

Acoustic Determination of the Critical Surfaces in the Ternary Systems $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ and $\text{CO} + \text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$ and in Their Binary Subsystems

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A simple acoustic method has been used to investigate the two ternary systems $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ and $\text{CO} + \text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$. Vapor–liquid equilibria data were measured for four of the six binary subsystems as well as the two ternary systems. The binary systems containing either CO_2 or a refrigerant (CH_2F_2 , $\text{CF}_3\text{CH}_2\text{F}$) have been investigated over the whole mole fraction range. For the subsystems containing CO , only the range from 0 to 40 mol % CO could be investigated. The ternary systems were measured by the quasibinary method (i.e. the ratio between two components being held constant). For the system $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$, three different quasibinary mixtures, with three different compositions each, were measured. For the ternary system $\text{CO} + \text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$, one quasibinary mixture with three different compositions was investigated. Additionally, two specific mixtures were investigated in the ternary system $\text{CO} + \text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$, because of the importance of this system in the synthesis of aliphatic polyketone polymers. For each mixture the critical point was determined. Different ways of presenting binary and ternary critical data and the topology of the resulting ternary critical surfaces are discussed with respect to thermodynamics. Some limitations of the acoustic method for probing phase behavior are explained. The critical data have been modeled using the Peng–Robinson equation of state.

Introduction

Supercritical mixtures are of increasing interest for chemical processes. However, reaction mixtures have to be homogeneous in order to exploit the advantages of supercritical fluids. Therefore, a knowledge of their phase envelopes and critical points is crucial. Even the simplest reaction system will be a ternary mixture (reactant, product, and solvent). Traditional methods of phase measurements (view-cell or sampling) are often very difficult to apply to some ternary mixtures where the density differences between the phases are small. Usually, therefore, properties of industrially important ternary fluid mixtures are estimated by investigating binary mixtures of their constituents and then predicting the properties of the ternary system. This procedure can lead to substantial errors, because the properties of the ternary is not necessarily the sum of those of the three binary subsystems. These errors can be reduced very substantially by data from even a modest number of experimental points on the ternary surface. In this paper we investigate two ternary systems of industrial interest,^{1–5} for which little data has so far been obtained. One system contains two refrigerants that are used as replacements for CFCs and represents an extension of our earlier work⁶ on mixtures of refrigerants with CO_2 . The second system $\text{CO} + \text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$ is already in use for the production of aliphatic polyketone polymers. Knowledge of the critical surface of this ternary system is essential to improve the synthesis of these

polymers, as the reaction mixture needs to be homogeneous in order to produce the polymer efficiently.

As mentioned in our previous work⁶ measurement of phase envelopes is difficult and is usually performed by visual methods or by sampling. Both methods have disadvantages; accurate sampling is difficult and time consuming, while determining a phase transition in a view-cell is often constrained by the subjectivity of the experimenter. This leads to uncertainties in the determination of the vanishing of the meniscus between the phases. In principle, the determination of vapor–liquid equilibria by an acoustic method overcomes these disadvantages.

Both systems were investigated with an acoustic method that we have already described in detail.^{6,7} Acoustic methods have a long history. A brief review of acoustic measurements was made in ref 6. Notable previous work includes Moldover,⁸ Colgate⁹ and Johnson¹⁰ and references therein. Our method is quite crude but gives satisfactory critical data for pure and binary systems,⁶ where critical temperatures were measured with an accuracy of ± 0.1 K and critical pressures with ± 0.1 bar. In this paper, we show that our acoustic technique gives satisfactory critical data for *ternary* mixtures.

For acoustic measurements, the key property of a fluid is its compressibility, which reaches a maximum whenever a phase transition occurs. The compressibility is related to the speed of sound of the fluid mixture, and hence, by measuring the speed of sound in the fluid, the phase envelope of the system can be obtained. Most authors who investigate multicomponent mixtures with acoustic methods operate their experiments only in the homogeneous region¹¹ to avoid condensation of the sample, hence avoiding errors in the measurement of the speed of sound.

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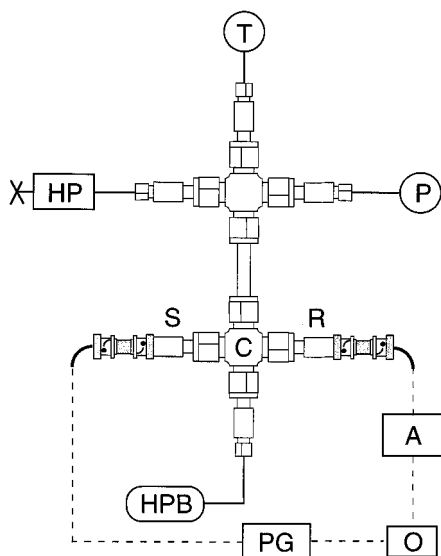


Figure 1. Schematic plan of the apparatus for acoustic measurements. Components are labeled as follows: A, amplifier; C, acoustic cell; HP, hand pump; HPB, high-pressure bomb; O, oscilloscope; P, pressure transducer; PG, pulse generator; R, acoustic receiver; S, acoustic sender; T, thermocouple.

In contrast to these highly accurate measurements of the speed of sound for pure components or homogeneous mixtures, our experiments cover the inhomogeneous region of the phase diagram. Therefore, no accurate speed of sound data are obtained; only the pressure–temperature coordinates for the minimum in the speed of sound were noted. We do not measure the speed of sound directly. Instead, we measure the transit time of a supersonic pulse. Changes in the transit time are inversely proportional to the speed of sound, and the maxima in transit time are used to determine the occurrence of phase transitions. Therefore, our experiments do not require high-precision acoustic measurements. Neither is the precise geometry of the acoustic cell a limiting factor for our accuracy. Here, we show that the depth of the minimum in the speed of sound at the vapor to liquid phase transition is dependent both on the number of components and on their physical properties. We demonstrate that an increasing amount of a permanent gas decreases the depth of the minimum in the speed of sound until it almost disappears. Nevertheless, despite these limitations, the acoustic method provides information about ternary systems for which no data are currently available.

Experimental Apparatus

The acoustic equipment has already been described in some detail.⁶ The apparatus has been modified as shown in Figure 1 for the investigation of ternary systems. The acoustic cell is now constructed from *two* standard stainless steel $1/4$ -in.-cross-piece (Swagelok 400-4), one of which has had its inner diameter bored out to provide an acoustic cavity of about 3 mL volume. The second cross-piece connects the manual high-pressure pump and the pressure transducer directly to the acoustic cell. In addition, the new cell design enables us to use the apparatus for liquid systems and has the option of inserting a miniature stirrer bar for more viscous fluids. Furthermore, the electrical connections are no longer in contact with the thermostating medium, avoiding the slow corrosion of the coaxial cables of the microphones, which had previously caused problems. Pressure was generated via a hand pump with 30 mL volume (High Pressure Equipment Co., Model 62-6-10), monitored with a solid-state pressure transducer (RDP-Electronics, Series TJE) and was constant within ± 0.01 MPa. The acoustic cavity and

the hand pump were thermostated with a circulating water thermostat (Haake, F3K), which held the temperature constant ± 0.02 K. The water is pumped through an aluminum thermostating jacket fitted to the cell, and good thermal contact is maintained by a layer of indium metal, cast *in situ*. All tubing is insulated with polyurethane foam; the cell and its heating jacket are insulated with a 25 mm thick layer of FIBERFRAX (ARCO East Midlands). Temperature was measured by a calibrated thermocouple and digital multimeter (Thurlby-Thandar TTI-1906) with an accuracy of ± 0.05 K in the temperature reading. The acoustic signal was provided by a pulse generator (Wayne Kerr, CT500), which produced a microsecond ultrasonic pulse at a repetition rate of ca. 100 Hz. The signal was then fed into the acoustic cavity via a ceramic transducer. A second, identical transducer monitored the signal at the other end of the cavity. The resulting signal was amplified and displayed on a digital oscilloscope (Gould, DSO 475), on which the transit time of the pulse across the acoustic cavity was measured. The observed maxima in the transit time were used to determine the critical point of the mixtures.

