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Vapor–Liquid Equilibrium of Binary Mixtures of Limonene with α-Pinene and β-Pinene at Reduced Pressures

M. Fátima Rodrigues and M. Gabriela Bernardo-Gil*

Departamento Engenharia Química, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

Vapor–liquid equilibrium data for the binary systems α-pinene + (*S*)-(−)-limonene and β-pinene + (*S*)-(-)-limonene were determined at 53.3 and 80.0 kPa in a modified miniature Othmer still. Parameters of the Wilson, NRTL, and UNIQUAC equations were calculated with the aid of a Nelder–Mead technique to minimize an objective function based on the total pressure. The results were compared with the predictions of the UNIFAC method.

Introduction

Pine rosin is one of the most important products of Portugal. The main constituents of the liquid phase obtained when steam distillation is applied to the pine rosin are α-pinene, β-pinene, and (*S*)-(−)-limonene. These components and/or their derivatives are used in the pharmaceutical and cosmetic industries.

Bernardo-Gil and Ribeiro (1989) determined experimental vapor–liquid equilibrium (VLE) data for binary mixtures of α-pinene + β-pinene, α-pinene + (*S*)-(−)-limonene and α-pinene + *p*-cymene at atmospheric pressure. The same authors (1993) reported data for β-pinene + (*S*)-(−)-limonene and β-pinene + *p*-cymene at 101.3 kPa. Nadais and Bernardo-Gil (1993) reported VLE results for α-pinene + (*S*)-(−)-limonene at 40.0, 66.7, and 101.3 kPa. Bernardo-Gil and Barreiros (1994) determined experimental VLE data of α-pinene + β-pinene at 80.0 and 53.3 kPa.

This paper reports the experimental VLE results for the binary systems α-pinene + (*S*)-(−)-limonene and β-pinene + (*S*)-(−)-limonene at 53.3 and 80.0 kPa. The Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) equations were used to describe the liquid phase activity coefficients. The virial equation of state was used to describe the vapor phase nonidealities, using the virial coefficients estimated by means of the Hayden and O'Connell method (1975). The UNIFAC model using the parameters of Skjold-Jorgensen *et al.* (1979) and of Macedo *et al.* (1983) for the interactions between the groups CH_2 and C=C were used.

Experimental Section

Materials. The α-pinene (Terpex, 95 mass %), β-pinene (Terpex, 93 mass %) and (*S*)-(−)-limonene (Fluka, >97 mass %) were distilled. This fractionation was carried out in a Vigreux column with 1.5 m length and 25 mm outside diameter. The purity of the distillate was checked with the aid of a 8700 Perkin-Elmer gas chromatograph equipped with a flame ionization detector and a Carbovax 20M column. The impurity contents were less than 0.1 mass % for α-pinene and limonene and 0.7 mass % for β-pinene. For each component the main impurities are the other two components and some camphene for β-pinene.

Apparatus and Procedure. The VLE values reported were measured in a modified miniature Othmer still. Equilibrium temperatures were measured by a platinum resistance thermometer coupled to a high-precision 6900 Comarc microprocessor (with a ±0.01 K resolution). The accuracy of the measurements was estimated as ±0.05 K. The pressure in the still was controlled with a mercury/platinum controller to within ±0.13 kPa and was measured with a mercury-filled U-tube manometer and a cathetometer to within ±0.013 kPa.

The compositions of the liquid and condensed vapor were determined using the same gas chromatograph that was used to determine the purity of the components. Calibrations were made in order to convert the peak-area ratios to actual mass compositions of the mixtures. The compositions determined were accurate to better than a mass fraction of 0.0005.

Table 1. Antoine Constants[a] and Molar Liquid Volume Constants[b] of Pure Components

	Antoine constants				mol liq vol consts	
component	*A*	*B*	*C*	temperature range/K	*D*	*E*
α-pinene	13.84793	3377.754	62.817	320–428.8	103.874	0.182
β-pinene	13.79453	3436.118	64.690	290–439.2	74.660	0.242
(*S*)-(−)-limonene	14.12371	3647.925	66.875	320–450.7	87.100	0.190

[a] $\ln(P/\mathrm{kPa}) = A - B/(T/\mathrm{K} - C)$. [b] $v_m\mathrm{L}/(\mathrm{cm}^3\ \mathrm{mol}^{-1}) = D + ET/\mathrm{K}$.

