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Fluid Phase Equilibria of Ethane + 2-Methylnaphthalene

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Phase boundary pressures between regions of one and two fluid phases have been measured as a function of temperature for 12 mixtures of ethane + 2-methylnaphthalene in the temperature range 278 K to 363 K by means of a synthetic method.

Introduction

Supercritical fluids like carbon dioxide or ethane are potential solvents for the separation of alkanes and aromatic compounds using supercritical extraction (de Haan, 1991). For an economically attractive design of such a separation process the phase behavior of the mixtures involved has to be known. The separation of mixtures of hexadecane and 2-methylnaphthalene using supercritical ethane is one of the separations that was investigated at the Delft University of Technology. The phase behavior of the system ethane + hexadecane was known from the literature (de Goede et al., 1989). For the system ethane + 2-methylnaphthalene only a limited data set of Estrera et al. (1987) is available.

Estrera et al. (1987) showed that in a p,T projection, the system ethane + 2-methylnaphthalene is characterized by the occurrence of a three-phase curve liquid−liquid−vapor, which ends at a high temperature (313 K) in an upper critical end point, where the ethane-rich liquid phase and the vapor phase become identical. At a low temperature (278.88 K) this curve ends in a quadruple point solid 2-methylnaphthalene−liquid−liquid−vapor, which is the point of intersection of the liquid−liquid−vapor curve and another three-phase curve, the solid 2-methylnaphthalene−liquid−vapor curve. This three-phase curve ends at a high temperature in the triple point of pure 2-methylnaphthalene.

Estrera et al. also measured two bubble-point isotherms at 298.15 K and 318.15 K, 2-methylnaphthalene mole fractions of 0.45 to 0.9 and pressures up to 5.5 MPa. In this paper we present fluid phase equilibrium data for this system over a wider range of temperature, composition, and pressure.

Experimental Section

Method. The measurements were carried out in a glass tube apparatus for use with pressures up to 15 MPa and temperatures up to 473 K. With this so-called Cailletet apparatus phase vanishing points, like dew points and bubble points, of mixtures of known composition can be measured visually. A detailed description of the apparatus and the procedure is given by de Loos et al. (1986).

Materials. The mole fraction purity of the ethane used (AGA) was greater than 0.999 95. The 2-methylnaphthalene used in this study was obtained from Merck with a minimum purity of 98 mol % and was purified further by recrystallization from ethanol (Feldman and Orchin, 1952). GC analyses showed that the final product had a minimum purity of 99.2 mol %.

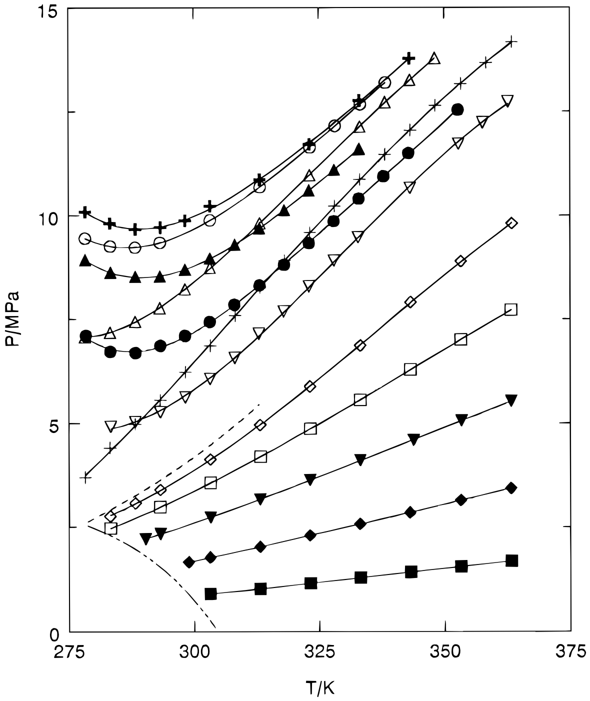

Figure 1. Fluid phase equilibria of {(1 − x)ethane + x2-methylnaphthalene}: phase boundary pressure as a function of temperature for indicated mole fraction x. Symbols, experimental data: (+) x = 0.057; (△) x = 0.087; (○) x = 0.125; (**+**) x = 0.188; (▲) x = 0.293; (●) x = 0.345; (▽) x = 0.378; (◊) x = 0.490; (□) x = 0.584; (▼) x = 0.696; (◆) x = 0.800; (■) x = 0.905. Full curves: best fit to the experimental data. (---) L_2L_1V curve (Estrera et al., 1987) (— - -) SL_2V curve (Estrera et al., 1987).

