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High-Pressure Vapor-Liquid Equilibrium Phase Properties of the Octafluoropropane (K-218)-Chlorodifluoromethane (Freon-22) Binary System

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Vapor and liquid equilibrium phase compositions were determined at 50, 60, 70, and 75 °C for the octafluoropropane-chlorodifluoromethane system. Measurements were made at pressures from the vapor pressure of the two pure components to the higher of the azeotropic or critical pressure for the binary systems at each temperature. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The azeotropic compositions and pressures were measured at 50, 65, and 70 °C. The critical pressure was determined at 70 and 75 °C.

Introduction

For process engineering and design calculations, it is frequently necessary to have available a suitable method for calculating the thermodynamic properties and phase behavior of multicomponent gaseous and liquid systems. Many of these methods rely extensively on the availability of pure component properties and binary interaction parameters for use in equations of state or other fluid property models.

In view of the perceived dangers to the ozone layer caused by chlorinated hydrocarbons, a great deal of interest has developed in fluorinated hydrocarbons. Recently, information on the behavior of octafluoropropane-chlorodifluoromethane at temperatures of 0 and 25 °C was published by Leu and Robinson (1). The object of the work undertaken in this study was to extend the temperature range and thereby explore the possibility of azeotropic behavior at higher temperatures. The potential for this had been indicated by the shape of the pressure-composition phase envelopes at 0 and 25 °C.

Experimental Method

The experiments were carried out in a variable-volume vapor-liquid equilibrium cell consisting of a transparent sapphire cylinder mounted between two steel headers. This has been described in detail by Robinson et al. (2). The body of the cell

had a 2.54-cm inside diameter with a length of 15.2 cm. The cell had an internal capacity of about 45 cm³. The main cell and all the necessary auxiliary lead lines and valves were mounted inside a controlled-temperature bath. The method of operation was basically the same as those described previously by Leu and Robinson (3).

Prior to commencing an experimental run, the equipment was thoroughly cleaned and evacuated. A suitable amount of octafluoropropane was then added to the cell, followed by sufficient chlorodifluoromethane to achieve the desired pressure range at the chosen temperature. Equilibrium was attained by mechanically rocking the entire assembly about a horizontal axis. The gas phase was sampled first by continuously drawing off a vapor stream through the sample valve under isobaric isothermal conditions. The withdrawn vapor was mixed with a stream of heated helium and circulated through the chromatographic switching valve. Samples were taken for analysis through the switching valve at periodic intervals.

After the remainder of the vapor phase plus a small interface portion of the liquid was removed, the liquid phase was then sampled and analyzed by using a similar procedure. At the completion of each pressure point, a new set of conditions was established by adjusting pressure and/or adding more material. The equilibration and sampling sequence was then repeated.

The azeotropic or critical region was approached isothermally by using an iterative experimental procedure involving changes in pressure and/or composition. After the equilibration process had been completed, the critical pressure corresponding to a given experimental temperature was determined by performing isothermal compression and expansion on either side of the critical point to observe both the phase boundary and the color changes taking place within the system. The critical composition was determined by taking a sample as described above, but the isobaric sampling pressure was kept at least 0.14 MPa higher than the observed critical pressure to ensure the mixture remained in the single phase.

Temperatures were measured with iron-constantan thermocouples which had been calibrated against a platinum resistance thermometer. This thermometer was calibrated for use in the range $t = -189$ to $+500$ °C on the International Practical Temperature Scale of 1968 (IPTS-68), amended edition of 1975. Each temperature was read on a digital voltmeter, such

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Table I. Equilibrium Pressure P , Liquid-Phase Mole Fraction x_1 , Vapor-Phase Mole Fraction y_1 , and Equilibrium Ratios $K_i = y_i/x_i$ of the Chlorodifluoromethane (1) + Octafluoropropane (2) System at Temperature t^a

