

Solubility of Hydrocarbons in Water Near the Critical Solution Temperatures

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Solubilities were measured for five binary hydrocarbon-water systems up to their critical solution temperatures and from 100 to 800 atm. Sharp maxima and double branches were observed in the solubility isotherms near the critical solution temperatures.

ALTHOUGH much has been published on hydrocarbon-water solubilities, there are no high temperature measurements above 200 atm. Therefore, five binary hydrocarbon-water systems were studied from about 50° C. below to a few degrees above the critical solution temperature (CST), at pressures to 800 atm. The hydrocarbons were: benzene, *n*-heptane, *n*-pentane, 2-methyl pentane, and toluene.

For each system, the solubility *vs.* pressure curve shows a sharp maximum near the critical solution temperature at about 300 atm. Beyond this maximum, pressure has a negative effect on solubility, and a second two-phase region appears at high pressures.

APPARATUS

The hydrocarbons were Phillips reagent grade with purities stated to be better than 99.8%. These purities were checked by gas chromatography. The water was distilled and deaerated.

The apparatus operates on the same principle as the familiar glass cloud-point tube in which a sample of known composition is sealed off and solubilities are determined from cloud-point temperatures. It differs in detail from the cloud-point tube in that pressures up to 800 atm. are possible, the pressure may be measured, and the composition may be varied easily.

Figure 1 is a schematic diagram of the solubility cell. This 100-cc. stainless-steel vessel has three injection points, one each for mercury, water, and hydrocarbon. Mixing is accomplished by a magnetically driven 1-inch steel ball. A light transmitted through a prism and window arrangement permits a view of the topmost portion of the cell interior. The windows are sealed against aluminum gaskets by an initial pressure of 800 atm. This seal is apt to break if the pressure is subsequently lowered below 100 atm.

The cell is thermostated in a salt bath, and temperature is measured and controlled with platinum resistance thermometers. Pressure is measured with Heise bourdon tube gages which were calibrated against a dead-weight gage. The hydrocarbon and water injected into the cell are displaced from thermostated reservoirs by mercury from Ruska pumps.

PROCEDURE

For a series of solubility determinations, the cell is evacuated, loaded with 15 grams of water, and brought to temperature. Mixing is started, and hydrocarbon is injected, until either a cloud or a small portion of a second phase appears at the top of the cell. Then mercury is injected to change the pressure and more hydrocarbon is injected, etc. Only the solubilities of hydrocarbons in water can be determined in this manner, because in the reverse case, the water-rich second phase will appear at the bottom of the cell, where it cannot be observed.

Occasional mercury leaks are inevitable with this apparatus, and while the salt bath is not permanently contaminated by any reasonably small leak, the mercury-vapor level in the air can temporarily reach very high levels. An instantaneous mercury-vapor detector is, therefore, a necessity.

ACCURACY OF RESULTS

The error in these determinations was the cumulative result of errors in temperature, pressure, and composition.

The total error in temperature probably did not exceed 0.02° C., because the liquid salt thermostat can be controlled to 0.01° C. and differences from point to point in the bath were less than 0.01° C.

Pressure was controlled to 0.5 atm., and it was measured with an accuracy of about 2 atm. Pressure errors were no more important than temperature errors except in the region where the isotherms split into two branches.

The greatest uncertainty was in determining the composition of the contents of the cell. Here, there were errors in the

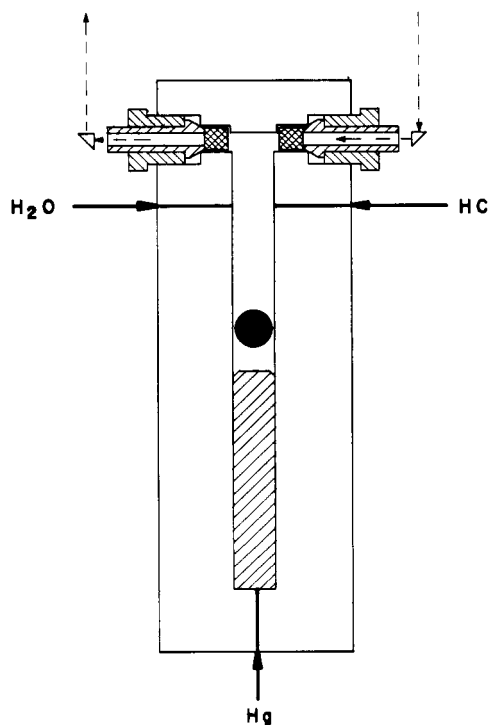


Figure 1. Solubility cell

quantities of hydrocarbon and water injected into the cell, errors in the detection of two phases, and errors due to decomposition and leaks.

