Probing Vapor/Liquid Equilibria of Near-Critical Binary Gas Mixtures by Acoustic Measurements

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Received: January 2, 1996; In Final Form: March 13, 1996[⊗]

Phase behavior is a fundamental aspect of supercritical fluids. A simple acoustic method is described for investigating vapor/liquid equilibria. The method is used to investigate three different pure components (CO_2, C_2H_6, and CF_3CH_2F, refrigerant R134a) and binary mixtures of CF_3CH_2F with CO_2 or C_2H_6. For the pure components, the reciprocal of the speed of sound was measured at selected temperatures around the critical point. The data obtained are in good agreement with literature values. The binary mixtures were investigated over the whole composition range (i.e., mole fraction of CF_3CH_2F from 0 to 1.0), and their critical curves were determined. The critical lines show the expected type I fluid phase behavior, but the critical line in $C_2H_6 + CF_3CH_2F$ shows an unusual pressure minimum and maximum. The resulting critical lines are discussed with respect to thermodynamics, the use of these mixtures for supercritical fluid chromatography and extractions, and the possibility of using CF_3CH_2F as a modifier.

Introduction

Supercritical mixtures are of increasing interest for chemical processes.[1] In order to exploit the advantages of a supercritical fluid, reaction mixtures have to be homogeneous. Therefore, a knowledge of their phase envelopes and critical points is crucial. Measurements of phase envelopes are 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. In principle, the determination of vapor−liquid equilibria by an acoustic method overcomes these disadvantages. First, acoustic measurements can be made in a totally opaque vessel, offering a completely objective route to obtaining data on phase transitions, and second, acoustic measurements should be applicable to nearly all types of fluid phase.

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,[2] and hence, by measuring the speed of sound in the fluid, the phase envelope of the system can be obtained. Furthermore, the specific dependence of the speed of sound on pressure and on temperature can be used to derive other thermodynamic properties of the fluid. For example, acoustic properties are often used to obtain data for the acoustic virial coefficients, which are related to the volumetric virial coefficients.[3,4] Therefore, acoustic measurements represent an independent source for thermophysical properties of pure fluids.

Measurements of acoustic properties of pure fluids were first reported[5] in the 1920s, although acoustic methods were already being investigated by the end of the past century.[6] However, these investigations were usually aimed at obtaining thermodynamic properties rather than critical data. In the 1980s,

extensive investigations began to measure critical properties via acoustic methods.[7−9] In the majority of this work, a spherical acoustic cavity was used as a resonator, because its geometry leads to standing acoustic waves in the cavity. Therefore, the signal-to-noise ratio is superior to other geometries. These pioneering experiments[7] proved that acoustic determination of critical data for pure substances could be of the same, if not better, precision than those previously obtained by visual determination.

On the other hand, acoustic measurements for binary mixtures are scarce.[10−12] Some investigations on binary mixtures were reported in the 1980s, but usually such mixtures are investigated by optical methods or by sampling. The acoustic behavior of a fluid mixture should also show distinctive variations depending on temperature and pressure. Therefore, its critical point should be locatable by an acoustic investigation. We have already reported briefly[13,14] how *photoacoustic* measurements can be used to locate the critical points of dilute mixtures of H_2 in CO_2 and N_2 in C_2H_6. The objective of this paper is to demonstrate that it is possible to detect critical points of refrigerant mixtures over a relatively wide temperature range, with a nonspherical acoustic resonator. A new technique is particularly important in this area because the visual determination of vapor−liquid critical points in refrigerant mixtures is often difficult, the consequence of the small density differences between the coexisting phases.[15] Visual methods take the vanishing point of the meniscus between coexisting phases as data point. In the vicinity of a critical point the density difference between vapor and liquid approaches zero, so the exact determination of the disappearance of the meniscus is biased by the subjectivity of the experimenter and can lead to substantial errors. By contrast, determination of the critical point with an acoustic method is completely objective and should therefore with sophisticated equipment, such as a spherical resonator, give an accuracy comparable to or even better than visual methods. For pure components the published data[7−9] already show a superior accuracy of the acoustic method in obtaining critical data.

