High-Temperature Mutual Solubilities of Hydrocarbons and Water

Part II: Ethylbenzene, Ethylcyclohexane, and *n*-Octane

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In Part I (Tsonopoulos and Wilson, 1983), the mutual solubilities of three C_6 hydrocarbons (benzene, cyclohexane, *n*-hexane) and water were experimentally investigated and, together with critically selected literature data, were correlated up to the three-phase critical end point. The present paper extends this analysis to the mutual solubilities of three C_8 hydrocarbons (ethylbenzene, ethylcyclohexane, *n*-octane) and water, which have been measured at the three-phase equilibrium pressure up to the critical temperatures (568, 561 and 539 K, respectively). A thermodynamic analysis of these new measurements and of available literature data has been performed up to the three-phase critical end point. Information is also provided on vapor-phase equilibrium compositions. The solubility of hydrocarbons in water has been used to calculate Henry's constants, while the solubility and volatility of water in hydrocarbons has been successfully correlated with several modifications of the Redlich-Kwong equation of state.

SCOPE

The importance of hydrocarbon/water mutual solubilities to the design and operation of process equipment in refineries and petrochemical plants was discussed by Tsonopoulos and Wilson (1983) [this reference will be cited as TW (1983)]. The same reference also discussed the correlation and prediction of mutual solubilities, Henry's constants for hydrocarbons in water, and the use of equations of state. All these were applied to C_6 hydrocarbons, for which much more is known than for other hydrocarbons.

Our work continues with C_8 hydrocarbons to study the effect of carbon number on mutual solubilities. But we have also expanded the scope of our study by including experimental data for the vapor composition and the three-phase critical end point, the highest temperature at which the vapor and the two liquid phases coexist.

CONCLUSIONS AND SIGNIFICANCE

New mutual solubility and vapor composition data are presented for water with ethylbenzene, ethylcyclohexane, or *n*-octane. These measurements were made up to 568 K at the three-phase equilibrium pressure, which is also reported. The solubility of hydrocarbons in water was measured by gas chromatography, while the concentration of water in hydrocarbon and vapor was determined 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 end point, whose properties were measured in a visual cell.

The solubility of C_8 hydrocarbons in water is, not surprisingly, significantly lower than that for the corresponding C_6 hydrocarbons. The minimum in the solubility at low temperature is again observed, although only for ethylbenzene can it clearly be established from the heat of solution data of Gill et al. (1976). The hydrocarbon solubilities are converted to Henry's constants, which go through a maximum at elevated temperatures and are higher than those for the corresponding C_6 hydrocarbons.

The solubility of water in C_8 hydrocarbons is very close to that in C_6 hydrocarbons. Although the carbon number effect is small, it is negative for aromatics (solubility decreases with increasing carbon number), but is positive for alkanes and naphthenes. The water solubility and the vapor composition are correlated with the Joffe-Zudkevitch, Soave, and Peng-Robinson modifications of the Redlich-Kwong equation of state. A temperature-independent binary constant (close to that for the corresponding C_6 hydrocarbon) suffices in correlating the water solubility data to within about 20 K of the three-phase critical temperature. Addition of a second binary constant significantly improves the agreement with experimental data, especially near the three-phase critical point.

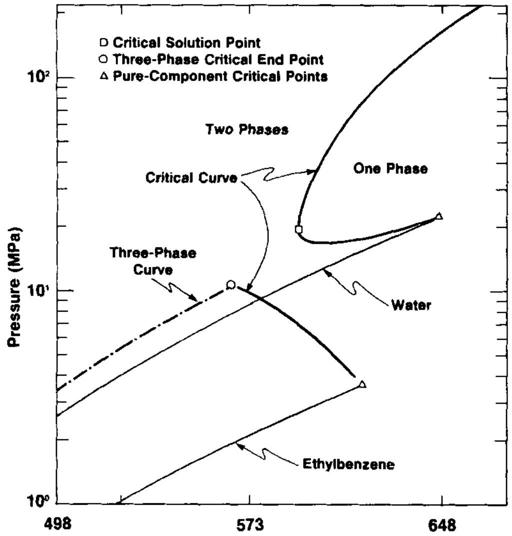

Figure 1. Pressure–temperature diagram for ethylbenzene/water.

HYDROCARBONS AND WATER AT HIGH TEMPERATURES

Figure 1 presents the pressure–temperature diagram for ethylbenzene/water. The pure-component vapor pressure curves (light solid lines) end at the respective critical points: 617.09 K and 3.609 MPa for ethylbenzene; 647.30 K and 22.12 MPa for water (Kudchadker et al., 1968). The gas-liquid critical curves (heavy solid line) ends at the pure-component critical points, but is broken into two pieces because it is intersected by the liquid-liquid curve; see also TW (1983).

The upper branch of the gas-liquid critical curve has been investigated by Alwani and Schneider (1969). The critical solution point, the minimum-temperature point in the critical curve, is at

$$T_c = 592 \pm 2\ \mathrm{K}$$
$$P_c = 19.5 \pm 2.0\ \mathrm{MPa}$$

No data have been located for the critical solution point of ethylcyclohexane/water or *n*-octane/water.

The lower branch of the critical curve, although not experimentally investigated, is shown in Figure 1 and begins at the critical point of ethylbenzene 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 also the maximum temperature of interest in this investigation; the lowest temperature of interest is 273.15 K or the melting point of the hydrocarbon.

As noted by TW (1983), a point below the three-phase equilibrium curve—the broken line in Figure 1—represents equilibrium between two phases, one of the two liquid phases and the vapor. A point above the line also represents equilibrium between two phases, the hydrocarbon-rich and water-rich liquid phases. Thus, the mutual solubilities can be investigated at $P \geq P_3$, and the vapor-liquid equilibrium behavior at $P \leq P_3$, where P_3 is the three-phase equilibrium pressure.

