948 *J. Chem. Eng. Data* **1995,** *40,* 948−949

Experimental Determination of Vapor−Liquid Equilibria in Binary Mixtures of Carbon Dioxide + Chloroform

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Bubble points of binary mixtures of carbon dioxide + chloroform at eight different mole fractions have been measured in the temperature region 280−370 K and at pressures up to 12 MPa by means of the synthetic method.

Introduction

In supercritical fluid extraction technology of pesticides from soils with carbon dioxide, chloroform might be a cosolvent candidate (*1*). For the modeling of systems consisting of a near-critical solvent, a cosolvent, and a solute, not only interaction parameters between the near-critical solvent and the solute have to be known, but also those between the near-critical solvent and the cosolvent (*1*). For that purpose, experimental data of these kinds of systems are a prerequisite. In the literature experimental data of binary mixtures of carbon dioxide and some cosolvents of interest for the supercritical extraction of pesticides from soils are scarce. To extend the availability of accurate experimental data on these systems, the underlying study was undertaken.

Recently, a new dynamic apparatus became available to meausre bubble points in systems of a near-critical solvent and less volatile cosolvents. Besides the vapor−liquid equilibria of the systems, also the density of the liquid phase could be measured with the apparatus. For details on this apparatus, one is referred to Kordikowski et al. (*2*). It turned out, however, that due to the relatively high vapor pressure of chloroform, the new apparatus was not appropriate to measure bubble points in the system carbon dioxide + chloroform. Therefore, it was decided to measure the vapor−liquid equilibrium of this system according to the synthetic method. To the best of our knowledge no experimental vapor−liquid data of this system are known in the literature.

Table 1. Bubble Point Temperatures and Pressures for the Binary Mixture Carbon Dioxide (1) + Chloroform (2)[a]

T/K	*p*/MPa	*T*/K	*p*/MPa	*T*/K	*p*/MPa
$x_2 = 0.0475$		$x_2 = 0.2636$		$x_2 = 0.6030$	
278.30	3.733	345.70	9.506	278.35	1.934
285.85	4.473	353.29	10.326	293.17	2.579
293.24	5.289	356.92	10.691	308.48	3.319
300.66	6.189	360.62	11.061	313.04	3.559
308.31	7.199	364.74	11.447	323.31	4.124
315.72	8.134	368.26	11.762	338.38	4.999
320.67	8.705	371.21	12.002	353.39	5.904
321.23	8.751			368.41	6.834
321.49*	8.771	$x_2 = 0.3739$			
		278.30	2.699	$x_2 = 0.7106$	
$x_2 = 0.1476$		293.24	3.684	278.18	1.487
278.32	3.350	308.26	4.839	293.33	1.967
288.31	4.205	323.34	6.139	308.31	2.502
298.29	5.176	338.31	7.530	323.42	3.097
308.34	6.271	345.58	8.224	338.27	3.727
318.27	7.446	353.41	8.979	348.37	4.167
328.35	8.686	360.88	9.679	353.14	4.382
335.97	9.602	368.45	10.374	368.42	5.082
343.29	10.398				
348.38	10.863	$x_2 = 0.4843$		$x_2 = 0.8658$	
353.40	11.248	278.18	2.332	278.25	0.737
356.03	11.424	283.30	2.597	293.25	0.967
356.36*	11.447	293.33	3.147	308.23	1.218
		307.62	4.037	323.24	1.503
$x_2 = 0.2636$		308.31	4.082	338.25	1.813
278.34	3.024	323.30	5.127	353.12	2.144
293.30	4.164	338.32	6.247	368.15	2.504
308.18	5.504	353.21	7.402		
323.32	7.049	363.19	8.177		
330.74	7.854	368.19	8.562		
338.22	8.681	371.25	8.802		

[a] Asterisk indicates critical point.

