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Vapor Pressure Measurements for 2-Chloromethylbenzoxazole and Vapor−Liquid Equilibrium Measurements for the Chlorobenzene + 2-Chloromethylbenzoxazole System

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Saturated vapor pressure of 2-chloromethylbenzoxazole was measured at temperatures from 347.65 K to 424.55 K and correlated with the Antoine equation. The isobaric VLE equilibrium data of the binary system 2-chloromethylbenzoxazole and chlorobenzene were determined at 7.92 kPa and 10.59 kPa and examined with the Herington thermodynamic consistency test and the χ^2 test. The experimental data were correlated with the UNIQUAC model. The optimum parameters of the UNIQUAC model were determined by the least-squares regression method. Deviations between experimental and calculated data were 0.00983 at 7.92 kPa and 0.01317 at 10.59 kPa.

Introduction

Vapor−liquid equilibrium (VLE) data are essential for the design and operation of separation process such as distillation, absorption, and extraction and the optimization of a process design or a flow sheet construction. Moreover, accurate VLE data are indispensable for developing and evaluating activity coefficient model. 2-Chloromethylbenzoxazole (boiling point, 115 °C/1330 Pa) is used as an important intermediate to manufacture the fluorescent whiting agent EBF[1] and dibenzazolyl compounds,[2] which are useful fluorescent whiting agents in dyestuff industry. 2-Chloromethylbenzoxazole was prepared by the direct reaction between o-aminophenol and chloracetyl chloride. The yield of 2-chloromethylbenzoxazole was more than 99 % of theory by analyzing the composition of the reacted mixture, which contains about 20 % chlorobenzene and less than 1 % other byproducts. Therefore, the separation of 2-chloromethylbenzoxazole from the binary mixture becomes an essential problem. Vacuum distillation could be used to solve this problem. The VLE data of 2-chloromethylbenzoxazole and chlorobenzene are important for this rectification. Unfortunately, a literature survey revealed that no data are available for systems involving 2-chloromethylbenzoxazole.

In this study, saturated vapor pressures of 2-chloromethylbenzoxazole and the VLE data of 2-chloromethylbenzoxazole and chlorobenzene were measured. The experimental data of vapor pressure and VLE were then correlated with the Antoine equation and the UNIQUAC model, respectively. The optimum Antoine constants and the binary interaction parameters of the UNIQUAC model were determined by means of the least-squares regression method.

Experimental Section

Materials. Chlorobenzene with purity 99.5+ mass % was purchased from Lingfeng Chemical Reagent Company of Shanghai. 2-Chloromethylbenzoxazole prepared in the laboratory was distilled prior to use. Its mass fraction purity, determined by GC, was better than 98.5 %.

Vapor Pressure. Vapor pressures were measured by the boiling point method.[3] The apparatus for vapor pressure measurement used here is similar to that of Huang et al.[4] Temperatures were measured with thermocouples with an uncertainty of ± 0.05 K, and the still pressure was controlled at the desired value by a U-tube mercury manometer with an uncertainty of ± 0.03 kPa. The U-tube mercury manometer and thermometers were calibrated before experimental measurements. The sample with an approximate volume of 150 mL of 2-chloromethylbenzoxaxole was placed in the vessel and evacuated to a proper degree of pressure. The sample was then heated and stirred well with a magnetic stirrer to prevent superheating. Both vapor and liquid phases were kept at the same temperature for more than 1 h.

VLE Measurement. The equipment and procedure for the measurement of low-pressure VLE are nearly the same as the one used by Huang et al.[4] The equipment is a recirculation type, in which vapor is continuously recirculation. The thermocouples with an uncertainty of ± 0.1 K were used here, and the manometer was the same as the one used in the measurement of the vapor pressure of 2-chloromethylbenzoxazole. For each experiment, about 120 mL of liquid mixture was fed into the still. 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. Then, the equilibrium temperature and pressure were recorded. The vapor and liquid samples were taken out separately. Then the samples were analyzed by gas chromatography (GC), to which the detail description is given in the following section.

