Vapor−Liquid Equilibrium Data of α-Pinene + *β*-Pinene + Limonene at 80 kPa and 101 kPa

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Vapor−liquid equilibrium data for the ternary system α-pinene + *β*-pinene + (*S*)-(−)-limonene were determined at 80.0 kPa and 101.3 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. Predictions of the ternary data by parameters determined using binary data were made. 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 pharmaceutical and cosmetic industries.

Bernardo-Gil and Ribeiro (1989) determined experimental 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 (53.3 and 80.0) kPa. Rodrigues and Bernardo-Gil (1995) reported VLE results for binary systems α-pinene + (*S*)-(−)-limonene and *β*-pinene + (*S*)-(−)-limonene at (53.3 and 80.0) kPa.

This paper reports the experimental data on VLE of the ternary system α-pinene + *β*-pinene + (S)-(−)limonene at (80.0 and 101.3) kPa.

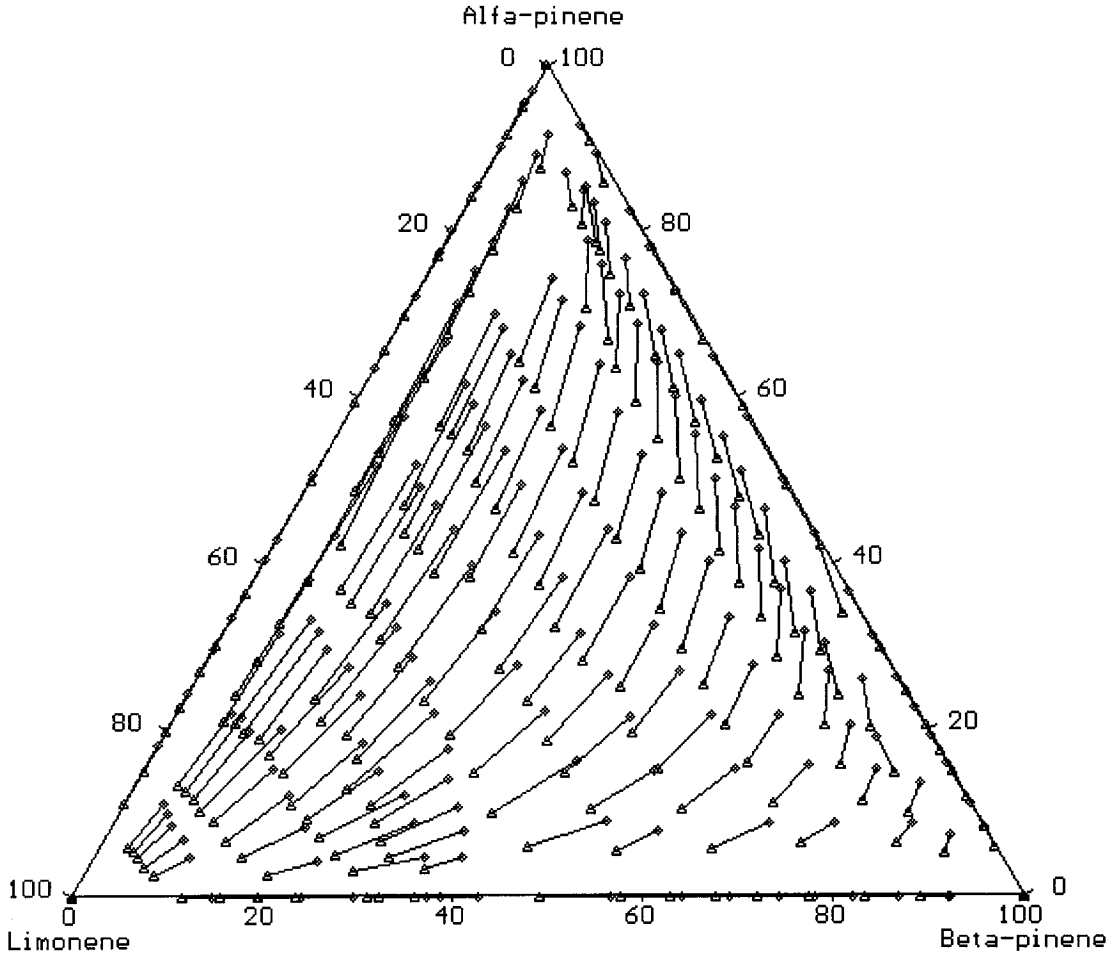

Figure 1. Tie lines of α-pinene + *β*-pinene + (*S*)-(−)-limonene at 80.0 kPa: (Δ) liquid phase; (◊) vapor phase.