Table 2. Pure Component Normal Boiling Points, Critical Properties, and Molecular Surface Area and Volume Constants

	boiling point/K		critical parameters				
component	exptl	lit	T_c/K	P_c/kPa	Z_c	*r*	*q*
α-pinene	428.75[a]	429.33[c]	620[c]	2500[c]	0.243[c]	6.05	4.76
β-pinene	439.15[b]	439.42[c]	635[c]	2500[c]	0.235[c]	6.06	4.76
(*S*)-(−)-limonene	450.65[a]	451.1[d]	655.33[e]	2831[e]	0.258[e]	6.28	5.21

[a] Obtained by Nadais and Bernardo-Gil (1993). [b] Obtained by Bernardo-Gil and Ribeiro (1993). [c] ESDU (1987). [d] Weast (1971–1972). [e] Predicted using the methods described by Quayle (1953).

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Table 3. Experimental Vapor-Liquid Equilibrium Data of α-Pinene + (*S*)-(−)-Limonene and β-Pinene + (*S*)-(−)-Limonene at 53.3 kPa

α-pinene + limonene			β-pinene + limonene		
T/K	x_1	y_1	*T*/K	x_1	y_1
426.4	0	0	426.4	0	0
425.6	0.030	0.054	425.6	0.056	0.076
425.0	0.053	0.092	425.0	0.099	0.140
424.0	0.093	0.159	424.5	0.138	0.187
422.7	0.140	0.223	423.9	0.184	0.238
421.9	0.180	0.285	423.2	0.239	0.301
420.7	0.223	0.349	422.8	0.263	0.332
419.6	0.269	0.400	422.4	0.296	0.370
418.9	0.296	0.434	422.0	0.332	0.411
417.8	0.343	0.492	421.5	0.372	0.457
416.9	0.389	0.538	421.0	0.413	0.504
415.4	0.456	0.605	420.8	0.427	0.511
413.7	0.542	0.692	420.4	0.468	0.548
412.4	0.605	0.737	420.3	0.469	0.559
411.7	0.636	0.769	419.6	0.541	0.625
410.8	0.690	0.804	419.1	0.579	0.657
410.0	0.735	0.837	418.6	0.625	0.697
408.7	0.798	0.883	418.5	0.632	0.701
408.0	0.836	0.905	417.7	0.701	0.762
407.3	0.884	0.934	417.4	0.733	0.796
406.4	0.931	0.962	415.9	0.880	0.903
406.0	0.960	0.979	415.4	0.928	0.945
405.3	1	1	415.1	0.961	0.974
			414.7	1	1

Table 4. Experimental Vapor−Liquid Equilibrium Data of α-Pinene + (*S*)-(−)-Limonene and β-Pinene+(*S*)-(−)-Limonene at 80.0 kPa

α-pinene + limonene			β-pinene + limonene		
T/K	x_1	y_1	*T*/K	x_1	y_1
441.3	0	0	441.3	0	0
439.0	0.112	0.182	440.0	0.115	0.148
437.2	0.151	0.244	439.7	0.155	0.195
436.1	0.199	0.297	439.0	0.195	0.241
435.5	0.227	0.337	438.4	0.235	0.295
434.3	0.271	0.406	437.4	0.310	0.372
433.6	0.303	0.431	437.2	0.322	0.388
432.3	0.365	0.506	436.8	0.360	0.427
429.1	0.500	0.636	435.3	0.492	0.567
427.3	0.594	0.722	434.2	0.576	0.642
426.1	0.657	0.774	433.6	0.631	0.691
425.3	0.697	0.801	433.3	0.677	0.743
424.0	0.771	0.853	433.0	0.721	0.781
422.6	0.841	0.902	432.2	0.776	0.821
421.6	0.917	0.955	431.8	0.833	0.869
420.8	0.950	0.969	431.2	0.892	0.922
420.1	1	1	431.1	0.893	0.924
			429.7	1	1

Results and Data Analysis

Pure Components. The Antoine constants used for the α-pinene and (*S*)-(−)-limonene (Nadais and Bernardo-Gil, 1993) and for the β-pinene (Bernardo-Gil and Ribeiro, 1993) are listed in Table 1. Molar liquid volumes of the pure components were calculated from the densities (Ribeiro and Bernardo-Gil, 1990) and were correlated linearly with temperature, the values of the parameters also being listed in Table 1.