Method of Analysis. The compositions of vapor- and liquid-phase samples were analyzed by GC (GC-930) with a FID detector. The column used was 10 % SE30, 80/100 supelcoport, and 20 ft by 1/8 in. The optimum operation conditions of GC are as follows: injector temperature, 170 °C; column temperature, 160 °C; FID temperature, 160 °C; carrier gas, pure hydrogen gas with a flow rate of 30 mL·min^{-1}; sample volume, 1.5 μL. A calibration curve was constructed before the experiment by the mole fraction and the peak area ratios of a set of

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Table 1. Experimental Vapor Pressure Data of 2-Chloromethylbenzoxazole

T/K	P_i^s/kPa	T/K	P_i^s/kPa	T/K	P_i^s/kPa
424.55	10.80	411.90	4.88	388.15	1.39
424.20	10.53	408.35	4.19	383.20	0.96
423.20	9.92	405.25	3.28	378.20	0.69
422.05	9.41	400.30	2.72	375.15	0.59
418.85	7.91	395.60	2.03	368.45	0.32
418.10	7.29	393.85	1.87	357.10	0.16
417.30	6.32	393.50	1.76	347.65	0.08

standard solutions of known compositions. The calibration curve of this system is

$$y = 2.0453x^4 - 3.021x^3 + 0.6329x^2 + 1.3424x \qquad (1)$$

where y is the mole fraction of 2-chloromethylbenzoxazole and x is the peak area ratios of 2-chloromethylbenzoxazole to chlorobenzene. The correlation coefficient R^2 value of this fit is 0.9973.

Results

Vapor Pressure. Saturated vapor pressures of 2-chloromethylbenzoxazole were measured at the temperatures from 347.65 K to 424.55 K. The experimental data given in Table 1 were then correlated with the Antoine equation,[5] and the optimum Antoine coefficients were obtained by the least-squares regression method. The results of Antoine coefficients A, B, and C can be found in Table 4.

The mole evaporation enthalpy $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ of 2-chloromethylbenzoxazole was obtained by the experimental data of vapor pressure correlated with the Clapeyron−Clausius equation:[6]

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H}{T(V_{\mathrm{G}} - V_{\mathrm{L}})} \qquad (2)$$

where P is pressure, T is temperature, ΔH is phase change enthalpy, V_{G} is vapor volume, and V_{L} is liquid volume.

For vaporization at low pressures, we could introduce reasonable approximations into eq 2 by assuming that the vapor phase is an ideal gas and that the mole volume of liquid is negligible as compared with the mole volume of vapor. So eq 2 becomes

$$\mathrm{d}\ln P^{\mathrm{s}} = \frac{-\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{R}\mathrm{d}\left(\frac{1}{T}\right) \qquad (3)$$

where P^{s} is saturated vapor pressure, $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ is the mole evaporation enthalpy, and R is mole vapor constant.

Equation 3 related the latent heat of vaporization directly to the vapor pressure P^{s} versus T curve. In fact, $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ could be given directly by the slope of a plot of ln P^{s} versus $1/T$ when the plot produced nearly a straight line.

The vapor pressure data of 2-chloromethylbenzoxazole are shown in Figure 1, from which it was seen that the plot of ln P^{s} versus $1/T$ was nearly a straight line with a R^2 value of 0.9987. So the $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ of 2-chloromethylbenzoxazole was obtained from Figure 1. The value is 79.61 kJ·mol^{-1}.

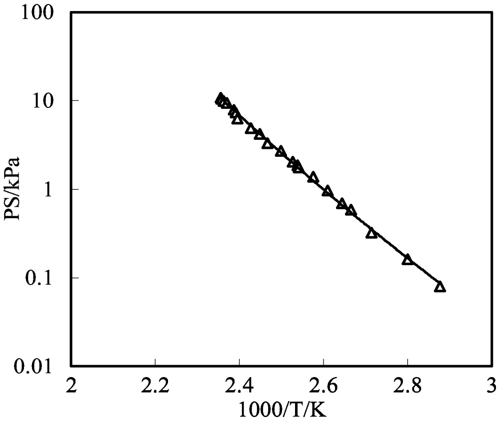

Figure 1. ln $P^{\mathrm{s}} - 1/T$ diagram of 2-chloromethylbenzoxazole: △, experimental values; —, regression curve.