Graphical Representation of Critical Data

Effective graphical representation of critical data is extremely important for multicomponent mixtures. Clearly the problems of representation increase with the number of components. Here we outline briefly the method that we introduced for binary subsystems in our earlier paper⁶ and then describe a previously unpublished method for the visualization of data for ternary systems.

Binary Systems. Three coordinates (pressure, temperature, and composition) are necessary to describe each data point in a binary system. All data can therefore conveniently be plotted in a three-dimensional graph, using temperature as the *x*-axis, composition as the *y*-axis and pressure as the *z*-axis, Figure 2a. Sometimes pure component data (vapor pressure curves, critical points) can be displayed on the front and back surface of the graph, but they are often omitted. The critical line can then be projected onto the *T*-*x*, *p*-*x*, or *p*-*T* surfaces of the cube, as shown in Figure 2a. We recently showed⁶ how these three projections can be grouped together as in Figure 2b, where all information about the critical line of a binary system is presented and no information about the system is lost.

Ternary Systems. *Four* coordinates are necessary to describe a data point completely in a ternary system (pressure, temperature, and *two* independent mole fractions). A simple way of representing ternary data has to be found, as there is no possibility of plotting in four dimensions. Some authors investigate ternary systems only at special fixed compositions,^{12,13} which simplifies the problem. Their preferred choice of graph is a *p*,*T* envelope, in which vapor–liquid equilibrium data and the critical point of the mixture are given. An example for a hypothetical isopleth (line of constant composition) is given in Figure 3a. The advantage of this kind of representation is that the dew and bubble points of the mixture are clearly visible and the specific phase behavior of that mixture can easily be visualized. The disadvantage is that only a few compositions can be represented on a single graph, and complete representation of ternary phase behavior is impossible, because each new composition will create another *p*,*T* envelope, which might overlap with the previous one.

Another method of representing ternary data is to plot them as a binary *p*,*T*-projection,¹⁴ where the three binary critical curves are plotted in the *p*,*T* surface. If all binary systems belong to type I of the classification of van Konynenburg and Scott,¹⁵ their perimeter describes the ternary critical surface, as

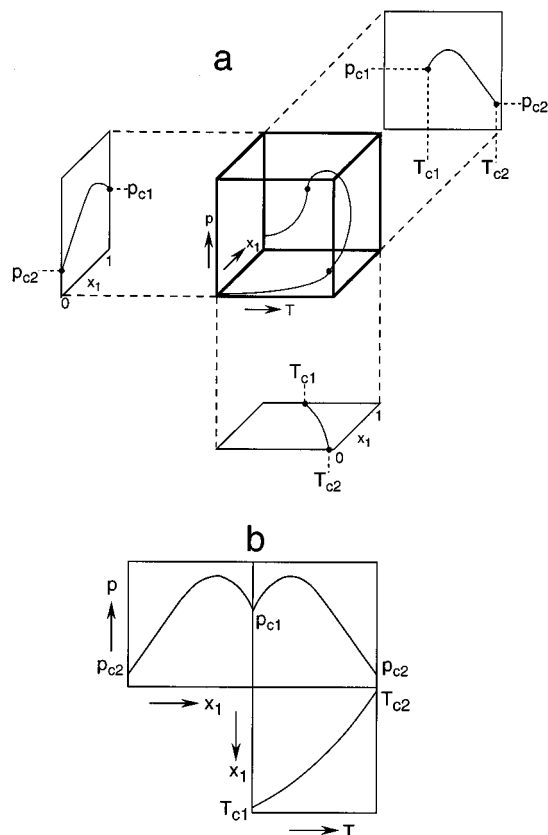


Figure 2. Different methods for plotting binary equilibrium data. (a) The p, T, x_1 cube showing the vapor pressure curves of the pure components with their critical points (black circles) and the binary critical curve connecting them. The three possible projections of the binary critical line on either the $p-x_1$, $T-x_1$ or $p-T$ surface are also shown as exploded view. (b) Shows the three two-dimensional projections of the binary critical curve displayed as if the cube is cut open along its axes.⁶

shown in Figure 3b. Although this method provides a reasonably simple representation of a ternary critical surface, it fails to give a clear visualization of the critical surface if any of the binary subsystems exhibits a more complicated kind of phase equilibrium.

Several authors have presented their data in a so-called phase prism,^{16–18} in order to represent the phase behavior over a wider range of compositions. Ternary data at a constant temperature and constant pressure can be plotted in a two-dimensional triangular graph, which is usually called a Gibbs–Triangle. Stacking several of these Gibbs–Triangles leads either to an isothermal or isobaric phase prism, as in Figure 3c. The obvious advantage of the prism over Figure 3a,b is that, for a constant temperature or pressure, all compositions are represented and the phase behavior is clearly visible, Figure 3c. In contrast to Figure 3b, which only showed the critical point of one ternary mixture, Figure 3c is capable of showing a ternary critical line. Unfortunately, only a single temperature or a single pressure can be plotted, and representation of the complete ternary phase behavior is still impossible. Furthermore, only data points which are obtained by the so-called “analytical method” (i.e. by means of composition variation) are suitable for this kind of graph. Data points obtained by the so-called “synthetic method” (i.e. by varying either pressure or temperature) will result in only one data point per phase prism.

Thus one must find a method for converting the four-dimensional information into three dimensions. The best way is to plot the ternary critical data in a so-called “phase cube”. There are two possible phase cubes which are topologically

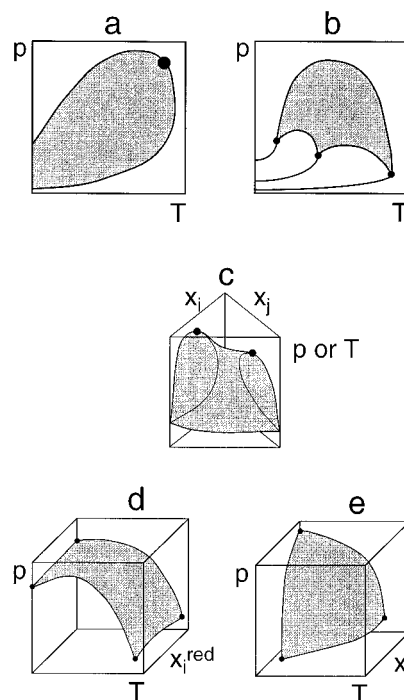


Figure 3. Different possibilities for plotting ternary equilibrium data. (a) Represents a ternary vapor to liquid equilibrium phase envelope (shaded) of constant composition exhibiting a ternary critical point (black circle). (b) Shows the vapor pressure curves and critical points of the pure components, the binary critical curves, and the ternary critical surface (shaded) plotted in a binary p, T projection. (c) An isobaric or isothermal ternary phase prism. The corners of the prism represent the pure components, while the vertical faces are sections through the corresponding binary subsystems, two of which exhibit a binary critical point. The ternary equilibrium data (shaded) are plotted inside of the prism. A ternary critical line connects the binary critical points. (d) and (e) are “phase-cubes” showing the complete ternary critical surface (shaded) and the corresponding critical lines of the binary subsystems connecting the pure components critical points.

equivalent.¹⁴ The first is shown in Figure 3d, where the data are plotted in a p, T, x_i^{red} cube. This method has been used previously to present ternary critical data,¹⁶ but it has never been discussed in detail. The key parameter is the renormalized mole fraction, x_i^{red} , which is obtained by dividing the mole fraction x_i by the sum of $x_i + x_j$. The renormalized mole fraction x_i^{red} then spans from 0 to 1. Additionally, x_i^{red} also represents the ratio of two of the three components. This way of plotting the data also results in a simple way of comparing data points, because ternary data are best measured in the so-called quasi-binary approach, where the ratio of two components is kept constant. The three binary critical curves are also represented, and additionally, the vapor pressure curves of the pure components can be added.

