Binary and Ternary Phase Behavior of α-Pinene, *β*-Pinene, and Supercritical Ethene

Miguel A. M. Costa, Henrique A. S. Matos, Manuel Nunes da Ponte,[†] and Edmundo J. S. Gomes de Azevedo*

Centro de Química Estrutural e Unidade de Química-Física de Materiais, ICEMS, Instituto Superior Técnico, Avenida Rovisco Pais, 1096 Lisboa, Portugal

High-pressure isothermal vapor−liquid equilibria have been measured for binary and ternary systems containing α-pinene, *β*-pinene, and supercritical ethene, at 288.15 K, 298.15 K, 308.15 K and pressures between 4 MPa and 8 MPa. Experimental results were obtained in an apparatus based on the synthetic method where the main feature is a variable-volume high-pressure cell with a glass window, making it possible to observe the phase behavior. A rod attached to the movable piston allowed the estimation of the density of the phase under study. Results show that the solubilities of both pinenes in supercritical ethene are very similar. The resulting binary pressure−temperature diagrams are of type I, according to the classification of Scott−van Konynenburg. The ternary systems are also of type I, according to the classification of McHugh−Krukonis. Three-phase liquid−liquid−gas regions are likely to exist in these systems but were not observed due to limitations in the apparatus used. To model the experimental results, we used the Peng−Robinson equation of state with van der Waals one-fluid mixing rules and Panagiotopoulos−Reid combining rules, which involves two binary interaction parameters to be determined from regression of experimental data. Deviations between experimental and calculated pressures were always less than 0.8%. Experimental vapor and liquid densities were compared with those generated by this equation. Ternary phase behavior was predicted using only binary interaction parameters retrieved from each binary system, resulting in mole fraction deviations less than 5% for the liquid phase and 3% for the vapor phase.

Introduction

The use of supercritical fluids is alternative to conventional distillation processes that normally require high temperatures which is inconvenient when dealing with natural products because of their thermal degradation. Moreover, supercritical fluids may be useful in the reduction of energy costs, which at present is still one of the main concerns in any industrial production facility. Gases at supercritical conditions have also been largely used in natural occurring mixtures, to extract products with high added value like flavors, fragrances, pharmaceutical chemicals, essential oils, etc., because they can advantageously replace toxic organic solvents.

Following this line, we have studied the possibility of separating α-pinene from *β*-pinene using supercritical fluid extraction, as an alternative to the high-energy-consuming conventional distillation. α-pinene and *β*-pinene are important chemicals used in the synthesis of a variety of chemicals, like synthetic resins and terpenic surfactants.

For this purpose we need relevant thermodynamic data on binary and ternary mixtures containing these constituents with supercritical fluid. Due to its convenient critical pressure (5.0318 MPa) and critical temperature (282.36 K), we selected ethene as the supercritical solvent. Since extraction takes advantage of the phase equilibria, the required data are mainly vapor−liquid equilibria (VLE). We report here VLE data and phase densities at three temperatures (288.15 K, 298.15 K, and 308.15 K) and pressures to 8 MPa for the binaries ethene + α-pinene, ethene + *β*-pinene and for the ternary ethene + α-pinene + *β*-pinene. Finally, to correlate and predict VLE data for those systems, we used the Peng−Robinson equation of state with van der Waals one-fluid mixing rules and Panagiotopoulos−Reid combining rules. This procedure requires two binary interaction parameters that are optimized from our binary phase equilibrium experimental data; they were used to predict the phase equilibrium of the ternary system.

Isobaric phase equilibria at atmospheric pressure were previously studied for the binaries α-pinene + *β*-pinene (Tucker and Hawkins, 1954; Bernardo-Gil and Ribeiro, 1989; Bernardo-Gil and Barreiros, 1994) and for these pinenes with other terpene hydrocarbons like limonene, *p*-cymene, etc. (Bernardo-Gil and Ribeiro, 1989, 1993; Farelo *et al.*, 1991). Low-pressure isothermal vapor−liquid equilibria for α-pinene + *β*-pinene and for α-pinene and *β*-pinene with non-terpenic hydrocarbons (heptane, cyclohexane, 1-octene, and cyclohexene) have been obtained by Reich and Sanhueza (1992) at 228.15 K and 388.15 K and pressures below atmospheric. For the system α-pinene with carbon dioxide, Pavlícek and Richter (1993) report high-pressure vapor−liquid equilibrium data at 313.15 K, 323.15 K, and 328.15 K and pressures from 3.5 MPa to 10 MPa.

Experimental Section

In the determination of VLE, we used the synthetic or indirect method, as described by Fornary *et al*. (1990). Mixtures of known composition are filled into the high-pressure cell and brought to conditions of temperature and pressure in the homogeneous range. Then, pressure is changed until the appearance of a second phase is detected by visual observation. No sampling is required by this technique.

