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PHASE EQUILIBRIA IN BINARY MIXTURES OF ETHANE AND HEXADECANE

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ABSTRACT

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This paper reports experimental results of a study of the phase behaviour of binary mixtures of ethane + hexadecane. In the near-critical region of ethane liquid + vapour and solid hexadecane + liquid two-phase boundaries have been measured. Also the three-phase equilibrium solid hexadecane + liquid + vapour has been determined experimentally. The experimental data cover the complete mole fraction range. Pressures up to 18 MPa were applied and the investigation was performed in a temperature region from about 260 K up to 450 K.

INTRODUCTION

This contribution is one of a series which studies the systematic change in phase behaviour with carbon number of ethane binaries with higher normal paraffins in the near-critical region of ethane. This phenomenon has been discussed in some previous papers by Peters (1986) and Peters et al. (1986). Excellent overviews of this subject have also been presented by Luks (Luks 1980, 1986). In these papers it has been shown how the phase behaviour changes systematically with increasing carbon number of the higher normal alkane. Binaries up to heptadecane are completely miscible in the liquid phase and binaries from octadecane up to tricosane show partial miscibility in the liquid phase with a lower and upper critical end point, indicated by LCEP and UCEP respectively. Examples of ethane binaries showing this

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type of phase behaviour have recently been discussed by Peters et al. (1987a, 1988) for ethane + eicosane and ethane + docosane respectively. Additional information on this type of phase behaviour has also been given quite recently by Estrera and Luks (1987) and Estrera et al. (1987).

Owing to the simultaneous shift of the triple point of the higher normal paraffin with increasing carbon number to higher temperature on the one hand and the shift of both the LCEP and UCEP to lower temperatures on the other hand, it has to be expected that there will be a carbon number at which the three-phase equilibrium solid higher normal paraffin + liquid + vapour interferes the three-phase equilibrium liquid + liquid + vapour. This phenomenon results in the existence of a quadruple point, i.e. a four-phase equilibrium solid higher normal paraffin + liquid + liquid + vapour. Recently Peters et al. (1987b, c) found this type of phase behaviour in the ethane binaries of pentacosane and tetracosane respectively. In both binaries a LCEP will no longer be present but a UCEP still exists. As the carbon number increases further stable liquid + liquid demixing will be obscured completely by solidification of the higher normal alkane and consequently a UCEP does not exist any longer. For a detailed discussion on this subject reference should be made to the papers cited previously.

So far experimental work has been concentrated on those binaries in which partial miscibility in the liquid phase occurs. This paper, however, reports on a binary without the occurrence of the three-phase behaviour liquid + liquid + vapour.

In the underlying investigation the carbon number of the higher normal alkane has been chosen as low as 16. To the best of our knowledge no experimental data on the binary ethane + hexadecane are available in the literature that allow a comparison with the data obtained in this investigation.

PHASE BEHAVIOUR OF MIXTURES OF ETHANE AND HEXADECANE

Specovius et al. (1981) discussed the fact that mixtures of ethane and higher n-alkanes up to heptadecane are completely miscible in the liquid phase. This type of phase behaviour can most conveniently be represented by means of a p, T, x projection, shown schematically in Fig. 1. In this figure A and B refer to ethane and hexadecane respectively. It can be seen that partial miscibility in the liquid phase will not occur and consequently a three-phase equilibrium liquid + liquid + vapour (l_1l_2g) does not exist. The three-phase equilibrium solid hexadecane + liquid + vapour (s_Blg) runs continuously from the quadruple point s_As_Blg through a maximum in pressure to the triple point of hexadecane. Also the critical locus l=g in this binary