EXPERIMENTAL PROCEDURE

The experimental procedure was very similar to that described by TW (1983) for C_6 hydrocarbons and water. The water concentration in the vapor was determined by Karl-Fischer titration. One significant difference was the determination of three-phase critical end points in the visual cell apparatus shown in Figure 2. This apparatus contains a Jergusen-type windowed cell with an internal volume of 185 cm^3. The large window area allowed very precise observation of the liquid levels and the characteristic critical opalescence in the region of the critical point.

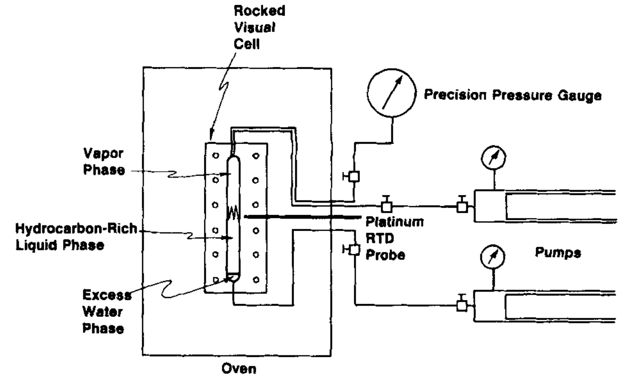

Figure 2. Diagram of visual cell for hydrocarbon/water three-phase critical end point measurements.

The materials were degassed before charging, and the cell was degassed in the charging procedure. No mercury was used in the measurement procedure. The critical density and critical composition were calculated from the amounts of the components charged, the cell volume, and volume of aqueous phase present at the critical end point. A slight excess of water was charged to the cell so that a separate aqueous phase was present at the bottom of the cell at the critical end point. The cell was continuously rocked inside a heated oven to ensure equilibrium between the phases as the critical end point was approached. This rocking was periodically interrupted in order to observe the relative amounts of the phases. (The oven was continuously purged with CO_2 in order to avoid the potentially unsafe condition of accidentally venting hydrocarbon vapor inside of the hot oven. The CO_2 purge eliminated the possibility of an explosion under such circumstances.)

The critical volume was approximated by maintaining nearly equal volumes of vapor and hydrocarbon phases as the critical point was approached. When this was done, the level appeared relatively stable as the critical end point was reached. Thus, the amounts charged probably corresponded fairly closely to the critical density. The calculation of the critical composition required a correction for the excess water remaining in the bottom of the cell. This level was read by means of a cathetometer, and the amount of excess water in the cell was estimated based on this level and the calculated density of water at the cell conditions. The correction for excess water was small because of the high concentration of water in the hydrocarbon-rich phase at the critical end point.

The hydrocarbons were purchased from Aldrich with a stated purity of 99+ mole%. Their water-free purity was checked by gas chromatography and found to be 99.9 mole% or better. Distilled water was used in all measurements.

EXPERIMENTAL RESULTS

Tables 1a, 1b, and 1c present the experimental results for water with, respectively, ethylbenzene, ethylcyclohexane, and *n*-octane. In each case,

TABLE 1a. MEASUREMENTS ON ETHYLBENZENE/WATER[a]

T (K)	P_3 (MPa)	x_{hc}	x_w	y_w
310.9	(0.0091)[b]	—	4.3×10^{-3}	(7.1×10^{-1})[b]
311.5	—	3.2×10^{-5}	—	—
367.6	0.111	8.6×10^{-5}	1.86×10^{-2}	7.26×10^{-1}
423.4	0.627	2.19×10^{-4}	5.96×10^{-2}	7.67×10^{-1}
479.5	2.32	6.0×10^{-4}	1.63×10^{-1}	7.78×10^{-1}
536.1	6.50	3.25×10^{-3}	4.08×10^{-1}	7.70×10^{-1}
550.4	8.27	—	4.72×10^{-1}	—
552.8	8.59	3.75×10^{-3}	—	—
568.1[c]	10.68	—	6.91×10^{-1}	6.91×10^{-1}

TABLE 1b. MEASUREMENTS ON ETHYLCYCLOHEXANE/WATER[a]

T (K)	P_3 (MPa)	x_{hc}	x_w	y_w
310.9	(0.0099)[b]	—	8.1×10^{-4}	(6.6×10^{-1})[b]
311.5	—	1.1×10^{-6}	—	—
367.6	0.117	2.4×10^{-6}	6.5×10^{-3}	7.12×10^{-1}
423.4	0.647	2.0×10^{-5}	3.0×10^{-2}	7.55×10^{-1}
479.5	2.36	1.21×10^{-4}	1.07×10^{-1}	7.54×10^{-1}
536.1	6.69	1.18×10^{-3}	2.90×10^{-1}	7.17×10^{-1}
552.8	8.83	2.37×10^{-3}	4.14×10^{-1}	6.71×10^{-1}
561.4[c]	9.93	—	6.03×10^{-1}	6.03×10^{-1}

TABLE 1c. MEASUREMENTS ON n-OCTANE/WATER[a]

T (K)	P_3 (MPa)	x_{hc}	x_w	y_w
310.9	(0.0103)[b]	1.2×10^{-7}	1.00×10^{-3}	(6.4×10^{-1})[b]
366.5	(0.117)[b]	4.8×10^{-7}	6.2×10^{-3}	(6.87×10^{-1})[b]
367.6	0.122	—	—	7.36×10^{-1}
422.0	0.655	3.8×10^{-6}	3.94×10^{-2}	—
423.4	0.674	—	—	7.36×10^{-1}
477.6	—	—	1.26×10^{-1}	—
479.5	2.51	4.0×10^{-5}	—	7.04×10^{-1}
533.1	—	—	3.87×10^{-1}	—
536.1	7.03	3.5×10^{-4}	—	6.52×10^{-1}
550.4[d]	—	—	5.49×10^{-1}	—
552.8[d]	8.86	6.0×10^{-4}	—	7.10×10^{-1}
539.1[c]	7.41	—	5.27×10^{-1}	5.27×10^{-1}

[a] All data (except three-phase critical end point measurements) were previously reported by Brady et al. (1982).

[b] Estimated from pure component vapor pressures.

[c] Measured three-phase critical end point.

[d] Not three-phase equilibrium measurement (above critical end point).

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 and the vapor.

