High-Pressure Phase Diagrams of Propane + 1,2,3,4-Tetrahydronaphthalene and Propane + 1-Methylnaphthalene Mixtures

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Equilibrium data on the propane + 1,2,3,4-tetrahydronaphthalene (tetralin) and propane + 1-methylnaphthalene at 394, 419, and 444 K are reported. The data have been obtained with a rather low-pressure cell (0–50 MPa, 293–473 K) and an infrared absorption method. In the absence of any literature data to which our results could be compared, the efficiency of the infrared calibration has been tested by applying the synthetic method for one point of the equilibrium curve of the propane + 1-methylnaphthalene mixture.

Introduction

Vapor–liquid equilibrium data are needed either to fix parameters in separation processes or to develop models that, in turn, will provide predicted data for more complex mixtures. Hydrocarbon binaries including methane have been studied frequently, most often with the sampling method, which can become inaccurate when high-molecular-weight solutes are included, or the synthetic method, which is accurate but very tedious to perform experimentally.

The infrared absorption method holds the advantages of in situ and real-time measurements of the concentrations of each species in both the gas and liquid phases. We have already used this method for the determination of vapor–liquid equilibria of methane with 1-methylnaphthalene,[1] hexane and benzene,[2] squalane and hexatriacontane,[3] and tetralin and 9,10-dihydrophenanthrene.[4] The mathematical treatment of the absorption spectra has been briefly described in some of the papers cited previously and more recently in a paper entirely devoted to improvement of the accuracy of the approach by a special treatment of the baselines.[4]

In the present paper, vapor–liquid equilibrium data on propane with tetralin (1,2,3,4-tetrahydronaphthalene) and 1-methylnaphthalene are reported. Experimental data on these binaries are rather scarce. Propane + tetralin has been studied at 273.15 and 293.15 K with a maximum pressure of 0.467 MPa.[5] Propane + 1-methylnaphthalene has been studied over a more extended range of temperature but under a pressure of about 1 bar.[6]

Experimental Section

Materials. The purity of propane was 99.95%. Tetralin and 1-methylnaphthalene were supplied by Aldrich with purities of 99% and 98%, respectively. Higher purities could not be found.

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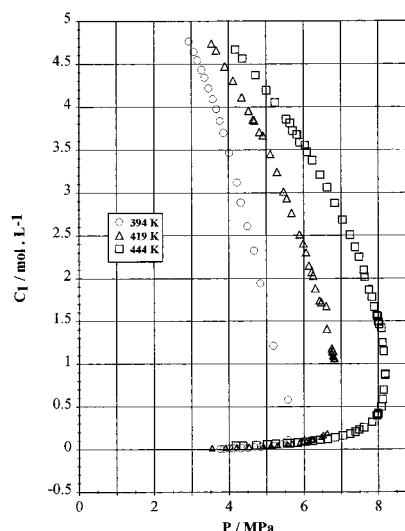
Figure 1. Concentration of tetralin as a function of pressure in the gas and liquid coexisting phases for the mixture propane + tetralin: ○, 394 K; △, 419 K; □, 444 K.

Accuracy. A great advantage of the infrared absorption method is that it provides direct access to the concentrations (in moles per liter) of each component in each of the liquid and gas phases. The mole fraction of propane is then obtained by calculating $x,y = C_2/(C_1 + C_2)$, where C_1 and C_2 are the concentrations of the heavy component and propane, respectively. The concentrations were obtained with an accuracy of better than 1%, and the uncertainty of the mole fraction can be calculated with

$$\frac{\Delta y}{y} = 2\frac{\Delta c}{c}(1 - y) \tag{1}$$

The pressure gauge accuracy, 0.05 MPa, was the main source of uncertainty.

