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Critical Point Measurements on Nearly Polydisperse Fluids

The critical temperatures, pressures and volumes of several mixtures containing CO_2, C_2H_6, C_3H_8, and C_4H_{10} have been measured using a heavy walled, variable volume, cylindrical glass vessel. In each mixture the relative proportions of the three hydrocarbon solutes to one another were changed; total solute mole fraction never exceeded 0.1. A detailed study of the mixture $CO_2 + C_3H_8$ shows that the critical temperature exhibits a minimum at a C_3H_8 mole fraction of 0.0265. Our mixture data are analyzed using a polydisperse model of dilute solutions.

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SCOPE

There now exist large collections of information about the properties of binary mixtures, such as the recent bibliographic collection of Hicks (1978), the classic data collection by Timmermans (1959), or the bibliographic collection of Wichterle et al. (1973, 1976, 1979). As the number of components in the mixture increases, the amount of information drops rapidly. Nonetheless, complex mixtures, those that contain dozens or even hundreds of components, are both common and, in some cases, economically important—industrial reaction mixtures and petroleum, to name two examples. The complexity of such materials makes all but the most narrow studies of their properties prohibitive. One way of approaching the problem of complex mixtures is to treat them as a special case of mixtures with an infinite number of components. In such a mixture, each molecular species is identified by the value of a continuous parameter, which may be multidimensional in character, and is inevitably connected to the physical properties of the species. Thus, as one would expect intuitively, species with similar values of the identification parameter would have similar properties. Unlike a mixture of discrete species, however, in which the composition would be characterized by a discrete set of values drawn from all possible values of the identification parameter, the infinite-component mixture would have components described by every possible value of that discriptor. Such a mixture is said to be "polydisperse." This kind of mixture model has been used extensively in the theory of high-polymer solutions and has been addressed at length for that special application by Flory (1978), Koningsveld (1969), and Scott (1952). This model has also been applied to hard-sphere mixtures by Blum and Stell (1979) and Vrij (1978). Recently the thermodynamics of the polydisperse mixture has been discussed by Salacuse (1978), Dickinson (1981), Kehlen (1981), and Gualtieri, Kincaid and Morrison (1982).

A special class of polydisperse mixture is one in which one component dominates the composition—acting as a solvent—and the remaining, infinite number of components are present collectively at a low concentration—a solute. In collaboration with Gualtieri (1982) we have described the thermodynamics of such a mixture in detail. In this paper we examine the critical properties of a similar, but far simpler, mixture, in which near-critical CO_2 is the solvent and various mixtures of ethane, propane and n-butane are the solute. The critical densities and temperatures of the mixtures are measured at 0.0, about 2.5 mol %, and about 9.0 mol % overall alkane composition. We have analyzed the data in two ways: first, by investigating the connection between the properties of the binary mixtures—that is, carbon dioxide and a single alkane—and the more complex mixtures; and, second, by modeling the mixture using our earlier analysis of the polydisperse impurity problems. For the second analysis, we have used the van der Waals free energy, the customary mixing rules for the unlike molecular interactions, a scheme for evaluating the molecular identification parameter, and have shown how information derived from the behavior of each solute component in the solvent leads to a scale for the identification parameter.

CONCLUSIONS AND SIGNIFICANCE

The critical loci of the binary mixtures $CO_2 + C_2H_6$, $CO_2 + C_3H_8$, and $CO_2 + C_4H_{10}$ at low alkane composition exhibit a simple dependence upon the alkane mole fraction. The heretofore unmeasured shallow minimum in the $CO_2 + C_3H_8$ critical temperature, Figure 2a, can be viewed as a natural consequence of the transition from $CO_2 + C_2H_6$ to $CO_2 + C_4H_{10}$ behavior. At low concentrations of a mixed solute, we show that the components act separately and that, under certain restrictive conditions, the effect of the mixed solute on the critical point of the mixture can be predicted by knowing the separate effect of each component of the solute. The analysis of the data in terms of the van der Waals binary mixture model shows clearly that effective

excluded volume and solvent-solute attraction parameters can be used to establish an identification label that increases with increasing carbon number. If the specific model calculations of the critical temperature shift of Gualtieri et al. (1982) are slightly extended to include higher-order terms in the solute mole fraction, we expect the van der Waals model to account for the observed critical temperature shift as well. Our results demonstrate that mixtures of straight chained alkanes with as few as three components have properties that will allow a polydisperse interpretation, and we expect that a polydisperse approach to modeling the properties of systems with many more alkane components may prove quite useful.

