High-Temperature Mutual Solubilities of Hydrocarbons and Water

Part I: Benzene, Cyclohexane and *n*-Hexane

The mutual solubilities at the three-phase equilibrium pressure of three C_6 hydrocarbons (benzene, cyclohexane and *n*-hexane) and water have been experimentally investigated up to 482 K. A thermodynamic analysis of these new measurements and of critically selected literature data has been carried out up to the three-phase critical end point. Information is also provided on the two-phase critical locus. The solubility of hydrocarbons in water has been used to calculate Henry's constants, while the solubility of water in the hydrocarbons has been correlated with a modified version of the Redlich-Kwong equation of state. Consideration is also given to the effect of pressure on the mutual solubilities.

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SCOPE

Knowledge of the hydrocarbon/water mutual solubilities is frequently of importance to the design and operation of process equipment in refineries and petrochemical plants. Hydrocarbons, like other pollutants, must be removed from refinery and petrochemical plant wastewater streams. Accordingly, the solubility and volatility of the hydrocarbons are needed to trace their phase distribution through the entire process sequence and to design separation equipment (such as sour water strippers) for their removal.

If the water present in a hydrocarbon mixture exceeds its solubility limit, a second liquid phase will form, the "free" water phase, that can affect product specifications and equipment operation. Perhaps the most common adverse process effect is corrosion. Even when a free-water phase does not form, the solubility of water in hydrocarbons at 470 K and above is so high that the phase distribution of water can affect both the operation of the equipment, say, a distillation tower, and the product quality. Sometimes, however, a water-rich phase is formed intentionally, for example, to remove salts that would otherwise deposit out. This case also requires the accurate prediction of the solubility limits.

The maximum temperature of interest in water pollution abatement is about 420 K, or even 470 K in certain cases, which can be reached in sour water strippers. On the hydrocarbon-rich side, the maximum temperature of interest can be much higher. Generally, it is the maximum temperature at which the hydrocarbon-rich liquid phase can exist. This is somewhat below the critical temperature of the hydrocarbon.

The process conditions at which hydrocarbon streams are contacted with water and lead to the formation of a second liquid phase need to be predicted reliably. The solution of water in hydrocarbons can be predicted accurately with an equation of state, using only a temperature-independent binary interaction parameter. The same procedure can then be used to predict the distribution of water between the vapor and hydrocarbon-rich liquid phases. On the other hand, the solubility of hydrocarbons in water is not predictable by such a procedure, unless the binary interaction parameter is made a strong function of temperature. The solubility of hydrocarbons in water is so low, however, that Henry's law is entirely adequate for representing the distribution of hydrocarbons between the vapor and the water-rich liquid phase.

Our work began with the C_6 hydrocarbons because their solubilities are better known than those of other hydrocarbons. Indeed, benzene/water has been the most extensively investigated system. Therefore, it provides a good starting point for checking the experimental techniques and even the data analysis and correlation. Cyclohexane and *n*-hexane have also been studied, but mostly around 298 K (which is even true of benzene). Thus, the high-temperature data presented here are considered a significant addition to the available data base.

CONCLUSIONS AND SIGNIFICANCE

New mutual solubility data are presented for water with benzene, cyclohexane or *n*-hexane. The solubilities were measured over the temperature range 311–482 K at the three-phase equilibrium pressure, which is also reported. As described in Appendix I, the solubility of hydrocarbons in water was measured by gas chromatography, while that of water in hydrocarbon by Karl-Fischer titration.

The new measurements were analyzed together with critically-selected literature data. Smoothed values are presented algebraically and graphically up to the three-phase critical temperature, the maximum temperature at which all three phases exist in equilibrium: water-rich, hydrocarbon-rich and vapor. For completeness, literature data are presented for the critical solution point, the minimum temperature on the water-rich liquid/gas critical curve.

The solubility of the C_6 hydrocarbons in water is very low and goes through a minimum at room temperature or below. This is well known for benzene (and alkylbenzenes), but there is insufficient solubility information to determine the minimum for cyclohexane and *n*-hexane. Recent calorimetric data by Gill et al. (1975, 1976) for the heat of solution clearly establish the solubility minima.

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The hydrocarbon solubilities are converted to Henry's constants, which go through a maximum at elevated temperatures. In view of the limited solubility of hydrocarbons in water (even at the three-phase critical temperature where it does not exceed 2.5 mol %), the vapor-liquid distribution of the hydrocarbons can be represented entirely satisfactorily by means of these Henry's constants.

The solubility of water in hydrocarbons is very substantial and increases rapidly with temperature (it is about 60 mol % for water in benzene at the three-phase critical temperature). The heat of solution is shown to be comparable to the hydrogen-bond energy (around 25 kJ•mol^{-1}). Because of the high solubility of water, Henry's law is inadequate in representing the vapor-liquid distribution of water. Instead, the water solubility is correlated with the Joffe-Zudkevitch modification of the Redlich-Kwong equation of state. A temperature-independent binary constant suffices in correlating the water solubility data to within about 20 K of the three-phase critical temperature.

Finally, it is shown that the three-phase equilibrium pressure (the pressure at which the three phases coexist) can be approximated by the sum of the pure-component vapor pressures up to high temperature. Furthermore, at pressures above the three-phase equilibrium pressure, the effect of pressure on the mutual solubilities is very slight but of opposite direction (at least up to 100 MPa): the hydrocarbon solubility increases, while the water solubility decreases, with increasing pressure.

HYDROCARBONS AND WATER AT HIGH TEMPERATURES

Figure 1 presents the *P-T* diagram for benzene/water to clarify what is meant by "high temperatures," three-phase equilibrium curve, and critical solution point. The *P-T* diagrams for cyclohexane/water and *n*-hexane/water are very similar.

First of all, the pure-component vapor pressure curves (light solid lines) end at the respective critical points: 562.09 K and 4.898 MPa for benzene; 647.30 K and 22.12 MPa for water (Kudchadker et al., 1968). The gas-liquid critical curve (heavy solid line) ends at the pure-component critical points, but is broken into two pieces because it is intersected by the liquid-liquid critical curve.

The upper branch of the gas-liquid critical curve initially has the expected behavior (it moves towards the critical point of benzene), but at about 579 K reaches a minimum in pressure and then turns up, reaches a minimum in temperature, and increases rapidly in pressure but slowly in temperature. This branch of the curve actually is a liquid-liquid critical curve—more properly, a fluid-liquid critical curve—and has been investigated up to 370 MPa by Alwani and Schneider (1967).

The minimum temperature point in the critical curve is the critical solution point, according to the definition of Connolly (1966)—the minimum temperature for mixing two substances in all proportion as liquid. Table 1 lists the critical solution point data for the three binaries of interest. Although there is agreement between Connolly and Schneider, it should be noted that Kay places the critical solution point at the pressure minimum in the critical curve, Table 1. However, Connolly considers the minimum temperature point to be more reproducible, and hence preferable as a "critical" point.

The lower branch of the critical curve in Figure 1 begins at the critical point of benzene and ends at the three-phase critical end point. This is the highest temperature at which all three phases coexist; above that, the hydrocarbon-rich liquid phase disappears.