Table 1. Vapor−Liquid Equilibrium Data for Tetraline (1) + Propane (2) at 394, 419, and 444 K

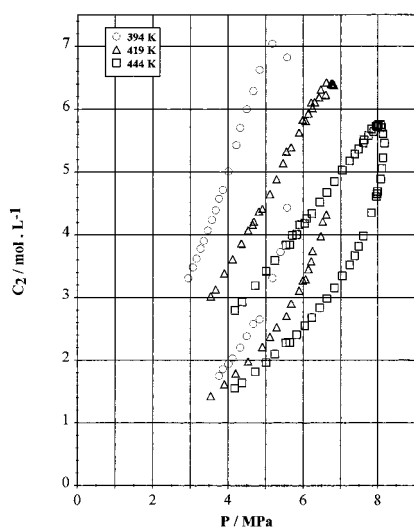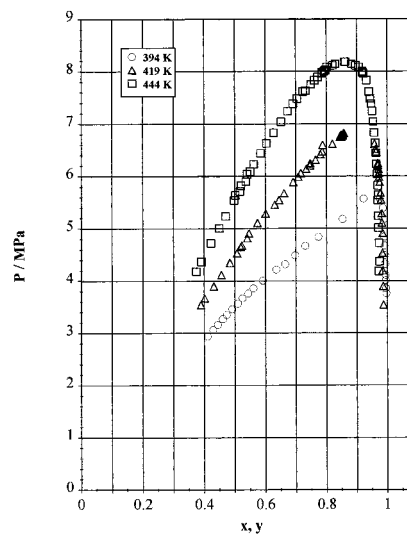|	gas phase		liquid phase			gas phase		liquid phase	
P (MPa)	C_1 (mol L^{-1})	C_2 (mol L^{-1})	C_1 (mol L^{-1})	C_2 (mol L^{-1})	P (MPa)	C_1 (mol L^{-1})	C_2 (mol L^{-1})	C_1 (mol L^{-1})	C_2 (mol L^{-1})
				$T = 394$ K					
2.94			4.763	3.311	4.01	0.012	1.943	3.465	5.013
3.06			4.642	3.485	4.11	0.013	2.031		
3.16			4.544	3.624	4.22			3.121	5.431
3.27			4.431	3.782	4.32	0.017	2.202	2.886	5.705
3.35			4.341	3.905	4.49	0.020	2.383	2.610	6.002
3.46			4.217	4.072	4.67	0.025	2.580	2.327	6.289
3.57			4.091	4.242	4.84	0.029	2.651	1.945	6.627
3.67			3.978	4.395	5.18	0.041	3.314	1.214	7.041
3.76	0.007	1.752	3.838	4.579	5.39	0.057	3.728		
3.86	0.010	1.859	3.698	4.720	5.57	0.110	4.435	0.581	6.823
				$T = 419$ K					
3.54	0.019	1.428	4.740	3.022	5.89	0.081	3.114	2.512	5.630
3.67			4.662	3.129	5.99	0.092	3.279	2.409	5.835
3.90	0.023	1.616	4.473	3.389	6.06	0.092	3.296	2.304	5.818
4.12			4.306	3.614	6.14	0.103	3.457	2.150	5.935
4.20	0.028	1.789			6.21	0.116	3.581	2.073	6.108
4.35			4.114	3.865	6.25	0.122	3.746	2.033	6.018
4.53	0.033	1.980	3.956	4.075	6.31			1.883	6.115
4.65			3.855	4.166	6.42			1.740	6.191
4.68			3.843	4.216	6.47	0.151	3.982	1.719	6.314
4.82			3.709	4.376	6.52	0.168	4.217		
4.91	0.035	2.215	3.668	4.417	6.60			1.675	6.229
5.11	0.043	2.375	3.451	4.653	6.62	0.190	4.325	1.409	6.425
5.29	0.048	2.528	3.244	4.887	6.75	1.129	6.410	1.182	6.403
5.46			3.013	5.143	6.77	1.088	6.393	1.156	6.398
5.55	0.057	2.708	2.936	5.331	6.79	1.082	6.393	1.146	6.407
5.68	0.066	2.906	2.763	5.394	6.82	1.051	6.384	1.068	6.389
				$T = 444$ K					
4.18	0.045	1.552	4.668	2.796	7.24	0.184	3.519	2.507	5.176
4.37	0.044	1.643	4.565	2.931	7.38	0.205	3.668	2.365	5.286
4.72	0.052	1.817	4.370	3.193	7.48	0.229	3.816	2.250	5.364
5.01	0.060	1.967	4.194	3.422	7.61	0.256	3.982	2.097	5.464
5.24	0.067	2.098	4.050	3.593	7.63			2.017	5.511
5.54	0.076	2.278	3.856	3.835	7.75			1.867	5.579
5.64	0.072	2.282	3.813	3.844	7.83	0.318	4.352	1.782	5.683
5.71			3.724	3.994	7.89			1.668	5.646
5.82	0.079	2.405	3.679	4.006	7.96	0.395	4.612	1.567	5.728
5.90			3.583	4.163	7.98	0.409	4.654	1.555	5.732
6.04	0.089	2.551	3.552	4.184	8.00	0.420	4.690	1.495	5.738
6.09			3.475	4.263	8.02			1.464	5.757
6.23	0.100	2.681	3.378	4.342	8.08	0.500	4.889	1.418	5.756
6.44	0.112	2.840	3.209	4.522	8.11	0.585	5.059	1.251	5.709
6.63	0.122	2.983	3.062	4.675	8.14	0.695	5.227	1.150	5.609
6.83	0.141	3.155	2.877	4.851	8.18	0.870	5.460	0.882	5.461
7.04	0.162	3.347	2.684	5.030					

