Phase Equilibria in the Critical Region

Binary Systems with Chlorotrifluoromethane

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KNOWLEDGE of phase equilibria is fundamental to the understanding of heterogeneous systems and to their use in separation processes and other chemical engineering operations. Phase equilibria in the critical region—the region at elevated pressures above the critical temperature of one of the compounds—are characterized by large nonidealities in the gas phase as well as possible liquid phase nonidealities. These nonidealities are manifested in interesting but generally unpredictable phenomena such as the solution of relatively large amounts of nonvolatile liquids and solids in supercritical gases, the existence of liquid phases consisting almost entirely of a supercritical component, phase inversions, gas-gas immiscibilities, etc. Unique separation processes might utilize the large changes in solubilities that occur over small temperature and pressure ranges in the critical region.

The present investigation is part of a continuing program at Princeton aimed at the understanding and generalization of phase equilibria just above the critical temperature of the gaseous component. Todd and Elgin (*16*) presented results of the original investigation of organic liquids with supercritical ethylene (T_c9.5° C.) which established the three types of pressure-composition isotherms that have also been found in all subsequent binary systems. This work was extended by Gottschlich (*7*), and ternary systems with ethylene were studied by Elgin and Weinstock (*5*). Snedeker (*15*) studied binary and ternary systems with carbon dioxide (T_c31.04° C.) and related his results to extensive work on subcritical carbon dioxide. The binary patterns observed with carbon dioxide were generally similar to those found with ethylene.

The purpose of the present work was to generalize the behavior patterns of binary systems in this region, utilizing previous results, theory, and experimental determinations with a different gaseous component. Behavior of previously studied systems, particularly the p-x isotherms with ethylene and with carbon dioxide, suggested ways in which the various patterns could be related to the properties of the pure components and the subcritical behavior of the systems. Theories of liquid solutions and nonideal gases, though not directly applicable, indicated the important variables and the trends to be expected. Vapor pressure and solubility parameter difference were chosen to correlate the results and develop a qualitative method of predicting the type of p-x isotherm to be observed just above the lower critical temperature. Equilibrium data were obtained for seven organic liquids with chlorotrifluoromethane (CTFM or Freon 13) to test and extend this correlation and to aid the understanding of behavior in this region.

CTFM was chosen for the gaseous component because it has a considerably lower solubility parameter than ethylene and carbon dioxide, with a comparable critical temperature (28.85° C.). The thermodynamic properties of pure CTFM were determined by Albright and Martin (*1*), but practically no solubility data could be found. The liquid components were chosen to give a wide range in vapor pressure and solubility parameter and to extend work on some liquids studied with the other gases. Pressure-composition and, in some cases, volume-composition isotherms were determined for these systems. The types of p-x isotherms found in the nonassociated systems agreed with the tentative predictions based on the isotherms found with ethylene and carbon dioxide. The method of prediction was improved by the utilization of the CTFM data.

A method was derived for calculating the partial molar volumes from the v-x isotherms at variable pressure; these calculations were carried out for systems of CTFM with toluene, *o*-xylene, and *m*-xylene.

BEHAVIOR PATTERNS

The three-dimensional p-T-x diagram is of interest for separation processes; Ricci (*14*) has illustrated the interrelations of the various cross sections and projections. It is convenient to consider the p-x cross sections in relation to the p-T-x phase boundaries as in Figure 1.

This study is limited to systems where solid regions do not intrude into the critical region, eliminating solid-fluid systems such as ethylene-naphthalene (*4*). The p-T projections of the loci of critical solution points can be divided into two major types: those in which these loci are continuous between the critical points of the two components, and those in which the critical loci are broken by liquid-liquid immiscibilities.

In the former type, the continuous critical locus may be of many forms. Systems with widely separated critical temperatures show critical curves that are convex upward as in the p-T-x diagram in Figure 1. Figure 2 shows how the maximum rise of the critical locus is higher for systems with greater differences in the critical temperatures of the components, giving some indication of the effect of temperature on the critical solution pressure. References to the systems used and their literature sources are available (*3*). Figure 1 shows that the Type I isotherm, with an observable critical solution point, will be found just above the critical temperature of the more volatile component. The Type II isotherm, with liquid-gas immiscibility to the maximum pressure of the apparatus, may be observed at higher temperatures as with the *n*-decane–carbon dioxide system at 50° C. (*16*).

Many systems have discontinuous critical curves as a result of three-phase immiscibilities in the critical region—a second liquid phase, L_2, forming. The phase rule indicates that three-phase equilibria in a binary system will be monovariant and can therefore be represented by a line on the p-T projection. Above the lower critical temperature, a L_1-L_2-V region leads to a Type III supercritical isotherm as shown in Figure 3. This line is terminated at high temperatures by what Ricci (*14*) calls a type-*k* singular point—in this case the invarient upper critical solution point at which the properties of the L_2 and V phases become identical in the presence of L_1. This point is joined to the critical point of the more volatile component by the $L_2 = V$ critical locus. At its lower end, the three-phase line may be terminated by another type-*k* singular point, $L_1 = L_2$, connected to the upper critical point by the other section of the critical locus as shown in Figure 3.