Figure 1 shows a schematic diagram of the experimental apparatus used in this study.

[†] Permanent address: Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal.

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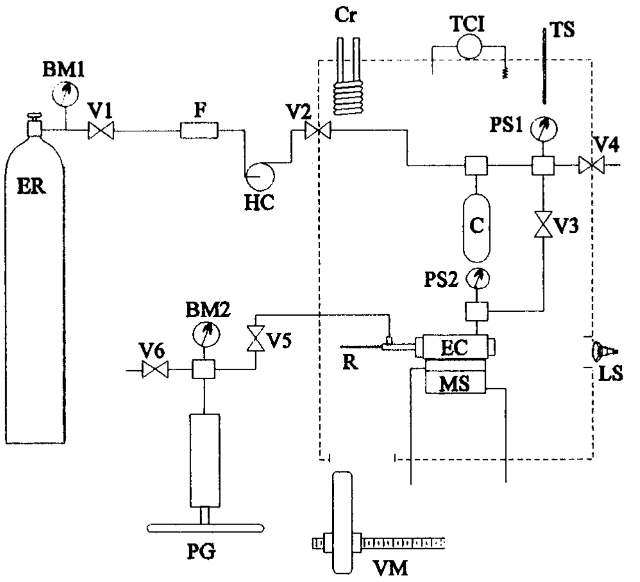

Figure 1. Schematic diagram of the experimental apparatus: BMi, Bourdon manometers; C, gas cylinder; Cr, cryostat; EC, equilibrium cell; ER, ethene reservoir; F, filter; HC, hand-operated compressor; LS, light source; MS, magnetic stirrer; PG, pressure generator; PS*i*, digital pressure sensors; R, rod; TCI, temperature controller indicator; TS, temperature sensor; V*i*, valves; VM, Vernier microscope.

The main component of the apparatus is a stainless steel variable-volume cell (EC in Figure 1) with an approximate volume in the range 9−25 cm^3, schematically shown in greater detail in Figure 2. It is constructed from 316 stainless steel, is 13 cm long, 5.8 cm o.d., and 2.2 cm i.d., and is fitted at one end with a 1.5 cm thick-walled viewing glass (Maxos, capable of operating to 20 MPa) that allows observation of the phase equilibria phenomena occurring inside the cell. This cell is an improvement over a previous one (Gomes de Azevedo *et al.*, 1993) since at the other end the cell has a movable stainless steel piston with a rod attached, which allows an approximate volume measurement of the phase under study.

The cell was immersed in a water bath, which temperature was controlled (to within ±0.01 K) by a thermostat Haake, model E3, and a cryostat Haake, model EK12. The temperature was measured with a digital thermometer Systemteknik, model S1224, provided with a Pt100 temperature sensor, model S935; we estimate that the overall uncertainty in temperature does not exceed ±0.02 K. Pressures were measured by Bourdon manometers VDO (BM in Figure 1) in the 200 bar range and, for more precise readings, by two digital pressure sensors, Setra Systems, model 206 (PS1), and Omega, model PX425 (PS2), with 5 kPa and 1 kPa precision, respectively.

Table 1. Critical Point of Pure Ethene

	this work	Daubert and Danner	% deviation
p_c/MPa	5.048	5.0318	0.32
V_c/(m^3 kmol^{-1})	0.1203	0.12907	7.29
T_c/K	282.31	282.36	0.004

A typical experimental run starts with the loading of the equilibrium cell with a known amount of solute (in this case, α-pinene or β-pinene or both). The uncertainty in composition of the mixtures is estimated to be ±0.001 in mole fraction. Ethene was then pressurized with a Newport Scientific hand-operated compressor, model 46-13310-2, into the volume between valves V2, V3, and V4 (see Figure 1). After pressure and thermal equilibrium was attained (that typically would take about 1 h), a known amount of supercritical ethene was transferred through V3 into the equilibrium cell. The amount of ethene was calculated from the pressure and temperature readings using an equation of state (Younglove, 1982). The solution in the cell was mixed with a Teflon-coated magnetic stir bar activated by an air-driven external magnet beneath the cell.

