Mutual Solubilities of Hydrocarbons and Water: III. 1-Hexene, 1-Octene, $C_{10}-C_{12}$ Hydrocarbons

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This article completes the analysis of high-temperature mutual solubilities of hydrocarbons and water. Part I (Tsonopoulos and Wilson, 1983) presented benzene, cyclohexane, and n-hexane, while Part II (Heidman et al., 1985) extended the investigation to ethylbenzene, ethylcyclohexane, and n-octane. Part III presents experimental data up to the three-phase critical end point for C_6, C_8, and C_{10} 1-alkenes, n-decane, n-butylcyclohexane, m-diethylbenzene, p-diisopropylbenzene, cis-decalin, tetralin, 1-methylnaphthalene, and 1-ethylnaphthalene. The thermodynamic analysis of Henry's constants for hydrocarbons in water is extended to the critical temperature of water, while the solubility and volatility of water in hydrocarbons are successfully correlated with several modifications of the Redlich-Kwong equation of state.

Introduction

The importance of hydrocarbon/water mutual solubilities to the design and operation of process equipment in refineries and petrochemical plants was discussed in Part I (Tsonopoulos and Wilson, 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 for three C_6 hydrocarbons: benzene, cyclohexane, and *n*-hexane. Part II (Heidman et al., 1985) extended the investigation to C_8 hydrocarbons—ethylbenzene, ethylcyclohexane, and *n*-octane—to study the effect of carbon number, but also expanded the scope 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.

Part III widens both the carbon number range and the types of hydrocarbon families investigated. In addition to alkylbenzenes (*m*-diethylbenzene and *p*-diisopropylbenzene), alkylcyclohexanes (*n*-butylcyclohexane), and alkanes (*n*-decane), Part III presents data for linear 1-alkenes (C_6, C_8, C_{10}) and condensed two-ring hydrocarbons (*cis*-decalin, tetralin, 1-methylnaphthalene, and 1-ethylnaphthalene).

Hydrocarbons and Water at High Temperatures

The high-temperature phase equilibrium behavior of C_6-C_8 hydrocarbon/water binaries is illustrated by Figure 1 of Part I (benzene/water) or Part II (ethylbenzene/water). This is Type III phase behavior according to the classification of van Konynenburg and Scott (1980). This type of behavior is also exhibited by the binaries investigated in Part III, *except* for those with the two-ring hydrocarbons. An example of Type III behavior is given in Figure 1 for *n*-decane/water (Brunner, 1990). The critical solution point (square) is at 631.9 K and 24.0 MPa. Also plotted in Figure 1 are Wang and Chao's (1990) measurements on the lower branch of the gas–liquid critical curve.

Type II phase behavior is observed for the two-ring hydrocarbon/water binaries, as shown for tetralin/water in Figure 2. A similar *P-T* diagram also describes the binaries of water with 1-methylnaphthalene, 1-ethylnaphthalene, and, most likely, *cis*-decalin. What is different from Figure 1 is that the three-phase equilibrium curve is *intersected* by the liquid–liquid critical curve. At this intersection (open circle in Figure 2), the hydrocarbon-rich and water-rich liquid phases become completely miscible. This intersection thus differs from the three-phase critical end point described in Parts I and II, and shown in Figure 1, above which the hydrocarbon-rich liquid phase disappears. (Another difference of Type II from Type III is the continuous gas–liquid critical curve.)

Jockers et al. (1977) investigated the tetralin/water binary

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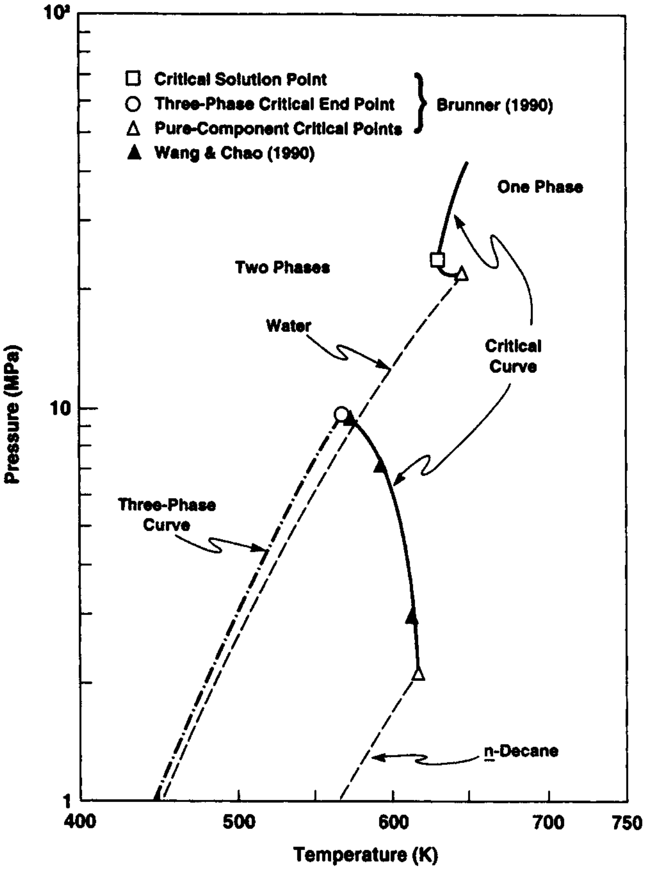

Figure 1. Pressure–temperature diagram for n-decane/water mixture (type III).

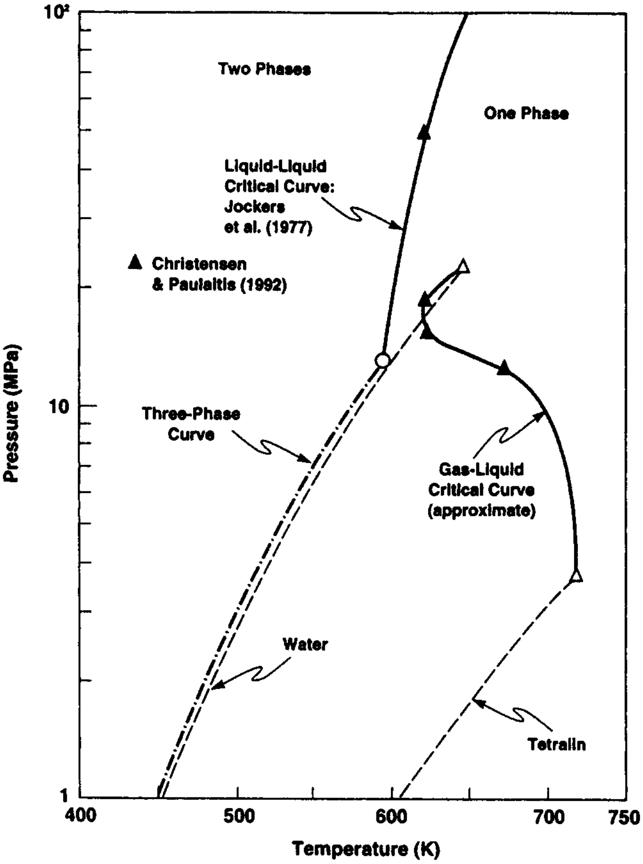

Figure 2. Pressure–temperature diagram for tetralin/water mixture (type II).

at 597–663 K at pressures up to 132 MPa. They located the three-phase critical end point (the open circle in Figure 2) at 597.2 K and 12.5 MPa, in very good agreement with our observation (see Table 1). Jockers et al. noted that the gas–liquid critical curve had not been investigated, but should run continuously from the critical point of water to that of tetralin. Christensen and Paulaitis (1992) recently confirmed this behavior (solid triangles in Figure 2) and also determined the three-phase critical end point. In addition, they investigated the 1-methylnaphthalene/water binary.

The three-phase critical temperature is the highest temperature of interest in this investigation. A point below the three-phase equilibrium curve represents equilibrium between the vapor and either of the two liquid phases, while a point above the curve represents equilibrium between the two 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. Because, as shown in Part I, mutual solubilities are very weakly pressure-dependent, solubilities at P moderately higher than P_3 are not too different from those at P_3. Both the vapor–liquid and liquid–liquid equilibrium behavior at P_3 are examined in this article.