The three-phase critical temperature is the maximum temperature of interest in this investigation; the lowest temperature is 273.15 K or the melting point of the hydrocarbon. Experimental data for the temperature and pressure at the three-phase critical end point are summarized in Table 2. There will be more on these properties when the analysis of the new data is discussed.

The final point on Figure 1 concerns the broken line, that is, the three-phase equilibrium curve. A point below this line represents equilibrium between two phases, one of the two liquid phases and the vapor. A point above the line also represents equilibrium be-

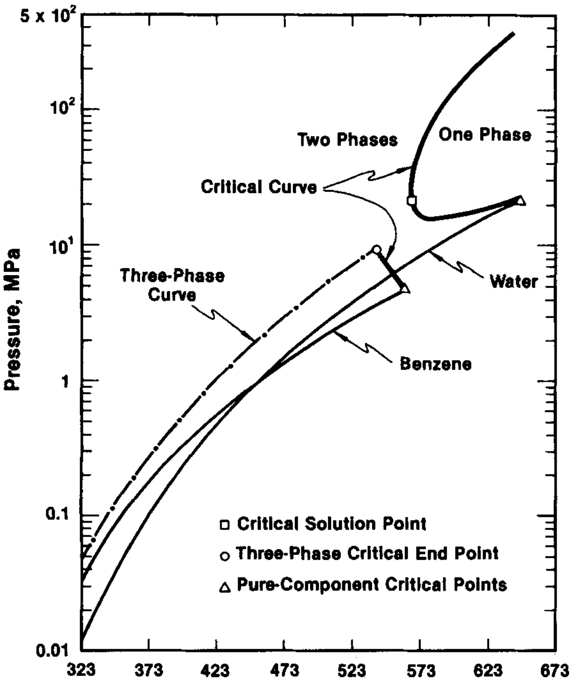

Figure 1. Pressure-temperature diagram for benzene/water.

TABLE 1. CRITICAL SOLUTION POINTS

Definition: minimum temperature for mixing of two substances in all proportions as liquid (Connolly, 1966)

	T_c, K	P_c, MPa	Reference
Benzene/Water	570 ± 2[a]	24.3 ± 1.0	Connolly (1966)
	567 ± 2	22.0 ± 2.0	Alwani & Schneider (1967)
Cyclohexane/Water	619 ± 1	35.5 ± 0.5[b]	Bröllos et al. (1970)
n-Hexane/Water	625 ± 2[c]	31.4 ± 1.0[c]	Connolly (1966)
	627.9 ± 0.2	31.0 ± 2.0	Loos et al. (1982)

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[a] Rebert and Kay (1959) observe that at 570 K the benzene-rich dense fluid phase and the water-rich liquid phase "have their maximum solubility." However, they locate the critical solution point at 579.6 K and 15.9 MPa. That point is where the critical curve in Figure 1 goes through a minimum in pressure. The same definition gives 633 K; 22.5 MPa for cyclohexane/water and 641 K; 22.6 MPa for *n*-hexane/water (Rebert and Hayworth, 1967).

[b] Figure 3 in Bröllos et al. (1970) suggests a critical pressure in the range 28 to 30 MPa.

[c] Results for 2-methylpentane/water; Connolly's measurements on *n*-pentane (624 K; 34.5 MPa) and *n*-heptane (626 K; 29.4 MPa) suggest that the P_c value for *n*-hexane may be closer to 32 MPa.

TABLE 2. THREE-PHASE EQUILIBRIUM END POINTS

	T_{3c}, K	P_{3c}, MPa	Reference
Benzene/Water	541.0	9.39	Scheffer (1914)
	541.5	9.404	Rebert & Kay (1959)
	542.6	9.460	Roof (1970)
Cyclohexane/Water	528.9	8.019	Rebert & Hayworth (1967)
	529.9	8.039	Roof (1970)
n-Hexane/Water	495.20	5.274	Scheffer (1913)
	497.4 ± 0.8	5.295	Roof (1970)

TABLE 3a. MEASUREMENTS ON BENZENE/WATER

T, K (°F)	P_3, MPa (psia)	x_{hc}	x_w
313.15 (104)	$0.0305\underline{4}$ (4.43)	$4.43\underline{5} \times 10^{-4}$	5.01×10^{-3}
373.15 (212)	0.2758 (40.0)	9.49×10^{-4}	2.08×10^{-2}
423.15 (302)	1.0549 (153.0)	2.42×10^{-3}	7.13×10^{-2}
473.15 (392)	3.020 (438.0)	5.40×10^{-3}	1.85×10^{-1}
313.15 (104)	—	—	4.71×10^{-3}
373.15 (212)	—	—	1.81×10^{-2}

TABLE 3b. MEASUREMENTS ON CYCLOHEXANE/WATER

T, K (°F)	P_3, MPa (psia)	x_{hc}	x_w
313.15 (104)	0.03151 (4.57)	1.56×10^{-5}	1.13×10^{-3}
373.15 (212)	0.2723 (39.5)	$(2.35 \times 10^{-5})^a$	5.12×10^{-3}
423.15 (302)	1.0032 (145.5)	1.30×10^{-4}	2.04×10^{-2}
473.15 (392)	2.965 (430.)	3.92×10^{-4}	7.89×10^{-2}
313.15 (104)	—	—	8.87×10^{-4}
373.15 (212)	—	3.79×10^{-5}	4.35×10^{-3}
423.15 (302)	—	—	2.40×10^{-2}
473.15 (392)	—	—	7.93×10^{-2}
313.15 (104)	—	$(1.99 \times 10^{-5})^b$	9.24×10^{-4}
422.04 (300)	—	1.03×10^{-4}	—
482.21 (408.3)	—	4.93×10^{-4}	—

TABLE 3c. MEASUREMENTS ON n-HEXANE/WATER

T, K (°F)	P_3, MPa (psia)	x_{hc}	x_w
313.15 (104)	0.04537 (6.58)	$(4.35 \times 10^{-6})^b$	1.23×10^{-3}
373.15 (212)	0.3482 (50.5)	6.21×10^{-6}	7.09×10^{-3}
423.15 (302)	1.2548 (182.)	3.39×10^{-5}	3.11×10^{-2}
473.15 (392)	3.516 (510.)	1.85×10^{-4}	1.10×10^{-1}
367.55 (201.92)	—	5.35×10^{-6}	5.95×10^{-3}
313.15 (104)	—	$(4.97\underline{5} \times 10^{-6})^b$	1.17×10^{-3}
310.93 (100)	—	2.38×10^{-6}	—
366.48 (200)	—	5.73×10^{-6}	—
422.04 (300)	—	2.71×10^{-5}	—

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[a] Discarded (too low).
[b] Discarded (too high).