The second phase cube representation, shown in Figure 3e, plots the data in a p, T, x_i -cube. One axis displays x_i , and because x_j is held in a fixed ratio to x_i under quasibinary conditions, x_j does not need to be plotted explicitly. The advantage of Figure 3e is that it contains no redundant information about the size and shape of the critical surface.¹⁴ Therefore, this plot is easier to interpret than the “quasibinary” graph, 3d, especially for more complicated ternary critical surfaces. However, Figure 3e cannot easily be used in studies such as ours, where the ratio of the two components i and j vary. Thus ternary data in this paper are presented as in Figure 3d. In both parts d and e of Figure 3, either isobaric or isothermal sections through the cubes provide condensed ternary information, which otherwise would be represented as a phase prism. Unfortunately, no specific

TABLE 1: Critical Point Data for Binary Refrigerant Mixtures^a

$\text{CO}_2 + \text{CH}_2\text{F}_2$		
$x(\text{CO}_2)$	p_c/bar	T_c/K
0.84	74.7	311.9
0.66	75.0	321.8
0.46	72.9	331.1
0.18	64.7	344.8
$\text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$		
$x(\text{CH}_2\text{F}_2)$	p_c/bar	T_c/K
0.72	54.5	357.3
0.50	50.8	362.5
0.31	47.8	366.7

^a See experimental section for errors in measurements.

information about vapor to liquid equilibria can be displayed in these ternary phase cubes. All that is possible is a “ternary dew point surface”, which represents the global minimum for the condensation of a given ternary mixture.

Results and Discussion

Our goal has been to obtain data for two ternary systems $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ and $\text{CO} + \text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$. In both cases, our strategy has been to apply our acoustic method to ternary mixtures of various compositions and to binary mixtures of the various components. This approach maximizes the opportunities for evaluating the acoustic method and for testing the validity of extrapolating from binary to ternary mixtures. We begin with the system $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$.

Fluorinated hydrocarbons are potentially attractive as modifiers for improving solubility in supercritical CO_2 . However, measurement of critical data for such compounds is notoriously difficult. The density differences between coexisting refrigerant phases are usually small, and determination of the vanishing point of the meniscus is biased by the subjectivity of the experimenter and can lead to substantial errors. Acoustic data for the system $\text{CO}_2 + \text{CF}_3\text{CH}_2\text{F}$ has been described by us earlier,⁶ and $\text{CO}_2 + \text{CH}_2\text{F}_2$ and $\text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$ have been studied in the literature,^{19,20} but for the refrigerant system only vapor to liquid equilibria data are available. Binary data for the systems $\text{CO}_2 + \text{CH}_2\text{F}_2$ and $\text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ are presented in Table 1.

$\text{CO}_2 + \text{CH}_2\text{F}_2$. Four mixtures covering the whole mole fraction range were investigated. The result for the critical line of this system is shown in Figure 4a. The system exhibits type I fluid phase behavior, according to the classification of van Konynenburg and Scott, which means that a continuous critical line connects the critical points of the two pure components. Only a small pressure maximum is visible. This suggests that CH_2F_2 should be a useful modifier for CO_2 . Its relatively low critical temperature (351.3 K) and its miscibility with CO_2 make it a good alternative to the heavier refrigerant $\text{CF}_3\text{CH}_2\text{F}$.⁶ As can be seen from Figure 4a, the maximum critical pressure of the system is only ca. 2 bar higher than that of pure CO_2 , corresponding to a mole fraction of CH_2F_2 of ca. 0.3 at a temperature of 315 K. This means that the solvation properties of the mixture will have substantially changed but the critical temperature remains reasonably low. As a result CH_2F_2 could conveniently be used to modify CO_2 .

$\text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ (Refrigerants R32 + R134a). Figure 4b shows results for the binary system $\text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ (R32 + R134a). Only three different mixtures were investigated with compositions corresponding to those used in the ternary system as quasibinaries. No maxima or minima in the projections of the critical line are visible. As expected, this binary system of

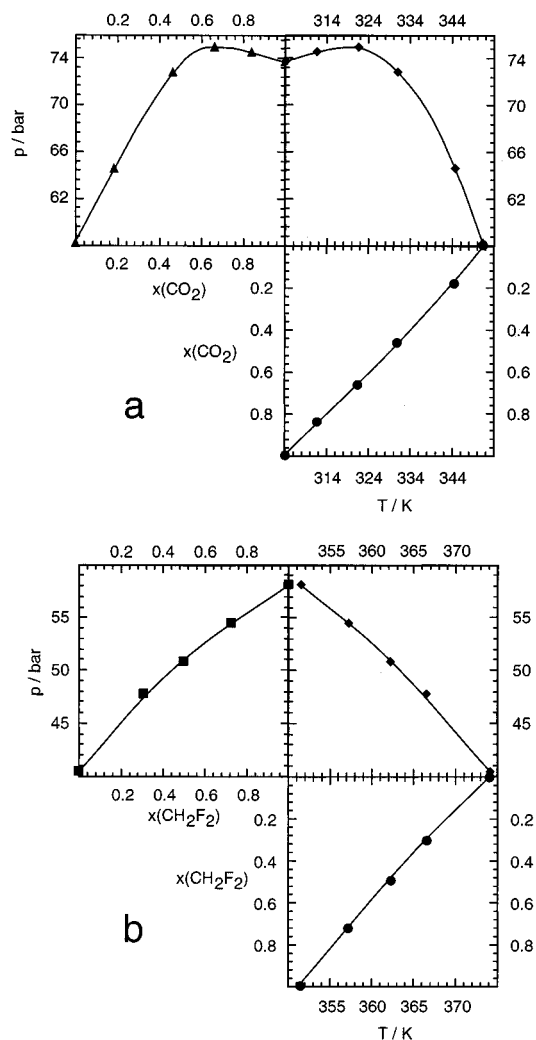


Figure 4. (a) Projections of the binary critical curve of the system $\text{CO}_2 + \text{CH}_2\text{F}_2$. (b) Projections of the binary critical curve of the system $\text{CF}_3\text{CH}_2\text{F} + \text{CH}_2\text{F}_2$. Symbols represent experimental critical data.

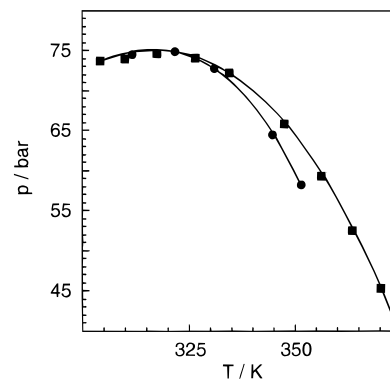


Figure 5. Comparison of the two binary refrigerant systems: ● ($\text{CO}_2 + \text{CH}_2\text{F}_2$) and ■ ($\text{CO}_2 + \text{CF}_3\text{CH}_2\text{F}$).

two refrigerants behaves almost ideally. The critical curves are almost straight lines connecting the critical points of the pure components.

$\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$. A comparison of the binary systems $\text{CO}_2 + \text{CH}_2\text{F}_2$, $\text{CO}_2 + \text{CF}_3\text{CH}_2\text{F}$ reveals that their critical lines are almost coincident over the temperature range of 303 to 318 K. A plot of the p, T projections of the critical curves of both binary systems is shown in Figure 5. We therefore concentrated our measurements of the ternary system in that area. Our goal was to check whether any unusual phenomena, such as pressure maxima or minima occurred in

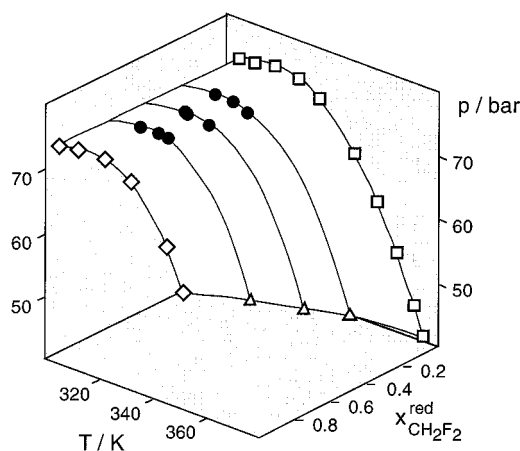


Figure 6. $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ system displayed in a p, T, x^{red} phase cube. The ternary critical surface is drawn as if opaque with additional lines for the coordinate system. Full symbols \bullet represent ternary critical data. Open symbols represent binary critical data, \diamond ($\text{CO}_2 + \text{CH}_2\text{F}_2$), \triangle ($\text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$), and \square ($\text{CO}_2 + \text{CF}_3\text{CH}_2\text{F}$); data for the last system taken from ref (6).

