

Three-Phase Critical Point in Hydrocarbon-Water Systems

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The pressure and temperature of the three-phase critical point have been determined from visual observations on 16 binary systems of water and a hydrocarbon—nine aliphatics, four naphthenics, and three aromatics. Both the temperature and (above four carbon atoms) the pressure of this critical point increase with molecular weight in a homologous series of hydrocarbons.

WHEN water and hexane were heated together under pressure, Scheffer (9) noted a three-phase critical point—a temperature and a pressure at which the vapor phase and the less dense liquid phase assumed identical properties. Data on the three-phase critical point have been reported for a few additional hydrocarbon-water systems (4, 6–8, 10).

In a one-component system the vapor-liquid critical state (at which vapor and liquid become identical) is a fixed, nonvariant point. Similarly, in a two-component system the vapor-liquid₁-liquid₂ critical state (at which vapor and liquid₁ become identical) is a fixed, nonvariant point. Application of the phase rule, as modified by Bowen (1),

$$F = C - P + 2 - R - r \quad (1)$$

shows this critical state to have zero degrees of freedom:

$$F = 2 - 3 + 2 - 0 - 1 = 0$$

In these hydrocarbon-water systems there is also a critical state at which vapor and the single liquid phase become identical. However, here there is one degree of freedom; there is a critical locus, with the critical pressure and the critical temperature dependent on the composition of the mixture. Data on this critical state of some hydrocarbon-water systems have been published (2, 6, 11).

EXPERIMENTAL

Apparatus. The hydrocarbon-water mixtures were confined over mercury in a vertical capillary of Corning Vycor glass (nominal 7- to 8-mm. o.d. and 1½- to 2½-mm. bore). A 15-inch length of this capillary was sealed off at the top, and connected at the bottom to a mercury pump and a pressure gage. The upper two thirds of the capillary was enclosed in an aluminum block furnace, shown in horizontal cross section in Figure 1. Four electrical heaters embedded in the block were fed by an auto-transformer to permit temperature changes. Air could be drawn through the eight air ducts for cooling the block.

Two opposed vertical slots, 4 inches long, through a portion of the furnace and its encompassing insulation permitted visual observation of the uppermost one third of the capillary. At right angles to the viewing slot were two chambers enclosing small magnets which could be moved vertically to lift a 1/16-inch magnetic stainless steel ball for agitation of the fluids.

The wall of the glass capillary was thickened at its lower end and ground to fit against a conical thrust washer of annealed copper in a pressure gland. Only glass, mercury, and stainless steel were in contact with the fluids at elevated temperature.

Pressures were estimated to the nearest even number of pounds per square inch on a Heise Bourdon gage which

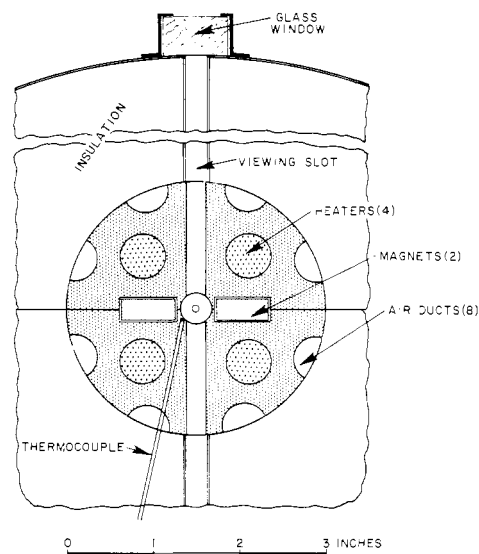


Figure 1. Horizontal section through furnace unit

had been calibrated against an Aminco dead-weight gage. Temperature was recorded continuously in terms of the e.m.f. generated by an iron-constantan thermocouple placed almost in contact with the capillary. Because of heat losses by convection through the sight slots and through imperfect contact of the two halves of the furnace, the effective temperature within the capillary was not that indicated by the thermocouple. Corrections were determined at three points by observing the critical temperature for three pure substances—butane, heptane, and benzene. An essentially linear relationship was found between the correction and the observed temperature, from a correction of -3° at 300° to -9° at 550° F.