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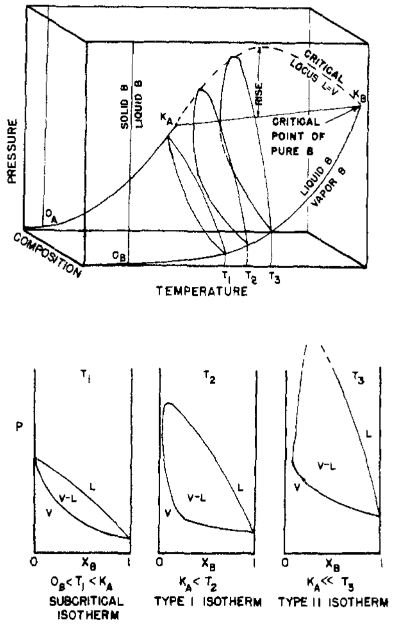

Figure 1. Phase diagrams for a binary system with a continuous critical locus

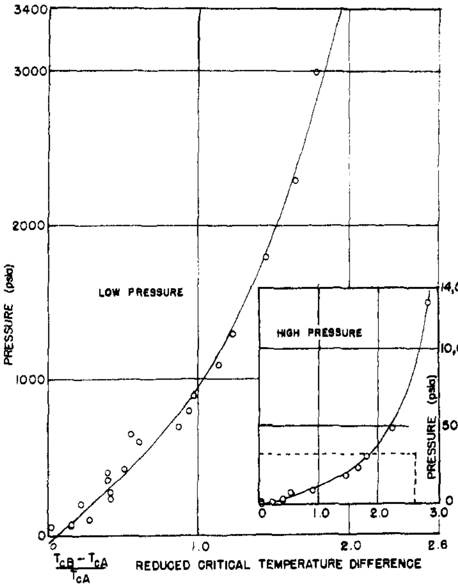

Figure 2. Rise of the critical locus above the critical pressures of the pure components for systems reported in the literature

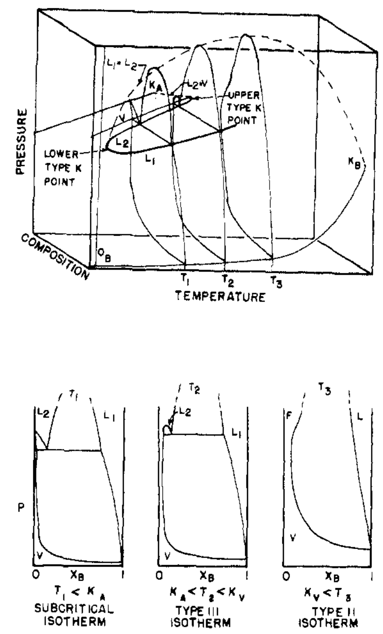

Figure 3. Phase diagrams for a binary system with liquid/liquid immiscibility cutting the critical locus

The extension of the subcritical immiscibility above the lower critical temperature suggests that methods of predicting nonidealities below the critical temperature may have some application in the critical region. This is not necessarily the case, however, since the three-phase line may be entirely above the critical temperature on one component. The system of ethylene-capronitrile reported by Todd (*16*) is an example of this behavior, giving a Type I isotherm 1° C. above the critical temperature of ethylene and a Type III isotherm 10° C. above the critical temperature. Other examples have also been reported (*4*).

Barker and Fock's (*2*) theory of upper and lower critical solution temperatures indicates that a lower type-*k* point is not to be expected unless the entropy of mixing deviates significantly from that of an ideal solution. With ideal entropy of mixing or where there is a high-melting solid in the system, the three-phase line will intersect a solid surface—e.g., methane with hydrogen sulfide (*10*). The same types of supercritical isotherms could be expected, however.

A fourth type of supercritical isotherm might be possible where the three-phase L_1-L_2-V line lies above the vapor pressure lines of both pure components as in the water-ether system (*9*).

