Table IV. Smoothed Pressure-Temperature-Composition Diagram in the Solid-Liquid-Vapor Region of the Ethylene-*n*-Dotriacontane System

press., atm	temp, K	composition of liquid phase, mole fraction ethylene	molar volume of liquid phase, mL/mol
10	339.9	0.178	487.0
20	337.7	0.325	401.5
30	336.0	0.435	347.0
40	334.5	0.523	303.8
50	333.1	0.598	264.1
60	331.7	0.657	233.8
70	330.4	0.707	207.9
80	329.2	0.752	183.6
90	328.1	0.798	159.5
100	327.4	0.830	142.6
120	326.7	0.863	126.0
140	326.4	0.879	118.0
160	326.2	0.886	114.0
180	326.0	0.895	109.8
200	325.9	0.900	107.0
220	325.7	0.915	99.2
240	325.7	0.917	98.2
260	325.6	0.927	93.2
271[a]	325.5		

[a] Type-K sineular point.

large standard deviations of pressure at high pressures in all of the data are due to the steepness of the curves with respect to the pressure variable. As before, the two critical end points make up two points on the binary L = V locus upper branch.

The S-L-V data in Tables II and IV can be correlated by using the Flory-Huggins theory (*4*, *5*) for the description of the nonideality of the liquid phase in concert with a solid-liquid fugacity equality formalism in the spirit of Prausnitz (*8*). However, to achieve a correlation of the accuracy desired for engineering design, one must modify the formalism in Prausnitz for pressure as the pressure effect is not negligible in these systems.

These systems presented herein also seem to be candidates for correlation using the perturbed hard-chain equation of state (*3*), which is designed parametrically for handling long molecules. We have not attempted to verify this conjecture.

Acknowledgment

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Glossary

CST	critical solution (temperature) point where two liquid phases become critical in the presence of the V phase
K	the critical end point, called the K point, where the L and V phases are critical in the presence of a third phase (either S or L)
L	liquid phase
P	pressure
Q	Q point, a four-phase invarient point, either S-L-L-V or S-S-L-V
S	solid phase
T	temperature
V	vapor phase

Literature Cited

(1) Colmenares, J. D. Ph.D. Thesis, University of Notre Dame, Notre Dame, IN, 1971.

(2) Diepen, G. A. M.; Scheffer, F. E. C. *J. Am. Chem. Soc.* **1948**, *70*, 4081.

(3) For example, see Donohue, M. D.; Prausnitz, J. M., Tulsa, OK, July 1977, Gas Processors Association, GPA Research Report RR-26.

(4) Flory, P. J. *J. Chem. Phys.* **1947**, *9*, 660; **1942**, *10*, 51.

(5) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440; *Ann. N. Y. Acad. Sci.* **1942**, *43*, 1.

(6) Lee, K. H.; Kohn, J. P. *J. Chem. Eng. Data* **1969**, *14*, 292.

(7) Miller, S. A., Ed. "Ethylene and Its Industrial Derivatives"; Ernest Benn Ltd.: London, 1969.

(8) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969; p 388 ff.

(9) Todd, D. B.; Elgin, J. C. *AIChE J.* **1955**, *1*, 20.

(10) van Gunst, C. A.; Scheffer, F. E. C.; Diepen, G. A. M. *J. Phys. Chem.* **1953**, *57*, 578.

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Supplementary Material Available: Complete tables of raw data (Tables A1-A4) for both binary systems (6 pages). Ordering information is given on any current masthead page.

Study of the Critical and Azeotropic Behavior of Binary Mixtures. 1. Critical States of Perfluoromethylcyclohexane–Isomeric Hexane Systems

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The *PVT–x* diagrams of five binary systems composed of the isomers of hexane with perfluoromethylcyclohexane as the common component were determined in the critical region. All of these systems form positive azeotropes and exhibit a minimum temperature point in their critical locus curves. The measured critical points in these systems and their correlation and prediction using an extended corresponding states principle are reported in this paper.

Introduction

The *PVT–x* relations of mixtures at elevated pressures are of great practical as well as theoretical interest. Of particular interest are those systems whose solutions deviate from ideality to such an extent that azeotropes are formed. Because of the difficulty in separating such mixtures by using conventional distillation techniques, data on the characteristic properties of azeotropes or reliable methods for their prediction are of importance to chemists and chemical engineers in the design and operation of chemical processes. From a theoretical point of view, the study of azeotropy is of considerable interest because it yields fundamental information on the molecular behavior of fluids.

