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Vapor–Liquid Equilibria for α-Pinene or β-Pinene with Anisole

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Low-pressure isothermal vapor–liquid equilibria (VLE) have been measured for binary systems of α-pinene or β-pinene with anisole at 393.15 and 403.15 K using a Stage and Fischer equilibrium still with circulation in both phases. The systems, investigated in the pressure range from 280 to 580 mbar, show positive deviations from Raoult's law and maximum pressure azeotropes. The VLE data are thermodynamically consistent.

Introduction

α- and β-pinenes, present in wood turpentine, are important compounds that are used in the synthesis of a variety of chemicals of added economical value, and that could also be used as potential solvents in extractive or azeotropic distillation.

Equilibrium calculations and the preliminary selection of potential solvents can be done if vapor–liquid equilibrium (VLE) information and activity coefficients are available. Predictive methods (*1, 2*) can be used for this purpose if basic information for the main group interaction parameters can be found.

Isobaric VLE information for α-pinene + β-pinene and for these pinenes with other terpene hydrocarbons like limonene, terpinolene, Δ^3-carene, *p*-cymene, and 1,8-cineole is available in the literature (*3–7*). Only recently, isothermal P–x–y VLE data for α-pinene and β-pinene with heptane, cyclohexane, 1-octene, cyclohexene, 1-butanol, and 1-pentanol, and infinite dilute activity coefficients for these same systems and with aromatics and ethers have been measured and published (*8–10*).

In this paper, new isothermal P–x–y VLE data are presented at two temperatures for α-pinene and β-pinene with anisole.

Experimental Section

VLE has been measured in a commercial Fischer LABODEST Model 601 dynamic phase equilibrium apparatus (*11*). The cell operates with circulation in both phases and has a volume of approximately 40 mL. It can operate under light overpressure up to 1500 mbar, atmospheric pressure, or vacuum down to 2.5 mbar and temperatures up to 525 K. Samples are taken via solenoid valves into screwable receivers. All the seals in the equipment are made of Viton to avoid the very strong solvent capacity of these pinenes, especially that of β-pinene. A 30-L steel buffer tank is used as a compensating vessel, and appropriate ice–water traps are used to capture condensating fluids in the system. All experiments have been carried out under an inert atmosphere of dry nitrogen to avoid exposure to moisture and oxygen.

The temperature in the VLE still has been determined with a Systemteknik S1224 digital temperature meter and a Pt100 Ω probe calibrated at the Swedish Statens Provningsanstalt in the IPTS-68 temperature scale. The accuracy is estimated as ±0.02 K.

The pressure in the system has been measured with a Fischer pressure transducer calibrated against an absolute mercury-in-glass manometer (22-mm-diameter precision tubing with cathetometer reading) with an uncertainty of ±0.1 mbar. The overall accuracy is estimated as ±0.2 mbar.

The compositions of the liquid and condensed vapor samples have been determined with a Bellingham+Stanley RFM 81 automatic refractometer with an accuracy in the refractive index of ±0.000 06. The uncertainty in the mole fraction compositions is estimated as ±0.002. Gravimetric calibrations were represented for interpolation purposes by a polynomial.

α-Pinene (98%), β-pinene (99%), and anisole (99%) were available from Aldrich Chemical Co. The purity was checked by gas chromatography. The liquids were rectified in a 1-m-long, 30-mm-diameter, Normschliffgerätebau adiabatic column (with 3 × 3 mm SS spirals), at 1:100 reflux. The evolution of the distillation was checked with refractive index determinations. The final products were obtained by discarding the upper 5% and lower 15% cuts and were dehydrated over molecular sieves.

The measured refractive indexes, together with the literature values, and the working purity of the pure chemicals, as used in the experiments, are given in Table I.

Table I. Source, Purity, Refractive Index n, and Normal Boiling Point T_b of the Pure Liquids

			n(D,293.15K)[a]		T_b (K)		
substance	source	purity (mol %)	this work	lit.	this work	lit. (*21*)	lit. (*14*)
α-pinene	Aldrich	99.9	1.465 89 (±)	1.465 8 (+)[b]	429.1	429.36	429.29
β-pinene	Aldrich	99.9	1.478 78 (–)	1.478 2 (–)[c]	438.9	439.19	439.19
anisole	Aldrich	99.8	1.517 18	1.517 91[d]	426.3	426.73	426.73

[a] Specific rotation: (±) $\alpha = 0$; (+) $\alpha > 0$; $\alpha < 0$. [b] Reference 18. [c] Reference 19. [d] Reference 20.

Table II. Antoine Constants A, B, and C, Equation 1, of the Pure Liquids and Standard Deviations sd(P)[a]

substance	no. of data points	A	B	C	temp range (K)	sd(P) (mbar)
α-pinene	16	7.076 588	1511.961	–57.730	365–430	0.3
β-pinene	15	7.067 997	1539.348	–59.937	364–439	0.2
anisole	12	7.117 773	1451.742	–73.252	382–429	0.4

[a] $\mathrm{sd}(P) = [\sum_{i=1}^{N}(P^{\mathrm{exptl}} - P^{\mathrm{calcd}})^2/(N-3)]^{1/2}$.