BASIS FOR CORRELATION

The immediate objective is the choice of variables for the qualitative prediction of behavior patterns. The usual liquid-solution and gas-mixture models do not seem directly applicable because of the unknown variations of molar volumes in the more miscible systems (Type I) and the inability to predict the formation of a second liquid phase in the critical region (Type III behavior). The magnitude of the intermolecular energy between unlike and like molecules is one of the most important parameters in gas-liquid solutions (*8*). Even though Hildebrand's regular solution model is of limited applicability here, the difference in the solubility parameters of the components is a convenient measure of this difference in intermolecular energy.

$$\delta_B - \delta_A = \left(\frac{E_{VB}}{v_B}\right)^{1/2} - \left(\frac{E_{VA}}{v_A}\right)^{1/2} \qquad (1)$$

For a liquid, E_V is essentially the heat of vaporization and v the molar volume. The regular solution model arises from the assumptions of no volume change on mixing, ideal entropy of mixing, and the "geometric mean rule" for intermolecular energy (*8*). Since the energy of vaporization is not defined for a gas, and a large volume change occurs when the gas dissolves in a liquid, a special method is required for the evalution of the solubility parameter of a gas. A modification of the method described by Prausnitz (*12*) was chosen for this study. This involves the evaluation of the solubility parameter of the supercritical component at that high pressure at which mixing of the pure gas and liquid occurs with no volume change. The difference in the internal energy of the pure gas between this pressure and zero pressure is set equal to E_V. The modification required near the critical point involves the use of a liquid corresponding-state isotherm (T reduced = 0.56) in place of an assumed constant compression for the gaseous component in solution. This change assures intersection with the gas-phase isotherm, even at high pressures near the critical point. (One would expect the compressibility of the supercritical component in both phases to decrease at higher pressures.)

Hildebrand and Scott (*8*) give several methods for obtaining the solubility parameters of liquids and present a table of values. Those used in the present work were obtained at 25° C. from published heats of vaporization, or from vapor pressure data using the methods given. Since the solubility parameter varies slowly with temperature, only a small error is introduced for these systems which are within 15° C. of this temperature.

Other factors will also affect the supercritical behavior patterns. Figure 2 shows that an increase in the critical temperature difference causes a rise in the critical locus and thus a decrease in the gas-in-liquid solubility. A decreased vapor pressure of the liquid component tends to reduce the mutual solubility in both phases. By analogy with liquid-liquid solutions, an increase in the molar volume of the liquid relative to a given gas tends to decrease the solubility because of heat effects. Fortunately, all these effects are related, and the higher members of a homologous series would be expected to be less miscible with a gas by all these criteria. The vapor pressure of the pure liquid component was chosen since it gives a generally self-consistent correlation, was more often available than the liquid critical temperature, and seemed to be closely related to the formation of a second supercritical liquid phase in the critical region.

If the vapor pressure of the liquid component is plotted against difference in solubility parameter each point will represent these physical properties of one system at a specific temperature. It was found that such a plot of systems with carbon dioxide and ethylene could be approximately divided into two regions, the points in one region giving Type I behavior and in the other, Type III behavior. Tentative predictions could be made from this graph. The experiments with CTFM described below were to check such predictions and to define better the boundaries between the various regions.

EXPERIMENTAL

Gaseous CTFM was compressed into an agitated chamber containing the liquid component. Provision was made for observation of the interfaces and removal of gas and liquid samples at constant pressure and temperature. Similar apparatus is described by Elgin and Weinstock (*5*).

The equilibrium chamber was a modified Jerguson liquid-level gage, fitted with a magnetically driven agitator, two removable sample tubes, and auxiliary equipment for charging and adjustment of the liquid level. The equilibrium chamber was submerged in a constant-temperature (±0.02° C.) water bath; this water was also circulated around the sample tubes.

A Heise 0- to 2000-p.s.i. Bourdon-tube gage graduated by 2-p.s.i. divisions was calibrated and used for primary pressure measurement for most of the systems. An Aschroft gage graduated from 0 to 1500 p.s.i.g. by 20-p.s.i. divisions was used for systems with propanol, tetradecane, and toluene

Sampling and Analysis. The liquid component of the system to be studied was introduced into the equilibrium chamber, followed by gaseous CTFM. When equilibrium had been attained (indicated by 45 minutes of constant pressure), a sample was taken by permitting the mercury in a sample tube to flow into the equilibrium chamber, displacing fluid into the sample tube.

After samples of two phases in equilibrium were taken, the sample tubes were disconnected, weighed on an analytical balance, cooled with dry ice, and slowly vented. They were then warmed to room temperature and reweighed to determine the amount of CTFM vented. The amount of the subcritical component was determined by weighing the liquid drained from the tube, rinsing the tube, and taking the refractive index of the solvent used as rinse. This was checked by weighing the tube before and after it was drained, rinsed, and dried. The details of the apparatus, experimental procedure, discussion of errors, materials used, and sample calculation are all available on microfilm (*3*).

RESULTS

The same three types of isotherms were observed in CTFM systems as with the other gases. With the lower solubility parameter of CTFM, mutual solubilities were generally lower and nonidealities leading to Type II and Type III behavior, greater than for the same liquids with ethylene and carbon dioxide.

