Solubilities of *n*-Alkanes (C_6 to C_8) in Water from 30 °C to 180 °C

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A solid-phase extraction method has been developed for measuring low solubilities of hydrocarbon in water. The solubilities of hexane, heptane, and octane in water were determined at temperatures ranging from (30 to 180) °C. The solubilities of alkanes in water at 30 °C decrease with increasing carbon number. At 30 °C, the mole fraction solubility is $(2.06 \pm 0.01) \times 10^{-6}$ for hexane and $(0.120 \pm 0.002) \times 10^{-6}$ for octane. The temperature effect on solubility in water is much more important for octane than for hexane. Increasing the temperature from (30 to 180) °C increases the solubilities by a factor of 23 for hexane and 110 for octane.

Introduction

Water is continuously present during the fluid reservoir formation and the exploitation of oil and gas reservoirs. Also, data concerning water−hydrocarbon systems are required for the design of a variety of chemical engineering separation operations, especially those concerned with water pollution abatement. Most of the time these processes are performed at high temperatures and pressures and it is necessary to have a correct knowledge of the water−hydrocarbon mutual solubilities.

There is a large amount of solubility data in the literature, and nearly all available data are at ambient conditions. For example, in the compilation of solubility data by Shaw,[1,2] few data are reported at temperatures above the normal boiling point of water and frequently these data are in poor agreement.

In a previous paper,[3] we reported solubility measurements in water for benzene and cyclohexane over the temperature range (70 to 150) °C. A static apparatus has been designed and constructed for these determinations. It allows for the on-line analysis by gas chromatography of the hydrocarbon saturated aqueous phase in equilibrium. But the solubility of alkanes in water is lower than the solubility of aromatics or cyclohexane. At 30 °C, the hexane mole fraction solubility is 200 times lower than the benzene mole fraction solubility[1,3,4] (respectively 2.07×10^{-6} and 4×10^{-4}). Detection of alkane trace levels in water was possible by changing the sensitivity of the flame ionization detector (FID). But increasing the sensitivity led to very poor reproducibility for the hexane chromatographic area because the detector signal was pertubated by water. The on-line method used for the determination of hydrocarbon solubilities was modified. Water saturation is still performed using the static method, but the sampling procedure is accomplished using the solid-phase extraction method. Trace hydrocarbon saturated water is trapped in a C18 column and then eluted by methanol. Methanol + hydrocarbon solutions are analyzed by GC-FID using an internal standard calibration method.

The present work reports the solubilities of hexane, heptane, and octane in water at temperatures from (30 to 180) °C.

Experimental Section

Experimental Procedure. Figure 1 shows a schematic diagram of the apparatus used to perform solubility measurements with a static method. The equilibrium cell has been described elsewhere.[3] Briefly, the stainless steel saturation cell (530 mL) was contained in the oven of an HP model 5880A gas chromatograph. The water temperature was determined using a calibrated thermocouple (with an accuracy of ±0.1 °C) inserted in the body of the cell. The pressure inside the cell was measured with a calibrated precision pressure gauge (accuracy of ±0.5%).

The cell was equipped with a sampling line. Approximately 20 mL of the liquid hydrocarbon was injected under vacuum and (200 to 450) mL of degassed water was introduced into the cell by a pneumatic pump (model MCP110, Haskel, Burbank, USA). To achieve a rapid equilibrium, a magnetic stirring alternative movement system was used to mix the water and the hydrocarbon. This system works with an induction motor (25 W, 1200 rpm, Sungshin P and Ind, Korea) coupled with a speed reducer (15/1) to avoid emulsion formations. The agitation is realized by back and forward movement of double helixes, connected to a stainless steel rod inside the cell.

The sampling procedure, in the equilibrium conditions, was realized by using the solid-phase extraction method.[5]

The experimental procedure is as follows: the mixture of water and hydrocarbon is stirred at the desired temperature over 12 h. After equilibration and in order to check for settling, a water sample is taken after 1 h and after 12 h of settling. The result of these measurements showed that there is no significative difference between the two samples. After the equilibration time, the cell is pressurized with nitrogen to about 7 bar, and the shut off valve of the water outlet (10) is slowly opened. The hydrocarbon saturated aqueous solution circulates through a HPLC column at a flow of 0.4 mL·min^{-1}. A HPLC column "silice Uptisphere