Experimental Procedure

The experimental procedure was described in Parts I (supplementary section) and II. Most hydrocarbons were purchased from Aldrich. Phillips was the source of n-decane; Pfaltz and Bauer of n-butylcyclohexane and 1-ethylnaphthalene; and Eastman Kodak was the source of 1-methylnaphthalene. The water-free purity of all hydrocarbons was checked by gas chromatography and was found to always exceed 99%. Distilled water was used in all measurements.

Experimental Results

Table 1 presents all of our experimental results. The information given at each temperature is P_3, the mole fraction of hydrocarbon in water, and the mole fraction of water in the hydrocarbon and the vapor. Also reported in the table are the experimentally determined CEP (three-phase critical end point) conditions. These measurements, first reported by Wilson et al. (1985), were performed in a visual cell apparatus (Part II), thus permitting direct observation of the critical point phenomena. However, the three-phase equilibrium measurements were made earlier (Part I and Brady et al., 1982) in a windowless cell and, inadvertently, some measurements were above the CEP temperatures and thus did not represent three-phase equilibrium conditions. Experimental solubilities above the CEP were not used in the data analysis.

Literature CEP measurements are compared with our data in Table 2. The agreement is very good for the n-decane, tetralin, and 1-methylnaphthalene binaries, but a substantial disagreement exists for the *cis*-decalin binary. Our P_3 curve intersects with the liquid–liquid critical curve of Jockers et al. (1977) at 610 K and 16.3 MPa, which may be a good compromise for the CEP of *cis*-decalin/water. This may also ex-

Table 1. Measurements on Hydrocarbons/Water

T (K)	P_3 (MPa)	x_{hc}	x_w	y_w
1-*Hexene/Water*[*]				
310.9*3*	0.2068[**]	1.2×10^{-5}	1.437×10^{-3}	—
366.4*8*	—	2.4×10^{-5}	—	—
366.65	0.3184	—	1.016×10^{-2}	0.2519
420.37	1.2473	—	4.329×10^{-2}	0.3459
422.0*4*	—	8.5×10^{-5}	—	—
475.2*6*	3.923	—	0.1533	0.4106
477.59	—	4.4×10^{-4}	—	—
494.2*6*[†]	—	7.3×10^{-4}	—	—
496.2*6*[†]	5.378	—	0.2207	0.4353
493.32[††]	5.316	—	0.312	0.312
1-*Octene/Water*[*]				
310.9*3*	—	5.0×10^{-7}	1.68×10^{-3}	—
366.4*8*	0.124[‡]	1.8×10^{-6}	8.70×10^{-3}	0.630
422.0*4*	0.662	1.4×10^{-5}	4.51×10^{-2}	0.672
477.59	2.423	9.1×10^{-5}	0.156	0.706
533.1*5*	6.840	6.2×10^{-4}	0.419	0.650
549.8*2*[†]	9.260	9.8×10^{-4}	0.538	0.587
539.2*1*[††]	7.467	—	0.517	0.517
1-*Decene/Water*				
374.1*5*	0.121[‡]	5.1×10^{-7}	1.33×10^{-2}	—
424.6*5*	0.552	1.4×10^{-6}	4.22×10^{-2}	—
475.1*5*	1.84	4.3×10^{-6}	0.128	—
576.1*5*[†]	11.36	5.5×10^{-5}	0.593	—
568.98[††]	9.942	—	0.700	0.700
n-Decane/Water				
374.1*5*	0.124[‡]	1.2×10^{-7}	8.42×10^{-3}	—
424.6*5*	0.531	3.3×10^{-7}	3.76×10^{-2}	—
475.1*5*	1.779	1.4×10^{-6}	0.118	—
576.1*5*[†]	11.238	4.9×10^{-5}	0.595	—
566.7*1*[††]	9.639	—	0.706	0.706
n-Butylcyclohexane/Water[*]				
310.9*3*	—	—	7.39×10^{-4}	—
366.4*8*	—	1.9×10^{-7}	6.13×10^{-3}	—
422.0*4*	0.5068	2.0×10^{-6}	2.87×10^{-2}	0.9132
477.59	1.9023	1.6×10^{-5}	0.101	0.9024
533.1*5*	5.4220	1.96×10^{-4}	0.266	0.8796
549.8*2*	7.1078	4.23×10^{-4}	0.347	0.8649
584.32[††]	11.84*5*	—	0.750	0.750
m-Diethylbenzene/Water[*]				
310.9*3*	—	4.3×10^{-6}	3.42×10^{-3}	—
366.4*8*	—	1.0×10^{-5}	1.62×10^{-2}	—
422.0*4*	0.5081	4.3×10^{-5}	5.93×10^{-2}	0.9171
477.59	1.8912	2.70×10^{-4}	0.157	0.8963
533.1*5*	5.405	1.57×10^{-3}	0.367	0.8553
549.8*2*	7.074	3.07×10^{-3}	0.457	0.8422
582.54[††]	11.71*4*	—	0.776	0.776
p-Diisopropylbenzene/Water[*]				
310.9*3*	—	3.7×10^{-7}	3.45×10^{-3}	—
366.4*8*	—	1.2×10^{-6}	1.57×10^{-2}	—
422.0*4*	0.4757	7.4×10^{-6}	6.00×10^{-2}	0.9519
477.59	1.799*5*	5.8×10^{-5}	0.167	0.9405
533.1*5*	5.081	4.5×10^{-4}	0.374	0.9199
549.8*2*	7.460	7.1×10^{-4}	0.462	0.9035
589.98[††]	12.44*5*	—	0.833	0.833
cis-Decalin/Water				
374.1*5*	0.110	4.1×10^{-7}	9.7×10^{-3}	—
424.6*5*	0.5468	2.0×10^{-6}	2.53×10^{-2}	—
451.1*5*	—	—	4.05×10^{-2}	—
475.1*5*	1.689	7.7×10^{-6}	5.40×10^{-2}	—
576.1*5*	10.273	8.8×10^{-5}	0.309	—
599.09[††,‡‡,§]	14.43*8*	—	0.791	0.791
Tetralin/water				
374.1*5*	0.1124	9.2×10^{-6}	2.06×10^{-2}	—
424.6*5*	0.5068	1.71×10^{-5}	4.40×10^{-2}	—
475.1*5*	1.689	3.6×10^{-5}	0.120	—
576.1*5*	9.942	1.66×10^{-4}	0.547	—
595.92[††,‡‡]	13.162	0.061	0.939	0.939
1-*Methylnaphthalene/water*[*]				
310.9*3*	—	4.3×10^{-6}	5.16×10^{-3}	—
366.4*8*	—	1.8×10^{-5}	2.23×10^{-2}	—
422.0*4*	—	1.1×10^{-4}	6.57×10^{-2}	0.9830
477.9*8*	—	5.6×10^{-4}	0.148	0.9740
533.5*4*	4.895	3.1×10^{-3}	0.363	0.9600
550.4*8*	6.412	4.9×10^{-3}	0.443	0.9539
589.4*3*[††,‡‡]	11.27*3*	0.078	0.922	0.922
1-*Ethylnaphthalene/water*[*]				
310.9*3*	—	1.3×10^{-6}	4.91×10^{-3}	—
366.4*8*	—	5.5×10^{-6}	2.12×10^{-2}	—
422.0*4*	0.4668	2.4×10^{-5}	6.23×10^{-2}	0.9901
477.59	1.7326	1.5×10^{-4}	0.151	0.9834
533.1*5*	4.833	8.4×10^{-4}	0.325	0.9684
549.8*2*	6.343	1.49×10^{-3}	0.407	0.9645
594.4*3*[††,‡‡]	12.23*8*	0.073	0.927	0.927

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

[**] Cell pressurized with helium.

[†] Above three-phase critical end point; not used in the data regression.

[††] Measured three-phase critical end point.

[‡] Probably high due to inadequate degassing of cell.

[‡‡] Hydrocarbon and water become completely miscible in the liquid phase.

[§] Originally identified as Type III system.

plain why at 599.1 K we observed a behavior closer to Type III (hydrocarbon phase disappears) rather than Type II (hydrocarbon-rich and water-rich phases become completely miscible).

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 in Parts I and II that, at least

Table 2. Three-Phase Critical End Points

	T_{3c} (K)		P_{3c} (MPa)	
	Literature	Our Work	Literature	Our Work
n-Decane/water (Type III)	569.*3*[*] 567.6[**]	566.7	9.625[*] 9.655[**]	9.639
cis-Decalin/water (Type II)[†]	613.2[††]	599.1	18.0[††]	14.44
Tetralin/water (Type II)	597.2[††] 593.2[‡]	595.9	12.5[††] 13.0[‡]	13.16
1-Methylnaphthalene/water (Type II)	586.2[‡]	589.4	11.2*5*[‡]	11.27

[*] Roof (1970).

