

# High-Pressure Phase Behavior of the Binary System Isobutane + Diamantane

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Solid–liquid and vapor–liquid equilibria for the binary system isobutane + diamantane were determined according to the synthetic method in the temperature range (320–530) K and the pressure range (0.3–10) MPa. Also, the three-phase curve solid diamantane–liquid–vapor was determined. The results show that the slope of this curve demonstrates a discontinuity, which can be explained by the existence of two solid modifications of diamantane. The two branches of this equilibrium intersect at the  $S_1$ – $S_2$  equilibrium line of diamantane. The influence of the occurrence of two modifications of diamantane on isobaric solid–liquid equilibria is less distinct.

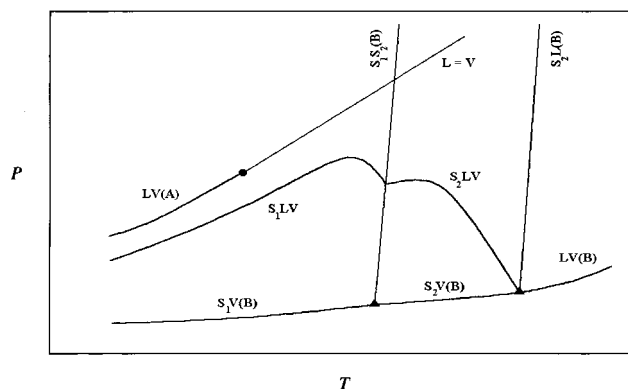
## Introduction

The phase behavior of systems of oil components and diamondoids is important for the recovery of hyperbaric reservoir fluids. The production of these reservoir fluids can be hampered by the precipitation of solid diamondoids such as adamantane or diamantane in pipelines and even in the reservoir.

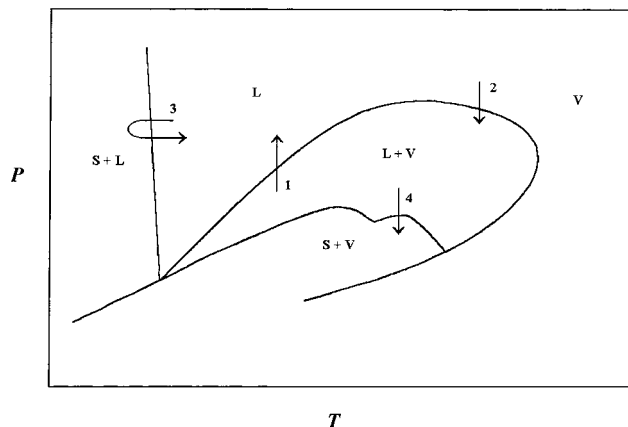
As a part of a systematic investigation on the phase behavior of light oil components and diamondoids, the high-pressure phase behavior of the binary system isobutane + diamantane is determined experimentally. The phase behavior of this binary system is schematically described by Figure 1. Since pure diamantane shows a solid–solid ( $S_1$ – $S_2$ ) transition line,<sup>1</sup> the curve representing the solid diamantane–liquid–vapor equilibrium (SLV) splits into two branches. One branch corresponds to the  $S_1$ –L–V equilibrium, and the other branch corresponds to the  $S_2$ –L–V equilibrium. Both branches intersect at the  $S_1$ – $S_2$  equilibrium line of pure diamantane. The  $S_1$ LV line starts at low temperature in the quadruple point solid methane–solid diamantane–liquid–vapor. The  $S_2$ LV line ends at higher temperature in the triple point of pure diamantane. The  $S_1$ – $S_2$  equilibrium line can be constructed using atmospheric data of Reiser et al.<sup>1</sup> and data for other binary diamantane systems.<sup>2</sup>

## Experimental Section

The experiments were carried out using a so-called Cailletet apparatus.<sup>3</sup> The top section of a Cailletet tube contains the mixture of isobutane and diamantane. This tube is placed in a thermostat bath filled with silicon oil. The temperature of the silicon oil was kept at a constant temperature within approximately 0.03 K. The temperature was measured with a platinum resistance thermometer (uncertainty  $\pm 0.01$  K), which was calibrated against a secondary standard thermometer. The pressure was measured with a dead weight pressure gauge (Budenberg, uncertainty  $\pm 0.003$  MPa at pressures below 5 MPa and  $\pm 0.01$  MPa at higher pressures) or, in case of the measure-



**Figure 1.**  $P$ – $T$  projection of the binary system of isobutane (A) and diamantane (B), with a discontinuity in the slope of the SLV equilibrium line at the intersection with the solid–solid transition line of diamantane.