Table 2. Experimental VLE Data of the 2-Chloromethylbenzoxazole (1) + Chlorobenzene (2) Binary Mixture at 7.92 kPa

no.	T/K	x_1	y_1	γ_1	γ_2
1	418.9	1.0000	1.0000	1.0000	
2	415.9	0.9950	0.8729	1.0617	1.4873
3	410.9	0.9883	0.7386	1.1930	1.4891
4	404.7	0.9798	0.6249	1.4524	1.4565
5	398.8	0.9616	0.3855	1.2964	1.4764
6	394.7	0.9476	0.2267	0.9947	1.5298
7	391.5	0.9356	0.1959	1.0643	1.4197
8	376.7	0.8708	0.0748	1.1689	1.2787
9	364.5	0.7727	0.0294	1.2577	1.1439
10	360.1	0.7170	0.0219	1.4265	1.0838
11	359.3	0.7123	0.0213	1.4876	1.0978
12	347.8	0.5584	0.0129	2.9725	1.1057
13	346.7	0.5050	0.0136	3.8036	1.0286
14	335.5	0.2317	0.0031	5.1810	1.0536
15	330.5	0.0000	0.0000		1.0000

Table 3. Experiment VLE Data of the 2-Chloromethylbenzoxazole (1) + Chlorobenzene (2) Binary Mixture at 10.59 kPa

no.	T/K	x_1	y_1	γ_1	γ_2
1	423.2	1.0000	1.0000	1.0000	
2	422.3	0.9969	0.8329	0.9593	3.6115
3	416.0	0.9913	0.6224	1.0100	3.3900
4	412.7	0.9781	0.5010	0.9795	3.2303
5	408.1	0.9712	0.3138	0.8023	3.0014
6	403.3	0.9593	0.2373	0.8074	2.8836
7	395.5	0.9527	0.1726	0.9513	2.7527
8	392.5	0.9235	0.1406	0.9413	2.6790
9	381.8	0.8460	0.0720	0.9986	2.4668
10	365.2	0.8186	0.0373	1.8490	2.1850
11	352.9	0.6939	0.0154	2.4573	1.7460
12	344.2	0.4322	0.0089	4.7822	1.3257
13	341.1	0.3224	0.0064	6.0279	1.2581
14	338.9	0.2044	0.0042	7.6832	1.1770
15	337.4	0.0000	0.0000		1.0000

Vapor−Liquid Equilibrium. The VLE data at the pressure of 7.92 kPa and 10.59 kPa are given in Tables 2 and 3 and are also plotted as Figures 2 and 3, respectively. We can find that the liquid and saturated vapor lines are far away from each other. This implies that it is easy to separate the mixture at these pressures. We also see that both VLE diagrams at these two different pressures are very similar except that the bubble temperatures are different.

Consistency Tests of Experimental Data

A set of experimental data must exhibit systematic or random errors and fail to represent the true behavior of a mixture. Thus, an experimental data set has to be carefully examined before it can be further implemented to design a separation column. The thermodynamic consistency must be satisfied.

The Herington consistency test[7] based on the principle of the Gibbs−Duhem theorem is an empirical method. It is usually considered as a criterion of a reliable experimental data set and is usually employed to verify our experimental data. A set of experimental data can be considered to meet the criterion if it

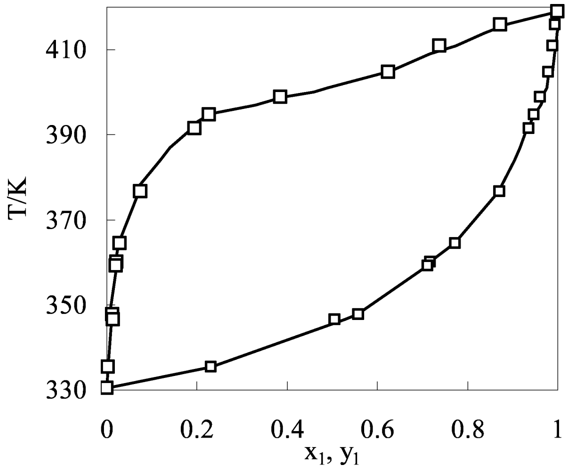

Figure 2. $T-x-y$ diagram of the 2-chloromethylbenzoxazole (1) + chlorobenzene (2) binary mixture at 7.92 kPa: □, experimental values; —, UNIQUAC model.

can satisfy the following:

$$|D - J| < 10 \tag{4}$$

where D and J are two parameters in the Herington test.

