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Measurement and Correlation of Vapor−Liquid Equilibrium Data for *β*-Pinene + *p*-Cymene + (*S*)-(−)-Limonene at Atmospheric Pressure

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ABSTRACT: Vapor−liquid equilibrium (VLE) data for binary systems of *β*-pinene + *p*-cymene and *β*-pinene + (*S*)-(−)-limonene and the ternary system of *β*-pinene + *p*-cymene + (*S*)-(−)-limonene were measured at 100.7 kPa using the modified Ellis equilibrium still. The experimental data of binary systems were tested for thermodynamic consistency with the method of Herington and point-to-point test of Van Ness. The parameters of four solution models—Wilson, nonrandom two-liquid (NRTL), universal quasichemical activity coefficient (UNIQUAC), and Liebermann−Fried—were calculated with the aid of the least-squares method to minimize an objective function based on the total pressure. The thermodynamic consistency of the VLE data of the ternary system was tested with the method of McDermott−Ellis, modified by Wisniak and Tamir. Also, the ternary system data were compared with the predicted values, using the parameters of Wilson model obtained from the binary systems. The predicted bubble-point temperature and the vapor composition for the ternary system were in good agreement with the experimental results.

INTRODUCTION

Turpentine oil, obtained by steam distillation of pine resins, is one of the richest resources of refined oil in the world. Its main constituents include *a*-pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene, CAS RN 80-56-8), *β*-pinene (6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane, CAS RN 127-91-3), *p*-cymene (1-methyl-4-(1-methylethyl)benzene, CAS RN 99-87-6), and (*S*)-(−)-limonene ((−)-1-methyl-4-(1-methylethenyl)cyclohexene, CAS RN 5989-54-8).[1] Turpentine oil is widely used in the synthesis of a variety of fine chemicals, such as synthetic resins and terpenic surfactants, and in the pharmaceutical and cosmetic industries.[2,3]

The usefulness of relevant thermodynamic data with the consideration of separating these components is evident. The vapor−liquid equilibrium (VLE) is the primary thermodynamic property for indicating the nonideal behavior of mixtures. Information about this basic mixture property is useful in the processing of turpentine.[4] VLE values for some binary mixtures containing pine resins have been reported,[5−9] but the ternary VLE information is severely limited. Rodrigues and Bernardo-Gil[2] reported VLE results for *a*-pinene + *β*-pinene + (*S*)-(−)-limonene at (80.0 and 101.3) kPa. Xu et al.[10] determined experimental VLE data for ternary mixtures of *a*-pinene + *β*-pinene + *p*-cymene at 100.7 kPa. The purpose of this work is to report the experimental VLE results for the ternary system *β*-pinene + *p*-cymene + (*S*)-(−)-limonene at 100.7 kPa.

EXPERIMENTAL SECTION

Materials. *β*-Pinene (Guangdong Maoming Aide Co. Ltd., with a minimum mass fraction 0.99), *p*-cymene (Shanghai Nuotai Chemical Co. Ltd., with a minimum mass fraction 0.98), and (*S*)-(−)-limonene (Fluka, with a minimum mass fraction 0.95) were distilled at reduced pressures. The purity of the distillate was determined with a 6890 Agilent gas chromatograph equipped with a flame ionization detector and a HP-1 column. The impurity contents were less than 0.005 (mass fraction) for *β*-pinene, 0.006 (mass fraction) for *p*-cymene, and 0.019 (mass fraction) for (*S*)-(−)-limonene. For each component the main impurities are the other two components in the ternary system in this work and lesser amounts of *a*-pinene.

Apparatus and Procedure. The VLE data were measured in a modified Ellis equilibrium still.[11] The cell operates with circulation in both liquid and vapor phases and has a volume of approximately 200 mL. All experiments were carried out under an inert atmosphere of dry nitrogen to avoid exposure to moisture and oxygen. The temperature was measured by a digital DTI-1000 thermometer, with an estimated accuracy of ± 0.01 K. The pressure of the system has been measured with a mercury-filled U-tube manometer equipped with a cathetometer to within ± 0.13 kPa. The system generally reached equilibrium conditions after (2 to 2.5) h of operation. Samples, taken by syringing 1.0 mL after the system had achieved equilibrium, were analyzed by gas chromatography, as described above. The column was 30 m long and 0.53 mm in diameter. Injector and detector temperatures were (553.15 and 563.15) K. The temperature of the GC oven was programmed from (353.15 to 533.15) K at 600 $K \cdot h^{-1}$ and held at 533.15 K for 300 s. Very good separation was achieved under these conditions, and calibration analysis was carried out to convert the peak ratio to the mass composition of the sample. At least three measurements were made for each composition. Concentration measurements were accurate to better than ± 0.0001 mol fraction.