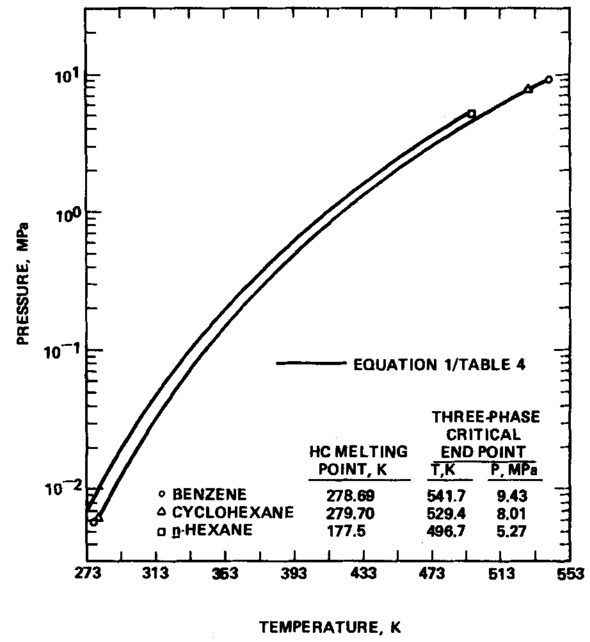

Figure 2. Three-phase equilibrium pressure for hydrocarbon/water binaries.

tween two phases, the hydrocarbon-rich and water-rich liquid phases. The mutual solubilities that will be presented are at P_3, the three-phase equilibrium pressure, which will also be reported. It will also be shown that the mutual solubilities are only weakly pressure-dependent; therefore, solubilities at $P > P_3$ are not drastically different from those at $P = P_3$. But it is important that P not be below P_3, because then the second liquid phase would disappear. Only the vapor-liquid equilibrium behavior at P_3 is of interest here.

EXPERIMENTAL RESULTS

The experimental procedure is described in Appendix I.

Tables 3a, 3b, and 3c present the experimental results for water with benzene, cyclohexane and n-hexane, respectively. In each case, the information given at each temperature is P_3, the mole fraction of the hydrocarbon in water, and the mole fraction of water in the hydrocarbon. The measurements are listed in chronological order.

The uncertainty in P_3 is about 1%. The repeatability of sequential analyses of the phases was generally within 5%, although larger deviations were not uncommon. Some hydrocarbon solubilities were clearly in error and were discarded (Tables 3b and 3c).

THREE-PHASE EQUILIBRIUM PRESSURE

P_3 is the pressure at which all three phases are present at equilibrium. At low temperatures, it is generally assumed that P_3 is equal to the sum of the pure-component vapor pressures. It was of interest to determine: (a) P_3 at high temperatures and (b) the relationship between P_3 and the pure-component vapor pressures.

There was generally good agreement between the new measurements and literature data. Data from the following sources were used in the regression:

Benzene

Scheffer (1914): 423.15 – 540.95 K
Rebert and Kay (1959): 453.15 – 541.45 K
Roof (1970): 542.59 K

Cyclohexane

Rebert and Hayworth (1967): 403.15 – 528.85 K
Roof (1970): 529.82 K

n-Hexane

Scheffer (1913): 450.55 – 495.20 K
Roof (1970): 496.48, 498 K

The results of the regression are listed in Table 4 and plotted in Figure 2, where the bottom curve represents the benzene and cyclohexane binaries. The temperature dependence of P_3 was adequately represented by a two-term equation:

$$ln\, P_3 = A + B/T \qquad (1)$$

The values of A and B are given in Table 4. Also included in Table 4 are predictions for the atmospheric azeotropic temperature and P_{3c}, the three-phase equilibrium critical pressure. In view of the simplicity of Eq. 1, the agreement with the data is entirely satisfactory.

Scheffer (1913, 1914) has demonstrated that

$$P_3 \cong P^s_{hc} + P^s_w \qquad (2)$$

up to high temperatures. For benzene/water, he found P_3 to be equal to the sum of the pure-component vapor pressures up to 443 K, 0.7% higher at 473 K, and only 3.3% at T_{3c}, 540.95 K (Scheffer, 1914). The deviations were larger for n-hexane/water, but Eq. 2 was still a reasonable approximation: P_3 was 3.6% higher at 468 K and 6.7% at T_{3c}, 495.20 K (Scheffer, 1913). Thus, at least up to 423 K, Eq. 2 is an excellent approximation.

SOLUBILITY OF HYDROCARBONS IN WATER

Much is known about the solubility of hydrocarbons in water, especially around 298 K (McAuliffe, 1963, 1966). At higher tem-

TABLE 4. THREE-PHASE EQUILIBRIUM PRESSURE
$ln\ P_3 = A + B/T$; P_3 in MPa and T in K

	A	B	Atmospheric Azeotropic T, K: Predicted	Atmospheric Azeotropic T, K: Observed[a]	T_{3c}, K[b]	P_{3c}, MPa: Predicted	P_{3c}, MPa: Observed[b]
Benzene	10.0744	−4241.29	343.1	342.40	541.7	9.432	9.42
Cyclohexane	10.0506	−4229.59	342.8	$342.\underline{4}$	529.4	7.850[c]	$8.02\underline{5}$
n-Hexane	9.8127	−4047.70	334.5	334.8	496.7	5.274	$5.29\underline{5}$

[a] The atmospheric azeotropic temperatures were taken from Horsley (1973). The value for cyclohexane/water is the average of two reported values (342.10 and 342.7 K).

[b] The T_{3c} and "observed" P_{3c} values are averages of the experimental results given in Table 2.

[c] A fit with $ln\ P_3 = A + B/T + C\ ln\ T$ gave a P_{3c} = 8.007 MPa.

TABLE 5. SOLUBILITY OF HYDROCARBONS IN WATER
$ln\ x_{hc} = A + B/T + C\ ln\ T$; T in K

	A	B	C	Solubility Minimum: T, K	Solubility Minimum: x_{hc}	Solubility at T_{3c}: T_{3c}, K	Solubility at T_{3c}: x_{hc}
Benzene[a]	−170.04018	6922.912	24.398795	283.8	3.954×10^{-4}	541.7	2.528×10^{-2}
Cyclohexane	−209.11689	8325.49	29.8231	279.2	1.193×10^{-5}	529.4	1.748×10^{-3}
n-Hexane	−367.98497	16128.646	52.820813	305.4	2.370×10^{-6}	496.7	4.982×10^{-4}

[a] Equation 4 predicts a solubility minimum at 292.1 K, where $x_{hc} = 3.974 \times 10^{-4}$.

peratures, only the solubility of benzene has been extensively investigated. For this reason, our experimental work began with benzene to test the experimental procedure and confirm that accurate solubility measurements could be obtained.

The analysis of the new measurements and selected literature data was carried out with a simple equation:

$$ln\ x_{hc} = A + B/T + C\ ln\ T \qquad (3)$$

(The thermodynamic basis of Eq. 3 will be discussed later.) The values of A, B and C for the three hydrocarbons are listed in Table 5. It is not claimed that Eq. 3 can provide the best possible fit from 273 K to T_{3c}. However, in view of the considerable uncertainty in the available information, Eq. 3 is entirely adequate to represent the temperature dependence of x_{hc}.

After the analysis of the solubility data with Eq. 3, the meager information on the heat of solution is examined, with particular reference to predicting the minimum in the solubility. Then, the effect of pressure on solubilities is examined and, finally the solubilities are converted to Henry's constants, which are needed for vapor-liquid equilibrium calculations.