Also reported in Tables 1a–c are the experimentally determined CEP (three-phase critical end point) conditions for each of the hydrocarbon/water binaries examined. As mentioned previously, these measurements were performed in a visual cell apparatus, thus permitting direct observation of the critical point phenomena. These measurements followed the three-phase equilibrium measurements at lower temperatures (where no visual observation was possible) and provided the upper temperature limit at which three phases exist simultaneously. In the case of n-octane (Table 1c), the experimental three-phase CEP indicated that two of the n-octane equilibrium measurements were above the CEP temperature and therefore did not represent three-phase equilibrium conditions. Consequently, these points were excluded from further analyses. The only CEP measurements available for comparison are those values of T_{3c} and P_{3c} reported by Roof (1970) for ethylbenzene (574 K, 11.22 MPa) and n-octane (540 K, 7.40 MPa). Table 1 shows that, while the CEP measurements for n-octane are in excellent agreement with those of Roof, those for ethylbenzene are significantly lower.

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. The uncertainties in the CEP measurements are estimated to be ±0.6 K in T_{3c}, ±0.04 MPa in P_{3c}, and ±0.02 mole fraction in the CEP composition.

THREE-PHASE EQUILIBRIUM PRESSURE

P_3 is the pressure at which all three phases are present at equilibrium. It was established by TW (1983) that, at least up to 423 K, P_3 is essentially equal to the sum of the pure-component vapor pressures.

The temperature dependence of P_3 was well represented by a three-term equation:

$$\ln P_3 = A + B/T + C \ln T \tag{1}$$

The results of the data regression and values of A, B, and C are given in Table 2. Also included in Table 2 are predictions for the atmospheric azeotropic temperature, given by Horsley (1973), and P_{3c}, the three-phase critical pressure. (Except for the CEP measurements of Roof, 1970, for ethylbenzene and n-octane, no additional literature data were found for the three-phase equilibrium pressures of these hydrocarbon/water systems.) The new measurements further established that P_3 is essentially equal to the sum of the pure-component vapor pressures up to about 423 K and increases to only about 5–10% higher than the vapor pressure sum at the CEP.

SOLUBILITY OF HYDROCARBONS IN WATER

The analysis of data for the solubility of hydrocarbons in water was carried out with an equation similar to Eq. 1:

$$\ln x_{hc} = A + B/T + C \ln T \tag{2}$$

The values of A, B, and C for the three hydrocarbons are listed in Table 3. The data and their fit with Eq. 2 are presented in Figures 3–5, which also include the solubility curves given in Part I for the corresponding C_6 hydrocarbons. As noted by TW (1983), Eq. 2 is not claimed to provide the best possible fit from 273 K to T_{3c}. However, in view of the considerable uncertainty in the available information, Eq. 2 is entirely adequate to represent the temperature dependence of x_{hc}. If more data at elevated temperatures become available, an additional temperature term may need to be added to Eq. 2.

Ethylbenzene in Water

The American Petroleum Institute *Technical Data Book* (1983) lists several literature references that report data on this binary. Of these, only Guseva and Parnov (1964a) investigated the hydrocarbon solubilities at high temperatures, but their data exhibit substantial scatter. Figure 3 presents the solubility of ethylbenzene in water up to T_{3c}, including both literature and new measurements. In addition to the data of Guseva and Parnov, the only data excluded from the final evaluation were the low-temperature measurements of Bohon and Claussen (1951). Although these data

TABLE 2. THREE-PHASE EQUILIBRIUM PRESSURE

$$\ln P_3 \text{ (MPa)} = A + B/T + C \ln T;\ T \text{ (K)}$$

				Atmospheric Azeotropic T (K)			P_{3c} (MPa)	
	A	B	C	Predicted	Observed[a]	T_{3c}(K)[b]	Predicted	Observed
Ethylbenzene	21.7487	−5,478.28	−1.53423	365.6	364.7	568.1	10.751	10.680
Ethylcyclohexane	26.2052	−5,724.84	−2.16651	364.3	—	561.4	9.903	9.928
n-Octane	27.9076	−5,821.38	−2.40256	363.1	362.7	539.1	7.370	7.412

[a] The atmospheric azeotropic temperatures were taken from Horsley (1973).

[b] The T_{3c} and Observed P_{3c} values are from this work.

TABLE 3. SOLUBILITY OF HYDROCARBONS IN WATER

$$\ln x_{hc} = A + B/T + C \ln T;\ T \text{ (K)}$$

				Solubility Minimum[a]		Solubility at T_{3c}	
	A	B	C	T (K)	x_{hc}	T_{3c}(K)	x_{hc}
Ethylbenzene	−185.1695	7,348.55	26.34525	279.0	2.82×10^{-5}	568.1	5.83×10^{-3}
Ethylcyclohexane	−334.2468	14,105.21	47.93102	294.3	9.66×10^{-7}	561.4	3.35×10^{-3}
n-Octane	−343.1497	13,862.49	49.24609	281.5	9.69×10^{-8}	539.1	4.61×10^{-4}

[a] Calorimetric data reported by Gill et al. (1976) for ethylbenzene in water predict a minimum in the solubility at about 292 K.

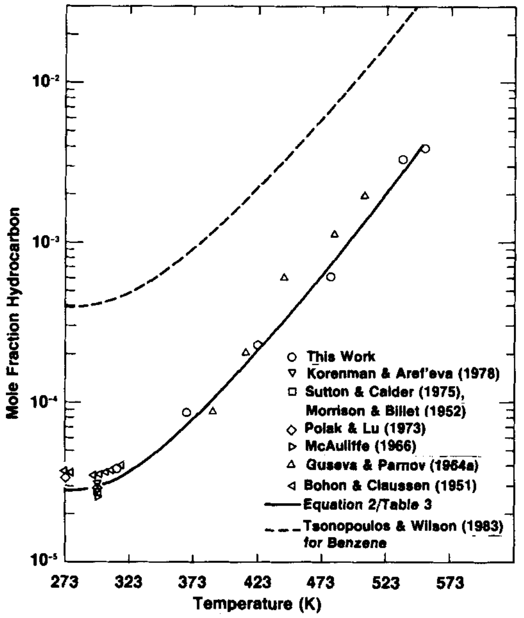

Figure 3. Solubility of ethylbenzene in water at three-phase equilibrium pressure.

are in relatively good agreement with other measurements near 298 K and exhibit a temperature dependence that is in excellent agreement with calorimetric data, they appear to be high by about 15–20% when compared to more recent, well-regarded measurements. Also shown in Figure 3 is the solubility of benzene in water from Part I.