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In spite of the existence of numerous azeotropic mixtures at atmospheric pressure, there have been few systematic measurements of such mixtures over a range of pressures, temperatures, and compositions. Kuenen (*9*, *10*) was the first to determine phase diagrams for systems which formed azeotropes in the critical region. He showed that in the binary systems N_2O–C_2H_6, CO_2–C_2H_6, and C_2H_2–C_2H_6 the critical locus curve possesses a point of minimum temperature, but he did not associate this property with the formation of azeotropic mixtures.

The general pattern of phase relations for critical azeotropic mixtures was established by Kay and co-workers, who studied the binary systems composed of the *n*-alkanes with perfluoro-*n*-heptane (*4*) and with acetone (*6*) as common components, and the *n*-alkyl alcohols with benzene as a common component (*16*). They found that the *PVT–x* diagrams for such systems may exhibit a great variety of forms depending on the difference in critical temperatures and pressures of the components. The present study deals with the relative effect of molecular structure on the phase diagrams of a series of binary systems composed of the isomers of hexane with perfluoromethylcyclohexane (PFMCH). These systems were found to form positive azeotropes which persist into the critical region.

Critical states of PFMCH–isomeric hexane mixtures and their correlation and prediction using an extended corresponding states principle are reported here. Measurements of dew and bubble points, as well as azeotropic states of these mixtures, are reported in the second part of the paper.

Experimental Section

The *PVT–x* relationships for the binary PFMCH–isomeric hexane systems were obtained by the determination of the *PT* and *VT* border curves of a series of mixtures of known composition. The relationships between any set of the variables were then obtained by appropriate cross plots of these curves. Also, for the *n*-hexane system, compressibility data in the superheated vapor and compressed liquid regions were taken.

The apparatus and experimental procedures employed were the same as those employed in studies previously reported (*5*, *7*, *8*). Very briefly, the operation consisted in confining a measured amount of an air-free sample over mercury in a precision-bore glass capillary tube, hereafter referred to as the experimental tube, which was surrounded by a constant temperature bath. The tube was fastened in a compressor block which was essentially a mercury-in-steel U-tube. This, in turn, was connected through a manifold to a high-pressure nitrogen gas cylinder. By admitting nitrogen gas to the system, pressure was applied via the mercury to the sample in the capillary. For the measurement of the compressibility of the superheated vapor, a dead-weight gauge was employed to measure the system pressure. Similarly, a bourdon gauge was employed to determine the pressure along the phase boundaries and in the compressed liquid region.

The constant-temperature bath surrounding the experimental tube consisted of a double-walled, silvered, and evacuated glass jacket with viewing slits and a side-arm boiling flask attached below the double wall. By refluxing the vapors of pure diethyl oxalate and diphenyl ether and controlling the pressure over the boiling liquid, we obtained a range of temperatures from 380 to 525 K constant to within ±0.02 K. The temperature of the bath was measured by a copper–constantan thermocouple with the aid of a sensitive potentiometer capable of reading the millivolt equivalent of 0.005 K.

The volume of the sample was determined by measuring the length of the tube occupied by the sample with a precision cathetometer reading to 0.02 mm. The volume of the tube per unit length had been determined by calibration with mercury, and the total volume was expressed analytically as a function of the distance from the sealed end of the tube. Equilibrium between the liquid and the vapor was attained by moving a magnetic stainless steel ball 0.159 cm in diameter through the sample by an external magnet held outside of the vapor jacket. This agitation also ensured an equilibrium distribution of the mercury vapor in the sample. The pressure gauges and the thermocouple were calibrated, the former by comparison with a calibrated dead-weight gauge and the latter by comparison with a platinum resistance thermometer which had been calibrated by the National Bureau of Standards.

Table I. Purity of Hexane Isomers

isomer	mol %	most probable impurity
n-hexane	99.96	methylcyclopentane
2-methylpentane	99.70	3-methylpentane
3-methylpentane	99.83	2-methylpentane
2,2-dimethylbutane	99.99	2,3-dimethylbutane
2,3-dimethylbutane	99.81	2,2-dimethylbutane

The *PVT* data were obtained by setting the temperature at a constant value, varying the pressure, and measuring the volume of the sample. Three types of phase boundary points were obtained: bubble points, dew points, and critical points. The bubble point was taken as the pressure at which a tiny bubble of vapor appeared in the liquid phase in the top of the tube. A dew point was observed when the first trace of liquid appeared at the mercury–vapor interface. This was viewed as a black spot—the contact of the ball with the liquid on the inner wall of the tube.