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

component	Antoine constants				mol liq vol const	
	A	*B*	*C*	temp 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] $\ln(P/\text{kPa}) = A - B/(T/\text{K}-C)$. [b] $v_m^L/\text{cm}^3\ \text{mol}^{-1} = D + ET/\text{K}$.

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

component	T_b/K		critical parameters			*r*	*q*
			T_c/K	P_c/kPa	Z_c		
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).

Table 3. Experimental Vapor−Liquid Equilibrium Data of α-Pinene (1) + *β*-Pinene (2) + (*S*)-(−)-Limonene (3) at 80.0 kPa

T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2
429.48	0.053	0.891	0.074	0.887	432.14	0.057	0.644	0.087	0.690	425.98	0.566	0.221	0.685	0.192	436.58	0.050	0.251	0.088	0.315
428.97	0.101	0.830	0.136	0.824	430.99	0.104	0.589	0.153	0.621	425.75	0.611	0.182	0.717	0.157	436.31	0.071	0.224	0.122	0.288
428.65	0.148	0.790	0.192	0.751	431.17	0.153	0.541	0.218	0.563	425.38	0.641	0.150	0.744	0.134	436.21	0.093	0.201	0.151	0.247
428.26	0.203	0.739	0.261	0.701	430.70	0.196	0.491	0.272	0.504	435.97	0.110	0.175	0.184	0.214	427.26	0.594	0.000	0.722	0.000
427.73	0.243	0.685	0.305	0.639	430.18	0.251	0.451	0.327	0.449	435.33	0.147	0.148	0.243	0.183	426.14	0.657	0.000	0.774	0.000
427.16	0.295	0.641	0.368	0.593	429.76	0.283	0.395	0.384	0.395	435.21	0.170	0.122	0.277	0.153	425.25	0.697	0.000	0.801	0.000
426.74	0.316	0.602	0.403	0.548	429.20	0.324	0.347	0.441	0.343	435.05	0.189	0.102	0.297	0.119	423.97	0.771	0.000	0.853	0.000
426.25	0.377	0.551	0.467	0.496	428.79	0.375	0.303	0.486	0.295	434.92	0.197	0.083	0.319	0.100	422.73	0.841	0.000	0.902	0.000
425.76	0.434	0.507	0.512	0.448	428.40	0.414	0.258	0.539	0.247	434.87	0.208	0.069	0.334	0.085	421.63	0.917	0.000	0.955	0.000
425.18	0.480	0.463	0.553	0.409	427.99	0.467	0.212	0.584	0.201	437.82	0.025	0.192	0.043	0.237	420.82	0.950	0.000	0.969	0.000
424.87	0.527	0.416	0.597	0.364	427.77	0.498	0.176	0.620	0.165	437.81	0.047	0.155	0.084	0.203	420.06	1.000	0.000	1.000	0.000
424.49	0.571	0.370	0.651	0.315	427.43	0.537	0.147	0.651	0.136	437.40	0.067	0.129	0.121	0.169	439.99	0.000	0.115	0.000	0.148