The observed minimum in the hydrocarbon solubility was examined at length by TW (1983). At the minimum, the heat of solution, $\Delta\bar{h}_i$, is zero since

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P \cong \frac{\Delta\bar{h}_i}{RT^2} \qquad (3)$$

Gill et al. (1976) measured the heat of solution of ethylbenzene in water from 288 to 308 K. These data are shown in Figure 6 and predict a minimum in the solubility, where $\Delta\bar{h}_i$ is zero, at about 292 K. In addition, Bohon and Claussen (1951) derived heats of solution from their solubility measurements from 280 to 308 K.

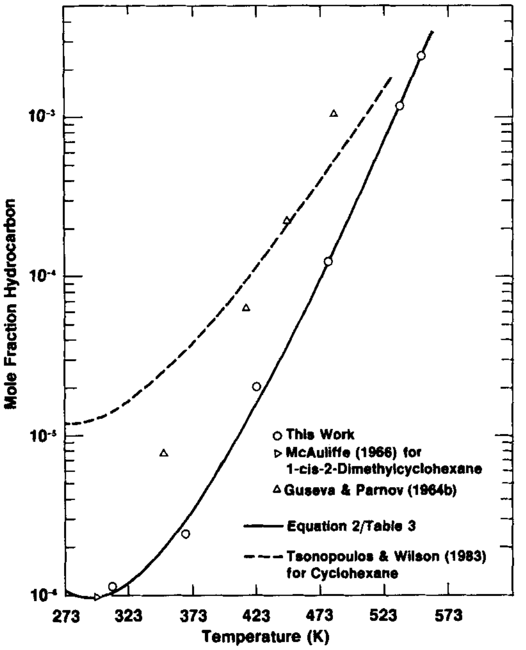

Figure 4. Solubility of ethylcyclohexane in water at three-phase equilibrium pressure.

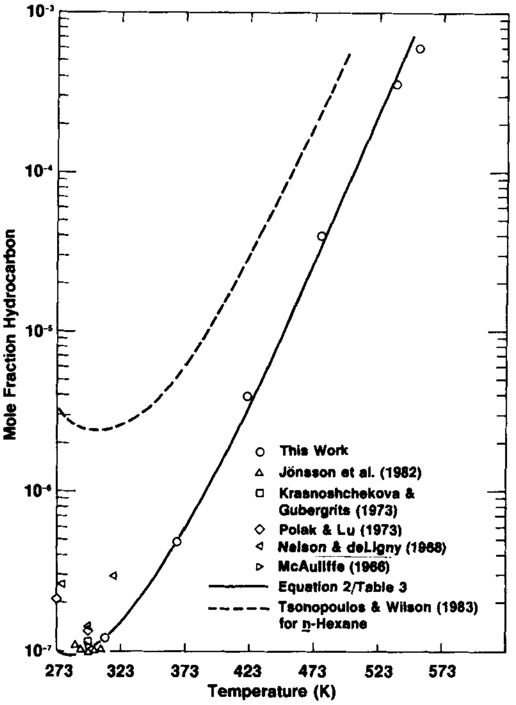

Figure 5. Solubility of *n*-octane in water at three-phase equilibrium pressure.

These are also shown in Figure 6 and are in excellent agreement with the calorimetric measurements of Gill et al. Equation 2, which emphasizes the high-temperature data, predicts a minimum in the solubility at a somewhat lower temperature, 279 K.

Ethylcyclohexane in Water

Figure 4 presents the solubility of ethylcyclohexane in water and shows that, as in the case of ethylbenzene, the solubility of the C_8 hydrocarbon is an order of magnitude less than the corresponding C_6 solubility. Again, only Guseva and Parnov (1964b) have measured the solubility of ethylcyclohexane in water at high temperatures, but these measurements are much higher than those obtained from this work. Furthermore, as shown in Figure 4, their high-temperature solubilities are of the same magnitude as those of cyclohexane in water, which is highly unlikely. Consequently, these data were not included in the final evaluation. Essentially no other literature information exists on ethylcyclohexane in water.

n-Octane in Water

Of the C_8 hydrocarbons examined in this work, *n*-octane is the least soluble in water and is more than an order of magnitude less soluble in water than *n*-hexane, as shown in Figure 5. Of the literature references, only Price (1976) and Guseva and Parnov (1965) measured the solubility of *n*-octane in water well above room temperature. However, Price's data are considerably lower than those obtained in this work as well as those reported by other investigators at near-ambient temperatures, while those of Guseva and Parnov are of very poor quality (as was the case for their *n*-hexane data; see TW, 1983). Consequently, the data from these two sources, which are not shown in Figure 5, were not included in our final analysis. In addition, low-temperature measurements shown in Figure 5 but not included in our analysis were the data of Nelson and de Ligny (1968) and Polak and Lu (1973). These data were much higher than other literature data in this temperature range and also exhibited excessive temperature dependence.

