Supercritical Fluids

Sensing the Critical Point of High-Pressure Mixtures[**]

Jie Ke, Robert M. Oag, P. J. King, Michael W. George, and Martyn Poliakoff**

Supercritical fluids are becoming increasingly attractive as solvents for chemical reactions and processes.[1–3] This development is creating a greater need for critical-point data for the multicomponent mixtures used in these applications. Critical-point data are important for the rigorous testing of computer models of the vapour–liquid equilibria, which are required to realize these chemical processes in practice. Surprisingly, most of the techniques available for locating critical points have hardly changed for more than a century and are time-consuming and often subjective.[4] Herein we describe a completely new approach, which is far more objective. Our strategy is to use a single, simple sensor in an unusual manner so as to distinguish between the dew point

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[*] Dr. J. Ke, Prof. M. W. George, Prof. M. Poliakoff
School of Chemistry
University of Nottingham
University Park, Nottingham NG7 2RD (UK)
Fax: (+44) 115-951-3058
E-mail: pcxjk2@unix.ccc.nottingham.ac.uk
martyn.poliakoff@nottingham.ac.uk

Dr. R. M. Oag, Dr. P. J. King
School of Physics and Astronomy
University of Nottingham
University Park, Nottingham NG7 2RD (UK)

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and bubble point curves of the mixture and hence to locate the point at which the two curves meet, the critical point.

In principle, the critical point of any pure, single-component substance can be found by simply observing the fluid as it is heated in a closed cell fitted with suitably pressure-resistant windows. The critical temperature and pressure, T_c and P_c, are the maximum values, for which gas and liquid can coexist. The problem becomes inherently more complicated with binary or multicomponent mixtures since additional components introduce extra degrees of freedom into the phase diagram. In particular, the critical point becomes just one of many points along the phase boundary and neither T_c nor P_c is necessarily the maximum value for coexistence. The critical point is now defined as the point at which all intensive properties are identical for the two coalescing phases; in particular the composition and density are the same for both phases. The critical point can therefore be recognized by the disappearance of the meniscus exactly halfway up the view cell when a liquid mixture is heated under a fixed volume. However, in practice, judging this condition is fraught with uncertainty. Our method relies on an alternative property of the critical point, namely, that it occurs at the intersection of the bubble point and dew point curves of the mixture.

Trying to monitor phase separation with a single sensor might seem to be a fruitless exercise because sensors tend to measure average properties of the phases. However we have overcome this problem by using a sensor that only responds to a density-dependent property of the fluid layer in immediate contact with the surface of the sensor. Hence, it gives substantially different signals for liquids and gases. The sensor is mounted near the bottom of a variable-volume cell fitted with a powerful stirrer.[5] Unlike traditional apparatus for phase measurements, there is no need for any window through which to observe the fluid.

Our method is based on the so-called "synthetic" approach in which one finds the temperature and pressure of the phase transition of a mixture of fixed composition in a sealed vessel. The experiment normally begins with the cell at high pressure and low volume, conditions under which the fluid mixture is in a single homogeneous phase. The volume of the cell is increased, the pressure drops and the density decreases smoothly until phase separation occurs. This separation registers as a discontinuity in the signal from the sensor. The key to our method is that this discontinuity is qualitatively different in form on the bubble and dew point curves of the fluid.

On the bubble point curve, phase separation involves the nucleation of small bubbles, which rise to the top of the cell, far removed from the sensor. Therefore, the sensor registers a modest increase in the density in the bulk of the fluid, Figure 1 a. In contrast, on the dew point curve, a thin film of liquid is formed on the walls of the cell and the surface of the sensor. This liquid is continually thrown around by the stirrer so that a liquid film is maintained on the surface of the sensor, which registers a sudden jump ($\Delta|Z|_{\min}$) from gas-like to liquid-like densities, Figure 1 b. The further the system is from the critical point, the greater the difference in density between the gas and liquid densities and the greater the jump. The procedure is repeated at a series of different temperatures and the critical point is located by extrapolating to the temperature at which $\Delta|Z|_{\min}$ tends zero.