Figure 2. Concentration of propane as a function of pressure in the gas and liquid coexisting phases for the mixture propane + tetralin: ○, 394 K; △, 419 K; □, 444 K.

Figure 3. Phase diagrams of propane + tetralin: ○, 394 K; △, 419 K; □, 444 K. $x,y = C_2/(C_1 + C_2)$ = mole fraction of propane.

Table 2. Vapor−Liquid Equilibrium Data for 1-Methylnaphthalene (1) + Propane (2) at 394, 419, and 444 K

	gas phase		liquid phase			gas phase		liquid phase	
P (MPa)	C_1 (mol L^{-1})	C_2 (mol L^{-1})	C_1 (mol L^{-1})	C_2 (mol L^{-1})	P (MPa)	C_1 (mol L^{-1})	C_2 (mol L^{-1})	C_1 (mol L^{-1})	C_2 (mol L^{-1})
				$T = 394$ K					
0.74			6.499	0.655	4.79	0.041	2.638	2.814	6.006
1.22			6.261	1.089	4.85			2.717	6.106
1.72			6.018	1.533	4.89	0.045	2.753	2.602	6.227
2.56	0.011	0.980	5.404	2.589	4.96	0.044	2.849	2.494	6.332
2.66	0.014	1.016	5.320	2.721	5.01	0.046	2.932	2.363	6.463
2.84	0.023	1.130	5.176	2.938	5.08	0.048	3.032	2.197	6.602
2.99	0.025	1.201	5.083	3.077	5.09	0.055	3.060	2.113	6.682
3.08	0.027	1.263	4.996	3.212	5.14	0.054	3.158	2.031	6.745
3.25	0.023	1.363	4.854	3.428	5.16			1.881	6.863
3.43	0.025	1.477	4.681	3.678	5.18	0.054	3.173	1.852	6.882
3.63	0.030	1.607	4.484	3.972	5.19	0.054	3.208		
3.77	0.025	1.715	4.346	4.183	5.22	0.060	3.301	1.847	6.887
3.82	0.023	1.769	4.309	4.233	5.24	0.056	3.254	1.784	6.925
3.96	0.027	1.860	4.147	4.450	5.26	0.060	3.361	1.722	6.969
4.08	0.031	1.943	4.009	4.648	5.30	0.066	3.456	1.585	7.042
4.42	0.033	2.239	3.365	5.387	5.36	0.067	3.527	1.411	7.122
4.55	0.036	2.353	3.177	5.611	5.41	0.072	3.669	1.289	7.166
4.63	0.039	2.454	3.097	5.698	5.46	0.078	3.779	1.205	7.186
4.68	0.037	2.500	3.013	5.790	5.49			1.094	7.198
4.73	0.038	2.566	2.916	5.896	5.52			1.034	7.194
				$T = 419$ K					
0.83			6.452	0.546	5.88	0.074	2.807	3.321	4.986
1.26			6.293	0.830	5.97	0.080	2.891	3.243	5.068
1.75			6.078	1.199	6.04	0.083	2.960	3.165	5.152
1.95			6.006	1.313	6.11	0.086	3.047	3.078	5.245
2.92	0.024	0.971	5.453	2.189	6.20	0.093	3.142	2.968	5.359
3.14	0.028	1.074	5.338	2.375	6.28			2.859	5.468
3.42	0.030	1.216	5.201	2.584	6.38	0.102	3.336	2.822	5.501
3.68	0.029	1.336	5.064	2.790	6.46	0.111	3.448	2.746	5.574