The temperature dependence of the solubility near 298 K appears to be well described by the measurements of Jönsson et al. (1982) from 288 to 308 K. The derived values of heats of solution

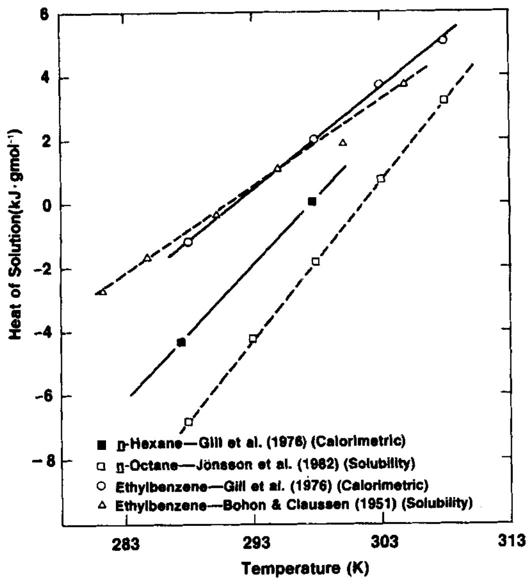

Figure 6. Heat of solution of hydrocarbons in water.

for n-octane in water are shown in Figure 6. Although somewhat displaced from the calorimetric measurements of Gill et al. (1976) on n-hexane in water (TW, 1983), the temperature dependence of the two data sets is nearly identical.

Henry's Constants

The Henry's constant, H_i, is frequently used to relate the volatility of a hydrocarbon to its solubility in water (TW, 1983):

$$y_iP \cong H_ix_i \cdot \left\{\frac{1}{\phi_i^V} \cdot \exp\left[\frac{v_i(P - P_w^s)}{RT}\right]\right\} \tag{4}$$

The terms within the brackets correct, respectively, for vapor-phase and liquid-phase non-idealities.

Henry's constants for ethylbenzene, ethylcyclohexane, and n-octane in water were derived as in Part I of this work (TW, 1983) and are presented in Figure 7. The temperature dependence of H_i is represented by a four-term equation:

$$\ln H_i = A + B/T + CT^2 + D\ln T \tag{5}$$

The coefficients for each hydrocarbon are listed in Table 4, along with the maximum values of H_i and the corresponding temperatures. Henry's constants are extremely large at nearly all temperatures investigated, even higher than those for the corresponding C_6 hydrocarbons. Thus, the soluble hydrocarbons can easily be removed from water by distillation.

VAPOR-LIQUID EQUILIBRIA OF WATER IN HYDROCARBONS

The solubility of water in the C_8 hydrocarbons investigated in this work is at least two orders of magnitude higher than the solubility of hydrocarbons in water. However, the solubility of water in the C_8 hydrocarbons is nearly identical to the solubility in the corresponding C_6 hydrocarbon, thus indicating a negligible carbon number effect. The solubility of water increases very rapidly with increasing temperature and reaches a very high value at the three-phase critical end point, T_{3c}. Unfortunately, there is little literature information available for the solubility of water at high temperatures, and no data were found on the volatility of water in these C_8 hydrocarbon systems.

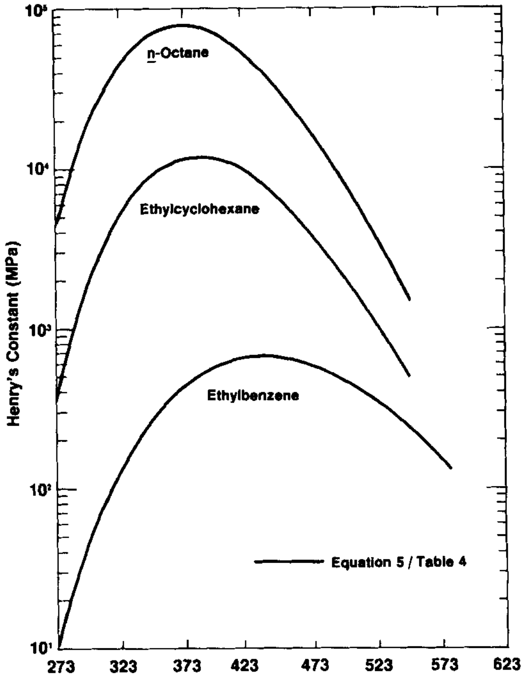

Figure 7. Henry's constants for C_8 hydrocarbons in water.

The water solubility and vapor-phase data obtained in this work suggest that the heat of solution for water in hydrocarbons approaches an infinite value as the temperature approaches T_{3c}. That is,

$$\lim_{T\to T_{3c}} \left(\frac{\partial \ln x_w}{\partial T}\right) \cong \lim_{T\to T_{3c}} \left(\frac{\Delta \bar{h}}{RT^2}\right) \to +\infty$$

Accordingly, the analysis of the water solubility data was carried out with an equation that was capable of reproducing this behavior:

$$\ln x_w = A + B\left(\frac{1}{T_r} - 1\right) + C(1 - T_r)^{1/3} + D(1 - T_r) \tag{6}$$

where $T_r = T/T_{3c}$. Solubility data from 273 K up to and including T_{3c} were incorporated in the final data analysis. Values of the four constants for the three C_8 hydrocarbon systems investigated are shown in Table 5, along with comparisons between predicted and observed solubilities at T_{3c}.

As discussed in Part I (TW, 1983), the high solubility of water in hydrocarbons means that its volatility in these systems cannot be accurately represented by Henry's constants. Furthermore, the availability of both water solubility and vapor-phase compositions at three-phase equilibrium conditions facilitates the evaluation of such data with an appropriate VLE (vapor-liquid equilibrium) model. In Part I, this evaluation was performed (using only water solubility information) with RKJZ, a modified Redlich-Kwong equation of state. This approach has been pursued in this work, but has been extended to include vapor-phase information in the data evaluation. Furthermore, the Soave (1972) and Peng-Robinson

TABLE 4. HENRY'S CONSTANTS FOR HYDROCARBONS IN WATER

$\ln H\ (\text{MPa}) = A + B/T + CT^2 + D\ln T;\ T\ (\text{K})$

					Maximum H	
	A	B	$C \times 10^6$	D	T(K)	H (MPa)
Ethylbenzene	146.152	−10,780.8	−16.9701	−18.3797	434.8	6.614×10^2
Ethylcyclohexane	325.570	−18,496.5	−10.9666	−44.7690	385.2	1.186×10^4
n-Octane	357.733	−19,363.1	−9.04865	−49.5296	372.1	7.836×10^4

TABLE 5. SOLUBILITY OF WATER IN HYDROCARBONS

$$\ln x_w = A + B\left(\frac{1}{T_r} - 1\right) + C(1 - T_r)^{1/3} + D(1 - T_r);\ T_r = T/T_{3c}$$

	A	B	C	D	Solubility at T_{3c}		
					T_{3c} (K)	Predicted x_w	Observed x_w
Ethylbenzene	−0.37215	−4.4626	−0.38596	−2.59850	568.1	0.689	0.691
Ethylcyclohexane	−0.50980	−7.4603	−1.05371	0.44796	561.4	0.601	0.603
n-Octane	−0.66037	−7.1130	−0.67885	−1.43381	539.1	0.517	0.527

(1976) modifications of the Redlich-Kwong equation of state, which will be referred to as RKS and P-R, respectively, were also used to evaluate the water solubility and volatility in the C_8 hydrocarbon systems. These equations are described briefly in the next section.