Solubility data examined but not included in the regression (and the reasons why) are reviewed in Appendix II.

Benzene in Water

Probably more measurements have been made on the solubility of benzene in water than of all other liquid hydrocarbons combined. No attempt has been made to collect all this information, which mostly covers the low-temperature range. Many of these references are included in the *API Data Book* (Chapter 9, 1983).

Figure 3 presents selected data between the melting point of benzene, 278.68 K, and the atmospheric azeotropic point, 342.40 K. Perhaps the most important reference in this range is Arnold et al. (1958); this reference also includes extensive literature information as well as data for the solubility of solid benzene. Figure 3 includes two lines; one calculated with Eq. 3 and one with Eq. 4:

$$ln\ x_{hc} = -442.92352 + 15{,}357.083/T - 0.061492742\ T + 70.54313\ ln\ T \qquad (4)$$

Because the data of Bradley et al. (1973) and Alexander (1959) were not used in the regression with Eq. 4, the fit is in closer agreement with the data of Arnold et al. and Franks et al. (1963). However, the addition of the T term in Eq. 4 leads to a concave-downwards curve above 450 K, which is incorrect. Accordingly, Eq. 4 was discarded in favor of the simpler Eq. 3.

Figure 4 presents the solubility of benzene in water up to T_{3c}. The only high-temperature data included in the final evaluation, other than the new measurements, where those of Thompson (1962; Thompson and Snyder, 1964) and the single values of Connolly (1966) and of Rebert and Kay (1959). As Figure 4 indicates, considerable uncertainty exists at 510–530 K. The fit with Eq. 3 with the coefficients in Table 5 is a reasonable compromise, but additional data at 490–530 K would be needed to firmly establish the solubility of benzene as T_{3c} is approached.

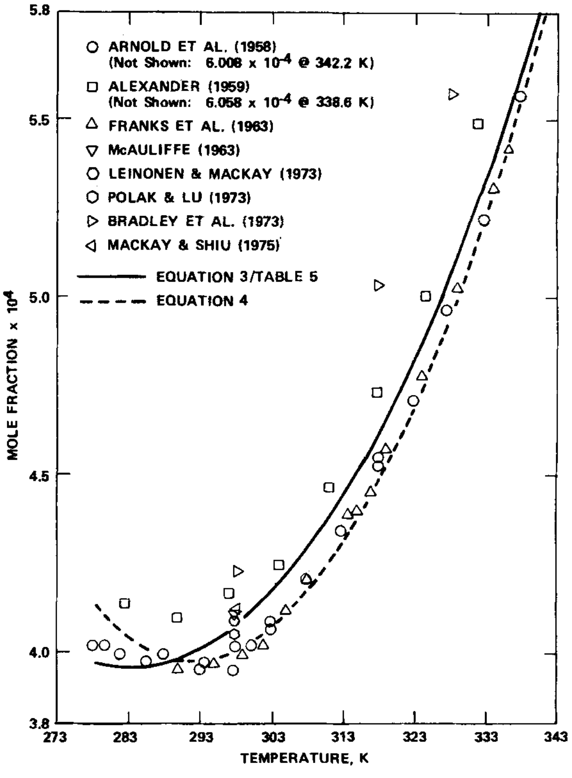

Figure 3. Low-temperature solubility of benzene in water.

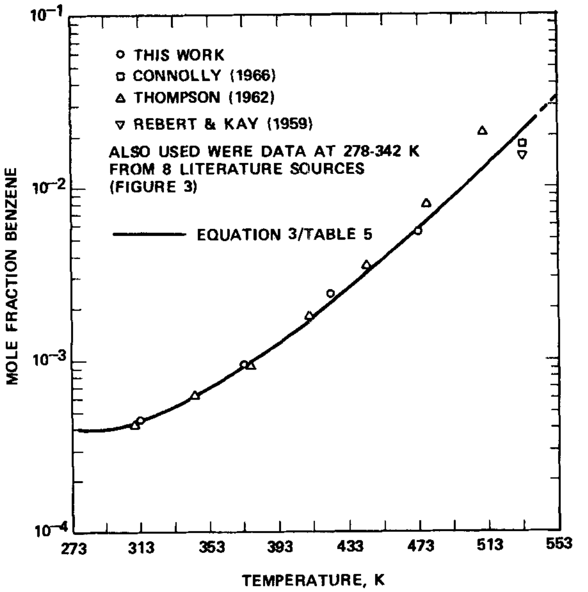

Figure 4. Solubility of benzene in water at three-phase equilibrium pressure.

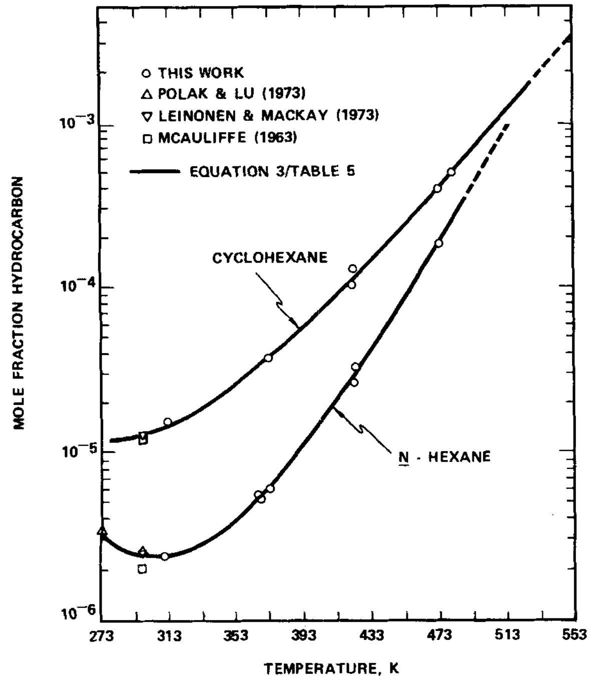

Figure 5. Solubility of cyclohexane and *n*-hexane in water at three-phase equilibrium pressure.

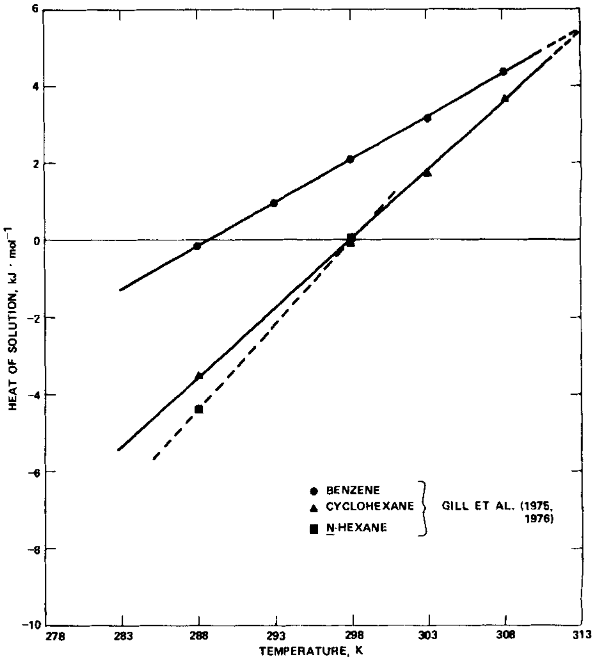

Figure 6. Heat of solution of hydrocarbons in water.