[**] Brunner (1990).

[†] Originally classified as Type III, but was changed to Type II in agreement with Jockers et al. (1977); see text.

[††] Jockers et al. (1977).

[‡] Christensen and Paulaitis (1992).

Table 3. Three-Phase Equilibrium Pressure
$\ln P_3$ (MPa) $= A + B/T + C \ln T$; T (K)

Hydrocarbon	A	B	C	Azeotropic T (K) Pred.	Azeotropic T (K) Obs.*	T_{3c} (K)**	P_{3c} (MPa) Pred.	P_{3c} (MPa) Obs.**
1-Butene†	−1.2305	−2308.02	1.36153	266.4	—	420.35	4.499	4.497
1-Hexene	2.6279	−3578.66	1.01502	331.1	330.9	493.32	5.301	5.316
1-Octene	26.4245	−5689.97	−2.20510	361.9	361.2	539.21	7.402	7.467
1-Decene	28.0120	−5972.36	−2.40186	371.2	369.9	568.98	9.761	9.942
n-Decane††	22.9179	−5691.36	−1.67619	372.4	370.4	566.71	9.472	9.639
n-Butylcyclohexane	29.1526	−6026.62	−2.57223	371.5	—	584.32	11.617	11.845
m-Diethylbenzene	28.7063	−6006.06	−2.50713	371.7	—	582.54	11.385	11.714
p-Diisopropylbenzene	24.6309	−5787.22	−1.92776	373.2‡‡	—	589.98	12.459	12.445
cis-Decalin	27.6600	−5946.94	−2.36028	372.1	—	599.09‡	13.991	14.438
Tetralin	28.9594	−6009.38	−2.55411	372.6	372.3	595.92‡	12.860	13.162
1-Methylnaphthalene	31.9855	−6159.32	−2.99949	373.0	373.0	589.43‡	11.042	11.273
1-Ethylnaphthalene	28.6530	−5973.50	−2.52507	373.7‡‡	—	594.43‡	11.879	12.238

*The atmospheric azeotropic temperature was taken from Horsley (1973).
**The T_{3c} and observed P_{3c} values are from this work.
†Data of Leland et al. (1955); approximate CEP presented in their Figure 3.
††Included in the regression the data of Brunner (1990) and of Sultanov and Skripka (1972).
‡Upper critical solution temperature (two liquid phases become identical).
‡‡Should actually be less than 373.2 K.

up to 420 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 3. (Because of the limited data for P_3, we included in the regression the sum of the pure-component vapor pressures at 273.15, 298.15, and 323.15 K.) Also included in Table 3 are predictions for the atmospheric azeotropic temperature, given by Horsley (1973), and P_{3c}, the three-phase critical pressure. The predicted azeotropic temperatures are higher than Horsley's, especially for 1-decene and n-decane.

Solubility of Hydrocarbons in Water

As in Parts I and II, the temperature dependence of the solubility of hydrocarbons in water was expressed by

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

This equation is very satisfactory up to T_{3c}, except for the two-ring hydrocarbons. In the latter case, the hydrocarbon and water phases become completely miscible at T_{3c}, and therefore, a more elaborate equation would be required to fit the data up to T_{3c}. Values of A, B and C for all the hydrocarbons are in Table 4, which also includes the values for 1-butene (Leland et al., 1955). The data and their fit with Eq. 2 have been plotted in Figures 3 (1-alkenes), 4 (n-decane), 5 (one-ring compounds), and 6 (two-ring compounds).

Linear 1-alkenes

Figure 3 includes the new data for C_6, C_8, and C_{10}, along with the limited literature information for C_6 and C_8 (Budantseva et al., 1976; Leinonen and Mackay, 1973; McAuliffe, 1966). To provide a better picture of the carbon-number effect on solubility, Figure 3 includes the data of Leland et al. (1955) for 1-butene.

Both the data and the fit with Eq. 2 look very reasonable for C_4, C_6, and C_8, but it is clear from Figure 3 that the solubility of 1-decene does not follow the pattern established by the C_4–C_8 1-alkenes. Furthermore, extrapolation of Eq. 2 for 1-decene to 25°C gives 1.83×10^{-7}, which is much higher

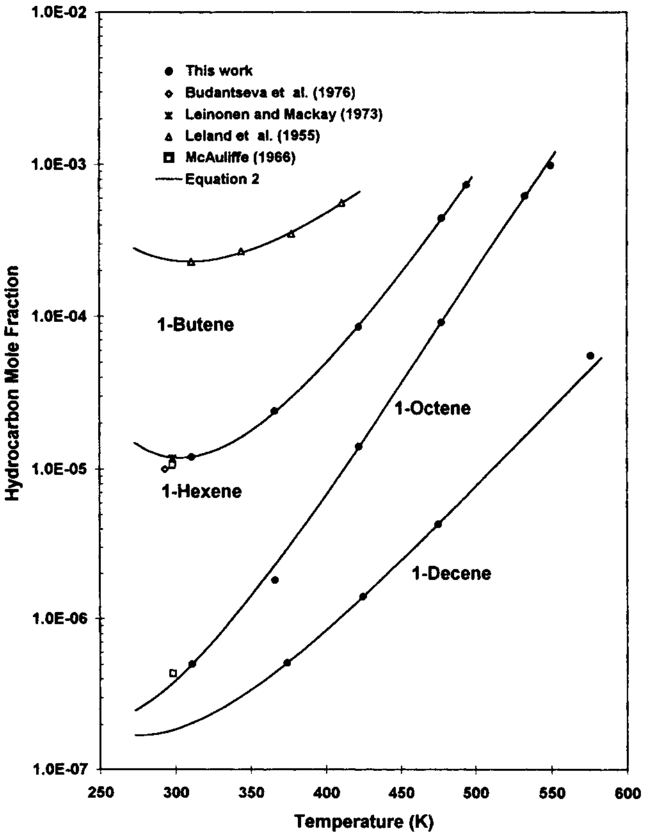

Figure 3. Solubility of linear 1-alkenes in water.

Table 4. Solubility of Hydrocarbons in Water
$\ln x_{hc} = A + B/T + C \ln T$; T (K)

Hydrocarbon	A	B	C	Solubility Minimum T (K)	Solubility Minimum x_{hc}	Solubility at T_{3c} T_{3c} (K)	Solubility at T_{3c} x_{hc}
1-Butene*	−170.9128	7473.51	24.13020	309.72	2.29×10^{-4}	420.35	6.36×10^{-4}
1-Hexene	−281.4372	12187.05	40.23222	302.92	1.19×10^{-5}	493.32	7.13×10^{-4}
1-Octene	−254.4458	9333.14	36.56667	(255.24)**	(2.45×10^{-7})**	539.21	8.02×10^{-4}
1-Decene	−186.3829	7103.48	25.80883	275.23	1.70×10^{-7}	568.95	3.82×10^{-5}
n-Decane	−365.2269	17208.95	51.19221	336.16	9.04×10^{-8}	566.71	3.33×10^{-5}
n-Butylcyclohexane	−301.0275	10936.28	43.31810	(252.46)**	(1.37×10^{-8})**	584.32	1.74×10^{-3}
m-Diethylbenzene	−287.2094	12083.60	41.11488	293.90	4.00×10^{-6}	582.54	9.36×10^{-3}
p-Diisopropylbenzene	−284.4905	11120.71	40.74943	(272.90)**	(2.57×10^{-7})**	589.98	3.50×10^{-3}
cis-Decalin††	—	—	—	—	—	599.09†	—
Tetralin††	—	—	—	—	—	595.92†	—
1-Methylnaphthalene	−196.2275	6610.86	28.35188	(233.17)**	(1.66×10^{-6})**	589.43†	—
1-Ethylnaphthalene	−227.7684	8347.76	32.6578	(255.61)**	(7.78×10^{-7})**	594.43†	—

*Data of Leland et al. (1955); approximate CEP presented in their Figure 3.
**Temperature lower than water freezing point (273.15 K).
†Upper critical solution temperature (two liquid phases become identical); Eq. 2 is not applicable at T_{3c}.
††Correlation not presented due to significant uncertainties at high temperature; see text and Figure 6.

than the value $2.5\ (\pm 0.5)\times10^{-8}$ that was obtained by extrapolating literature data at 25°C for C_4–C_8 1-alkenes.