In this paper, we first show that our acoustic technique gives satisfactory critical data for pure substances, CO_2, C_2H_6, and the refrigerant R134a (CH_3CH_2F). Then, we investigate binary

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J. Phys. Chem., Vol. 100, No. 22, 1996 **9523**

mixtures CO_2 + R134a and C_2H_6 + R134a. Our aim is to evaluate the possible use of R134a as a modifier for improving the solvent power of supercritical CO_2 and C_2H_6, because neat R134a has considerably better solvent properties than either. However, to be a good modifier for these fluids, R134a should increase the solvent power without altering the critical temperatures and pressures significantly.

Theoretical Background

Our experiment is carried out by measuring the transit time of an ultrasonic pulse between two piezoelectric transducers through a fluid mixture. The transit time is proportional to the reciprocal of the speed of sound. The speed of sound at zero frequency, c_0, of a pure component, neglecting absorption and dispersion, is given by eq 1, where ρ is the density of the fluid,[2] which can be transformed simply into eq 2.

$$c_0 = \left(\frac{\partial p}{\partial \rho}\right)_S^{0.5} \qquad (1)$$

$$c_0 = \left(\frac{V}{M\beta_S}\right)^{0.5} \qquad (2)$$

Given the definition of the isentropic compressibility β_S in eq 3,

$$\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \qquad (3)$$

eq 2 can be rewritten as eq 6 via eq 4, eq 5, and γ, the ratio of the heat capacities.

$$\left(\frac{\partial V}{\partial p}\right)_S = \frac{(\partial S/\partial p)_v}{(\partial S/\partial V)_p} = \frac{(\partial S/\partial T)_v(\partial T/\partial p)_v}{(\partial S/\partial T)_p(\partial T/\partial V)_p} \qquad (4)$$

$$c_\sigma = T\left(\frac{\partial S}{\partial T}\right)_\sigma \qquad \text{with } \sigma: \ V \text{ or } p \qquad (5)$$

$$c_0 = V\left[-\frac{\gamma}{M}\left(\frac{\partial p}{\partial V}\right)_T\right]^{0.5} \qquad (6)$$

However, eq 6 cannot be applied at the critical point because $(\partial p/\partial V)_T = 0$ and γ shows positive infinity, but using the relationship between the heat capacities c_p and c_v given in eq 7, eq 6 can be rearranged to eq 8.

$$c_p = c_v - T\left(\frac{\partial p}{\partial T}\right)_v^2 \bigg/ \left(\frac{\partial p}{\partial V}\right)_T \qquad (7)$$

$$c_0 = V\left(\frac{T}{Mc_v}\right)^{0.5}\left(\frac{\partial p}{\partial T}\right)_v\left[1 - \frac{c_v}{T}\frac{(\partial p/\partial V)_T}{((\partial p/\partial T)_v)^2}\right]^{0.5} \qquad (8)$$

The right-hand term in the square brackets in eq 8 tends to unity, as the fluid approaches its critical point, leading to eq 9, the thermodynamic expression for the speed of sound of a pure component at its critical point.

$$c_{0\text{(critical)}} = V\left(\frac{T}{Mc_v}\right)^{0.5}\left(\frac{\partial p}{\partial T}\right)_v \qquad (9)$$

Experimental Apparatus

The acoustic cell is constructed from a standard stainless steel $^1/_4$ in. cross piece (Swagelok 400-4), with its inner diameter bored out to provide an acoustic cavity of about 2 mL volume. A schematic representation of the experimental equipment is
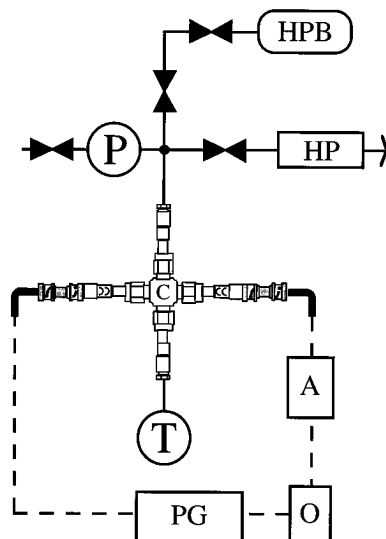

Figure 1. Schematic representation of the acoustic equipment. The components are labeled as follows: A, amplifier; C, cell; HP, hand pump; HPB, high-pressure bomb; O, digital oscilloscope; P, pressure transducer; PG, pulse generator; T, thermocouple.

shown in Figure 1. Pressure was generated via a hand pump (High Pressure Equipment Co., Model 62-6-10) and monitored with a solid-state pressure transducer (RDP-Electronics, Series TJE). Pressure 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. Temperature was measured via a thermocouple and digital readout (Kayne-May Ltd., KM-42), with an accuracy of ±0.1 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 A and then displayed on an oscilloscope (Gould, DSO 475), from which the transit time of the pulse across the acoustic cavity, the reciprocal of the speed of sound, was obtained.

