Apparatus for the On-line GC Determination of Hydrocarbon Solubility in Water: Benzene and Cyclohexane from 70 °C to 150 °C

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An apparatus has been designed and constructed to measure liquid hydrocarbon solubility in water. On-line analysis coupled with gas chromatography has been applied to the determination of binary mixtures of water with benzene and cyclohexane for the temperature range (70 to 150) °C. Measurements obtained for benzene show good agreement with literature values and allow us to validate this new method. Increasing the temperature from 70 °C to 150 °C increases the mole fraction solubility of cyclohexane in water from $(19.7 \pm 0.02) \times 10^{-6}$ to $(131 \pm 3) \times 10^{-6}$.

Introduction

Knowledge of water−hydrocarbon phase behavior is of tremendous interest in the environmental sciences and in the chemical and petroleum industries. Notably, the main application of this knowledge is in the field of design requirements by engineers for various chemical engineering separation processes, especially those dealing with water pollution abatement.

Generally, these processes are performed at elevated temperatures and pressures, using water vapor, and so the variation of the solubility of hydrocarbons in water as a function of the temperature and pressure needs to be known.

Many studies have been reported in the literature, but the agreement between the results obtained by different investigators is poor. The present study reports a new approach for determining the solubility of hydrocarbons in water in the temperature range 70 °C to 150 °C, and the first results obtained with this method are presented.

A static apparatus, completely automated, has been designed and constructed. It allows for on-line analysis by gas chromatography of the saturated aqueous phase in equilibrium. The reliability of the new method is demonstrated through the comparison of benzene solubility results with literature values. In addition, solubility measurements of cyclohexane in water are reported.

Experimental Section

Experimental Procedure. The solubility measurement of hydrocarbons in water at elevated temperatures is difficult due to the fact that the analyses must be made for very low concentrations of solutes. Special precautions are required to sample the equilibrated phases, and different key points had to be addressed to successfully design this device.[1−3]

Most of the problems arise due to the difficulties in transferring an aliquot of the equilibrated mixture from the equilibrium cell to an appropriate analytical instrument, without composition change.

Different factors can interfere during this transfer: entrainment of small droplets of one phase into the other while sampling can lead to very large errors; adsorption of the dilute solute on the sample line surfaces can lead to depletion of the solute from the sample phase, thus changing the composition of the sample; changes in temperature and pressure in the sample line while sampling can alter composition uniformity; temperature drops can lead to liquid−liquid-phase splits, while pressure drops during sampling can lead to vapor−liquid flashing.

Thus, the key point is to be sure of the representativity of the analyzed sample to be certain of the correct water analysis in equilibrium conditions. A static apparatus, completely automated, has been designed and constructed according to these constraints.

A schematic diagram of the experimental apparatus is shown in Figure 1. This device is coupled on-line with a gas chromatograph. The three major parts are the equilibrium cell, the calibration system, and the gas chromatograph.

The equilibrium cell was a stainless steel autoclave. Its total internal volume was about 530 mL. All heated components were placed in the oven of a HP model 5880A gas chromatograph. The cell is equipped with a charging line and a sampling line. Furthermore, two openings allow us to evacuate and pressurize the cell. Moreover, three openings are provided for subsequent apparatus evolution.

Approximately 20 mL of the liquid hydrocarbon is injected under vacuum and 200 mL of degassed water is introduced into the cell by using a pneumatic pump (model MCP110, Haskel, Burbank, USA). To achieve a rapid equilibrium, a magnetic stirring alternative movement system is 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 emulsions. The agitation is realized by a double helixes system having a back and forward movement, which is connected with a stainless steel rod inside the cell.

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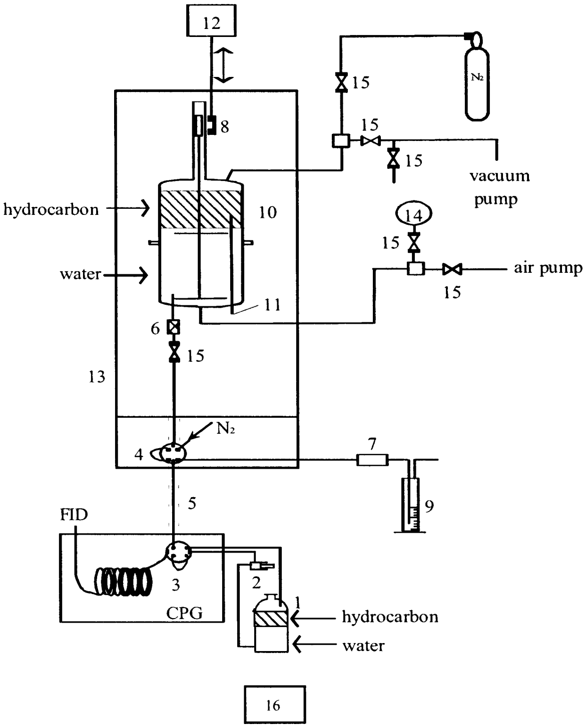