TABLE 2: Ternary Critical Data for the System $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$

$x(\text{CH}_2\text{F}_2)$	$x(\text{CF}_3\text{CH}_2\text{F})$	p_c/bar	T_c/K
Ratio $\text{CH}_2\text{F}_2:\text{CF}_3\text{CH}_2\text{F} \approx 1:3$			
0.06	0.13	74.3	316.3
0.09	0.21	74.3	322.9
0.12	0.28	73.4	328.2
Ratio $\text{CH}_2\text{F}_2:\text{CF}_3\text{CH}_2\text{F} \approx 1:1$			
0.10	0.10	74.7	318.3
0.12	0.12	74.9	318.2
0.17	0.17	73.9	326.5
Ratio $\text{CH}_2\text{F}_2:\text{CF}_3\text{CH}_2\text{F} \approx 3:1$			
0.12	0.04	74.3	313.7
0.17	0.07	74.5	321.3
0.22	0.08	74.3	324.6

the ternary critical surface, although such phenomena would be unlikely for this system because the binary mixtures show only slight deviations from ideality. These phenomena, termed “cosolvency” for a pressure minimum and “island” for a pressure maximum, have been previously reported for various ternary systems.^{15,21}

Our measurements were carried out with a quasibinary approach, with the ratio between two of the three components held constant throughout a series of measurements. Three different mixtures with a ratio of CH_2F_2 to $\text{CF}_3\text{CH}_2\text{F}$ of roughly 3:1, 1:1, and 1:3 were prepared. Ternary mixtures containing various amounts of CO_2 were prepared using these binary mixtures. Three different amounts of CO_2 were chosen for each quasibinary composition with the mole fraction of CO_2 varying from 0.60 to 0.85. The critical point for each mixture was measured acoustically, and a compilation of the ternary data for the system $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ is given in Table 2. The ternary critical points and the corresponding binary critical curves are plotted in a p, T, x^{red} cube, Figure 6.

The three different quasibinary mixtures are clearly visible, and as expected, the ternary data points lie on a straight line connecting the critical point of CO_2 with the critical point of the corresponding binary refrigerant mixture. No global pressure maximum or minimum could be detected in the ternary critical surface. Only a very flat local pressure maximum connecting the two maxima in the binary critical curves of the systems $\text{CO}_2 + \text{CH}_2\text{F}_2$ and $\text{CO}_2 + \text{CF}_3\text{CH}_2\text{F}$ is visible. This confirms our initial expectation that the ternary system should behave ideally and that this ternary system can be expressed as

the sum of the three binaries. No problems were encountered in the acoustic determination of critical data in this system. Further compositions could have been studied had it been necessary.

$\text{CO} + \text{C}_2\text{H}_4$ and $\text{CO} + \text{CH}_3\text{CHCH}_2$. Unlike the other components in this paper, CO is a permanent gas with a value of T_c (132.95 K) well below ambient. Although we have previously reported acoustic measurements⁷ involving CO_2 with permanent gases (H_2 , He , or N_2), the mole fractions of these gases were generally small, and the critical temperatures of the mixtures were close to those of the pure CO_2 . Although we report that the presence of CO limits the range of data that can be obtained acoustically, we show that the method can provide information where none existed before.

The binary system $\text{CO} + \text{C}_2\text{H}_4$ was studied with three different compositions, and five mixtures were investigated for the system $\text{CO} + \text{CH}_3\text{CHCH}_2$. For reasons explained below only small parts of both critical lines could be measured. No literature data were available for either system, but the correctness of our assumption about the shape of the critical curves can be verified by comparing $\text{CO} + \text{CH}_3\text{CHCH}_2$ with the system $\text{CO} + \text{C}_3\text{H}_8$. As the critical properties of propene and propane are almost identical, the shape of the binary critical curves should be very similar. Literature data²² for the system $\text{CO} + \text{C}_3\text{H}_8$ show a large pressure maximum in the critical curve with the maximum pressure exceeding 150 bar. Test measurements by Widdoes and Katz²² proved that vapor–liquid equilibrium data for both systems are almost identical. Therefore, our system should show qualitatively the same behavior in its critical curve. Although the critical pressures of CH_3CHCH_2 and CO are similar, the binary system exhibits the expected large pressure maximum in the critical curve, Figure 7b. This maximum is the result of physical differences (i.e. large differences in size of the molecules and their critical temperature) between CH_3CHCH_2 and CO . The corresponding curves for $\text{CO} + \text{C}_2\text{H}_4$ are shown in Figure 7a. For both alkenes, the projections of the critical lines show large pressure maxima, which exceed the critical pressures of the pure components by a factor of 2–3. Unfortunately, neither maximum could be determined accurately. In the case of $\text{CO} + \text{C}_2\text{H}_4$, our data were limited by the fact that the critical temperature of the mixtures fell below the minimum operating temperature of our equipment (248 K) as the mole fraction of CO increased. For $\text{CO} + \text{CH}_3\text{CHCH}_2$, we observed an interesting effect that limited the range of our acoustic measurements because phase transitions and critical points are determined by locating a maximum in the transit time of the supersonic pulse. Usually this maximum is very narrow and pronounced, but, in this system, the maximum broadens and disappears as the amount of CO present in the mixture is increased. The critical temperature of the mixtures are far above the critical point of CO ($T_c = 132.95$ K). As mentioned in the Introduction, the speed of sound can be related to the compressibility of the fluid. At the critical temperatures of the binary mixtures, the compressibility of CO increases monotonically with falling pressure. This means that the speed of sound in pure CO increases correspondingly, so generating a constant background signal. Thus the maximum in the transit time becomes less pronounced and broadens with an increasing mole fraction of CO . Finally, at ca. 40 mol % CO , this effect renders the peak at the phase transition undetectable. One might think that the broadening of the maximum is due to complex formation. However, the same effect can be observed with other permanent gases,⁷ such as H_2 or He . Data for both binary systems are collected in Table 3.

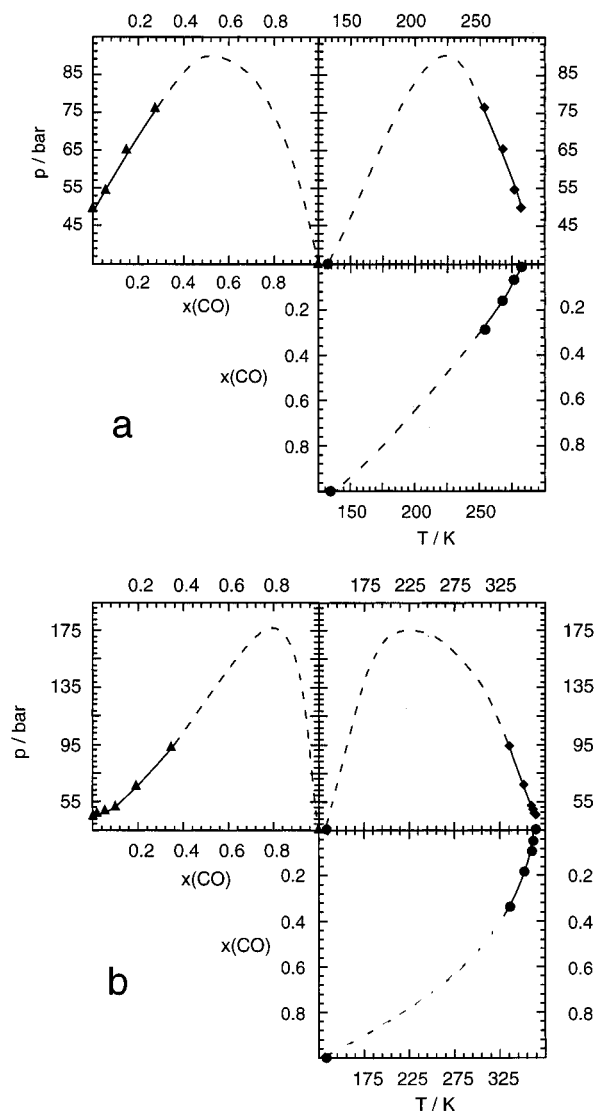


Figure 7. (a) Projections of the binary critical curve of the systems CO + C₂H₄, (b) Projections of the binary critical curve of the system CO + CH₃CHCH₂. Symbols represent experimental critical data. The shapes of the binary critical curves are estimated by the dashed lines.