In Figure 4, the large points indicate the specific type of isotherm observed with each of the CTFM systems in relation to the liquid vapor pressure and the solubility parameter difference. The previously mentioned systems with ethylene and carbon dioxide are also plotted. The shape of the point indicates the type of isotherm observed. The CTFM systems fall into the areas that would be expected from the previous results. The isotherms for nonassociated liquids (Table I) with all three gases were used to draw the more precise boundaries in Figure 4. The division is for approximately 4° C. above the gas critical temperature. Since Todd's data (*16*) were taken at other temperatures, there is some uncertainty about the behavior at the temperature of comparison. More precise location of the boundaries will require data on more systems—particularly the boundary between Type II and Type III regions, which now depends on only one Type II system. As the

Table I. Data for Nonassociated Systems

(Referred to in Fig. 4)

Liquid	Gas	Temp., ° C.	Vapor Pressure, Mm. Hg	$\delta_B - \delta_A$ (Cal. /Cc.)$^{1/2}$	Type Isotherm
n-Heptane	C_2H_4	10.5	21	1.0	I
		19.5	34		I
n-Decane	C_2H_4	10.5	0.51	1.2	I
		19.5	1.0		I
n-Cetane	C_2H_4	10.5	3.2×10^{-4}	1.4	(III)
		19.5	9.1×10^{-4}		(I ?)
Toluene	C_2H_4	10.5	13	2.0	I
		19.5	22		I
Propyl propionate	C_2H_4	10.5	5.1	1.7	I
		19.5	9.2		I
Hexaldehyde	C_2H_4	10.5	5.4	2.6	I
		19.5	9.4		I
o-Dichlorobenzene	C_2H_4	11.4	0.55	2.3	III
p-Dichlorobenzene	C_2H_4	11.4	1.0	2.7	(I)
		20.8	2.0		(I)
n-Heptane[a]	CO_2	35	75	−0.3	I
n-Decane[a]	CO_2	35	3.2	−0.2	I
		50	7.5		(II)
n-Tetradecane[a]	CO_2	32.1	0.028	−0.1	III
n-Cetane[a]	CO_2	35	4.9×10^{-3}	−0.1	(II or III)
Toluene[a]	CO_2	35	47	0.5	I
Chlorobenzene[a]	CO_2	35	19	0.9	I
Acetone[a]	CO_2	35	350	1.1	I
n-Tetradecane	CTFM	32.75	0.03	2.0	III
Decane	CTFM	30.0	2.5	1.9	I
Toluene	CTFM	32.75	43	2.59	I
o-Xylene	CTFM	32.75	12	2.64	I
m-Xylene	CTFM	32.75	13	2.54	I
Phenyl ether	CTFM	32.75	0.12	3.3	II
Bromoform	CTFM	32.75	9.2	3.9	III

[a] Reference (*15*); first eight liquids (*16*).

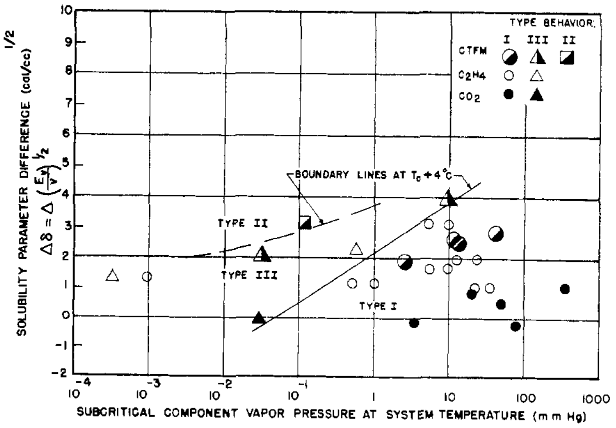

Figure 4. Type of supercritical isotherm as a function of solubility parameter difference and subcritical component vapor pressure

temperature is raised and the upper type-*k* point exceeded, the Type II–Type III boundary will move down, approaching the other boundary.

Prediction of Behavior in Other Systems. To use this correlation for the prediction of patterns in other nonassociated systems, the solubility parameter difference between the liquid and the gas must first be calculated by methods mentioned above. The vapor pressure of the liquid component at the system temperature can usually be interpolated or extrapolated from published data. These properties of the binary system become its coordinates in Figure 4, and the type of isotherm to be expected is given by the region into which the system falls. Until more data are available, predictions close to the boundaries should be considered tentative.

No point representing the 1-propanol–CTFM system is shown in Figure 4, since in hydrogen-bonded systems the solubility parameter difference is no longer a valid measure of the interaction energy. A plot similar to Figure 4, but for hydrogen-bonded systems, shows the same general trends, but indicates no precise boundaries (*3*).

