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Apparatus for the Determination of Water Solubility in Hydrocarbon: Toluene and Alkylcyclohexanes (C_6 to C_8) from 30 °C to 180 °C

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An apparatus has been designed and constructed to measure mutual solubilities of (water + hydrocarbon). The solubility of water in toluene, cyclohexane, methylcyclohexane, ethylcyclohexane, and (*cis* + *trans*)-1,2-dimethylcyclohexane were determined at temperatures ranging from (30 to 180) °C. Measurements obtained for toluene show good agreement with literature values and allow us to validate this new method. As expected, increasing the temperature increases the solubilities of water in the alkylcyclohexanes. Furthermore, the solubility of water in alkylcyclohexanes increases with the number of carbon atoms.

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 concerning water pollution abatement. Most of the time these processes are performed at high temperatures and pressures, and it is necessary to be able to accurately predict in order to have a correct knowledge of water−hydrocarbon mutual solubilities.

In the present study, new data of the solubility of water in hydrocarbons are reported. In previous papers,[1−3] solubility measurements for benzene, cyclohexane, and alkanes (C_6−C_8) and some alkycyclohexanes in water were reported. A static apparatus has been designed and constructed for these determinations. To measure water solubility in organics, the sampling procedure has been modified. The organic phase saturated with water is sampled in dehydrated methanol. The solution is analyzed by coulometric titration according to the Karl-Fisher method. The present work reports the solubility of water in toluene, cyclohexane, methylcyclohexane, ethylcyclohexane, and ($Z + E$)-1,2-dimethylcyclohexane at temperatures ranging 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 in detail elsewhere.[1] Briefly, the stainless steel saturation cell (530 mL) was contained in the oven of an HP model 5880A gas chromatograph. The temperature of the organic phase was determined using a calibrated thermocouple (with an uncertainty of ± 0.1 °C) inserted in the body of the cell. Pressure inside the cell was measured with a calibrated precision pressure gauge (uncertainty of ± 0.5 %).

The cell was equipped with a charging line and a sampling line. Approximately 200 mL of the liquid hydrocarbon was injected under vacuum, and 30 mL of degassed water was introduced into the cell using a pneumatic pump (model MCP110, Haskel, Burbank, CA). 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 emulsions. The agitation is realized by a system of double helixes having a backward and forward movement, which is connected with a stainless steel rod inside the cell.

The sampling procedure adopted for this work was as follows: the water and hydrocarbon mixture was stirred at the desired temperature during 3 h. Previous studies have shown that 3 h is enough to reach equilibrium. After the equilibration time, the cell was pressurized with nitrogen to about 7 bar. The organic phase saturated with water was sampled in a closed flask containing a known amount of dehydrated methanol to limit the volatilization of water from the sample. The sampling flask was inserted at the place of the connector (8 in Figure 1) in the closed loop. By opening the valve (10) and closing the valve (11), the saturated organic phase was then tapped in the flask. Then by closing the valve (10) and opening the valve (11), the organic outlet tubing (between the valve (10) and the connector (8)) was rinsed by dehydrated methanol in order to recover the possible water traces adsorbed. This mixture was injected using a dried syringe into the coulometer cell for the analysis.

The quantity of water present in the flask (hydrocarbon + méthanol mixture) was then determined by coulometric titration according to the Karl-Fisher method. The solubility of water in the hydrocarbon is determined after taking into account the water content in the methanol.

Karl Fisher Titration. All analyses were performed using a KF 756 coulometer (Methrom, France) equipped with a titration vessel with a magnetic stirrer and double platinum electrodes without diaphragm.