The constants representing the molecular sizes and surface areas, q_i and r_i, of the UNIQUAC and UNIFAC equations were obtained from atomic and molecular structure data and the van der Waals molecular volumes and surface areas, V_i and A_i:

$$r_i = V_i/15.17 \qquad (1)$$

$$q_i = A_i/(2.5 \times 10^9) \qquad (2)$$

The normalization factors 15.17 and 2.5×10^9 are those derived by Abrams and Prausnitz (1975).

Table 5. Root Mean Square Deviations between Experimental and Calculated Data and Absolute Deviation in Pressure and Vapor Mole Fraction Obtained in the Consistency Tests for the System α-Pinene + (*S*)-(−)-Limonene

	root mean square deviations		consistency tests	
models	*P*/kPa	*y*	Δ*P*/kPa	Δ*y*
P = 53.3 kPa			0.05	0.002
Wilson	0.06	0.004		
NRTL (α = 0.4)	0.06	0.004		
UNIQUAC	0.06	0.004		
UNIFAC[a]	0.68	0.005		
UNIFAC[b]	0.68	0.005		
ideal solution (γ = 1)	0.06	0.004		
P = 80.0 kPa			0.16	0.004
Wilson	0.19	0.005		
NRTL (α = 0.4)	0.19	0.005		
UNIQUAC	0.19	0.005		
UNIFAC[a]	0.71	0.005		
UNIFAC[b]	0.72	0.005		
ideal solution (γ = 1)	0.45	0.005		

[a] Using parameters from Skjold-Jorgensen *et al.* (1979). [b] Using parameters from Macedo *et al.* (1983).

Table 6. Root Mean Square Deviations between Experimental and Calculated Data and Absolute Deviation in Pressure and Vapor Mole Fraction Obtained in the Consistency Tests for the System β-Pinene + (*S*)-(−)-Limonene

	root mean square deviations		consistency tests	
models	*P*/kPa	*y*	Δ*P*/kPa	Δ*y*
P = 53.3 kPa			0.027	0.003
Wilson	0.12	0.004		
NRTL (α = 0.4)	0.07	0.004		
UNIQUAC	0.07	0.004		
UNIFAC[a]	0.32	0.004		
UNIFAC[b]	0.32	0.005		
ideal solution (γ = 1)	0.22	0.005		
P = 80.0 kPa			0.32	0.003
Wilson	0.37	0.004		
NRTL (α = 0.4)	0.37	0.004		
UNIQUAC	0.37	0.004		
UNIFAC[a]	0.94	0.006		
UNIFAC[b]	0.93	0.005		
ideal solution (γ = 1)	0.38	0.004		

[a] Using parameters from Skjold-Jorgensen *et al.* (1979). [b] Using parameters from Macedo *et al.* (1983).

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

Binary Data. The experimental VLE results for α-pinene + (*S*)-(−)-limonene and β-pinene + (*S*)-(−)-limonene at 53.3 and 80.0 kPa are presented in Tables 3 and 4, respectively.

The thermodynamic consistency of the data was tested using the Van Ness method, described by Fredenslund *et al.* (1977). The fugacities of the pure components at saturation and the fugacities of the components in the vapor mixture were calculated using the volume-explicit virial equation terminated after the second virial coefficient. The virial coefficients were estimated by means of the method developed by Hayden and O'Connell (1975). The excess molar Gibbs free energy was described by Legendre polynomials. The vapor−liquid equilibrium data are considered to be consistent if the average absolute deviation between the experimental and calculated vapor mole fractions is less than 0.01. The results are presented in the Tables 5 and 6.

Table 7. Model Parameters for the System α-Pinene (1) + (*S*)-(−)-Limonene (2)

equation	A_{12}/K	A_{21}/K
	$P = 53.3$ kPa	
Wilson	−2.449	4.504
NRTL (α = 0.4)	28.01	−26.99
UNIQUAC	−57.70	58.82
	$P = 80.0$ kPa	
Wilson	6.141	7.064
NRTL (α = 0.4)	30.53	−18.24
UNIQUAC	−55.94	58.98

Table 8. Model Parameters for the System β-Pinene (1) + (*S*)-(−)-Limonene (2)

equation	A_{12}/K	A_{21}/K
	$P = 53.3$ kPa	
Wilson	363.6	−260.8
NRTL (α = 0.4)	−19.86	28.99
UNIQUAC	−102.6	115.4
	$P = 80.0$ kPa	
Wilson	126.7	−120.6
NRTL (α = 0.4)	−73.11	75.01
UNIQUAC	−67.30	68.86

The data were reduced by means of a Nelder−Mead technique to minimize the following objective function (Bernardo-Gil and Soares, 1982):

$$F = \sum_{j=1}^{N} (P_j^{\text{calcd}} - P_j^{\text{exptl}})^2 \tag{3}$$

where N is the number of data points and P^{exptl} and P^{calcd} are the experimental and calculated values of the total pressure.