3.94	0.033	1.469	4.917	3.007	6.50			2.677	5.632
4.20	0.038	1.618	4.748	3.255	6.53	0.116	3.547	2.638	5.668
4.44	0.041	1.755	4.588	3.467	6.55	0.119	3.524		
4.70	0.045	1.913	4.401	3.729	6.60	0.123	3.644	2.566	5.744
4.93	0.045	2.053	4.237	3.947	6.64	0.131	3.687	2.511	5.773
5.13	0.052	2.202	4.099	4.124	6.71	0.137	3.794	2.386	5.874
5.17	0.057	2.237			6.76	0.148	3.878	2.378	5.881
5.26	0.059	2.309			6.83	0.158	3.998	2.208	6.003
5.33	0.061	2.341			6.88	0.163	4.092	2.207	6.004
5.34	0.061	2.368	3.911	4.358	6.96	0.177	4.192	2.077	6.102
5.36			3.869	4.342	7.00	0.192	4.282	2.015	6.134
5.43	0.063	2.341			7.08	0.207	4.469	1.880	6.211
5.51			3.685	4.565	7.14	0.239	4.644	1.767	6.261
5.52	0.064	2.501			7.20	0.265	4.803	1.642	6.309
5.59	0.065	2.534	3.619	4.644	7.28	0.324	5.073	1.478	6.352
5.68	0.070	2.613	3.534	4.747	7.40	0.962	6.196	1.268	6.348
5.73	0.071	2.653	3.494	4.794	7.47	0.871	6.217	0.883	6.205
5.79	0.073	2.726	3.392	4.909					
				$T = 444$ K					
1.26			6.267	0.714	7.38			3.157	4.898
1.52			6.181	0.855	7.42	0.147	3.362	3.152	4.918
2.01			6.010	1.145	7.49	0.147	3.342	3.070	4.988
2.53			5.808	1.456	7.53	0.152	3.453	3.077	4.992
2.82	0.023	0.844	5.657	1.719	7.59	0.165	3.545	3.008	5.047
3.14	0.024	0.960	5.527	1.912	7.67	0.169	3.583	2.981	5.084
3.38	0.031	1.055	5.426	2.064	7.73	0.174	3.685	2.879	5.169
3.62	0.036	1.159	5.327	2.214	7.78	0.179	3.689	2.876	5.185
3.86	0.037	1.246	5.221	2.369	7.81	0.177	3.643		
4.11	0.037	1.340	5.113	2.527	7.83	0.188	3.783	2.759	5.270
4.33	0.040	1.435	5.013	2.673	7.89	0.195	3.819	2.775	5.268
4.58	0.046	1.567	4.900	2.839	7.92	0.187	3.768		
4.83	0.038	1.676	4.776	3.006	7.94	0.205	3.900	2.654	5.362
5.08	0.046	1.817	4.639	3.189	7.98	0.207	3.930	2.681	5.346
5.34	0.053	1.937	4.516	3.356	8.00	0.225		2.578	5.418
5.59	0.064	2.080	4.385	3.536	8.03	0.205	3.894		
5.78	0.069	2.162	4.230	3.655	8.09	0.209	3.966		
5.86	0.067	2.242	4.223	3.736	8.10	0.227	4.059		
5.94	0.075	2.258	4.128	3.792	8.17	0.224	4.043		
6.08	0.078	2.345	4.038	3.896	8.12	0.239		2.474	5.502
6.16	0.079	2.393	4.028	3.940	8.22	0.260		2.369	5.580
6.18	0.082	2.414	3.971	3.985	8.24	0.246	4.127		
6.30	0.086	2.497	3.896	4.072	8.25	0.243	4.132		
6.36	0.087	2.510	3.909	4.084	8.31			2.276	5.640