Natarajan and Venkatachalam (1972) measured the solubility of C_6, C_7, C_8, and C_{10} 1-alkenes in 0.001 M aqueous HNO_3. These data were not included in our analysis. The reported solubility at 25°C for 1-decene is 7.39×10^{-7} (mole fraction), which is higher than McAuliffe's (1966) value for 1-octene (see Figure 3).

Guerrant (1964) reported mutual solubilities of 1-hexene/water at 555.4 K (540°F), which is considerably above the T_{3c} (493.3 K). The solubility of 1-hexene (1.11 wt. % or $x_{hc} = 2.4\times10^{-3}$) is about one-half that determined with Eq. 2 and the parameters in Table 4. His data for 1-hexene/water were not included in our analysis.

n-Decane

Figure 4 includes all known data for the solubility of *n*-decane in water. The literature data are those of Becke and Quitzsch (1977) at 20°C; Baker (1959), Franks (1966), Krasnoshchekova and Gubergrits (1973), McAuliffe (1969) at 25°C; and the high-temperature data of Guerrant (1964).

The literature data for *n*-decane at 25°C cover the range of 1.1 to 6.6×10^{-9}. Extrapolation of C_9-normal alkane data gives 3.0×10^{-9}, which is very close to the numerical average of the four experimental values. The new measurements are much higher (when extrapolated) than the literature data at 20 and 25°C, but are much lower than Guerrant's (1964) high-temperature data, two of which are at $T > T_{3c}$. The fit in Figure 4 (with Eq. 2 and the parameters in Table 4) was based entirely on the new measurements. It is consistent with the fit for 1-decene (see Figure 3), but is clearly inconsistent even with the highest literature value at 25°C: 6.58×10^{-9} (McAuliffe, 1969). Interestingly, perhaps, the only literature value that is close to the curve in Figure 4 is one of the two approximate values of Mackay et al. (1975) reported but rejected by Shaw (1989): 1.6×10^{-7}, probably at 25°C.

One-ring hydrocarbons

Figure 5 is a plot of the solubility data for *n*-butylcyclohexane, *m*-diethylbenzene, and *p*-diisopropylbenzene in water. The only known literature data are Guerrant's (1964) data for *m*-diethylbenzene. As in every other case, Guerrant's data for the solubility of hydrocarbons were not used in the data regressions summarized in Table 4 and illustrated in Figure 5.

Two-ring hydrocarbons

The solubility of two-ring hydrocarbons in water cannot be adequately represented by Eq. 2 up to the CEP because, at

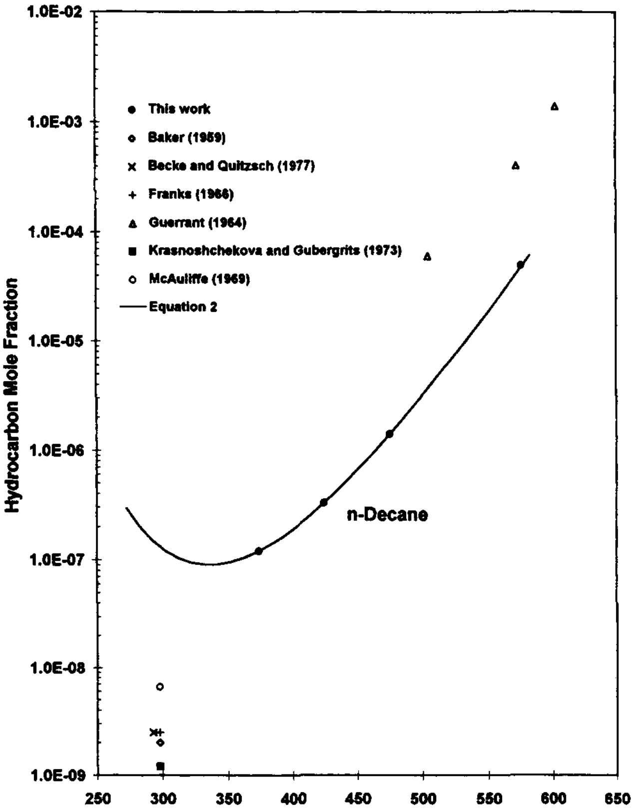

Figure 4. Solubility of *n*-decane in water.

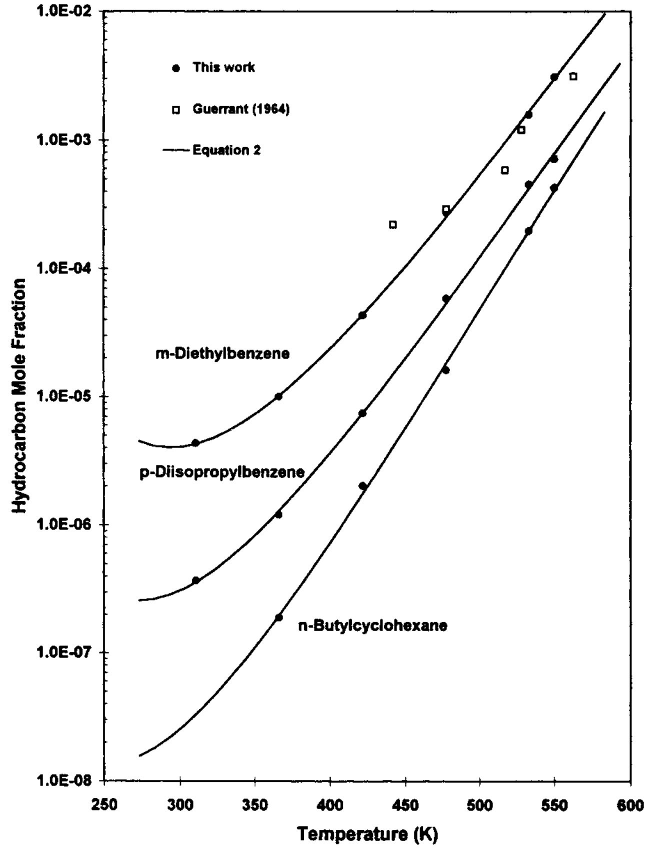

Figure 5. Solubility of one-ring hydrocarbons in water.

that point, the solubility is fairly substantial. However, Eq. 2 is probably satisfactory up to within a few degrees of T_{3c}.

Figure 6 indicates that the solubility of *cis*-decalin and tetralin increases much less rapidly with temperature than that for the two alkylnaphthalenes. This difference may be real, but it should also be noted that *cis*-decalin and tetralin were investigated together with 1-decene and *n*-decane. The solubility of all four hydrocarbons exhibits a relatively flat dependence on temperature; that is, the heat of solution (above the minimum) appears to be significantly smaller than that of the other hydrocarbons.

For both *cis*-decalin and tetralin, our measurements are consistent with the low-temperature literature data (Burris, 1985; Deno and Berkheimer, 1960; Price, 1976), but are *much* lower than the high-temperature literature data (Christensen and Paulaitis, 1992; Guerrant, 1964). In view of these significant discrepancies, we ignored the high-temperature literature data in the regression, but consider our results to be tentative. Additional high-temperature data are needed for the solubility of *cis*-decalin and tetralin in water to resolve the discrepancies illustrated in Figure 6.

The solubility of 1-methylnaphthalene and 1-ethylnaphthalene in water is well established at room temperature (Almgren et al., 1979; Burris, 1985; Eganhouse and Calder, 1976; Mackay and Shiu, 1977; Schwarz, 1977). The new measurements indicate a very rapid increase in solubility at high temperatures. The solubility of 1-methylnaphthalene in water at 299.9°C reported by Christensen and Paulaitis (1992) is much higher than our data (possibly because it is close to the CEP) and was excluded from the analysis.