The critical point was determined by following the bubble point line to the temperature and pressure at which the meniscus disappeared and was replaced by a band of opalescent fog. Lastly, the isothermal compressibility measurements were made from 1.72 to 15.5 bar; above 15.5 bar; the precision bourdon gauge was employed. Further details of the apparatus and procedure are given in the ref *2*.

Source and Purity of Materials

The five isomeric hexanes employed in this investigation were obtained from the Phillips Petroleum Co., who furnished the data given in Table I concerning their purity.

The perfluoromethylcyclohexane was supplied by the E. I. du Pont de Nemours Co. It was treated with di-*n*-butylamine to remove possible traces of hydrofluorocarbons by using the method of Grafstein (*3*). This consisted in refluxing two volumes of the PFMCH with one volume of the amine for 2 h, followed by decanting the amine layer. This treatment was repeated three times. The PFMCH layer then was washed with 10% sulfuric acid to remove traces of the amine, dried over anhydrous potassium carbonate, and finally distilled. The standard boiling point was measured in an ebulliometer and found to be 349.56 K. A determination of the bubble and dew points of a sample at a series of constant temperatures from 373 K to near the critical point showed a difference in pressure that varied from ~0.14 bar to zero pressure with increasing temperature, indicating the presence of a trace of impurity. That this was not due to the presence of air in the sample was indicated by the fact that the vapor–liquid branch of the isotherm was linear with no sudden increase in pressure as the bubble point was approached. Rowlinson and Thacker (*14*) in the purification of PFMCH by fractional distillation found traces of three impurities by vapor phase chromatography which they attributed to traces of isomers having boiling points very nearly the same as PFMCH. We believe that this is the explanation of the isothermal difference in pressure between the bubble and dew points that was noted in the case of our sample.

Degassing and Loading the Sample

Air and other noncondensable gases were removed from the liquid sample by a series of operations which involved freezing with liquid nitrogen and pumping off the residual gas over the solid, followed by melting and distillation at low pressure. This cycle of operations was performed three times. The sample was then transferred by distillation to a side-arm flask and isolated from the degassing train by a stopcock. The sample was kept at low temperature by surrounding the flask with a dry ice bath. This was done for each of the five isomeric hexanes and PFMCH.

In the preparation of a binary mixture of known composition of PFMCH and a hexane isomer, a quantity of liquid was transferred by distillation from the appropriate storage flask to a small capillary whose total volume per unit length had been previously determined. From the length of the tube occupied by the sample at 273.16 K (measured with a cathetometer reading to 0.05 mm) and the density of the liquid at 273.16 K, the weight of the sample was calculated. A correction was made for the weight of the vapor over the liquid by using the perfect gas law and a knowledge of the vapor pressure and the total volume. The measured sample was then transferred by distillation to the experimental tube and frozen in the tip by surrounding the end of the tube with a bath of liquid nitrogen. In like manner, the second component was measured and transferred to the experimental tube. With the mixture frozen, mercury was then added until the tube was filled (*8*). The tube was then transferred to the compressor block.

Precision and Accuracy of the Experimental Measurements

Pressure. For the compressibility measurements in the super-heated vapor region, a dead-weight gauge was employed to measure the system pressure. It was estimated to have a precision of ca. ±0.0014 bar and an accuracy of ±0.0069 bar. Similarly, a bourdon gauge was employed to determine the pressure along the phase boundaries and in the compressed liquid region. Because of the hysteresis of the gauge, and the inability to read the pressure to better than ±0.014 bar, the overall accuracy of the gauge amounted to 0.069 bar. The precision was estimated to be ±0.027 bar.

Temperature. The temperature was measured with a copper-constantan thermocouple in conjunction with a sensitive potentiometer. The precision of this measurement was estimated to be ±0.01 K, but in lieu of such factors as temperature gradients caused by fractionation of the boiling liquid, radiation to the surroundings, calibration of the thermocouple, and balancing the potentiometer, the accuracy was estimated to be ca. ±0.1 K.

Volume. Two experimental tubes were employed in this study. For the PFMCH-*n*-hexane system, a tube having a relatively large volume and consisting of two sections of different diameter (4.6 and 2.0 mm i.d.) was employed. This tube was well studied for obtaining compressibility measurements and had a total volume of ~4.25 cm^3. For the remaining four systems, a uniform 2.0-mm i.d. tube was employed and had a volume of ~0.75 cm^3.

A sensitive cathetometer reading to within ±0.005 cm was employed in the determination of the volume in terms of the length of the tube. Consequently, this length measurement limited the accuracy of the sample volume. In the small 2-mm bore section of either tube, the precision amounted to ±0.25 vol %, while the accuracy was estimated to be ±0.05 vol %. In the large 4.6-mm bore section, the precision was estimated to be ±0.05 vol % and the accuracy to be ±0.10 vol %.