Cyclohexane in Water

Cyclohexane is much less soluble in water than benzene is: Figure 5. Of the literature data, only the measurements at 298 K of McAuliffe (1963) and of Leinonen and Mackay (1973) were included in the regression. Still, a minimum in solubility was predicted, although at a temperature (279.16 K) below the melting point of cyclohexane (279.70 K). The extrapolation to T_{3c} is reasonable, but data above 480 K would clearly be welcome, especially since some literature data are markedly different from our measurements (Appendix II).

n-Hexane in Water

Paraffins are the least soluble hydrocarbons in water. In the case of the C_6 hydrocarbons, the mole fraction at room temperature is of the order of 10^{-4} for benzene, 10^{-5} for cyclohexane, and only 10^{-6} for n-hexane. Such low solubilities are a challenge to measure accurately, but the measurements of McAuliffe (1963), Leinonen and Mackay (1973), and of Polak and Lu (1973) are in reasonably good agreement among themselves and with our data, as shown in Figure 5.

The fit of the data with Eq. 3 leads to a predicted minimum at 305.4 K and a mole fraction at T_{3c} of 4.982×10^{-4}. Even for the much more soluble benzene, the solubility at T_{3c} is only about 2.5 mol % (Table 5). Thus, properties such as the density and enthalpy of the water-rich phase should not be much different from those of water.

Heat of Solution

In view of the observed minimum in the solubility of the hydrocarbons, it would be valuable to have accurate data for the heat of solution because, at the minimum, the heat of solution should be zero.

The relationship between solubility and heat of solution is given by

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P \cong \frac{\Delta \bar{h}_i}{RT^2} \qquad (5)$$

$\Delta \bar{h}_i$, the heat of solution, is the difference between the enthalpy of the hydrocarbon i in solution and the enthalpy of the pure hydrocarbon:

$$\Delta \bar{h}_i = \bar{h}_i \text{ (in solution)} - h_i \text{ (pure } hc) \qquad (6)$$

Thus, $\Delta \bar{h}_i = \bar{h}_i^E$, the partial molar excess enthalpy of component i.

Gill et al. (1975, 1976) have measured the heat of solution over a temperature range, using a flow-microcalorimetric technique. Their results are plotted on Figure 6. Gill's measurements strongly suggest that the heat of solution is a linear function of temperature; therefore, the heat capacity of solution (or the partial molar excess heat capacity) is constant. Integration of Eq. 5, where $\Delta \bar{h}_i$ is expressed as a linear function of temperature, leads to Eq. 3.

The predicted minima in the solubility (where $\Delta \bar{h} = 0$) and the values of $\Delta \bar{c}_p$ from the data of Gill et al. are compared in Table 6 with the results obtained from the analysis of the solubility data. The agreement is far from perfect, but more data (solubility and calorimetric) may lead to better agreement.

TABLE 6. TEMPERATURE DEPENDENCE OF HYDROCARBON SOLUBILITY

	Solubility Minimum T, K		$\Delta\bar{c}_p$, J·mol^{-1}·K^{-1}	
	Solubility Data	Calorimetric Data[a]	Solubility Data	Calorimetric Data
Benzene	283.8 (Eq. 3) 292.1 (Eq. 4)	288.9 ± 0.2	203 282[b]	225 ± 5
Cyclohexane	279.2	298.2 ± 0.5	248	360 ± 30
n-Hexane	305.4	298.2 ± 0.5	439	440 ± 45

[a] Gill et al. (1976) give the minima at 289.0 ± 0.2, 298.5 ± 0.3, and 298.2 ± 0.5 K, respectively.

[b] Equation 4 predicts a weakly temperature-dependent $\bar{c}_p$:

T, K	$\Delta\bar{c}_p$, J·mol^{-1}·K^{-1}
288	292
293	287
298	282
303	276
308	271

Effect of Pressure; Volume of Solution

The solubility of hydrocarbons in water, like most other liquid-phase properties, is a weak function of pressure. In Figure 7, the solubility of benzene has been plotted as a function of pressure.

Thompson (1962) measured the solubility at 6.996 MPa (1,000 psig) and 34.575 MPa (5,000 psig). These data were linearly extrapolated to P_3, as shown in Figure 7. At 510.9 K, the solubility was measured only at the higher pressure and was extrapolated to P_3 by using the slope determined at 477.6 K.

Thompson's results demonstrate that the effect of pressure is small but positive. That is, solubility increases with increasing pressure. Connolly's (1966) measurements at 533.15 K suggest that the pressure effect is even smaller. They also disagree with Thompson's result at 510.9 K. The results at P_3 from both sources are plotted in Figure 4.

In contrast to Thompson and Connolly, Kudchadker and McKetta (1962) found an extremely large pressure effect. Their 310.9 K isotherm is included in Figure 7. Such a large pressure effect is suspect.

The thermodynamic relationship for the effect of pressure on the solubility is given by (Bradley et al., 1973):

$$\left(\frac{\partial \ln x_i}{\partial P}\right)_T \cong -\frac{\Delta\bar{v}_i}{RT} \tag{7}$$

where $\Delta\bar{v}_i$ is the volume of solution (or the partial molar excess volume of component i, $\bar{v}_i^E$):

$$\Delta\bar{v}_i = \bar{v}_i \text{ (in solution)} - v_i \text{ (pure } hc) \tag{8}$$

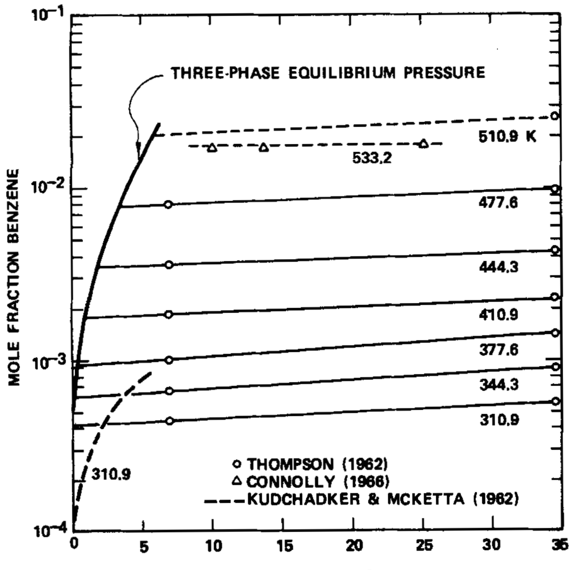

Figure 7. Effect of pressure on solubility of benzene in water.