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Table III. Experimental Vapor–Liquid Equilibrium Results for Anisole (1) + α-Pinene (2) at 393.15 and 403.15 K: Total Pressure P, Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, and Average Absolute Deviations $\Delta(P)$ and $\Delta(y_1)$

T = 393.15 K[a]			T = 403.15 K[a]		
P (mbar)	x_1	y_1	P (mbar)	x_1	y_1
370.6	0.000	0.000	500.5	0.000	0.000
383.9	0.081	0.109	504.6	0.018	0.023
393.6	0.124	0.169	530.3	0.126	0.162
400.0	0.168	0.218	544.3	0.189	0.244
410.5	0.238	0.305	553.2	0.242	0.301
418.5	0.323	0.372	563.6	0.322	0.375
425.3	0.438	0.473	574.4	0.442	0.473
427.0	0.517	0.521	577.0	0.504	0.516
426.6	0.617	0.581	576.3	0.678	0.642
423.3	0.696	0.648	565.9	0.801	0.740
418.3	0.795	0.720	559.3	0.846	0.783
413.3	0.842	0.768	550.8	0.895	0.841
406.1	0.890	0.822	540.8	0.951	0.906
397.7	0.942	0.891	534.9	0.971	0.938
388.6	0.981	0.951	526.5	0.990	0.973
383.3	0.997	0.985	521.4	1.000	1.000
379.9	1.000	1.000			

[a] $\Delta(P)$ (mbar) = 0.8 and $\Delta(y_1)$ = 0.014 for T = 393.15 K. $\Delta(P)$ (mbar) = 1.0 and $\Delta(y_1)$ = 0.011 for T = 403.15 K. $\Delta(P) = [\sum_{i=1}^{N}(P^{\text{exptl}} - P^{\text{calcd}})/N]$. $\Delta(y_1) = [\sum_{i=1}^{N}(y_1^{\text{exptl}} - y_1^{\text{calcd}})/N]$.

Table IV. Experimental Vapor–Liquid Equilibrium Results for Anisole (1) + β-Pinene (2) at 393.15 and 403.15 K: Total Pressure P, Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, and Average Absolute Deviations $\Delta(P)$ and $\Delta(y_1)$

T = 393.15 K[a]			T = 403.15 K[a]		
P (mbar)	x_1	y_1	P (mbar)	x_1	y_1
280.7	0.000	0.000	382.7	0.000	0.000
298.5	0.093	0.139	400.7	0.073	0.115
312.9	0.146	0.232	411.4	0.100	0.160
330.3	0.227	0.336	428.0	0.163	0.243
344.0	0.314	0.430	440.1	0.204	0.306
356.4	0.406	0.497	447.6	0.226	0.337
360.9	0.457	0.530	462.2	0.291	0.415
371.9	0.594	0.630	471.2	0.342	0.455
378.3	0.685	0.718	479.9	0.397	0.497
379.7	0.723	0.750	489.3	0.447	0.550
381.4	0.797	0.801	505.0	0.581	0.645
382.1	0.878	0.870	514.6	0.677	0.715
382.0	0.928	0.914	518.3	0.719	0.746
381.5	0.950	0.931	521.4	0.790	0.801
380.2	0.983	0.971	523.3	0.878	0.871
379.9	1.000	1.000	523.5	0.927	0.916
			522.8	0.959	0.950
			521.4	1.000	1.000

[a] $\Delta(P)$ (mbar) = 0.7 and $\Delta(y_1)$ = 0.008 for T = 393.5 K. $\Delta(P)$ (mbar) = 0.9 and $\Delta(y_1)$ = 0.006 for T = 403.15 K.

Results and Discussion

The pure component vapor pressures, of the same batch of chemicals as was used in the mixture experiments, were measured in the Fischer still. The experimental vapor pressures were correlated with the Antoine equation:

$$\log(P/\text{mbar}) = A - B/[(T/\text{K}) + C] \qquad (1)$$

where the constants A, B, and C were determined with a least-squares procedure. The pure component vapor pressures for α-pinene, β-pinene, and anisole are included in the experimental VLE data sets which follow and are shown with their Antoine constants in Table II. Normal boiling point temperatures calculated from eq 1 and from the literature are compared in Table I.

Table V. Basic Properties for the Pure Substances:[a] Critical Temperature T_c, Critical Pressure P_c, Mean Radius of Gyration R_d, Critical Compressibility Factor Z_c, Dipolar Moment D, Association Parameter η, and Acentric Factor ω

property	α-pinene[b]	β-pinene[b]	anisole
T_c (K)	632.0[c]	643.0[c]	641.65
P_c (bar)	27.6[c]	27.6[c]	41.746
R_d (Å)	3.418	3.617	3.719
Z_c	0.265	0.261	0.264
D (D)	0.36[c]	0.36[d]	1.36
η	0.0[c]	0.0[c]	0.0[c]
ω	0.2862	0.3252	0.3689

[a] Reference 14. [b] Racemic mixture. [c] Estimated. [d] Not available; assigned.