The hydrocarbon-water injection system was thermostated except for the narrow transfer lines (0.2 mm. I.D.). Because injection was directly into the interior of the cell, there was no unmixed dead space portion other than the volume held up in

the line between the close-off valve and the interior of the cell (0.05 cc.). Thus, the total injection error should be less than 0.02 gram.

The existence of two phases was indicated either by the appearance of a cloud or, more usually, by the appearance of a small portion of a second phase. Formation of about 0.05 cc. of the second phase was necessary for positive identification. In

Table I. Solubilities of Hydrocarbons in Water

Temp., ° C.	Pres- sure, Atm.	Wt. % Hydro- carbon	Temp., ° C.	Pres- sure, Atm.	Wt. % Hydro- carbon	Temp., ° C.	Pres- sure, Atm.	Wt. % Hydro- carbon	Temp., ° C.	Pres- sure, Atm.	Wt. % Hydro- carbon
Benzene											
260	100	7.1	287.5	735	13.9	295	450	22.9	300	470	49.5
	250	7.3		295	135		18.2	690		18.2	470
	500	7.2		160	22.8		300	145		22.8	470
281	800	6.6		185	27.0		155	27.3		470	40.0
	150	13.7		210	31.3		160	30.9		480	37.5
	250	13.8		225	34.0		160	34.3		490	34.3
287.5	500	13.3		230	35.3		165	37.5		505	31.0
	600	12.7		240	35.5		165	40.0		555	27.3
	165	17.2		250	35.3		160	43.0		665	22.9
	195	18.1		265	34.0		160	46.1			
	320	18.1		290	31.3		490	56.0			
	380	17.3		350	27.0		480	52.5			
<i>n</i> -Heptane											
295	170	1.1 ^a	350	195	3.7	355	230	10.3	355	300	24.8
	250	1.1		210	5.7		240	13.5		305	19.5
	500	1.1		260	9.6		250	19.5		345	13.5
	700	1.1		280	10.0		245	24.7		390	10.3
330	200	3.3		310	9.6		320	41.7			
	300	3.3		370	8.1		310	35.1			
	500	3.3		550	5.7		300	29.3			
<i>n</i> -Pentane											
300	150	1.3 ^a	340	230	5.2	350	325	15.5	352	385	36.5
	185	1.7		250	6.1		350	15.5		380	34.0
	350	1.7		275	6.9		395	13.9		375	31.4
	600	1.6		330	7.6		445	12.0		375	28.5
	700	1.5		350	7.6		510	10.3		375	25.4
330	170	2.1		470	6.9		590	9.0		375	23.3
	195	3.3		620	5.7	352	280	15.8		380	21.0
	220	4.0	350	240	7.8		280	18.4	390	18.4	
	260	4.6		255	9.0		280	21.0	420	15.7	
	350	4.9		265	10.3		280	23.3			
	485	4.7		280	12.1		400	40.7			
	670	4.0		300	13.9		390	38.7			
2-Methyl Pentane											
300	140	1.1 ^a	330	500	3.7	350	275	11.6	355	385	37.4
	275	1.3		210	4.5		290	12.5		380	35.1
	475	1.3		235	5.4		310	12.8		380	32.8
	700	1.3		265	6.3		335	12.5		380	30.2
330	160	1.8		300	6.9		365	11.6		380	27.4
	185	2.7		370	6.4		405	10.5		380	24.3
	215	3.9		485	5.3	355	245	13.0		385	21.0
	245	4.0	350	230	7.1		245	14.9	395	17.3	
	300	4.2		240	8.2		250	17.4			
410	4.1	260		10.4	250		21.0				
Toluene											
280	150	6.8	305	200	19.5	310	180	33.1	310	260	33.1
	250	6.8		250	19.0		180	36.3		275	29.6
	410	6.6		285	18.0		270	50.5		295	26.7
300	600	5.8	310	145	18.0		265	48.6		325	23.8
	170	14.2		150	19.6	260	46.5	405	19.5		
	250	14.1		155	21.7	260	44.3	455	18.0		
	300	14.0		165	23.9	260	41.9				
305	160	18.0		170	26.7		260	39.2			
	180	19.0		175	29.6		260	36.3			