Composition. Binary mixtures of known composition were prepared by combining measured amounts of the air-free, liquid components in the experimental tube. This was accomplished by separately charging the perfluorocarbon and hydrocarbon samples into a 1-mm bore, calibrated, glass loading tube; measuring the volume at a known temperature; and distilling these measured quantities into the experimental tube. The compositions of the mixtures obtained in this manner were estimated to be accurate within ±0.1 mol %.

Table II. Critical Properties of the Pure Material

ref	T_c, K	P_c, bar	V_c, cm^3/mol	ρ_c, g/cm^3
Perfluoromethylcyclohexane				
this work	485.91	20.1871	570.09	0.614
n-Hexane				
this work	507.86	30.3162	366.53	0.235
Chun (*1*)	507.96	30.1659	371.43	0.232
Rossini (*13*)	507.90	30.316	368.26	0.234
Kay (*5*)	507.7	30.3369	369.84	0.233
2-Methylpentane				
this work	497.78	30.3203	368.43	0.234
Chun (*1*)	497.86	30.3093	366.69	0.235
Rossini (*13*)	498.10	30.3438	366.69	0.235
Kay (*5*)	498.1	30.3438	366.69	0.235
3-Methylpentane				
this work	504.60	31.2442	368.71	0.234
Chun (*1*)	504.63	31.2794	368.43	0.234
Rossini (*13*)	504.40	31.2401	366.69	0.235
Kay (*5*)	504.4	31.2401	366.70	0.235
2,3-Dimethylbutane				
this work	500.08	31.4524	360.15	0.239
Chun (*1*)	500.24	31.4731	356.08	0.242
Rossini (*13*)	500.30	31.3986	357.56	0.241
Kay (*5*)	500.4	31.3986	357.56	0.241
2,2-Dimethylbutane				
this work	489.25	31.0236	358.10	0.241
Chun (*1*)	489.02	30.8553	357.56	0.237
Rossini (*13*)	489.40	31.0608	359.05	0.240
Kay (*5*)	489.4	31.0746	359.05	0.240

Experimental Results

The following experimental data are presented in this paper: (1) the critical properties of all six pure substances; (2) the experimental *PVT* data at saturation for pure PFMCH; (3) critical states of binary mixtures of PFMCH-isomeric hexanes. Measurements along the saturation boundaries of mixtures and azeotropic states are presented in part 2 of this paper.

Critical Properties of the Pure Substances. Table II presents the experimentally determined critical constants for PFMCH and the five isomers of hexane, together with reliable values obtained from the literature. In this investigation, all values of the critical volume were determined from the law of rectilinear diameters.

A summary of the experimental thermodynamic properties at saturation from 383.16 K to the critical temperature of perfluoromethylcyclohexane is presented in Table III. Columns 1-4 give the following experimental quantities: the temperature T, the saturated vapor pressure P, and the specific volumes of the saturated liquid and vapor, V^L and V^G. The values of the vapor pressure, given in column 2, represent the numerical average of the experimental bubble and dew point pressures at temperature T. In no case did the bubble and dew point pressures differ by greater than 0.138 bar.

Column 5 gives the difference between the saturated vapor and liquid volumes ΔV_{vap}. The enthalpy of vaporization ΔH_{vap} given in column 6 was calculated from the rigorous, thermodynamic equation

$$\Delta H_{vap} = T \Delta V_{vap}(dP/dT) \qquad (1)$$

The slope of the vapor pressure curve (dP/dT) was obtained in the manner outlined by Reid and Sherwood (*12*) from the vapor pressure-temperature data by using the Douglass-Avakian method of numerical differentiation. Finally, the internal energy of vaporization ΔU_{vap} was obtained from eq 2.