The fluid mixture was filled into a high-pressure bomb of about 50 mL capacity (Whitey, HDF4-50). A mixture with a desired composition was obtained as follows. The bomb was weighed empty and then connected to a high-pressure reservoir of the first component. The vessel was cooled with liquid nitrogen, and a certain amount of the first component was frozen in. The bomb was then thawed and weighed. The same procedure was repeated to add the second component to the bomb. The mass differences were converted into moles to calculate the mole fractions of the system; the accuracy in mole fraction depended only on the balance (Mettler, PM4000) and was ±1%. The filled bomb was then used to load the hand pump. The pump was filled with an initial pressure in the bomb, which was below the dew pressure of the mixture, so that a homogeneous vapor phase was necessarily present in the bomb at the outset. Subsequent filling of the cell also began at a pressure lower than the dewpoint to ensure homogeneity of the mixture without stirring. For more complex mixtures stirring would probably be necessary. The acoustic signal of the mixture was monitored while the mixture was heated with an industrial heat gun. Temperature and simultaneously pressure were raised until a change in the acoustic signal, from a gaslike to a liquidlike signal, occurred. The equipment was disconnected from the bomb, and the pressure was increased with the hand pump until only minute changes in the acoustic signal were
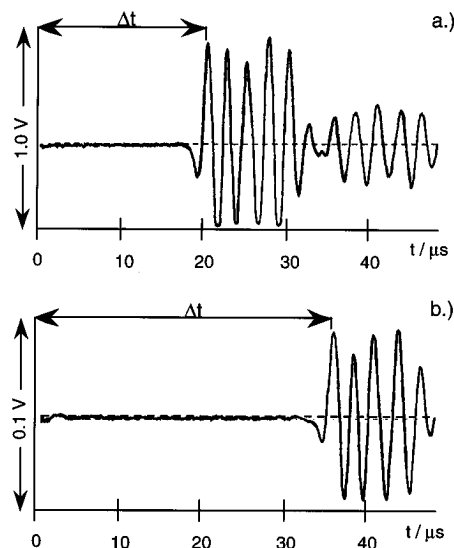
Figure 2. Typical acoustic traces for pure CO_2 recorded in our apparatus: (a) for liquid CO_2; (b) for gaseous CO_2. Note the different ordinate scales in the two traces.

observed, meaning that a liquidlike state with a low compressibility was present in the acoustic cell. The system was allowed to equilibrate for at least 20 min at the desired start temperature. This procedure guaranteed that a homogeneous liquid phase was present prior to any experiment. After equilibration, the pressure was slowly decreased, and for each pressure, the corresponding time delay was measured. The pressure was lowered until a maximum in time delay was observed. This procedure was repeated for different temperatures until the absolute maximum of the time delay was located. R134a (1,1,1,2-tetrafluoroethane, ICI, KLEA Division) had a purity of 99.98%. CO_2 and C_2H_6 were supplied by BOC and had purities greater than 99.9%. All gases were used without further purification.

Safety Warning. *Such experiments involve high pressures and must therefore only be carried out with appropriately rated equipment.*

Results

Pure Components. Acoustic measurements were carried out with pure CO_2, C_2H_6, and R134a to determine whether the equipment produced reliable results. For CO_2, C_2H_6, and R134a several isotherms were measured in the vicinity of the critical temperature. Figure 2 shows the raw data for two different pressures of CO_2, and Figure 3a–c summarizes the acoustic measurements for each substance. It can be seen that, as expected, the time delay increases when the sample approaches its critical point. Table 1 shows that the critical pressure and temperature of these substances measured in our apparatus are in good agreement with the literature data.[16–18]