Modifications of the Redlich-Kwong Equations of State

The R-K (Redlich-Kwong) equation of state can be written in the form suggested by Soave (1972):

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{7}$$

where

$$a = 0.42748\ldots\left(\frac{R^2T_c^2}{P_c}\right)(\alpha) \tag{8}$$

$$b = 0.08664\ldots\left(\frac{RT_c}{P_c}\right) \tag{9}$$

The α term in Eq. 8 introduces temperature dependence in a and is given by

$$\alpha = 1/T_r^{0.5} \tag{10}$$

in the original equation proposed by Redlich and Kwong (1949). However, in its original form, the R-K equation was unsatisfactory for VLE calculations.

In 1972, Soave recommended the generalized relationship

$$\alpha = [1 + m(1 - T_r^{0.5})]^2 \tag{11}$$

where

$$m = 0.480 + 1.574\,\omega - 0.176\,\omega^2 \tag{12}$$

Soave demonstrated that Eq. 11, developed from pure-component vapor pressure data for hydrocarbons and nonpolar gases, resulted in a modified R-K equation that was capable of accurately predicting the VLE behavior of nonpolar systems. Later, Graboski and Daubert (1978) modified Eq. 12 to:

$$m = 0.48508 + 1.55171\,\omega - 0.15613\,\omega^2 \tag{13}$$

in order to improve pure-component vapor pressure predictions.

Peng and Robinson (1976) proposed a modified R-K equation of state capable of predicting the liquid density as well as vapor pressure in order to further improve VLE predictions. Their equation is given by:

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

$$a = 0.45724\ldots\left(\frac{R^2T_c^2}{P_c}\right)(\alpha) \tag{15}$$

$$b = 0.07780\ldots\left(\frac{RT_c}{P_c}\right) \tag{16}$$

The additional $b(v - b)$ volume term in Eq. 14 greatly improves the prediction of liquid density without making b a function of temperature. The temperature dependence of α as obtained from vapor pressure data is given by Eq. 11, but with

$$m = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2 \tag{17}$$

Previous to both Soave and Peng and Robinson, Zudkevitch and Joffe (1970) proposed that the R-K equation be modified such that both a and b in Eq. 7 are functions of temperature. In the form recommended by Joffe et al. (1970) and Gray (1977), the RKJZ parameters a and b are determined by simultaneously matching liquid density and equating the vapor and liquid fugacities at the pure component's vapor pressure. Above the critical temperature, a and b are set equal to their respective values at the critical temperature. The RKJZ equation of state has been successfully applied to a wide variety of systems, including those containing hydrogen (Gray et al., 1983) and water (TW, 1983).

Mixing Rules for Equations of State

The mixing rules in the cubic equations of state provide formulas for predicting the a and b of mixtures. The most common set of mixing rules is

$$a_m = \sum_i \sum_j z_i z_j a_{ij} \tag{18}$$

$$a_{ij} = (a_i a_j)^{0.5}(1 - C_{ij}) \tag{19}$$

$$b_m = \sum_i z_i b_i \tag{20}$$

$C_{ij} = 0$ is a reasonable assumption for most hydrocarbon/hydrocarbon binaries, especially at or above ambient temperature. However, non-zero C_{ij}'s are required when the components are very different in molecular size; for example, for H_2/hydrocarbon mixtures. Non-zero C_{ij}'s may also be required at very low temperatures, for calculations in the critical region, or for polar mixtures such as the water/hydrocarbon systems.

Although the use of only one binary constant (C_{ij}) was shown to satisfactorily correlate the solubility of water in C_6 hydrocarbon systems (TW, 1983) to within 20 K of T_{3c}, it is tempting to consider what a second binary constant will do. This is typically accomplished by replacing Eq. 20 with:

$$b_m = \sum_i \sum_j z_i z_j b_{ij} \tag{21}$$

$$b_{ij} = 0.5(b_i + b_j)(1 + D_{ij}) \tag{22}$$

Setting $D_{ij} = 0$ in Eq. 22 results in the original mixing rule, Eq. 20. A non-zero D_{ij} has been found to help in fitting VLE data for nonhydrocarbon-containing binaries (e.g., H_2 binaries; Gray et al., 1983). Thus, the first step in the data analysis is to determine optimum C_{ij}'s (and D_{ij}'s) by regressing the binary vapor-liquid (hydrocarbon-rich) equilibrium data at P_3. The mixing rules defined by Eqs. 18 and 21 were employed for all three equations of state.