Figure 1. Schematic diagram of the water solubility apparatus: 1, calibration saturation cell; 2, HPLC pump; 3 and 4, rotary six-port valve; 5, heating capillary stainless steel tube; 6, filter; 7, HPLC column; 8, magnet; 9, graduated flask; 10, equilibrium cell; 11, thermocouple; 12, motor; 13, GC oven; 14, pressure gauge; 15, valves; 16, magnetic stirrer.

The sampling procedure adopted for this work is that the water + hydrocarbon mixture is stirred at the desired temperature during 3 h. Previous studies have shown that 3 h is enough to reach equilibrium. Moreover, a check for sample settling was performed. The sample was analyzed after 1 h or overnight settling. The results of the two measurements showed that there is no significative difference between samples taken after 1 h and after 24 h of settling.

The sampling of the aqueous phase, in the equilibrium conditions, is made by using a rotary 6-port valve (VICI$_{AG}$; valve, UWT; 0.16 mm; 0.4 mm; USA) with an about 20 μL external loop. The valve is thermostated at 30 °C above the sample temperature to limit adsorption. A 2-μm filter (SSI-05-0105; 0.16 mm; Touzart et Matignon-France), placed before the outlet valve, avoids plugging of the valve by possible particles coming from the autoclave. Loading of the loop is accomplished by pressurization of the cell with nitrogen to about 17 bar. A HPLC column generates a head loss to ensure a flow rate within the range from (0.2 to 1.2) mL·min^{-1} through the loop. Excess water flowed into a graduated flask for the control of the water level in the equilibrium cell.

In the injection mode, the outlet of the valve is connected to the gas chromatography device by a heating capillary stainless steel tube. The water temperature was measured by means of a calibrated thermocouple inserted in the body of the cell, with an accuracy of ±0.1 °C. Pressure was measured by means of a calibrated precision pressure gauge, connected at the top of the cell, with an accuracy of ±0.5%.

Concerning the calibration system, the analytical conditions for the standard solution must be as close as possible to those of the sample. A hydrocarbon saturated aqueous solution at 30 °C and at atmospheric pressure is used as calibration solution. Benzene and cyclohexane solubilities in water, at 30 °C, have been previously measured in our laboratory.[4] The measured mole fraction solubility is 402 × 10^{-6} for the benzene and 13 × 10^{-6} for the cyclohexane.

This solution is generated by a saturation system, coupled with the gas chromatography device. This system consists of a thermostated double jacket glass cell,[4] where the water and the liquid hydrocarbon are mixed in using a magnetic stirrer.

At the bottom part of the cell, an orifice allows the sampling of the saturated aqueous phase. Saturated water is continuously recycled by means of a HPLC pump (Milton Roy Company; NSI-33R; USA).

A thermostated rotary six-port valve (VICI$_{AG}$; valve, UWT; 0.16 mm; 0.4 mm; USA) at 75 °C with an approximately 20 μL external loop is used for the injection of the standard solution into the gas chromatograph.

The calibration is realized every day in order to take into account the variation of the detector response in time. The determination of the hydrocarbon solubility in water at a given temperature was calculated with the following relation:

$$x_1(t) = x_1(30\ °\mathrm{C})R_{\mathrm{loop}}\frac{A_1(t)}{A_1°(30\ °\mathrm{C})} \tag{1}$$

with $x_1(t)$ the mole fraction solubility of hydrocarbon at the measured temperature (t °C), $x_1(30\ °\mathrm{C})$ the mole fraction solubility of hydrocarbon at 30 °C, $A_1(t)$ the chromatographic area measured for the sample at t °C, and $A_1°(30\ °\mathrm{C})$ the chromatographic area measured for the calibration solution at 30 °C.

A loop ratio is defined as

$$R_{\mathrm{loop}} = \frac{A_1°(30\ °\mathrm{C})}{A_1(30\ °\mathrm{C})}$$

Indeed in this apparatus, two six-port valves with two different loop volumes are used: for the same temperature, the chromatographic areas measured for the calibration solution and for the sample are different.