With this apparatus we can visualize several phenomena related to the phase equilibria, namely dew points, bubble points, and critical points. The determination of any of these equilibrium points was obtained by changing only the cell's internal volume where the mixture was contained. This was achieved by varying the volume inside the cell, through the axial movement of the piston. This movement was performed by pressurizing water into the backside of the piston using a manual pressure generator (PG) supplied by High Pressure Equipment, model 37-6-30. For a given mixture, the volume of the cell was increased until the two phases were clearly seen. The volume of the cell was then reduced until the vapor phase disappeared and the liquid filled the entire cell. The bubble point was obtained when the first bubble of vapor appears, with the increasing of the cell's volume. A dew point was characterized by the appearance of the first drop of liquid (in the form of a fine mist) in equilibrium with the vapor phase. Similarly, the position of the piston was changed until the vapor phase filled the cell. At each bubble point or dew point, the values of temperature (at TS), pressure (at PS2), and position of the rod were registered. The position of the piston was determined by reading the displacement of the rod with the Vernier microscope (Precision Tool & Instrument, with an accuracy of ±0.005 μm). Since the volumes of the cell at different rod positions were previously calibrated with pure ethene at saturation, we obtained an estimate of the phase density. Mole fractions were calculated from the amounts of substances loaded into the cell. A different

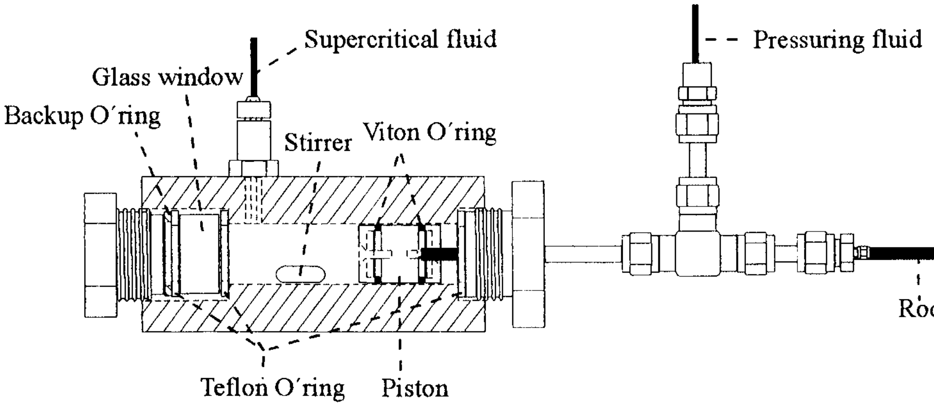

Figure 2. Schematic diagram of the high-pressure view cell.

Table 2. Experimental Pressure (p) and Density (ρ) as a Function of Liquid Mole Fraction (x_1) and Vapor Mole Fraction (y_1) for the Binary Ethene (1) + α-Pinene (2)

x_1	p/MPa	ρ/kmol m^{-3}	x_1	p/MPa	ρ/kmol m^{-3}	y_1	p/MPa	ρ/kmol m^{-3}
				T = 288.15 K				
0.7690	4.471	9.87	0.9446	5.201	10.52	0.9962	5.488	6.98
0.7920	4.579	10.24	0.9560	5.251	10.73	0.9970	5.407	5.37
0.8114	4.663	10.54	0.9631	5.288	10.86	0.9974	5.316	4.86
0.8339	4.754	10.92	0.9746	5.333	12.48	0.9978	5.207	4.46
0.8554	4.833	11.40	0.9798	5.376	9.58	0.9980	5.116	4.20
0.8731	4.898	11.80	0.9826	5.395	9.65			
0.8951	4.968	12.49	0.9858	5.425	9.60			
0.9111	5.024	12.94	0.9879	5.444	9.55			
0.9176	5.086	9.90	0.9897	5.462	9.54			
0.9263	5.124	10.13	0.9938	5.488	7.66			
0.9332	5.154	10.28	0.9950	5.489	7.29			
				T = 298.15 K				
0.7525	5.226	9.73	0.9210	6.194	10.94	0.9815	6.382	8.44
0.7688	5.327	9.98	0.9318	6.237	11.02	0.9838	6.379	8.17
0.7888	5.458	10.27	0.9454	6.287	11.23	0.9918	6.294	6.55
0.8104	5.573	10.55	0.9528	6.314	10.99	0.9931	6.245	5.88
0.8333	5.710	10.90	0.9584	6.334	10.79	0.9939	6.209	5.73
0.8532	5.817	11.21	0.9648	6.358	10.54			
0.8685	5.899	11.36	0.9714	6.383	8.95			
0.8816	5.960	11.48	0.9756	6.385	8.84			
0.8963	6.031	11.50	0.9782	6.386	8.60			
				T = 308.15 K				
0.7471	5.973	9.44	0.8959	7.143	12.10	0.9572	7.358	9.94
0.7902	6.356	10.08	0.9089	7.215	12.18	0.9614	7.356	9.60
0.8137	6.539	10.49	0.9140	7.241	11.41	0.9747	7.342	7.87
0.8473	6.814	11.79	0.9283	7.325	11.24	0.9782	7.319	7.78
0.8659	6.964	12.08	0.9401	7.362	10.76	0.9822	7.252	7.54
0.8786	7.049	12.12	0.9521	7.369	10.14	0.9848	7.162	7.29
						0.9879	6.975	6.44