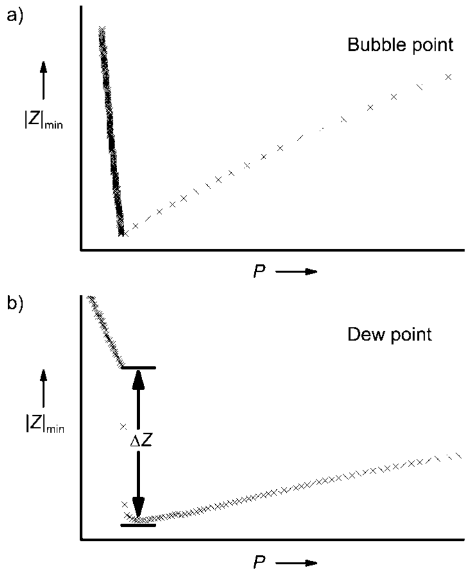

Figure 1. Shear-mode sensor responses ($|Z|_{\min}$) as a function of pressure along two isotherms showing the difference in the discontinuity caused by phase transitions on a) the bubble point and b) the dew point. In b) a new liquid phase appears from the gas phase after the phase separation, which results in a sudden jump ($\Delta|Z|_{\min}$) that is related to the difference in density between the two coexisting phases.

We have used two different types of sensor to validate this method. The first is a quartz "shear-mode" sensor,[6] which is set up to register its equivalent resistance, $|Z|_{\min}$, an indication of the acoustic coupling between the sensor and the fluid. $|Z|_{\min}$ is proportional to "γ", the square root of the product of density and viscosity of the fluid. The sensor gives a high value of $|Z|_{\min}$ in a liquid-like environment and a low value in a gas-like fluid. Similar sensors are used in quartz microbalances for monitoring volatile organic compounds[7] and as shear-mode sensors for chiral discrimination.[8] The second sensor is a fiber-optic reflectometer,[9] in which U, the ratio of the intensity of the light entering the fiber to that back-reflected by the end of the fiber, depends on the difference in the refractive index between the fiber and the fluid, and hence on the density of the fluid. Its response is the inverse of that of the shear-mode sensor, high for gas and low for liquid-like densities. For the first study, CO_2 + MeOH, both sensors were mounted simultaneously in the same cell.

CO_2 + MeOH is an extremely well studied mixture,[10–14] particularly because of the widespread use of MeOH as a cosolvent to enhance the rather low solvent power of pure CO_2. Even so, there are considerable differences in the value of T_c reported by different studies on mixtures of apparently similar composition.[10–14] Figures 2 a and b show the traces recorded from the two sensors over the section of the phase boundary, which includes the critical point. As expected, for each temperature the two sensors agree within experimental error on the pressure at which phase separation occurs and the data agree well with literature values.[11] The traces recorded by both sensors at higher temperatures display the

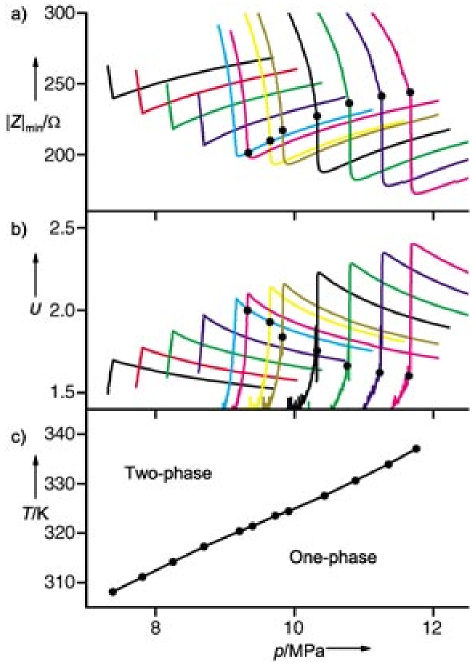

Figure 2. The binary mixture of MeOH + CO_2 with $x_{MeOH} = 0.139$. a) Plot of the shear-mode sensor response ($|Z|_{min}$) to pressure along 12 isotherms, with temperature increasing from left to right. The minimum on each isotherm indicates the phase transition. For those isotherms on the right-hand side, a "jump" can be seen after the phase transition, as indicated by (●). b) Optic-fiber reflectometer response measured simultaneously with the data shown in a). The signal U is normalized with respect to the response in air. The *maximum* on each of these isotherms indicates the phase transition, and the sudden decreases in U are marked as (●). c) The P–T phase boundary (●, indicates measured points); note that there is no obvious indication of precisely where the critical point is located on this featureless curve.