RESULTS AND DATA ANALYSIS

Pure Components. The Antoine constants used for the *β*-pinene and (*S*)-(−)-limonene[2] and for the *p*-cymene[10] are listed

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Table 1. Antoine Constants[a] A, B, and C and Density Constants[b] a and b of Pure Components β-Pinene, (S)-($-$)-Limonene, and p-Cymene

component	Antoine constants				density constants	
	A	B	C	T range/K	a	$10^4(-b)$
β-pinene	13.79453[c]	3436.118[c]	64.690[c]	290−439.2[c]	0.8852[b]	7.92[b]
(S)-($-$)-limonene	14.12371[c]	3647.925[c]	66.875[c]	320−450.7[c]	0.8603[b]	7.64[b]
p-cymene	14.37985[d]	3741.421[d]	66.761[d]	429−450.3[d]	0.8716[b]	7.86[b]

[a] $\ln(P/\mathrm{kPa}) = A - B/(T/\mathrm{K} - C)$. [b] $d/\mathrm{g\cdot cm^{-3}} = a + bt/°\mathrm{C}$, from ref 12. [c] From ref 2. [d] From ref 10.

Table 2. Normal Boiling Points T_b, Critical Parameters T_c, P_c, and Z_c, and Molecular Surface Area and Volume Constants q and r of Pure Component β-Pinene, (S)-($-$)-Limonene, and p-Cymene

component	T_b/K		T_c/K	P_c/kPa	Z_c	r	q
	expt.	lit.					
β-pinene	439.03	439.42[a]	635.00[a]	2500[a]	0.235[a]	6.06[a]	4.76[a]
(S)-($-$)-limonene	450.40	451.10[a]	655.33[a]	2831[a]	0.258[a]	6.28[a]	5.21[a]
p-cymene	449.73	450.30[b]	651.15[b]	2854[b]	0.250[b]	6.91[b]	5.46[b]

[a] From ref 2. [b] From ref 10.

Table 3. Experimental Vapor−Liquid Equilibrium Data of the Binary Systems: β-Pinene (1) + p-Cymene (2) and β-Pinene (1) + (S)-($-$)-Limonene (3) at 100.7 kPa

β-pinene (1) + p-cymene (2)					β-pinene (1) + (S)-($-$)-limonene (3)				
T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_3
449.39	0.0000	0.0000		1.0000	450.34	0.0000	0.0000		1.0000
448.80	0.0632	0.0864	1.0789	1.0005	449.36	0.0735	0.1003	1.0630	0.9965
448.02	0.1123	0.1513	1.0828	1.0007	448.93	0.1015	0.1377	1.0674	0.9955
447.39	0.1579	0.2081	1.0750	1.0004	448.56	0.1314	0.1739	1.0503	0.9957
446.44	0.2285	0.2927	1.0684	0.9995	448.05	0.1662	0.2182	1.0544	0.9943
445.75	0.2833	0.3526	1.0551	1.0027	447.53	0.2018	0.2588	1.0426	0.9976
445.35	0.3161	0.3876	1.0494	1.0043	446.97	0.2459	0.3086	1.0338	0.9990
444.75	0.3672	0.4406	1.0416	1.0072	446.24	0.3001	0.3697	1.0324	0.9996
444.09	0.4259	0.4996	1.0344	1.0104	445.41	0.3605	0.4352	1.0317	1.0012
443.53	0.4786	0.5505	1.0281	1.0143	444.74	0.4213	0.4949	1.0201	1.0065
443.02	0.5283	0.5967	1.0219	1.0195	443.78	0.5019	0.5743	1.0166	1.0101
442.35	0.5977	0.6587	1.0133	1.0297	442.95	0.5723	0.6373	1.0092	1.0239
441.84	0.6542	0.7085	1.0082	1.0372	442.40	0.6258	0.6822	1.0011	1.0400
441.44	0.7001	0.7493	1.0061	1.0396	441.43	0.7198	0.7661	1.0006	1.0483
440.74	0.7838	0.8201	1.0004	1.0544	440.17	0.8532	0.8795	0.9992	1.0653
440.13	0.8594	0.8837	0.9976	1.0652	439.57	0.9198	0.9352	1.0001	1.0652
439.59	0.9332	0.9448	0.9954	1.0798	439.02	0.9803	0.9846	1.0014	1.0456
439.31	0.9765	0.9808	0.9943	1.0757	438.95	1.0000	1.0000	1.0000	
438.95	1.0000	1.0000	1.0000						