Bradley et al. (1973) have measured the solubility of benzene up to about 120 MPa between 308 and 333 K. Bradley's results show that x_{hc} increases with pressure, but the effect is a very small one in agreement with Connolly (1966). At 310.9 K, Bradley's measurements lead to a $(-\Delta\bar{v}) \cong 4.5$ cm^3·mol^{-1}; Thompson's give 21.5 cm^3·mol^{-1} (almost five times higher, but still a small effect), while the measurements of Kudchadker and McKetta lead to the extraordinarily high value of 2,890 cm^3·mol^{-1}, more than 600 times that obtained from Bradley's results.

The evidence is in favor of only a slight increase of the hydrocarbon solubility with pressure, at least up to pressures of about 100 MPa. At higher pressures, the measurements of Bradley et al. (1973) on toluene up to 300 MPa suggest a reverse, but still small, effect: the solubility decreases with increasing pressure.

Henry's Constants

Solubilities cannot be used directly in distillation calculations. What is needed there is the volatility of the hydrocarbon. In view of the very low solubility of the hydrocarbons, their volatility, that is, their partial pressure over the aqueous solution, can be expressed by Henry's law (Prausnitz, 1969):

$$\varphi_i^V y_i P \cong H_i x_i \exp \frac{v_i (P - P_w^s)}{RT} \tag{9}$$

H_i is determined in the limit of the infinitely dilute hydrocarbon i:

$$H_i = \lim_{x_i \to 0} \frac{\varphi_i^V y_i P}{x_i} \tag{10}$$

Therefore, H_i is determined at the vapor pressure of water.

Equations 9 and 10 are more often used to describe the solubility of gases. In the present case, the mutual solubilities can be converted to activity coefficients based on the symmetric convention (Raoult's rather than Henry's law). Then, H_i is related to the infinite-dilution activity coefficient (symmetric convention) as follows:

$$H_i \cong \gamma_i^\infty P_i^s \varphi_i^s \exp \frac{v_i (P_w^s - P_i^s)}{RT} \tag{11}$$

In Eq. 11, as well as in Eq. 9, v_i is the volume of the liquid hydrocarbon and is assumed to be independent of pressure.

Henry's constants for benzene, cyclohexane, and n-hexane in water calculated with Eq. 11 are plotted in Figure 8. φ_i^s was determined with the correlation of Lyckman et al. (1965). The temperature dependence of H was represented with Eq. 12:

$$\ln H = A + B/T + CT^2 + D \ln T \tag{12}$$

The coefficients for each hydrocarbon are listed in Table 7, along with the temperature at which H_i attains its maximum value. Even

TABLE 7. HENRY'S CONSTANTS FOR HYDROCARBONS IN WATER

$\ln H = A + B/T + CT^2 + D \ln T$

H in MPa; T in K

	A	B	C	D	Maximum H	
					T, K	H, MPa
Benzene	132.977	−9463.47	-1.50638×10^{-5}	−16.9273	423.7	2.557×10^2
Cyclohexane	244.272	−13539.9	-2.03342×10^{-6}	−33.6554	394.9	4.699×10^3
n-Hexane	413.539	−21622.5	-1.26465×10^{-6}	−58.2501	369.1	3.507×10^4

TABLE 8. SOLUBILITY OF WATER IN HYDROCARBONS

$\ln x_w = A + B/T + CT + D \ln T$; T in K

	A	B	C	D	Solubility at T_{3c}	
					T_{3c}, K	x_w
Benzene[a]	−1.64055	−2029.41	0.00900544	—	541.7	0.601[b]
Cyclohexane	−62.7645	−654.027	—	9.99967	529.4	0.276[c]
n-Hexane	−45.1714	−1635.73	—	7.53503	496.7	0.185[d]

---

[a] The use of the A, B and C terms led to a slightly better fit than that with A, B and D.

[b] Rebert and Kay (1959) report the value 0.6012 at 541.5 K; Umano and Hayano (1957) make no mention of T_{3c}, but report a solubility of 0.5925 at 544.7 K (where there should be no hydrocarbon-rich liquid phase).

[c] Rebert and Hayworth (1967) report a solubility at their T_{3c} (528.9 K) that is clearly in error: 17.2 wt.% water or $x_w = 0.493$. That would make water more soluble in cyclohexane than it is in benzene, which is unlikely. It is possible that 17.2 should have been 7.2 wt.% water or $x_w = 0.266$. This lower value is consistent with a solubility reported by Rebert and Hayworth at 516.4 K: 5.2 wt.% water or $x_w = 0.204$.

[d] Rebert and Hayworth (1967) quote the results of Scheffer (1913), but there is an apparent error in the solubility: they report $x_w = 0.322$, while Figure 2 in Scheffer's paper gives $x_w = 0.268$.

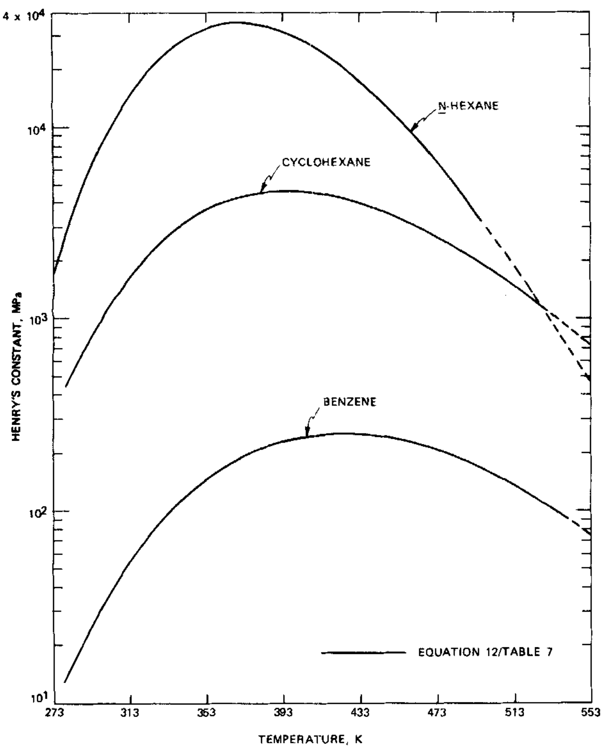

Figure 8. Henry's constants for hydrocarbons in water.

away from their maximum, the H_i values are extremely large, and thus the soluble hydrocarbons can be easily removed from water by distillation.

SOLUBILITY OF WATER IN HYDROCARBONS

Water is much more soluble in hydrocarbons than the hydrocarbons in water. Furthermore, the solubility of water increases very rapidly with increasing temperature—there is no minimum in the solubility of water—and reaches a very high value at T_{3c}. However, the available information at high temperature is just as limited as it is for the solubility of hydrocarbons in water. As before, much more is known about water/benzene than any other water/hydrocarbon system.

The analysis of the water solubility data was carried out with an equation that has one more term than Eq. 3:

$$\ln x_w = A + B/T + CT + D \ln T \tag{13}$$

The values of the four constants for the three systems of interest are listed in Table 8; only three constants were used for each system.

The high solubility of water means that its volatility—from the saturated to the infinitely-dilute solution—*cannot* be adequately represented by means of a Henry's constant. It is necessary to introduce the effect of composition on volatility. For this reason, the water solubility has also been fitted with a modified Redlich-Kwong equation of state, which can then be used in vapor-liquid equilibrium calculations.