^a Because the absolute uncertainties of the low solubilities are nearly as great as those of the high solubilities, the relative error in the low solubility region is very large.

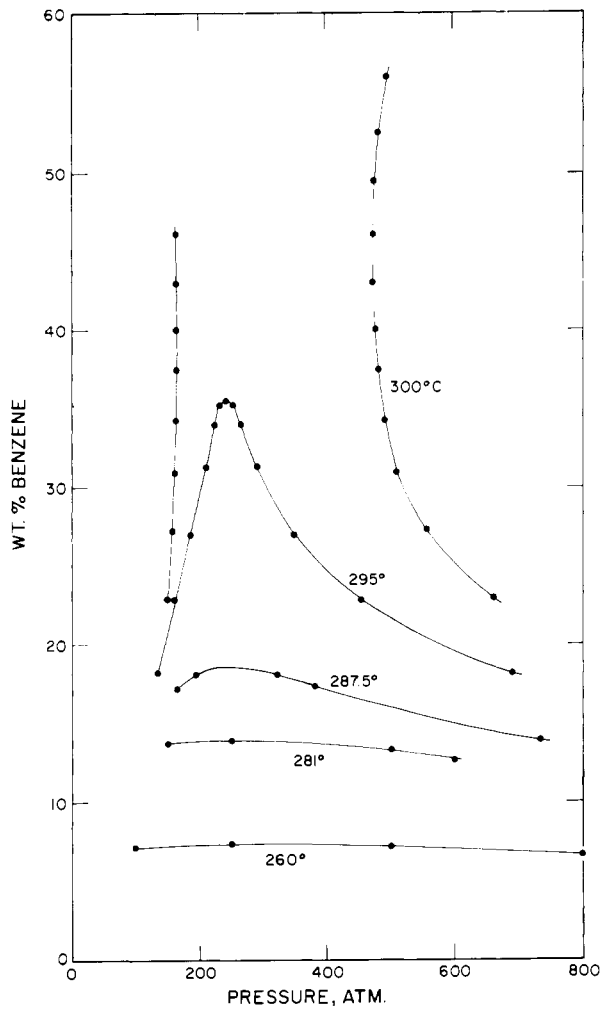


Figure 2. Solubility of benzene in water

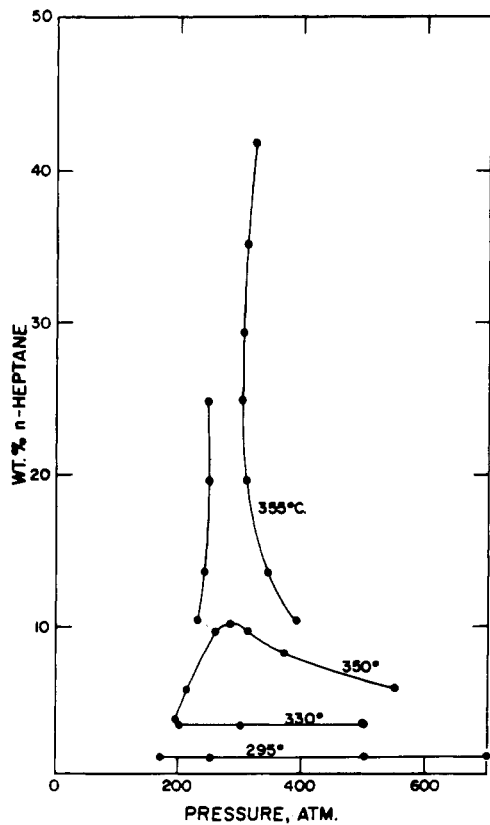


Figure 3. Solubility of *n*-heptane in water

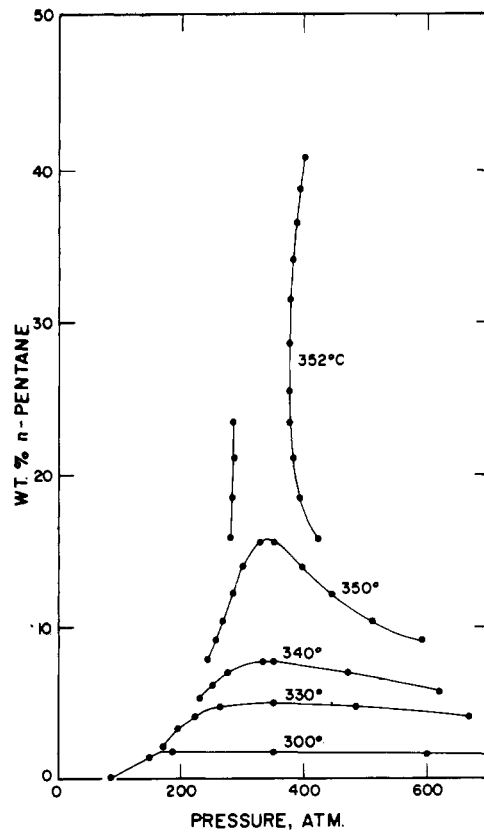