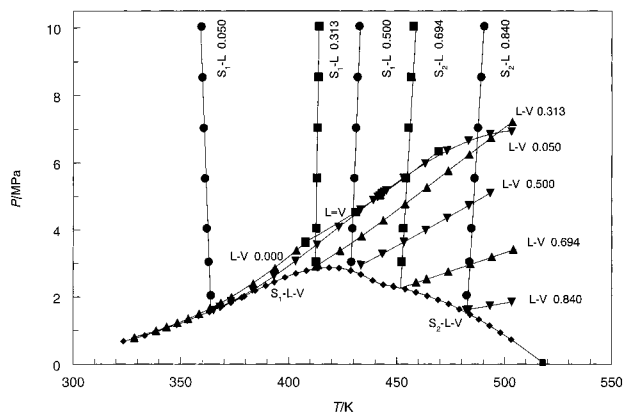


**Figure 2.** Experimental path taken in order to determine the equilibria.

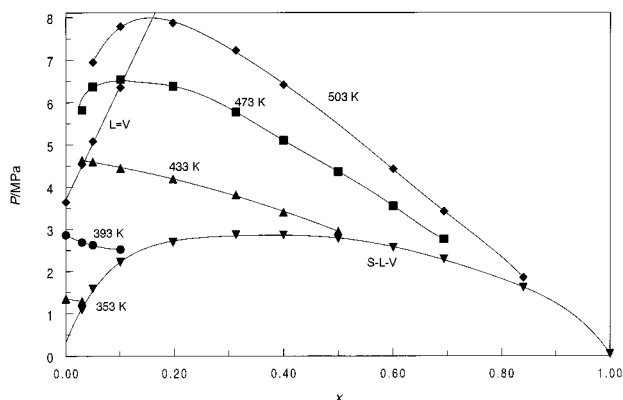
ments of SLV equilibria, with a manometer (Heise, uncertainty  $\pm 0.01$  MPa). The manometer was calibrated against a dead weight gauge.

To measure the L–V equilibria, the pressure was gradually increased until the last gas-bubble disappeared (bubble points, line 1 in Figure 2) or decreased until the first liquid-

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**Figure 3.** Phase diagrams of  $(1-x)$  isobutane +  $x$  diamantane at the indicated mole fraction of diamantane.



**Figure 4.** Isothermal  $P$ - $x$  cross sections of the L-V equilibrium and  $P$ - $x$  projection of the SLV equilibria and the critical curve of  $(1-x)$  isobutane +  $x$  diamantane.

droplet appeared (dew points, line 2 in Figure 2). For the measurements of the  $(S+L)/L$  boundary curves, the temperature was, under constant pressure, first decreased until small nuclei appeared. Then the temperature was (gradually) increased until the last crystal dissolved (line 3 in Figure 2).

The S-L-V equilibrium for a binary system has, according to the Gibbs' phase rule, only one degree of freedom. To measure this equilibrium at a fixed temperature, starting from the LV region, the pressure was decreased until solid diamantane was formed and equilibrium was reached (line 4 in Figure 2).

## Materials

The diamantane used during the experiments was obtained from Chevron. To increase the purity, it was sublimated under vacuum. GC analysis showed that the purity was better than 99 mol %.