In this study, the values of $|D - J|$ are 3.1 and 4.4 for the experimental data at 7.92 kPa and 10.59 kPa, respectively. Thus we might say that the experimental data satisfy the Herington test. Nevertheless, we cannot still guarantee the reliability of the data because it is possible that unreliable experimental data could satisfy the Herington test resulting from their errors cancelling each other. So it is necessary to check the consistency of the data with statistical analysis of the χ^2 test that is proposed by Neau and Peneloux.[8] Neau and Peneloux demonstrated that an experimental data set is consistent if the minimum objective function,[9] $S_{\min}$, given in eq 6, was confined in the χ^2 region with degrees of freedom $2n - p$ and a significant level α. This criterion is expressed as

$$S_{\min} < \chi^2_{1-\alpha}(2n - p) \tag{5}$$

where S is the minimum objective function value defined in eq 6, n is the number of experimental points, and p is the number of parameters:

$$S_{\min} = \sum_i \left\{ \left(\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{\sigma_{P_i}^{\text{est}}} \right)^2 + \left(\frac{T_i^{\text{exp}} - T_i^{\text{cal}}}{\sigma_{T_i}^{\text{est}}} \right)^2 + \left(\frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{\sigma_{x_i}^{\text{est}}} \right)^2 + \left(\frac{y_i^{\text{exp}} - y_i^{\text{cal}}}{\sigma_{y_i}^{\text{est}}} \right)^2 \right\} \tag{6}$$

where the pressure and temperature variances, σ_P^2 and σ_T^2, were estimated by the uncertainty of the measurement and the experimenter's reading error, while liquid and vapor composition variances were determined by the inaccuracy of the calibration curve. All the standard deviations used for our calculations were $\sigma_P = 0.03$ kPa, $\sigma_T = 0.1$ K, $\sigma_x = 0.01$, and $\sigma_y = 0.01$.

In this study, the significant value α is 0.05 and both of the freedom degrees, $2n - p$, are 28 for experiments at 7.92 kPa and 10.59 kPa. Then the χ^2 distribution value obtained from the table of a statistics textbook is $\chi_{0.95}{}^2(28) = 15.379$. After comparison of these two values with the minimum objective function values $S_{\min}$ in Table 5, we concluded that this consistency test was also satisfied.

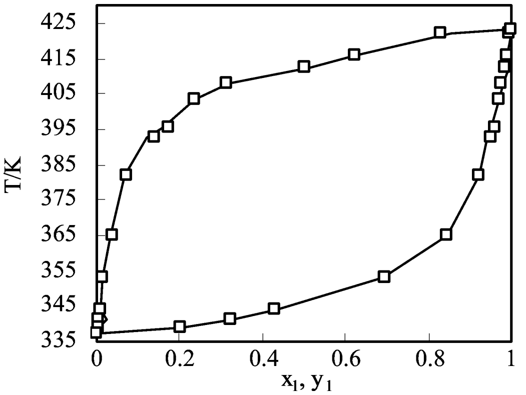

Figure 3. $T-x-y$ diagram of the 2-chloromethylbenzoxazole (1) + chlorobenzene (2) binary mixture at 10.59 kPa: □, experimental values; —, UNIQUAC model.

Table 4. Molecular Structure[10,11] and Antoine Parameters Used in Present Work

	2-chloromethylbenzoxazole	chlorobenzene
r	5.3776	3.8127
q	3.836	2.844
q'	3.836	2.844

Antoine coefficients	$Y* = A_i - B_i/(T/K + C_i)$ $Y* = \lg(P_i^{\text{sat}}/\text{mmHg})$	 $Y* = \ln(P_i^{\text{sat}}/\text{mmHg})$
A_i	9.6947	16.0676
B_i	2703.1910	3295.12
C_i	−78.2028	−55.60

Table 5. Regression Results of the UNIQUAC Model

		7.92 kPa	10.59 kPa
model parameters	$\Delta u_{12}/R$	76.80 ± 23.42	150.59 ± 15.26
	$\Delta u_{21}/R$	924.06 ± 293.15	1589.89 ± 321.42
sum square of residual	$S_{\min}$	14.21	6.50
estimated variance of fit	$\sigma_{fit}^{2,est}$	0.00983	0.01317
mean deviations of T	ΔT	0.018 %	0.017 %
mean deviations of y	Δy	0.412 %	0.547 %

