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Solubilities of Alkylcyclohexanes in Water from 30 °C to 180 °C

Céline Marche,*,† Corinne Ferronato,‡ and Jacques Jose†

Laboratoire des Sciences Analytiques, Université Claude Bernard-Lyon 1, Bât J. Raulin, 2 ème étage,
43 Boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France, and
Laboratoire d'Application de la Chimie à l'Environnement, Université Claude Bernard-Lyon 1, Bât J. Raulin,
4 ème étage, 43 Boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France

A solid-phase extraction method has been developed for measuring low solubilities of hydrocarbons in water. The solubilities in water of methylcyclohexane, ethylcyclohexane, *trans*-1,2-dimethylcyclohexane, and a mixture of 1,2-dimethylcyclohexane isomers (respectively, 89.3 mol % and 10.7 mol % of the cis and trans isomers) were determined at temperatures ranging from (30 to 180) °C. At 30 °C, the mole fraction solubility is $(2.96 \pm 0.03) \times 10^{-6}$ for methylcyclohexane, $(0.699 \pm 0.007) \times 10^{-6}$ for ethylcyclohexane, and $(0.80 \pm 0.02) \times 10^{-6}$ for *trans*-1,2-dimethylcyclohexane. The mole fraction solubility is $(1.09 \pm 0.01) \times 10^{-6}$ and $(0.91 \pm 0.01) \times 10^{-6}$, respectively, for *cis*-1,2-dimethylcyclohexane and *trans*-1,2-dimethylcyclohexane (from the mixture). Temperature effect on solubility in water for ethylcyclohexane and for the dimethylcyclohexanes is very similar. Increasing the temperature from (30 to 180) °C increases the solubilities by a factor of approximately 40.

Introduction

Water is continuously present during the fluid-reservoir formation and the exploitation of oil and gas reservoirs. Also, knowledge of water−hydrocarbon phase behavior is of tremendous interest in the environmental sciences and in the chemical and petroleum industries.

There is a large amount of solubility data in the literature, and nearly all available data are at ambient conditions, or these data are in poor agreement.

In a previous paper,[1] we reported solubility measurements in water for benzene and cyclohexane over the temperature range of (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 and alkylcyclohexanes in water is lower than the solubility of aromatics or cyclohexane. The on-line method previously described and used[1] was not adapted and was modified.[2] Water saturation is still performed using the static method, but the sampling procedure is accomplished using the solid-phase extraction method.[3] Trace hydrocarbon saturated water is trapped in a C18 column and then eluted by methanol. Methanol + hydrocarbon solutions are analyzed by gas-chromatography flame-ionization detection (GC-FID) using an internal standard calibration method.

The present work reports the solubility in water of methylcyclohexane, ethylcyclohexane, *trans*-1,2-dimethylcyclohexane, and of a mixture of 1,2-dimethylcyclohexane isomers (cis + trans) 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 using a static method. The equilibrium cell has been described elsewhere.[1] Briefly, the stainless-steel saturation cell (530 mL) was contained in the oven of an HP model 5880A gas chromatograph. Pressure inside the cell was measured with a calibrated precision pressure gauge (uncertainty of ±0.5%). The water temperature was determined using a calibrated thermocouple (with an uncertainty of ±0.1 °C) inserted in the body of the cell.

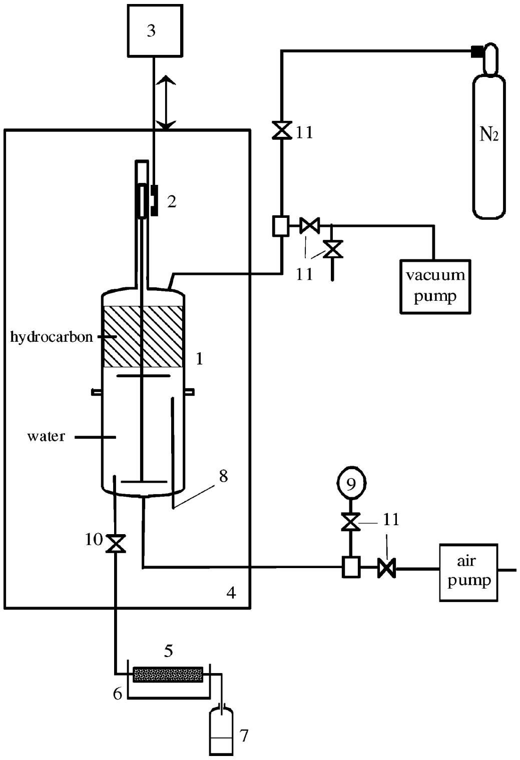

Figure 1. Schematic diagram of the water solubility apparatus: 1, equilibrium cell; 2, magnet; 3, motor; 4, GC oven; 5, HPLC column; 6, ice bath; 7, recovering flask; 8, thermocouple; 9, pressure gauge; 10, outlet valve; 11, valves.