Water in Ethylbenzene

Figure 8 presents the VLE data for water in ethylbenzene at the three-phase equilibrium pressure up to T_{3c}. The high-temperature water solubilities obtained in this work appear to be consistent with most low-temperature measurements available in the literature. However, the low-temperature solubilities of Filippov and Furman (1952) exhibit a much stronger temperature dependence than other available data in this range, and thus were not included in the final data analysis. Also shown in Figure 8 is the water concentration in the vapor-phase, y_w, at P_3. These new measurements establish that

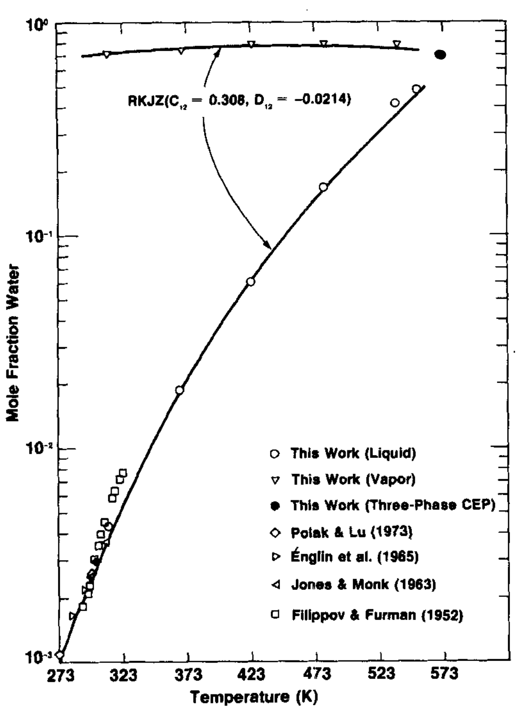

Figure 8. VLE and solubility of water in ethylbenzene at three-phase equilibrium pressure.

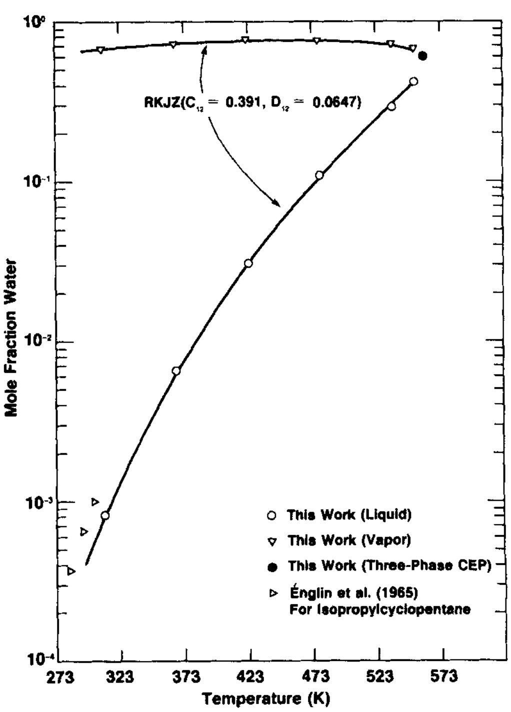

Figure 9. VLE and solubility of water in ethylcyclohexane at three-phase equilibrium pressure.

y_w can be estimated to within 2–3% from the pure-component vapor pressures according to:

$$y_w \cong \frac{P_w^s}{P_w^s + P_{hc}^s} \tag{23}$$

up to about 423 K. This observation is similar to that previously discussed for the estimation of P_3 from the sum of component vapor pressures.

The curves shown in Figure 8 demonstrate that the RKJZ equation of state can correlate the VLE behavior very accurately up to within 10 K of T_{3c} when both C_{ij} (0.308) and D_{ij} (−0.0214) are used. Table 6 summarizes the data analyses for all equations of state using only C_{ij} or both C_{ij} and D_{ij}. These results show that RKJZ correlates these data more accurately than either the RKS or P-R equation. Furthermore, significant improvement is gained by the addition of the second interaction parameter, D_{ij}. Much of this improvement is obtained in the region just below T_{3c}, as will be discussed later. Finally, the similar deviations in the water K-value (y_w/x_w) and the water solubility (x_w) suggest that essentially all of the error in the correlated K-values is due to errors in the predicted liquid-phase composition.

Water in Ethylcyclohexane

Figure 9 presents the VLE and solubility data for water in ethylcyclohexane at P_3. Unfortunately, no literature data were found for comparison. Énglin et al. (1965) report low-temperature solubilities in another C_8 naphthene (isopropylcyclopentane) which, although higher by nearly 50%, exhibit a temperature dependence similar to that for water in ethylcyclohexane. (Clearly, more experimental data are needed.) Finally, as for water in ethylbenzene, the water content in the vapor at P_3 can be estimated to within 2–3% by Eq. 23 up to about 423 K.

Figure 9 also demonstrates that the VLE behavior is accurately correlated by the RKJZ equation of state to within 5 K of T_{3c} using both C_{ij} (0.391) and D_{ij} (0.0647). In addition, Table 6 shows that, although slightly less accurate than RKJZ, the RKS and P-R equations of state correlate these data very well.

Water in *n*-Octane

Figure 10 shows VLE and solubility data for water in n-octane at P_3. Although no high-temperature solubility data could be found in the literature, the data obtained in this work appear to be consistent with the low-temperature measurements of Polak and Lu (1973). However, the data of Énglin et al. (1965) and, particularly, Black et al. (1948) are much higher and are probably in error; see TW (1983). Data from these two sources were omitted from further analyses.

Figure 10 also shows that the VLE data are well correlated by RKJZ to within 10 K of T_{3c} using both C_{ij} (0.330) and D_{ij} (0.0984). Furthermore, Table 6 shows that both RKS and P-R are also capable of accurately correlating these data with either C_{ij} or C_{ij} and D_{ij}.

TABLE 6. ANALYSIS OF VAPOR-LIQUID EQUILIBRIA OF WATER IN HYDROCARBONS AT THREE-PHASE EQUILIBRIUM PRESSURE WITH CUBIC EQUATIONS OF STATE

	RKJZ				RKS			P-R		
			AAD(%)[a]				AAD(%)[b]			AAD(%)[b]
	C_{ij}	D_{ij}	(y_i/x_i)	x_w	C_{ij}	D_{ij}	(y_i/x_i)	C_{ij}	D_{ij}	(y_i/x_i)
Ethylbenzene	0.284	—	4.35/2.70	4.15	0.324	—	8.06/12.60	0.305	—	6.54/13.61
	0.308	−0.0214	3.82/1.90	3.96	0.387	−0.0574	4.45/10.78	0.348	−0.0385	4.08/12.28
Ethylcyclohexane	0.465	—	5.56/2.24	5.02	0.507	—	3.75/10.31	0.481	—	5.46/12.61
	0.391	0.0647	0.84/1.66	0.80	0.537	−0.0264	1.92/4.37	0.508	−0.0239	4.30/6.97
n-Octane	0.450	—	7.07/1.44	6.64	0.495	—	1.77/2.84	0.467	—	4.10/3.99
	0.330	0.0984	1.16/2.01	1.13	0.451	0.0365	1.54/3.86	0.367	0.0822	2.65/6.52

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[a] AAD (absolute average deviation) is given by $\Sigma|(K_{calc} - K_{expt})/K_{expt}| \cdot 100/n$ for the K-values (y_i/x_i) of water/hydrocarbon, respectively, or, similarly, for the solubility of water in hydrocarbon (x_w).