The effects of temperature and pressure on the solubility of water are related, respectively, to the heat and volume of solution. The heat of solution is shown to be comparable to the energy of a hydrogen bond, while the volume of solution is small but positive (rather than negative, as it is for hydrocarbons in water).

Solubility data examined but not included in the regression (and the reasons why) are reviewed in Appendix II.

Water in Benzene

Figure 9 presents selected data for the low-temperature solubility of water in benzene. Figure 10 presents the solubility of water in benzene up to T_{3c}. The fit of the data with Eq. 13 is very satisfactory and the predicted x_w at T_{3c} is in good agreement with the data of Rebert and Kay (1959) and of Umano and Hayano (1957). The value of Thompson (1962) at 510.9 K is an extrapolation from a measurement at a higher pressure and will be discussed again later. The new measurements at 373 K are unaccountably too low.

RKJZ Equation of State

Figure 10 also includes a heavier line that was calculated with a modification of the Redlich-Kwong equation of state proposed by Zudkevitch and Joffe (1970). This equation of state, which will be referred to by the initials RKJZ, was recently used by Wilson et al. (1981) in a study of the volatility of coal liquids.

Briefly, in the RK equation:

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5}\, v\, (v + b)} \tag{14}$$

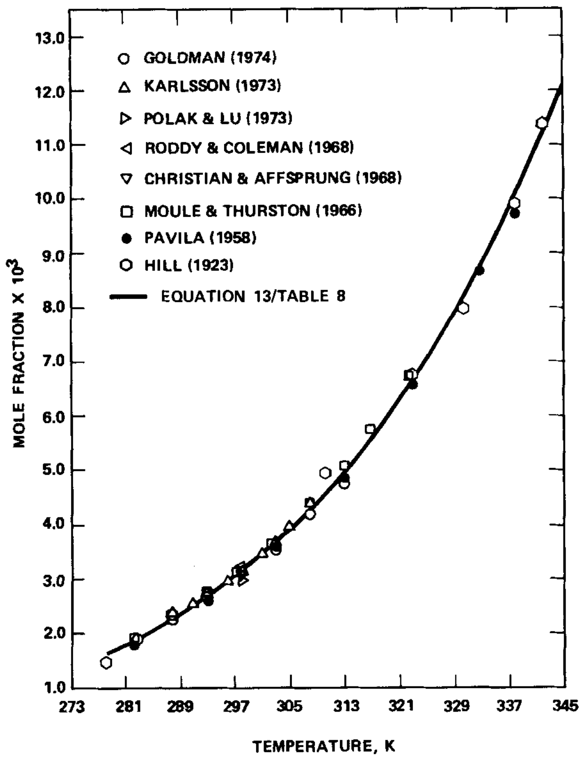

Figure 9. Low-temperature solubility of water in benzene.

The temperature dependence of a and b is determined by simultaneously matching the liquid density and forcing the vapor and liquid fugacities to be equal at the pure component's vapor pressure. In addition, a modification was made in the mixing rule for a. For a binary mixture, this is given by:

$$a_m = z_1^2 a_1 + 2z_1z_2(a_1a_2)^{1/2}(1 - C_{12}) + z_2^2 a_2 \qquad (15)$$

C_{12}, which is assumed to be independent of temperature, corrects for the deviation of a_{12} from the geometric mean.

The C_{ij} turns out to be equal to zero for most hydrocarbon/hydrocarbon binaries, especially near ambient temperature. However, nonzero C_{ij}'s may be required when the two components are very different in molecular size, for calculations in the critical region, or for polar components. Thus, the first step in the use of RKJZ is to determine the C_{ij} values for the key binaries.

The heavy line in Figure 10 demonstrates that RKJZ with $C_{12} = 0.260$ correlates the solubility data very adequately up to 475 K. Above 495 K, however, RKJZ breaks down. The problem is with the computational algorithm. In the vicinity of the three-phase critical end point, the calculations converge to the wrong density.

A closer look will be taken at the critical region in a future paper. It is clear, however, that RKJZ with a constant C_{ij} can adequately correlate the solubility data up to at least 470 K, the maximum temperature of interest in water pollution abatement work. It will, therefore, be possible to use RKJZ, with the C_{ij} determined from the water solubility, to predict the vapor-liquid equilibrium behavior of water/hydrocarbon systems. However, the water-rich liquid will have to be excluded from such treatment because RKJZ, or any other similar equation of state, cannot predict the solubility or volatility of hydrocarbons in water, as long as a constant C_{ij} is used. To correlate the solubility of hydrocarbons in water, it is necessary to make C_{ij} a very strong function of temperature, thus significantly minimizing the utility and usefulness of an equation of state (Peng and Robinson, 1980).

Water in Cyclohexane

Figure 11 presents selected data for the solubility of water in cyclohexane. The literature data extend only up to 313 K. Although our measurements at 313 K are too high (our procedure for measuring the solubility of water proved to be unreliable at $x_w \lesssim 0.001$), they are considered reliable at higher temperatures.

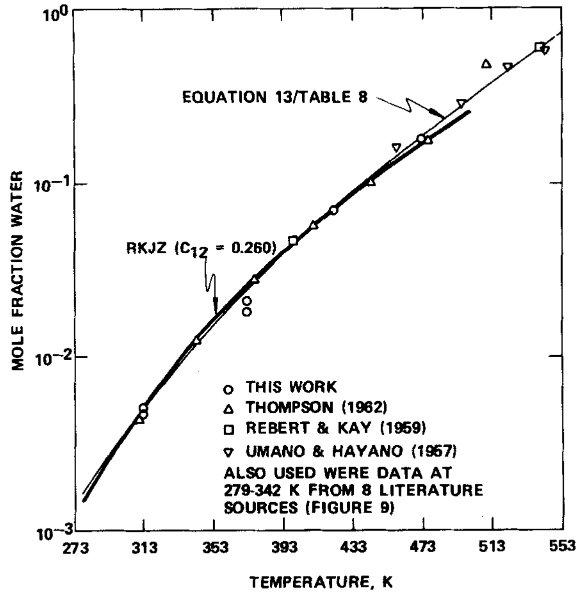

Figure 10. Solubility of water in benzene at three-phase equilibrium pressure.

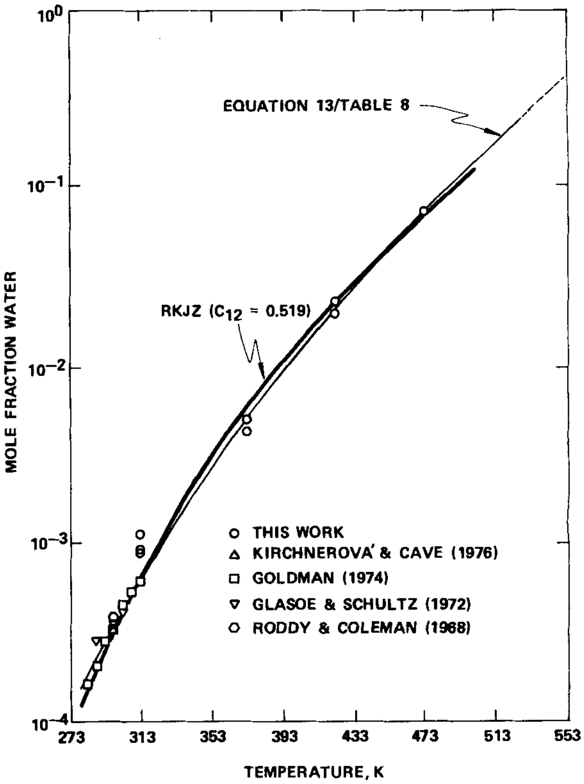

Figure 11. Solubility of water in cyclohexane at three-phase equilibrium pressure.