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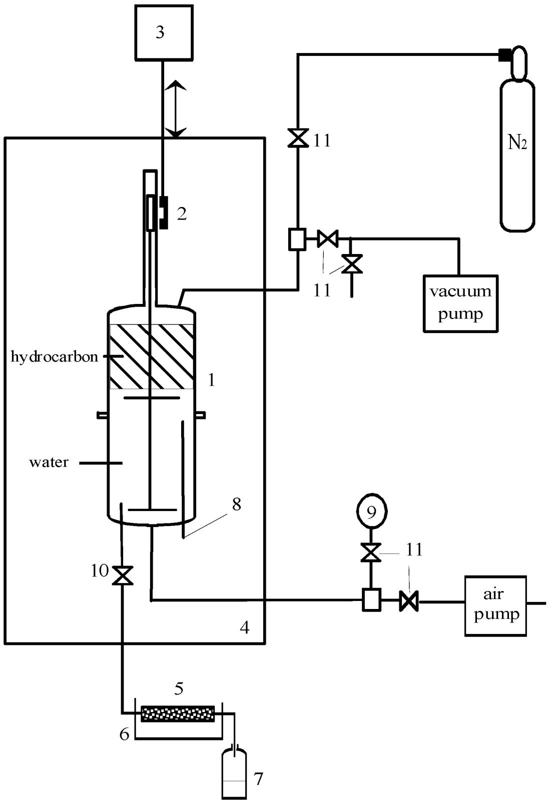

Figure 1. Schematic diagram of the water solubility apparatus: (1) equilibrium cell; (2) magnet; (3) motor; (4) GC oven; (5) HPLC column; (6) ice bath; (7) recovering flask; (8) thermocouple; (9) pressure gauge; (10) outlet valve; (11) valves.

HDO C18" (33 mm × 4.60 mm, 4.9 μm) was used. For solubility measurements at elevated temperatures, the saturated aqueous water was cooled before entering the HPLC column to avoid damage to the stationary phase. Tubes and the column were immersed in an ice bath.

The volume of saturated water passing through the HPLC column was determined according to the estimated hydrocarbon solubility at the studied temperature. Water volumes varied from (200 to 400) mL. For a 10^{-7} mole fraction solubility in water, a minimum of about 200 mL of saturated aqueous phase is required to accumulate a sufficient amount of alkane in the C18 column. After the collection of the aqueous sample, pressurization is stopped and the oven is cooled at 30 °C to allow disconnection of the water outlet tubing from the cell. Hydrocarbon previously retained in the column is then eluted in the backflush mode with 10 mL of methanol. This elution is accomplished by a HPLC pump (Water 590) with a flow rate of 0.5 mL·min^{-1}. Different elution volumes of methanol were tested. 10 mL of methanol was sufficient for total elution of the absorbed solute for all conditions. Also, the column and the water outlet tubing are washed with deionized water prior to subsequent use. After the elution, the 10 mL of (hydrocarbon + methanol) is weighed to ±0.1 mg before and after internal standard addition necessary for the quantitative determination by GC/FID. Internal standards are chosen that eluted near and similar to the solute of interest during gas-chromatography analysis. They are included heptane for hexane, octane for heptane, and ethylcyclohexane for octane.

Materials. The solutes tested in this work were linear alkanes: hexane, heptane, and octane. All solutes were with a specified purity of 99+%, and they are obtained from Acros Organics. Deionized water was used in all cases.

Table 1. Mole Fraction Solubility of Hexane in Water

	$10^{-6}(x \pm \sigma^a)$	$10^{-6}x$	
T/°C	exptl	lit.	calc by eq 1
30.8	2.06 ± 0.01	2.1(1) (at 30 °C)	2.09
70.3	2.77 ± 0.04	3.3(1) (at 70 °C)	3.14
100.6	6.16 ± 0.08	5.6(1) (at 100 °C) 6.21(10) (at 100 °C)	6.33
130.8	14.46 ± 0.08		15.89
151.1	26.7 ± 0.3	27.1(10) (at 148.9 °C) 33.9(10) (at 150 °C)	32.3
170.0	48.0 ± 0.3		65.5

[a] Standard deviations (σ) are based on five chromatographic analyses.