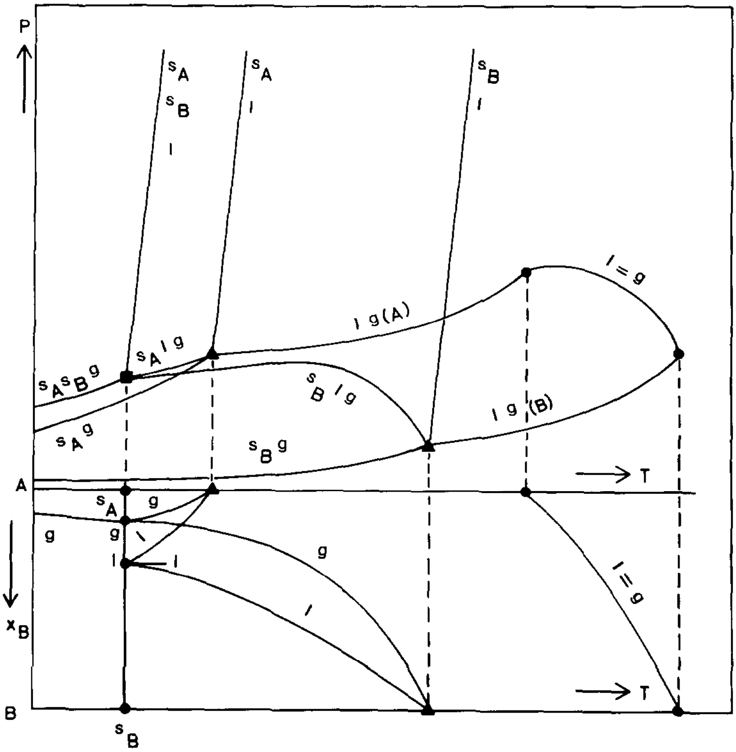

Fig. 1. Schematic *p*, *T*, *x* projection of the phase behaviour of the binary ethane + hexadecane (A, ethane; B, hexadecane).

has a continuous course from the critical point of ethane to the critical point of hexadecane.

EXPERIMENTAL DETAILS

The experimental work has been carried out in a Cailletet apparatus. With this equipment pressures up to approximately 18 MPa are possible and a temperature region from 250 K up to 450 K can be covered. A detailed description of this equipment was given by van der Kooi (1981), de Loos et al. (1983) and Peters (1986). The experimental techniques and procedures to determine the various types of phase equilibria have been discussed in detail by Glaser et al. (1985), Peters (1986) and Coorens et al. (1988).

For pressures lower than 5.0 MPa the accuracy was 0.002 MPa, and for pressures above this value an accuracy of 0.01 MPa could be attained. Over the whole temperature range of interest, the temperature could be determined to an accuracy within 0.01 K. The experimental procedure for

TABLE 1

Experimental p, T data of the two-phase equilibrium vapour+liquid (x, mole fraction hexadecane in the liquid phase)

T (K)	p (MPa)	T (K)	p (MPa)
$x = 0.054$			
262.25	1.748	341.21	9.216
263.22	1.792	350.67	10.373
264.84	1.866	360.35	11.447
265.77	1.910	370.08	12.442
266.70	1.954	370.44	12.467
267.67	2.003	370.67	12.491
268.55	2.047	371.18	12.540
269.37	2.086	373.06	12.722
274.49	2.361	374.93	12.883
278.75	2.601	389.19	14.085
283.38	2.905	399.31	14.786
288.44	3.248	411.26	15.477
293.41	3.611	422.23	15.576
303.21	4.440	422.36	15.992
312.89	5.391	432.29	16.316
322.81	6.681	444.20	16.610
332.84	8.078		
$x = 0.125$			
268.00	1.928	337.51	7.920
272.85	2.153	342.56	8.560
277.80	2.418	342.87	8.613
282.48	2.683	347.34	9.165
282.71	2.708	352.41	9.770
287.78	3.021	352.89	9.809
292.64	3.351	357.13	10.540
298.65	3.805	362.21	10.920
303.65	4.205	362.96	10.956
308.88	4.690	372.99	11.956
312.80	5.065	383.02	12.967
317.79	5.560	393.05	13.839
322.78	6.120	403.08	14.624
327.66	6.705	413.12	15.271
332.57	7.300		
$x = 0.208$			
270.89	1.901	352.62	8.472
272.83	1.986	362.67	9.502
274.15	2.051	372.65	10.492
277.58	2.221	382.74	11.424
282.57	2.486	392.68	12.291
292.50	3.066	402.72	13.080
302.38	3.746	412.73	13.801
322.64	4.556	422.79	14.439

TABLE 1 (continued)

T (K)	p (MPa)	T (K)	p (MPa)
332.44	6.371	432.81	15.003
342.24	7.376	442.87	15.483
342.33	7.381	452.94	15.890
342.68	7.442		
$x = 0.282$			
275.14	1.833	342.96	6.007
275.69	1.857	352.80	6.791
276.82	1.906	362.83	7.576
279.42	2.019	372.83	8.355
283.56	2.202	382.78	9.106
288.42	2.437	392.80	9.836
293.39	2.692	402.83	10.527
298.44	2.957	412.84	11.180
303.29	3.236	422.88	11.793
313.16	3.849	433.04	12.342
323.08	4.531	442.91	12.822
332.90	5.242	452.97	13.273
$x = 0.394$			
279.31	1.598	361.53	5.427
279.50	1.612	371.37	5.964
282.91	1.730	381.15	6.483
287.85	1.902	390.93	7.018
292.75	2.088	400.72	7.523
302.65	2.485	410.55	8.003
312.56	2.922	420.39	8.494
322.36	3.382	430.39	8.910
332.82	3.907	439.41	9.288
341.50	4.372	449.95	9.700
351.57	4.887		
$x = 0.561$			
284.11	1.224	342.21	2.769
284.54	1.234	352.04	3.078
285.50	1.254	361.84	3.392
287.51	1.297	371.83	3.715
292.37	1.410	381.85	4.038
297.35	1.533	391.79	4.352
302.00	1.645	401.77	4.661
308.24	1.828	411.80	4.965
313.98	1.985	422.04	5.269
318.00	2.098	432.14	5.549
323.81	2.264	442.17	5.818
327.80	2.377	452.50	6.063
332.73	2.524		