423.93	0.610	0.329	0.681	0.280	427.19	0.555	0.122	0.682	0.113	437.40	0.090	0.105	0.153	0.135	439.65	0.000	0.155	0.000	0.195
423.57	0.649	0.290	0.723	0.240	426.99	0.566	0.104	0.699	0.095	437.35	0.102	0.083	0.201	0.119	439.04	0.000	0.195	0.000	0.241
423.15	0.709	0.233	0.767	0.199	433.00	0.055	0.546	0.078	0.577	437.39	0.116	0.071	0.198	0.087	438.44	0.000	0.235	0.000	0.295
422.84	0.747	0.194	0.811	0.157	432.68	0.104	0.494	0.150	0.538	437.43	0.127	0.057	0.216	0.071	437.42	0.000	0.310	0.000	0.372
422.56	0.776	0.169	0.834	0.133	432.09	0.147	0.445	0.216	0.479	437.39	0.133	0.045	0.221	0.057	437.19	0.000	0.322	0.000	0.388
422.88	0.787	0.158	0.855	0.113	431.66	0.187	0.406	0.267	0.431	439.43	0.025	0.074	0.047	0.100	436.75	0.000	0.360	0.000	0.427
421.94	0.808	0.133	0.850	0.114	431.28	0.234	0.361	0.316	0.377	439.34	0.036	0.059	0.069	0.084	435.26	0.000	0.492	0.000	0.567
421.77	0.831	0.111	0.870	0.086	430.88	0.273	0.314	0.385	0.324	439.29	0.046	0.046	0.085	0.063	434.24	0.000	0.576	0.000	0.642
429.98	0.065	0.835	0.089	0.840	430.56	0.321	0.270	0.434	0.274	439.27	0.055	0.039	0.099	0.052	433.61	0.000	0.630	0.000	0.691
429.10	0.115	0.774	0.154	0.770	429.13	0.385	0.226	0.495	0.225	439.27	0.059	0.030	0.113	0.041	433.33	0.000	0.677	0.000	0.743
428.75	0.158	0.730	0.205	0.716	429.48	0.390	0.186	0.536	0.188	421.82	0.877	0.054	0.917	0.043	433.04	0.000	0.721	0.000	0.781
428.13	0.206	0.689	0.271	0.660	429.15	0.418	0.156	0.565	0.153	422.67	0.828	0.054	0.893	0.043	432.23	0.000	0.776	0.000	0.821
427.92	0.243	0.644	0.320	0.610	428.97	0.437	0.131	0.591	0.128	423.50	0.777	0.055	0.861	0.045	431.80	0.000	0.833	0.000	0.870
427.61	0.287	0.598	0.370	0.561	429.22	0.472	0.113	0.615	0.107	424.41	0.726	0.055	0.828	0.047	431.21	0.000	0.891	0.000	0.922
427.08	0.337	0.556	0.418	0.513	434.19	0.058	0.449	0.091	0.517	425.41	0.675	0.058	0.786	0.050	431.09	0.000	0.893	0.000	0.924
426.62	0.378	0.513	0.468	0.465	433.67	0.101	0.391	0.163	0.450	426.48	0.622	0.060	0.753	0.048	429.73	0.000	1.000	0.000	1.000
426.21	0.416	0.473	0.503	0.426	433.49	0.149	0.348	0.224	0.386	427.46	0.572	0.054	0.713	0.050	420.35	0.910	0.090	0.929	0.071