Figure 4. Solubility of *n*-pentane in water

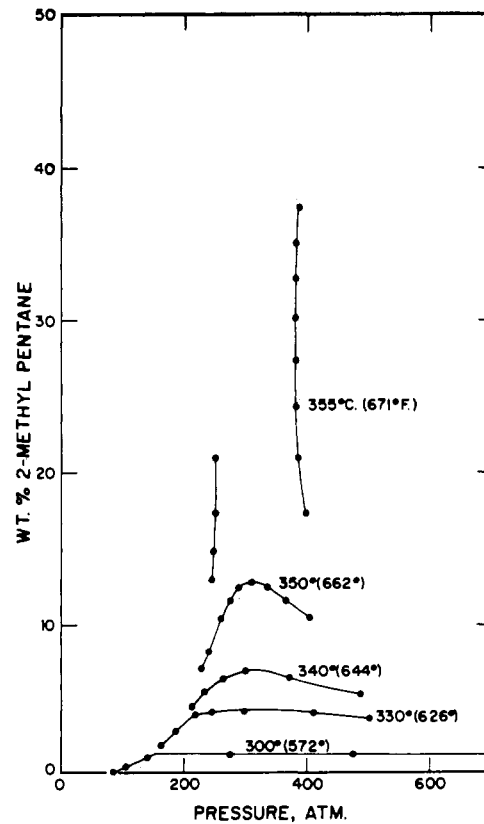


Figure 5. Solubility of 2-methyl pentane in water

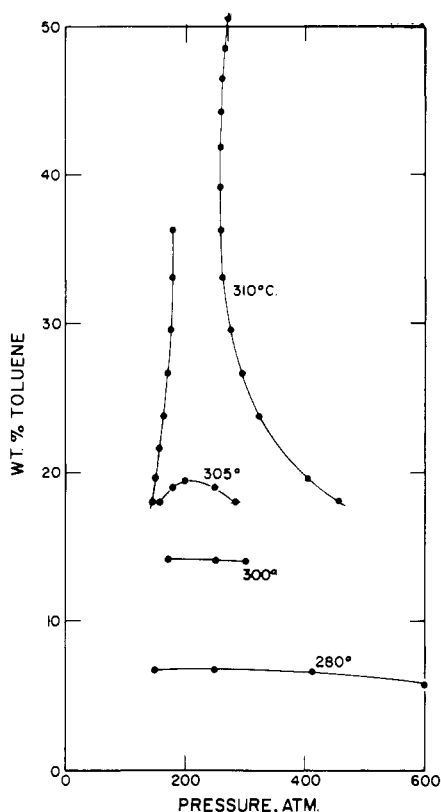


Figure 6. Solubility of toluene in water

addition, the geometry of the cell was such that 0.03 cc. of volume was above the view-port. Approximate corrections were made for these effects.