Table 2 (Continued)

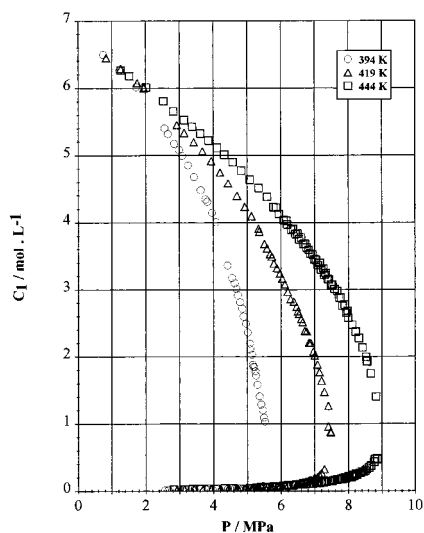|	gas phase		liquid phase			gas phase		liquid phase	
P (MPa)	C_1 (mol L^{-1})	C_2 (mol L^{-1})	C_1 (mol L^{-1})	C_2 (mol L^{-1})	P (MPa)	C_1 (mol L^{-1})	C_2 (mol L^{-1})	C_1 (mol L^{-1})	C_2 (mol L^{-1})
				$T = 444$ K					
6.43	0.094	2.566	3.830	4.155	8.35	0.269	4.274		
6.49			3.834	4.175	8.36	0.268	4.289		
6.54	0.097	2.661	3.752	4.241	8.41	0.286	4.402		
6.60			3.776	4.243	8.42			2.136	5.727
6.66	0.102	2.746	3.681	4.328	8.44	0.287	4.381		
6.71	0.103	2.772	3.682	4.349	8.50	0.302	4.463		
6.76	0.107	2.823	3.629	4.394	8.53	1.993	5.795		
6.82	0.108	2.849	3.595	4.449	8.54	0.328	4.582	1.928	
6.87	0.111	2.898	3.537	4.492	8.57			1.926	5.829
6.94	0.112	2.941	3.522	4.526	8.61	0.344	4.603		
6.99	0.119	2.988	3.453	4.585	8.67	0.376	4.759	1.746	5.893
7.04	0.117	3.012	3.446	4.615	8.77	0.433	4.960		
7.09	0.125	3.080	3.365	4.679	8.79	0.471	5.081		
7.15	0.123	3.102	3.394	4.670	8.80	0.475	5.075		
7.19	0.132	3.157	3.299	4.747	8.82			1.404	5.938
7.26	0.132	3.182	3.317	4.749	8.85	0.471	5.040		
7.29	0.140	3.248	3.220	4.832	8.86	0.483	5.080		
7.33	0.140	3.273	3.247	4.823					