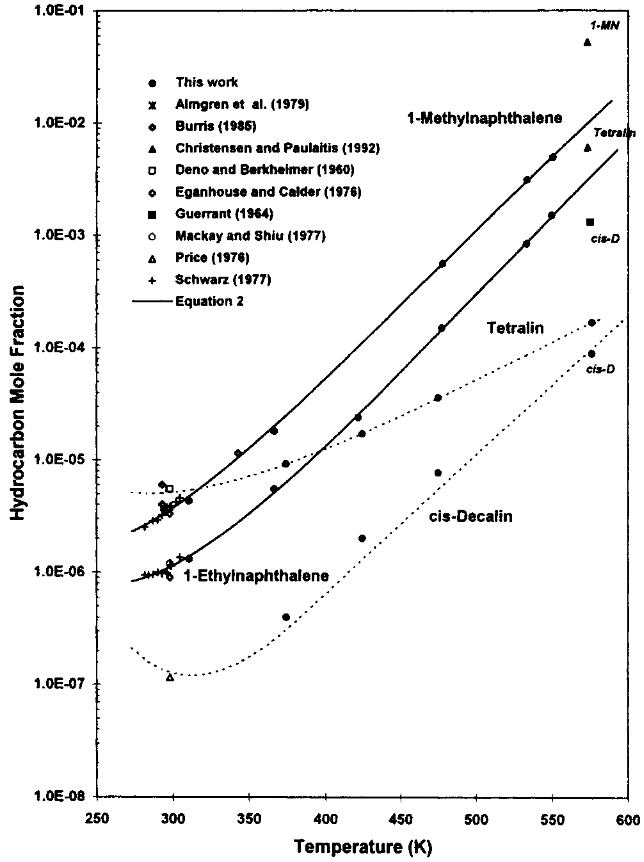

Figure 6. Solubility of two-ring hydrocarbons in water.

For *cis*-decalin and tetralin, the dashed line was drawn through the data measured in this work but further experimental data are needed.

Henry's constants

In view of the very low solubility of hydrocarbons in water, their volatility, that is, their partial pressure over the aqueous solution, can be expressed by Henry's law (Tsonopoulos and Wilson, 1983):

$$y_iP \cong H_ix_i\left\{\frac{1}{\phi_i^V}\exp\left[\frac{v_i(P-P_w^s)}{RT}\right]\right\}, \qquad (3)$$

where H_i is the Henry's constant and the terms within the braces correct, respectively, for vapor-phase and liquid-phase nonidealities due to compressibility.

A very useful characteristic of the temperature dependence of Henry's constants was first described by Beutier and Renon (1978), who showed for all solutes i in a solvent j:

$$H_{i,j} = \phi_i^\infty P_{c,j} \quad \text{at} \quad T_{c,j}, \qquad (4)$$

where ϕ_i^∞ is the fugacity coefficient of solute i at infinite dilution at the solvent critical point. This is extremely helpful in extrapolating Henry's constants (or solubilities) to high temperatures. Furthermore, Beutier and Renon (1978) demonstrated that

$$\lim_{T \to T_{c,j}} \frac{\partial(H_i/\phi_i^\infty)}{\partial T} = -\infty. \qquad (5)$$

An improved derivation of Eqs. 4 and 5 was proposed by Schotte (1985).

Harvey and Levelt Sengers (1990) correlated the Henry's constant for light gases in water from 0°C up to the water critical point using the expression:

$$T\ln\left(\frac{H_i}{P_w^s\phi_i^\infty}\right)=T\ln(K_i^\infty)=T\ln\left(\lim_{x_i\to 0}\frac{y_i}{x_i}\right)$$

$$=B(\rho_w^s-\rho_{c,w})+CT\rho_w^s\exp\left[\frac{273.15-T}{\tau}\right], \quad (6)$$

where ρ_w^s and $\rho_{c,w}$ are the saturated-liquid density and critical density of water; and B, C, and τ are parameters regressed from the experimental data. In this work, we used a modification of Eq. 6 that satisfies Eqs. 4 and 5 to correlate the Henry's constant for hydrocarbons in water over the entire temperature range:

$$T\ln\left(\frac{H_{hc}}{P_w^s\phi_{hc}^\infty}\right)=T\ln(K_{hc}^\infty)=T\ln\left(\lim_{x_{hc}\to 0}\frac{y_{hc}}{x_{hc}}\right)$$

$$=B(\rho_w^s-\rho_{c,w})+C(T-T_{c,w})\rho_w^s\exp\left[\frac{273.15-T}{\tau}\right], \quad (7)$$

where $T_{c,w}$ is the water critical temperature (647.3 K). Regressed parameters B, C, and τ for the hydrocarbons examined in this work are given in Table 5. In addition, Eq. 7 was used to correlate Henry's constants for hydrocarbons in water for the hydrocarbons examined in Parts I and II. In Figures 7 and 8, $T\ln(K_{hc}^\infty)$ is plotted as a function of temperature for different families of hydrocarbons. Included in Figure 7 are values for *n*-hexane (Tsonopoulos and Wilson, 1983) and *n*-octane (Heidman et al., 1985).

Because of the uncertainty in the experimental data for *cis*-decalin and tetralin solubility in water, the Henry's constants for these hydrocarbons in water are not included. Furthermore, Figure 7 indicates that the (K_{hc}^∞) values for *n*-decane and 1-decene are not consistent with those of the other components of their corresponding families. These observations are related to the problems, discussed previously, with our solubility data for these four hydrocarbons in water.

Vapor-Liquid Equilibria of Water in Hydrocarbons

The solubility of water in the 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 hydrocarbons exhibits 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 are relatively few literature data available for the solubility or volatility of water at high temperatures.

As noted in Part II, 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,

$$\lim_{T\to T_{3c}}\left(\frac{\partial\ln x_w}{\partial T}\right)\equiv\lim_{T\to T_{3c}}\left(\frac{\Delta\bar{h}_i}{RT^2}\right)\to+\infty. \quad (8)$$

Table 5. Henry's Constant for Hydrocarbons in Water $T\ln(K_{hc}^\infty)=T\ln(H_{hc}/P_w^s\phi_{hc}^\infty)=B(\rho_w^s-\rho_{c,w})+C(T-647.3)\rho_w^s\exp[(273.15-T)/\tau]$; $K(-)$, T (K), ρ (mol/L)

Hydrocarbon	B (L·K/mol)	C (L/mol)	τ (K)
1-Butene	119.986	0.04030	159.861
1-Hexene	124.870	0.04808	71.412
1-Octene	132.624	0.04389	80.930
1-Decene	224.608	0.23978	2,415.863
n-Hexane	138.816	0.05663	67.651
n-Octane	148.549	0.07751	57.221
n-Decane	214.105	0.23194	324.160
Cyclohexane	120.331	0.04250	127.090
Ethylcyclohexane	127.250	0.06922	55.116
n-Butylcyclohexane	140.768	0.06151	81.067
Benzene	80.311	0.02078	47.990
Ethylbenzene	95.848	0.05303	90.777
m-Diethylbenzene	101.205	0.06632	90.030
p-Diisopropylbenzene	114.481	0.07678	104.103
cis-Decalin*	—	—	—
Tetralin*	—	—	—
1-Methylnaphthalene	65.852	0.03510	70.763
1-Ethylnaphthalene	81.277	0.06513	105.738

*Henry's constants not determined (see also text).

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

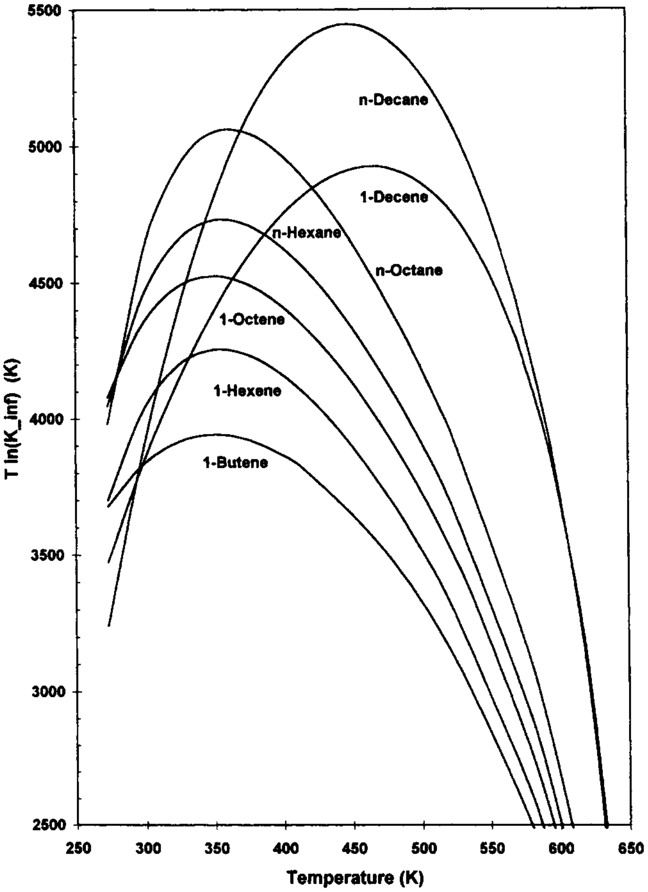

Figure 7. Henry's constant for *n*-alkanes and linear 1-alkenes in water.