TABLE 1 (continued)

T (K)	p (MPa)	T (K)	p (MPa)
$x = 0.801$			
289.14	0.536	352.68	1.164
293.09	0.560	353.02	1.148
298.11	0.599	357.61	1.225
303.10	0.648	363.36	1.291
308.15	0.698	374.81	1.412
313.27	0.752	384.83	1.522
318.52	0.800	394.07	1.644
322.52	0.838	403.46	1.742
327.97	0.899	413.46	1.840
333.06	0.951	423.18	1.958
338.27	1.005	433.21	2.066
342.90	1.056	443.12	2.164
347.84	1.115	453.15	2.262

preparing the samples, as described previously by Peters et al. (1987b), makes possible an accuracy of 0.002 in the mole fraction.

The ethane used in this work was an AGA product with a minimum purity of 99.995 mol.%. This purity was verified by measuring the saturated vapour pressure curve. Excellent agreement with measurements of Douslin and Harrison (1973) was obtained. The hexadecane used was a Merck product and its purity was specified to be better than 99.0 mol.%. From gas chromatography as well as differential scanning calorimetry it was found that the purity of the hexadecane was at least 99.0 mol.%. Both chemicals were used without further purification.

EXPERIMENTAL RESULTS

For seven different overall compositions two-phase boundaries vapour + liquid (lg) and solid hexadecane + liquid (s_Bl) have been determined experimentally. In Table 1 the bubble points (lg data) and in Table 2 the points of crystallization (s_Bl data) are summarized. A graphical representation of the data of Tables 1 and 2 is shown in Fig. 2. In this figure the full curves are best polynomial fits to the experimental data. Figure 2 also shows that intersection of a lg boundary with the corresponding s_Bl boundary — i.e. boundaries of the same overall composition — results in a point of the three-phase equilibrium solid hexadecane + liquid + vapour (s_Blg). In Table 3 these points of intersection are given. The three-phase equilibrium s_Blg was also measured directly in a similar way as discussed previously by Peters (1986). A disadvantage of the latter method is that only p, T data of this

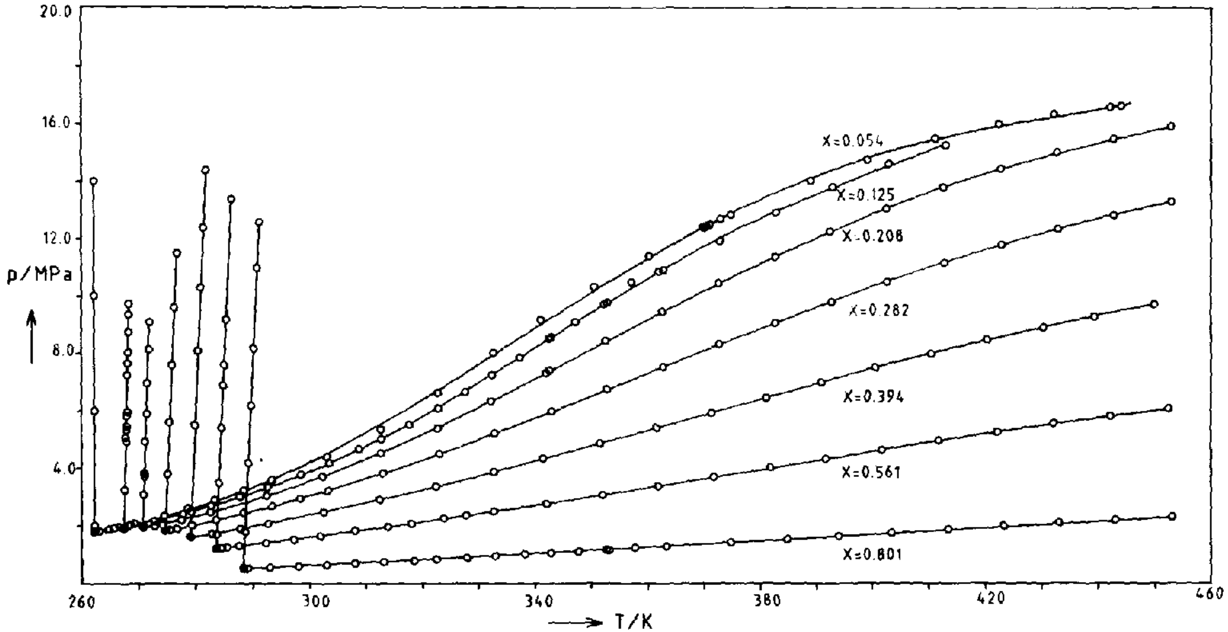

Fig. 2. Experimental data (○) of lg and s_Bl two-phase boundaries. (●) points of intersection between corresponding isopleths. Full curves are obtained by least squares polynomial fit.