TABLE 3: Critical Point Data for Binary Mixtures Containing CO

CO + C ₂ H ₄		
<i>x</i> (C ₂ H ₄)	<i>p_c</i> /bar	<i>T_c</i> /K
0.95	55.9	277.1
0.85	65.7	267.7
0.73	75.7	254.5
CO + CH ₃ CHCH ₂		
<i>x</i> (CH ₃ CHCH ₂)	<i>p_c</i> /bar	<i>T_c</i> /K
0.98	46.9	363.5
0.95	49.0	362.5
0.91	52.1	360.6
0.81	66.6	351.7
0.66	94.3	335.9

CO + C₂H₄ + CH₃CHCH₂. The ternary system CO + C₂H₄ + CH₃CHCH₂ is of industrial relevance in the production of aliphatic polyketone polymers.^{1–5} Therefore, precise knowledge about its critical surface could improve existing production processes as the mixture has to be homogeneous. As with the refrigerants, this ternary system was investigated by the quasibinary method, but additionally two mixtures of particular industrial relevance were investigated. Only one quasibinary

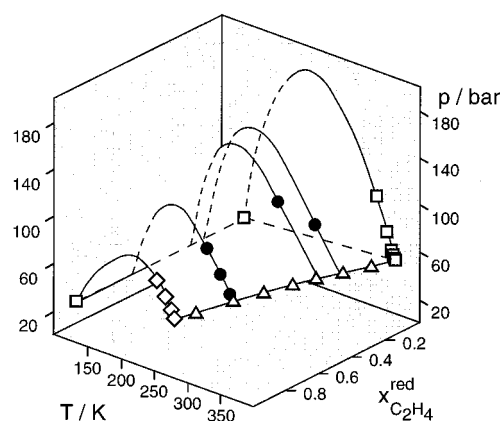


Figure 8. The system CO + C₂H₄ + CH₃CHCH₂ in a *p*, *T*, *x^{red}* phase cube. The ternary critical surface is drawn as if opaque with dotted lines for easy visualization of the shape of the surface. Full symbols represent ternary critical data. Open symbols represent binary critical data; ◇ (CO + C₂H₄), □ (CO + CH₃CHCH₂), and △ (C₂H₄ + CH₃CHCH₂) taken from ref 20.

TABLE 4: Ternary Critical Data for the System CO₂ + C₂H₄ + CH₃CHCH₂

Ratio C ₂ H ₄ :CH ₃ CHCH ₂ ≈ 3:1			
<i>x</i> (C ₂ H ₄)	<i>x</i> (CH ₃ CHCH ₂)	<i>p_c</i> /bar	<i>T_c</i> /K
0.51	0.17	89.7	269.4
0.59	0.20	71.1	287.8
0.71	0.24	67.6	300.8
Compositions for Industrial Polymer Production			
0.16	0.48	90.6	325.8
0.18	0.39	115.0	302.1

mixture with three different compositions was measured. All data for this system are summarized in Table 4.

The results are again presented in a *p*, *T*, *x^{red}* cube, Figure 8. The ternary critical surface shows a pronounced local pressure maximum reflecting the maxima in the corresponding binary systems. Although the critical surface could only be determined partly, it seems to be unlikely that there is a global pressure maximum, hence an “island system”. Quasibinary mixtures with a ratio of C₂H₄:CH₃CHCH₂ of 3:1 lie on a continuous and straight line, which connects the critical point of CO with the critical point of the pure quasibinary mixture. The other two mixtures, which contained larger quantities of CO, have compositions similar to those used for the production of aliphatic polyketone polymers. These mixtures also lie on the critical surface but in the region of high CH₃CHCH₂ mole fractions. The same effect of the “disappearing transition maximum” was experienced with the ternary mixtures as we found in the CO + CH₃CHCH₂ binary.

Modeling

Although the systems presented in this study are of industrial interest, it is difficult to obtain accurate data over the entire pressure, temperature, composition (*p*–*T*–*x*) space for these systems. Therefore, the aim of this section is to extend the impact of our critical-mixture data by fitting the data to the Peng–Robinson (PR) equation of state²³ to obtain temperature-independent interaction parameters that are used to generate *p*–*x* isotherms and ternary phase diagrams. The PR equation of state is used with the following mixing rules

$$p = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (1)$$

$$a_{\text{mix}} = \sum_{ij} x_i x_j a_{ij} \quad (2)$$

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \quad (3)$$

$$b_{\text{mix}} = \sum_{ij} x_i x_j b_{ij} \quad (4)$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})(1 - l_{ij})] \quad (5)$$

where k_{ij} and l_{ij} are mixture parameters and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson.²³ With these mixing rules the expression for the fugacity coefficient becomes

$$\ln \phi_i = \frac{b'_i}{b_{\text{mix}}} (Z - 1) - \ln(Z - B) - \frac{A}{2.828B} \left(\frac{2 \sum_j x_j a_{ij}}{a_{\text{mix}}} - \frac{b'_i}{b_{\text{mix}}} \right) \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \quad (6)$$

where

$$Z = \frac{pV}{RT} \quad A = \frac{a_{\text{mix}} R^2 T^2}{p} \quad B = \frac{b_{\text{mix}} RT}{p}$$

The term b'_i is defined as

$$b'_i = \left[\frac{\partial(b_{\text{mix}} N)}{\partial N_i} \right]_{T, V, N_{j \neq i}} = 2 \sum_k x_k b_{ik} - b_{\text{mix}} \quad (7)$$

where N is the total number of moles in the mixture. If l_{ij} is set equal to zero, the mixing rule for b_{mix} reduces to a single summation in mole fraction, b'_i becomes equal to b_i , and the equation for the fugacity coefficient of component i reduces to the expression given by Peng and Robinson.²³ The PR equation is fit to experimental critical-mixture data by calculating P - x isotherms and obtaining the best fit of the critical point at each temperature with mixture parameters that do not vary with temperature. Additionally, the vapor pressures of the pure components are calculated with the PR equation of state. Table 5 shows that accepted values for pure component critical points^{24,25} are in good agreement with values obtained with the PR equation of state for the substances investigated in this work.

Table 6 lists the interaction parameters obtained for the binary systems considered in this study. Figure 9 shows that a reasonable fit of the isotherms for the three refrigerant systems is obtained with both interaction parameters set equal to zero. This is not entirely unexpected since we have shown in our earlier work⁷ that mixtures of refrigerants with CO_2 behave almost ideally. There are two features that appear in the calculated P - x isotherms for these refrigerant systems. The two-phase region is very narrow and the calculated critical-mixture composition is not as close to experimental observation as the calculated critical-mixture pressure. Figure 10 shows the calculated critical-mixture curves of the three binary refrigerant systems. The predicted critical-mixture curves confirm the proposed type I fluid phase behavior of these systems.