425.87	0.467	0.426	0.555	0.379	432.92	0.193	0.301	0.278	0.330	428.52	0.534	0.058	0.665	0.061	420.62	0.860	0.130	0.896	0.104
425.23	0.503	0.388	0.600	0.336	432.65	0.234	0.254	0.343	0.273	429.22	0.487	0.054	0.630	0.055	421.20	0.781	0.219	0.825	0.175
424.96	0.550	0.342	0.643	0.295	432.12	0.275	0.206	0.398	0.221	430.22	0.422	0.071	0.577	0.061	421.58	0.729	0.271	0.782	0.218
424.41	0.595	0.297	0.689	0.251	431.94	0.309	0.169	0.443	0.181	431.52	0.380	0.058	0.533	0.055	421.97	0.669	0.331	0.728	0.272
423.98	0.634	0.256	0.724	0.215	431.71	0.340	0.143	0.470	0.148	432.43	0.328	0.054	0.516	0.062	422.83	0.588	0.412	0.650	0.350
423.78	0.669	0.229	0.761	0.178	431.17	0.353	0.117	0.492	0.120	433.45	0.282	0.054	0.435	0.059	423.37	0.496	0.504	0.577	0.423
423.57	0.707	0.187	0.789	0.150	431.02	0.370	0.098	0.519	0.103	434.48	0.243	0.051	0.382	0.059	424.39	0.424	0.576	0.503	0.497
431.29	0.063	0.736	0.087	0.758	436.51	0.032	0.354	0.047	0.387	435.62	0.211	0.054	0.317	0.059	425.05	0.340	0.640	0.438	0.562
430.83	0.113	0.682	0.158	0.697	436.29	0.048	0.308	0.079	0.372	436.34	0.000	0.000	0.000	0.000	425.82	0.300	0.700	0.367	0.633
429.80	0.161	0.631	0.217	0.635	435.93	0.066	0.291	0.108	0.351	438.11	0.112	0.000	0.182	0.000	426.27	0.247	0.753	0.315	0.685
429.83	0.207	0.584	0.279	0.578	435.41	0.087	0.274	0.140	0.326	437.24	0.151	0.000	0.244	0.000	426.83	0.205	0.795	0.264	0.736
429.39	0.254	0.537	0.336	0.523	435.39	0.110	0.259	0.177	0.307	436.13	0.199	0.000	0.297	0.000	427.14	0.175	0.825	0.228	0.772
428.83	0.298	0.493	0.404	0.469	434.86	0.130	0.225	0.221	0.271	435.46	0.227	0.000	0.337	0.000	427.61	0.151	0.849	0.195	0.805
428.41	0.345	0.447	0.437	0.424	434.56	0.166	0.217	0.258	0.248	434.32	0.271	0.000	0.406	0.000	428.00	0.120	0.880	0.160	0.840
427.86	0.395	0.401	0.486	0.377	434.15	0.194	0.193	0.287	0.214	433.59	0.303	0.000	0.431	0.000	428.47	0.082	0.918	0.113	0.887
427.37	0.431	0.357	0.532	0.333	433.72	0.211	0.157	0.323	0.180	432.25	0.365	0.000	0.506	0.000	428.80	0.060	0.940	0.082	0.918
426.61	0.477	0.311	0.581	0.284	433.52	0.237	0.138	0.354	0.153	429.07	0.501	0.000	0.636	0.000					
426.28	0.521	0.267	0.639	0.237	436.91	0.029	0.280	0.048	0.347										