The cell was equipped with a sampling line. Approximately 20 mL of the liquid hydrocarbon was injected under vacu-

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* To whom correspondence should be addressed. E-mail: marche@univ-lyon1.fr. Fax: +33-4-72-43-13-30.

† Laboratoire des Sciences Analytiques.

‡ Laboratoire d'Application de la Chimie à l'Environnement.

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um and (200−450) 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.[1] 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 sampling procedure, in the equilibrium time, was realized by using the solid-phase extraction method.

The sampling procedure adopted for this work has been decribed elsewhere.[2] Briefly, water + hydrocarbon was stirred at the desired temperature over 12 h. After the equilibration time, the cell was pressurized with nitrogen to about 7 bar to allow the sampling. The hydrocarbon-saturated aqueous solution circulated through a high-performance liquid chromatogrpahy (HPLC) column at a controlled flow (0.4 mL·min^{-1}). The HPLC column used was a "Silice Uptisphere HDO C18" (33 mm × 4.60 mm, 4.9 μm). After the collection of the aqueous sample, hydrocarbon previously retained in the column was eluted in the back-flush mode with 10 mL of methanol. Previous studies have shown that 10 mL of methanol was sufficient for total elution of the absorbed solute. After the elution, the 10 mL (hydrocarbon + methanol) sample was weighted to ±0.1 mg before and after internal standard addition necessary for the quantitative determination by GC-FID. The internal standards were octane for methylcyclohexane and ethylcyclohexane and nonane for *cis*-1,2-dimethylcyclohexane and *trans*-1,2-dimethylcyclohexane (uncertainty on composition of ± .1%).

Materials. The specified purity of methylcyclohexane, ethylcyclohexane, and *trans*-1,2-dimethylcyclohexane was 99+%. For the *cis*-1,2-dimethylcyclohexane, a mixture of (cis + trans) isomers (97+%) was used. The composition of the mixture has been determined by GC analysis: 89.3% of *cis*-1,2-dimethylcyclohexane (molar) and 10.7% of *trans*-1,2-dimethylcyclohexane (molar), using the trans isomer standard solution. All were obtained from Fluka. Deionized water was used in all cases.

Gas Chromatographic Analysis. A DELSI DI-700 gas chromatograph equipped with an FID was used for sample analysis. Chromatographic separations were accomplished with a 50-m CP-Sil-5CB column (0.53 mm i.d., 2 μm film thickness, Chrompack). The splitless injection mode was used.

All analyses were realized under isothermal conditions: 80 °C for methylcyclohexane; 95 °C for ethylcyclohexane; 100 °C for (cis + trans)-1,2-dimethylcyclohexane; and 85°C for *trans*-1,2-dimethylcyclohexane. The injector temperature and the detector temperature were, respectively, 160 °C and 180 °C.

The GC analysis gave the concentration of the studied hydrocarbon in methanol. Also, the solubility was calculated on the basis of the mole fraction of the hydrocarbon in the 10 mL of methanol vs the volume of saturated water having circulated through the HPLC column. Four-point calibration lines were generated for each solute to determine its detector response with respect to the internal standard. The standard solutions were prepared gravimetrically over the range in which the actual analysis would be conducted. All standards were immediately analyzed to establish calibration curves.

Results and Discussion

Tables 1−4 and Figures 2−4 present measured solubility for methylcyclohexane−, ethylcyclohexane−, *cis*- and *trans*-1,2-dimethylcyclohexane−, and *trans*-1,2-dimethylcyclohexane−water systems. Reported data solubilities have been calculated from the mean values of five chromatographic analyses with the corresponding standard deviations.

Table 1. Mole Fraction Solubility of Methylcyclohexane in Water

	10^{-6} ($x \pm \sigma^a$)	10^{-6} x	
t/°C	exp	lit	calc from eq 2
26.1	2.96 ± 0.03	$2.94^{(4)}$ (at 26.1 °C)	2.93
70.5	5.04 ± 0.08	$4.0^{(4)}$ (at 70 °C)	4.76
100.5	10.06 ± 0.05	$6.2^{(9)}$ (at 99.1 °C)	9.01
131.0	24.4 ± 0.4	$20.0^{(4)}$ (at 130 °C)	
151.4	42.3 ± 0.7	$44.8^{(9)}$ (at 149.5 °C); $46.0^{(4)}$ (at 150 °C)	
170.8	70.8 ± 0.6		