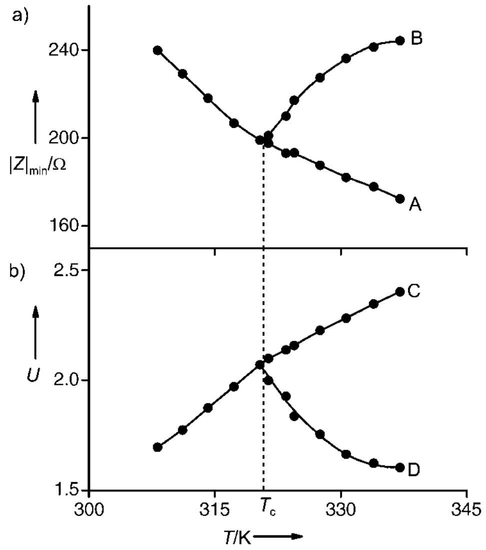

Figure 3. Locating the critical temperature (T_c) by using a) the shear-mode sensor, and b) the optic fiber sensor. Curves A and C correspond the phase-transition curves, and Curves B and D are the sensor responses from the new liquid phase after the phase transition, marked as (●) in Figure 2a, b, respectively. Curve A was fitted with a cubic spline and B was fit with a cubic polynomial; the point at which the curves A and B intersect is the critical point. Similar treatments were made on curves C and D in Figure 3b. The dashed line indicates the critical temperature.

characteristic "jump" indicative of the dew point curve (Figure 2). The optic fiber sensor, which has an extremely small active area compared to the shear-mode sensor, sometimes gave a "noisier" signal at the dew point because of the comparable dimension of the fiber tip and the liquid droplets. Extrapolation of these jumps back to the phase boundary locates the critical temperature, T_c, of the mixture. Figure 3 shows that the two sensors yield very similar values of T_c, 320.9 ± 0.2 K (shear-mode) and 320.8 ± 0.3 K (optic fiber). The critical pressure, P_c, (9.30 MPa and 9.29 MPa respectively) can be found from the phase boundary in Figure 2c. In this way, the critical point can be identified in a relatively objective manner on a phase boundary that is essentially featureless.

The second mixture $N_2(0.14) + CO_2(0.86)$ is of great historical interest. It was studied by Thomas Andrews[15] in 1871–2, the first binary gas mixture ever to be studied in this way. His experiments involved compressing the mixture with a mercury "piston" in a vertical glass capillary tube sealed at the upper end. Andrews was concerned that the mixture might not be properly mixed in the narrow tube and he was unable to explain the mysterious evaporation of liquid on increasing the pressure. This was subsequently recognized as retrograde condensation.[15] Therefore, until 2003, Andrews's work remained unpublished[15] and, surprisingly, no one had studied this mixture in the intervening 132 years.[16–19]

Figure 4 shows the results of studying Andrews's mixture with the shear-mode sensor. The traces look more complicated than for CO_2 + MeOH because of the curvature of the phase boundary. Figure 4b compares the experimental T,P phase envelope with the line derived from Andrews's notebook.[15] Excitingly, this shows that Andrews's value of the maximum temperature of the phase envelope 21 °C (294 K), is extremely close to our measured value, 293.6 ± 0.2 K, although the true error could be marginally greater because the composition of our mixture and Andrews's might be slightly different. Interestingly, we also agree on the temperature at which the maximum pressure is observed, 282 K, but the maximum pressure itself, 9.8 MPa, is about 1.0 MPa lower than estimated[15] from his results.

