High-pressure phase behaviour of the binary system {CO₂ + *cis*-decalin} from (292.75 to 373.75) K

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ARTICLE INFO

ABSTRACT

The phase behaviour of the {CO₂ (1) + *cis*-decalin (2)} binary system has been experimentally studied at temperatures ranging from (292.75 to 373.75) K. Saturation pressures, ranging from (15.9 to 490.5) bar, were obtained using a variable volume high-pressure cell by visual observation of phase transitions at constant overall composition. For this system, no literature data are available and the results obtained in this study reveal the occurrence of vapor–liquid, liquid–liquid, and vapor–liquid–liquid phase transitions in the investigated temperature range. A total of 133 experimental points are reported including bubble points, dew points, liquid–liquid phase equilibria, and coordinates of the three-phase line. The experimental data can be reasonably predicted by the PPR78 model in which the temperature-dependent binary interaction parameter is calculated by a group contribution method.

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1. Introduction

Phase equilibrium data of mixtures containing carbon dioxide are required for the design and the improvement of many industrial operations such as gas injection in reservoir fluids [1–7] or supercritical fluid extraction [8,9]. Moreover, reliable experimental data are needed for the development of predictive thermodynamic models [10–13], to compare equation of state (EOS) or to fit model parameters. For example, to build a group contribution method (GCM), many phase equilibrium data are needed for the adjustment of group interaction parameters. Furthermore, these data must concern several binary systems involving the same groups in the largest temperature/pressure range.

Broadly speaking, binary mixtures containing CO₂ have been extensively measured and there is a vast amount of reliable experimental phase equilibria and critical data. However, our bibliographical investigations enabled us to note that very few vapor–liquid equilibrium (VLE) data were available for two kinds of binary systems: {CO₂ + branched alkanes} and {CO₂ + branched naphthenes}. This work is part of a continuing study on the phase behaviour of CO₂ with hydrocarbons. A few years ago, we investigated the solubility of CO₂ in three branched alkanes: 2,2,4-trimethyl pentane; 2,5-dimethyl hexane; and 3-methyl pentane [14]. In 2007, new high-pressure saturation points for a sys-

tem containing CO₂ and five hydrocarbons were measured [1]. Recently, measurements were reported for two binary mixtures containing CO₂ and a branched single-ring naphthenic compound: {CO₂ + methyl cyclopentane} and {CO₂ + isopropyl cyclohexane} [15].

The objective of this work is to obtain experimental data concerning a binary system containing CO₂ and a two-ring naphthenic compound. In the open literature, VLE data are available [16–19] for the binary system {CO₂ (1) + *trans*-decalin (2)} at temperatures from (273.15 to 523.60) K. On the other hand, from our knowledge, no paper has been published regarding to the binary system consisting of CO₂ and *cis*-decalin (*cis*-decahydro naphthalene). We thus decided to measure the phase equilibria for the system {CO₂ (1) + *cis*-decalin (2)}. The experiments were conducted in a high-pressure cell with two sapphire windows allowing us direct observation of the phase transitions. The experimental results were predicted with the PPR78 model [20–24].

2. Experimental section

2.1. Materials

The carbon dioxide used in this study was supplied by Messer France and had a minimum mass fraction purity higher than 0.999. *cis*-Decalin was supplied by Aldrich with a minimum molar fraction purity higher than 0.990 and was used without any further purification.

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2.2. Apparatus and procedure

Saturation points were measured using a variable volume high-pressure cell (Top Industrie S.A., France). The equipment used and the technique employed were extensively discussed in our previous studies [1,15,25–27].

Briefly, the technique used to carry out phase equilibrium measurement was based on a synthetic method which avoids sampling and analyses of the phases. The high-pressure cell was equipped with a moving piston and two sapphire windows allowing a visual observation of the equilibrium cell. A video acquisition system, connected to a screen, was placed right in front of a window. The

TABLE 1

Experimentally determined fluid–fluid phase transitions (VLE and LLE) for the {CO_2 (1) + *cis*-decalin (2)} binary system at 12 different CO_2 mole fractions