$$\Delta U_{vap} = \Delta H_{vap} - P \Delta V_{vap} \qquad (2)$$

Table III. Experimental Thermodynamic Properties of Perfluoromethylcyclohexane

T, K	P, bar	V^L, cm³/mol	V^G, cm³/mol	ΔV_{vap}, cm³/mol	ΔH_{vap}, kcal/mol	ΔU_{vap}, kcal/mol
383.06	2.7799	221.14	10829.70	10608.56	6.75	6.05
393.06	3.5198	231.55	8437.53	8205.98	6.41	5.72
403.07	4.3947	243.16	6652.22	6409.06	6.06	5.39
413.07	5.4427	248.49	5295.63	5047.14	5.71	5.05
423.00	6.2224	256.45	4259.95	4003.50	5.33	4.70
433.08	8.1234	268.55	3325.01	3056.46	4.92	4.33
433.05	9.7533	279.45	2608.10	2328.65	4.51	3.97
453.09	11.6900	294.51	2133.77	1839.26	4.05	3.54
458.10	12.7484	302.97	1899.97	1597.00	3.79	3.30
463.04	13.8667	312.29	1673.18	1360.89	3.51	3.06
468.10	15.0685	323.91	1470.20	1146.29	3.23	2.82
473.10	16.3895	338.72	1260.88	0922.16	2.87	2.51
478.10	17.8236	361.76	1062.57	0700.81	2.40	2.10
483.05	19.2770	402.59	851.83	0449.24	1.77	1.56
485.15	19.6307	419.05	785.13	0366.08	1.42	1.25
485.16	19.9375	444.64	725.66	0281.02	1.04	0.91
485.50	20.0258	462.58	683.89	0221.31		
485.66	20.0982	496.71	656.94	0160.23		
485.91	20.1871	570.09	570.09	0000.00	0.00	0.00

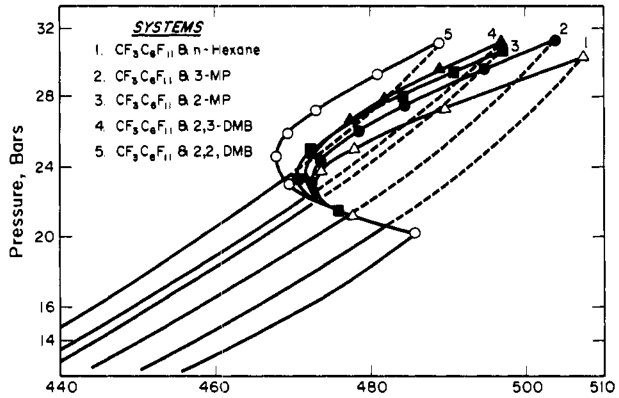

Figure 1. Vapor pressure curves of pure components and *PT* critical locus curves of binary systems of PFMCH with the isomeric hexanes.

The vapor pressure–temperature data were fit to a Clausius–Clapeyron type equation by using a least-squares technique (eq 3), where P is in bars and T is in K.

$$\log P = -1551.7/T + 4.49177 \tag{3}$$

Critical Properties for the Binary Mixtures. Table IV represents a summary of the experimental critical properties of the various mixtures associated with the five systems investigated, and therefore defines the critical locus curve for each system. The data of Table IV were plotted in Figure 1 as a composite diagram. The vapor pressure curves for the hexane isomers were taken from the data of Kay (*5*). It is apparent from Figure 1 that each of the isomers of hexane exhibit, with perfluoromethylcyclohexane, the characteristic minimum in critical temperature associated with the formation of positive azeotropes.

Correlation and Prediction of Critical States

The critical states measured in this investigation have been used to extensively test and develop an extended form of the corresponding states principle (*15*, *17–20*). This method has been used previously (*17–20*) for the calculation of critical and azeotropic states of mixtures of hydrocarbons. It is shown here that the method can be used for the prediction of critical states of mixtures containing PFMCH and also that extension of any isomeric system can be made quantitatively from a knowledge of the properties of another isomeric system.