Just as with CO_2 + MeOH, the sensor registers a jump at the points along the dew-point curve. However, the curvature of the lines, shown in Figure 5a makes locating the intersection of the curves less certain than in Figure 3a. Therefore, we have tried a different approach by finding the temperature at which $\Delta|Z|_{min}$ extrapolates to zero (Figure 5b). $\Delta|Z|_{min}$ is defined as the difference in $|Z|_{min}$ between liquid and gas at the dew point. This gives 290.9 ± 0.2 K for T_c and 9.42 MPa for P_c. Thus, T_c is 2.7 K lower than the maximum temperature, thereby explaining why Andrews could not understand the nature of the effect, which he observed over a narrow temperature range close to T_{max}. This contrasts with the predictions of the Peng–Robinson equation of state (EOS), one of the most common EOS for supercritical mixtures, which predicts 293.4 K for T_c only 0.2 K below T_{max}. By a

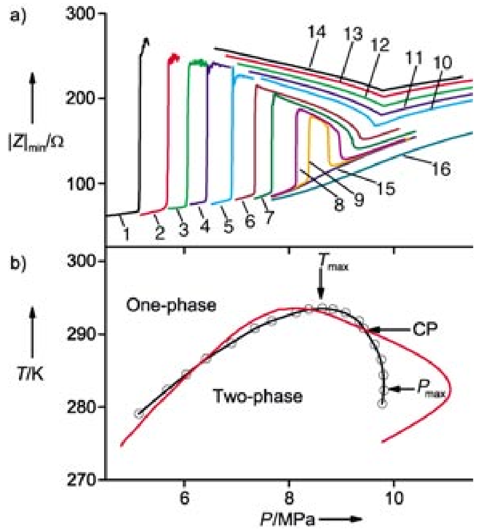

Figure 4. The binary mixture of N_2 and CO_2 with $x_{N2} = 0.14$, the same composition[15] as used by Andrews in 1871–72. a) Plot of the variation of $|Z|_{min}$ with pressure at various temperatures in the critical region. Isotherms 1–9 (279.1–293.4 K) display a dew point "jump" in $|Z|_{min}$ after the phase transition; some isotherms (e.g., 9) have two jumps for a given temperature, thus indicating that there are two dew points along that isotherm, at which the retrograde condensation occurs. Isotherms 10–14 (280.5–288.6 K) show the "tick-shape" discontinuity characteristic the bubble-point on the phase boundary. Isotherms 15–16 (293.9 K and 297.0 K, respectively) have no discontinuities because they are above the maximum temperature of two-phase coexisting region. b) The points (○) indicate the experimental P–T phase boundary derived from a), together with the phase boundary (——) deduced from Andrews's notebook;[15] CP indicates the critical point.

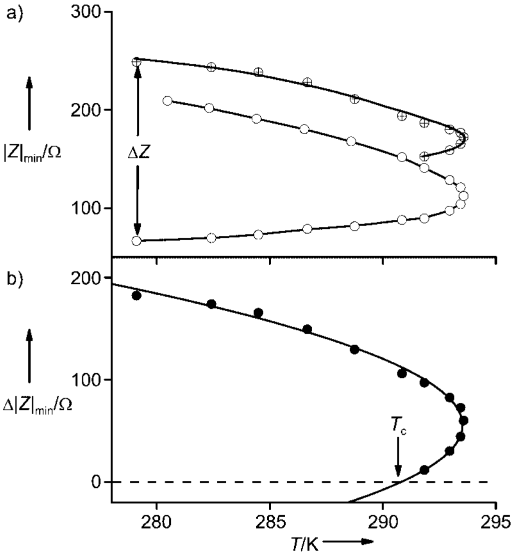

Figure 5. a) $|Z|_{min}$,T projection: (○) from bulk phase at the phase boundary (⊕) from the new liquid phase after the phase separation. b) $\Delta|Z|_{min}$–T curve. This curve was fitted with a cubic polynomial and extrapolated to $\Delta|Z|_{min} = 0$ to find T_c. At the dew point, $\Delta|Z|_{min}$ represents the difference in $|Z|_{min}$ between liquid and gas which is indicated by the arrows in a).

strange quirk of fate, Figure 4b shows that Andrews's phase boundary and ours intersect almost exactly at the critical point!

We have described a new, general and objective approach to locating critical points of fluid mixtures. It is new because it exploits the fact that the liquid phase forms preferentially on the surface of the sensor. It is general because it can be used with any type of surface-sensitive sensor and it is objective because it is based on the numerical output of a sensor rather than the visual image normally used for phase equilibrium studies.

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