P /MPa	x_1	y_1	K_1	K_2
$t = 50.0\text{ }^\circ\text{C}$				
1.652	0.0	0.0		1.00
1.743	0.041	0.080	1.94	0.60
1.949	0.174	0.272	1.56	0.882
2.117	0.312	0.416	1.33	0.849
2.157	0.375	0.452	1.21	0.876
2.228	0.492	0.530	1.08	0.925
2.252	0.595	0.613	1.03	0.957
2.270	0.626*	0.626	1.00	1.00
2.259	0.665	0.644	0.968	1.06
2.239	0.750	0.708	0.945	1.17
2.187	0.851	0.783	0.920	1.45
2.082	0.935	0.890	0.920	1.45
2.082	0.935	0.890	0.951	1.70
1.955	1.0	1.0		1.00
$t = 65.0\text{ }^\circ\text{C}$				
2.304	0.0	0.0		1.00
2.393	0.035	0.061	1.72	0.974
2.708	0.182	0.260	1.43	0.905
2.946	0.316	0.405	1.28	0.870
2.996	0.365	0.432	1.18	0.894
3.121	0.527	0.552	1.05	0.947
3.129	0.591	0.603	1.02	0.969
3.136	0.628*	0.628	1.00	1.00
3.123	0.657	0.652	0.993	1.01
3.105	0.762	0.734	0.963	1.12
3.001	0.864	0.824	0.954	1.29
2.941	0.924	0.889	0.963	1.45
2.823	0.969	0.935	0.972	1.71
2.710	1.0	1.0		1.00
$t = 70.0\text{ }^\circ\text{C}$				
2.554	0.0	0.0		1.00
2.632	0.0271	0.0347	1.28	0.992
2.739	0.0629	0.0734	1.17	0.989
2.808	0.0933	0.102	1.09	0.991
2.845	0.115†	0.115	1.00	1.00
3.432	0.475†	0.475	1.00	1.00
3.472	0.520	0.546	1.05	0.946
3.845	0.588	0.605	1.03	0.959
3.498	0.616*	0.616	1.00	1.00
3.492	0.644	0.630	0.978	1.04
3.475	0.686	0.669	0.975	1.05
3.461	0.731	0.704	0.963	1.10
3.273	0.907	0.868	0.958	1.41
3.174	0.949	0.921	0.971	1.54
3.145	0.962	0.941	0.977	1.58
3.003	1.0	1.0		1.00
$t = 75.0\text{ }^\circ\text{C}$				
3.331	1.0	1.0		1.00
3.350	0.998	0.997	0.998	1.90
3.445	0.971	0.949	0.978	1.74
3.612	0.894	0.852	0.952	1.40
3.758	0.792	0.761	0.961	1.15
3.780	0.774	0.751	0.972	1.10
3.780	0.772	0.749	0.970	1.10
3.818	0.700	0.686	0.979	1.05
3.829	0.683	0.672	0.983	1.04
3.843	0.659†	0.659	1.00	1.00

^a Azeotropic and critical compositions are indicated with the following symbols: *, azeotropic composition; †, critical composition.

that temperatures are believed known to within $\pm 0.1\text{ }^\circ\text{C}$ or better. Pressures were measured by a strain gauge pressure transducer (Statham UTC-UC3/UGP4-200, range 0–200 psi, and Statham UTC-UC3/UGP4-500, range 0–500 psi), calibrated with a precision dead-weight gauge. Each pressure was read on a digital voltmeter. The pressures are believed known to within $\pm 0.2\%$ of full scale.

The phase compositions were determined with a Hewlett-Packard Model 5750B gas chromatograph coupled with an HP-3353 data acquisition system. A thermal conductivity detector on isothermal mode was used for this binary system. The column used was a 2.44-m-length by 3.18-mm-diameter stainless steel tube packed with Porapak-QS. It was maintained at $65\text{ }^\circ\text{C}$ for this study. Helium gas at a flow rate of $25\text{ cm}^3/\text{min}$ was used as carrier gas for gas chromatograph analysis. The response factor for conversion from area fraction to mole fraction relative to chlorodifluoromethane was 1.3347 for octafluoropropane. This factor was obtained by calibrations made for each component using a gravimetric method to prepare the standard solution for gas chromatographic analysis. At least five samples of each phase were taken for analysis so that the reported compositions are the result of averaging at least four out of five determinations. The precision of the analysis was generally within better than 2% of the relative standard deviation.

In determining the physical properties in the critical region, the given experimental temperature was considered as the critical temperature. The corresponding critical pressure was determined by averaging the two values obtained from isothermal compression and expansion observations. The associated composition was determined as described above.