The 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 parametersof Skjold-Jorgensen *et al.* (1979) and of Macedo *et al.* (1983) for the interactions between the groups CH_2 and C═C was also used.

Experimental Section

Materials. The α-pinene (Terpex, 95 mass %), *β*-pinene (Terpex, 93 mass %), and (*S*)-(−)-limonene (Fluka, >97 mass %) were distilled. These fractions were carried out

Table 4. Experimental Vapor−Liquid Equilibrium Data of α-Pinene (1) + *β*-Pinene (2) + (*S*)-(−)-Limonene (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2	T/K	x_1	x_2	y_1	y_2
432.35	0.763	0.139	0.792	0.150	441.32	0.208	0.368	0.302	0.385	435.69	0.381	0.543	0.462	0.502	445.45	0.155	0.000	0.000	0.000
433.23	0.692	0.209	0.771	0.170	442.07	0.176	0.410	0.247	0.429	435.35	0.426	0.518	0.509	0.456	444.35	0.200	0.000	0.000	0.000
434.44	0.596	0.299	0.681	0.256	442.57	0.139	0.432	0.208	0.466	434.71	0.472	0.472	0.555	0.411	442.55	0.281	0.000	0.000	0.000
434.91	0.487	0.400	0.595	0.342	442.83	0.115	0.454	0.174	0.498	434.49	0.506	0.438	0.592	0.375	441.05	0.343	0.000	0.469	0.000
435.95	0.402	0.490	0.502	0.432	442.96	0.097	0.476	0.143	0.520	434.10	0.552	0.391	0.635	0.332	439.75	0.409	0.000	0.542	0.000
436.79	0.333	0.556	0.422	0.508	443.16	0.079	0.486	0.115	0.534	433.61	0.598	0.344	0.682	0.286	438.35	0.484	0.000	0.625	0.000
437.40	0.276	0.612	0.356	0.572	443.31	0.067	0.500	0.104	0.558	433.21	0.646	0.297	0.715	0.251	436.75	0.593	0.000	0.710	0.000
438.03	0.233	0.659	0.296	0.631	443.49	0.057	0.510	0.087	0.570	432.75	0.688	0.253	0.762	0.205	435.65	0.650	0.000	0.748	0.000
438.43	0.193	0.693	0.254	0.661	439.22	0.440	0.056	0.599	0.061	432.59	0.727	0.215	0.793	0.175	435.25	0.668	0.000	0.754	0.000
438.83	0.162	0.725	0.217	0.704	440.13	0.387	0.087	0.546	0.087	432.24	0.759	0.182	0.819	0.148	434.85	0.695	0.000	0.778	0.000
439.08	0.115	0.772	0.158	0.763	440.77	0.335	0.138	0.479	0.141	432.07	0.780	0.158	0.838	0.127	433.95	0.740	0.000	0.816	0.000
439.44	0.102	0.784	0.140	0.783	441.47	0.283	0.189	0.416	0.199	431.73	0.806	0.137	0.845	0.121	433.55	0.764	0.000	0.838	0.000
433.34	0.739	0.056	0.833	0.057	442.03	0.236	0.239	0.352	0.256	431.57	0.827	0.117	0.873	0.094	433.25	0.765	0.000	0.840	0.000
433.98	0.689	0.107	0.776	0.094	442.72	0.190	0.286	0.287	0.312	431.33	0.841	0.103	0.888	0.080	432.65	0.815	0.000	0.884	0.000
434.95	0.596	0.201	0.699	0.177	443.39	0.152	0.322	0.240	0.361	431.14	0.851	0.090	0.878	0.089	431.55	0.852	0.000	0.915	0.000
436.10	0.492	0.295	0.601	0.265	443.65	0.123	0.353	0.192	0.395	447.43	0.033	0.193	0.095	0.236	429.95	0.931	0.000	0.963	0.000
436.84	0.376	0.386	0.508	0.356	443.92	0.101	0.378	0.156	0.426	447.44	0.057	0.163	0.098	0.209	450.65	0.000	0.000	0.000	0.000
437.80	0.324	0.459	0.407	0.435	444.18	0.067	0.413	0.108	0.475	447.10	0.073	0.134	0.136	0.131	449.45	0.000	0.075	0.000	0.103
438.42	0.263	0.517	0.356	0.499	444.35	0.082	0.396	0.130	0.453	447.01	0.097	0.106	0.168	0.136	449.05	0.000	0.097	0.000	0.132
438.82	0.220	0.564	0.291	0.554	444.51	0.055	0.421	0.090	0.488	446.78	0.113	0.084	0.197	0.110	448.65	0.000	0.122	0.000	0.164
439.38	0.173	0.599	0.250	0.601	444.67	0.055	0.424	0.073	0.500	446.61	0.130	0.071	0.214	0.089	448.15	0.000	0.156	0.000	0.201