Operation. The capillary unit was charged in an inverted position. The higher boiling of the two components was introduced (to a depth of ½ to ¾ inch) and degassed by cycles of successive freezing, evacuation, and thawing. Then the lower boiling constituent was added and the degassing cycle repeated. Degassing in a capillary tubing is not particularly efficient, but the alternative of distilling any except the most volatile constituents into the evacuated capillary was not practical at the pressures obtainable with the simple vacuum system available for this work. The possible presence of small amounts of residual air was perhaps the major limitation in the accuracy of these measurements of critical properties. While the capillary unit was still in the inverted position and the charge frozen, mercury was introduced. Then the unit was turned to its upright position and the charge thawed.

The temperature of the furnace was brought up rapidly for an initial rough determination of the critical point; manual adjustments of the autotransformer then caused the temperature to cycle slowly across the critical temperature. Several such temperature cycles were made to obtain a value of both critical temperature and critical pressure. The steel ball was moved slowly up and down in the capillary as an aid in achieving equilibrium compositions and detecting changes in the interface as the critical point was approached. The disappearance of the interface into an opalescent hazy zone was chosen as the critical state.

Materials. Freshly boiled distilled water was used. Sources of the hydrocarbons are given in Table I.

RESULTS

Observations on three-phase critical points are summarized in Table I and Figure 2. Values given are averages of several heating-cooling cycles for a mixture. The rising- and falling-temperature values generally differed by about 1° F. and the pressure by about 2 p.s.i. As shown in Table I, two separate fillings of the capillary usually gave values of temperature agreeing within 1° and pressure within a few pounds per square inch.

Contamination by air affected the three-phase critical point. At one time three consecutive runs gave critical pressures which were evidently too high. An unexpected source of air leakage was found and eliminated; then repeat runs gave pressures from 80 to 150 pounds per square inch lower and temperatures averaging about 1° higher than in the suspected runs.

Included in Figure 2 is a curve for the vapor pressure of water as a function of temperature. Other solid curves connect the critical points for homologs of the different types of hydrocarbons. The dashed lines serve merely to

guide the eye in connecting the critical point of hydrocarbon with the three-phase critical point of the same hydrocarbon when mixed with water.

In some cases included in this study the hydrocarbon-rich liquid is iso-optic with—i.e., has the same refractive index as—the water-rich liquid at elevated temperatures and pressures. When the equilibrated liquid phases have the same refractive index, the interface is difficult to detect visually, especially if the two liquids have about the same dispersion of refractive index with wavelength. Some erroneous reports of miscibility have entered the literature through misinterpretation of iso-optics (3). Except for an exploratory survey of the *n*-heptane-water system, no observations were recorded on iso-optics. In the heptane-water system the pressure at which the two liquid phases were iso-optic was essentially a linear function of temperature from 500 p.s.i. at 350° F., to 2300 p.s.i. at 460° F.

DISCUSSION

Scheffer (9) reported in 1913 that when hexane and water are heated together under pressure there is a three-phase critical point, at which temperature and pressure the vapor phase and the less dense liquid phase assume identical properties. He gave quantitative data on the hexane-water system and, later, on the benzene-water system (10) as well as a mixed pentanes-water system. Other workers have presented quantitative data on compositions of coexistent phases in benzene-water (7), cyclohexane-water (6), propane-water (4), and *n*-butane-water (8), which data include the three-phase critical point. The latter two studies were made in a blind cell.

Our observed three-phase critical point for *n*-butane-water differs considerably from the published value. We agree more closely with published values for the propane-, *n*-hexane-, benzene-, and cyclohexane-water systems.

Table I. Critical Points in Hydrocarbon and Hydrocarbon-Water Systems

Hydrocarbon ^a	Critical Points			
	Hydrocarbon (Two-Phase) (5)		Hydrocarbon-Water (Three-Phase) ^b	
	Temp., ° F.	Pressure, p.s.i.a.	Temp., ° F.	Pressure, p.s.i.a.
Propane ^c	206.01	616.3	(205.7) (4) 206 206	(637) (4) 628 626
Butane ^d	305.62	550.7	(305) (8) 302 301	(637.5) (8) 612 612
<i>n</i> -Pentane	385.7	488.6	375	658
<i>n</i> -Hexane	453.6	436.9	(431.7) (9) 437 434	(764.9) (9) 768 768
<i>n</i> -Heptane	512.6	396.8	474 475	916 912
<i>n</i> -Octane	564.10	360.6	513	1074
<i>n</i> -Nonane	610.5	335	540	1240
<i>n</i> -Decane	651.7	304.5	565	1396
2,2-Dimethylbutane	420.04	446.8	410	692
Cyclopentane	461.3	653.8	439	986
Methylcyclopentane	499.24	548.9	473	1028
Cyclohexane	536.5	591	(492) (6) 494	(1163) (6) 1166
Methylcyclohexane	570.15	503.5	520	1208
Benzene ^e	552.09	710.4	(514) (10) (515) (7) 517	(1362) (10) (1364) (7) 1372
Toluene ^f	605.43	595.9	545	1464
Ethylbenzene	651.09	523.5	574 574	1624 1630

^a Unless otherwise indicated, all hydrocarbons were Phillips pure grade (99%). ^b Data in parentheses are from literature; all others from this investigation. ^c Phillips research grade (99.99%). ^d Phillips instrument grade (99.5%). ^e Baker's analyzed.