Results. The p,T behavior in the temperature range of 278 K to 363 K of the 12 binary (1 − x)ethane + x2-methylnaphthalene mixtures investigated is given in Table 1 and plotted in Figure 1 together with the liquid−liquid−vapor curve and solid 2-methylnaphthalene−liquid−vapor curve, as measured by Estrera et al. (1987). x is the 2-methylnaphthalene mole fraction. The full curves are third-order or fourth-order polynomials fitted to the data. The data for x = 0.057, x = 0.087, and x = 0.125 represent at low temperature the transition $L_2 + L_1 \rightarrow L_1$ and at high temperature the transition $L_2 + V \rightarrow V$. L_2 is richer in 2-methylnaphthalene and has a higher density than L_1. For x = 0.293, x = 0.345, and x = 0.378 the transition is at low temperature $L_2 + L_1 \rightarrow L_2$ and at high temperature $L_2 + V \rightarrow L_2$. For x = 0.188 the meniscus disappears almost in the middle over the whole temperature range, so the isopleth for this composition more or less represents the critical curve. For x = 0.490 and higher the transitions are always $L_2 + V \rightarrow L_2$.

From the polynomials fitted to the p,T data isothermal p,x sections were obtained by interpolation. Figure 2 shows

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Table 1. Fluid Phase Equilibria of {(1 − x)Ethane + x 2-Methylnaphthalene}: Phase Boundary Pressure p as a Function of Temperature T for Given Mole Fraction x

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
		$x = 0.057$			
278.30	3.692	313.23	8.253	338.24	11.473
283.23	4.407	318.17	8.903	343.27	12.048
288.24	4.979	323.13	9.588	348.26	12.638
293.26	5.563	328.15	10.228	353.31	13.163
303.27	6.233	333.20	10.868	358.31	13.668
298.28	6.864	338.20	11.468	363.44	14.168
308.26	7.588				
		$x = 0.087$			
278.26	7.078	298.24	8.213	333.19	12.138
283.25	7.178	303.21	8.728	338.21	12.718
288.29	7.438	313.17	9.813	343.17	13.253
293.20	7.763	323.15	10.973	348.13	13.778
		$x = 0.125$			
278.32	9.453	303.26	9.888	328.25	12.157
283.32	9.258	313.22	10.688	333.30	12.672
288.27	9.228	323.25	11.647	338.30	13.192
293.25	9.348				
		$x = 0.188$			
278.34	10.093	298.28	9.875	323.12	11.715
283.26	9.810	293.23	10.229	333.09	12.755
288.31	9.670	313.19	10.869	343.08	13.770
293.35	9.713				
		$x = 0.293$			
278.35	8.923	298.26	8.688	318.11	10.128
283.38	8.618	303.22	8.958	323.04	10.603
293.25	8.518	308.21	9.293	328.08	11.102
298.26	8.523	313.13	9.688	333.05	11.602
		$x = 0.345$			
278.45	7.108	303.18	7.434	328.00	9.864
283.32	6.728	308.11	7.844	332.97	10.409
288.32	6.698	313.15	8.309	337.93	10.949
293.30	6.868	318.07	8.804	342.91	11.504
298.24	7.104	323.05	9.329	352.75	12.539
		$x = 0.378$			
283.38	4.924	308.17	6.575	332.85	9.474
288.26	5.039	312.99	7.149	343.18	10.664
293.29	5.275	317.98	7.679	352.83	11.724
298.28	5.629	323.04	8.279	357.66	12.234
303.22	6.070	328.02	8.904	362.65	12.739
		$x = 0.490$			
283.25	2.762	313.20	4.962	343.26	7.902
288.29	3.073	323.19	5.892	353.29	8.887
293.26	3.398	333.25	6.868	363.42	9.812
303.26	4.127				
		$x = 0.584$			
283.31	2.468	313.27	4.194	343.21	6.289
293.23	2.978	323.25	4.869	353.24	7.009
303.28	3.563	333.22	5.564	363.24	7.714
		$x = 0.696$			
290.28	2.214	313.20	3.164	343.87	4.593
293.27	2.333	323.18	3.629	353.37	5.068
303.28	2.729	333.21	4.103	363.26	5.538
		$x = 0.800$			
298.91	1.668	323.19	2.298	353.24	3.143
303.21	1.778	333.16	2.573	363.19	3.433
313.19	2.029	343.13	2.848		
		$x = 0.905$			
303.22	0.909	333.23	1.293	353.26	1.558
313.19	1.029	343.26	1.428	363.31	1.693
323.25	1.163				