Binary Mixtures. Differences in composition should lead to differences in the acoustic properties of a mixture. Binary mixtures containing the refrigerant R134a and CO_2 or C_2H_6 were studied in order to investigate the use of R134a as a possible modifier. CO_2 + R134a and C_2H_6 + R134a were measured across the whole mole fraction range. For both systems, eight different isopleths were investigated, so that the critical line of the system could be determined accurately. A representative set of data points for one composition of CO_2 + R134a is shown in Figure 4. Some of the subcritical isotherms show two maxima in time delay (indicated by arrows in the figure), leading to the conclusion that the maximum at high pressure represents a bubble pressure, while the lower maximum pressure represents a dew pressure. Unfortunately, the dew pressure cannot be
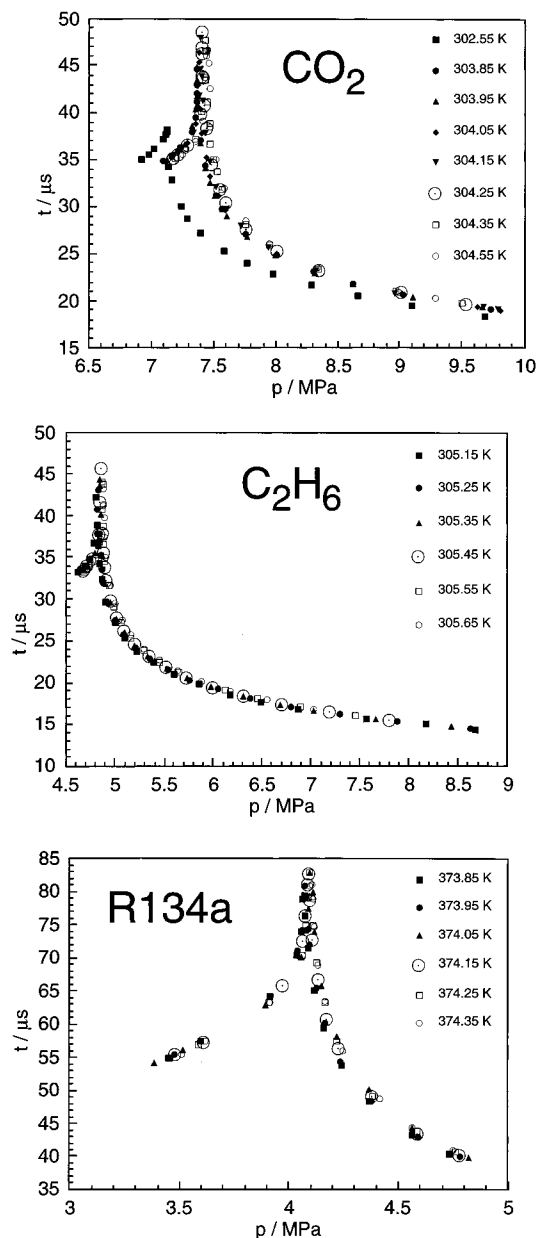

Figure 3. (a, top) Time delay (μs) versus pressure for near-critical isotherms of pure CO_2 in the temperature range 302.55–304.55 K. Subcritical isotherms are marked with filled black symbols, supercritical isotherms with outline symbols, and the critical isotherm with a center-dotted circle. Note that the time delay changes by 30% over a temperature range of only 2 K and by nearly 250% over the pressure range from 7 to 10 MPa. (b, middle) Time delay (μs) versus pressure for near-critical isotherms of pure ethane in the temperature range 305.15–305.65 K. The isotherms are marked in the same way as in (a). (c, bottom) Time delay (μs) versus pressure for near-critical isotherms of pure R134a in the temperature range 373.85–374.35 K. The isotherms are marked in the same way as in (a).

TABLE 1: Critical Parameters for Pure Substances Measured with the Acoustic Cell Shown in Figure 1

substance	T_c/K	$T_c - T_c$(lit.)/ K	p_c/MPa	$p_c - p_c$(lit.)/ MPa
CO_2	304.25 ± 0.1	+0.05[a]	7.41 ± 0.03	+0.03[a]
C_2H_6	305.45 ± 0.1	+0.05[b]	4.85 ± 0.03	−0.02[b]
CF_3CH_2F	374.15 ± 0.1	+0.10[c]	4.08 ± 0.03	+0.02[c]

[a] Reference 17. [b] Reference 18. [c] Reference 19.