Table IV. Critical Properties of Mixtures

x_1	T_c, K	P_c, bar	V_c, cm³/mol	ρ, mol/L
Perfluoromethylcyclohexane–*n*-Hexane				
1.0000	485.91	20.1871	570.09	1.7541
0.8172	476.21	21.5564	517.05	1.9340
0.6604	473.96	22.1824	501.99	1.9920
0.4830	473.59	23.3125	459.12	2.1780
0.3342	478.37	24.8107	423.78	2.3597
0.1732	489.95	27.5493	408.45	2.4482
0.000	507.86	30.3162	366.53	2.7282
Perfluoromethylcyclohexane–2-Methylpentane				
1.0000	485.91	20.1871	570.09	1.7541
0.7980	476.54	21.7012	524.46	1.9067
0.6087	471.14	22.7237	496.07	2.0158
0.4104	471.01	24.2647	448.79	2.2282
0.3077	474.01	25.2547	429.25	2.3296
0.2059	479.13	26.5241	399.89	2.5009
0.0913	487.76	28.6442	390.80	2.5588
0.0000	497.78	30.3203	368.43	2.7142
Perfluoromethylcyclohexane–3-Methylpentane				
1.0000	485.91	20.1871	570.09	1.7541
0.7951	478.21	21.7819	530.65	1.8844
0.5869	472.83	23.1574	487.94	2.0494
0.4045	474.65	24.7625	434.60	2.3009
0.2952	478.76	25.9304	425.70	2.3490
0.2062	484.53	27.4859	406.26	2.4614
0.0855	495.17	29.6391	385.09	2.5968
0.0000	504.60	31.2442	368.71	2.7121
Perfluoromethylcyclohexane–2,3-Dimethylbutane				
1.0000	485.91	20.1871	570.09	1.7541
1.8173	477.96	21.8184	517.18	1.9335
0.5930	472.23	23.2119	472.15	2.1179
0.4417	471.90	24.3212	442.92	2.2577
0.2875	476.01	26.0959	397.45	2.5160
0.2030	481.54	27.6514	394.04	2.5378
0.1078	488.97	29.6136	376.40	2.6567
0.0000	500.08	31.4524	360.15	2.7766
Perfluoromethylcyclohexane–2,2-Dimethylbutane				
1.0000	485.91	20.1871	570.09	1.7541
0.8330	477.71	21.6860	521.47	1.9177
0.6353	470.26	23.0050	470.69	2.1245
0.4025	467.85	24.7107	444.25	2.2510
0.2943	469.75	25.8539	421.09	2.3748
0.2056	473.28	27.1694	412.18	2.4261
0.0848	481.65	29.3033	381.66	2.6201
0.0000	489.25	31.0236	358.10	2.7925

Briefly, the method starts with the known *PVT* properties of a reference substance (methane has been used as a reference substance in all calculations presented below) and yields the properties of any substance which is conformal to the reference substance from a knowledge of its critical temperature and volume. Nonconformal substances can be included in the treatment using shape factors (*11*) whose magnitude is proportional to the difference in acentric factors of that substance and the reference substance. The method can be extended to mixtures via the van der Waals one-fluid model, which is used to obtain the pseudocritical temperature and volume of a hypothetical pure substance which has the same properties as the mixture:

$$V_{cm}T_{cm} = \sum\sum x_i x_j T_{cij} V_{cij} \quad (4)$$

$$V_{cm} = \sum\sum x_i x_j V_{cij} \quad (5)$$

In using the van der Waals one-fluid model, the like terms ($i = j$) are obtained from pure component properties, but unlike terms ($i = j$) require mixture data for their evaluation. The usual procedure is to write

$$T_{cij} = \xi_{ij}(T_{cii}T_{cjj})^{1/2} \quad (6)$$

$$V_{cij} = (V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \quad (7)$$

where the binary interaction coefficient is an adjustable constant which must be obtained from experimental data. In general, it is sufficient to characterize each binary system by means of one adjustable coefficient, and no further information is required to predict the properties of ternary and higher mixtures. The values ξ_{ij} calculated from corresponding states correlations of various thermodynamic properties and phase equilibria agree very well with each other (*21*). It is believed that the value of ξ_{ij} for any binary mixture is a measure of intermolecular forces in that mixture and is not an artifact of the method of calculation. To demonstrate this point, the single value of ξ_{ij} used in *all* calculations presented below was obtained from the correlation of the critical states of PFMCH–*n*-hexane mixtures. It was assumed that the intermolecular interactions in all other mixtures containing the isomers of *n*-hexane were similar to those in the PFMCH–*n*-hexane system. Hence critical states in the PFMCH–*n*-hexane system have been correlated, whereas critical states in the other systems have been *predicted* by using only the critical points and acentric factors of the *pure* components. (As will be seen below, agreement with experiment is truly remarkable.)

Critical states of binary mixtures which exhibit azeotropic behavior in the critical region satisfy the following equations (*20*):

$$A_{2x}A_{2v} - A_{xv}^2 = 0 \quad (8)$$

$$A_{3x}A_{2v}^3 - 3A_{2xv}A_{xv}A_{2v}^2 + 3A_{x2v}A_{2v}A_{xv}^2 - A_{3v}A_{xv}^3 = 0 \quad (9)$$

where the subscripts denote derivatives, e.g., $A_{2xv} = \partial^3 A/\partial x^2 \partial V$. Hence, if the Helmholtz free energy and its derivatives are available, then the two equations may be solved for any two of the three variables T_c, V_c, x_c. In the calculations presented here, the Helmholtz free energy and its derivatives were obtained by using the extended corresponding states principle, and the two equations were solved for T_c and V_c at various values of x_c, thus yielding the complete critical locus. (P_c may be obtained by using the corresponding states equations when T_c, V_c, and x_c are known or have been calculated.)