Table 3. Experimental Pressure (p) and Density (ρ) as a Function of Liquid Mole Fraction (x_1) and Vapor Mole Fraction (y_1) for the Binary Ethene (1) + β-Pinene (3)

x_1	p/MPa	ρ/kmol m^{-3}	x_1	p/MPa	ρ/kmol m^{-3}	y_1	p/MPa	ρ/kmol m^{-3}
				T = 288.15 K				
0.7232	4.373	9.11	0.9369	5.173	10.17	0.9976	5.412	5.77
0.7482	4.506	9.50	0.9494	5.226	10.48	0.9978	5.353	5.26
0.7754	4.629	9.88	0.9596	5.274	10.74	0.9986	5.054	4.26
0.7947	4.709	10.18	0.9683	5.316	11.07			
0.8162	4.798	10.49	0.9729	5.339	11.28			
0.8404	4.883	10.82	0.9845	5.422	8.70			
0.8631	4.951	11.24	0.9884	5.462	8.72			
0.8792	4.994	11.54	0.9913	5.485	8.47			
0.9087	5.061	13.12	0.9933	5.487	8.02			
0.9262	5.134	9.84						
				T = 298.15 K				
0.7591	5.197	10.52	0.9288	6.267	10.22	0.9847	6.393	8.37
0.7827	5.416	10.91	0.9402	6.309	10.43	0.9893	6.390	8.11
0.8095	5.638	11.37	0.9493	6.339	10.52	0.9906	6.353	7.65
0.8293	5.777	11.66	0.9566	6.358	10.42	0.9917	6.323	7.36
0.8476	5.895	11.84	0.9625	6.380	10.23	0.9927	6.273	6.91
0.8631	5.979	11.98	0.9677	6.395	9.97	0.9938	6.218	6.47
0.8780	6.055	12.05	0.9753	6.404	9.17			
0.8899	6.110	11.82	0.9776	6.405	9.02			
0.9026	6.159	12.02	0.9804	6.405	8.78			
0.9114	6.198	11.87						
				T = 308.15 K				
0.7228	6.052	9.21	0.8933	7.305	11.70	0.9512	7.496	10.81
0.7671	6.440	9.87	0.9095	7.365	11.60	0.9581	7.488	10.39
0.7986	6.709	10.40	0.9216	7.454	12.47	0.9649	7.472	9.74
0.8270	6.909	11.20	0.9374	7.498	11.80	0.9803	7.412	9.65
0.8503	7.060	11.56	0.9439	7.499	11.34	0.9832	7.367	8.87
0.8710	7.187	11.67				0.9862	7.273	7.97
						0.9880	7.200	7.44
						0.9902	7.055	6.77

amount of ethene was added to the previous mixture, and the procedure was repeated. The data presented are the mean values of at least three different runs.

Ethene, supplied by Air Liquide, was 99.95 mol % pure and was used as received. Both pinenes were obtained from Aldrich and were used without further purification; α-pinene was 99 mass % pure, and β-pinene was 98 mass % pure. Their purity was confirmed by gas chromatography. Before any measurements, the liquids were degassed in the cell.

Table 4. Experimental Pressure (p) and Density (ρ) as a Function of Liquid Mole Fraction (x_1) and Vapor Mole Fraction (y_1) for the Ternary Ethene (1) + α-Pinene (2) + β-Pinene (3)

x_1	x_2	p/MPa	ρ/kmol m^{-3}	y_1	y_2	p/MPa	ρ/kmol m^{-3}
			T = 288.15 K				
0.7153	0.1424	4.217	9.18	0.9918	0.0041	5.478	8.08
0.7603	0.1199	4.457	9.87	0.9950	0.0025	5.483	7.13
0.7911	0.1044	4.606	10.35	0.9958	0.0021	5.476	6.77
0.8279	0.0861	4.761	11.04	0.9973	0.0013	5.411	5.67
0.8597	0.0702	4.879	11.62	0.9981	0.0010	5.142	4.38
0.8914	0.0543	4.986	12.41	0.9984	0.0008	4.984	4.01
0.9140	0.0430	5.056	13.06				
0.9293	0.0354	5.141	10.76				
0.9454	0.0273	5.209	11.13				
0.9590	0.0205	5.270	11.57				
0.9663	0.0169	5.302	12.03				
0.9741	0.0130	5.341	12.53				
0.9759	0.0121	5.351	12.64				
0.9776	0.0112	5.391	9.28				
0.9829	0.0086	5.437	8.62				
0.9869	0.0065	5.471	8.63				
0.9899	0.0051	5.492	8.60				
			T = 298.15 K				
0.8028	0.0986	5.540	10.95	0.9875	0.0063	6.362	7.74
0.8218	0.0891	5.662	11.39	0.9923	0.0039	6.337	7.15
0.8367	0.0816	5.768	11.68	0.9933	0.0033	6.310	6.86
0.8573	0.0713	5.880	12.21	0.9943	0.0028	6.271	6.57
0.8742	0.0629	5.971	12.36				
0.8901	0.0549	6.048	12.44				
0.9014	0.0493	6.099	12.47				
0.9131	0.0434	6.149	12.36				
0.9155	0.0422	6.164	10.47				
0.9225	0.0387	6.188	12.27				
0.9245	0.0377	6.203	10.69				
0.9326	0.0337	6.233	10.77				
0.9402	0.0299	6.262	10.79				
0.9510	0.0245	6.300	10.86				
0.9603	0.0199	6.335	10.67				
0.9729	0.0135	6.353	8.90				
0.9772	0.0114	6.371	8.73				
0.9816	0.0092	6.372	8.59				
0.9835	0.0082	6.373	8.38				
			T = 308.15 K				
0.7642	0.1179	6.237	9.74	0.9632	0.0184	7.400	9.60
0.8080	0.0960	6.628	10.32	0.9680	0.0160	7.385	9.22
0.8311	0.0844	6.813	10.70	0.9810	0.0095	7.367	9.36
0.8556	0.0722	6.988	11.64	0.9850	0.0075	7.295	8.44
0.8760	0.0620	7.105	11.78	0.9875	0.0062	7.216	7.68
0.8921	0.0539	7.208	11.66	0.9900	0.0050	7.095	6.88
0.9062	0.0469	7.277	11.61				
0.9125	0.0437	7.301	11.46				
0.9313	0.0344	7.355	11.23				
0.9397	0.0302	7.377	11.01				
0.9491	0.0254	7.397	10.55				
0.9551	0.0224	7.402	10.34				