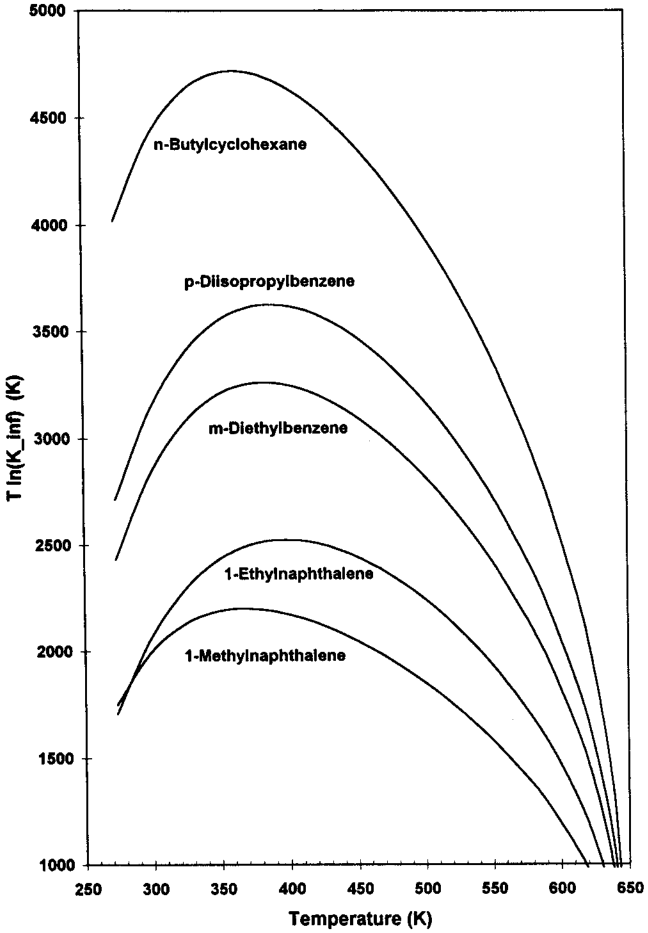

Figure 8. Henry's constant for one- and two-ring hydrocarbons in water.

$$\ln x_w = A + B(1/T_r - 1) + C(1 - T_r)^{1/3} + D(1 - T_r), \quad (9)$$

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 hydrocarbon systems investigated are shown in Table 6, along with comparisons between predicted and observed solubilities at T_{3c}.

As discussed in Part I, the high solubility of water in hydrocarbons means that its volatility in these systems cannot be represented accurately by Henry's law. 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 EoS (equation of state) proposed by Zudkevitch and Joffe (1970). This approach was extended in Part II to include vapor-phase information in the data evaluation. Furthermore, the Soave (1972) and Peng and Robinson (1976) modifications of the Redlich-Kwong EoS, which will be referred to as RKS and PR, respectively, were also used to evaluate the water solubility and volatility in the hydrocarbon systems. These equations were described in Part II. Only the mixing rules are discussed here.

Mixing rules for equations of state

The mixing rules in the cubic EoS provide formulas for predicting the a and b parameters of mixtures. The most common set of mixing rules used for these EoS parameters is often referred to as the van der Waals mixing rules:

$$a_m = \sum_i \sum_j z_i z_j a_{ij} \quad (10)$$

$$a_{ij} = (a_i a_j)^{0.5}(1 - C_{ij}) \quad (11)$$

$$b_m = \sum_i z_i b_i. \quad (12)$$

$C_{ij} = 0$ is a reasonable assumption for most hydrocarbon/hydrocarbon binaries, especially at or above ambient temperature. However, nonzero C_{ij} are required when the components are very different in molecular type or size, for example, for H_2/hydrocarbon mixtures. Nonzero C_{ij} 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 (Tsonopoulos and Wilson, 1983) to

Table 6. Solubility of Water in Hydrocarbons
$\ln x_w = A + B(1/T_r - 1) + C(1 - T_r)^{1/3} + D(1 - T_r)$; $T_r = T/T_{3c}$

						Solubility at T_{3c}	
Hydrocarbon	A	B	C	D	T_{3c} (K)	Pred. x_w	Obs. x_w
1-Butene*	−2.97639	−7.72697	−0.11404	−2.24872	420.35	0.0510	0.0514
1-Hexene	−1.16505	−7.93967	−1.28572	0.53914	493.32	0.312	0.312
1-Octene	−0.67479	−4.91952	−0.10000	−4.88719	539.21	0.501	0.517
1-Decene	−0.35073	−3.85350	−0.10000	−5.55748	568.98	0.700	0.700
n-Decane	−0.33494	−6.84452	−0.93296	−0.55233	566.71	0.715	0.706
n-Butylcyclohexane	−0.28919	−7.48699	−0.84473	0.67511	584.32	0.749	0.750
m-Diethylbenzene	−0.25546	−4.94353	−0.30200	−1.89054	582.54	0.775	0.776
p-Diisopropylbenzene	−0.18712	−4.79819	−0.11802	−2.34481	589.98	0.829	0.833
cis-Decalin	−0.20794	−7.23668	−2.86276	4.88165	599.09	0.812	0.791
Tetralin	−0.06902	−1.63345	−0.77109	−6.23732	595.92	0.933	0.939
1-Methylnaphthalene	−0.07871	−4.13940	−0.81054	−1.74710	589.43	0.924	0.922
1-Ethylnaphthalene	−0.07510	−4.62273	−0.98539	−0.52654	594.43	0.928	0.927

*Data of Leland et al. (1955) and Wehe and McKetta (1961); approximate CEP presented in Figure 3 of Leland et al. (1955).

Table 7. Liquid–Liquid Equilibrium Analysis of Water–Hydrocarbon Mixtures at Three-Phase Equilibrium Pressure with Cubic Equations of State

	RKJZ		RKS		PR	
Hydrocarbon	C_{ij}	% AAD*	C_{ij}	% AAD*	C_{ij}	% AAD*
1-Butene	0.372	8.5	0.387	20.7	0.383	19.3
1-Hexene	0.390	2.3	0.410	7.9	0.400	3.9
1-Octene	0.379	7.9	0.402	14.9	0.387	11.0
1-Decene	0.332	18.8	0.359	25.7	0.342	21.5
n-Decane	0.444	5.2	0.468	13.0	0.448	2.0
n-Butylcyclohexane	0.468	10.5	0.492	6.0	0.472	8.9
m-Diethylbenzene	0.291	5.7	0.315	11.2	0.300	6.8
p-Diisopropylbenzene	0.290	3.8	0.314	10.4	0.299	6.1
cis-Decalin	0.460	17.4	0.474	25.1	0.456	19.0
Tetralin	0.287	20.3	0.319	26.4	0.301	23.4
1-Methylnaphthalene	0.263	7.2	0.284	8.1	0.267	6.6
1-Ethylnaphthalene	0.268	4.8	0.287	11.3	0.271	6.3

*% AAD (average absolute deviation) of water solubility in hydrocarbon from fit of data with Eq. 9.

within 20 K of T_{3c}, a second binary constant was considered for the C_8 hydrocarbon systems (Heidman et al., 1985). This is typically accomplished by replacing Eq. 12 with

$$b_m = \sum_i \sum_j z_i z_j b_{ij} \qquad (13)$$

$$b_{ij} = 0.5(b_i + b_j)(1 + D_{ij}). \qquad (14)$$

(Setting $D_{ij} = 0$ in Eq. 14 results in the original mixing rule, Eq. 12.) However, the use of D_{ij} improves the prediction of the water solubility only close to T_{3c}. In this work, only C_{ij} was used.