EXPERIMENTAL DETAILS

Samples for this study were prepared by distilling measured quantities of each of the components, commercially available research grade materials, from a gas buret into a small, stainless steel thermocompressor at liquid nitrogen temperature. Analyses of each of the components used are shown in Table 1. The amounts of each of the components were determined in two ways: first, by using the temperature-pressure-volume measurements from the gas buret and the second virial coefficients from the compilation by Dymond and Smith (1969); second, by weighing the thermocompressor after each successive addition of the components. The two determinations typically agreed with one another to ±0.2% for the amounts of the minor components. The mixtures were then displaced with mercury from the thermocompressor into a heavy-walled cylindrical borosilicate glass cell shown in Figure 1. The total volume of the cell was approximately 7.0 cm^3; however, the volume of the sample could be varied by raising or lowering the mercury level in the cell.

The cell was immersed in a water bath whose temperature was controlled to ±0.0003 K. The temperature was measured with a quartz crystal thermometer calibrated with an NBS calibrated platinum resistance thermometer. The volume of the sample was determined by measuring the distance between the top of the cell and the mercury meniscus; corrections for the shape of the mercury meniscus and two small ball bearings used for stirring were also made. The volume of the cell was calibrated using triply distilled mercury as a reference. The volume along the length of the cell was known to ±0.002 cm^3. Pressures were measured by the voltage induced by the deflection of a magnetic steel diaphram inside a linear variable differential transformer. The diaphragm was calibrated against a dead weight gauge. The pressure was measured to ±0.01 bar.

Ideally, the critical points of the mixtures would be determined by the direct observation of the appearance and disappearance of the meniscus at the exact middle of the sample. Realistically, such a measurement is not experimentally practicable. The critical conditions were determined by interpolation of data taken when the meniscus appeared just above the middle (fraction of the upper phase $\gtrsim 0.4$) and just below the middle of the cell (fraction of the upper phase $\lesssim 0.6$). The temperature for these interpolated points was determined to ±0.001 K. In all cases, the appearance of the meniscus was used as a criterion for determining the temperature. Typically, vigorous stirring would warm the sample enough to move above the separation temperature; upon standing, the sample would cool and separate once again. Using the criterion of disappearance of the meniscus without stirring on warming is not satisfactory because the diffusion process is too slow to destroy the composition difference between the two phases. The maximum difference between total volumes in such sets of measurements was no more than 1.5%. The differences between the temperatures and pressures of these measurements depend upon the shape of the p-V-T-x two-phase region around the critical point; the reasons for this are explained well, for example, by Rowlinson (1969) and will not be dwelled upon here.

As an indication of the accuracy of our measurements, our measured critical points for CO_2 and C_2H_6 are compared in Table 2 with the determinations of others.

TABLE 1. ANALYSES OF RESEARCH GRADE MATERIALS*

CO_2	99.995%
C_2H_6	99.96%
C_3H_8	99.97%
n-C_4H_{10}	99.9%

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* These analyses were provided by the Matheson Co., the source of these materials. The source is given for reasons of scientific completeness, not for a recommendation by the authors, the National Bureau of Standards, or the U.S. Government.

EXPERIMENTAL RESULTS

The three hydrocarbons, ethane, propane, and n-butane were chosen as the solutes in this set of measurements for a variety of reasons. First, they, like the solvent, carbon dioxide, are readily available as highly purified materials. Second, these hydrocarbons, as well as the solvent, are all gases at ambient pressure and temperature; consequently, they are easy to handle in sample preparation and transfer. Third, they offer a variety of simple critical behavior in mixtures with CO_2. The family of CO_2 + hydrocarbon critical lines has been reviewed in detailed by Schneider (1978a,b). In mixtures with CO_2, ethane has an azeotrope; the critical temperature falls with the addition of ethane to pure CO_2. That system has been studied in detail by Khazanova et al (1966). The mixtures CO_2 + propane and CO_2 + propane and CO_2 + n-butane have been somewhat less thoroughly studied; however, the measurements of Olds et al. (1948) on CO_2 + n-butane indicates that we would find a positive value for dT_c/dx_4 for that system. The measurements of Poettman et al. (1945) suggested that we would also find a positive value for dT_c/dx_3, but that it would fall between the values for ethane and n-butane. Carbon dioxide was chosen as the solvent because it has a particularly accessible critical point. Finally, one must also recognize the interest in CO_2 as a solvent in its near-critical state both in enhanced oil recovery and as a supercritical extractant in industrial processes.