Results

Using the experimental procedure described above, we obtained VLE data for binary and ternary systems containing ethene, α-pinene, and β-pinene, at 288.15 K, 298.15 K, and 308.15 K. As a test of our apparatus, we measured the critical point of the pure ethene used in these measurements. As Table 1 shows, our experimental data are in good agreement with the tabulated critical constants (Daubert and Danner, 1989) for ethene.

Binary Systems. Binary isothermal VLE data (pressure and density at saturation as a function of liquid and vapor compositions) are presented in Table 2 for the binary ethene (1) + α-pinene (2) at 288.15 K, 298.15 K, and 308.15 K. Table 3 shows similar results for the binary ethene (1) + β-pinene (3) at 288.15 K, 298.15 K, and 308.15 K.

Ternary System. Isothermal vapor−liquid equilibria were also obtained for the ternary system ethene (1) + α-pinene (2) + β-pinene (3). We used the same experimental technique described before, starting with a binary liquid mixture of α-pinene + β-pinene at a 1:1 mole ratio. Table 4 presents the experimental results obtained for this ternary mixture at the same temperatures, 288.15 K, 298.15 K, and 308.15 K.

Table 5. Pure Component Data Used with PR-EOS (T_c, Critical Temperature; p_c, Critical Pressure; ω, Acentric Factor)

component	T_c/K	p_c/MPa	ω
ethene (1)	282.31[a]	5.048[a]	0.0852[b]
α-pinene (2)	632.00[b]	2.76[b]	0.2862[b]
β-pinene (3)	643.00[b]	2.76[b]	0.3252[b]

[a] This work. [b] Daubert and Danner, 1989.

The experimental densities of the several mixtures presented in Tables 2−4 show occasionally a discrepancy between consecutive values. This is attributed to uncertainties associated with the relative importance of the dead volumes which depend on the position of the piston. These uncertainties become more important as the volume of the

Table 6. Binary Interaction Parameters and Quality of Fit for Ethene (1) + α-Pinene (2) and Ethene (1) + β-Pinene (3) Obtained from the PR-EOS[a]

	ethene (1) + α-pinene (2)			ethene (1) + β-pinene (3)		
T/K	k_{12}	k_{21}	Δp/MPa	k_{13}	k_{31}	Δp/MPa
288.15	0.1272	0.049 69	0.00988	0.1640	0.051 46	0.0268
298.15	0.1127	0.044 31	0.0104	0.1543	0.041 91	0.0574
308.15	0.1175	0.039 78	0.0294	0.1581	0.044 98	0.0454

[a] Δp are the average absolute pressure deviations, defined as $\Delta p = [\sum_{i=1}^{n}(p_i^{\mathrm{exp}} - p_i^{\mathrm{calc}})^2/(n - 1)]^{1/2}$, where n is the number of experimental points.