TABLE 2

Experimental p, T data of the two-phase equilibrium solid hexadecane + liquid (x, mole fraction hexadecane in the liquid phase)

T (K)	p (MPa)	T (K)	p (MPa)
$x = 0.054$			
262.27	2.000	262.26	10.000
262.27	6.000	262.26	14.000
$x = 0.125$			
267.77	3.250	268.19	7.250
267.87	5.050	268.22	8.750
267.91	5.450	268.32	8.750
267.91	5.350	268.32	9.350
267.95	5.850	268.33	7.650
267.97	5.850	268.33	8.050
268.11	5.950	268.50	9.750
268.19	7.650		
$x = 0.208$			
271.02	3.100	271.55	5.900
271.14	3.850	271.75	7.000
271.18	3.750	271.95	8.150
271.35	4.950	272.14	9.100
271.49	5.900		
$x = 0.282$			
275.17	3.800	276.43	9.600
275.59	5.600	276.89	11.500
276.00	7.600		
$x = 0.394$			
279.31	2.500	281.03	10.300
279.94	5.500	281.51	12.400
280.54	8.100	281.99	14.400
$x = 0.561$			
283.67	1.700	285.08	7.600
284.10	3.500	285.43	9.200
284.56	5.400	286.39	13.400
284.91	6.900		
$x = 0.801$			
288.66	1.820	290.22	8.200
289.24	4.200	290.89	11.000
289.73	6.200	291.32	12.600

equilibrium can be obtained. In Table 4 the p, T data of the three-phase equilibrium $s_B lg$ are given. Figure 3 compares the data from Table 3 and Table 4.

TABLE 3

p, T, x data of the three-phase equilibrium solid hexadecane + liquid + vapour (x, mole fraction hexadecane in the liquid phase)

T (K)	p (MPa)	x
262.29	1.804	0.054
267.53	1.890	0.125
270.80	1.923	0.208
274.66	1.820	0.282
279.12	1.597	0.394
283.55	1.205	0.561
288.28	0.522	0.801

TABLE 4

p, T data of the three-phase equilibrium solid hexadecane + liquid + vapour

T (K)	p (MPa)	T (K)	p (MPa)
263.96	1.789	279.87	1.521
265.69	1.846	281.75	1.348
268.14	1.887	283.64	1.125
271.81	1.890	285.53	0.837
273.71	1.846	288.22	0.515
275.57	1.787	289.22	0.356
277.96	1.660	290.24	0.182

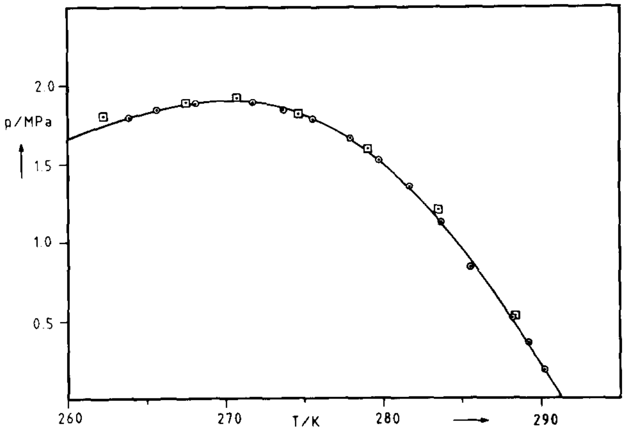

Fig. 3. Experimental data of the three-phase equilibrium solid hexadecane + liquid + vapour. Open circles are taken from Table 4 and the open squares are taken from Table 3. Full curve is a best fit to the experimental data.

DISCUSSION

It has already been pointed out that no experimental data are available in the literature for comparison.

In comparison with the lg points of Table 1 the s_Bl data points of Table 2 are somewhat less accurate; the mole fraction of 0.054 especially provides rather inaccurate experimental results. This is caused by the steepness of the s_Bl-boundary (see Fig. 2). Figure 3 compares the data of the three-phase equilibrium $s_B$lg obtained by intersection (Table 3) with the experimental data obtained by direct measurements (Table 4). From this figure it can be concluded that both kinds of experimental data are in complete agreement.

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