Figure 11 shows calculated P - x isotherms for binary systems with CO , C_2H_4 , and CH_3CHCH_2 . Figure 11a shows that a good fit of the isotherms at -18 , -5 , and $+4$ °C for the $\text{CO} + \text{C}_2\text{H}_4$ system is obtained with k_{ij} equal to -0.100 and $l_{ij} = -0.180$. This is the only binary system considered in this study that required two mixture parameters to fit the observed critical

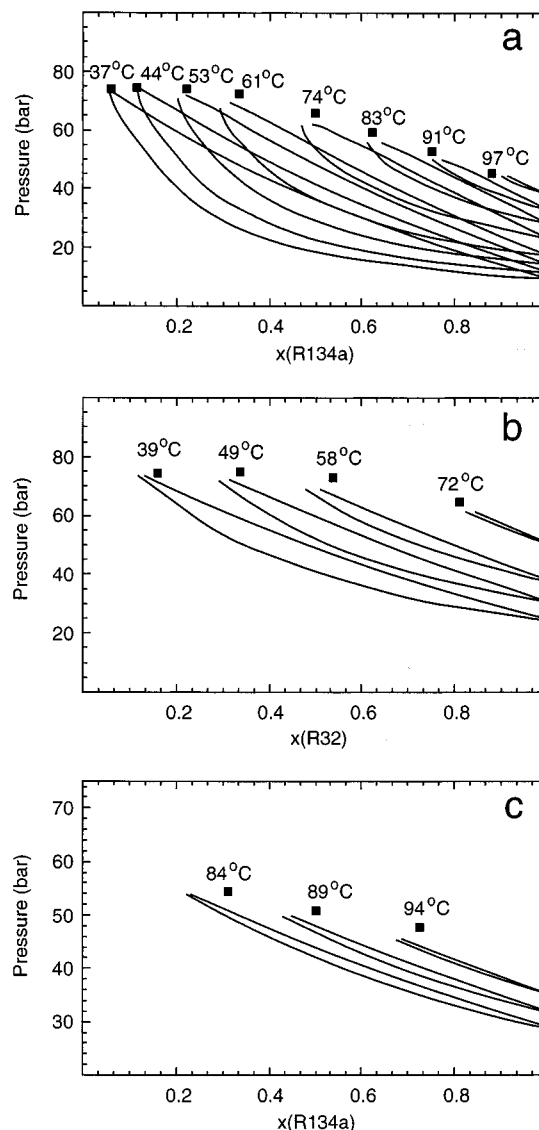


Figure 9. Calculated pressure-composition isotherms determined with both k_{ij} and l_{ij} set equal to zero: (a) $\text{CO}_2 + \text{CF}_3\text{CH}_2\text{F}$, (b) $\text{CO}_2 + \text{CH}_2\text{F}_2$, (c) $\text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$. The solid squares represent experimental data obtained in this study.

TABLE 5: Pure Component Critical Parameters

component	critical parameters			critical parameters calculated with PR EOS		
	p_c/bar	T_c/K	$\rho_c/\text{g cm}^{-3}$	p_c/bar	T_c/K	$\rho_c/\text{g cm}^{-3}$
CO	35.0	132.9	0.300	34.32	132.51	0.233
CO_2	73.8	304.1	0.468	73.22	305.01	0.361
C_2H_4	50.4	282.4	0.215	48.30	280.71	0.143
CH_3CHCH_2	46.0	364.9	0.232	44.31	363.04	0.154
CH_2F_2	58.3	351.6	0.431	57.49	350.95	0.283
$\text{CF}_3\text{CH}_2\text{F}$	40.6	374.15	0.509	40.21	373.74	0.377

TABLE 6: Binary Interaction Coefficients

system	k_{ij}	l_{ij}
$\text{CO}_2 + \text{CH}_2\text{F}_2$	0.00	0.00
$\text{CO}_2 + \text{CF}_3\text{CH}_2\text{F}$	0.00	0.00
$\text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$	0.00	0.00
$\text{CO} + \text{C}_2\text{H}_4$	-0.10	-0.18
$\text{CO} + \text{CH}_3\text{CHCH}_2$	-0.16	0.00
$\text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$	0.00	0.00

points. Without this second parameter it was not possible to fit simultaneously the critical-mixture composition and pressure. Calculated P - x isotherms are also shown for temperatures that are much lower than those experimentally investigated. At

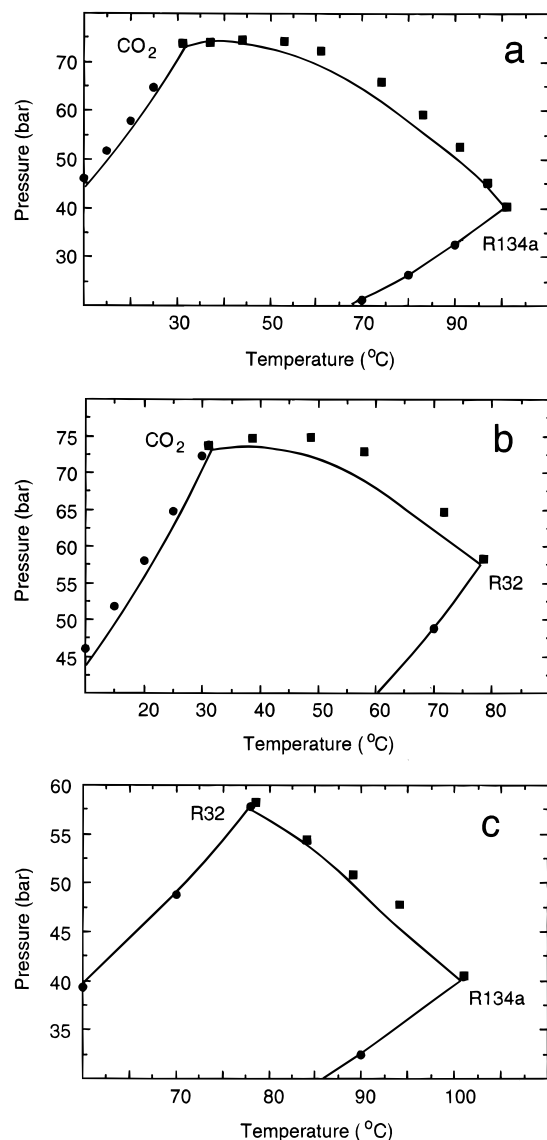


Figure 10. P , T projection of pure component vapor pressures and binary critical lines calculated with the PR EOS for the systems (a) $\text{CO}_2 + \text{CF}_3\text{CH}_2\text{F}$, (b) $\text{CO}_2 + \text{CH}_2\text{F}_2$, and (c) $\text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$. The calculated curves were obtained with both k_{ij} and l_{ij} set equal to zero. Solid circles represent vapor pressures taken from refs 24 and 25. Solid squares represent experimental data points from acoustic measurements.

temperatures of -120 , -130 , and -145 °C, the PR equation of state indicates the presence of a three-phase (LLV) line shown by a discontinuity in the P - x loop. The discontinuity in the P - x isotherms is represented by dashed lines in Figure 11a, and it suggests that the $\text{CO} + \text{C}_2\text{H}_4$ system does exhibit type I phase behavior following the classification of van Konynenburg and Scott.¹⁵

Similar fits are obtained for the P - x isotherms and the critical-mixture curve for the $\text{CO} + \text{CH}_3\text{CHCH}_2$ system shown in Figure 11b. However, in this instance, k_{ij} is equal to -0.160 and l_{ij} is equal to zero. In addition, a maximum of ca. 180 bar is predicted at a temperature of -50 °C compared to a maximum of ca. 90 bar also at ca. -50 °C for the $\text{CO} + \text{C}_2\text{H}_4$ system. For the $\text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$ both interaction parameters are set equal to zero since binary mixtures of hydrocarbons behave almost ideally.²³ The p , T projections for the three hydrocarbon systems are shown in Figure 12. These systems exhibit type I fluid phase behavior, except for the $\text{CO} + \text{C}_2\text{H}_4$ system shown in Figure 12a. However, the calculated phase behavior near the critical point of CO is not physically realistic and is therefore