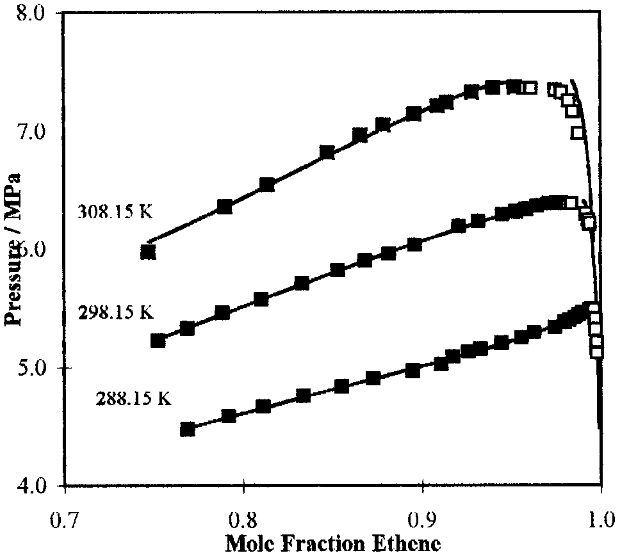

Figure 3. Vapor–liquid equilibrium for the binary ethene (1) + α-pinene (2) at 288.15 K, 298.15 K, and 308.15 K. (—) Calculated from PR-EOS with the binary interaction parameters listed in Table 6. Experimental: (■) liquid; (□) vapor.

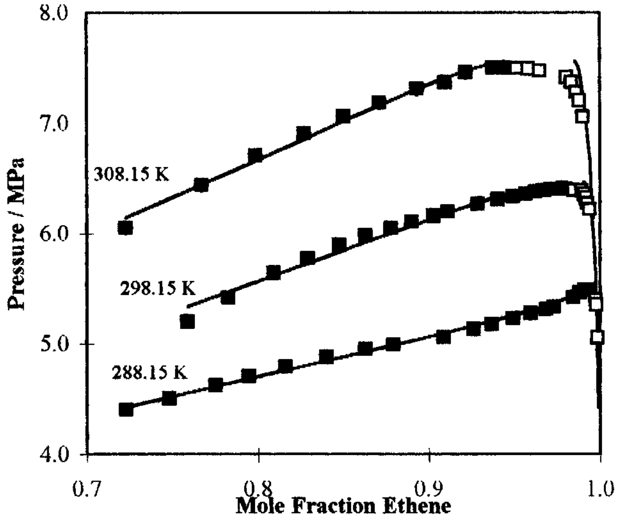

Figure 4. Vapor–liquid equilibrium for the binary ethene (1) + β-pinene (3) at 288.15 K, 298.15 K, and 308.15 K. (—) Calculated from PR-EOS with the binary interaction parameters listed in Table 6. Experimental: (■) liquid; (□) vapor.

cell approaches its minimum, i.e., when the piston is pushed at its maximum. Therefore, some of the experimental density measurements presented in Tables 2–4 have an error that in the worst case may reach 10%.

Modeling with the Peng–Robinson Equation of State

Using the pure component data shown in Table 5, binary experimental data were correlated by the Peng–Robinson equation of state (PR-EOS) (1976) with van der Waals one-fluid mixing rules and Panagiotopoulos–Reid combining rules (1986). At each temperature, an oriented-search technique was used to obtain the two binary interaction parameters characteristic of each binary system that minimized the objective function $\sum_{i=1}^{n}(p_i^{\mathrm{exp}} - p_i^{\mathrm{calc}})^2$ where n is the number of experimental points and p^{exp} and p^{calc} are respectively the experimental and calculated total pressures.