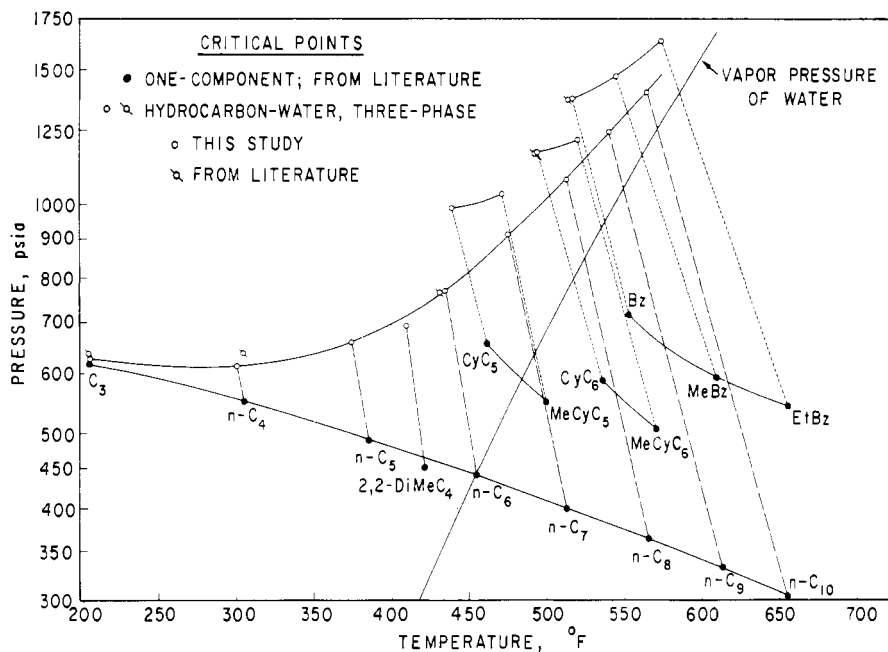


Figure 2. Critical points

[Since Scheffer's pentane was stated (10) to be a mixture of *n*- and isopentane, no comparison can be made with our result on *n*-pentane.] Our lower value for the *n*-butane-water point appears to be more consistent on a pressure-*vs.*-temperature plot of all data (Figure 2) than the previously reported value for this system.

Scheffer (9) noticed that the total pressure in the system at the three-phase critical point was considerably greater (approximately 48 p.s.i.) than the sum of the vapor pressure of water and of hexane at that temperature. He commented on this unexpected result and subsequently showed the same phenomenon to exist in systems involving benzene or mixed pentanes with water.

In each of our experiments the confining mercury was at the same temperature as the other fluids. At the highest temperature (575° F.) the vapor pressure of mercury is nearly 5 p.s.i. Although we do not know how the presence of mercury affects the three-phase critical point, we suspect that it may have an effect similar to that of air, small amounts of which increase the critical pressure without greatly affecting the critical temperature. However, the good agreement of these values with those from the literature for the three-phase critical points of hexane-water, benzene-water, and cyclohexane-water systems indicates that the errors in these measurements are not large.

NOMENCLATURE

- C* = number of chemical compounds in system
- F* = number of degrees of freedom
- P* = number of phases
- R* = number of reversible chemical reactions occurring
- r* = number of pairs of phases having same concentration

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CORRECTION

In the article "Thermodynamic Functions of 1,2-*trans*-Difluorodiazine" by Emile Ruther [*J. CHEM. ENG. DATA* **7**, 398 (1962)], the following corrections should be noted. A correction of -0.32 should be applied to all data in the column presently headed by S^0/R . For example, the value at 100° K. which is shown as 22.11 should read 21.79. All other values from 100° to 6000° K. should correspondingly be reduced. The column headings S^0/R and $-(F^0 - E^0)/RT$ should be transposed.