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

Table 2. Mole Fraction Solubility of Ethylcyclohexane in Water

	10^{-6} ($x \pm \sigma^a$)	10^{-6} x	
t/°C	exp	lit	calc from eq 1
30.3	0.699 ± 0.007		0.987
70.4	1.41 ± 0.01	$1.6^{(6)}$ (at 70 °C)	1.66
100.5	4.52 ± 0.06	$3.4^{(5)}$ (at 100 °C)	3.40
131.0	10.9 ± 0.1		8.5
151.2	17.77 ± 0.03	$20.0^{(6)}$ (at 150.4 °C)	16.65
170.8	29.4 ± 0.1		33.4

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

Table 3. Mole Fraction Solubility of *trans*-1,2-Dimethylcyclohexane in Water

t/°C	10^{-6} ($x_{\text{trans}} \pm \sigma^a$)
30.2	0.80 ± 0.02
70.3	1.91 ± 0.07
100.7	4.7 ± 0.5
131.0	10.8 ± 0.5
151.0	22.3 ± 0.4
170.1	35.6 ± 0.4

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

Table 4. Mole Fraction Solubility of 1,2-dimethylcyclohexane (cis + trans) in Water

	10^{-6} (x ± σ^a)	
t/°C	x_{cis}	x_{trans}
30.0	1.09 ± 0.01	0.91 ± 0.01
70.0	2.16 ± 0.03	1.81 ± 0.03
100.2	4.36 ± 0.02	3.6 ± 0.2
130.5	9.87 ± 0.07	8.1 ± 0.1
150.5	19.6 ± 0.5	16.8 ± 0.9
170.5	43.6 ± 3	34 ± 5

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

In these tables are reported data solubilities given by Shaw[4,5] for each hydrocarbon. However, his compilation shows that independently obtained values at a given temperature often differ by an order of magnitude.

In these figures are reported the correlations proposed by Heidman et al.[6] (eq 1) and Yaws et al.[7] (eq 2) and are expressed by

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

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

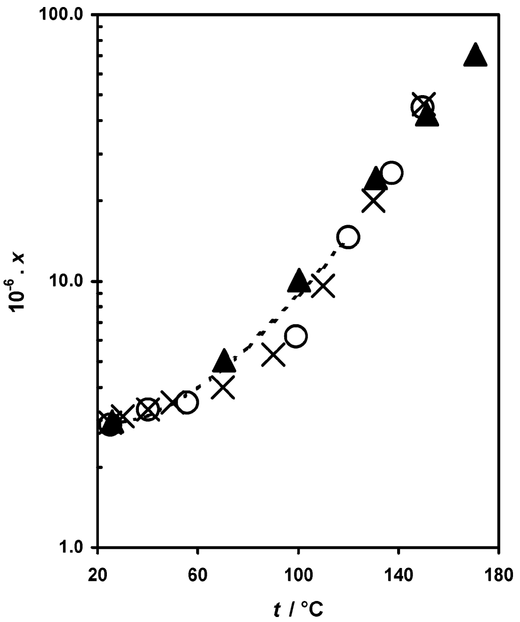

Figure 2. Mole fraction solubility (x) of methylcyclohexane in water: dashed line, Yaws et al.;[7] ○, Price;[9] ×, literature experimental data from *Solubility Data Series*;[4] ▲, this work.

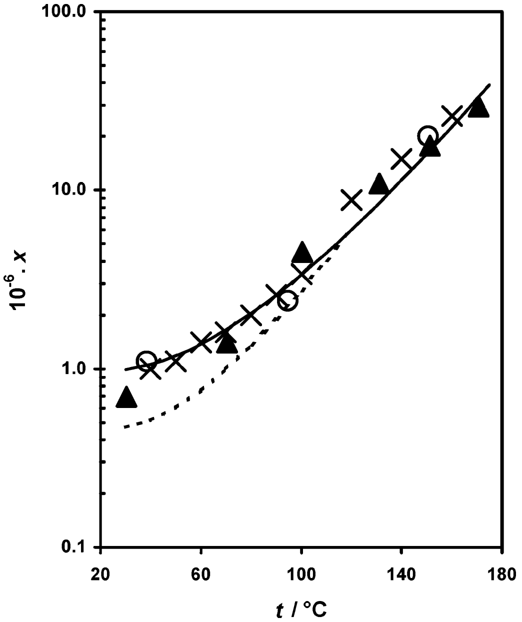

Figure 3. Mole fraction solubility (x) of ethylcyclohexane in water: dashed line, Yaws et al.);[7] solid line, Heidman et al.;[6] ○, Heidman et al.;[6] ×, literature experimental data from *Solubility Data Series*;[5] ▲, this work.