The analytical condition meets an important difficulty because a small quantity of hydrocarbon in a large amount of water is injected by the valve in the gas chromatograph which is equipped with a flame ionization detector, since the FID is sensitive to the hydrocarbon and water is not detected. Two chromatographic columns, allowing separation of trace level of hydrocarbon in a large volume of water, have been tested in a gas chromatograph equipped with a thermal conductivity detector. The advantage of the thermal conductivity detector is that the water signal is recorded. The tested columns are a Carbowax column, which is a polar phase, and a Porapak Q column, which is an adsorbent phase. The results obtained with these two columns are similar, and no water signal perturbation has been observed.

In addition, monitoring solutions were prepared for each solute in organic solvent, to verify the linearity of the detector response. These solutions are prepared gravimetrically over the range (0 to 130) g·L^{-1} in order to be in the range of mass of solute injected by valve 4. These injected masses are about 430 μg for the benzene and 17 μg for the cyclohexane at 150 °C. The response of the detector was linear up to 700 μg of benzene injected.

Gas Chromatography Analysis. A DELSI DI 200 gas chromatograph equipped with a flame ionization detector was used for sample analysis. Chromatographic separa-

Table 1. Mole Fraction Solubility of Benzene in Water

	$10^{-4}(x \pm \sigma)^a$	$10^{-4}x$	
t/°C	exp	lit.	calc by eq 2
70.0	5.75 ± 0.01	6.17,[7] 6.25[1]	5.97
100.8	9.22 ± 0.03	9.50,[1] 9.49,[2] 10.2[3]	9.23
131.1	16.20 ± 0.07		15.41
151.2	23.2 ± 0.5	24.2 (at 150 °C),[2] 22.8 (at 149.8 °C)[3]	22.37

[a] Standard deviations (σ) are based on five on-line analyses at each condition.

Table 2. Mole Fraction Solubility of Cyclohexane in Water

	$10^{-6}(x \pm \sigma)^a$	$10^{-6}x$	
t/°C	exp	lit.	calc by eq 5
70.0	19.7 ± 0.2	21.66[7]	21.55
100.1	35.0 ± 0.2, 34.5 ± 0.3		37.37
130.5	61 ± 1		71.93
151.0	131 ± 3	130 (at 150.15 °C)[2]	116.28

[a] Standard deviations (σ) are based on five on-line analyses at each condition.

tions were accomplished with a 0.9 m Porapak Q (50/80 mesh) packed column (0.635 cm o.d.). For the benzene, the column oven temperature was held at 100 °C during 4 min, followed by a rise of 39.9 °C·min^{-1} to a final temperature of 210 °C during 11 min. For the cyclohexane, the analysis was realized under isothermal conditions at 170 °C. The detector temperatures were 210 °C for the benzene and 180 °C for the cyclohexane. The injector temperature was 160 °C for both cases.

Materials. The specified purity of cyclohexane was 99.5%, and that of benzene was 99.7%. They were obtained from R.P. Normapur Prolabo. Deionized water was used in all cases.

Results and Discussion

An advantage of this method is that it is relatively simple to determine the solubility of a hydrocarbon in water at various temperatures by raising the temperature of the GC oven containing the cell. An on-line analysis is performed on the sample in the equilibrium conditions, and the advantage is the avoidance of any loss or contamination of the sample.

For the sampling, the cell is pressurized with nitrogen to about 17 bar. This has negligible effect on the mole fraction solubilities of the studied solutes within the experimental temperature range.[5,6]

Very few water solubility data at elevated temperature are available in the literature, except for benzene. For example, Shaw[7] has reported multiple solubility data for benzene up to 80 °C. The validation of our apparatus is based on comparison of our benzene aqueous solubilities with the literature.

Solubilities of both benzene and cyclohexane in water, at different temperatures, are reported in Tables 1 and 2 and in Figures 2 and 3. The solubilities of benzene and cyclohexane in water at 30 °C have been previously determined in our laboratory.[4] The measured mole fraction solubility was 402 × 10^{-6} for the benzene and 13 × 10^{-6} for the cyclohexane.[4]

Table 1 shows the results obtained for benzene at (70, 100.8, 131.1, and 151.2) °C using our method and literature results around these temperatures. Also shown are the values calculated by the correlation proposed by Tsonopoulos and Wilson.[2] Good agreement between the literature data and our values validates our method and demonstrates the capability and the reliability of our technique for the determination of the solubility of a hydrocarbon in water. Furthermore, the mean deviation between our experimental values and calculated values from Tsonopoulos' correlation[2] was 3.2%.