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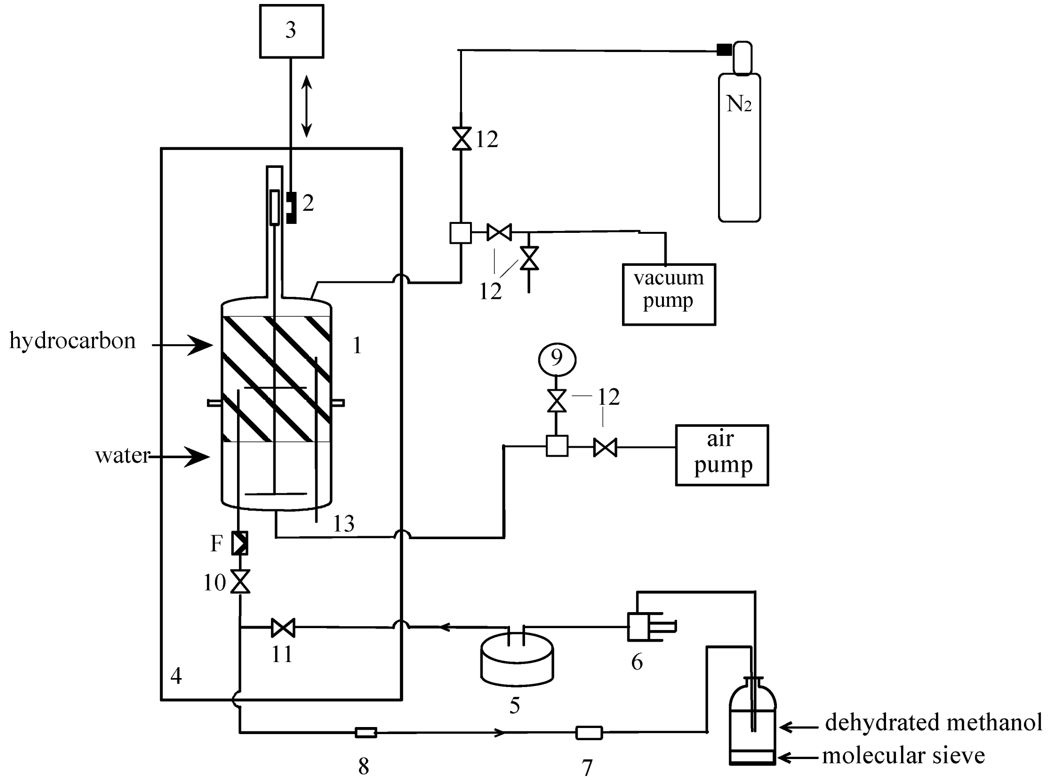

Figure 1. Schematic diagram of the apparatus used for water solubility measurements: 1, equilibrium cell; 2, magnet; 3, motor; 4, GC oven; 5, pulsation damper; 6, HPLC pump; 7, pressure regulator; 8, connector; 9, pressure gauge; 10, outlet valve; 11, outlet valve; 12, valves; 13, thermocouple.

Materials. The solutes tested in this work were as follows: toluene (Acros Organics, > 99 %), cyclohexane (Acros Organics, > 99.5 %), methylcyclohexane (Fluka, > 98 %), and ethylcyclohexane (Fluka, > 99 %). For the 1,2-dimethylcyclohexane, a mixture of ($Z + E$) isomers (> 97 %) was used. The composition of the mixture has been determined by GC analysis:[3] 89.3 % of Z-1,2-dimethylcyclohexane and 10.7 % of E-1,2-dimethylcyclohexane using the trans isomer standard solution.

The impurities of the solutes had no effect on the coulometric titration of water. The reagent for coulometric titration was Hydranal-Coulomat AG from Riedel-de Haën. The methanol is obtained from Merck (purity > 99.8 %) and was dehydrated, during 3 days before its use, with molecular sieves (3 Å, vacuum activated at 450 °C) under agitation. Deionized water was used in all cases.

Results and Discussion

Table 1 and Figures 2 to 6 present measured solubility of water in toluene, cyclohexane, methylcyclohexane, ethylcyclohexane, and ($Z + E$)-1,2-dimethylcyclohexane. Reported data solubilities have been calculated from the mean value of five coulometric titrations with the corresponding standard deviations.

These figures also report the correlations proposed by Tsonopoulos and Wilson[4] (eq 1) for cyclohexane, by Heidman et al.[5] (eq 2) for ethylcyclohexane, and by Hibbard and Schalla[6] (eq 3) for cyclohexane and methylcyclohexane, which are expressed by

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

$$\ln x = A' + B' \times \left(\frac{1}{Tr} - 1\right) - C' \times (1 - Tr)^{1/3} + D' \times (1 - Tr) \tag{2}$$

$$\log x = -\left(4200 \times \frac{\mathrm{H}}{\mathrm{C}} + 1050\right)\left(\frac{1}{(T/\mathrm{K})} - 0.0016\right) + 2.00 \tag{3}$$

where x is the mole fraction solubility of water in hydrocarbon and T is the absolute temperature:

$$Tr = \frac{T}{T_{3c}} \text{ and } T_{3c} = 561.4\ \mathrm{K} \text{ (for the ethylcyclohexane)}$$

The parameters of these equations are reported in Table 2.

Table 1 shows the results obtained for the solubility of water in toluene. The validation of our apparatus is based on comparison of these values with the literature data. Our experimental value at 30 °C $\{(3.30 \pm 0.03) \times 10^{-3}\}$ is in good agreement with the (3.14×10^{-3}) value obtained by Englin et al.[7] Figure 2 shows good agreement between the literature data and our values, which validates our method and demonstrates the capability and the reliability of our technique for the determination of the solubility of water in a hydrocarbon. As expected, increasing temperature increases the mole fraction solubility of water in toluene. For example at 173.8 °C, the mole fraction solubility of water rises approximately 32 times as compared with that at 30.0 °C.