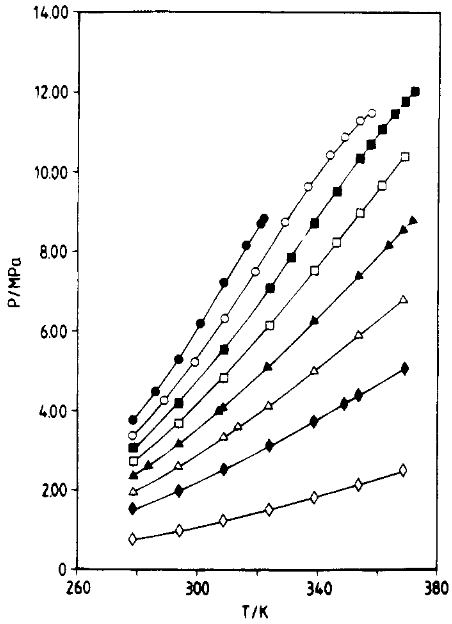

Figure 1. Bubble point measurements of the binary mixture carbon dioxide (1) + chloroform (2). Symbols, experimental data: ●, x_2 = 0.0475; ○, x_2 = 0.1476; ■, x_2 = 0.2636; □, x_2 = 0.3739; ▲, x_2 = 0.4843; △, x_2 = 0.6030; ◆, x_2 = 0.7106; ◇, x_2 = 0.8658. Full curves: best fit to the experimental data.

Experimental Section

Method. The experimental work was carried out in a Cailletet apparatus and has been described already in various references. For details one is, for instance, referred to Van der Kooi (*3*), De Loos et al. (*4*), Peters (*5*), and Peters et al. (*6*). Also the experimental procedures and accuracy of the method have been described previously by Van der Kooi (*3*), Peters (*5*), Peters et al. (*7, 8*), and Coorens et al.

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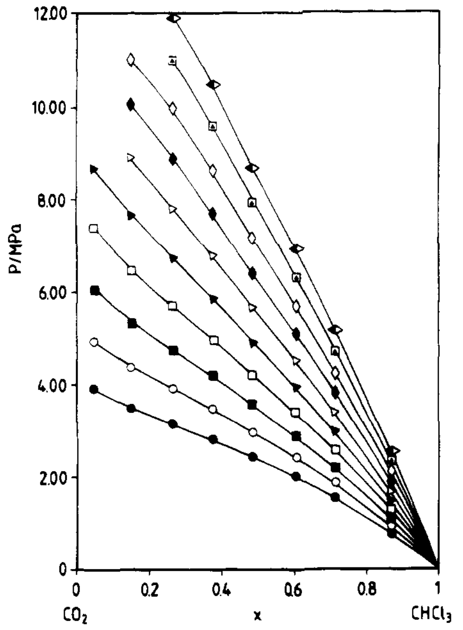

Figure 2. Isothermal data of the binary mixture carbon dioxide (1) + chloroform (2). Symbols, interpolated experimental data: ●, T = 280 K; ○, T = 290 K; ■, T = 300 K; □, T = 310 K; ▲, T = 320 K; △, T = 330 K; ♦, T = 340 K; ◇, T = 350 K; triangle in a box, T = 360 K; horizontal diamond, left solid, T = 370 K. Full curves: best fit to the experimental data.

(*9*). Carbon dioxide was supplied by Air Products, and the purity was 99.9 mol %. The purity of chloroform (supplied by Baker) was better than 99 mol %. Both substances were used without further purification.

Results. In Table 1, the experimental series of (p, T) bubble point data or isopleths are summarized, and Figure 1 represents the data graphically. The full curves are best fits to the results. Using a suitable interpolation technique from the (p, T) data, isothermal (p, x) cross-sections can be obtained. For round values of the temperature, Figure 2 shows the (p, x) cross-sections at various temperatures.

Discussion and Conclusions

This paper presents bubble point measurements of the system carbon dioxide + chloroform. Because no experimental information was available in literature, no comparison could be made with data from other sources. From Figure 2 it can be seen that all isotherms show positive deviations from Raoult's law. This figure also shows that the isotherms have an inflection point which becomes less pronounced toward higher temperatures.

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Received for review January 20, 1995. Accepted March 31, 1995.[⊗]

JE9500183

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1995.