The first step in the data analysis is to determine optimum C_{ij} by regressing the binary vapor–liquid (hydrocarbon-rich) or the liquid–liquid equilibrium data at P_3. Since we do not have experimental data for the vapor phase composition for many of the mixtures examined, C_{ij} were determined from the water solubility data. Experimental solubilities at the three-phase critical end point were not included in the regressions. The C_{ij} values obtained from the water solubility data are very similar to the values obtained from the vapor–liquid equilibrium data. In Part II, C_{ij} were determined using both vapor–liquid and water solubility data, and the values obtained from the two different analyses were very close. The C_{ij} parameters for the three cubic EoS for all the hydrocarbons examined in this work and the %AAD (average absolute deviation) of the water solubility in hydrocarbons are shown in Table 7.

Water in linear 1-alkenes

The solubility of water in 1-alkenes has a negligible dependence on the carbon number of the hydrocarbon. In Figure 9, experimental data are shown for water in 1-octene. The solubilities of water in 1-butene (Leland et al., 1955; Wehe and McKetta, 1961), 1-hexene and 1-decene are very similar, except as their T_{3c} is approached. The experimental data of Budantseva et al. (1976) for 1-hexene at 20°C, and those of Englin et al. (1965) for 1-hexene at 30°C (not shown here) and for 1-octene (shown in Figure 9) appear to be inconsistent with the new data. RKJZ is the most accurate EoS for the correlation of water solubility in all four 1-alkenes. In Figure 9, EoS predictions and experimental data are also shown for the vapor-phase composition. All three EoS give similar results except near the T_{3c}.

Water in n-decane

In Figure 10, experimental data and EoS correlations are shown for the solubility of water in *n*-decane. The data of Guerrant (1964) are consistently lower than our data. On the other hand, the data of Sultanov and Skripka (1972) (later

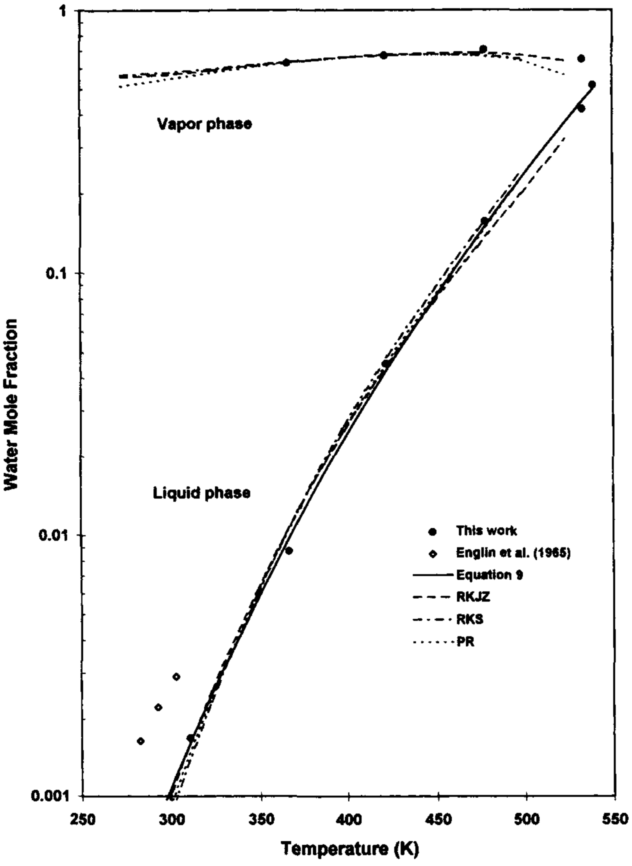

Figure 9. Vapor–liquid equilibria of water/1-octene mixture.

versions of the same data are reported on pages 304–306 of Shaw (1989), Vol. 38) are between our data and those of Guerrant (1964). The PR EoS is the most accurate of the three equations in correlating the experimental data. From the solubility data, we calculated the heat of solution of water in *n*-decane to be equal to 33.6 kJ/mol at 298.15 K and 33.8 kJ/mol at 313.14 K. The experimental values measured by Nilsson (1986) are 37.1 and 36.3 kJ/mol, respectively.

Water in one-ring hydrocarbons

Figure 11 shows experimental data and EoS correlations for the water solubility in *n*-butylcyclohexane and *m*-diethylbenzene. The water solubility in *p*-diisopropylbenzene is not shown because it essentially coincides with the water solubility in *m*-diethylbenzene. Again, the data of Guerrant (1964) for *m*-diethylbenzene are inconsistent with our data, while the low-temperature data of Englin et al. (1965) for water in diethylbenzene (unspecified isomer) are higher than our data. RKS is the most accurate EoS for the water solubility in *n*-butylcyclohexane, while RKJZ is the most accurate for the water solubility in *m*-diethylbenzene and *p*-diisopropylbenzene (not shown in Figure 11).

Water in two-ring hydrocarbons

Experimental data and their correlation with Eq. 9 are shown in Figure 12 for the water solubility in *cis*-decalin, tetralin, and 1-methylnaphthalene. The data for 1-ethylnaphthalene nearly coincide with those of 1-methylnaphthalene and are not shown for clarity. The limited data available in the literature for these hydrocarbons are those of Englin et al. (1965) for water in 1-methylnaphthalene and decalin at low temperature; Guerrant (1964) for water in *cis*-decalin at 574.8 K; and Christensen and Paulaitis (1992) at 573.15 K for water in tetralin and 1-methylnaphthalene.

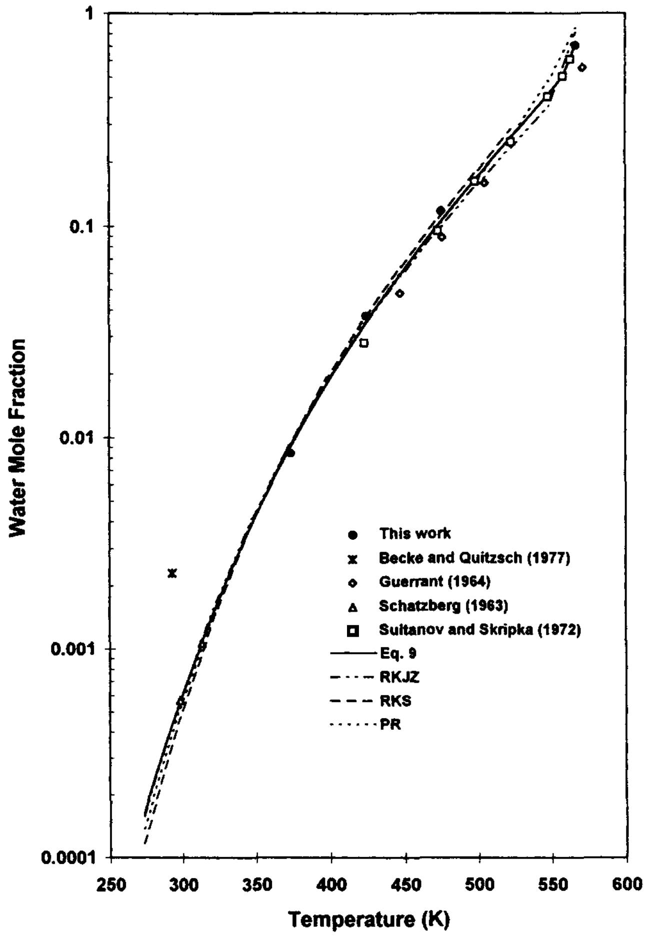

Figure 10. Solubility of water in n-decane.

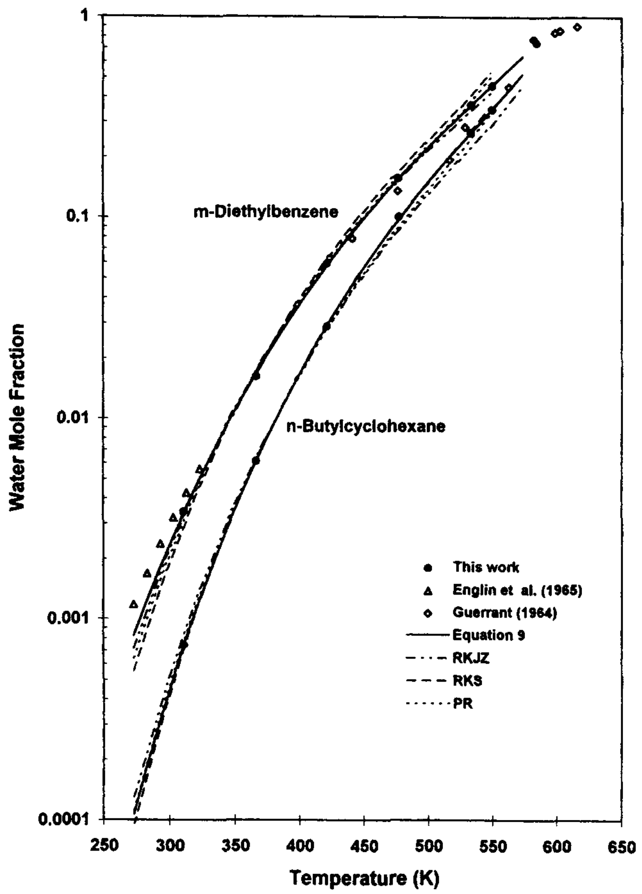

Figure 11. Solubility of water in *n*-butylcyclohexane and *m*-diethylbenzene.