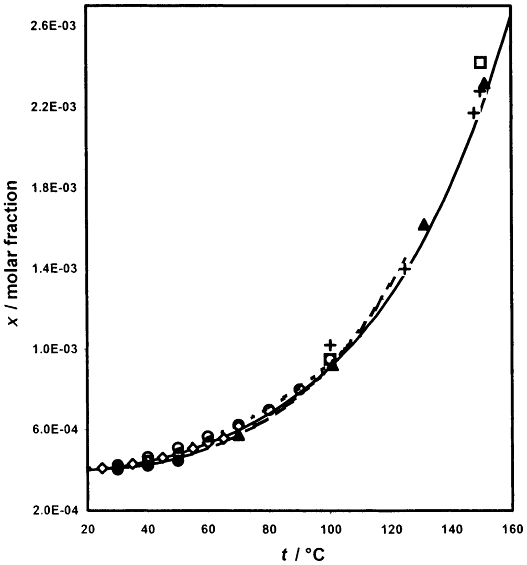

Figure 2. Mole fraction solubility (x) of benzene in water: —, Tsonopoulos and Wilson;[2] ···, Chen and Wagner;[1] - - -, Yaws et al.;[8] □, Tsonopoulos and Wilson;[2] +, Anderson and Prausnitz;[3] ◇, data recommended in *Solubility Data Series*;[7] ○, Chen and Wagner;[1] ●, De Hemptinne et al.;[4] ▲, this work.

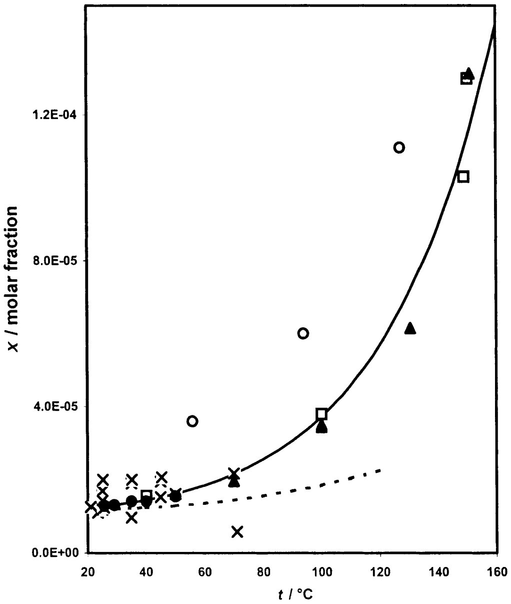

Figure 3. Mole fraction solubility (x) of cyclohexane in water: —, Tsonopoulos and Wilson;[2] - - -, Yaws et al.;[8] ○, Guseva and Parnov;[11] □, Tsonopoulos and Wilson;[2] ×, literature experimental data derived from *Solubility Data Series*;[7] ●, De Hemptinne et al.;[4] ▲, this work.

As expected, increasing the temperature increases the mole fraction solubility of benzene in water. For example, an increase of the temperature from 70 °C to 151.2 °C increases the mole fraction solubility of benzene more than 4 times from (5.75 ± 0.01) × 10^{-4} to (23.2 ± 0.5) × 10^{-4}.

Figure 2 shows good agreement between our experimental solubility values, previously reported experimental data, and those calculated by the three following correlations:

(1) the correlation of Tsonopoulos and Wilson[2] for the mole fraction solubility of benzene (x) in the temperature range (0 to 270) °C, expressed by

$$\ln x = -170.0418 + \frac{6922.912}{(T/\mathrm{K})} + 24.3987 \ln(T/\mathrm{K}) \tag{2}$$

(2) that one of Chen and Wagner[1] for the mole fraction solubility of benzene (x), valid between 0 °C and 125 °C, expressed by

$$\ln x = 6.191 - \frac{7887.82}{(T/\mathrm{K})} + \frac{11.097 \times 10^5}{(T/\mathrm{K})^2} \tag{3}$$

(3) and the correlation proposed by Yaws et al.,[8] valid between (25 and 121) °C, expressed by

$$\log S = 11.994 - \frac{5214.537}{(T/\mathrm{K})} + \frac{776966}{(T/\mathrm{K})^2} \tag{4}$$

where S is the solubility in water in parts per million by mass.

Only the correlation of Tsonopoulos and Wilson[2] is for high temperatures. Our experimental data fit closely with the three correlations, as can be seen in Figure 2.

The values of solubility obtained for the cyclohexane in water are given in Table 2. Also given are the experimental data available in the literature at the studied temperatures and the calculated values from eq 5.