in Table 1. Density constants[12] for the linear correlation of temperature are also listed in Table 1. The constants representing the molecular sizes and surface areas, q_i and r_i, of the UNIQUAC equation were obtained from atomic and molecular structure data. The van der Waals molecular volumes and surface areas, V_i and A_i,[8] can be calculated by following equations.

$$r_i = V_i/15.17 \tag{1}$$

$$q_i = A_i/(2.5\cdot 10^9) \tag{2}$$

The normalization factors 15.17 (10^{-6} $\mathrm{m^3\cdot mol^{-1}}$) and $2.5\cdot 10^9$ (10^{-4} $\mathrm{m^2\cdot mol^{-1}}$) are those derived by Abrams and Prausnitz.[13]

Table 2 presents the critical properties, normal boiling temperatures, and molecular volume and area constants of the pure components.

Binary Data. The experimental VLE data of β-pinene + p-cymene and β-pinene + (S)-($-$)-limonene at 100.7 kPa are presented in Table 3, together with the activity coefficients γ_i which were calculated from the following equation, which is suitable for low pressure sytems:[14]

$$\gamma_i = Py_i/P_i^S x_i \tag{3}$$

where P is the total pressure and P_i^S is the vapor pressure of the pure component, x_i is the liquid phase mole fraction of component i, and y_i is the vapor phase mole fraction of component i. The activity coefficients reported in Table 3 indicate that the measured systems exhibit moderate deviations from ideal behavior and no azeotrope is present. In eq 3, also known as modified Raoult's law, the vapor phase is assumed to be an ideal gas, and the pressure dependence of the liquid-phase fugacity is neglected.

The vapor−liquid equilibrium data reported in Table 3 were found to be thermodynamically consistent by the Herington method[15] and the point-to-point method of Van Ness et al.[16] as modified by Fredenslund et al.[17] The results are shown in Table 4.

The fit of the data were evaluated by minimizing the following objective function:[18]

$$F = \sum_{j=1}^{N_d} (P_j(\mathrm{calc}) - P_j(\mathrm{expt}))^2 \tag{4}$$

where N_d is the number of data points and P_j(expt) and P_j(calc) are the experimental and calculated values of the total pressure, respectively.

The numerical values of binary Wilson, nonrandom two-liquid (NRTL), universal quasichemical activity activity coefficient (UNIQUAC), and Liebermann−Fried parameters A_{ij} and A_{ji}, obtained from experimental data, are presented in Table 5 for the systems β-pinene + p-cymene and β-pinene + (S)-($-$)-limonene. According

Table 4. Results of Herington and Van Ness Thermodynamic Consistency Test of System β-Pinene (1) + *p*-Cymene (2) and β-Pinene (1) + (*S*)-(−)-Limonene (3)

system	Herington			Van Ness	
	D	*J*	*D*−*J*	Δ*y*	Δ*P*/kPa
β-pinene (1) + *p*-cymene (2)	9.8021	3.2403	6.5618	0.0024	0.1
β-pinene (1) + (*S*)-(−)-limonene (3)	3.8206	3.5329	0.2877	0.0018	0.1