Table 2. Mole Fraction Solubility of Heptane in Water

	$10^{-6}(x \pm \sigma^a)$	$10^{-6}x$	
T/°C	exptl	lit.	calc by eq 1
32.7	0.474 ± 0.001	0.41(1) (at 30 °C)	0.450
70.4	0.915 ± 0.007		0.697
100.7	2.04 ± 0.06; 2.12 ± 0.02	1.0(1) (at 100 °C)	1.47
131.0	4.00 ± 0.08	4.90(12) (at 136.7 °C)	3.94
151.3	8.8 ± 0.2		8.36
170.5	17.63 ± 0.06		17.93
170.6	17.42 ± 0.01		18.01

[a] Standard deviations (σ) are based on five chromatographic analyses.

Gas Chromatographic Analysis. All analyses were performed using a DELSI DI-700 gas chromatograph equipped with a flame ionization detector. Chromatographic separations were accomplished with a 50 m CP-Sil-5CB column (0.53 mm i.d., 2 μm film thickness, Chrompack). Splitless injection mode was used.

All analyses were realized under isothermal conditions: 40 °C for hexane; 70 °C for heptane; and 95 °C for octane. Injector temperature and detector temperature were respectively 160 °C and 180 °C.

The GC analysis gave the concentration of the studied hydrocarbon in methanol. Also, the solubility is calculated on the basis of the mole fraction of the hydrocarbon in the 10 mL of methanol versus the volume of saturated water having circulated through the HPLC column. Four point calibration lines are generated for each solute to determine its detector response with respect to the internal standard. The standard solutions are prepared gravimetrically over the range in which the actual analysis would be conducted. All standards were immediately analyzed to establish calibration curves. Furthermore, a "monitoring solution" containing the analytes in the concentration range of the standard was also prepared. This solution was periodically analyzed to control the stability of the GC system.

Results and Discussion

For realizing the sampling, the cell is pressurized with nitrogen to about 7 bar. This low system pressure used for these determinations has a negligible effect on the mole fraction solubilities of the studied solutes.[6,7]

Tables 1−3 and Figures 2−4 present measured solubilities for the hexane, heptane, and octane−water systems. Reported data solubilities have been calculated from the mean values of five chromatographic analyses with the corresponding standard deviations. Thus, some water−hydrocarbon equilibria were repeated at 100 °C and 170 °C for heptane and at 124 °C and 131 °C for octane. The

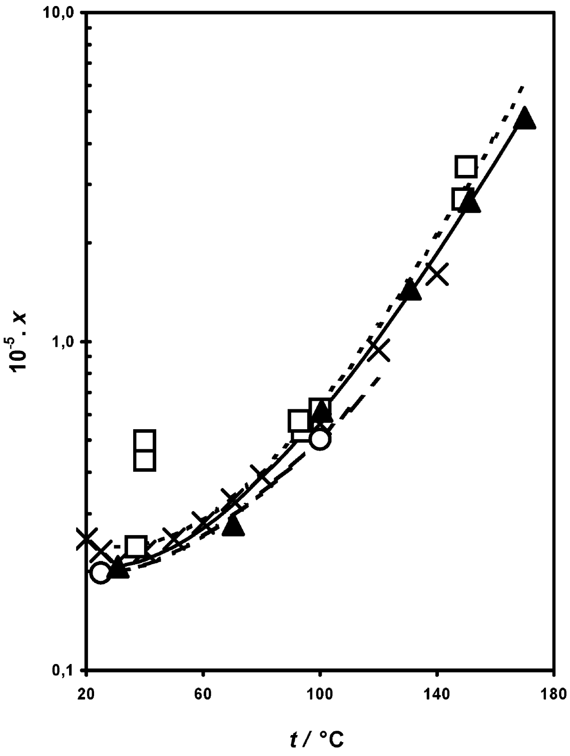

Figure 2. Mole fraction solubility (x) of hexane in water: - - -, Tsonopoulos;[8] — — —, Yaws et al.;[9] —, our correlation; □, Tsonopoulos and Wilson;[10] ○, Yaws et al.;[11] ×, literature experimental data from *Solubility Data Series*;[1] ▲, this work.