The correlation of Tsonopoulos and Wilson[2] for the solubility of cyclohexane in water, x, is valid between (0 and 256) °C and expressed by

$$\ln x = -209.11689 + \frac{8325.49}{(T/\mathrm{K})} + \frac{29.8231}{(T/\mathrm{K})^2} \tag{5}$$

The correlation proposed by Yaws et al.[8] is only valid between (25 and 120) °C and expressed by

$$\log S = 6.403 - \frac{2773.806}{(T/\mathrm{K})} + \frac{413297.1}{(T/\mathrm{K})^2} \tag{6}$$

where S is the solubility in water in parts per million by mass.

At the studied temperatures there are some deviations between the results reported in our work and those available in the literature, as can be seen in Figure 3. There is a large amount of solubility data in the literature, but nearly all of these values are in the range (20 to 70) °C. Shaw,[7] who compiled the literature data from 1928 to 1983 in the temperature range from 5 °C to 70 °C, recommends only one data set, at 25 °C. At the other temperatures, the data are too scattered to enable a satisfactory recommendation. For example, at 35 °C, the experimental value of solubility realized by De Hemptinne et al.[4] is 14.1×10^{-6}, while the one measured by Kudchadker and McKetta[9] is 9.7×10^{-6} and the other value, by Pierotti and Liabastre,[10] is 20.1×10^{-6}, leading to a factor of 2 between the results of these two last investigators.

Our experimental data are very close to the correlation, eq 5. The mean deviation between our data and calculated values from eq 5 is 10.9%, and at 151 °C, the experimental value of $(131 \pm 3) \times 10^{-6}$ is identical to the experimental value reported by Tsonopoulos and Wilson[2] of 130×10^{-6} at 150.1 °C.

The correlation proposed by Yaws et al.[8] does not fit the experimental data well. For cyclohexane, increasing the temperature from 70 °C to 150 °C increases the mole fraction solubility of cyclohexane more than 6.5 times from $(19.7 \pm 0.2) \times 10^{-6}$ to $(131 \pm 3) \times 10^{-6}$.

Conclusion

A static apparatus has been designed and constructed for the determination of the hydrocarbon solubility in water. Studies were made from 70 °C to 150 °C.

The validity of our methodology and the reliability of our technique have been demonstrated by the determination of the solubility of benzene in water. The results are in good agreement with literature data in the range of temperatures between 70 °C and 150 °C. The solubility of cyclohexane in water has also been determined by this method. It is proposed to study further the solubility of hydrocarbons in water.

Literature Cited

(1) Chen, H.; Wagner, J. An apparatus and procedure for measuring mutual solubilities of hydrocarbons + water: benzene + water from 303 to 373 K. *J. Chem. Eng. Data* **1994**, *39*, 470−474.
(2) Tsonopoulos, C.; Wilson, G. M. High-temperature mutual solubilities of hydrocarbons and water. Part I: Benzene, Cyclohexane and *n*-Hexane. *AIChE J.* **1983**, *29* (6), 990−999.
(3) Anderson, F. E.; Prausnitz, J. M. Mutual solubilities and vapor pressures for binary and ternary aqueous systems containing benzene, toluene, *m*-xylene, thiophene and pyridine in the region 100−200 °C. *Fluid Phase Equilib.* **1986**, *32*, 63−76.
(4) De Hemptinne, J. C.; Delepine, H.; Jose, J. C.; Jose, J. Aqueous solubility of hydrocarbon mixtures. *Rev. Inst. Fr. Pet.* **1998**, *53* (4), 409−419.
(5) Miller, D. J.; Hawthorne, S. B. Solubility of liquid organics of environmental interest in subcritical (hot/liquid) water from 298K to 473K. *J. Chem. Eng. Data* **2000**, *45*, 78−81.
(6) Chen, H.; Wagner, J. An efficient and reliable gas chromatographic method for measuring liquid−liquid mutual solubilities in alkylbenzene + water mixtures: toluene + water from 303 to 373 K. *J. Chem. Eng. Data* **1994**, *39*, 475−479.
(7) Shaw, D. G., Ed. Hydrocarbons with water and seawater; part I: Hydrocarbons C_5 to C_7. *Solubility Data Series*; Pergamon Press: Oxford, 1989.
(8) Yaws, C. L.; Bu, L.; Nijhawan, S. Calculate the solubility of aromatics. *Chem. Eng.* **1995**, 113−115.
(9) Kudchadker, A. P.; McKetta, J. J. Solubility of cyclohexane in water. *AIChE J.* **1961**, *7*, 707.
(10) Pierotti, R. A.; Liabastre, A. A. Structure and properties of water solutions. *U. S. Nat. Technol. Inf. Serv.* **1972**, 113.
(11) Guseva, A. N.; Parnov, E. I. The solubility of aromatic hydrocarbons in water. *Khimiya* **1963**, *18*, 76−79.

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