Figure 4. Concentration of 1-methylnaphthalene as a function of pressure in the gas and liquid coexisting phases for the mixture propane + 1-methylnaphthalene: ○, 394 K; △, 419 K; □, 444 K.
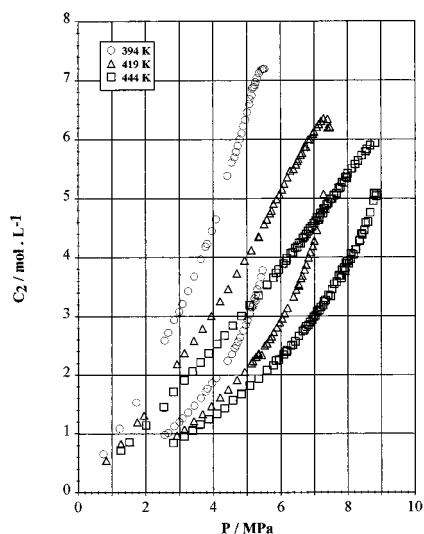

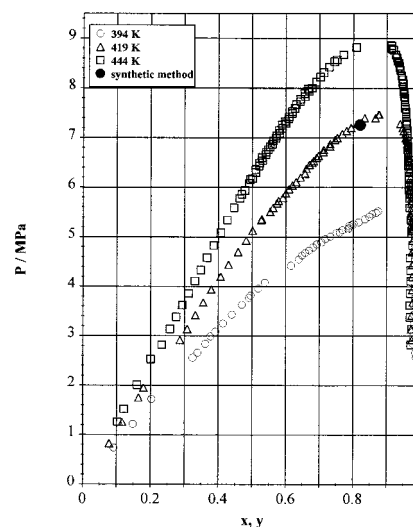**Figure 5.** Concentration of propane as a function of pressure in the gas and liquid coexisting phases for the mixture propane + 1-methylnaphthalene: ○, 394 K; △, 419 K; □, 444 K.

Figure 6. Phase diagram of propane + 1-methylnaphthalene: ○, 394 K; △, 419 K; □, 444 K. $x,y = C_2/(C_1 + C_2)$ = mole fraction of propane; solid circle = synthetic method.

Results

Propane + Tetralin Mixture. Vapor−liquid equilibrium data for the propane + tetralin mixture are reported in Table 1. Tetralin (C_1) and propane (C_2) concentrations in each phase are given at various pressures. Figures 1 and 2 show plots of tetralin and propane concentrations as a function of pressure along the coexistence lines. Pressure−mole fraction plots at 394, 419, and 444 K are shown in Figure 3. It should be noted that the mixture critical pressure increases with temperature, which is opposite to the behavior observed for the methane + tetralin mixture.[4] Because infrared absorption is a very fast method, a great number of measurements could be performed over very small pressure intervals. However, because of the very high compressibility of such a mixture in that temperature range, several fillings of the cell, with various initial compositions of the mixture, were needed to cover the entire pressure range.

Propane + 1-Methylnaphthalene Mixture. Vapor−liquid equilibrium data for the propane + 1-methylnaphthalene mixture are reported in Table 2. 1-Methylnaphthalene (C_1) and propane (C_2) concentrations in each phase

are given at various pressures. Figures 4 and 5 show plots of 1-methylnaphthalene and propane concentrations as a function of pressure along the coexistence lines. Pressure–mole fraction plots at 394, 419, and 444 K are shown in Figure 6. A test of the accuracy of the infrared absorption method was performed by applying the synthetic method to this mixture at 419 K. For that purpose, the composition of the mixture was determined by weighing the components introduced into the cell. Next, starting from a pressure high enough that the system was in a one-phase state, the pressure–volume diagram was plotted versus decreasing pressure. The liquid–gas equilibrium pressure was then reached when a change in the slope is observed. The result obtained is represented by the solid circle in Figure 6. The agreement with the infrared measurements is quite good.

As in the case of the tetralin + propane mixture, several fillings of the cell were required to cover the entire pressure range. Furthermore, the respective volumes of the gas and liquid phases near the critical region sometimes prevented a recording of the infrared spectrum.

List of Symbols

T = temperature, K
P = pressure, MPa
C_1 = concentration of the heavy component (tetralin or 9,10-dihydrophenanthrene)

C_2 = concentration of methane
x = mole fraction of propane in the liquid phase
y = mole fraction of propane in the gas phase

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