As we will explain in the next section, our analysis of the data for the mixtures that contain binary and ternary solutes requires information about the effect of the single-component solutes on the critical temperature of CO_2. Those data are found in Table 3. The mixtures CO_2 + C_2H_6 and CO_2 + n-C_4H_{10} behaved in much the way we expected, thus no measurements

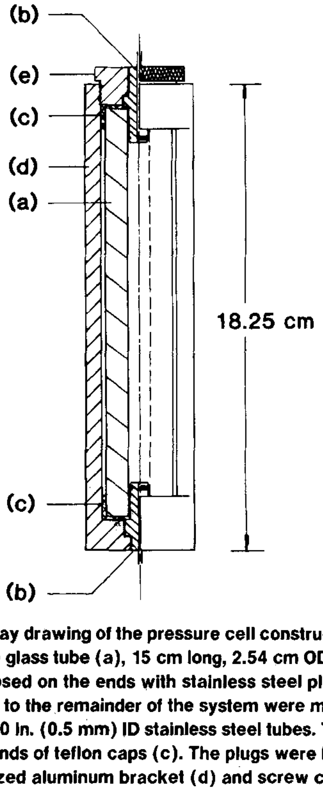

Figure 1. A cut-away drawing of the pressure cell constructed from a heavy-walled borosilicate glass tube (a), 15 cm long, 2.54 cm OD, 0.871 cm ID. The glass tube was closed on the ends with stainless steel plugs (b) with o-ring seals; connections to the remainder of the system were made through 1/16 in. (1.6 mm) OD, 0.020 in. (0.5 mm) ID stainless steel tubes. The glass tube was protected on the ends of teflon caps (c). The plugs were held in place by an anodized aluminum bracket (d) and screw cap (e).

TABLE 2. COMPARISON OF MEASURED CRITICAL POINTS

T_c/K	ρ_c/mol dm^{-3}	p_c/10^5 Pa	Source
CO_2:			
304.206(±.001)	10.642 ± 0.008	73.84 ± 0.01	This Work
304.127(±0.004)	16.63 ± 0.05	73.753 ± 0.007	Moldover (1974)
304.202			Morrison (1981)
C_2H_6:			
305.393(±.001)	6.862 ± 0.005	47.78 ± 0.01	This Work
305.33	6.870	47.718	Douslin and Harrison (1973)
305.379			Morrison (1981)

TABLE 3a. $CO_2 + C_2H_6$

x_2 (±0.0004)	ΔT_c/K (±0.001)	ρ_c/mol dm^{-3} (±0.008)	p_c/10^5 Pa (±0.01)
0.0	0.0	10.642	73.84
0.0261	−1.543	10.511	72.50
0.0975	−5.291	10.180	69.35

for $0 \le x_2 \le 0.0975$

$\Delta T_c = x_2(67.96x_2 - 60.89)$

TABLE 3b. $CO_2 + C_3H_8$

x_3 (0.0004)	ΔT_c/K (±0.001)	ρ_c/mol dm^{-3} (±0.008)	p_c/10^5 Pa (±0.01)
0.0	0.0	10.642	73.84
0.0105	−0.038		73.24
0.0143	−0.058		72.43
0.0261	−0.071		72.29
0.0266	−0.074	10.471	72.30
0.0282	−0.068		72.00
0.0333	−0.062		71.83
0.0341	−0.055		71.78
0.0391	−0.039		71.58
0.0496	0.073		71.08
0.0985	1.140	9.965	69.50

For $0 \le x_3 \le 0.0496$

$\Delta T_c = x_3(-3.862 - 31.69x_3 + 2789.5x_3^2)$

TABLE 3c. $CO_2 + C_4H_{10}$

x_4 (±0.0004)	ΔT_c/K (±0.001)	ρ_c/mol dm^{-3} (±0.008)	p_c/10^5 Pa (±0.01)
0.0	0.0	10.642	73.84
0.0252	1.943	10.436	73.36
0.0856	8.272	9.894	76.63

for $0 \le x_4 \le 0.0856$

$\Delta T_c = x_4(323.4x_4 + 68.95)$

other than the ones needed for this study are given. Conversely, the mixture $CO_2 + C_3H_8$ exhibits a complex behavior at low concentrations of C_3H_8; our data for that mixture are more detailed, Figures 2a and 2b.