T/K	P/bar		T/K	P/bar		T/K	P/bar	
				$x_1 = 0.1009$				
293.15	15.9	L + V → L	303.05	18.6	L + V → L	312.95	21.0	L + V → L
323.25	23.5	L + V → L	333.15	25.9	L + V → L	343.25	28.2	L + V → L
352.95	30.5	L + V → L	363.15	32.7	L + V → L	372.95	34.6	L + V → L
				$x_1 = 0.2073$				
293.15	29.9	L + V → L	302.95	34.3	L + V → L	312.85	38.8	L + V → L
323.05	43.4	L + V → L	333.15	47.9	L + V → L	343.25	52.3	L + V → L
353.25	56.4	L + V → L	363.05	60.2	L + V → L	373.15	63.9	L + V → L
				$x_1 = 0.3010$				
292.75	40.3	L + V → L	302.95	47.0	L + V → L	313.05	53.6	L + V → L
323.05	60.5	L + V → L	333.25	67.2	L + V → L	343.55	73.7	L + V → L
353.45	79.8	L + V → L	362.95	85.3	L + V → L	373.35	91.0	L + V → L
				$x_1 = 0.4006$				
293.05	49.8	L + V → L	302.95	58.9	L + V → L	312.85	68.3	L + V → L
323.25	78.1	L + V → L	333.25	87.8	L + V → L	343.35	96.9	L + V → L
353.25	105.5	L + V → L	363.75	114.2	L + V → L	373.05	121.2	L + V → L
				$x_1 = 0.5002$				
292.85	55.9	L + V → L	302.85	67.9	L + V → L	313.05	81.0	L + V → L
322.95	94.4	L + V → L	333.25	107.7	L + V → L	343.55	120.8	L + V → L
353.45	132.5	L + V → L	363.05	142.6	L + V → L	373.05	152.4	L + V → L
				$x_1 = 0.6005$				
294.05	369.3	L + L → L	295.55	263.3	L + L → L	297.25	212.2	L + L → L
299.55	173.1	L + L → L	303.65	138.6	L + L → L	308.35	120.8	L + L → L
313.05	114.7	L + V → L	323.05	120.5	L + V → L	333.15	134.0	L + V → L
342.55	147.7	L + V → L	352.35	161.3	L + V → L	362.15	173.9	L + V → L
373.05	186.6	L + V → L						
				$x_1 = 0.7002$				
301.15	441.5	L + L → L	303.25	316.5	L + L → L	308.05	227.4	L + L → L
313.05	192.0	L + V → L	318.25	175.8	L + V → L	323.85	170.0	L + V → L
333.45	172.1	L + V → L	343.15	181.2	L + V → L	353.15	193.3	L + V → L
362.85	205.0	L + V → L	373.15	217.1	L + V → L			
				$x_1 = 0.8001$				
303.25	490.5	L + L → L	304.75	375.1	L + L → L	308.15	277.7	L + L → L
313.55	223.8	L + V → L	318.25	203.9	L + V → L	323.25	194.2	L + V → L
327.85	191.6	L + V → L	333.25	192.6	L + V → L	343.25	200.5	L + V → L
353.25	211.3	L + V → L	363.25	222.8	L + V → L	373.05	233.7	L + V → L
				$x_1 = 0.8703$				
303.05	437.1	L + L → L	307.05	283.3	L + L → L	309.25	252.2	L + L → L
313.25	220.2	L + V → V	318.25	200.9	L + V → V	323.05	192.7	L + V → V
327.65	190.5	L + V → V	333.05	191.8	L + V → V	343.25	200.0	L + V → V
353.25	211.3	L + V → V	363.15	223.3	L + V → V	373.15	234.4	L + V → V
				$x_1 = 0.9300$				
298.25	311.6	L + L → L	300.95	237.6	L + L → L	308.05	180.2	L + L → L
313.15	168.0	L + V → V	323.35	165.9	L + V → V	333.35	175.4	L + V → V
343.15	189.2	L + V → V	353.25	202.9	L + V → V	363.45	216.1	L + V → V
373.75	227.8	L + V → V						
				$x_1 = 0.9600$				
293.05	106.8	L + L → L	303.35	100.4	L + L → L	313.25	115.2	L + V → V
323.35	133.0	L + V → V	333.35	151.4	L + V → V	343.15	168.0	L + V → V
353.05	183.2	L + V → V	363.35	196.7	L + V → V	372.95	207.1	L + V → V
				$x_1 = 0.9792$				
293.05	56.6	L + V → L	302.95	70.7	L + V → L	313.15	90.4	L + V → V
323.15	113.4	L + V → V	333.05	133.2	L + V → V	343.05	149.8	L + V → V
353.25	163.4	L + V → V	363.15	174.7	L + V → V	373.15	182.7	L + V → V