Table 3. Mole Fraction Solubility of Octane in Water

	$10^{-6}(x \pm \sigma^a)$	$10^{-6}x$	
T/°C	exptl	lit.	calc by eq 1
29.9	0.122 ± 0.001	0.096(2) (at 30°C)	0.097
30.3	0.120 ± 0.002		0.097
69.2	0.239 ± 0.003		0.151
70.0	0.352 ± 0.006	0.240(2)	0.154
99.9	0.480 ± 0.006		0.334
101.1	0.538 ± 0.008		0.347
124.0	1.23 ±0.01 1.42 ± 0.01		0.75
131.0	1.77 ± 0.03 1.93 ± 0.05		0.97
151.2	3.92 ± 0.02	3.80(14) (at 149°C) 1.86(12) (at 149.6 °C)	2.12
165.1	6.90 ± 0.04		3.77
165.4	6.82 ± 0.04		3.82
183.0	13.37 ± 0.06		8.17

[a] Standard deviations (σ) are based on five chromatographic analyses.

repeated solubility measurements were in good agreement. These experiments confirmed good reproducibility of the saturation, solid-phase extraction, and methanol elution steps.

In these tables, are reported data solubilities given by Shaw[1,2] for each hydrocarbon. However, his compilation shows that independently obtained values often differ by an order of magnitude.

In these figures are reported the correlations proposed by Tsonopoulos[8] (eq 1) and Yaws et al.[9] (eq 2), which are expressed by

$$\ln x = A + \frac{B}{(T/\mathrm{K})} + C \ln(T/\mathrm{K}) \qquad (1)$$

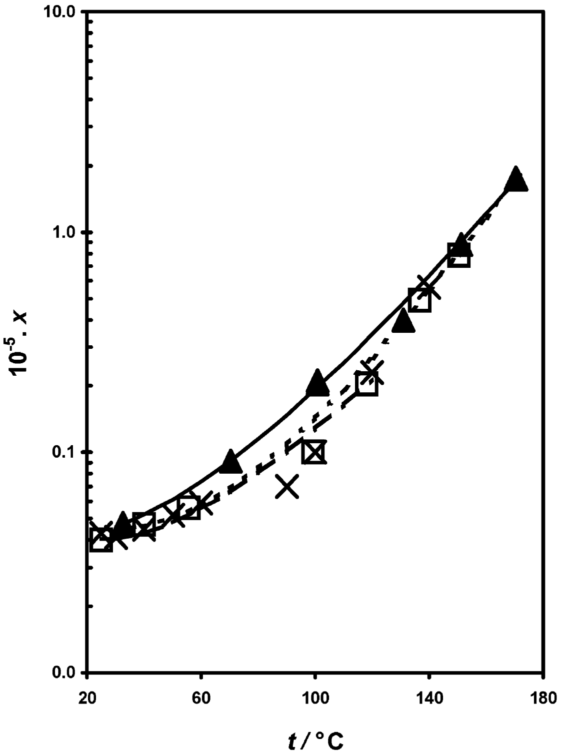

Figure 3. Mole fraction solubility (x) of heptane in water: - - -, Tsonopoulos;[8] — — —, Yaws et al.;[9] —, our correlation; □, Price;[12] ×, literature experimental data from *Solubility Data Series*;[1] ▲, this work.

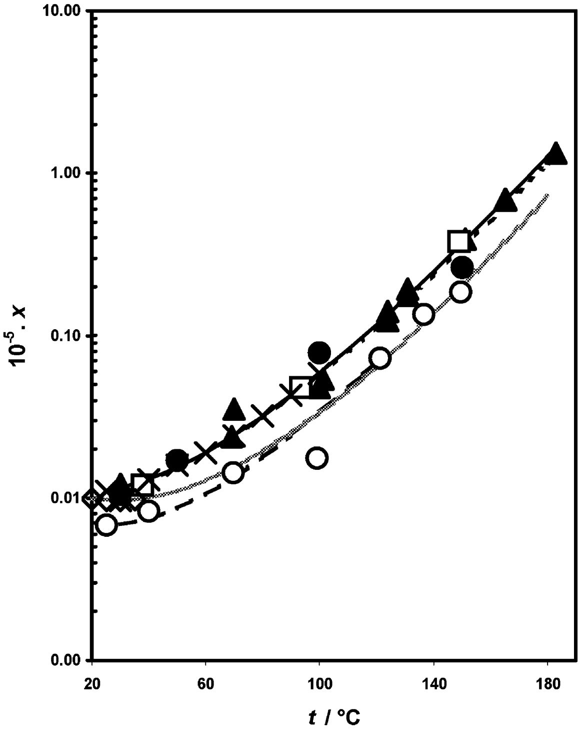

Figure 4. Mole fraction solubility (x) of octane in water: ···, Tsonopoulos;[8] - - -, Heidman et al.;[14] — — —, Yaws et al.;[9] —, our correlation; ○, Price;[12] □, Heidman et al.;[14] ×, literature experimental data from *Solubility Data Series*;[1] ●, Bergin;[13] ◇, Jönsson et al.;[15] ▲, this work.