Table VI. Correlation Energy Parameters for Equation 4: Temperature T, Molar Liquid Volumes of Pure Components V_1 and V_2, Energy Parameters a_{12} and a_{21}, and Average Absolute Deviations in the Pressure $\Delta(P)$, Temperature $\Delta(T)$, and Liquid-Phase $\Delta(x_1)$ and Vapor-Phase $\Delta(y_1)$ Mole Fractions

T (K)	V_1[a] (cm^3 mol^{-1})	V_2[a] (cm^3 mol^{-1})	a_{12} (cal mol^{-1})	a_{21} (cal mol^{-1})	$\Delta(P)$ (mbar)	$\Delta(T)$/(K)	$\Delta(x_1)$	$\Delta(y_1)$
			Anisole (1) + α-Pinene (2)					
393.15	117.5	185.2	312.56	168.24	0.21	0.06	0.003	0.013
403.15	119.0	187.5	317.52	140.49	0.15	0.05	0.002	0.010
			Anisole (1) + β-Pinene (2)					
393.15	117.5	182.6	384.28	−56.98	0.31	0.06	0.003	0.009
403.15	119.0	184.8	263.79	76.54	0.24	0.07	0.003	0.007

[a] Estimated with the modified Rackett equation (*24*). [b] $\Delta(T) = [\sum_{i=1}^{N}(T^{\text{exptl}} - T^{\text{calcd}})/N]$. [c] $\Delta(x_1) = [\sum_{i=1}^{N}(x_1^{\text{exptl}} - x_1^{\text{calcd}})/N]$.

The binary VLE measurements were determined in the same Fischer still. For the α-pinene mixtures, the compositions were obtained by adding progressively one component to the other, initially as a pure component, this procedure being reversed at mole fractions close to 0.60. As for the β-pinene mixtures, due to some reactivity that was detected at high temperatures or in extended runs, fresh chemicals were charged into the cell for each new composition.

The experimental binary VLE results for the systems α-pinene and β-pinene + anisole at 393.15 and 403.15 K are presented in Tables III and IV. The systems deviate positively from Raoult's law and show maximum pressure azeotropes.

These redundant data sets have been checked for thermodynamic consistency with a program that uses the differential test. The excess Gibbs energy of the VLE data has been represented by the highly flexible Legendre polynomials, which are similar to the Redlich–Kister expansion (*1*). A fourth-order polynomial has been used for this purpose, and the correlation constants have been obtained by a least-squares regression technique, where the sum of the squared differences between the experimental and the calculated pressures is minimized. This is equivalent to Barker's method (*12*). The vapor-phase nonidealities have been corrected with the virial equation of state truncated after the second coefficient (*13*).

The absolute average deviations in the pressure $\Delta(P)$ and in the vapor mole fraction $\Delta(y_1)$ are shown in Tables III and IV. The basic pure component properties used in this and other programs have been taken from a recent data compilation (*14*) and are shown in Table V. It has to be emphasized that the critical properties and the dipole moments of both pinenes available in this compilation are estimated values.

Accordingly, taking into account the uncertainties present in the physical properties of the pinenes, and considering that an average absolute deviation in the vapor mole fraction $\Delta(y_1)$ of less than 0.01 is normally taken as reasonable in the literature, these new VLE data sets can be considered thermodynamically consistent.

Finally, the VLE data sets have been correlated with the Wilson two-parameter activity coefficient γ_i equation (*15*):

$$\ln \gamma_1 = \left[-\ln(x_1 + \Lambda_{12}x_2) + \frac{\Lambda_{12}x_2}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}x_2}{x_2 + \Lambda_{21}x_1}\right] \quad (2)$$

$$\ln \gamma_2 = \left[-\ln(x_2 + \Lambda_{21}x_1) + \frac{\Lambda_{21}x_1}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}x_1}{x_1 + \Lambda_{12}x_2}\right] \quad (3)$$

where

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(\frac{-a_{12}}{RT}\right) \qquad \Lambda_{21} = \frac{V_1}{V_2}\exp\left(\frac{-a_{21}}{RT}\right) \quad (4)$$

V_1 and V_2 are molar liquid volumes, and a_{12} and a_{21} are adjustable energy parameters.

The energy parameters a_{12} and a_{21} have been estimated by a nonlinear regression method based on the maximum-likelihood principle (*16, 17*) and are shown, together with the average absolute deviations in the pressure $\Delta(P)$, temperature $\Delta(T)$, and liquid-phase $\Delta(x_1)$ and vapor-phase $\Delta(y_1)$ compositions, in Table VI. A fit of all the P–T–x–y data have been considered, minimizing the errors in all the experimental measurements. The truncated virial equation of state has also been used here to correct for vapor-phase nonidealities (*13*).

Glossary

N	number of experimental points
P	total pressure
T	temperature
V_i	molar liquid volume of pure component i
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
a_{ij}	adjustable binary energy parameter in eq 4

Superscripts

exptl	experimentally measured value
calcd	calculated value

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