Quantitative Results. The different types of isotherms are the results of continuous changes in behavior patterns. Understanding of the relationship of these changes to the system parameters is aided by consideration of the details of the *p*-*x* isotherms and volumetric behavior of the system.

The systems of CTFM with toluene and *m*- and *o*-xylene are well within the Type I region and give very similar Type I isotherms, as seen in Figure 5. For comparison, Todd's toluene-ethylene results (*16*) are plotted against the "corresponding-pressure ratio." This ratio removes the first order (Henry's law) effects of critical temperature and pressure by dividing the system pressure by the extrapolated vapor pressure of the supercritical component. The solubility parameter difference is greater with toluene-CTFM than with toluene-ethylene or toluene–carbon dioxide, and the initial solubility of the gas is less, relative to Henry's law. In all these cases, the two-phase region is still closed and touches the axes at one point, the vapor pressure of the pure liquid. Because this vapor pressure is low, the major portion of the vapor branch of the curve lies nearly on the bottom and left-hand axes. No data were taken along this section of the curve; it can be calculated approximately from Raoult's law (dotted line). As the critical pressure and density of the CTFM are approached in the gaseous phase, the solubility of the liquid component increases over that predicted by Raoult's law.

The maxima indicate critical coalescence which was observed after iterative adjustment of the total concentration in the equilibrium chamber. Coalescence was characterized by deep orange colors in both phases, as well as the flattening and disappearance of the miniscus.

Figure 6 shows the liquid *v*-*x* isotherms for the Type I systems. Since the relative variation of the mean molar volume is much smaller than that of the pressure, the *v*-*x* plot offers a sensitive means of spotting erratic samples. A more important use of the *v*-*x* isotherms is as a basis for the calculation of the partial molar volumes of the components. This cannot be done directly from equilibrium data by the Bakhuis-Rooseboom method, since this depends on an assumption of constant pressure for the evaluation of the partial derivative. These data may be used, however, if the effect of pressure on volume is correctly utilized. The appropriate equation (*3*) is

$$v_A = v - x_B \left(\frac{dv}{dx_B}\right)_{T,\,\text{coex.}} + x_B \left(\frac{\partial v}{\partial p}\right)_{T,\,x} \left(\frac{dp}{dx_B}\right)_{T,\,\text{coex.}} \tag{2}$$

with the x_B derivatives evaluated at constant temperature along the coexistence line of the two phases in equilibrium, rather than at constant temperature and pressure.

The first two terms on the right side correspond to those in the Bakhuis-Rooseboom method and can be similarly evaluated from the intercepts of the tangents to the *v*-*x* plot (*13*). Using the *p*-*x* isotherm, the third term can be evaluated if one assumes that the compressibility of the supercritical component in solution is equal to that of the pure gas at the pressure at which their respective molar volumes are equal. In these cases, the third term turns out to be a small correction to the other two over most of the concentration range, making the assumption relatively uncritical. The resulting partial molar volumes are plotted against composition in Figure 7. As the liquid phase becomes predominantly CTFM, the partial molar volume of the CTFM begins to increase at a progressively faster rate until, at the critical pressure, it equals that of the dense gas

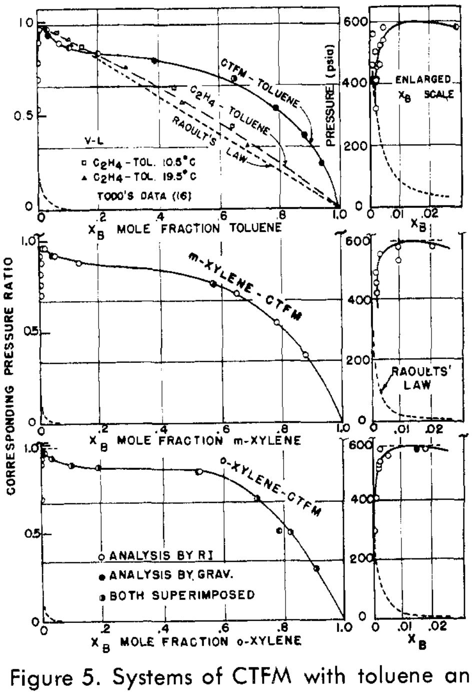

Figure 5. Systems of CTFM with toluene and xylenes give Type I pressure-composition isotherms at 32.75° C.