Table 5. Model Parameters A_{ij}, A_{ji}, and α_{ij} or β for Two Binary Systems of β-Pinene (1) + *p*-Cymene (2) and β-Pinene (1) + (*S*)-(−)-Limonene (3)

system	model	A_{ij}	A_{ji}	α_{ij} or β
1	β-pinene (1) + *p*-cymene (2)			
	Wilson	887.8	818.6	
	NRTL	−1622.3	2242.0	0.3
	UNIQUAC	−145.2945	−21.9672	
	Liebermann−Fried	0.5674	1.6363	2
2	β-pinene (1) + (*S*)-(−)-limonene (3)			
	Wilson	−3014.8	1977.5	
	NRTL	2604.3	−1976.0	0.3
	UNIQUAC	102.4698	−14.3342	
	Liebermann−Fried	0.9002	1.0823	2

Table 6. Average Absolute Deviations δ*y* and δ*T* between Calculated and Experimental VLE Data for *y* and Temperature *T* of the Binary Systems β-Pinene (1) + *p*-Cymene (2) and β-Pinene (1) + (*S*)-(−)-Limonene (3) at 100.7 kPa, Respectively

model	δ*y*	δ*T*/K	δ*y*	δ*T*/K
	β-pinene (1) + *p*-cymene (2)		β-pinene (1) + (*S*)-(−)-limonene (3)	
Wilson	0.0016	0.04	0.0012	0.08
NRTL	0.0025	0.05	0.0027	0.02
UNIQUAC	0.0149	0.05	0.0156	0.02
Liebermann−Fried	0.0064	0.40	0.0044	0.19

to refs 19 and 20 the NRTL nonrandomness parameter α_{ij} and the Liebermann−Fried parameter β are assumed to be 0.3 and 2, respectively.

The average absolute deviations between the experimental and the calculated values of temperature and vapor mole fraction are shown in Table 6. The deviations between the experimental and the calculated values of vapor mole fraction and bubble-point temperature are shown in Figures 1 to 4. The proposed four models yield similar deviations, but the best fit for the miscible mixtures is obtained with the Wilson model. It gives not only an expression for the activity coefficients as a function of composition but also an estimate of the variation of the activity coefficients with temperature. This property is a practical advantage in isobaric calculations where the temperature varies as the composition changes.

Ternary Data. The VLE data of the ternary system β-pinene + *p*-cymene + (*S*)-(−)-limonene at 100.7 kPa are presented in Table 7. The thermodynamic consistency of the VLE data in Table 7 was tested by the McDermott−Ellis method[21] as modified by Wisniak and Tamir.[22] According to these references, any two experimental points *a* and *b* in the system are considered to be thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \tag{5}$$

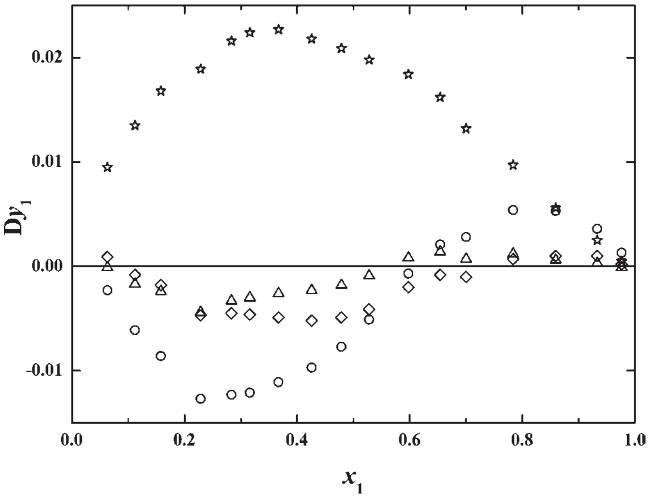

Figure 1. Deviations $Dy_1 = y_1(\text{calc}) - y_1(\text{expt})$ between calculated and experimental vapor mole fractions of component 1 for the binary system of β-pinene (1) + *p*-cymene (2): △, Wilson; ◇, NRTL; ☆, UNIQUAC; ○, Liebermann−Fried.