Materials

Chlorodifluoromethane of 99.9+ mol % purity and octafluoropropane of 99.5+ mol % purity were obtained from Matheson Gas Products, Canada, Inc. Gas chromatograms were run on these compounds, but no detectable impurities were found. Thus, these materials were used without further purification. The octafluoropropane was degassed in the equilibrium cell before the addition of chlorodifluoromethane.

Results and Discussion

The experimentally measured equilibrium liquid (x_i) and vapor (y_i) compositions for the octafluoropropane (1) + chlorodifluoromethane (2) system are presented in Table I. The vapor- and liquid-phase envelopes for this system are shown graphically in Figure 1 for each of the four isotherms studied. For completeness, the earlier results reported by Leu and Robinson (1) at 0 and $25\text{ }^\circ\text{C}$ are also included in the figure. The calculated equilibrium ratios $K_i = y_i/x_i$ for each component in the binary system at the four higher temperatures are also given in Table I. They are shown graphically in Figure 2 for three isotherms at 50, 65, and $75\text{ }^\circ\text{C}$ along with the earlier work reported by Leu and Robinson (1) at 0 and $25\text{ }^\circ\text{C}$.

Information on the critical and azeotropic conditions in the mixtures of octafluoropropane and chlorodifluoromethane is given in Table II. The critical and azeotropic loci are shown graphically in Figure 3. The vapor pressure of the pure components has been reported in the literature at temperatures in

Table II. Critical Temperature t_c and Pressure P_c and Azeotropic Temperature t_{AZ} and Pressure P_{AZ} of the Chlorodifluoromethane (1) + Octafluoropropane (2) System

system	$t_c/^\circ\text{C}$	P_c/MPa	$t_{AZ}/^\circ\text{C}$	P_{AZ}/MPa	ref
chlorodifluoromethane	96.0	4.975			4
chlorodifluoromethane + octafluoropropane	75.0	3.843	70.0	3.498	this work
	70.0	3.432	65.0	3.136	this work
	70.0	2.849	60.0	2.270	this work
octafluoropropane	71.9	2.675			5, 6

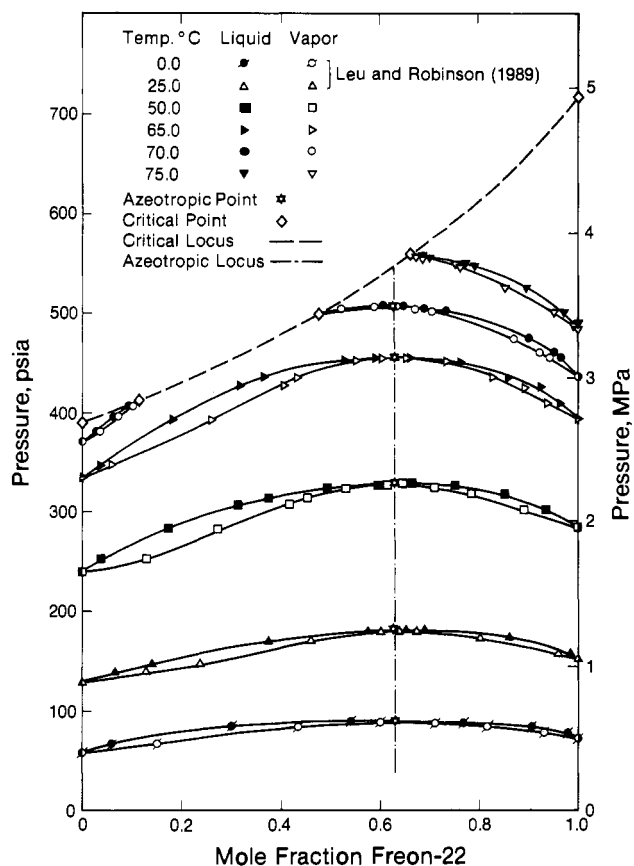


Figure 1. Pressure-composition phase diagram for the octafluoropropane-chlorodifluoromethane binary system at six temperatures.