The results obtained for the solubility of water in cyclohexane are presented in Table 1. Figure 3 shows our experimental solubility values, previous reported experimental data, and those calculated by the two following correlations: the correlation of Tsonopoulos and Wilson[4] valid between (0 and 280) °C, expressed by eq 1, and the correlation of Hibbard and Schalla[6] valid between (0 and 352) °C and expressed by eq 3. However, the Hibbard and Schalla correlation is very poor for cyclohexane and all cycloalkanes.

Figure 3 shows a global good agreement between our experimental solubility values and previously reported experimental data. However, our values are lower than below those calculated by the Hibbard and Schalla,[6] the experimental data obtained by Englin et al.,[7] and those of Plenkina et al.[8] The value of solubility obtained at 30.1 °C is $(0.68 \pm 0.02) \times 10^{-3}$.

Table 1. Mole Fraction Solubility of Water x in Various Hydrocarbon

t/°C	$10^3 (x \pm \sigma^a)$	$10^3 x$ (lit.)
	Toluene	
30.0	3.30 ± 0.03	3.14(7), 2.91(9)
50.0	6.75 ± 0.05	5.30(9)
100.1	22.4 ± 0.2	22.6(9)
128.6	41.0 ± 0.4	
150.3	73.0 ± 0.8	58.0(10) (at 149.4 °C)
173.8	107 ± 1	98.4(10) (at 175.2 °C)
	Cyclohexane	
30.0		0.65(11), 0.45(13), 0.96(7)
30.1	0.68 ± 0.02	
49.9	1.30 ± 0.02	1.49(11), 2.29(7) (at 50.0 °C)
69.8	2.78 ± 0.01	
100.2	5.98 ± 0.01	5.12(4), 4.35(4) (at 100.0 °C)
120.7	11.2 ± 0.1	36.0(8) (at 130 °C)
150.2	26.3 ± 0.1	20.4(4), 24.0(4) (at 150.0 °C)
173.0	44.5 ± 0.1	93.0(8) (at 163 °C)
	Methylcyclohexane	
29.9	1.02 ± 0.01	0.98(7)
49.8	1.72 ± 0.01	
70.0	3.06 ± 0.01	
100.3	6.74 ± 0.02	
120.8	14.4 ± 0.1	
150.8	29.1 ± 0.1	
151.8	31.1 ± 0.1	
172.8	51.3 ± 0.1	
	Ethylcyclohexane	
34.0	1.54 ± 0.02	0.81(5) (at 37.9 °C)
49.7	2.38 ± 0.01	
69.8	3.72 ± 0.01	
99.9	7.23 ± 0.04	6.5(5) (at 94.6 °C)
120.1	15.43 ± 0.01	
150.0	30.00 ± 0.01	30.0(5) (at 150.4 °C)
172.6	53.32 ± 0.07	
	($Z + E$)-1,2-Dimethylcyclohexane	
32.0	1.62 ± 0.01	
49.3	2.47 ± 0.03	
69.8	3.90 ± 0.01	
99.9	7.27 ± 0.02	
120.8	15.23 ± 0.01	
150.1	31.36 ± 0.01	
173.0	60.98 ± 0.03	

[a] Standard deviations (σ) are based on five coulometric titrations.

However, the experimental values in the literature are very poor, thus our values cannot be compared with the literature data.

The increase of the solubility with temperature is very similar to that observed for toluene. For example, increasing the temperature from 30.1 °C to 173.0 °C results in a 65 times enhancement in mole fraction solubility from $(0.68 \pm 0.02) \times 10^{-3}$ to $(44.5 \pm 0.1) \times 10^{-3}$.

For the solubility of water in methylcyclohexane: To our knowledge, very few such data are available. In Figure 4, we report our experimental solubility values, the two values obtained by Englin et al.[7] at 25 °C and 30 °C, and the correlation proposed by Hibbard and Schalla[6] (expressed by eq 3). However, this correlation is similar to that used for cyclohexane.