$$\log S = A' + \frac{B'}{(T/\mathrm{K})} + \frac{C'}{(T/\mathrm{K})^2} \qquad (2)$$

where x is the solubility of hydrocarbon in water in molar

Table 4. Parameters of Eqs 1 and 2

	parameters of eq 1			parameters of eq 2		
alkanes	*A*	*B*	*C*	*A′*	*B′*	*C′*
hexane	−374.908 04	16 327.128	53.895 82	10.992	−5969.484	889 453.1
heptane	−396.939 79	17 232.298	56.959 27	12.811	−7426.389	1 106 532
octane	−415.756 3(8)	17 975.386(8)	59.554 51(8)	16.865	−10269.140	1 530 102
	−343.149 7(14)	13 862.386(14)	49.246 09(14)			

fraction, *S* is the solubility of hydrocarbon in water in parts per million by mass, and *T* is the temperature in Kelvin. The parameters of these equations are reported in Table 4.

Table 1 shows the results obtained for the hexane using our method and solubility values cited in the literature at temperatures close to those of our experiment. Also are presented the solubility values calculated by the correlation proposed by Tsonopoulos.[8] Our experimental value at 30 °C ((2.06 ± 0.01) × 10^{-6}) is in good agreement with the (2.07×10^{-6}) value recommended by Shaw.[1]

As expected, increasing temperature increases the mole fraction solubility of hexane in water. For example, at 130.8 °C, the mole fraction solubility of hexane rises approximately 7 times compared with that at 30.8 °C, while increasing the temperature from 30.8 °C to 170.0 °C increases the mole fraction solubility of hexane more than 23 times to 48×10^{-6}.

Figure 2 shows global good agreement between our experimental solubility values and previous reported experimental data. However, our values are below those calculated by the Tsonopoulos correlation[8] for temperatures higher than 130 °C. The two correlations reported in Figure 2 are the correlation of Tsonopoulos[8] in the temperature range (0 to 220) °C and expressed by eq 1, and the correlation proposed by Yaws et al.,[9] valid between (25 and 120) °C, expressed by eq 2.

Table 2 shows the results obtained for the solubility of heptane in water. Also reported are the experimental data available in the literature at the studied temperatures and the calculated data from the correlation of Tsonopoulos.[8] Figure 3 shows our experimental solubility values, previous reported experimental data, and those calculated by the two following correlations: the correlation of Tsonopoulos[8] valid between (0 and 256) °C, expressed by eq 1, and the correlation of Yaws et al.[9] valid between (25 and 120) °C and expressed by eq 2.

At 32.7 °C, the experimental value of (0.474 ± 0.001) × 10^{-6} is close to the value reported by Shaw [1] of 0.410×10^{-6} at 30 °C. Increasing the temperature from 32.7 °C to 170.5 °C raises the mole fraction solubility of heptane more than 37 times to (17.63 ± 0.06) × 10^{-6}.

Table 3 shows the results obtained for the solubility of octane in water. The value of solubility obtained at 29.9 °C is (0.120 ± 0.002) × 10^{-6}, and that proposed by Shaw[1] is 0.096×10^{-6}. A similar increase of the solubility with the temperature is obtained. For example, raising the temperature from 29.9 °C to 183 °C results in a 110 times enhancement in mole fraction solubility from (0.120 ± 0.002) × 10^{-6} to (13.37 ± 0.06) × 10^{-6}. This enhancement with respect to temperature is even more significant for solutes with very low solubilities at ambient temperature.

Figure 4 shows our experimental solubility values, previous reported experimental data, and those calculated by the three following correlations: the correlation of Tsonopoulos[8] and that of Heidman et al.[14] valid in the temperature range (0 to 266) °C and expressed by eq 1, and the correlation proposed by Yaws et al.,[9] valid between (25 and 120) °C, expressed by eq 2.