439.86	0.152	0.632	0.213	0.635	446.14	0.025	0.363	0.043	0.440	446.55	0.131	0.056	0.231	0.072	447.65	0.000	0.194	0.000	0.250
439.97	0.127	0.658	0.156	0.669	445.98	0.041	0.338	0.067	0.409	446.49	0.142	0.047	0.243	0.054	446.95	0.000	0.245	0.000	0.307
440.16	0.115	0.670	0.145	0.695	445.68	0.066	0.310	0.103	0.370	448.79	0.025	0.078	0.059	0.106	445.95	0.000	0.315	0.000	0.389
440.62	0.077	0.683	0.124	0.719	445.29	0.092	0.287	0.142	0.338	446.30	0.042	0.235	0.073	0.282	444.95	0.000	0.389	0.000	0.470
440.86	0.073	0.711	0.097	0.724	444.77	0.113	0.264	0.179	0.313	447.17	0.034	0.189	0.061	0.243	443.95	0.000	0.475	0.000	0.557
439.66	0.059	0.719	0.086	0.743	444.52	0.136	0.243	0.215	0.285	448.66	0.049	0.050	0.110	0.076	443.05	0.000	0.550	0.000	0.630
435.12	0.652	0.053	0.777	0.047	444.13	0.175	0.194	0.277	0.228	448.60	0.059	0.040	0.113	0.056	442.25	0.000	0.624	0.000	0.695
435.72	0.594	0.103	0.730	0.089	443.57	0.214	0.161	0.331	0.182	448.76	0.062	0.032	0.115	0.043	441.35	0.000	0.713	0.000	0.764
436.25	0.552	0.142	0.669	0.138	443.04	0.245	0.132	0.371	0.149	448.57	0.074	0.027	0.122	0.035	440.75	0.000	0.778	0.000	0.823
436.44	0.502	0.227	0.615	0.208	442.69	0.265	0.108	0.403	0.122	439.50	0.063	0.830	0.085	0.826	440.15	0.000	0.847	0.000	0.874
437.24	0.459	0.250	0.571	0.236	442.46	0.281	0.090	0.418	0.100	440.19	0.052	0.795	0.075	0.821	439.75	0.000	0.913	0.000	0.925
438.00	0.394	0.293	0.520	0.275	442.01	0.298	0.075	0.449	0.083	439.28	0.115	0.772	0.158	0.763	439.35	0.000	0.971	0.000	0.976
438.44	0.349	0.338	0.440	0.329	446.32	0.025	0.260	0.064	0.330	438.35	0.036	0.964	0.053	0.947	439.13	0.000	1.000	0.000	1.000
439.06	0.293	0.387	0.396	0.383	446.20	0.050	0.245	0.086	0.306	435.55	0.097	0.903	0.134	0.866	429.29	1.000	0.000	1.000	0.000
439.94	0.248	0.427	0.349	0.433	445.96	0.073	0.222	0.120	0.273	436.75	0.161	0.839	0.206	0.794					
440.59	0.196	0.467	0.295	0.481	445.82	0.092	0.200	0.156	0.242	436.05	0.226	0.774	0.299	0.701					
441.02	0.171	0.508	0.243	0.523	445.46	0.128	0.160	0.208	0.196	435.15	0.319	0.681	0.385	0.615					
441.40	0.150	0.538	0.208	0.559	445.09	0.157	0.131	0.294	0.165	434.35	0.420	0.580	0.488	0.512					
441.80	0.113	0.560	0.161	0.591	444.76	0.176	0.107	0.279	0.129	433.45	0.516	0.484	0.589	0.411					
442.04	0.097	0.578	0.143	0.611	444.49	0.194	0.089	0.305	0.113	432.85	0.586	0.414	0.655	0.345					
442.28	0.089	0.601	0.108	0.611	444.44	0.208	0.073	0.324	0.086	432.25	0.654	0.346	0.729	0.271					
437.44	0.506	0.069	0.653	0.082	444.12	0.219	0.066	0.346	0.072	431.35	0.751	0.249	0.810	0.190					
437.92	0.430	0.108	0.623	0.101	439.14	0.052	0.891	0.073	0.887	431.25	0.790	0.210	0.829	0.171					
438.96	0.425	0.149	0.567	0.148	438.44	0.101	0.842	0.134	0.827	430.35	0.855	0.145	0.887	0.113					
439.05	0.373	0.199	0.520	0.191	438.11	0.150	0.791	0.199	0.763	430.25	0.864	0.136	0.896	0.104					
439.71	0.337	0.240	0.462	0.239	437.58	0.197	0.745	0.256	0.706	429.55	0.919	0.081	0.945	0.055					
440.33	0.273	0.296	0.395	0.289	437.04	0.243	0.699	0.310	0.653	428.75	0.992	0.008	0.995	0.005					
440.94	0.251	0.321	0.355	0.333	436.43	0.289	0.653	0.360	0.601	448.85	0.050	0.000	0.077	0.000					
436.32	0.333	0.610	0.413	0.552	447.05	0.097	0.000	0.000	0.000										