The critical line for the mixture $CO_2 + C_3H_8$ has a minimum in temperature about 0.074 K below T_{co} for CO_2; the minimum occurs at about 0.0265 mol % propane. Although this behavior adds a complication to our analysis of the mixed hydrocarbon solutes, it is what one would expect for a smooth transition from the behavior of the $CO_2 + C_2H_6$ system to the CO_2 + n-C_4H_{10} system. As the critical temperature of the hydrocarbon is raised from 32.24°C for C_2H_6 to 152.3°C for n-C_4H_{10}, the minimum in the critical line is "pulled up" eventually to be "snapped out" at the CO_2 critical point. Apparently, in that progression, C_3H_8 falls just before the disappearance of the minimum. A minimum in the critical line can also suggest the presence of the intersection of an azeotropic locus with the critical line. The measurements of the pressure and temperature of the critical locus, Table 3b and Figures 2a and 2b, do not indicate such an intersection; the critical locus for the mixture appears never to be above the liquid-vapor line for CO_2 of Levelt Sengers (1972) which is consistent with our data.

The results for the CO_2 + hydrocarbon mixtures are given in Table 4.

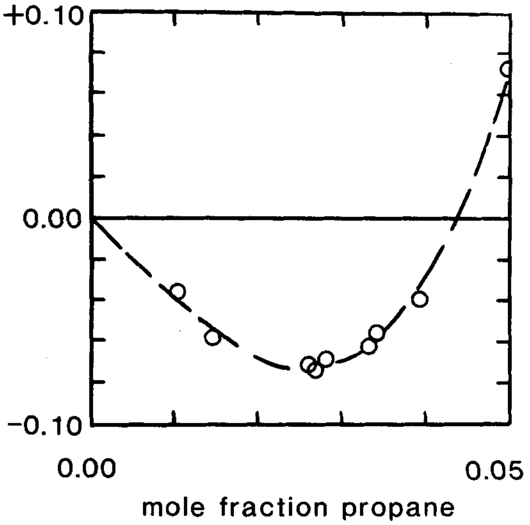

Figure 2a. Effect of small concentrations of propane on the critical temperature of CO_2. The lowest concentration point, reported by Poettmann et al. (1945), outside the range of this figure, is at $x_3 = 0.061$, $\Delta T/K = 0.16 \pm 0.3$.

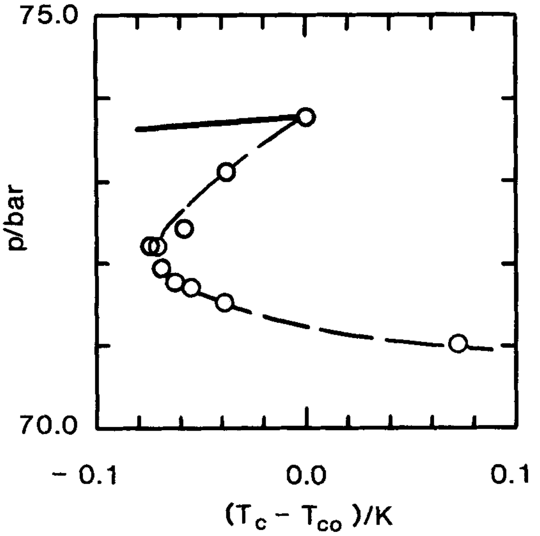

Figure 2b. Critical locus of $CO_2 + C_3H_8$ near the critical point of CO_2. The lowest concentration point reported by Poettman (1945) is at $\Delta T/K = 0.16 \pm 0.3$ and p/bar = 70.35 ± 0.34. The heavy line extending left from the critical point of CO_2, is the liquid vapor line reported by Levelt Sengers and Chen (1972).

Finally, at the bottom of each of the parts of Table 3, and in Table 4b, one will find expressions for the temperature of the critical line for the appropriate mixtures. These expressions have been used to interpolate our data, when that was necessary, and to estimate limiting slopes of the critical lines; they apply to the very limited composition range we indicate and are not intended for any broader interpretation.