Isobutane, or 2-methyl-propane, was supplied by Hoek Loos, with a minimum purity of 99.95 vol %. To check the purity of the isobutane, the vapor pressure was measured from 330 K up to its critical point (407.83 K, 3.64 MPa). These experimental results agreed within the experimental accuracy ( $\pm 0.003$  MPa) with the literature data.<sup>4</sup>

## Results

Figure 3 shows a selection of the experimental results. The figure shows  $(S+L) \rightarrow L$  and  $(L+V) \rightarrow L$  boundary curves for mixtures of constant composition and the three-phase curves  $S_1LV$  and  $S_2LV$ .

**Table 1.** Vapor-Liquid Equilibria in the System  $[(1-x)$  Isobutane +  $x$  Diamantane]: Phase Boundaries at Constant Diamantane Mole Fraction  $x$

		$P$		$P$		$P$	
		$T/K$	MPa	$T/K$	MPa	$T/K$	MPa
$x = 0.000$	L $\rightarrow$ V	328.58	0.79	358.57	1.50	393.63	2.86
		338.56	0.99	363.57	1.66	403.66	3.39
		343.51	1.10	368.52	1.82	407.70	3.62
		348.56	1.23	373.52	1.99	407.74	3.63
		353.50	1.35	383.60	2.40		
$x = 0.030$	L $\rightarrow$ L + V	345.23	1.099	383.13	2.271	423.81	4.211
		353.18	1.296	393.13	2.687	428.13	4.409
		363.17	1.578	403.11	3.151	430.58	4.515
		373.12	1.902	413.10	3.657	430.88	4.527
		431.01	4.530				
	L = V	431.13	4.537	443.29	5.05	472.02	5.82
		431.29	4.545	453.20	5.40	483.05	5.94
		433.33	4.631	463.11	5.69	493.04	5.86
		431.01	4.530				
		431.13	4.537	443.29	5.05	472.02	5.82
$x = 0.050$	L $\rightarrow$ L + V	365.20	1.607	403.16	3.069	441.09	4.99
		368.18	1.700	413.13	3.558	442.13	5.03
		373.20	1.863	423.14	4.078	442.98	5.07
		383.19	2.221	433.13	4.60		
		393.18	2.623	439.12	4.89		
	L = V	443.13	5.08				
		443.23	5.09	453.15	5.55	493.11	6.86
		443.61	5.10	463.10	5.98	503.09	6.94
		444.09	5.13	473.13	6.37		
		445.17	5.18	483.13	6.67		
$x = 0.101$	L $\rightarrow$ L + V	486.07	2.229	403.34	2.940	443.40	5.00
		386.65	2.252	413.33	3.404	453.33	5.54
		388.49	2.325	423.33	3.905	463.45	6.06
		393.37	2.518	433.37	4.443	468.28	6.30
		469.27	6.35				
	L = V	473.38	6.54	493.91	7.44		
		483.37	7.00	503.48	7.78		
		401.67	2.682	434.00	4.184	483.92	6.92
		402.64	2.722	443.99	4.670	493.89	7.41
		403.92	2.772	453.87	5.25	503.90	7.86
$x = 0.198$	L $\rightarrow$ L + V	413.96	3.208	463.87	5.83		
		424.00	3.678	473.92	6.38		
		412.53	2.910	443.77	4.282	483.57	6.25
		413.64	2.958	453.90	4.775	493.56	6.75
		423.74	3.377	463.94	5.271	503.48	7.22
$x = 0.313$	L $\rightarrow$ L + V	433.74	3.813	473.87	5.77		
		421.26	2.932	453.27	4.225	493.24	5.98
		423.30	3.006	463.28	4.658	503.20	6.41
		433.35	3.396	473.26	5.10		
		443.29	3.804	483.25	5.55		
$x = 0.400$	L $\rightarrow$ L + V	433.40	2.947	463.31	3.996	493.25	5.099
		443.32	3.284	473.31	4.361		
		453.29	3.636	483.32	4.731		
		438.22	2.572	463.19	3.260	493.29	4.124
		443.34	2.713	473.20	3.546	503.30	4.421
$x = 0.500$	L $\rightarrow$ L + V	453.44	2.994	483.23	3.841		
		453.79	2.329	473.78	2.758	503.99	3.419
		458.88	2.436	483.98	2.988		
		463.74	2.537	494.00	3.198		
		482.15	1.613	493.16	1.737		
$x = 0.600$	L $\rightarrow$ L + V	483.17	1.623	503.26	1.852		