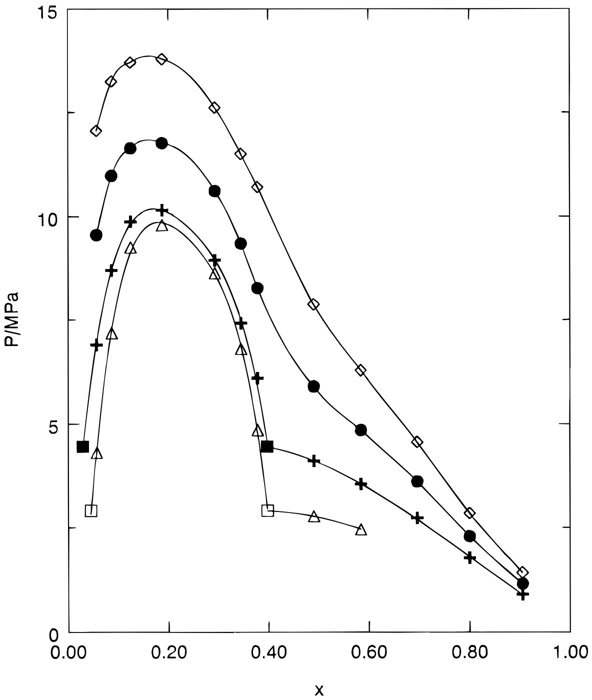

Figure 2. Fluid phase equilibria of {(1 − x)ethane + x2-methylnaphthalene}: isothermal p,x data. Symbols, interpolated experimental data: (△) T = 283.15 K; (+) T = 303.15 K; (●) T = 323.15 K; (◇) T = 343.15 K. Full curves: best fit to experimental data. Symbols, data from L_2L_1V equilibria (Estrera et al., 1987): (□) T = 283.15 K; (■) T = 303.15 K.

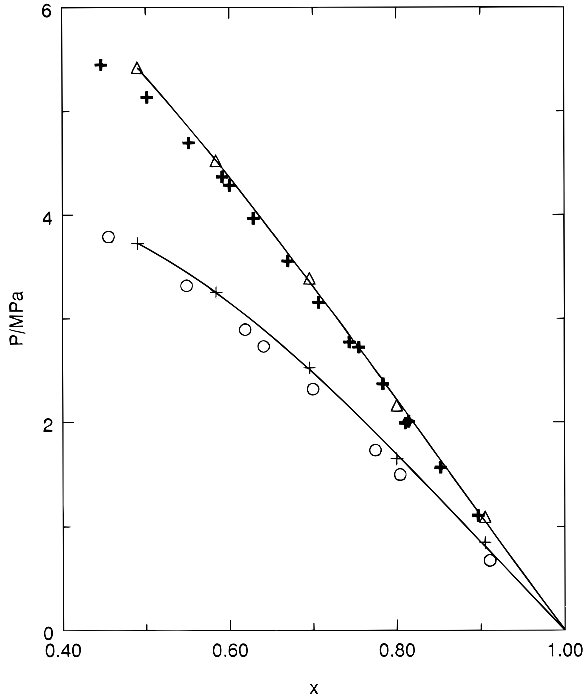

Figure 3. Fluid phase equilibria of {(1 − x)ethane + x2-methylnaphthalene}: isothermal bubble point data. Symbols, interpolated experimental data: (+) T = 298.15 K; (△) T = 318.15 K. Full curves: best fit to experimental data. Symbols, data from Estrera et al. (1987): (○) T = 298.15 K; (+) T = 318.15 K.

these sections at (283.15, 303.15, 323.15, and 343.15) K. At 283.15 K and 303.15 K also the composition of the L_2 and the L_1 phase on the liquid−liquid−vapor curve as found by Estrera et al. (1987) is plotted. At these temperatures a $L_2 + L_1$ equilibrium is found at high pressure and at low pressure a $L_2 + V$ equilibrium. At low mole fractions and pressures higher than the three-phase pressure also a two-phase equilibrium $L_1 + V$ should be found, but no data were collected for this equilibrium. At 323.15 K and 343.15 K the curves represent the $L_2 + V$ equilibrium.

In Figure 3 a comparison is made between the bubble point data as found by Estrera et al. (1987) at 298.15 K and 318.15 K and our bubble point data. The curves show that there is a small but systematic deviation of our results from the data of Estrera et al.

Discussion and Conclusions

This paper presents fluid phase equilibrium data for the system ethane + 2-methylnaphthalene. The results confirm the occurrence of a liquid−liquid−vapor equilibrium at temperatures lower than 313 K. The three-phase pressure at 293.4 K was found to differ only 0.01 MPa from the three-phase pressure found by Estrera et al. However, at a 2-methylnaphthalene mole fraction higher than 0.45, our bubble points can show deviations up to 0.1 MPa from the data of Estrera et al. (1987).

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