TABLE 4a. CO_2 + BINARY OR TERNARY HYDROCARBON MIXTURES

x_2	x_3 (±0.0004)	x_4	ΔT_c/K (±0.001)	ρ_c/mol dm^{-3} (±0.008)	$p_c/10^5$ Pa (±0.01)
0.0	0.0	0.0	0.0	10.642	73.84
0.0123	0.0126	0.0	−0.597	10.499	72.56
0.0193	0.0063	0.0	−1.028	10.473	72.63
0.0063	0.0186	0.0	−0.296	10.481	72.51
0.0127	0.0	0.0127	0.290	10.441	72.79
0.0	0.0132	0.0129	0.977	10.419	72.78
0.0081	0.0084	0.0085	0.146	10.454	72.62
0.0484	0.0443	0.0	−2.235	10.107	69.37
0.0445	0.0	0.0440	1.920	9.985	72.12
0.0	0.0443	0.0441	4.887	9.939	72.31
0.0282	0.0356	0.0323	1.862	10.018	71.28

TABLE 4b. TEMPERATURE SHIFT EQUATIONS FOR MIXTURES IN TABLE 3a, EXPERIMENTAL AND PREDICTED

i Mixtures where $x_2 = x_3, x_4 = 0$

$\Delta T_c = (x_2 + x_3)(19.26(x_2 + x_3) - 24.5)$

$$\left.\frac{dT_c}{dx}\right|_{x=0} = -24.5 \text{ K}$$

$$\left.\frac{dT_c}{dx}\right|_{x=0,\text{predicted}} = -32.4 \text{ K}$$

ii Mixtures where $x_2 = x_4, x_3 = 0$

$\Delta T_c = (x_2 + x_4)(162.9(x_2 + x_4) + 7.3)$

$$\left.\frac{dT_c}{dx}\right|_{x=0} = 7.3 \text{ K}$$

$$\left.\frac{dT_c}{dx}\right|_{x=0,\text{predicted}} = 4.1 \text{ K}$$

iii Mixtures where $x_3 = x_4, x_2 = 0$

$\Delta T_c = (x_3 + x_4)(286.5(x_3 + x_4) + 30.0)$

$$\left.\frac{dT_c}{dx}\right|_{x=0} = 30.0 \text{ K}$$

$$\left.\frac{dT_c}{dx}\right|_{x=0,\text{predicted}} = 32.5 \text{ K}$$

ANALYSIS AND DISCUSSION OF THE DATA

In an earlier paper (Gualtieri et al., 1982) we examined in detail the problem of the effect of a complex impurity on the critical point of a solvent. When expressed in its most general terms, the effect on the critical temperature and critical density are as follows:

$$T_c = T_{co} + \sum_i T_{c1}(i)x_i + \dots \tag{1}$$

$$\rho_c = \rho_{co} + \sum_i \rho_{c1}(i)x_i + \dots , \tag{2}$$

where the constants $T_{c1}(i)$ and $\rho_{c1}(i)$ depend only on the microscopic properties of species i and the properties of the solvent. In the polydisperse van der Waals model we found that

$$T_{c1}(i) = T_{co}(9a(i)^2 - 4a(i) - 6a(i)b(i) + b(i)^2)/4 \tag{3}$$

and

$$\rho_{c1}(i) = \rho_{co}[1 - (18a(i)^2 - 2b(i)^2 + 27a(i)^2b(i) - 27a(i)^3 - 9a(i)b(i)^2 + b(i)^3)/8]. \tag{4}$$

Here the excluded volume parameters, $b(i)$, and the solvent-solute attraction parameters, $a(i)$, are normalized such that $b(CO_2) = 1$ and $a(CO_2) = 1$.

In this section, we shall examine the meaning of these expressions in two ways: first, in a general sense, without applying any particular mixture model to interpret the data reported in Tables 3 and 4; and, second, by using the van der Waals mixture model to establish a scheme for the identity parameter for mixtures of hydrocarbons in carbon dioxide.

The simplest interpretation of Eqs. 1 and 2 is that, in the limit of infinite dilution, the effect of a complex impurity on the critical point of the solvent is the appropriately averaged sum of the effect of each constituent of the impurity. This treatment is different from treating the impurity as if it were a single averaged molecular species since the averages of products and powers of quantities are different from products and powers of averaged quantities.

