JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Determination and Correlation of Vapor−Liquid Equilibrium Data for the Ethyl Acetate + Hexamethyl Disiloxane System at 101.3 kPa

Wenlin Zhang,* Nan Meng, Ruyi Sun, and Chunli Li

School of Chemical Engineering, Hebei University of Technology, Tianjin, 300130, China

ABSTRACT: Vapor−liquid equilibrium (VLE) data of ethyl acetate (EAC) + hexamethyl disiloxane (HMDSO) system at 101.3 kPa were measured by using a double circulating VLE still. The thermodynamic consistency of the VLE data was examined by the Herrington method. Experimental data were correlated by the Wilson, nonrandom two-liquid (NRTL), and universal quasichemical activity coefficient (UNIQUAC) parameter models. All of the models were satisfactorily correlated with the VLE data. The result showed that the NRTL model was the most suitable one to represent experimental data satisfactorily, the system had a minimum temperature azeotrope at 350.31 K, and the mole azeotropic composition was 0.0330.

■ INTRODUCTION

Hexamethyl disiloxane (HMDSO, 1) is a significant chemical raw material used as silazane stock, silicon rubber, medicines, gas chromatography fixed fluid, analytical reagent, moisture repellent, and so on. It is widely used in organic chemical industry and pharmaceutical chemicals.

Ethyl acetate (EAC, 2) is a very important organic chemical product which is used as industrial solvents in coatings, ethyl cellulose, artificial leather, linoleum colorants, artificial fiber, and other products. It is also used as an extraction agent in drug and organic acid production. It is the main raw material for some fruit essences and perfume.[1]

Nowadays, along with the rapid development of pharmaceutical intermediate industry, distillation can be used in separation of the HMDSO + ester mixture. Vapor−liquid equilibrium (VLE) data always need to be added gradually so as to meet the needs of distillation. Up to now, there are few VLE data for those systems. In this work, isobaric VLE data for the HMDSO (1) + EAC (2) system were investigated at 101.3 kPa. The results of the binary system were tested for thermodynamic consistency by the Herington method. Meanwhile, the Wilson,[2] nonrandom two-liquid (NRTL),[3] and universal quasichemical activity coefficient (UNIQUAC)[4] equations were applied to fit with experimental data.

■ EXPERIMENTAL SECTION

Chemicals. HMDSO (AR), supplied by Shanghai Nuotai Chemical Factory, was further purified by distillation. EAC (AR) was supplied by Tianjin Reagent Factory in the same batch.

All of the chemicals had been analyzed by gas chromatography (GC), and no detectable impurity was observed. The properties of the experimental materials are shown in Table 1.

Table 1. Physical Properties of the Pure Components

property	HMDSO (1)[9]	EAC (2)[1]
formula	$C_6H_{18}Si_2O$	$C_4H_8O_2$
MW/(g·mol^{-1})	162.38	88.11
T_b/K	373.67	350.21
T_c/K	518.70	523.30
P_c/MPa	1.9140	3.8800
n_{20}^{D}	1.378	1.3724

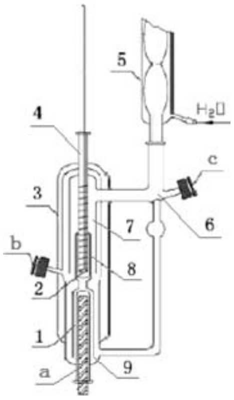

Figure 1. Double circulating still. 1, Boiling room; 2, liquid-phase sample reservoir; 3, vacuum thermal insulating jacket; 4, thermometer casing; 5, vapor-phase condenser; 6, vapor-sample reservoir; 7, vapor-phase separator room; 8, vapor-liquid riser; 9, vapor-liquid mixed room; a, inner heater tube; b, liquid-phase sample port; c, vapor-phase sample port.