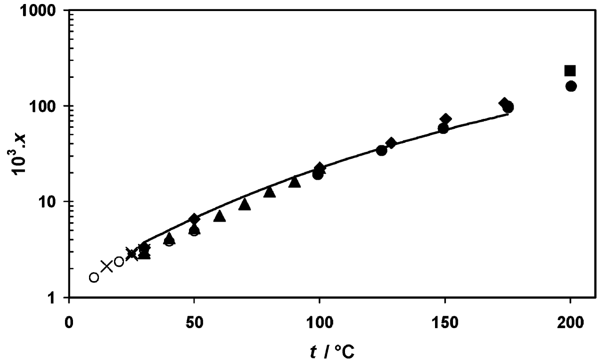

Figure 2. Mole fraction solubility (x) of water in toluene: solid line, our correlation; ○, ref 7; ●, ref 10; ▲, ref 9; ×, literature experimental data from ref 11; ■, ref 12; ◆, this work.

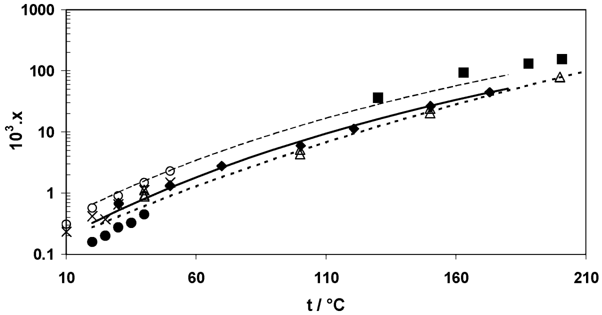

Figure 3. Mole fraction solubility (x) of water in cyclohexane: solid line, our correlation; dotted line, ref 4; dashed line, ref 6; ○, ref 7; ■, ref 8; ●, ref 13; Δ, ref 4; ×, literature experimental data from ref 11; ◆, this work.

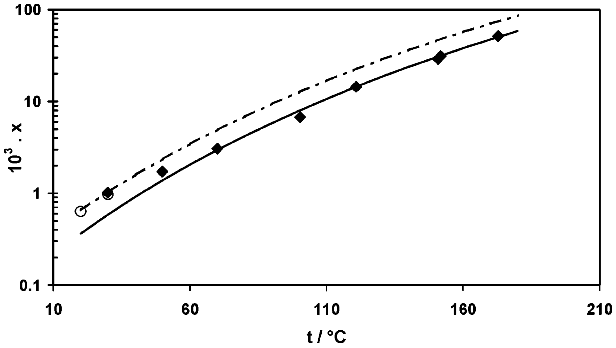

Figure 4. Mole fraction solubility (x) of water in methylcyclohexane: solid line, our correlation; dashed line, ref 6; ○, ref 7; ◆, this work.

At 29.9 °C, the experimental value of $(1.020 \pm 0.002) \times 10^{-3}$ is close to the value reported by Englin et al.[7] of 0.975×10^{-3} at 30 °C. Increasing the temperature from 29.9 °C to 172.8 °C raises the mole fraction solubility of water more than 50 times to $(51.3 \pm 0.1) \times 10^{-3}$.

Table 1 shows the results obtained for the water solubility in ethylcyclohexane. As expected, increasing temperature increases the mole fraction solubility of water. For example, increasing the temperature from 34.0 °C to 172.6 °C raises the mole fraction solubility of water in ethylcyclohexane more than 34 times to $(53.32 \pm 0.07) \times 10^{-3}$.

Table 2. Parameters of Equations 1, 2, and 3

	parameters of equations							
	(1)			(2)[a]				(3)
alkylcyclohexanes	A	B	C	A'	B'	C'	D'	H/C
cyclohexane	−62.7645	−654.027	9.99967					0.168
methylcyclohexane								0.168
ethylcyclohexane				−0.5098	−7.4603	−1.05371	0.44796	-

[a] With $Tr = T/T_{3c}$ and $T_{3c} = 561.4$ K (for ethylcyclohexane).

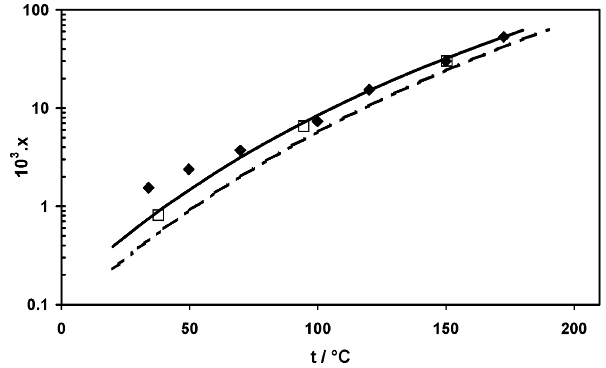

Figure 5. Mole fraction solubility (*x*) of water in ethylcyclohexane: solid line, our correlation; dashed line, ref 5; Δ, ref 5; ◆, this work.