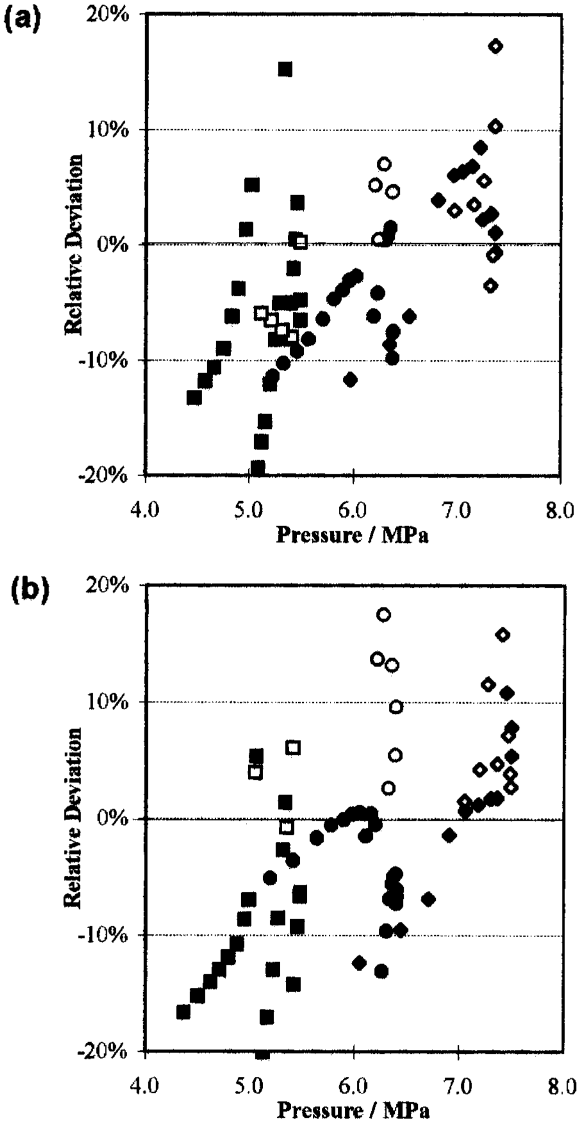

Figure 5. Relative deviations of calculated (PR-EOS with the binary interaction parameters listed in Table 6) and experimental densities for the binaries (a) ethene + α-pinene and (b) ethene + β-pinene at 288.15 K (■), 298.15 K (●), and 308.15 K (◆). Filled symbols refer to liquid and open symbols refer to vapor.

The resulting binary interaction parameters are listed in Table 6. Since α-pinene and β-pinene are structurally similar, their liquid mixtures show small deviations from Raoult's law (i.e., $k_{23} = k_{32} = 0$), as shown by the experimental p–x–y binary data at 373.15 K and 388.15 K obtained by Reich and Sanhueza (1992). As Table 6 shows, the binary interaction parameters are slightly temperature dependent. It turned out that the temperature dependence of these parameters could be neglected without significant loss in accuracy in the calculated results.

Figures 3 and 4 compare experimental with calculated VLE data for the binaries ethene (1) + α-pinene (2) and

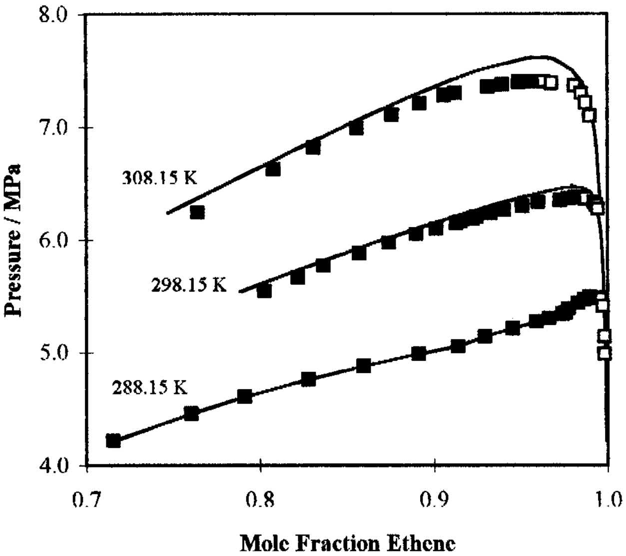

Figure 6. Vapor−liquid equilibrium for the pseudobinary ethene + (α-pinene + β-pinene) with the pinenes at a 1:1 mole ratio, at 288.15 K, 298.15 K, and 308.15 K. (—) Calculated from PR-EOS with the binary interaction parameters listed in Table 6. Experimental: (■) liquid; (□) vapor.

ethene (1) + β-pinene (3), respectively, at the three temperatures reported here. As shown, the model used represents well these particular systems. Pressure deviations do not exceed 0.8% for any of the systems studied. Even in the critical region, which is normally difficult to predict with a cubic equation of state, we obtain a fairly good representation. Any of the curves represented in Figures 3 and 4 show no evidence of three-phase formation. Yet the form of the curve at 288.15 K suggests that liquid−liquid immiscibility may exist at lower temperatures. Limited three-phase (liquid−liquid−gas) regions were observed (Gomes de Azevedo *et al.*, 1993) in similar systems (ethene + limonene and ethene + cineole) in the range 285−301 K.

For both systems there is good agreement between calculated and experimental results. For any of the isotherms, deviations in the calculated liquid mole fractions do not exceed 0.6% of the experimental values, being the largest deviations observed mostly as the critical region is approached. For the vapor mole fractions, the largest deviations (about 2%) are found at the 308.15 K isotherm. For the other two isotherms, deviations do not exceed 0.5%.

Figure 5 compares experimental molar densities with those generated by the Peng−Robinson equation of state (using again the binary interaction parameter data listed in Table 6). Shown are the relative deviations defined as $[(\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{calc}})/\rho_i^{\mathrm{exp}}] \times 100\%$ as a function of pressure for ethene (1) + α-pinene (2) and ethene (1) + β-pinene (3) mixtures at 288.15 K, 298.15 K, and 308.15 K.

As Figure 5 shows, density measurements show some scattering at certain pressures. As mentioned above, this behavior is associated with the relative magnitude of dead volumes to the total volume inside the cell, which become more important as the volume of the cell is closer to its minimum. However, even with limitation, the deviations between experimental and calculated density values are in most cases less than 10%.