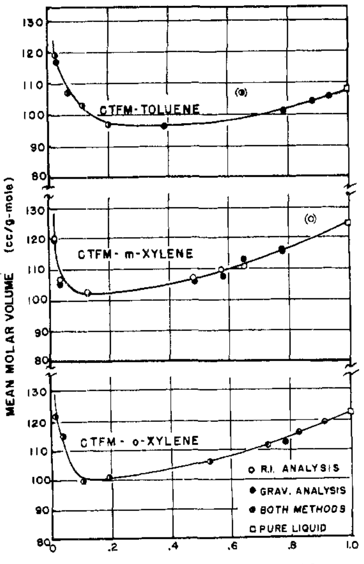

Figure 6. The mean molar volume of the liquid phase of a Type I system decreases then increases as the critical composition is approached, giving a minimum in the volume-composition isotherm

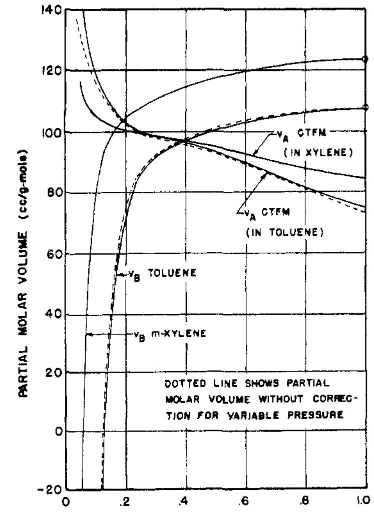

Figure 7. Partial molar volumes of both components in the liquid phase show rapid changes as the critical composition is approached

phase. The partial molar volume of the subcritical component falls off very rapidly and actually becomes negative. This means that a small amount of toluene added to the liquid in this composition range will cause a net decrease in the total volume as mixed bonds are formed at the expense of weaker bonds between the CTFM molecules. The subcritical component tends to be a condensing agent for the expanded CTFM in the region of its extrapolated vapor pressure.

The system *n*-tetradecane–CTFM, shown in Figure 8, indicates the Type III behavior given by a low vapor pressure liquid below its upper type-*k* point. The observed maximum of the very small V-L_2 dome is only about 5 p.s.i. above the three-phase line. This dome disappears above the upper type-*k* point at 34.2° C. By comparison with the tetradecane–carbon dioxide data (*15*), one can see the effect of the increased solubility parameter difference on the gas-in-liquid solubility. At approximately 735 p.s.i.a., the dense but compressible L_2 phase becomes heavier than the L_1 phase, and the positions of the two phases are inverted. Such barotropic phenomena have been reported previously at much higher pressures (*11*).

The Type III isotherm appears differently for the bromoform-CTFM system (Figure 9), showing the combined effect of high vapor pressure and very large solubility parameter difference. The latter is responsible for the very low gas-in-liquid solubility and the low solubility of bromoform in the CTFM phase at high pressures. This is partly counteracted in the region of the three-phase pressure by the high vapor pressure of bromoform; the V-L_2 dome is approximately the same size as the tetradecane-CTFM system.

The system of CTFM with phenyl ether at 32.75° C. gives the Type II isotherm shown in Figure 10. The system will give Type III behavior between 28.85° C. (the critical temperature of CTFM) and 30.0° C. (the upper type-*k* point of the system). The proximity of these two temperatures and the very small fluid-phase solubility of the phenyl ether are the result of the combination of low vapor pressure and relatively high solubility parameter difference. The vapor branch of the curve at 32.75° C. shows a definite concavity, giving rise to a shoulder in the critical pressure region—the incipient L_2-V dome. The solubility parameter difference lies between that of the bromoform-CTFM system and those of the systems with hydrocarbons; this system also shows an intermediate gas-in-liquid solubility. The three-phase line intersects a solid surface at about 24° C., giving an invariant quadruple point.

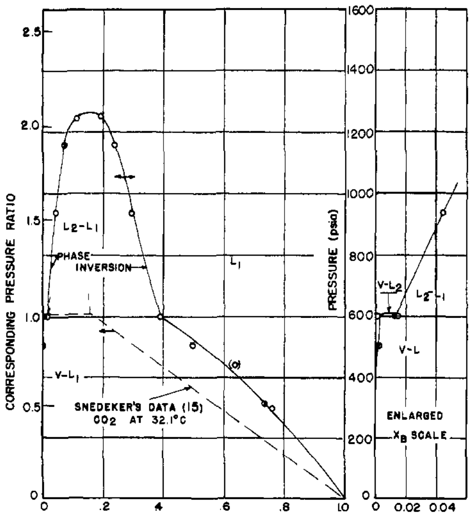

Figure 8. As with CO_2, tetradecane withCTFM at 32.75° C. gives a Type III *p-x* isotherm but with generally reduced solubility. The third phase arises from the large difference in vapor pressures (volumes) not solubility parameter difference