Data Regression

The vapor phase was treated as an ideal gas since the pressure is so low that the pressure effect on the phase equilibrium was neglected. The vapor liquid equilibrium equation[4] for binary mixture is

$$y_i P = x_i \gamma_i P_i^{\text{s}} \quad i = 1, 2 \tag{7}$$

In this study, the binary VLE data were correlated using the activity coefficient model of UNIQUAC[10] for liquid-phase activity coefficients, γ_i, and the Antoine equation was used to calculate the vapor pressures of the pure components. All the pure component molecular structure parameters used in the UNIQUAC[10] model and the Antoine parameters used in this study are given in Table 4. After all the methods and formulations for the evaluations of thermodynamic properties were determined, the experimental data were regressed by the least-square method.

The regression results at 7.92 kPa and 10.59 kPa are shown in Table 5. The optimum binary interaction parameters of the UNIQUAC model, the minimum objective function value, and the estimated variance of fit are given in Table 5. Figures 2 and 3 show the comparisons between the experimental and

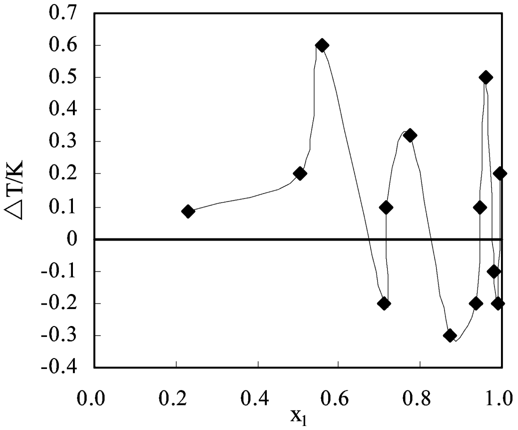

Figure 4. Deviations between calculated and measured bubble temperatures vs liquid mole fractions of 2-chloromethylbenzoxazole (1) + chlorobenzene (2) at 7.92 kPa.

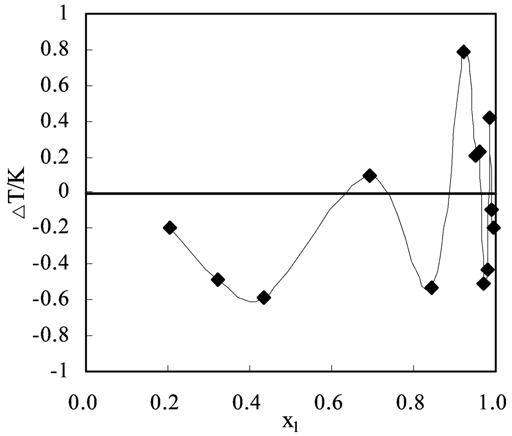

Figure 5. Deviations between calculated and measured bubble temperatures vs liquid mole fractions of 2-chloromethylbenzoxazole (1) + chlorobenzene (2) at 10.59 kPa.

predicted VLE values of this binary mixture at each pressure, which revealed that the model of UNIQUAC could be used to describe the VLE of the mixture.

The optimum parameters of the UNIQUAC model were then used to estimate the bubble temperatures. The mean deviations between the experimental and the calculated values of bubble temperatures and vapor-phase compositions at 7.92 kPa and 10.59 kPa can be seen in Table 5, respectively. Also, deviations between calculated and measured bubble temperatures versus liquid mole fractions of 2-chloromethylbenzoxazole (1) + chlorobenzene (2) at 7.92 kPa and 10.59 kPa are shown in Figures 4 and 5. These two figures showed the reasonable estimations by the UNIQUAC model.

Conclusions

In this study, Antoine coefficients of 2-chloromethylbenzoxazole were determined at temperatures from 347.65 K to 424.55 K, and isobaric VLE data for 2-chloromethybenzoxazole + chlorobenzene were collected separately at 7.92 kPa and 10.59 kPa. The experimental VLE data satisfied both the Herington thermodynamic consistency test and the statistical χ^2 test. The UNIQUAC model could represent the VLE data of this binary mixture, which are useful for process design to separate this mixture.

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