First, let us consider the effect of composition on the limiting slopes for the critical temperature loci for different hydrocarbon mixtures. The estimated values for these slopes are indicated in Table 4b. Within the uncertainty inherent in these slopes, ±1.5 K and ± 3.0 K for the experimental values for the single-component and two-component impurities respectively, and ±3.0 K for the predicted values of the slopes, the prediction that each component acts independently appears to be correct.

Let us now try to predict the effect of the hydrocarbon mixture solutes on the critical temperature and density of the mixture using the scheme suggested by Gualtieri et al. (1982). In Tables 5a and 5b, the experimental and predicted relative changes in the temperature—in columns headed by τ's—and in the density—in columns headed with $\Delta\rho_c/\rho_{co}$—are given. Let us consider the effect on density first. The densities of the CO_2 + single hydrocarbon mixtures versus mole fraction are shown in Figure 3. If we assume that the total change in density is the sum of the change effected by each component were it present alone in the solvent at its given concentration we find the relative changes to be those predicted in the column headed $(\Delta\rho_c/\rho_{co})_{calc}$. At both overall concentrations of the impurity this prescription appears to predict the change in density to within 0.2% of the measured value. This

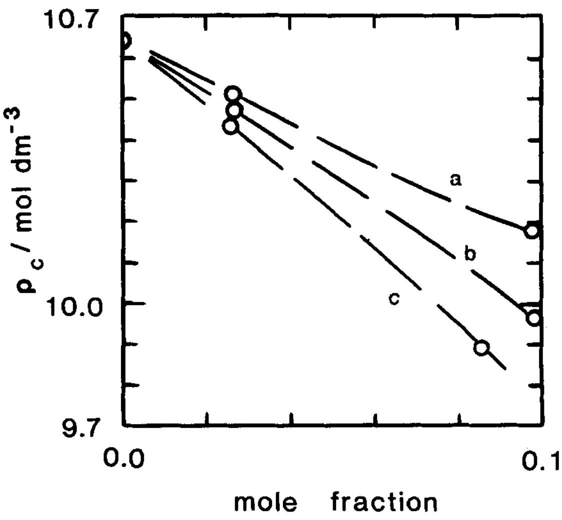

Figure 3. Critical density of the mixtures CO_2 + hydrocarbon vs. the mole fraction of the hydrocarbon. The line indicated by *a* is for $CO_2 + C_2H_6$; by *b*, for $CO_2 + C_3H_8$; by *c*, for $CO_2 + C_4H_{10}$.

TABLE 5a. $X_{\text{hydrocarbon}}$ ~0.025

X_2	X_3	X_4	τ_{exp}	τ_1	τ_2	τ_3	$(\Delta\rho/\rho_{co})$ exp	$(\Delta\rho/\rho_{co})$ calc
			10^{-3}				10^{-2}	
0.0123	0.0120	0.0	−1.96	−2.64	−2.59	−2.51	−1.34	−1.34
0.0193	0.0063	0.0	−3.38	−3.94	−3.87	−3.81	−1.59	−1.29
0.0063	0.0186	0.0	−0.91	−1.50	−1.47	−1.40	−1.51	−1.42
0.0127	0.0	0.0127	0.95	0.34	0.54	0.75	−1.89	−1.57
0.0	0.0132	0.0129	3.21	2.76	2.94	3.16	−2.10	−1.79
0.0081	0.0084	0.0085	0.48	0.20	0.29	0.50	−1.77	−1.54
			(±0.01)	(±0.12)	(±0.18)	(±0.18)	(±0.15)	(±0.20)

TABLE 5b. $X_{\text{hydrocarbon}}$ ~0.09

x_2	x_3	x_4	τ_{exp}	τ_1	τ_2	τ_3	$(\Delta\rho/\rho_{co})_{\text{exp}}$	$(\Delta\rho/\rho_{co})_{\text{calc}}$
			10^{-3}				10^{-2}	
0.0484	0.0443	0.0	−7.35	−10.3	−9.2	−7.1	−5.03	−4.98
0.0445	0.0	0.0440	6.31	1.07	3.52	6.1	−6.17	−5.55
0.0	0.0443	0.0441	16.1	9.43	12.1	15.6	−6.60	−6.31
0.0282	0.0356	0.0323	6.12	1.22	2.76	7.8	−5.86	−5.96
			(±0.01)	(±0.12)	(±0.12)	(±0.18)	(±0.15)	(±0.20)

difference is consistent with the uncertainty in the measurements themselves. Even at the higher concentrations of the impurity the calculated and measured density shifts agree within the uncertainties of both for all but one of the mixtures.