Apparatus and Procedure. The double circulating still of modified Othmer type[5] was used to measure VLE data. The still was equipped with a digital manometer and a vacuum pump that measured to maintain the system under constant pressure within ± 0.1 kPa. The diagram for the still is shown in Figure 1. The mixture was heated in the boiling room. Some of the boiled liquid was taken with some gas spills up through the vapor−liquid riser to the vapor−liquid separator room. The gas was separated from

Special Issue: Kenneth N. Marsh Festschrift

Received: September 2, 2011
Accepted: October 10, 2011
Published: October 21, 2011

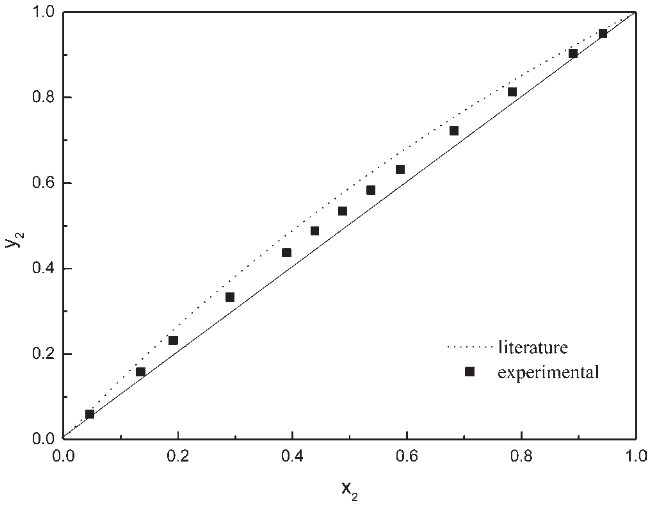

Figure 2. $y-x$ diagram for EAC (2) + IPAC (3).

Table 2. VLE Data of HMDSO (1) + EAC (2) at 101.3 kPa

T (K)	x_1	x_2	y_1	y_2
350.23	0.0000	1.0000	0.0000	1.0000
350.27	0.0241	0.9759	0.0251	0.9749
350.30	0.0566	0.9434	0.0584	0.9416
350.49	0.0844	0.9156	0.0801	0.9199
350.57	0.1028	0.8972	0.0975	0.9025
350.77	0.1605	0.8395	0.1264	0.8736
350.94	0.2013	0.7987	0.1526	0.8474
351.13	0.2378	0.7622	0.1707	0.8293
351.50	0.2816	0.7184	0.2084	0.7916
351.74	0.3178	0.6822	0.2294	0.7706
351.84	0.3428	0.6572	0.2457	0.7543
353.02	0.4240	0.5760	0.2769	0.7231
353.69	0.4537	0.5463	0.2888	0.7112
354.70	0.5317	0.4683	0.3104	0.6896
355.83	0.5880	0.4120	0.3525	0.6475
357.46	0.6332	0.3668	0.3943	0.6057
359.27	0.7142	0.2858	0.4445	0.5555
361.67	0.7878	0.2122	0.5287	0.4713
364.43	0.8502	0.1498	0.6068	0.3932
368.52	0.9206	0.0794	0.7821	0.2179
372.73	1.0000	0.0000	1.0000	0.0000

the liquid and went into the vapor-phase condenser. Meanwhile, the separated liquid dropped into the liquid-phase sample reservoir. The gas was condensed by the circulation of cooling water to shape droplets and collected in the vapor-phase sample reservoir. Liquid formed in the liquid-phase sample reservoir and vapor-phase sample reservoir mixed with each other and flowed back into the boiling room where it was heated continuously. It took approximately 2 h to reach stabilization of the studied system.

About 45 mL of the mixture of known composition obtained by weight using a balance with a resolution of 10^{-4} g was put into the still. The equilibrium temperature was measured by a digital thermometer with an error of less than 0.3 K.

Table 3. Antoine Equation Parameters

	HMDSO	EAC
temperature units	K	K
pressure units	MPa	MPa
C_{1i}	37.1135	53.0085
C_{2i}	−5597	−6227
C_{3i}	0	0
C_{4i}	0	0
C_{5i}	−4.1262	−6.4100
C_{6i}	$6.3815 \cdot 10^{-18}$	$1.7914 \cdot 10^{-18}$
C_{7i}	6	6
C_{8i}	199.75	189.6
C_{9i}	532	523.3

To test the suitability of the equilibrium still, the VLE data of EAC (2) + 2-propyl acetate (IPAC, 3) system were compared with the literature data. The results are shown in Figure 2.