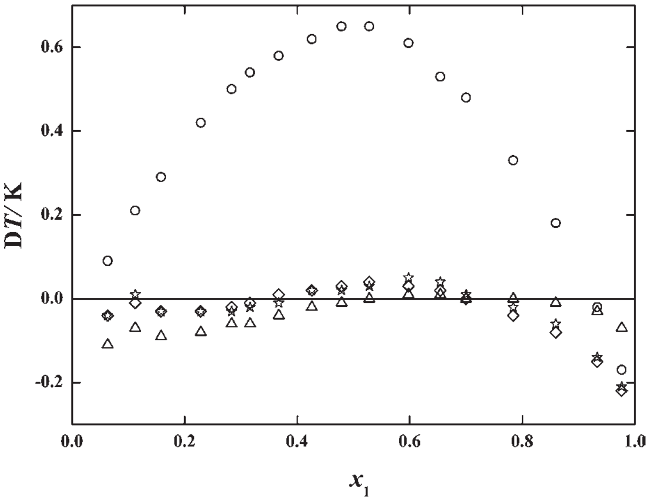

Figure 2. Deviations $DT = T(\text{calc}) - T(\text{expt})$ between calculated and experimental boiling points for the binary system of β-pinene (1) + *p*-cymene (2): △, Wilson; ◇, NRTL; ☆, UNIQUAC; ○, Liebermann−Fried.

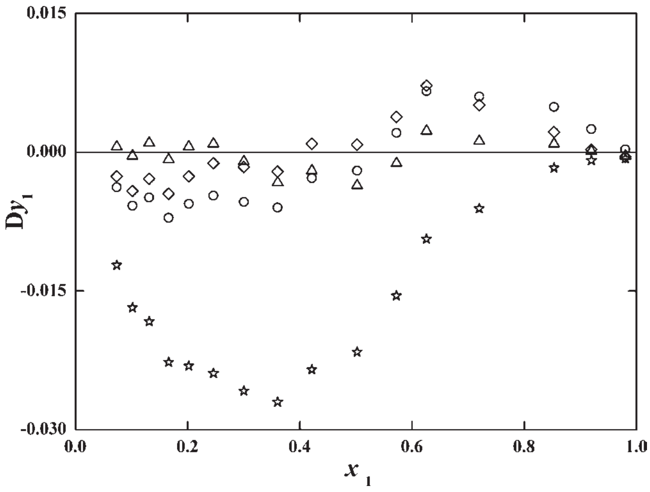

Figure 3. Deviations $Dy_1 = y_1(\text{calc}) - y_1(\text{expt})$ between calculated and experimental vapor mole fractions of component 1 for the binary system of β-pinene (1) + (*S*)-(−)-limonene (3): △, Wilson; ◇, NRTL; ☆, UNIQUAC; ○, Liebermann−Fried.

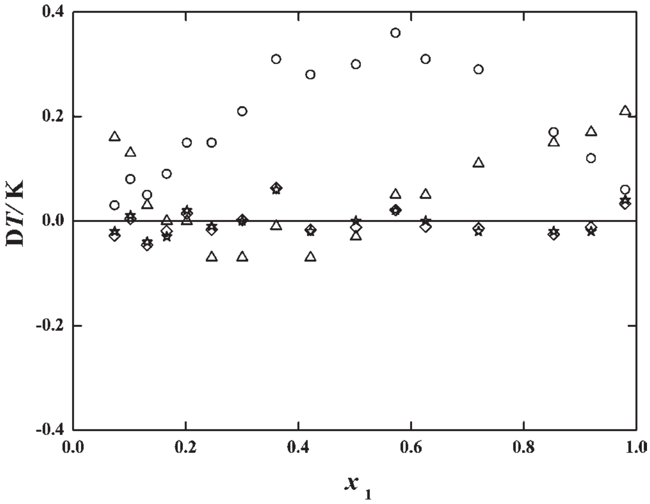

Figure 4. Deviations $DT = T(\text{calc}) - T(\text{expt})$ between calculated and experimental boiling points for the binary system of β-pinene (1) + (*S*)-(−)-limonene (3): △, Wilson; ◇, NRTL; ☆, UNIQUAC; ○, Liebermann−Fried.

where the local deviation D is given by

$$D = \sum_{i=1}^{N_c} (x_{ia} + x_{ib})(\ln \gamma_{ia} - \ln \gamma_{ib}) \tag{6}$$

and N_c is the number of components. The maximum deviation $D_{\max}$ is given by

$$D_{\max} = \sum_{i=1}^{N_c} (x_{ia} + x_{ib}) \left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}} \right) \Delta x + 2 \sum_{i=1}^{N_c} |\ln \gamma_{ib} - \ln \gamma_{ia}| \Delta x + \sum_{i=1}^{N_c} (x_{ia} + x_{ib}) \frac{\Delta P}{P} + \sum_{i=1}^{N_c} (x_{ia} + x_{ib}) B_i \{(T_a + C_i)^{-2} + (T_b + C_i)^{-2}\} \Delta T \tag{7}$$