measured, when the system is close to its critical point, because the maxima become increasingly shallow and eventually coalesce as T_c is approached.
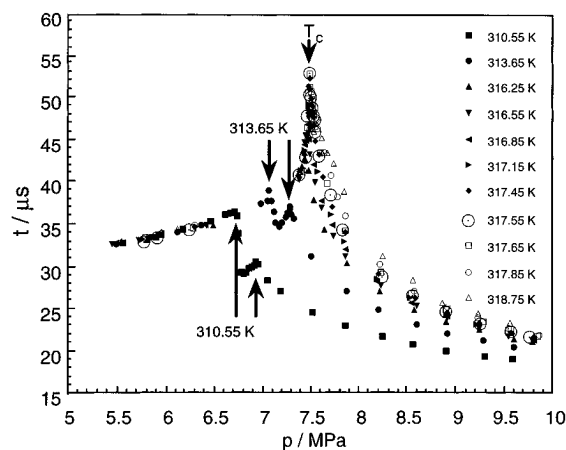
Figure 4. Near-critical isotherms for a mixture of CO_2 + R134a with $x(CO_2) = 0.88$. The arrows indicate the double maxima observed at 310.55 and 313.65 K. Some data points in the vicinity of the maxima were omitted for clarity. The isotherms are marked in the same way as in Figure 3.
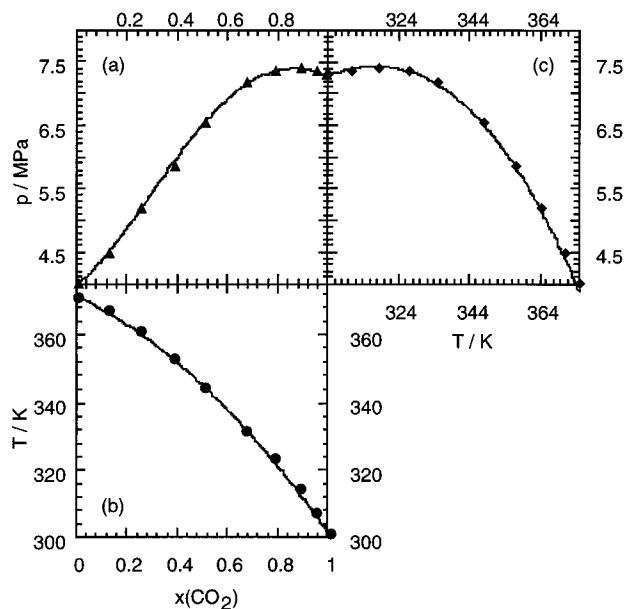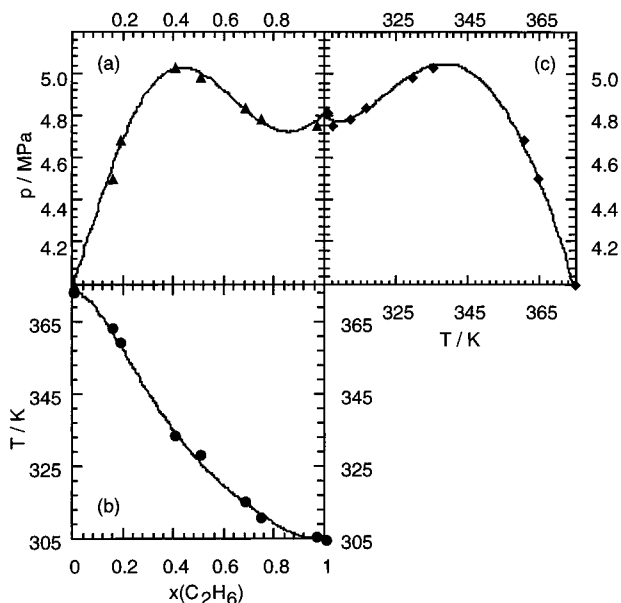

Figure 6. Projections of the critical curve of the system C_2H_6 + R134a.

0.85 (Figure 6a). There is also a pressure *maximum* with $x(C_2H_6) = 0.46$. The T,x projection (Figure 6b) of this system shows negative deviation from ideality. Although alkane—fluorocarbon mixtures usually show liquid—liquid immiscibility due to large excess Gibbs energies,[19] in this system no liquid—liquid immiscibility could be found in the investigated temperature range.

Discussion

Qualitatively, the binary systems CO_2 + R134a and C_2H_6 + R134a display similar behavior over the temperature range which we have investigated; the critical points of both systems are connected by a continuous critical line. Because no liquid—liquid immiscibility was found, we conclude that both systems belong to type I, as classified by van Konynenburg and Scott.[20] In the system containing CO_2, the critical line exhibits a slight pressure maximum at high mole fractions of CO_2, but only marginally higher than p_c of pure CO_2. This suggests that R134a might indeed be a useful modifier for supercritical carbon dioxide. Mixtures with up to 10 mol % of R134a have a similar critical temperature and pressure as pure CO_2, so the mixture can easily be transferred to a homogeneous state, but the solubility properties of the mixture should be enhanced.