Decomposition was not a problem with benzene and toluene. However, some of the paraffins did decompose at the highest temperatures—e.g., at the end of a 48-hour series of measurements, 2-methyl pentane was found to contain 0.2% C_3 paraffin and 0.5% C_4 olefin. These impurities would not change the solubilities by more than the size of the points in Figures 2 through 6. Attempts to measure the solubility of a C_6 olefin were frustrated by dimerization.

The most troublesome portion of this method is its sensitivity to small leaks. Because the runs usually lasted a few days, leakage from the system had to be kept below 10^{-3} ml. of liquid per hour. The window seals behaved erratically, but when they were working properly leaks could be kept below 10^{-5} ml. per hour. A mass balance was made at the end of each run. For a successful run, this balance was within 0.05 gram in a total sample weight of 30 grams.

Rebert and Kay(3) have made a thorough study of the benzene-water system at moderate pressures. Their agreement with the present work is satisfactory in the small region where comparison is possible—i.e., they report 22.0 wt. % benzene in water at 295° C. and 159 atm. compared to the author's value of 21.6 wt. %.

A more recent study (4) gives a value of 10.2 wt. % benzene in water at 238° C. and 340 atm. Because this is in conflict with

Table II. Critical Solution Temperatures for Hydrocarbon-Water Systems

Hydrocarbon	CST, °C.	Pressure, Atm.
Benzene	297	240
<i>n</i> -Heptane	353	290
<i>n</i> -Pentane	351	340
2-Methyl pentane	352	310
Toluene	308	220

the author's value of 7.2 wt. % in the 100 to 500 atm. interval at 260° C., a Kay-type apparatus (1) was used to obtain a check. This gave 7.0 wt. % at 260° C. and 135 atm.

SOLUBILITIES

The solubility isotherms, which are listed in Table I and plotted in Figures 2 through 6, behave normally at the lower temperatures, and then show a sharp maximum near the CST. That the maximum is most pronounced in the case of benzene is in part due to the choice of temperatures. In each system the highest temperature isotherm is separated into two branches, with a region of complete miscibility intervening between 2 two-phase regions.

As shown in Figures 2 and 3, the solubility of the aromatic is many times that of the paraffin at the same temperature and pressure. This selectivity would be reduced in a ternary system. Figures 3 through 5 indicate that the solubility of paraffins in water increases with decreasing chain length while branching has little effect. Figure 6 shows that toluene is about one-half as soluble as benzene.

CRITICAL SOLUTION TEMPERATURES

The CST is usually defined as the minimum temperature for mixing of two substances in all proportions as liquid; or it is the maximum temperature of a binary system for two liquid phases in equilibrium (2). Normally both parts of this definition are the same. But for the present work they are not, and a choice was necessary. In quoting a CST for the benzene-water system, Rebert and Kay (3) chose the second part. However, the existence of maxima in the solubility isotherms shows that the first part also gives a unique temperature. For the benzene-water system, the first part gives a temperature which is 9° C. below that given by the second part. Because the lower values are much easier to determine in the author's apparatus, they are referred to as critical solution temperatures and are listed in Table II. The uncertainty in the CST is about 2° C. and that of the corresponding pressure, about 10 atm.

LITERATURE CITED

- (1) Connolly, J.F., Kandalic, G.A., *Phys. Fluids* **3**, 463 (1960).
- (2) Francis, A.W., *Advan. Chem. Ser.* **31**, 1 (1961).
- (3) Rebert, C.J., Kay, W.B., *A.I.Ch.E.J.* **5**, 285 (1959).
- (4) Thompson, W.H., Snyder, J.R., *J. CHEM. ENG. DATA* **9**, 516 (1964).

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