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Vapor−Liquid Equilibria for the Binary Mixture α-Pinene + Octane

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Isothermal and isobaric vapor−liquid equilibria (VLE) were measured for the binary mixture α-pinene + octane at the temperatures (348.15, 363.15, and 383.15) K and at the pressures (26.66 and 53.33) kPa with an inclined ebulliometer. The experimental results are analyzed using the UNIQUAC equation with temperature-dependent binary parameters with satisfactory results.

Introduction

α-Pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene, CAS RN 80-56-8) is a substance present in wood turpentine, is one of the intermediates of vitamin synthesis, and is a leuco transparent liquid with a strong odor.[1] Isobaric vapor−liquid equilibria (VLE) data for α-pinene with terpene hydrocarbons and isothermal VLE data for α-pinene with alkanes and alkenes are available in the literature.[2−4] Unfortunately, the isobaric and isothermal VLE data of pinene + octane are scarce in the literature.[5] To further understand the nature of α-pinene and to optimize separation processes during the process of linalool and vitamin E production, VLE data of α-pinene + octane are indispensable.

In this paper, the isothermal and isobaric VLE for α-pinene + octane at the temperatures (348.15, 363.15, and 383.15) K and at the pressures (26.66 and 53.33) kPa are reported. The binary VLE data are correlated by using the UNIQUAC equation with temperature-dependent binary parameters.

Experimental Section

Materials. α-Pinene (highest commercial grade, Zhejiang NHU Co., Ltd.) was maintained under special conditions before its use. It was distilled by using a 150 cm high column under a pressure of 10.0 kPa. Octane (analytical reagent grade, Shanghai Chemical Co.) was refluxed over freshly activated CaO for at least 2 h and then fractionally distilled. Pure materials were stored over type 0.4 nm molecular sieves. The purities of the materials were determined in our laboratory by gas chromatography to be as follows :α-pinene, 99.80 mass %; octane, 99.85 mass %. The physical properties of the pure materials are listed in Table 1 along with literature values.[6]

Apparatus and Procedures. The isothemal and isobaric VLE measurements were done by using an inclined ebulliometer with a pumplike stirrer, as described previously.[7−9] The ebulliometric method is based on the overall concentration $x°$ instead of the equilibrium concentration x of the liquid phase. The ebulliometer was connected to a pressure controlling system. The temperature inside the ebulliometer was measured with a standard platinum resistance thermometer connected to a digital multimeter (Keithley 195A) with a sensitivity of 0.01 K. The accuracy of the temperature was estimated to be 0.05 K. The pressure was indirectly measured by the boiling temperature of pure water in a separate ebulliometer. The estimated uncertainty of the indirect pressure measurements was 40 Pa. All mixtures were prepared by mass; the uncertainty of the composition measurements was estimated to be 0.0001 mole fraction. The detailed procedure was described elsewhere.[7]

Table 1. Physical Properties of the Pure Solvents

	d(293.15 K)/kg·m^{-3}		n_D(293.15 K)		T_b(101.325 kPa)/K	
solvent	expt	lit.	expt	lit.	expt	lit.
α-pinene	858.06	858.2[6]	1.4657	1.4658[6]	429.24	429.35[6]
octane	702.44	702.5[6]	1.3973	1.3974[6]	398.79	398.85[6]

Table 2. VLE Data for (x)α-Pinene (1) + (1 − x)Octane (2)

	p/kPa			T/K	
x_1	348.15 K	363.15 K	383.15 K	26.66 kPa	53.33 kPa
0.0000	19.31	33.52	64.25	356.74	376.95
0.1121	18.21	31.26	61.57	358.09	378.69
0.2021	17.02	29.71	57.18	359.62	381.29
0.2529	16.59	28.63	55.08	360.64	382.52
0.3034	15.98	27.47	52.96	361.80	383.06
0.3990	14.86	25.67	49.69	363.73	385.89
0.5015	13.75	23.65	45.54	366.08	388.92
0.5994	12.51	21.40	41.01	369.12	392.37
0.8003	10.05	17.54	34.51	375.67	398.92
0.8966	8.74	15.65	30.67	378.94	401.82
1.0000	7.35	13.32	26.98	382.79	405.54

Results and Discussion

The measured binary VLE data are listed in Table 2. The data were correlated by using the UNIQUAC equation with temperature-dependent binary parameters.