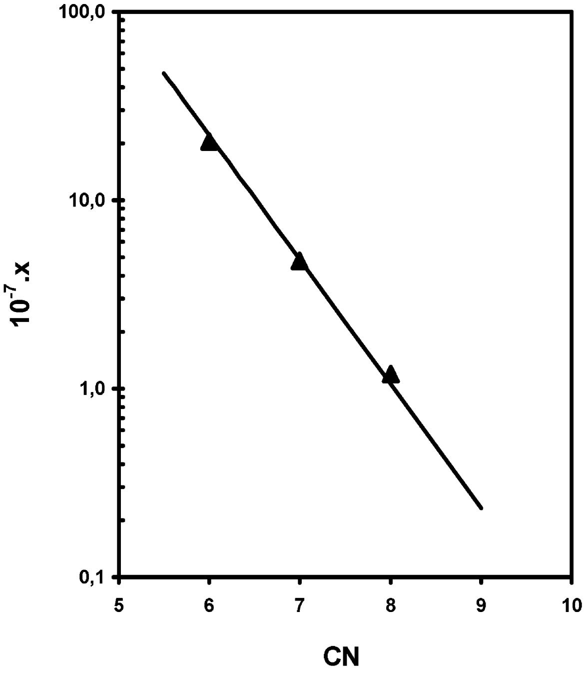

Figure 5. Mole fraction solubility of normal alkanes in water at 30 °C as a function of carbon number CN: —, calculated by eq 3; ▲, this work.

The correlations of Tsonopoulos[8] and Yaws et al.[9] do not fit the experimental data well, except the experimental data of Price.[12] The experimental data fit closely with the correlation of Heidman et al.,[14] as can be seen in Figure 4.

The solubilities of liquid normal alkanes in water at ambient temperature decrease steeply with increasing molar volume, which is proportional to the carbon number (CN). This step decrease in solubility with increasing carbon number is approximately given by the equation

$$\ln x_{\mathrm{hc}} = -3.9069 - 1.51894(\mathrm{CN}) \tag{3}$$

which was obtained by regressing the solubility data for $5 \le \mathrm{CN} \le 9$ from Shaw.[1,4]

Also, Figure 5 presents measured solubilities for hexane, heptane, and octane and those from eq 3 at around 30 °C. The values obtained in this work confirm the validity of eq 3.

These measured solubilities were correlated by Tsonopoulos[8] and Yaws and al.[9] for the three studied alkanes.

These correlations result from the relationship between solubility and heat of solution given by

$$\left(\frac{\partial \ln x_i}{\partial T}\right) = \frac{H_i^{\mathrm{E}}}{RT^2} \tag{4}$$

H_i^{E} is the partial molar excess enthalpy of component *i*.

Integration of eq 4, where H_i^{E} is expressed as a linear function of temperature, leads to eq 5:

Table 5. Parameters for Calculation of the Mole Fraction Solubility of Hydrocarbons in Water with Eq 5

	A	*B*	*C*
hexane	−317.569	13 522.116	45.478
heptane	−278.215	11 022.128	39.771
octane	−362.618	14 904.474	52.067

Table 6. Comparison of ΔC_p

	$\Delta\overline{C_p}$ (J·K^{-1}·mol^{-1})	
hexane	379	448$^{(8)}$
heptane	331	474$^{(8)}$
octane	433	495$^{(8)}$

$$\ln x_{hc} = A + \frac{B}{(T/K)} + C \ln (T/K) \qquad (5)$$

with x_{hc} the mole fraction solubility of hydrocarbon in water.

The values of *A*, *B*, and *C* can be calculated from our experimental data by adjustment by the method of least-squares. These obtained values are listed in Table 5. These equations, available from (30 to 180) °C, are graphically represented in Figures 2−4. The heat capacity of a solution is given by the relation $\Delta\overline{C_p} = RC = 8.31451C$ (J·K^{-1}·mol^{-1}). Our values, reported in Table 6, are lower than previous data from Tsonopoulos,[8] especially for heptane.

Conclusion

The modification of a previously reported method for determining hydrocarbon solubilities in water by GC on-line analysis allows the determination of very low solubilities of hydrocarbon in water by using a solid-phase extraction method. The quality of the obtained results for hexane, heptane, and octane in water, over the temperature range (30 to 180) °C, allows us to envisage the determination of lower solubilities of hydrocarbon in water. From our experimental measurement, correlations are proposed for the estimation of the solubilities of hexane, heptane, and octane in water between (30 and 180) °C.

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