Analysis of the temperature data is complicated by the pronounced curvature of the temperature shift lines; we will thus examine the data for temperature in three somewhat different ways. If the infinite dilution value for (dT_c/dx) for each of the components were used so that the change in temperature were calculated by

$$\Delta T_c = \sum_i x_i \left(\frac{dT_c}{dx_i}\right)\bigg|_{x_i=0} = \sum_i x_i T_{c1}(i), \tag{5}$$

the relative temperature changes under the column headed τ_1 would be predicted. This approach always leads to a lower temperature than actually measured for these mixtures. It works marginally well in the low composition mixtures and very poorly indeed in the mixtures at higher concentration. Such a result should not be surprising when one considers the curvature of the critical loci for the single component impurities. If one assumes that the effect of each of the components on the temperature is independent of the others in the spirit of Gualtieri et al. (1982), the temperature effect could be predicted by summing the temperature changes were each component present alone in the solvent—the same approach used in predicting changes in the density.

$$\Delta T_c = \sum_i \Delta T_i(x_i)\cdot \tag{6}$$

The relative temperature shifts predicted by this approach are shown in Tables 5a and 5b under the column headed τ_2. In all cases, the predicted temperature shift is closer to the experimental value than determined in the first scheme; however, in all cases, the predicted temperature is still too low. The final scheme we include here works very well indeed. As we shall indicate, it appears that under restricted conditions, it is the correct predictive scheme. Suppose we determine the temperature change effected by each component not at its actual composition but at the total composition of the impurity and then sum the temperature changes according to the relative amount of each component present

$$\Delta T_c = \frac{\sum_i x_i \Delta T_i \left(\sum_j x_j\right)}{\sum_i x_i}. \tag{7}$$

The relative temperature changes predicted by this scheme are given in Tables 5a and 5b under the columns headed by τ_3. The agreement between the measured and predicted values all the mixtures is substantially better than the results calculated from the other schemes, typically within 50 mK.

We must address the problem of why, in a certain sense, each component acts as if it were present at the total impurity concentration. Surely, at $x = 0.09$, the most important interaction felt by the impurity molecules is with the CO_2 and the most important interaction felt by CO_2 molecules is with other CO_2's. For the hydrocarbon mixtures used in these experiments, whether the solute is a single species or a mixture, the effect of the impurity on the volume—and presumably also the microscopic structure—of the solution is substantially the same. Thus, an ethane molecule in a solution with an impurity of $x = 0.09$ would find itself in much the same surrounding regardless of the specific nature of the impurity. The third approach for estimating the critical temperature of the mixtures, for which a qualitative explanation has been given, represents a special solution to the critical point equations given by Gualtieri et al. in their Eqs. B5 and B15. In this restricted solution, the change in the density of the solvent that results from the addition of the mixed solute must equal the mole-fraction-weighted sum of the changes in solvent density due to each solute alone at a composition equal to the overall solute composition. Under this special circumstance, the change in critical temperature will equal the mole-fraction-weighted sum of the critical temperature changes due to each solute but at the total solute composition. Our examination of the density indicates we are working in this regime for these mixtures. It is not clear that this would be true at our experimental compositions if the molecules in the hydrocarbon mixture were very different in size. This kind of observation is presently beyond the work explicitly set down Gualtieri et al. (1982) but should certainly appear when that calculation is carried to higher impurity concentration ranges. The van der Waals model predictions for the temperature and density shifts are given by Eqs. 3 and 4. Our data indicates, that the temperature shift is linear in the impurity mole-fraction only when $x_i \lesssim 0.01$, whereas the density shift for which the data are less precise remains nearly linear over the entire range considered $(0 \lesssim x_i \lesssim 0.09)$. Thus we do not expect these limiting concentration expressions to correlate all the temperature shifts successfully.