At vapor−liquid equilibrium,

$$p y_i \phi_i = p_i^{S} \phi_i^{S} x_i \gamma_i \exp[v_i^{L}(p_i - p_i^{S})/RT] \tag{1}$$

where p is the total pressure, y_i is the vapor mole fraction of component i, and ϕ_i is the fugacity coefficient of component i, calculated from the virial equation,

$$\ln \phi_i = (2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij}) p/RT \tag{2}$$

where the second virial coefficients of pure substances B_{ii} and mixtures B_{ij} were calculated according to the method of Hayden and O'Connell,[10] x_i is the liquid mole fraction of component i, and v_i^{L} is the pure liquid molar volume

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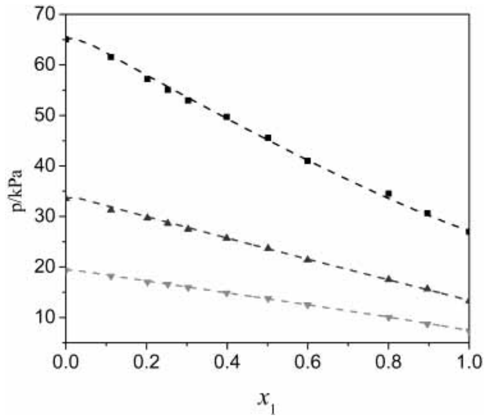

Figure 1. $p-x_1$ for α-pinene (1) + octane (2) at constant temperature: ■, 383.15 K; ▲, 363.15 K; ▼, 348.15 K; - - -, UNIQUAC correlation.

Table 3. Correlation Results for the Binary System and Root-Mean-Square Deviations for $\delta p/p$ and δT

system	a_{12}/K	a_{21}/K	$10^2\delta p/p$	δT/K
α-pinene (1) + octane (2)	$125.53 - 58.04T_r - 35.50T_r^2$	$99.18 - 41.04T_r - 34.57T_r^2$	0.998	0.30

calculated from the modified Rackett equation.[11] The p_i^S is the saturated vapor pressure, calculated from the Antoine equation,

$$\log(p_i^S/\text{kPa}) = A - B/(C + T/\text{K}) \tag{3}$$

For α-pinene and octane, the constants used are from the *DECHEMA Chemistry Data Series*.[12] The liquid-phase activity coefficient γ_i was calculated from the UNIQUAC equation[13] with temperature-dependent binary parameters. The pure component structural parameters for each component are as follows: for α-pinene, $r = 6.06$, $q = q' = 4.76$; and for octane, $r = 5.85$, $q = q' = 4.94$. The temperature dependence of a_{ij} is given by

$$a_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)}T_r + a_{ij}^{(2)}T_r^{\ 2} \tag{4}$$

where $T_r = T/T_0$, and T_0 is an arbitrarily chosen reference temperature, in this case 315 K.

To obtain the temperature-dependent parameters, a modified Powell optimization method[14] was used to minimize the objective function,

$$J = \sum_j (p - p_{\text{exp}})_j^2/p_{\text{exp},j}^2 \tag{5}$$

The root-mean-square deviations (RMSDs) between the experimental and calculated values of the measured variables—δp for pressure and δT for temperature—and the optimum binary parameters α_{ij} are listed in Table 3. The results show that the RMSDs in pressure and temperature for the binary systems are 0.998% and 0.30 K, respectively. Figure 1 shows the isothermal vapor−liquid equilibria for α-pinene + octane at (348.15, 363.15, and 383.15) K. Figure 2 shows the isobaric vapor−liquid equilibria for α-pinene + octane at (26.66 and 53.33) kPa. The experimental and fitted values are in good agreement. The results indicate that the isothermal and isobaric binary VLE data of α-pinene + octane can be satisfactorily correlated by using the UNIQUAC equation with binary temperature-dependent parameters.