in a Vigreux column 1.5 m long and with a 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 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 experimental equilibrium data were measured in a modified miniature Othmer still. Equilibrium temperatures were measured with a platinum resistance thermometer coupled to a high-precision 6900 Comarc microprocessor to within ±0.01 K, the accuracy of the measurements being 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 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 components. Calibrations were carried out 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.

Results and Data Analysis

Pure Components. The Antoine constants used for α-pinene and (*S*)-(−)-limonene (Nadais and Bernardo-Gil, 1993) and for *β*-pinene (Bernardo-Gil and Ribeiro, 1993) are listed in Table 1. Molar liquid volumes of the pure components were calculated from densities (Ribeiro and Bernardo-Gil, 1990) and were correlated linearly with temperature, the values of parameters being also 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, the van der Waals molecular volumes and surface areas V_i and A_i (Bondi, 1968):

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

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

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

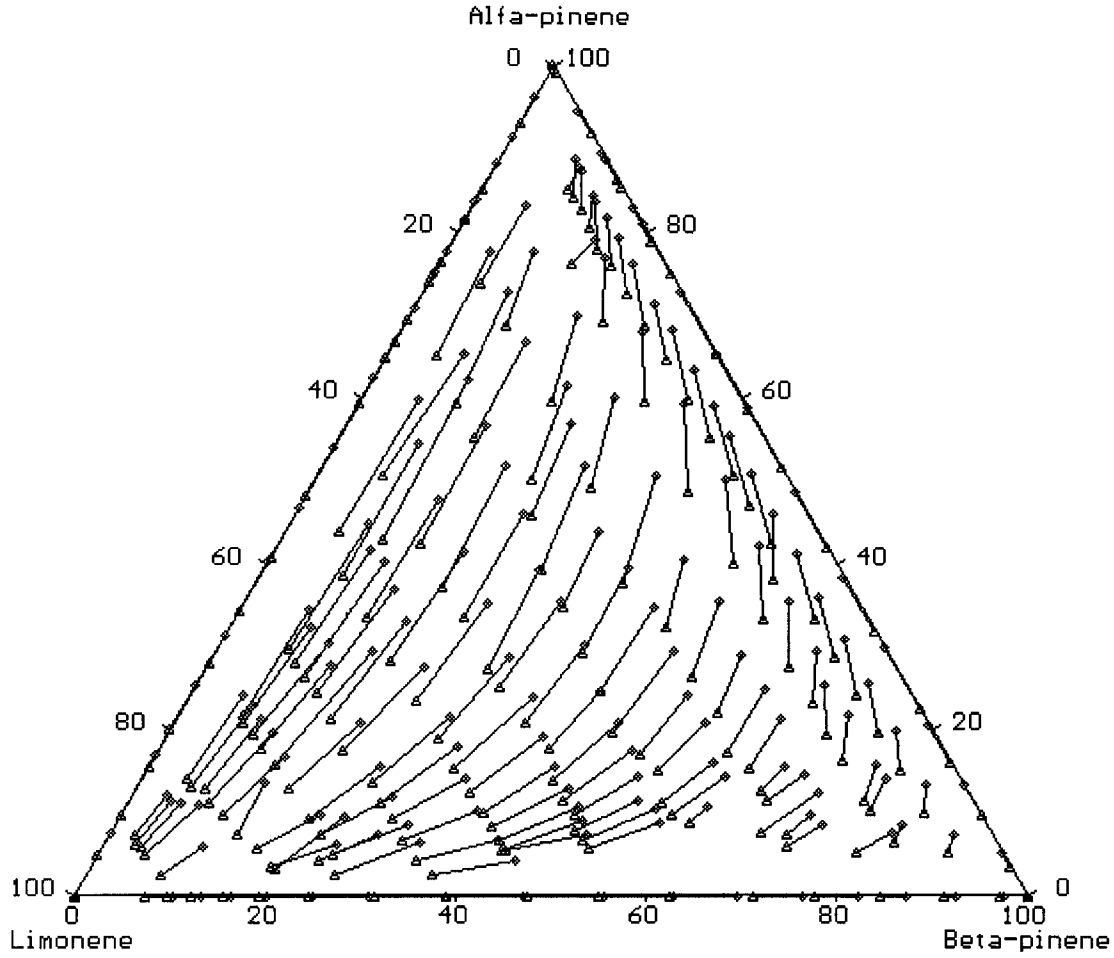

Figure 2. Tie lines of α-pinene + *β*-pinene + (*S*)-(−)-limonene at 101.3 kPa. (Δ) liquid phase; (◊) vapor phase.

Table 5. Root Mean Square Deviations between Experimental and Calculated Data, Using Direct Correlation (DC) and Using Parameters Obtained by Correlation of Binary Data (PR), and Absolute Deviation in Vapor Mole Fraction Obtained in the Consistency Tests, for the System α-Pinene + *β*-Pinene + (*S*)-(−)-Limonene at 80.0 kPa

	root mean square deviations		consistency tests
models	Δ*P*/kPa	Δ*y*	Δ
			0.03
	DC		
Wilson	1.54	0.034	
NRTL (α = 0.4)	0.65	0.013	
UNIQUAC	2.43	0.018	
	PR		
Wilson	1.54	0.033	
NRTL (α = 0.4)	0.73	0.012	
UNIQUAC	3.96	0.024	
UNIFAC[a]	0.95	0.013	
UNIFAC[b]	0.94	0.013	
ideal solution ($\gamma = 1$)	1.00	0.013	