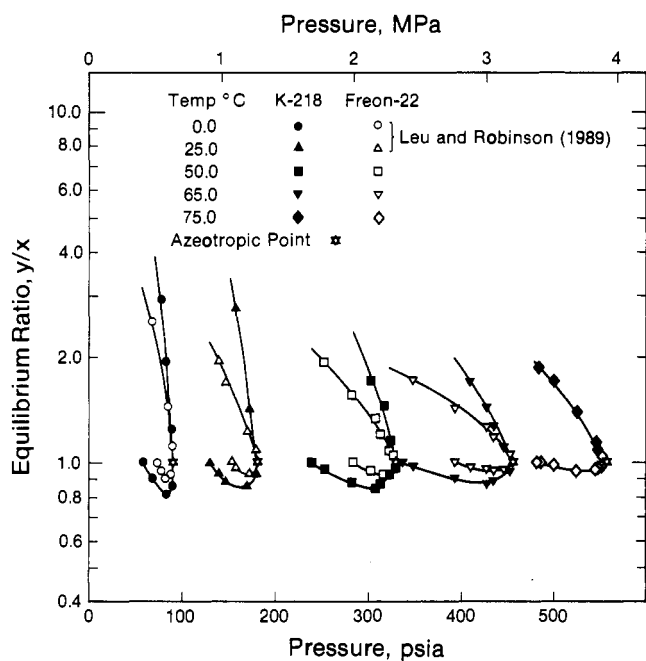


Figure 2. Equilibrium ratios for octafluoropropane and chlorodifluoromethane in the binary system at five temperatures.

the 50–75 °C range. The values obtained in this work are compared to the work of other authors in Table III.

This study is the first reported on the equilibrium phase behavior of the octafluoropropane + chlorodifluoromethane binary system in the temperature range which encompasses the azeotropic and critical region and extends beyond the critical temperature of octafluoropropane. The information obtained will be useful for evaluating the interaction parameters required in equations of state used for describing the behavior of the

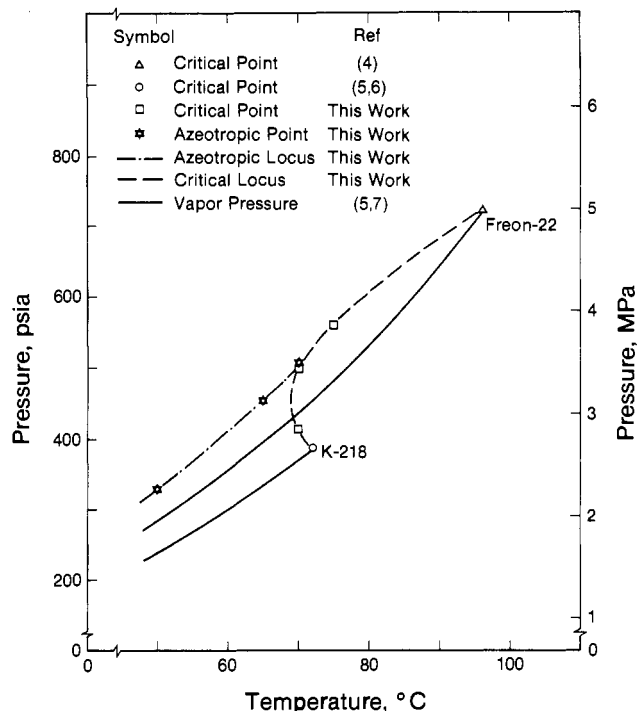


Figure 3. Azeotrope and critical behavior in the octafluoropropane-chlorodifluoromethane binary system.

Table III. Vapor Pressure of Chlorodifluoromethane and Octafluoropropane

$t/^\circ\text{C}$	P/MPa					
	ref 8	refs 7, 9	ref 10	ref 11	ref 12	this work
Chlorodifluoromethane						
50	1.920	1.958	1.937			1.955
65	2.730	2.719	2.694			2.710
70	3.030	3.014	2.991			3.003
75	3.390	3.330	3.312			3.331
Octafluoropropane						
50				1.651	1.641	1.652
65				2.298	2.310	2.304
70				2.547	2.553	2.554

binary pairs. This should help to improve the reliability of vapor-liquid equilibrium and fluid property predictions made for mixtures containing these compounds.