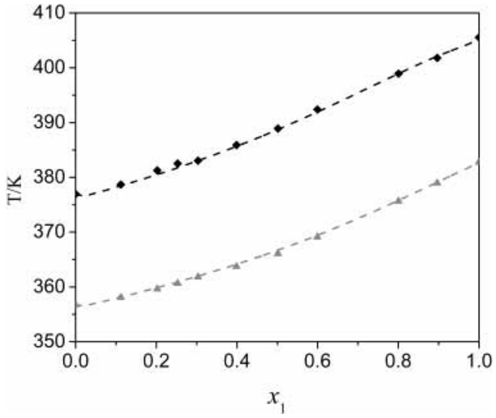

Figure 2. $T-x_1$ for α-pinene (1) + octane (2) at constant pressure: ▲, 26.66 kPa; ◆, 53.33 kPa; - - -, UNIQUAC correlation.

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Literature Cited

(1) Hawkins, J. E.; Armstrong, G. T. Physical and thermodynamic properties of terpenes. *J. Am. Chem. Soc.* **1954**, *76*, 3756−3758.
(2) Farelo, F.; Santos, F.; Serrano, L. Isobaric vapor-liquid equilibria in binary mixtures of α-pinene, limonene and 1,8-cineole. *Can. J. Chem. Eng.* **1991**, *69*, 794−799.
(3) Tucker, W. C.; Hawkins, J. E. Vapor-liquid equilibria of alpha-pinene − beta-pinene system. *Ind. Eng. Chem* **1954**, *46*, 2387−2390.
(4) Reich, R.; Sanhueza, V. Vapor-liquid equilibria for α-pinene and β-pinene and for these pinenes with heptane, cyclohexane, 1-octene and cyclohexene. *Fluid Phase Equilib.* **1992**, *77*, 313−325.
(5) Reich, R.; Sanhueza, V. Vapor-liquid equilibria for α-pinene and β-pinene with 1-butanol and 1-pentanol. *Fluid Phase Equilib.* **1992**, *78*, 239−248.
(6) Robert, C. W.; Melvin, J. A.; Willian, H. B. *The CRC Handbook of Chemisty and Physics*, 66th ed.; CRC Press: Boca Raton, FL, 1986.
(7) Li, H.; Han, S.; Teng, Y. Bubble points measurement for system chloroform-ethanol-benzene by inclined ebulliometer. *Fluid Phase Equilib.* **1995**, *113*, 185−195.
(8) Li, H.; Han, S. Isothermal and isobaric (vapor+liquid) equilibria of (ethanol + benzene + hexane). *J. Chem. Thermodyn.* **1997**, *29*, 921−927.
(9) Wang, C.; Li, H.; Zhu, L.; Han, S. Isothermal and isobaric vapor + liquid equilibria of N, N-dimethylformamide + *n*-propanol + *n*-butanol. *Fluid Phase Equilib.* **2001**, *189*, 119−127.
(10) Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem., Process. Des. Dev.* **1975**, *14*, 209−216.
(11) Spencer, C. F.; Danner, R. P. Improved equation for prediction of saturated liquid density. *J. Chem. Eng. Data* **1972**, *17*, 236−241.
(12) Gmehling, J. G.; Onken, U. *Vapor-liquid equilibrium data collection*; DECHEMA Chemistry Data Series Vol. 1; DECHEMA: Frankfurt, 1977.
(13) Anderson, T. F.; Prausnitz, J. M. Application of the UNIQUAC equation to calculation of multicomponent phase equilibria. *Ind. Eng. Chem., Process. Des. Dev.* **1978**, *17*, 552−561.
(14) Powell, M. J. D. An efficient method for finding the minimum of a function of several variables without calculating derivatives. *Comput. J.* **1964**, *7*, 155−162.

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