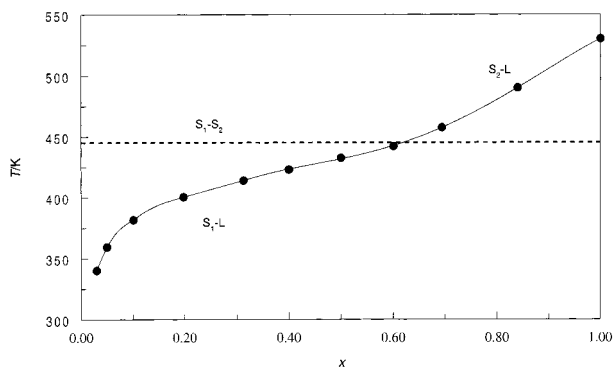
The plotted SLV data were obtained as described earlier. In principle, the point of intersection of a  $(S+L) \rightarrow L$  boundary curve and a  $(L+V) \rightarrow L$  boundary curve of the same composition should also yield a SLV point. SLV points determined in this way agree with the directly measured SLV points within the experimental accuracy.

**L-V Equilibria.** The experimentally determined LV equilibrium points are given in Table 1. The LV equilibrium was measured up to 503 K. Also three critical points were obtained at low diamantane mole fractions. From these data  $P$ - $x$  cross sections are constructed in Figure 4. Figure 4 also contains the  $P$ - $x$  projection of the composition of the liquid phase along the SLV equilibrium curve and of the binary critical curve  $L=V$ .

For the lowest composition ( $x_{\text{diamantane}} = 0.030$ ) a liquid-vapor transition could no longer be observed at 503 K.

**Table 2. Solid-Liquid Equilibria in the System [(1 - x) Isobutane + x Diamantane]: Phase Boundaries at Constant Diamantane Mole Fraction x**

		$P$		$P$		$P$	
		$T/K$	$MPa$	$T/K$	$MPa$	$T/K$	$MPa$
$x = 0.030$	$L \rightarrow L + S_1$	343.72	2.047	341.87	5.55	340.07	10.05
		343.22	3.047	341.36	7.05		
		342.67	4.047	340.76	8.55		
$x = 0.050$	$L \rightarrow L + S_1$	363.90	2.045	361.20	5.54	359.41	10.04
		362.92	3.045	360.52	7.04		
		362.08	4.045	359.92	8.54		
$x = 0.101$	$L \rightarrow L + S_1$	385.58	2.218	382.88	6.05	381.60	10.05
		384.40	3.549	382.27	7.55		
		383.87	4.549	381.78	9.05		
$x = 0.198$	$L \rightarrow L + S_1$	401.22	3.051	400.59	6.05	400.44	10.05
		400.90	4.051	400.53	7.05		
		400.73	5.05	400.44	8.55		
$x = 0.313$	$L \rightarrow L + S_1$	412.66	3.047	413.05	5.647	413.76	8.55
		412.77	4.047	413.35	7.05	414.07	10.05
		420.33	3.049	421.26	5.549	422.46	8.55
$x = 0.400$	$L \rightarrow L + S_1$	420.33	3.049	421.26	5.549	422.46	8.55
		420.72	4.049	421.85	7.05	423.07	10.05
		428.88	3.048	430.28	5.55	431.73	8.55
$x = 0.500$	$L \rightarrow L + S_1$	429.44	4.048	431.01	7.05	432.61	10.05
		438.07	3.050	439.54	5.55	441.53	8.55
		438.65	4.050	440.57	7.05	442.26	10.05
$x = 0.600$	$L \rightarrow L + S_1$	438.07	3.050	439.54	5.55	441.53	8.55
		438.65	4.050	440.57	7.05	442.26	10.05
		452.13	3.048	454.15	5.55	456.54	8.55
$x = 0.694$	$L \rightarrow L + S_2$	453.00	4.048	455.32	7.05	457.64	10.05
		482.30	2.051	485.87	5.55	490.33	10.05
		483.52	3.051	487.41	7.05		
$x = 0.840$	$L \rightarrow L + S_2$	484.48	4.051	488.89	8.55		

**Figure 5.** Solid-liquid solubility curve of (1 - x) isobutane + x diamantane at 10 MPa. The dotted line represents the transition temperature, at which diamantane shows a solid-solid transition ( $S_1-S_2$ ).