From Figure 2, the experimental data agreed well with the literature data. It proved that the still was reliable for this measurement.

Sample Analysis. To determine the liquid and vapor samples, gas chromatography (GC3420A, BeiFen Co.) was used with a 30 m long capillary column (HJ-OV-1701, 0.32 mm in diameter and 0.5 μm film thickness) and a hydrogen flame ionization detector (FID). The column, injector, and detector temperatures were 343.15 K, 443.15 K, and 443.15 K, respectively. The carrier gas was nitrogen (99.999 %) at a constant flow rate of 30 $\mathrm{mL \cdot min^{-1}}$. Hydrogen (99.99 %) and compressed air were used at a constant flow rate of (30 and 300) $\mathrm{mL \cdot min^{-1}}$, respectively. The injected sample was 0.4 μL. Each sample was analyzed at least thrice to ensure accuracy with an error within ± 0.02. Then, the data were calibrated by a series of standard mixtures which were prepared at a 5 % increase gravimetrically.

RESULTS AND DISCUSSION

Experimental Data. The VLE data for the binary systems of HMDSO (1) + EAC (2) were measured at 101.3 kPa and are shown in Table 2, where x and y are the mole fractions of the liquid phase and vapor phase, respectively. T is the temperature (K).

Thermodynamic Consistency Test. Since the equilibrium pressures were sufficiently low in the investigated system, the vapor phase could be considered as the ideal gas. The activity coefficients equation was simplified to:

$$\gamma_i = P y_i / x_i P_i^s \tag{1}$$

where γ_i are the activity coefficients of the component i; P is the total pressure; P_i^s is the vapor pressure of pure component i; x_i is the mole fraction of component i in the liquid phase; y_i is the mole fraction of component i in the vapor phase.

The vapor pressure of pure component was calculated by the modified Antoine equation as follows:

$$\ln P_i^s = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i} T + C_{5i} \ln T + C_{6i} T^{C_{7i}}$$
$$C_{8i} \le C_{9i} \tag{2}$$

where $C_{(1-7)i}$ are component-specific coefficients and $C_{(8-9)i}$ are the scopes of application temperatures. The parameters are shown in Table 3.

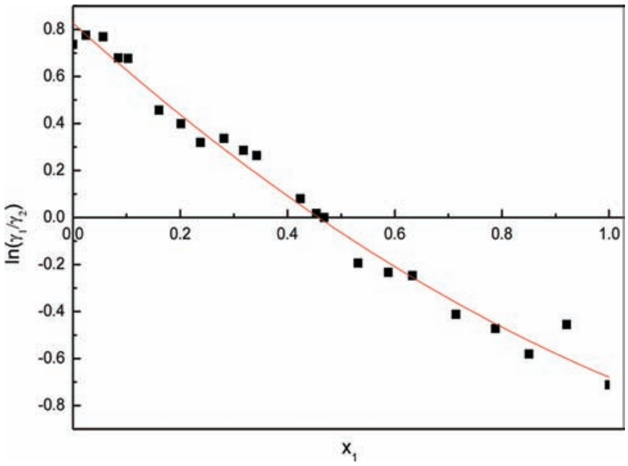

Figure 3. Herington test.

Table 4. Binary Interaction Parameters of NRTL, UNIQUAC, and Wilson Models

	NRTL	UNIQUAC	Wilson
	$\tau_{ij} = B_{ij}/T$	$\tau_{ij} = \exp(B_{ij}/T)$	$\ln A_{ij} = B_{ij}/T$
B_{12}	−110.12	−95.76	−315.23
B_{21}	407.63	22.33	24.13
ΔT_{AD}	0.3078	0.3056	0.3083
ΔT_{MD}	0.7612	0.7537	0.7576
σ_T	0.3844	0.3808	0.3892
Δy_{AD}	0.00235	0.00281	0.00255
Δy_{MD}	0.04219	0.04291	0.04162
σ_y	0.16984	0.17181	0.17189