Glossary

K	equilibrium ratio, y/x
P	pressure, MPa or psia
t	temperature, °C
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase

Subscripts

i	component ($i = 1$, octafluoropropane; $i = 2$, chlorodifluoromethane)
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Equilibrium Phase Properties of the Methanol-Isobutane Binary System

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Vapor and liquid equilibrium phase compositions were determined at 0.0, 50.0, 100.0, 125.0, 131.0, 133.0, and 150.0 °C for the methanol-isobutane binary system. Measurements were made at each temperature from the vapor pressure of the methanol to the vapor pressure of the isobutane or to the maximum azeotropic or critical pressure, whichever was higher. Equilibrium ratios for each component were calculated at each temperature from the phase composition data. The azeotropic pressures and associated compositions were measured, and an expression relating azeotropic pressure and composition was developed. The critical temperatures and corresponding critical pressure were measured, and the critical locus was constructed.

Introduction

The phase behavior of methanol-alkane binary mixtures has received increased interest in recent years. This interest has arisen for a variety of reasons, including in particular the role of methanol as a hydrate inhibitor in gas transportation and processing operations and the use of methanol and other alcohols and ethers in motor gasoline. In addition to this industrial interest, methanol-alkane mixtures are often used as model systems for understanding polar-nonpolar mixture behavior and for developing mixing rules and interaction parameters for equation of state work for this class of systems. Vapor-liquid equilibrium in the *n*-butane-methanol binary system was studied by Leu et al. (1) at 0, 50, and 100 °C, and the azeotropic behavior of this system has been reported by Churkin et al. (2). No previous published work has been found for the methanol-isobutane system. In view of the importance of the system and the lack of data on it, the present study was undertaken. The objective was to determine vapor-liquid equilibrium data in the range from 0 to 150 °C and to explore the azeotrope and critical regions wherever they occurred.

Experimental Section

The equipment used and the method of operation for this study were basically the same as that described previously by Huang et al. (3).

Equilibrium was attained by mechanically rocking the entire assembly. The gas phase was sampled first by continuously drawing off a vapor stream through the sample valve under

isobaric isothermal conditions. The withdrawn vapor was mixed with a stream of heated helium and circulated through the chromatographic switching valve. Samples were taken for analysis through the switching valve at periodic intervals. After the remainder of the vapor phase plus a small interface portion of the liquid was removed, the liquid phase was then sampled and analyzed by using a similar procedure.

The azeotropic region was approached isothermally by adjusting pressure or altering the composition through appropriate addition of more material. After the equilibration process had been completed, the azeotropic pressure corresponding to a given experimental temperature was determined using the equilibrium phase compositions as a guide. When the composition difference between the vapor and liquid phases was less than 2×10^{-4} mole fraction, the azeotropic point was considered to have been attained.

The critical point was obtained at isothermal conditions by using an iterative experimental procedure involving changes in pressure and/or composition. As equilibrium was approached in the critical region, minor isothermal adjustments in the pressure were made to observe changes along the phase boundary and to note the critical opalescence. When the critical pressure had been determined, the pressure was increased well into the single-phase region so that the system could be sampled and analyzed to obtain the composition at the critical point.

Temperatures were measured with iron-constantan thermocouples which had been calibrated against a platinum resistance thermometer. Each temperature was read out on a digital voltmeter (HP-3455A). Temperatures are believed known to within ± 0.1 °C or better. Pressures were measured with various strain gauge pressure transducers, depending on the range and magnitude of the pressures encountered during the experiment. These had been calibrated with a precision dead-weight gauge. The various transducers were Druck PA-110/W (0-15 psia; 0.1% full scale (FS)); Statham PA208TC-100-350 (0-100 psia; 0.15% FS); and Statham UGP4-200 (0-200 psig; 0.15 FS), -500 (0-500 psig; 0.15% FS), and -1000 (0-1000 psig; 0.15 FS). The pressure is believed known to within $\pm 0.15\%$ of the full scale or better.

The phase compositions were determined with a Hewlett-Packard Model 5750B gas chromatograph coupled with an HP-3353 data acquisition system. A thermal conductivity detector on isothermal mode was used for this binary system. The column used was a 2.44-m-length by 3.18-mm-diameter stainless steel tube packed with Porapak-QS and was maintained at 105 °C. The response factor for converting from area fraction to mole fraction for isobutane was 1.7393 with respect

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