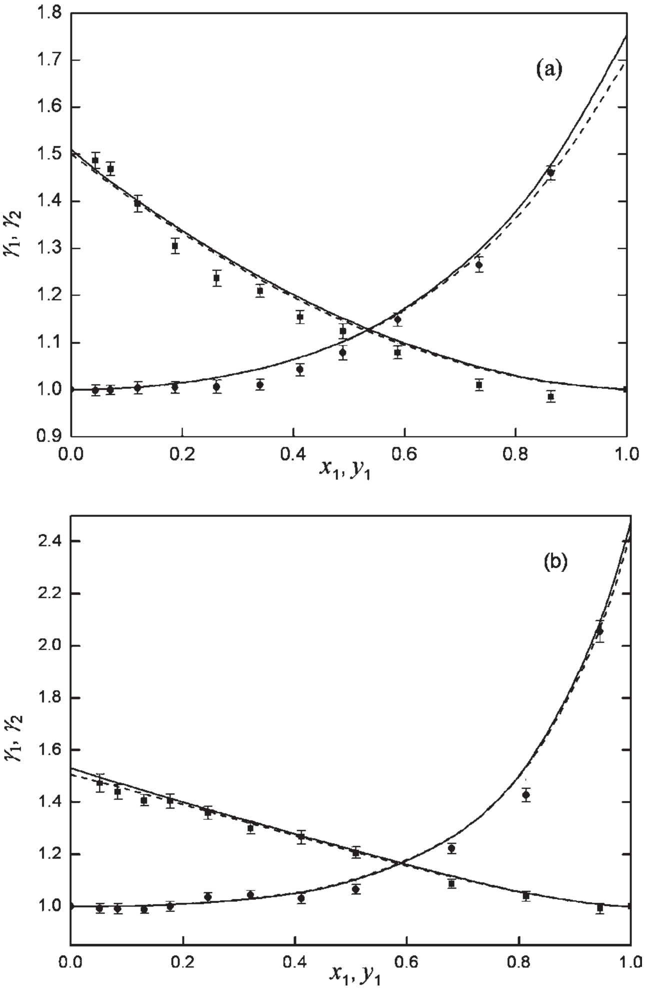

Figure 4. Activity coefficient−composition diagram for the *N,N*-dimethylaniline (1) + 2-amino-3-methylpyridine (2) system at P = pressure: (a) P = 5.158 kPa; (b) P = 8.041 kPa; ■, γ_1 from the data; ●, γ_2 from the data; - -, γ_1, γ_2 from the Van Laar model; —, γ_1, γ_2 from the UNIQUAC model. The error bars are the uncertainties for the experimental values.

On the basis of eqs 2 to 4 and the data in Tables 1 and 2, the values of (D, J) are calculated for the system at 5.158 kPa (3.699, 11.59) and 8.041 kPa (0.9687, 11.21), respectively. The results show that $D < J$, which means the data for the binary system (2-amino-3-methylpyridine + *N,N*-dimethylaniline) are thermodynamically consistent.

Data Regression. The isobaric VLE data were correlated using the activity coefficient models (Van Laar[15] and UNIQUAC[15] models). The binary interaction parameters of the two models were determined by the minimization of the following objective function (OF)[16]

$$\text{OF} = \sum_{k=1}^{n}\sum_{i=1}^{2}\left(\frac{\gamma_{i,k}^{\text{exp}} - \gamma_{i,k}^{\text{cal}}}{\gamma_{i,k}^{\text{exp}}}\right)^2 \tag{5}$$

where $\gamma_{i,k}^{\text{exp}}$ and $\gamma_{i,k}^{\text{cal}}$ are the experimental and the calculated liquid-phase activity coefficients of species i. $\gamma_{i,k}^{\text{cal}}$ is calculated by

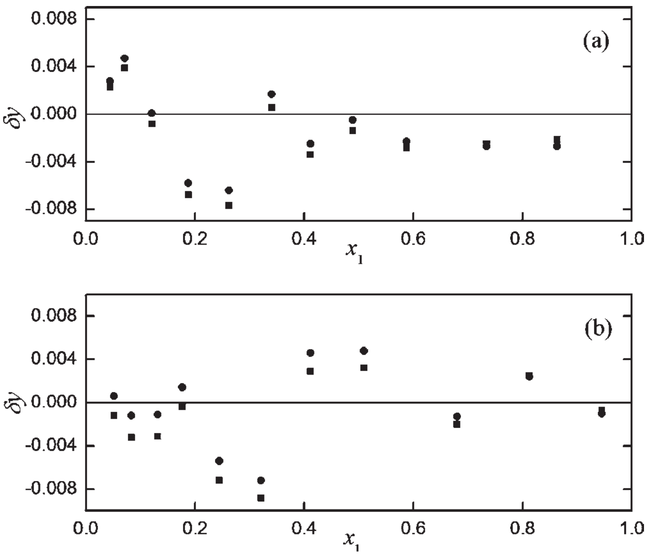

Figure 5. Point test for the *N*,*N*-dimethylaniline (1) + 2-amino-3-methylpyridine (2) system at P = pressure: (a) P = 5.158 kPa; (b) P = 8.041 kPa; ●, Van Laar model; ■, UNIQUAC model.

the Van Laar and UNIQUAC models. The molecular structure parameters,[17,18] r and q, used in the UNIQUAC model are listed in Table 3.

The correlated binary interaction parameters, including A_{12} and A_{21} of the Van Laar and Δu_{12} and Δu_{21} of the UNIQUAC, are listed in Table 4. The activity coefficient at infinite dilution (γ_i^∞) and the average absolute deviations (AAD) of bubble-point temperature, vapor mole fraction, and activity coefficient for the system are also presented in Table 4. AAD is defined as follows

$$\mathrm{AAD}(z) = \frac{1}{N}\left(\sum_{i=1}^{N}\frac{|z_{i,\exp} - z_{i,\mathrm{cal}}|}{z_{i,\exp}}\right) \qquad (6)$$

where z represents T, y_1, and γ, respectively.

The AAD between the experimental data and calculated ones for T, y_1, and γ are less than 0.13 %, 0.70 %, and 2.6 %, respectively. Figures 2 to 3 (y_1−x_1 and T−x_1−y_1) illustrate the comparison between the experimental and calculated VLE data of the mixture at each pressure, while the γ_1−γ_2−x diagrams for the system are presented in Figure 4. It can be seen from Figures 2 to 4 that the differences among the vapor-phase mole fraction, boiling temperature, and activity coefficient calculated by the Van Laar and UNIQUAC models are indistinct. Close observation of these graphs reveals that the curves of two models are almost overlapping the other, which means both models represent good agreement with the VLE properties of the system.

The point test[19] for thermodynamic consistency requires that the vapor composition residual (δy) scatters evenly about the x-axis. Furthermore, the average absolute deviation of the residual should be less than 0.01 as suggested by Danner and Gess.[20,21] The results of the point test for the binary system are shown in Figure 5, and the average absolute deviation of the residual is 0.003, which is less than 0.01. So the measured data sets passed the test.

The data obtained with the current binary system can be used for the calculation of the multiphase VLE system[15] by using the UNIQUAC model, and the parameters (Δu_{ij}) used in the model are determined from the binary system data.

■ CONCLUSION

Isobaric VLE data have been measured for the binary system composed of *N*,*N*-dimethylaniline and 2-amino-3-methylpyridine at (5.158 and 8.041) kPa. The data have been shown to be thermodynamically consistent. For the system, both the Van Laar and UNIQUAC models give similar good representation of the data, which means two models are capable of correlating the VLE data of the investigated system.

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