Table 7. Experimental Vapor−Liquid Equilibrium Data of the Ternary System β-Pinene (1) + *p*-Cymene (2) + (*S*)-(−)-Limonene (3) at 100.7 kPa for Different Mole Fraction *x* and *y* of the Components in the Liquid and Vapor State, Respectively

T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2
448.87	0.0584	0.8255	0.0820	0.8116	448.76	0.0523	0.5472	0.0713	0.5428
448.07	0.1108	0.7854	0.1489	0.7564	447.94	0.0986	0.5020	0.1306	0.4896
447.23	0.1751	0.7113	0.2244	0.6711	447.28	0.1466	0.4521	0.1898	0.4353
446.26	0.2451	0.6501	0.3053	0.6032	446.57	0.2034	0.4013	0.2553	0.3741
445.48	0.2887	0.6025	0.3567	0.5530	446.08	0.2531	0.3517	0.3124	0.3295
444.99	0.3214	0.5661	0.3885	0.5128	445.35	0.3124	0.2979	0.3745	0.2786
444.45	0.3758	0.5171	0.4423	0.4645	444.51	0.3843	0.2115	0.4491	0.1977
444.13	0.4189	0.4735	0.4838	0.4230	443.88	0.4404	0.1585	0.5016	0.1505
443.31	0.4786	0.4168	0.5442	0.3671	443.18	0.5073	0.1007	0.5694	0.0881
442.76	0.5421	0.3445	0.6010	0.3046	442.62	0.5632	0.0355	0.6253	0.0289
442.08	0.6042	0.2901	0.6604	0.2531	448.78	0.0625	0.4286	0.0856	0.4249
441.76	0.6654	0.2289	0.7159	0.1980	447.75	0.1221	0.3745	0.1602	0.3658
441.37	0.7149	0.1751	0.7597	0.1511	446.76	0.1836	0.3204	0.2324	0.3023
440.66	0.7915	0.1025	0.8234	0.0919	446.18	0.2341	0.2695	0.2893	0.2595
439.90	0.8504	0.0512	0.8770	0.0387	445.49	0.2791	0.2251	0.3396	0.2079
448.83	0.0750	0.7187	0.0998	0.7029	445.07	0.3303	0.1625	0.3931	0.1573
447.89	0.1256	0.6764	0.1652	0.6495	444.78	0.3798	0.1266	0.4468	0.1153
446.83	0.1867	0.6112	0.2386	0.5664	444.50	0.4337	0.0604	0.4971	0.0645
445.89	0.2435	0.5497	0.3040	0.5071	448.49	0.0750	0.3040	0.1042	0.2971
445.38	0.3004	0.5023	0.3648	0.4586	447.78	0.1467	0.2254	0.1895	0.2260
444.62	0.3843	0.4175	0.4490	0.3729	446.94	0.2134	0.1631	0.2694	0.1548
443.96	0.4464	0.3526	0.5095	0.3158	446.62	0.2531	0.1287	0.3177	0.1250
443.22	0.5233	0.2768	0.5826	0.2464	445.95	0.3121	0.0763	0.3811	0.0753
442.62	0.5638	0.2078	0.6226	0.1774	445.62	0.3487	0.0457	0.4136	0.0504
441.81	0.6449	0.1321	0.6951	0.1202	449.03	0.0388	0.2552	0.0524	0.2548
441.51	0.7035	0.0758	0.7501	0.0702	448.16	0.1034	0.1965	0.1392	0.1991
447.88	0.0830	0.6175	0.1119	0.6022	447.54	0.1476	0.1572	0.1936	0.1587
446.98	0.1346	0.5571	0.1744	0.5359	447.03	0.1952	0.1054	0.2496	0.1011
446.53	0.2007	0.4934	0.2540	0.4666	446.65	0.2453	0.0504	0.3076	0.0486
445.58	0.2647	0.4326	0.3251	0.3941	449.41	0.0402	0.1568	0.0535	0.1602
445.17	0.3182	0.3671	0.3798	0.3393	448.56	0.0901	0.1131	0.1210	0.1201
444.93	0.3596	0.3337	0.4225	0.3067	448.12	0.1271	0.0815	0.1709	0.0839
444.38	0.4251	0.2585	0.4917	0.2306	447.72	0.1673	0.0325	0.2200	0.0289
443.26	0.5245	0.1765	0.5864	0.1537	449.85	0.0389	0.0631	0.0591	0.0633
442.85	0.5739	0.1248	0.6286	0.1165	449.34	0.0642	0.0357	0.0876	0.0411
442.27	0.6222	0.0678	0.6765	0.0585					