The numerical values of binary Wilson, NRTL, and UNIQUAC parameters A_{12} and A_{21}, in K, obtained from experimental data, are presented in Tables 7 and 8 for the systems α-pinene + (*S*)-(−)-limonene and β-pinene + (*S*)-(−)-limonene, respectively. The NRTL nonrandomness parameter, α_{12}, was assumed to be 0.4.

The root mean square deviations between the experimental and calculated values of pressure and vapor mole fraction are shown in Tables 5 and 6. In these tables root mean square deviations for P and y considering the solution as ideal are also presented.

The UNIFAC parameters reported by Skjold-Jorgensen *et al.* (1979) and by Macedo *et al.* (1983) were used to predict the VLE data of these systems at the pressures studied. The root mean square deviations obtained for P and y using this model are also presented in Table 5 and 6.

Conclusions

Consistent experimental VLE data for the mixtures α-pinene + (*S*)-(−)-limonene and β-pinene + (*S*)-(−)-limonene for two different pressures have been reported. The data were correlated in terms of different models used for the description of liquid phase activity coefficients. The results show that the models are appropriate and give almost the same deviations, although the deviations found for the UNIFAC model are greater than for the other equations, at least for pressure. The root mean square deviations, considering the solution as ideal, are similar to those found using the models in vapor composition.

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Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of multicomponent liquid mixtures: a new expression for the excess Gibbs Energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.

Bernardo-Gil, M. G.; Soares, L. J. S. Vapour-liquid equilibria: correlation of binary data. *Rev. Port. Quim.* **1982**, *24*, 118−132.

Bernardo-Gil, M. G.; Ribeiro, M. A. Vapour-liquid equilibria of binary systems based on pine resin. *Fluid Phase Equilib.* **1989**, *53*, 15−22.

Bernardo-Gil, M. G.; Ribeiro, M. A. Vapour-liquid equilibria of binary mixtures of β-pinene with limonene and p-cymene at atmospheric pressure. *Fluid Phase Equilib.* **1993**, *85*, 153−160.

Bernardo-Gil, M. G.; Barreiros, A. Vapour-liquid equilibria of α-pinene +β-pinene at 53.3 and 80 kPa. *Fluid Phase Equilib.* **1994**, *100*, 283−291.

ESDU International - Engineering Sciences Data - Physical Data, Chemical Engineering, Vol 1- General - Melting points, boiling points and critical properties; ESDU International plc, 1987; 87028 (Rc 1.2).

Fredenslung, A., Gmehling, J.; Rasmussen, P. *Vapour-liquid Equilibria using UNIFAC*; Elsevier: Amsterdam, 1977.

Hayden, J. G.; O'Connell, J. P. A generalised Method for predicting Second virial coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

Macedo, E. A., Weidlich, U., Gmehling, J.; Rasmussen, P. Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. 3. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 676−678.

Nadais, M. H.; Bernardo-Gil, M. G. Vapour-liquid equilibria of α-pinene +limonene at reduced pressures. *Fluid Phase Equilib.* **1993**, *91*, 321−330.

Quayle, O. R. The parachors of organic compounds. *Chem. Rev.* **1953**, *53*, 439−589.

Renon, H.; Prausnitz, J. M. Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

Ribeiro, M. A.; Bernardo-Gil, M. G. Densities and refractive indices of Components of Pine Resin. *J. Chem. Eng. Data* **1990**, *35*, 204−206.

Skojld-Jorgensen, S. S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. Vapour-Liquid equilibria by UNIFAC group contribution: revision and extension. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714−722.

Weast, R. C. *Handbook of Chemistry and Physics*, 52nd ed.; CRC Press: Cleveland, 1971−1972.

Wilson, G. M. VLE - A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−133.

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