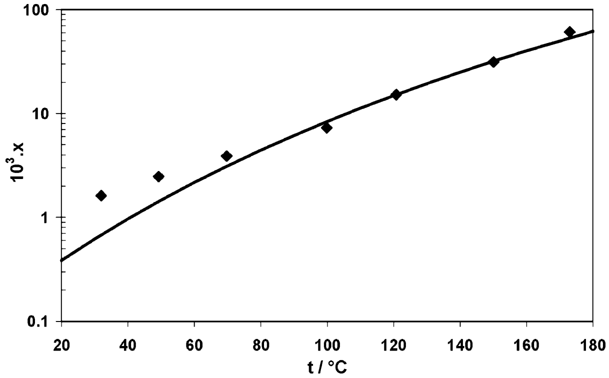

Figure 6. Mole fraction solubility (*x*) of water in 1,2-dimethylcyclohexane (cis + trans**)**: solid line, our correlation; ◆, this work.

Figure 5 shows our experimental solubility values, previously reported experimental data, and those calculated by the correlation of Heidman et al.[5] valid between (0 and 295) °C (expressed by eq 2). Our experimental solubility data are in good agreement with the experimental data of Heidman et al.[5] but lie above the calculated data from the correlation of Heidman et al.[5]

The results obtained for the solubility of water in ($Z + E$)-1,2-dimethylcyclohexane are presented in Table 1. A similar increase of the solubility with the temperature is obtained: raising the temperature from 32.0 °C to 173.0 °C results in a 37 times enhancement in mole fraction solubility from $(1.62 \pm 0.01) \times 10^{-3}$ to $(60.98 \pm 0.03) \times 10^{-3}$. The experimental data are reported in Figure 6. To our knowledge, no data are available in the literature.

Equations 1 and 2 work quite well respectively for cyclohexane and ethylcyclohexane. Equation 3, which expresses x_w as function of the H/C weight ratio, is very poor for alkanes and alkylbenzenes. This correlation is identical for the alkylcyclohexanes at a given temperature because all cycloalkanes have the same H/C ratio. In addition, the Hibbard−Schalla correlation incorrectly predicts that the solubility of water in cycloalkanes is higher than that in the corresponding alkanes.

Tsonopoulos[14] proposed a correlation where x_w is correlated with a two-parameter equation:

$$\ln x = A + \frac{B}{(T/\mathrm{K})} \tag{4}$$

where *x* is the mole fraction solubility of water in hydrocarbon and *T* is the absolute temperature. The correlation fits the data well to within around 50 K of the three-phase critical temperature.

Table 3. Parameters for Calculation of the Mole Fraction Solubility of Water in Hydrocarbon with Equation 4

	A	*B*
toluene	3.9350	−2886.53
cyclohexane	6.3226	−4209.53
methylcyclohexane	6.4449	−4209.53
ethylcyclohexane	6.5081	−4209.53
($Z + E$)-1,2-dimethylcyclohexane	6.5003	−4209.53

The values of *A* and *B* have been calculated from our experimental data by adjustment using the least-squares method. These obtained data are listed in Table 3. These equations, available from (30 to 180) °C, are graphically represented in Figures 2 to 6. At low temperatures, our experimental values are higher than the data calculated using our correlation.

For the parameter *A*, the mean deviation between our calculated values and Tsonopoulos[14] values was 3 % for the alkycylohexane family.

The calculated parameter *B* is the same as that proposed by Tsonopoulos.[14] This parameter is the same for all the compounds of a given family. Furthermore, the heat of solution is given[14] by the relation $\Delta\bar{h} = -RB = -\,8.31451B$ (J·mol^{-1}). The heats of solution obtained from our parameter *B* were 35 kJ·mol^{-1} for the alkycyclohexanes and 24 kJ·mol^{-1} for toluene. These values are the same as the literature data cited in Tsonopoulos.[14]

Conclusion

In this work, we have determined the solubilities of water in toluene, cyclohexane, methylcyclohexane, ethylcyclohexane, and a 1,2-dimethylcyclohexane mixture (89.3 % Z + 10.7 % E) over the temperature range of (30 to 180) °C. These measurements have been realized using a static method for the equilibration between the organic and the water phases. The samples were analyzed by coulometric titration according to the Karl-Fisher method. The validity of our methodology and the reliability of our technique have been demonstrated using literature data concerning water solubility in toluene. The results are in good agreement with the literature data. Finally, new values for the solubility of water in alkylcyclohexanes are reported in the temperature range between 30 °C and 180 °C, and the solubility of water in alkylcyclohexane increases slightly with the number of carbon atoms.

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