[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, Using Direct Correlation (DC) and Using Parameters Obtained by Correlation of Binary Data (PR), and Absolute Deviation in Vapor Mole Fraction Obtained in the Consistency Tests, for the System α-Pinene + *β*-Pinene + (*S*)-(−)-Limonene at 101.3 kPa

	root mean square deviations		consistency tests
models	Δ*P*/kPa	Δ*y*	Δ
			0.03
	DC		
Wilson	1.60	0.020	
NRTL (α = 0.4)	0.98	0.017	
UNIQUAC	1.53	0.021	
	PR		
Wilson	1.84	0.036	
NRTL (α = 0.4)	2.82	0.020	
UNIQUAC	1.91	0.020	
UNIFAC[a]	1.35	0.016	
UNIFAC[b]	1.35	0.016	
ideal solution ($\gamma = 1$)	1.52	0.016	

[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.

Ternary Data. The experimental VLE data of α-pinene + *β*-pinene + (*S*)-(−)-limonene at 80.0 kPa and 101.3 kPa are presented in Tables 3 and 4, respectively. In Figures 1 and 2 representations of tie lines, respectively at 80.0 kPa and 101.3 kPa, are shown.

The thermodynamic consistency of the data was tested using the McDermott two points consistency test, described by McDermott and Ellis (1965), based on the Gibbs−Duhem equation in isothermal and isobaric conditions

$$\sum_{i=1}^{M} x_i d(\log \gamma_i) = 0 \qquad (3)$$

Table 7. Model Parameters for the System α-Pinene (1) + β-Pinene (2) + (*S*)-(−)-Limonene (3), at (80.0 and 101.3) kPa, Obtained by Correlation of Ternary Data (DC)

equation	A_{12}/K	A_{13}/K	A_{21}/K	A_{23}/K	A_{31}/K	A_{32}/K
			$P = 80.0$ kPa			
Wilson	1.584	−16.09	30.93	1.731	20.06	−162.7
NRTL (α = 0.4)	−1.498	−17.03	32.41	178.8	19.43	−183.1
UNIQUAC	−4.563	45.76	3.455	292.4	−99.64	−203.0
			$P = 101.3$ kPa			
Wilson	−5.405	36.51	2.143	255.6	−19.73	−246.6
NRTL (α = 0.4)	−25.97	10.55	23.17	−229.9	3.026	227.6
UNIQUAC	−24.75	6.091	22.34	−234.9	2.252	180.5

where M is the number of components in the mixture, x_i is the liquid mole fraction of the component i, and γ_i is the activity coefficient of the component i.

After integration and reduction to a couple of points (c and d) the resulting formula for application is

$$\sum_{i=1}^{N}(x_{i,c} + x_{i,d})\left(\log \frac{\gamma_{i,d}}{\gamma_{i,c}}\right) \tag{4}$$

With McDermott's two points test it is possible to analyze the consistency of each point, by itself. A P, T, x_i, y_i (where P is the pressure, T is the temperature, and y_i is the vapor mole fraction of the component i) data point is consistent if the deviations between a point and its neighbors is less than 3%. Results on the consistency of ternary data are presented in Tables 5 and 6, in terms of Δ, the sum of all the deviations for each isotherm.

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

$$F = \sum_{j=1}^{N}(P_j^{\text{cal}} - P_j^{\text{exp}})^2 \tag{5}$$

where N is the number of data points.

The root mean square deviations between the experimental and calculated values of pressure and vapor mole fraction, using the ternary experimental data to obtain the parameters for the equations referred to as DC, are shown in Tables 5 and 6. The numerical values of these binary parameters (A_{ij} and A_{ji}, in K) for the system studied, at each pressure, are presented in Table 7. The NRTL nonrandomness parameter, α_{ij}, was assumed to be 0.4.

Predictions of ternary data using parameters obtained from binary data (Bernardo-Gil and Ribeiro, 1993; Bernardo-Gil and Barreiros, 1994; Rodrigues and Bernardo-Gil, 1995) were made. In Tables 5 and 6, the root mean square deviations for P and y, using these parameters (PR), are shown. In these tables root mean square deviations for P and y, considering the solution as ideal, and those obtained when the UNIFAC parameters of Skjold-Jorgensen *et al.* (1979) and of Macedo *et al.* (1983) are used, are also presented.

No significant differences were found in the deviations when one or another equation is used, although the best results were obtained when the NRTL equation was used.

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