In the present study, the error in the measurements was estimated to be $\Delta P = \pm\, 0.27$ kPa and $\Delta T = \pm\, 0.02$ K, where $\Delta x = \pm\, 0.0002$ in mole fraction units.[22] B_i and C_i are the Antoine constants of pure components *i*. T_a and T_b are the temperatures of point *a* and point *b*, respectively. For the data reported in this study, the value of D was always smaller than that of $D_{\max}$, which illustrates the thermodynamic consistency of the VLE data.

The ternary VLE data were predicted using the Wilson model for the activity coefficients of the components with the binary interaction parameters obtained in the study of the binary subsystems. The values of the binary interaction parameters for the system *p*-cymene + (*S*)-(−)-limonene were obtained using the data of Tong et al.,[23] and the corresponding parameters of system β-pinene + *p*-cymene and β-pinene + (*S*)-(−)-limonene were calculated in this work. The absolute average deviations for the ternary system was $\delta T = 0.17$ K, $\delta y_1 = 0.0038$, $\delta y_2 = 0.0015$, and $\delta y_3 = 0.0037$, respectively.

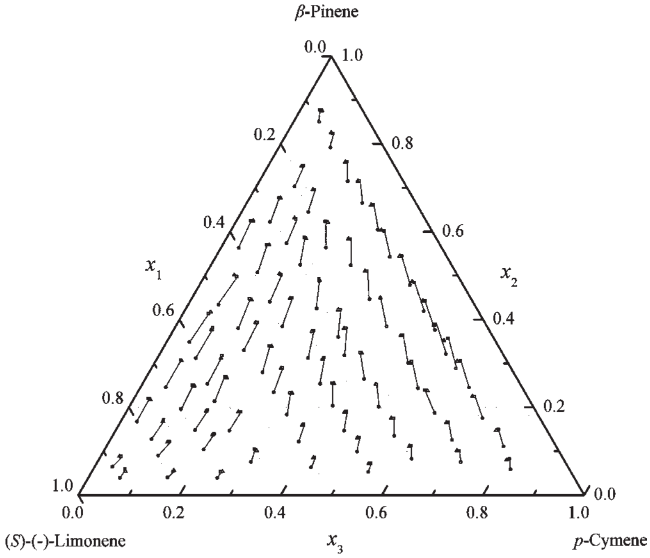

Figure 5. Diagram of VLE for the ternary system β-pinene (1) + *p*-cymene (2) + (*S*)-(−)-limonene (3) at 100.7 kPa: ○, liquid phase mole fractions; □, the experimental vapor phase mole fractions; △, calculated vapor phase mole fractions.

In Figure 5 representations of tie lines and calculated vapor phase mole fractions at 100.7 kPa are shown. It can be observed that the binary contributions allow a good prediction of the behavior of the ternary system.

CONCLUSIONS

Thermodynamically consistent experimental VLE data for the mixtures β-pinene + *p*-cymene, β-pinene + (*S*)-(−)-limonene, and β-pinene + *p*-cymene + (*S*)-(−)-limonene at 100.7 kPa have been reported. The data were compared with the results of different solution models (i.e., Wilson, NRTL, UNIQUAC, and Liebermann−Fried) for determining the liquid-phase activity coefficients. The results show that the four models yield similar deviations, but the Wilson model gave the best fit. The VLE data for the ternary system of β-pinene + *p*-cymene + (*S*)-(−)-limonene were also predicted by Wilson equation using the interaction parameters obtained from the related binary systems. The predicted results were in good agreement with the experimental results.

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