By contrast, the critical line for C_2H_6 + R134a exhibits a pressure *minimum* as well as a pressure *maximum*. The minimum pressure of the critical curve is about 0.1 MPa lower than the critical pressure of pure ethane. Alkane + fluorocarbon systems often display a pressure minimum in their critical curve,[19,21] but the appearance of both a pressure maximum and a pressure minimum is unusual. Unfortunately, there are few published reports of critical properties of binary systems containing partially fluorinated alkanes with alkanes. As far as we are aware, no other alkane + fluorocarbon system has been shown to exhibit this behavior. We assume, however, that the pressure minimum occurs because of specific interactions between the two components. R134a is capable of forming hydrogen bonds with itself. The largest nonidealities are to be expected when R134a is dilute and the hydrogen bonds have to be broken. Investigations with vibrational spectroscopy might be able to monitor spectroscopic changes between "bonded" and "nonbonded" refrigerant molecules, but this is beyond the scope of the present study. The system NH_3 + cyclohexane also exhibits a critical curve with a pressure maximum and

Figure 5. Projections of the critical curve of the system CO_2 + R134a.

In the system CO_2 + R134a, the critical line in its p,T projection starts with a slight positive slope, exhibiting a pressure maximum around 318 K. It then descends toward the critical point of R134a; see Figure 5c. Looking at the p,x projection of the critical curve (Figure 5a), the pressure maximum is located around a mole fraction of $x(CO_2) = 0.88$, while the T,x projection (Figure 5b) shows only a slight positive deviation from ideality. No liquid—liquid immiscibility was found above 253 K.

Although C_2H_6 and CO_2 are quite similar in their critical properties, mixtures of alkanes with partially or totally fluorinated alkanes usually show a very different fluid phase behavior from that of mixtures with CO_2. Bubble and dew point data for the binary systems propane or propene with R134a have been reported.[15] Both systems show positive azeotropy, because the vapor pressure curves of these alkanes and R134a are almost identical. Unfortunately, no data for the critical curves were measured. For this reason, we have measured C_2H_6 + R134a. As shown in Figure 6a—c the projections of the critical curve are quite different from those of CO_2 + R134a in Figure 5. The most striking difference is the presence of a pressure *minimum* in the p,T projection (Figure 6c) at temperatures around 310 K, corresponding to the mole fraction $x(C_2H_6) =$

minimum.[22] Like R134a, NH_3 is capable of forming strong hydrogen bonds, but in contrast to our system the pressure minimum occurs at high mole fractions of ammonia. Additionally, measurements of excess properties, especially excess volumes, for this system would clearly be most valuable. No liquid−liquid immiscibility was found in our experiments, although this might be obscured by crystallization of the mixture, as has been reported[23] for the system $C_2H_6 + C_2F_6$.

Conclusions

We have shown that our simple acoustic equipment can be used to determine liquid−vapor equilibrium data for binary systems as well as pure components. The deviations between the literature data and the measured data for the pure components are within the experimental error of our equipment. Future investigations will include mixtures containing permanent gases and also ternary or quaternary mixtures. The acoustic method is a reliable and fast method for the determination of fluid phase equilibria, independent of the nature of the fluid. It has wide applicability and provides an objective method for obtaining data points, making it advantageous to optical techniques.

Ideally, a modifier should not change the critical pressure and temperature of the extraction solvent but should change its solvent charateristics. The p,x projections of the critical curves for both $CO_2 + R134a$ and $C_2H_6 + R134a$ show that R134a is likely to be an effective modifier. R134a changes the critical parameters in both systems only marginally. With mole fractions of up to 10%, only a slight increase in the critical pressure is observed. Indeed, there is even a modest *decrease* of the critical pressure in $C_2H_6 + R134a$, while in both systems the critical temperatures rise only a few kelvin above those of the pure CO_2 or C_2H_6. Bearing in mind that pure R134a is a good solvent for polar components, we conclude that R134a shows promise as a modifier for CO_2 or C_2H_6 in supercritical extractions.

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