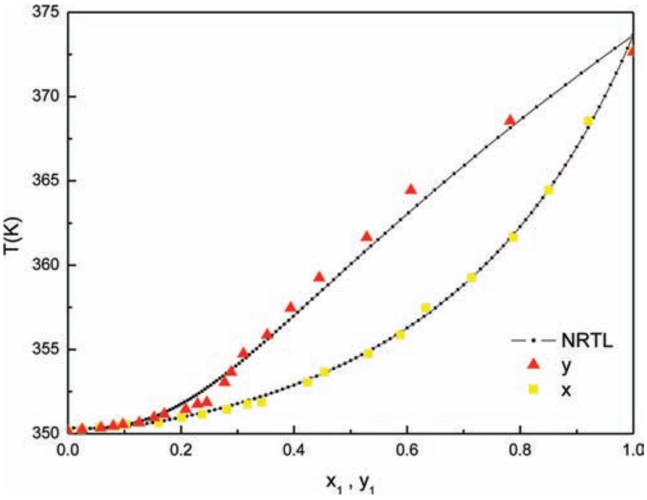

Figure 4. $T-x-y$ diagram for HMDSO (1) + EAC (2).

The thermodynamic consistency of VLE data for the system was tested by the Herington method. According to this method, D was 2.79, J was 9.64, and the check result $D-J$ was −6.85 which was less than 10. Therefore, the VLE data passed the Herington test.[6] The result of the Herington test is shown in Figure 3.

Correlation of the System. For the binary system, the Wilson, NRTL, and UNIQUAC equations were used to calculate the VLE data. Model parameters were obtained using the minimization of the objective function as follows:

$$F = \sum_{i=1}^{N} \left(\left[\frac{T_{\exp,i} - T_{\mathrm{cal},i}}{\sigma_T} \right]^2 + \left[\frac{y_{\exp,i} - y_{\mathrm{cal},i}}{\sigma_y} \right]^2 \right) \qquad (3)$$

where N is the number of the data; σ is the standard deviation of the measured variables. In the calculations, the values of σ are set to 0.5 K for temperature and 0.005 for vapor phase composition.

The results of the calculated values of the equations and binary parameters are shown in Table 4, where AD is the average deviation and MD is the maximum deviation.

From Table 4, the NRTL average deviations in temperature and vapor-phase composition were better than others. The NRTL correlation ($\alpha = 0.3$[7,8]) values with the experimental $T-x-y$ data are shown in Figure 4. The system had a minimum temperature azeotrope at 350.31 K and $x_1 = 0.0330$.

CONCLUSIONS

VLE data for the EAC + HMDSO system at 101.3 kPa were measured by using a double circulating VLE still. NRTL, Wilson, and UNIQUAC model parameters were obtained with satisfactory correlation. The NRTL model was better than the others. The system had a minimum temperature azeotrope at 350.31 K and $x_1 = 0.0330$. Those data will be useful to distillation in organic chemical industry and pharmaceutical chemicals.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ctstzwl@hebut.edu.cn.

REFERENCES

(1) Cheng, N. *Solvents Handbook*; Chemical Industry Press: Beijing, 2002.

(2) Wilson, G. M. Vapor−Liquid Equilibium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86* (6), 127–130.

(3) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess function for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(4) Abrams, D.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for Gibbs energe of partly or completely miscible System. *AIChE J.* **1975**, *21*, 116–128.

(5) Zhang, W.-L.; Hou, K.-H.; Mi, G.-J. Study on Isobaric VLE Data for the Binary System of Thiophene and Octane. *J. Chem. Eng. Chin. Univ.* **2007**, *21* (6), 911–913.

(6) Abobott, M. M.; Van Ness, H. C. *Theory and Problems of Thermodynamics*; McGraw-Hill: New York, 1972.

(7) Zhang, W.; Hou, K.; Mi., G. Liquid-Liquid Equilibria of Ternary Systems Sulfide + Octane + Solvents at Different Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 2275–2281.

(8) Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: Boston, 1985.

(9) Guirong, M.; Xiaochun, C. Determination of LLE data for toluene-hexamethyldisiloxane-sulfolane ternary system. *Beijing Huagong Daxue Xuebao, Ziran Kexueban* **2003**, *30* (3), 5–9.