Figure 12 shows that the temperature dependence of the water solubility in tetralin is not consistent with that in other two-ring hydrocarbons. Furthermore, all three cubic EoS exhibit considerable deviations in their correlation of water solubilities in *cis*-decalin and tetralin (Table 7). This poor representation is illustrated in Figure 12, which also shows the correlations with RKJZ for both *cis*-decalin and tetralin.

Considering also the apparent inconsistency of the experimental solubility of *cis*-decalin and tetralin in water (Figure 6), and the inability of Eq. 7 to represent their Henry's constants in water, we may conclude that our data for both these systems are in error. Finally, the EoS accurately correlate the solubility of water in the two alkylnaphthalenes, with PR being the most accurate for 1-methylnaphthalene and RKJZ the most accurate for 1-ethylnaphthalene.

VLLE of Water–Hydrocarbon Mixtures Using Elaborate Mixing Rules

Considerable effort has been devoted in the literature to-

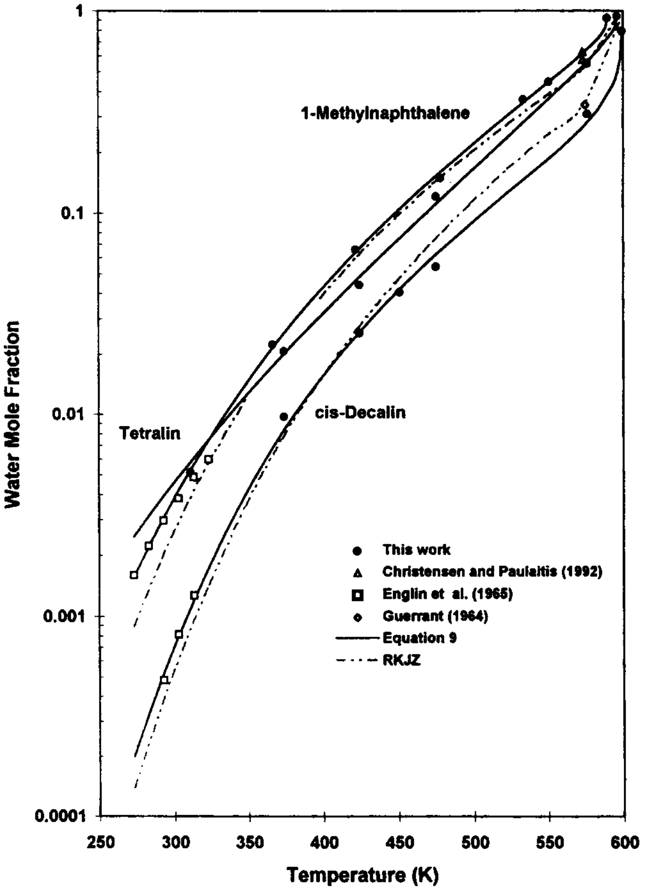

Figure 12. Solubility of water in two-ring hydrocarbons.

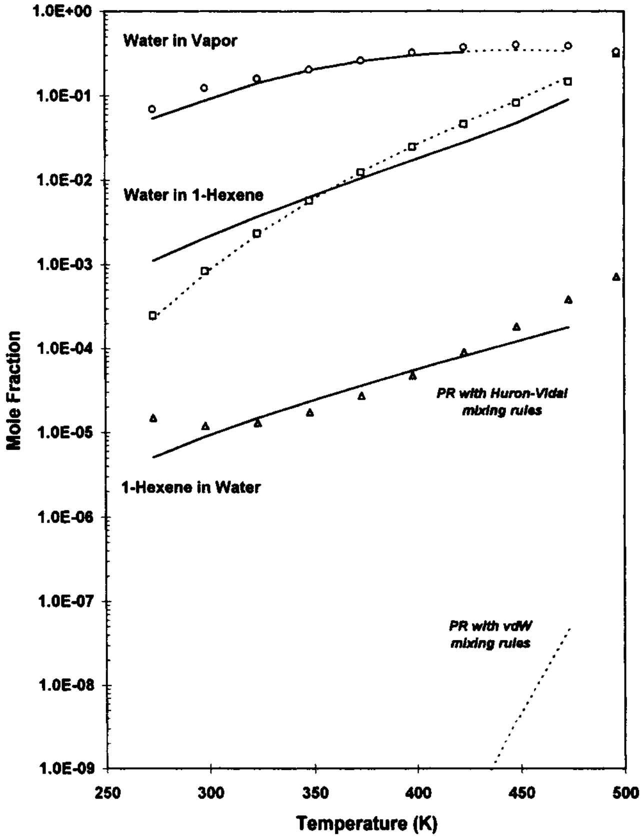

Figure 13. Vapor-liquid-liquid equilibria of water/1-hexene mixture.

ward the development of more elaborate mixing rules in order to accurately describe highly nonideal mixtures such as those examined in this work. For example, we attempted to use the PR EoS with the local composition mixing rules given by Huron and Vidal (1979) to correlate the experimental VLLE of water/1-hexene. As shown in Figure 13, these more elaborate mixing rules provide some qualitative improvement over the van der Waals mixing rules (Eqs. 10–12) of the solubility of 1-hexene in water. However, this improvement results in an inferior correlation of the water solubility in 1-hexene. In addition, the PR EoS with Huron–Vidal mixing rules predicts a somewhat lower three-phase critical end point than it does with the van der Waals mixing rules. This confirms the previous similar observations by Tsonopoulos and Heidman (1986) for the water/ethylbenzene mixture.

Many other mixing rules can be found in the literature. An example of an unconventional mixing rule is that proposed by Michel et al. (1989), who accounted for the hydrophobic effect by introducing a strong composition dependence in the water–water parameter a_{ii} in Eq. 11. The additional adjustable parameters enabled Michel et al. to fit simultaneously x_w and x_{hc}, but they found that for VLE calculations they also needed to introduce a density dependence.

Conclusions

New experimental data are reported for the mutual solubilities of water with 1-hexene, 1-octene, 1-decene, *n*-decane, *n*-butylcyclohexane, *m*-diethylbenzene, *p*-diisopropylbenzene, *cis*-decalin, tetralin, 1-methylnaphthalene, and 1-ethylnaphthalene from ambient temperatures up to the three-phase critical end point. Vapor-phase compositions are also reported. The new data are critically analyzed and compared with data available in the literature. In addition, the Henry's constants of hydrocarbons in water are evaluated and correlated using a modification of the expression proposed by Harvey and Levelt Sengers (1990) that satisfies the limiting behavior close to the water critical point. From the data analysis, we conclude that the mutual solubility data for water/tetralin and water/decalin are likely in error. Furthermore, the solubilities of *n*-decane and 1-decene in water do not follow the qualitative behavior of other hydrocarbons in their respective homologous series. Consequently, additional measurements for these hydrocarbons with water at moderate and high temperatures are needed.

The solubility of water and the VLE of water/hydrocarbon mixtures is correlated with the RKJZ, RKS, and PR EoS. Classical van der Waals mixing rules with one temperature-independent binary parameter (C_{ij}) provide quantitative agreement with the experimental data from ambient temperature up to within 20 K of the three-phase critical end point. The use of the more elaborate Huron–Vidal mixing rules appears not to improve the correlation of the VLLE of these mixtures. In a separate paper (Economou and Tsonopoulos, 1996), we examine the accuracy of higher order EoS for the correlation of water/hydrocarbon VLLE.

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