In addition to the fit of the data with Eq. 13, which was extrapolated to T_{3c} (Table 8), Figure 11 also presents the fit with RKJZ. The correlation of the data with $C_{12} = 0.519$ (twice the value for water in benzene) is satisfactory up to 475 K. As in the case of water in benzene, however, RKJZ falters above 495 K due to convergence to the wrong density root of the equation of state.

Water in *n*-Hexane

Perhaps a surprising result about the solubility of water in *n*-hexane is that it is higher than that in cyclohexane. (Cyclohexane

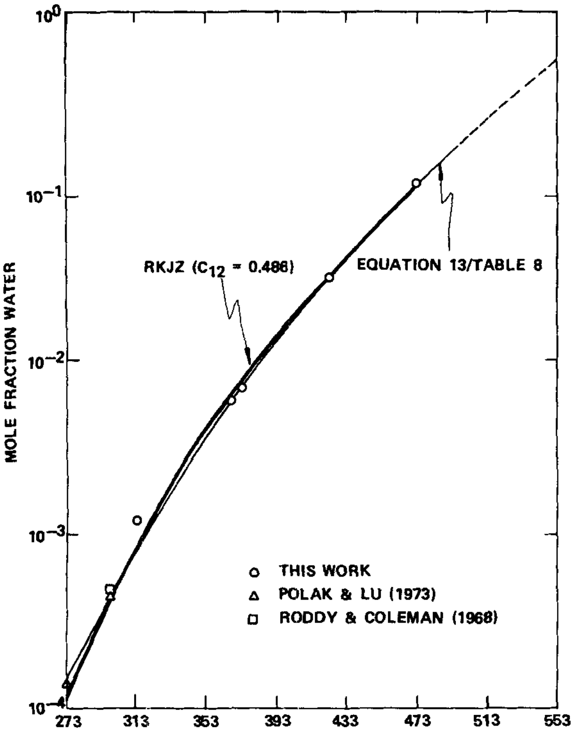

Figure 12. Solubility of water in *n*-hexane at three-phase equilibrium pressure.

is significantly more soluble in water than *n*-hexane is.) There is relatively limited literature information for water in *n*-hexane, Figure 12, but the comparisons in Figures 9 and 11 suggest that the data of Polak and Lu (1973) and of Roddy and Coleman (1968) are reliable.

The fit of the data with Eq. 13 and its extrapolation to T_{3c} are summarized in Table 8. RKJZ with $C_{12} = 0.486$ is satisfactory up to 475 K, but again breaks down in the vicinity of the three-phase critical end point.

Heat of Solution

The relationship between solubility and heat of solution is given by Eqs. 5 and 6. The difference here is that $\bar{h}_i$ is the enthalpy of water in solution and h_i is the enthalpy of pure water. A more important difference is that the heat of solution for water in hydrocarbons is much larger than that for hydrocarbons in water (Figure 6). In the case of water, the heat of solution in the three hydrocarbons at 298 K is:

	$\Delta\bar{h}_w$, kJ·mol^{-1}
Benzene	23.5
Cyclohexane	30.2
n-Hexane	32.3

These values were calculated by substituting Eq. 13 into Eq. 5.

What is striking about these large values for the heat of solution is that their magnitude is close to that of the hydrogen-bond energy. Typical values for the energy of a hydrogen bond range between 21 and 29 kJ·mol^{-1} (more recognizable as 5 to 7 kcal·mol^{-1}; Prausnitz, 1969). Thus, not surprisingly, the dissolution of *n* water molecules leads to the breaking of about *n* hydrogen bonds. The increase in heat of solution from benzene to cylohexane to *n*-hexane may be related to the relative affinity of the hydrocarbon molecules towards water. Since *n*-hexane has the least affinity, it can be tentatively concluded that 32.3 kJ·mol^{-1} (7.7 kcal·mol^{-1}) is a better measure of the hydrogen-bond energy in hydrocarbon/water systems. Physical interactions between water and benzene lead to a lowering of the heat of solution.

Effect of Pressure; Volume of Solution

The effect of pressure on the solubility is related to the volume of solution, as shown in Eqs. 7 and 8 where $\bar{v}_i$ and v_i now refer to water rather than a hydrocarbon component *i*.

The measurement of Thompson (1962) on the solubility of water in benzene at 6.996 MPa (1,000 psig) and 34.575 MPa (5,000 psig) lead to the following value for the volume of solution:

$$\Delta\bar{v}_w = 13 \text{ cm}^3\text{·mol}^{-1}$$

This value is the average over the range 310.9 to 477.6 K. At 510.9 K, Thompson measured the solubility only at 34.575 MPa, making the extrapolation to P_3 uncertain (Figure 10).

The value 13 cm^3·mol^{-1} is, in absolute magnitude, about half that for benzene in water, also from the measurements of Thompson. Thus, pressure affects the solubility of water even less than it affects the solubility of benzene (and other hydrocarbons) in water. The difference, however, is that the solubility of water decreases with increasing pressure.

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NOTATION

a,b = parameters in the Redlich-Kwong equation of state, Eq. 14
A,B,C,D = empirical constants in Eqs. 1, 3, 4, 12 and 13
C_{12},C_{ij} = characteristic binary constant, Eq. 15
h = molar enthalpy
$\bar{h}_i$ = partial molar enthalpy of component *i*
H_i = Henry's constant for component *i* (in water)
P = pressure
R = gas constant
T = temperature (absolute)
v = molar volume
$\bar{v}_i$ = partial molar volume of component *i*
x_i = liquid mole fraction of component *i*
y_i = vapor mole fraction of component *i*
z_i = mole fraction of component *i* (phase undefined)

Greek Letters

γ_i^∞ = infinite-dilution activity coefficient of component *i*
$\Delta\bar{c}_{pi}$ = molar heat capacity of solution of component *i*
$\Delta\bar{h}_i$ = molar heat (enthalpy) of solution of component *i*
$\Delta\bar{v}_i$ = molar volume of solution of component *i*
φ_i = fugacity coefficient of component *i*

Subscripts

c = critical property
hc = hydrocarbon property
$i, j(1, 2)$ = property of component *i*, *j*(1, 2)
m = mixture property
w = water property
3 = three-phase equilibrium property
$3c$ = three-phase critical end point property

Superscripts

E = excess property, Eqs. 6 and 8

V = vapor-phase property
s = saturated pure-component property

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