Figure 6 compares calculated with experimental VLE data for the pseudobinary ethene + (α-pinene + β-pinene), the pinenes being at a 1:1 mole ratio. Again, the calculated results use the binary interaction parameters of Table 6 and are in reasonably good agreement with the experimental data. Nevertheless, larger deviations are observed in this case as expected, because contrary to the previous cases the calculated results in Figure 6 represent true predictions whereas the calculated lines presented in Figures 3−5 result from data correlation. The calculated results shown in Figure 6 show deviations not larger than 5% for the liquid mole fractions and 3% for the vapor mole fractions.

Figure 7 presents calculated and experimental VLE data for the ternary ethene + α-pinene + β-pinene system at 288.15 K, 298.15 K, and 308.15 K. These calculated curves are a true prediction since no ternary data were used in the fitting. As shown, at the three temperatures, the calculated ternary results using the binary interaction parameters listed in Table 6, are in good agreement with

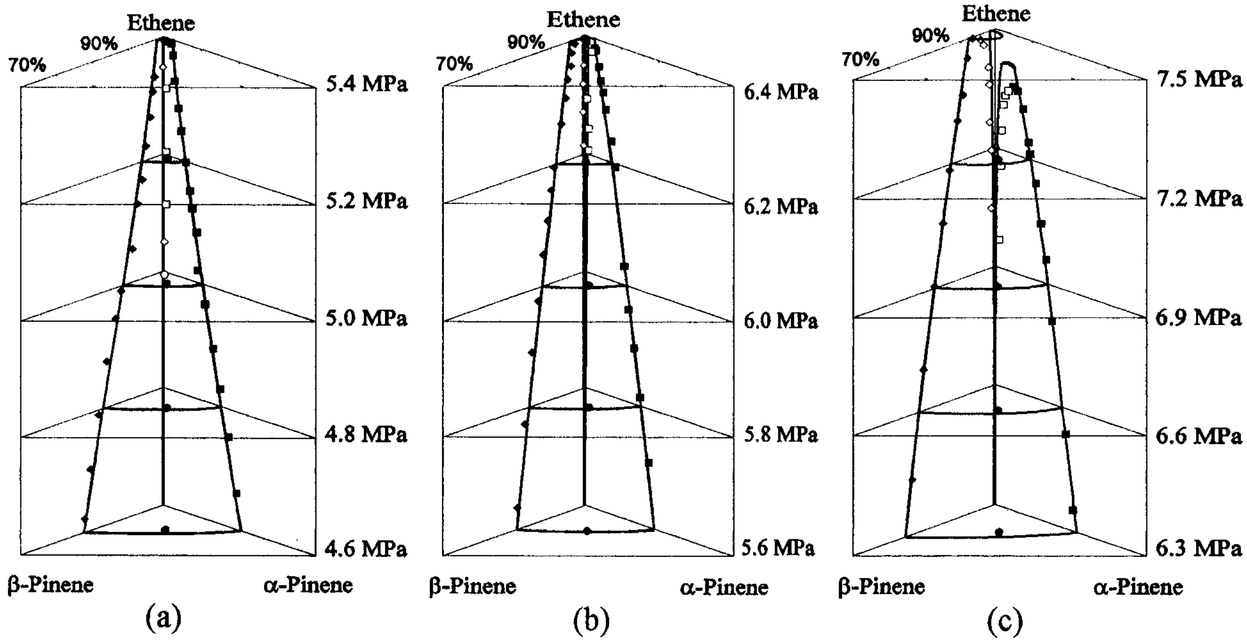

Figure 7. Phase equilibrium behavior for the ternary ethene + α-pinene + β-pinene at (a) 288.15 K, (b) 298.15 K, and (c) 308.15 K. (—) Calculated from PR-EOS with the binary interaction parameters listed in Table 6. Experimental binary data: (◆, ■) liquid; (◇, □) vapor. Experimental ternary data: (●) liquid; (○) vapor.

the experimental data. The isobaric sections of the prisms shown in Figure 7 are predictions from the Peng−Robinson EOS as well as interpolations from the experimental points for the pressures listed. The faces of the prisms compare experimental with calculated results for each binary system and are therefore the results previously presented for the binary systems.

The solubility results obtained for each terpene in supercritical ethene show that under the conditions investigated here, both systems have similar solubilities in supercritical ethene. We believe that this same trend will not change under different temperature and/or pressure conditions. Supercritical ethene exhibits similar selectivities for both pinenes and therefore is not suitable as an extraction agent.

Similarly to a previous investigation involving the binaries ethene + limonene and ethene + cineole and the ternary ethene + limonene + cineole (Matos *et al.*, 1994), we conclude that this technique may not be suitable for the separation of these pinenes, because there is not a significant enrichment of one of the components in the vapor phase. It is likely that the use of a suitable entrainer may change these conclusions.

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