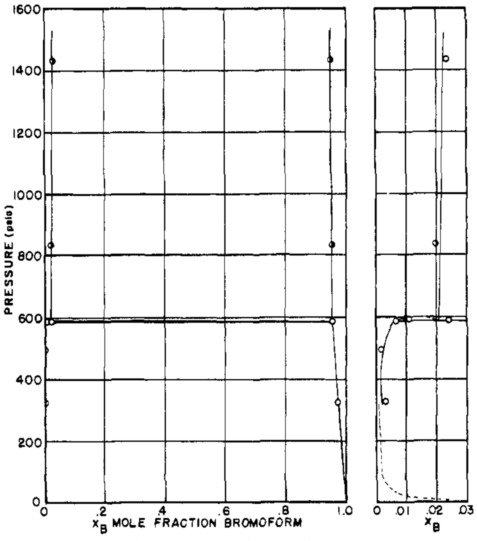

Figure 9. The bromoform-CTFM system at 32.75° C. gives a highly immiscible Type III *p-x* isotherm as predicted from the large solubility parameter difference

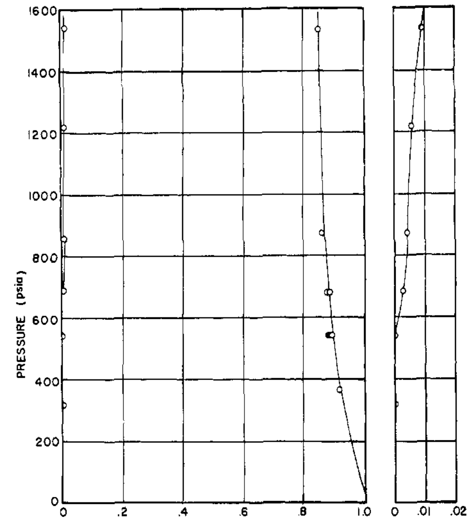

Figure 10. The phenyl ether–CTFM system at 32.75° C. gives a Type II *p-x* isotherm as the result of low vapor pressure and large solubility parameter difference

Franck (*6*) predicted from statistical calculations the proportionality of $1/v$ to the log of the concentration of a solid solute in a supercritical fluid at moderate densities. With a liquid solute, the first-order effects of varying liquid composition can be removed by using the ratio x_B (fluid)/ x_B (liquid). No attempt is made to account for variation in the liquid-phase activity coefficient. A plot of the log of this ratio against $1/v$ in Figure 11 shows that at large gas volumes (low pressure), the vapor pressure largely determines the concentration of the subcritical component. The solubility parameter difference seems to determine the slope of the curve, however, and therefore has a large effect on the solubility at higher pressure. The tetradecane-CTFM curve clearly deviates from the linear relationship as the critical solution pressure is approached.

The presence of a small amount of the subcritical component in the fluid phases has only a limited effect on their volumetric behavior. The mean molar volumes of the V

and L_2 phases, which are predominantly CTFM, deviate from the pure CTFM isotherm in only two regions. First, this occurs as the L_1-L_2 critical solution pressure is approached and appreciable amounts of the liquid—e.g., tetradecane—dissolve in the L_2 phase. Second, in the region of the extrapolated vapor pressure of CTFM, the tendency for pure CTFM to condense is greatly strengthened by even small amounts of the subcritical component. The reduction in volume is appreciable even when no condensation occurs (Type II behavior with phenyl ether), as well as when the V-L_2 dome forms. This p-v isotherm can be obtained (*3*).

The upper type-k point for the 1-propanol–CTFM system is at 31.6° C., giving Type II behavior at 32.75° C. The p-x isotherm was determined at 30.0° C. where Type III behavior is observed (Figure 12). As in the case of bromoform, the L_1-L_2 dome remains open to the maximum pressure of the apparatus. The previously studied systems of propanol with ethylene and carbon dioxide are also plotted against the corresponding pressure ratio in Figure 10. The nonidealities increase from Type I behavior with carbon dioxide to Type II behavior with ethylene, and to highly immiscible Type III and II behavior with CTFM.

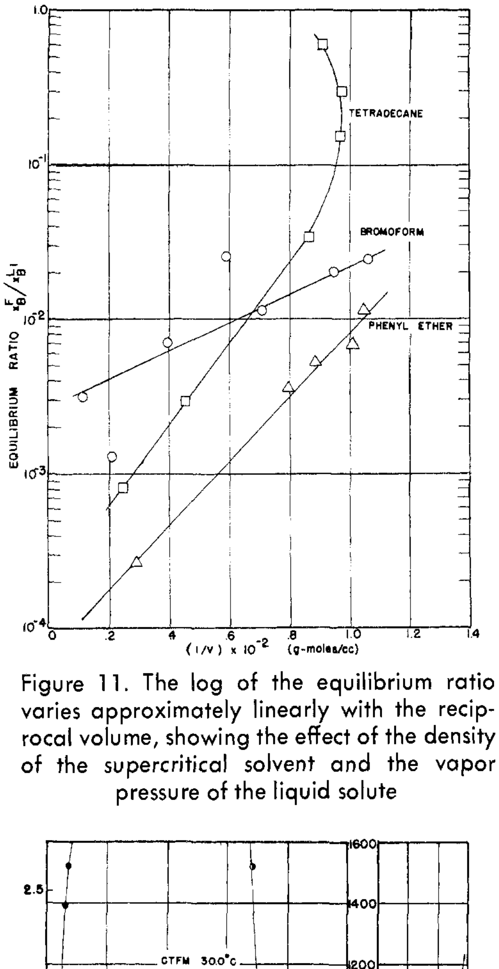

Figure 11. The log of the equilibrium ratio varies approximately linearly with the reciprocal volume, showing the effect of the density of the supercritical solvent and the vapor pressure of the liquid solute