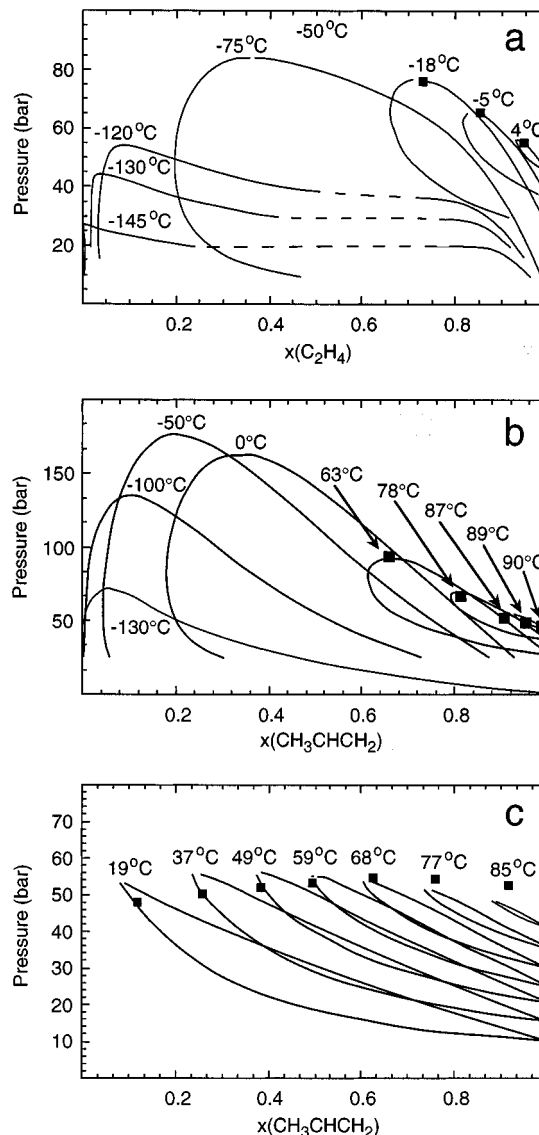


Figure 11. Calculated pressure-composition isotherms using the PR EOS with adjustable parameters k_{ij} and l_{ij} for the following binary systems (a) $\text{CO} + \text{C}_2\text{H}_4$ with $k_{ij} = -0.10$ and $l_{ij} = -0.18$. The dashed lines at -120 , -130 , and -145 °C indicate the presence of a calculated, three-phase LLV line at temperatures near the critical point of CO. (b) $\text{CO} + \text{CH}_3\text{CHCH}_2$ with $k_{ij} = -0.16$ and $l_{ij} = 0.0$. (c) $\text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$ with k_{ij} and $l_{ij} = 0.0$. Solid squares represent experimental data points.

not presented in the diagram. More than likely the mixture parameters that were obtained over only a limited range at much higher temperatures are not applicable at these cold temperatures. As expected, the systems containing CO exhibit a large pressure maximum in their critical curve, as proposed by our experimental data and estimated in the literature.²² This is reflected in the strongly negative interaction coefficients used in the PR equation of state to model these systems.

Since most of the binary systems considered in this study exhibit type I fluid phase behavior, similar behavior is expected for the ternary mixtures. The ternary systems are modeled using only the binary interaction coefficients. Predicted and experimental data points are plotted in Gibbs triangles for easy visualization of the results. For the ternary system $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$, the experimental critical data could not be calculated at the given experimental pressure of interest, because the PR equation of state predicts a single phase under these conditions. Therefore, ternary vapor to liquid equilibrium are calculated at pressures less than the experimental pressure but

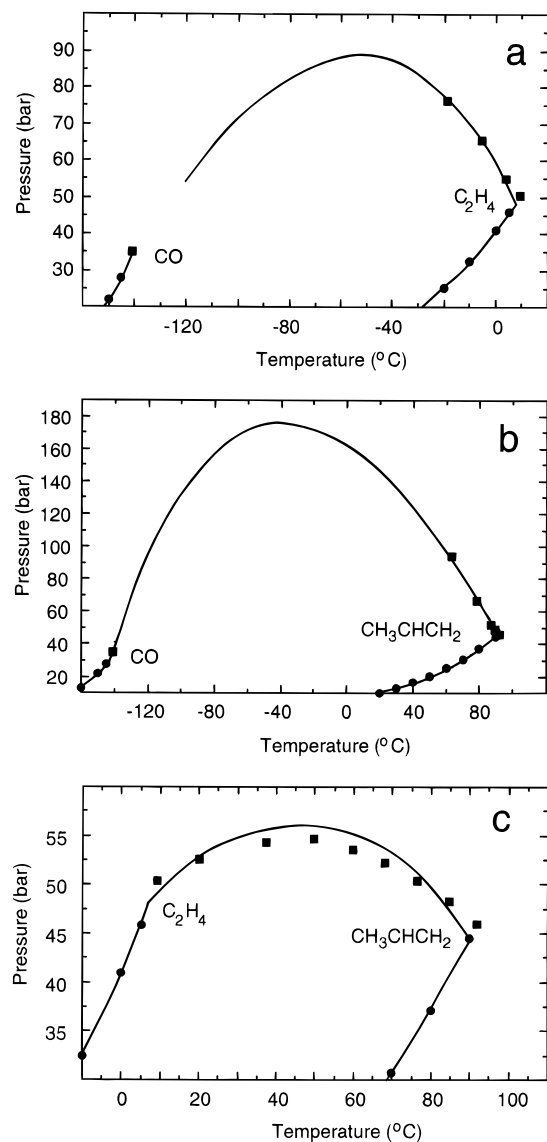


Figure 12. P,T projection of pure component vapor pressures and binary critical lines calculated with the PR EOS for the systems (a) $\text{CO} + \text{C}_2\text{H}_4$ with $k_{ij} = -0.10$ and $l_{ij} = -0.18$, (b) $\text{CO} + \text{CH}_3\text{CHCH}_2$ with $k_{ij} = -0.16$ and $l_{ij} = 0.0$, and (c) $\text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$ with k_{ij} and $l_{ij} = 0.0$. Solid circles represent vapor pressures taken from ref 24.

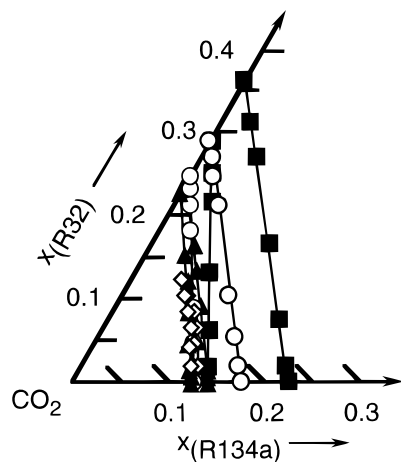


Figure 13. Calculated isothermal ternary vapor to liquid equilibria at 318.25 K in the system $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$: ■ 65 bar, ○ 70 bar, ▲ 73 bar, and ◇ 73.6 bar.

only at one temperature (318.25 K) as shown in Figure 13. Since the calculated tie-lines for the ternary system are very small,

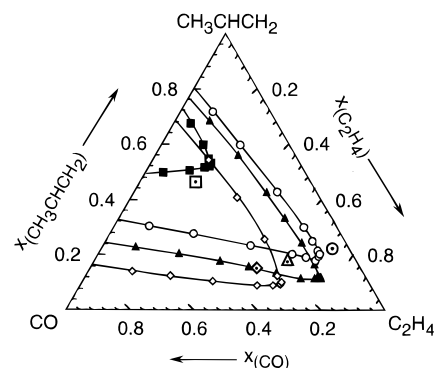


Figure 14. Calculated ternary vapor to liquid equilibria in the system $\text{CO} + \text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$: ■ 325.8 K and 90.6 bar, ○ 300.0 K and 67.6 bar, ▲ 287.8 K and 71.1 bar, ◇ 269.4 K and 89.7 bar. Open symbols with center dot represent the experimental critical points at the corresponding temperature and pressure, as determined by our acoustic measurements.