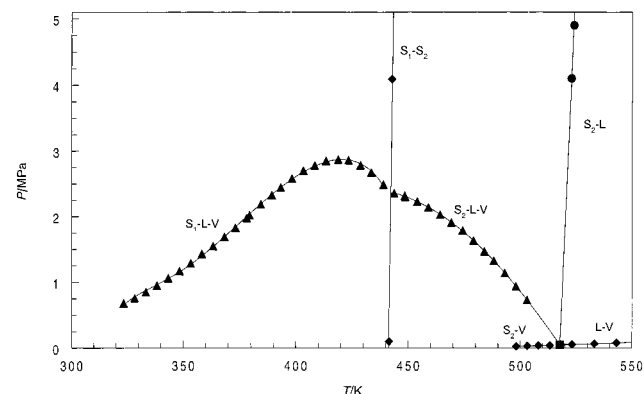
**$S_1-L$  Equilibria and  $S_2-L$  Equilibria.** The experimental results of the equilibrium-points are given in Table 2. From these data a  $T-x$  cross section at 10 MPa is constructed in Figure 5. From this figure we observe that at the temperature of the solid-solid transition of pure diamantane also a change in the slope of the liquidus is observed.

**$S_1-L-V$  Equilibria and  $S_2-L-V$  Equilibria of Isobutane and Diamantane.** The experimental results for these equilibria are given in Table 3. The  $S_1-L-V$  equilibrium line is measured from 320 K up to higher temperatures. As stated in the Introduction; the  $S-L-V$  equilibrium line is split into two branches. The experimental data also show that the intersection of these two branches lies at the constructed  $S_1-S_2$  equilibrium line.<sup>1,2</sup> A  $P-T$  projection of the experimental results is plotted in Figure 6.

The  $P-x$  projection of the  $S-L-V$  equilibrium was already constructed in Figure 4.

**Table 3. Solid Diamantane-Liquid-Vapor Curve in the Binary System Isobutane + Diamantane**

$T/K$	$P/MPa$	$T/K$	$P/MPa$	$T/K$	$P/MPa$	$T/K$	$P/MPa$
323.41	0.68	373.16	1.83	418.69	2.87	464.10	2.03
328.35	0.76	378.16	1.98	423.34	2.86	469.10	1.91
333.32	0.85	379.38	2.02	428.66	2.78	474.11	1.79
338.30	0.95	384.51	2.19	433.40	2.67	478.97	1.63
343.28	1.06	389.35	2.33	438.87	2.49	483.87	1.47
348.27	1.17	393.33	2.45	443.67	2.36	488.01	1.33
353.28	1.29	398.33	2.58	448.38	2.32	492.95	1.14
358.27	1.43	403.34	2.70	448.61	2.30	498.02	0.94
363.26	1.55	408.34	2.78	453.96	2.23	503.03	0.73
368.32	1.69	413.31	2.85	458.88	2.14	517.65	0.05

**Figure 6.** Three-phase equilibria of isobutane + diamantane. Also, the phase equilibrium lines of pure diamantane are presented in this figure.<sup>1,2</sup>

## Conclusions

The binary system of isobutane and diamantane shows a discontinuity in the slope of the SLV equilibrium line. This line is split into two sections: an  $S_1LV$  and  $S_2LV$  equilibrium line. These lines intersect at the  $S_1-S_2$  equilibrium line of pure diamantane which was constructed from previous measurements on other binary systems of diamantane. Also, the isobaric  $T-x$  cross section at 10 MPa for the solid-liquid equilibria shows a change in slope at the solid-solid transition temperature of diamantane.

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