Results of the calculations are shown in Figures 2–4. As mentioned above, a single value of the binary interaction coefficient $\xi_{12} = 0.885$, obtained from a "best fit" of the critical properties of PFMCH–*n*-hexane mixtures, has been used for all systems. It is apparent from the figures that agreement with experiment for all five mixtures and for all critical properties (critical temperature, critical pressure, and critical density as a function of composition) is excellent. This demonstrates the power and truly predictive capabilities of the corresponding states approach. Further details of the method of calculation are given elsewhere (*17*, *20*).

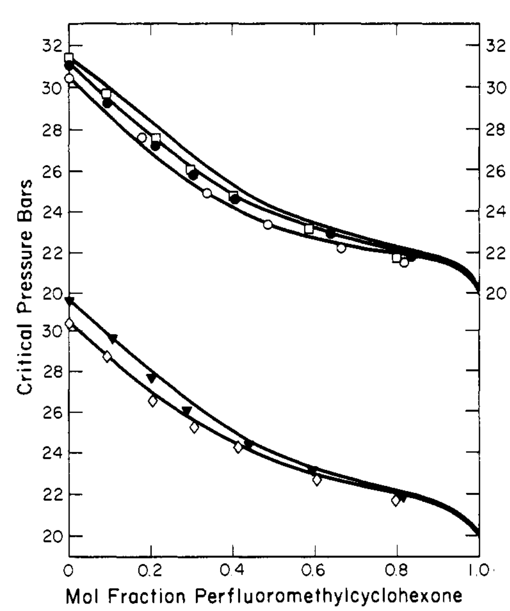

Figure 2. Critical pressure–composition relations of binary systems of PFMCH with the isomeric hexanes. Predicted values: (—). Experimental points: (●) 2,2-dimethylbutane; (□) 3-methylpentane; (○) *n*-hexane; (▽) 2,3-dimethylbutane; (◇) 2-methylpentane.

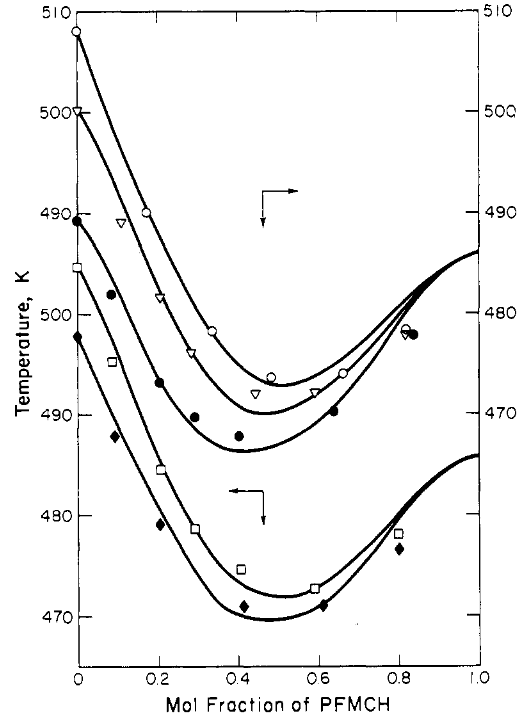

Figure 3. Critical temperature–composition relations of binary systems of PFMCH with isomeric hexanes. Predicted values: (—). Experimental points: (○) *n*-hexane; (▽) 2,3-dimethylbutane; (●) 2,2-dimethylbutane; (□) 3-methylpentane; (◇) 2-methylpentane.

Glossary

A	Helmholtz free energy
H	enthalpy
P	pressure
R	gas constant
T	thermodynamic temperature
U	internal energy
V	volume
x	mole fraction

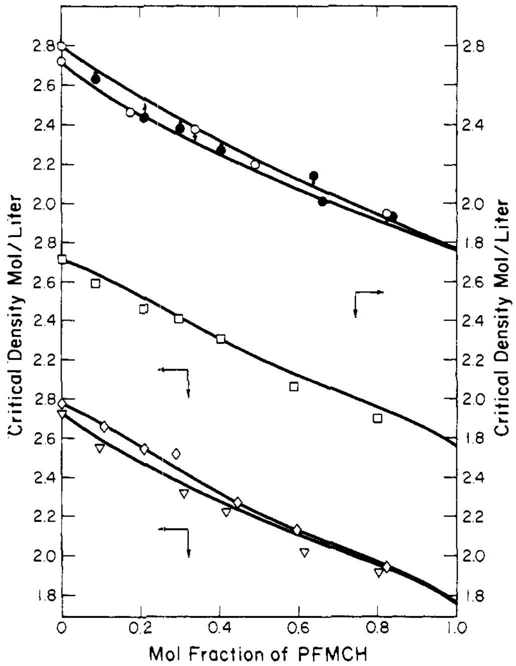

Figure 4. Critical density-composition relations of binary systems of PFMCH with isomeric hexanes. Predicted values: (—). Experimental points: (●) 2,2-dimethylbutane; (○) *n*-hexane; (◇) 2-methylpentane; (▽) 2,3-dimethylbutane; (□) 3-methylpentane. $\xi = 0.885$ for all systems.