Using the binary mixture data we have obtained estimates for $T_{c1}(i)$ and $\rho_{c1}(i)$. Substituting these estimates into Eqs. 3 and 4 we find the following values for b and a: $b(C_2H_6) = 1.50$, $b(C_3H_8) = 1.60$, $b(C_4H_{10}) = 1.74$, $a(C_2H_6) = 1.15$, $a(C_3H_8) = 1.29$, and $a(C_4H_{10}) = 1.44$. These values differ somewhat from the values found in the *CRC Handbook:* 1.50, 1.98, 2.87, 1.22, 1.55 and 2.01, respectively. This difference is to be expected; the CRC van der Waals constants are determined from single component critical point data. Except for C_2H_6, all the temperatures reported here

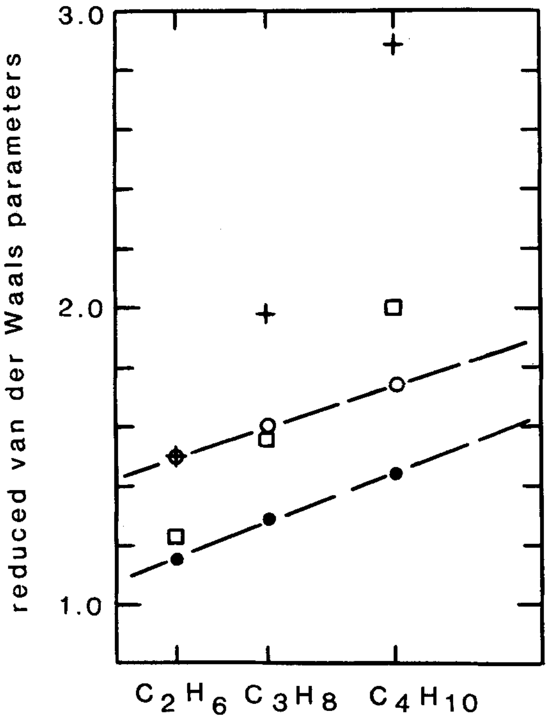

Figure 4. Reduced van der Waals parameters *b(I)* and *a(I)*. Values obtained by using binary mixture data and Eqs. 3 and 4 are denoted by the open and filled circles respectively. The crosses indicate scaled values of *b(I)* and the open squares, scaled values of *a(I)* determined from *CRC Handbook* values.

are far from hydrocarbon critical points so that one would not expect the effective van der Waals a and b to be the same as those determined from pure critical data. (The geometric mean was used to obtain the a's.) Both sets of values show the same expected increasing trend as the carbon number increases. In Figure 4 we plot the derived values of b and a and compare them to the *CRC Handbook* values. The ordering of components along the abscissa in Figure 4 has been chosen so that our derived values of $b(i)$ lie on a straight line. Note that the derived values of $a(i)$ are nearly linear in i as well.

When we use the values of $b(i)$ and $a(i)$ derived from the binary mixture data to calculate the critical temperature and density shifts we obtain the values listed in Table 4 under the columns τ_1 and $(\Delta\rho_c/\rho_{co})_{calc}$, respectively. As expected τ_1 does not provide a good estimate of τ_{exp}, while $(\Delta\rho_c/\rho_{co})_{exp}$ and $(\Delta\rho_c/\rho_{co})_{calc}$ agree quite well. The important feature of this analysis is that within the range of validity of the model calculations there exists an assignment of molecular parameters, the b's and the a's, that are simple functions of an identity label. Thus we expect that mixtures of many more alkanes with CO_2 can be represented as a polydisperse mixture.

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NOTATION

p_{co} = critical pressure of CO_2
p_c = critical pressure
T_{co} = critical temperature of CO_2
T_c = critical temperature
$T_{c1}(i)$ = coefficient in the expansion of T_c
x_2 = mole fraction of C_2H_6
x_3 = mole fraction of C_3H_8
x_4 = mole fraction of C_4H_{10}
ΔT_c = $T_c - T_{co}$
$\Delta\rho_c$ = $\rho_c - \rho_{co}$
$(\Delta\rho_c/\rho_{co})_{calc}$ = predicted relative critical density shift
$(\Delta\rho_c/\rho_{co})_{exp}$ = observed relative critical density shift
ρ_{co} = critical density of CO_2
ρ_c = critical density
$\rho_{c1}(i)$ = coefficient in the expansion of ρ_c
τ_{exp} = observed relative critical temperature shift, $(T_c - T_{co})/T_{co}$
τ_i = predicted relative critical temperature shift

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