TABLE 7: Calculated Compositions of Light and Heavy Phases for the System $\text{CO}_2 + \text{CH}_2\text{F}_2 + \text{CF}_3\text{CH}_2\text{F}$ at 318.25 K for Various Pressures^a

light phase			heavy phase		
$x(\text{CO}_2)$	$x(\text{R32})$	$\rho/\text{g cm}^{-3}$	$\rho/\text{g cm}^{-3}$	$x(\text{CO}_2)$	$x(\text{R32})$
$p = 65.0$ bar					
0.8479	0.0176	0.264	0.628	0.7643	0.0218
0.8251	0.0617	0.261	0.617	0.7438	0.0766
0.7880	0.1342	0.257	0.600	0.7102	0.1666
0.7457	0.2175	0.252	0.580	0.6717	0.2701
0.7293	0.2504	0.249	0.572	0.6565	0.3130
$p = 70.0$ bar					
0.8637	0.0184	0.316	0.553	0.8166	0.0215
0.8497	0.0467	0.314	0.547	0.8036	0.0545
0.8247	0.0905	0.311	0.538	0.7834	0.1056
0.7834	0.1834	0.304	0.519	0.7409	0.2137
0.7687	0.2141	0.302	0.512	0.7269	0.2497
0.7607	0.2309	0.300	0.509	0.7192	0.2693
$p = 73.0$ bar					
0.8713	0.0096	0.379	0.482	0.8527	0.0103
0.8667	0.0191	0.379	0.481	0.8484	0.0205
0.8537	0.0493	0.372	0.425	0.8438	0.0512
0.8353	0.0881	0.371	0.460	0.8191	0.0939
0.8180	0.1258	0.367	0.458	0.8015	0.1345
0.8043	0.1572	0.361	0.435	0.7906	0.1663
$p = 73.6$ bar					
0.8645	0.0246	0.397	0.447	0.8554	0.0256
0.8532	0.0494	0.395	0.430	0.8468	0.0506
0.8420	0.0695	0.406	0.445	0.8350	0.0724
0.8331	0.0899	0.405	0.440	0.8269	0.0911
0.8258	0.1097	0.391	0.398	0.8243	0.1103
0.8201	0.1299	0.367	0.368	0.8199	0.1301

an enlargement of the “ CO_2 -rich” corner of the phase triangle is shown. The predicted difference between vapor and liquid phase composition close to the critical point is only 1.5 mol %, which suggests why it is difficult to obtain accurate view-cell data for these systems. A critical point is calculated at 318.25 K for a pressure of 73.6 bar, which shows good agreement with the experimentally determined critical point at slightly higher pressure. A comparison between experimental and calculated ternary critical data is given in Table 7.

The vapor to liquid equilibrium for the system $\text{CO} + \text{C}_2\text{H}_4 + \text{CH}_3\text{CHCH}_2$ was calculated at four different temperatures and pressures, which all match the experimentally obtained critical values for the quasibinary mixtures. Selected tie-lines calculated for each temperature and the experimental critical point are shown in Figure 14. The predictions from the PR equation of state do not coincide precisely with any of the experimental data points. Nevertheless, the agreement between experimental

TABLE 8: Calculated Compositions of Light and Heavy Phases at Observed Critical Temperatures and Pressures for the System CO + C₂H₄ + CH₃CHCH₂

light phase			heavy phase		
$x(\text{CO})$	$x(\text{C}_2\text{H}_4)$	$\rho/\text{g cm}^{-3}$	$\rho/\text{g cm}^{-3}$	$x(\text{CO})$	$x(\text{C}_2\text{H}_4)$
$T = 325.8 \text{ K}, p = 90.6 \text{ bar}$					
0.4411	0.0517	0.201	0.352	0.2693	0.0485
0.3560	0.1318	0.227	0.312	0.2679	0.1274
0.3052	0.1710	0.252	0.282	0.2759	0.1690
0.2844	0.1853	0.265	0.274	0.2756	0.1846
experimental critical point				0.36	0.16
$T = 300.0 \text{ K}, p = 67.6 \text{ bar}$					
0.5824	0.1033	0.118	0.468	0.1775	0.0960
0.4557	0.2570	0.127	0.434	0.1499	0.2432
0.2965	0.4584	0.144	0.376	0.1189	0.4430
0.1833	0.6047	0.171	0.317	0.0994	0.5939
0.1449	0.6540	0.188	0.285	0.0960	0.6462
0.1195	0.6816	0.208	0.252	0.0988	0.6782
0.1022	0.6905	0.234	0.244	0.0978	0.6895
experimental critical point				0.05	0.71
$T = 287.8 \text{ K}, p = 71.1 \text{ bar}$					
0.6623	0.0981	0.121	0.496	0.2016	0.1022
0.5387	0.2431	0.129	0.461	0.1740	0.2564
0.4202	0.3898	0.141	0.419	0.1510	0.4128
0.3427	0.4874	0.151	0.386	0.1391	0.5150
0.2653	0.5866	0.168	0.344	0.1305	0.6142
0.1981	0.6720	0.194	0.296	0.1290	0.6917
0.1545	0.7185	0.227	0.251	0.1398	0.7234
0.1416	0.7295	0.242	0.248	0.1384	0.7305
0.1359	0.7347	0.249	0.252	0.1341	0.7353
experimental critical point				0.21	0.59
$T = 269.4 \text{ K}, p = 89.7 \text{ bar}$					
0.7161	0.1310	0.161	0.508	0.2770	0.1697
0.6049	0.2578	0.175	0.464	0.2534	0.3302
0.4814	0.4013	0.198	0.405	0.2430	0.3897
0.3500	0.5500	0.246	0.322	0.2660	0.5967
0.3004	0.5998	0.276	0.308	0.2658	0.6202
0.2770	0.6188	0.294	0.297	0.2743	0.6204
experimental critical point				0.32	0.51

and predicted data is remarkably good, in view of the difficulty in obtaining experimental data for this system. A comparison between experimental and calculated ternary critical data is given in Table 8. The critical points at 269.4, 287.8, and 300.0 K belong to a quasibinary mixture. It can be seen that the overall miscibility on the quasibinary isopleth does not increase monotonically with temperature. Furthermore, it can be seen from Table 8 that addition of CH₃CHCH₂ to the system, with an almost constant mole fraction of CO, changes its critical pressure only marginally, although the critical temperature is increased by more than 55 K. Both results have consequences for an industrial process using these mixtures, because it is crucial to work in a homogeneous phase for production of polymer. Again, reasonable agreement is obtained considering that the sets of binary mixture parameters were not adjusted for these ternary calculations. Also, note that mixture densities are obtained with these calculations.

Conclusions

We have shown that our improved acoustic cell can provide ternary critical data for two systems that are chemically and physically very different. Adding a third component had no substantial effect on the signal strength at the phase transition, although the signal shape can be influenced by the physical properties of the components even in a binary system. This effect leads to a substantial limitation for the detection of phase equilibria with an acoustic method in a multicomponent system.

In the system CO₂ + CH₂F₂ + CF₃CH₂F, we showed that even the small differences in the binary subsystems could be detected in the ternary mixture and that the existence of a global

pressure maximum is impossible. Furthermore, the data from the subsystem CO₂ + CH₂F₂ suggest that CH₂F₂ might be used to modify the properties of CO₂ in supercritical fluid chromatography and supercritical fluid extraction. Indeed, CH₂F₂ might be preferable to modifiers like CH₃OH, since polar modifiers are usually not completely miscible with CO₂, or increase the critical parameters substantially. Furthermore, CH₃OH strongly self-associates, which limits its effectiveness as a cosolvent.

By contrast, the critical surface exhibits a pronounced pressure maximum in the system CO + C₂H₄ + CH₃CHCH₂, as a result of chemical differences between CO and the alkenes. The critical pressure changes rapidly with composition and with temperature, which has implications for the industrial production of aliphatic polyketone polymers. Since the reaction mixture must be homogeneous, precise control of all reaction parameters must be implemented, especially if polymers with a high CH₃-CHCH₂ content are to be produced because the changes are largest on the "CH₃CHCH₂-rich" side of the phase diagram.

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