ρ	density
ξ	interaction coefficient

Subscripts

1, 2	component 1, 2
c	critical
cm	pseudocritical value for mixture
i, j	component i, j
vap	vaporization
x, v	differentiation with respect to x, v

Superscripts

G	gas
L	liquid

Literature Cited

(1) Chun, S. W. Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1964.
(2) Genco, J. M. Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1965.
(3) Grafstein, D. *Anal. Chem.* **1954**, *26*, 523.
(4) Jordan, L. W.; Kay, W. B. *Chem. Eng. Prog., Symp. Ser.* **1963**, *59*, 46.
(5) Kay, W. B. *J. Am. Chem. Soc.* **1946**, *68*, 1336.
(6) Kay, W. B. *J. Phys. Chem.* **1964**, *68*, 827.
(7) Kay, W. B.; Rambosek, G. M. *Ind. Eng. Chem.* **1953**, *45*, 221.
(8) Kay, W. B.; Donham, W. E. *Chem. Eng. Sci.* **1955**, *4*, 1.
(9) Kuenen, J. P. *Philos. Mag.* **1895**, *40*, 173.
(10) Kuenen, J. P. *Philos. Mag.* **1897**, *44*, 174.
(11) Leland, T. W.; Chappelear, P. S. *Ind. Eng. Chem.* **1968**, *60*, 15.
(12) Reid, R. C.; Sherwood, T. K. "The Properties of Gases and Liquids", 2nd ed.; McGraw-Hill: New York, 1966, p 89.
(13) Rossini, F. D. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons"; American Petroleum Institute, Carnegie Press: Pittsburgh, 1953.
(14) Rowlinson, J. S.; Thacker, P. *Trans. Faraday Soc.* **1957**, *53*, 1.
(15) Rowlinson, J. S.; Watson, I. D. *Chem. Eng. Sci.* **1969**, *24*, 1565.
(16) Skaates, J. M.; Kay, W. B. *Chem. Eng. Sci.* **1964**, *19*, 431.
(17) Teja, A. S.; Rowlinson, J. S. *Chem. Eng. Sci.* **1973**, *28*, 529.
(18) Teja, A. S.; Kropholler, H. W. *Chem. Eng. Sci.* **1975**, *30*, 435.
(19) Teja, A. S.; *AIChE J.* **1975**, *21*, 618.
(20) Teja, A. S. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 435.
(21) Teja, A. S. *Chem. Eng. Sci.* **1978**, *33*, 609.

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Study of the Critical and Azeotropic Behavior of Binary Mixtures. 2. *PVT–x* Data and Azeotropic States of Perfluoromethylcyclohexane–Isomeric Hexane Systems

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***PVT–x* data for five binary systems composed of the isomers of hexane with perfluoromethylcyclohexane as the common component are reported in this paper. All of these systems form positive azeotropes which persist in their critical regions. The locus of azeotropic points for each system and its prediction using an extended corresponding states principle is also reported.**

Introduction

An investigation of the *PVT–x* relations of a series of binary systems composed of the isomers of hexane with perfluoromethylcyclohexane (PFMCH) as a common component was undertaken to obtain information on the relative effect of molecular structure on the phase diagrams of such mixtures. These systems were found to form positive azeotropes which persist up to the critical locus curve. The critical loci of PFMCH–isomeric hexane mixtures and their correlation and prediction using an extended corresponding states principle were reported in part 1 of this paper (*1*). It was found that the critical loci of all these systems exhibit a minimum temperature point which is characteristic of systems which form positive azeotropes in their critical region. It was further shown that the critical loci of PFMCH–isomeric hexane systems could be predicted by the extended corresponding states approach, using only a single adjustable binary interaction coefficient obtained from the correlation of the critical states of PFMCH–*n*-hexane mixtures.

In this paper, we report the measurements of dew and bubble points as well as azeotropic states of PFMCH–isomeric hexane systems. The predictive capabilities of the extended corre-

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