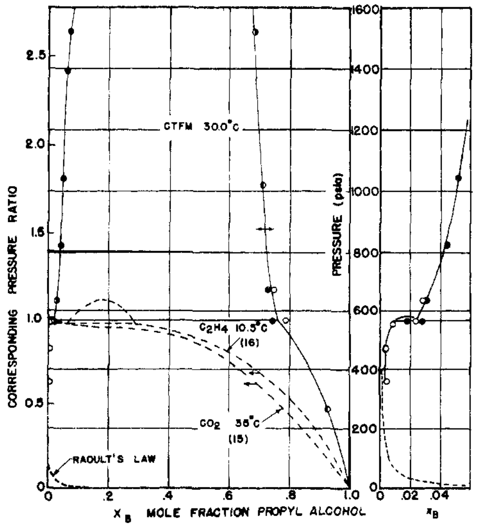

Figure 12. CTFM with propyl alcohol at 30.0° C. gives a Type III isotherm

SUMMARY

The same three general types of supercritical p-x isotherms were found in systems with CTFM as were previously found with ethylene and carbon dioxide, but with generally reduced miscibility. Based on the results of these three gases, a method is proposed for the correlation and prediction of the type of p-x isotherm to be found with a specific nonassociated system just above the critical temperature of its more volatile component.

A small amount of the subcritical component in a predominantly CTFM phase acts as a condensing agent, decreasing the volume of the phase and leading to negative partial molar volumes in some cases. A method was derived to calculate partial molar volumes from variable pressure data.

NOMENCLATURE

E_{VA}, E_{VB} = energies of vaporization
F = fluid phase (V or L_2)
K_A, K_B = critical points of pure components
K_V = upper type-k singular point
L_1, L_2 = first and second liquid phases (identification only)
O_A, O_B = triple points of pure components
p = pressure
T = temperature
T_{cA} = critical temperature of pure supercritical component
V = gas (fluid or vapor) phase
v = mean molar volume (total vol./total no. moles)
v_A, v_B = partial molar volumes of supercritical and subcritical components
x_B = mole fraction of the subcritical component
δ = solubility parameter, defined by Equation 1

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LITERATURE CITED

(1) Albright, L.F., Martin, J.J., *Ind. Eng. Chem.* **44**, 188 (1952).
(2) Barker, J.A., Fock, W., *Discussions Faraday Soc.* **15**, 188 (1953).
(3) Chappelear, D.C., Ph.D. dissertation, Princeton University, Princeton, N. J., February 1960. Univ. Microfilms, L.C. Card No. Mic. 60-4969.
(4) Diepen, G.A.M., Scheffer, F.E.C., *J. Am. Chem. Soc.* **70**, 4081, 4085 (1948).
(5) Elgin, J.C., Weinstock, J.J., J. CHEM. ENG. DATA **4**, 3 (1959).
(6) Franck, E.U., *Z. physik. Chem. (Frankfurt)* **6**, 345 (1956).
(7) Gottschlich, C., M.S. thesis, Princeton University, Princeton, N. J., September 1953.
(8) Hildebrand, J.H., Scott, R.L., "The Solubility of Nonelectrolytes," 3rd ed., Chap. VII, VIII, Reinhold, New York, 1950.
(9) Intern. Critical Tables, vol. III, pp. 381-2, McGraw-Hill, New York, 1926.
(10) Kohn, J.P., Kurata, K., *A.I.Ch.E. Journal* **44**, 211 (1958).
(11) Lindros, A.E., Dodge, B.F., *Chem. Eng. Progr. Symposium Ser. No. 3*, **48**, 10 (1952).
(12) Prausnitz, J.M., *A.I.Ch.E. Journal* **4**, 269 (1958).
(13) Prigogine, I., Defay, R., "Chemical Thermodynamics," trans. by D.H. Everett, Chap. XXV, Longmans Green, New York, 1954.
(15) Snedeker, R.A., Ph.D. dissertation, Princeton, University, Princeton, N. J., June 1955.
(16) Todd, D.B., Elgin, J.C., *A.I.Ch.E. Journal* **1**, 20 (1955).

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