[b] The AAD values for the solubility of water in hydrocarbon predicted by RKS and P-R are nearly identical to those for the water K-value (y_w/x_w).

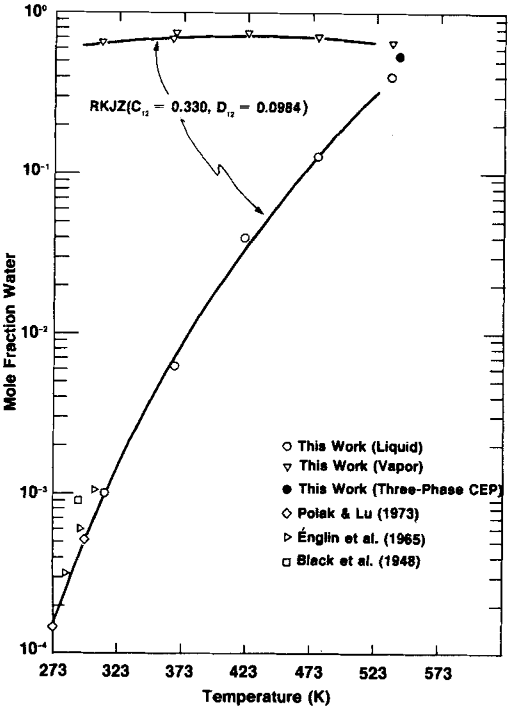

Figure 10. VLE and solubility of water in *n*-octane at three-phase equilibrium pressure.

VLE Behavior Near Three-Phase CEP

As the temperature approaches T_{3c} at the three-phase equilibrium pressure, the water concentrations of the hydrocarbon-rich liquid and vapor phases converge until, at T_{3c}, the compositions of both phases are identical. This behavior is clearly illustrated in Figure 11 for water in ethylcyclohexane. Also shown are the compositions predicted by the RKJZ equation using either only a single interaction parameter ($C_{ij} = 0.465$) or both C_{ij} (0.391) and D_{ij} (0.0647). Up to about 473 K, the predictions obtained from either one or two parameters are very similar (although addition of the D_{ij} term improves the temperature dependence and reduces the average deviation by about a factor of two). However, as the temperature approaches T_{3c}, the two approaches diverge and that with the single interaction parameter increasingly underpredicts the water solubility while overpredicting the vapor-phase water concentration. Furthermore, errors in the predicted water solubility in this region can easily exceed 20% when only C_{ij} is used. (These errors are usually larger for the RKS and P-R equations of state.)

As shown in Figure 11, the use of both C_{ij} and D_{ij} greatly improves the prediction of the water solubility in the CEP region. Errors in solubility predictions are reduced to about 1–2% up to within 5 K of T_{3c}, while the accuracy in the vapor concentration predictions is not significantly affected. In addition, there appears to be a remarkable intercorrelation between C_{ij} and D_{ij}. For the three C_8 hydrocarbon systems examined, the sum of the optimum C_{ij} and D_{ij} parameter values is nearly equal to the optimum value of C_{ij} when only C_{ij} is used. This is true for all of the equations of state evaluated in this work and suggests that, for hydrocarbon/water systems, generalizing the equation of state approach with two interaction parameters may be only marginally more difficult than a single-parameter generalization. Finally, no temperature dependence in either C_{ij} or D_{ij} is needed to correlate the VLE behavior of water in hydrocarbons up to T_{3c}, which further simplifies any effort to generalize the equation of state approach. Such an effort will be discussed in a future paper.

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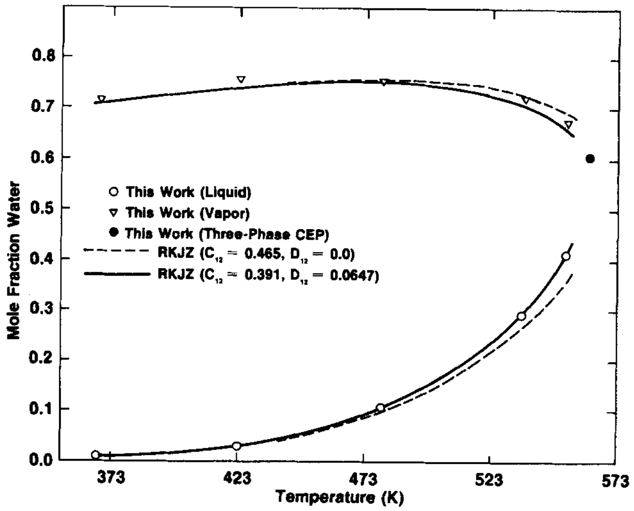

Figure 11. VLE behavior of water in ethylcyclohexane near three-phase critical end point.

NOTATION

a,b = parameters in the RK, RKS, RKJZ, and Peng-Robinson equations of state
A,B,C,D = empirical constants in Eqs. 1, 2, 5, 6
C_{12},C_{ij} = characteristic binary constant; see Eq. 19
D_{12},D_{ij} = characteristic binary constant; see Eq. 22
$\bar{h}_i$ = partial molar enthalpy of component i
H_i = Henry's constant for component i (in water)
m = parameter in RKS and Peng-Robinson equations of state
P = pressure
R = gas constant
T = temperature (absolute)
v = molar volume
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

α = parameter in the RK, RKS, and Peng-Robinson equations of state
$\Delta\bar{h}_i$ = molar heat (enthalpy) of solution of component i
ϕ_i = fugacity coefficient of component i
ω = acentric factor

Subscripts

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

Superscripts

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

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