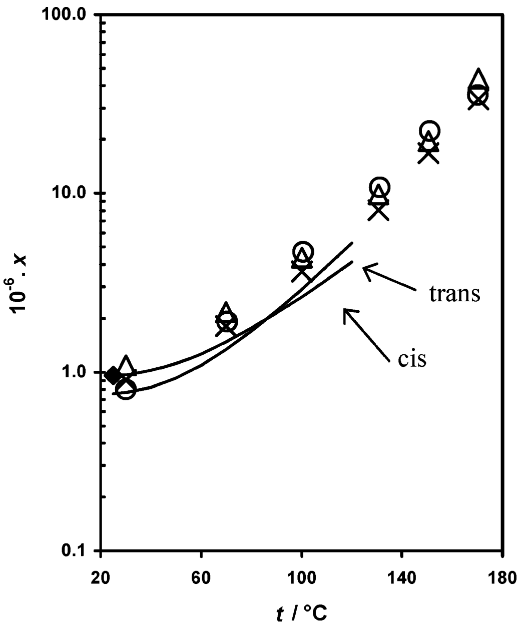

Figure 4. Mole fraction solubility (x) of 1,2-dimethylcyclohexane in water: solid line, Yaws et al.;[7] ○, *trans*-1,2-dimethylcyclohexane; △, *cis*-1,2-dimethylcyclohexane from mixture; ×, *trans*-1,2-dimethylcyclohexane from mixture; ◆, McAuliffe[8] (*cis*-1,2-dimethylcyclohexane).

where x is the mole fraction solubility of hydrocarbon in water, S is the solubility of hydrocarbon in water in ppm by mass, and T is the temperature in K.

The parameters of these equations are reported in Table 5.

Table 1 shows the results obtained for methylcyclohexane using our method and solubility values cited in the literature at a temperature close to those of our experiment. Also are presented the solubility values calculated by the correlation proposed by Yaws et al.[7] Our experimental value at 26.1 °C ($(2.96 \pm 0.03) \times 10^{-6}$) is in good agreement with the (2.94×10^{-6}) value recommended by Shaw.[4]

As expected, increasing temperature increases the mole fraction solubility of methylcyclohexane in water. For example, increasing the temperature from 26.1 °C to 170.8 °C raises the mole fraction solubility of methylcyclohexane more than 23 times to $(70.8 \pm 0.6) \times 10^{-6}$.

Figure 2 shows our experimental solubility values, previously reported experimental data, and those calculated by the correlation of Yaws et al.,[7] valid between (25 and 120) °C and expressed by eq 2. Our experimental solubility data fit closely with the correlation of Yaws et al.[7] and are above experimental data from the literature between 60 °C and 130 °C.

Table 2 shows the results obtained for the solubility of ethylcyclohexane in water. Also are reported the experimental data available in the literature at the studied temperatures and the calculated data from the correlation of Heidman.[6] Figure 3 shows our experimental solubility values, previously reported experimental data, and those calculated by the two following correlations: the correlation of Heidman et al.,[6] valid between (0 and 288) °C, expressed by eq 1, and the correlation of Yaws et al.,[7] valid between (25 and 120) °C, expressed by eq 2.

A similar increase of the solubility with the temperature is obtained. For example, raising the temperature from 30.3 °C to 170.8 °C results in a 42-time enhancement in mole fraction solubility from $(0.699 \pm 0.007) \times 10^{-6}$ to $(29.4 \pm 0.1) \times 10^{-6}$.

Tables 3 and 4 show the solubility results obtained for the 1,2-dimethylcyclohexane isomers in water. We first measured the solubility of the *trans*-1,2-dimethylcyclohexane in water, and then we measured the solubility of *cis*- and the *trans*-1,2-dimethylcyclohexane in water using the mixture of isomers (respectively, 89.3 mol % and 10.7 mol % of the cis and trans isomers). If the isomers mixture is considered as an ideal solution, the solubility of each isomer in water (in molar fraction) can be calculated by the following relation

$$x_{\text{i pure}} = \frac{x_{\text{i mixture}}}{X_{\text{i mixture}}} \qquad (3)$$

where $x_{\text{i pure}}$ is the solubility of the pure isomer in water, $x_{\text{i mixture}}$ is the measured solubility in water of the consid-

Table 5. Parameters of Equations 1 and 2

	parameters of eq 1[a]			parameters of eq 2[b]		
alkylcyclohexanes	A	B	C	A′	B′	C′
methylcyclohexane				13.091	−7085.522	1055594
ethylcyclohexane	−334.02468	14105.21	4793102	19.501	−11345.870	1690535
cis-1,2-dimethylcyclohexane				11.610	−6455.945	961943.2
trans-1,2-dimethylcyclohexane				15.082	−8586.692	1279417

[a] $\ln x = A + B/(T/\mathrm{K}) + C \ln(T/\mathrm{K})$. [b] $\log S = A' + B'/(T/\mathrm{K}) + C'/(T/\mathrm{K})^2$.

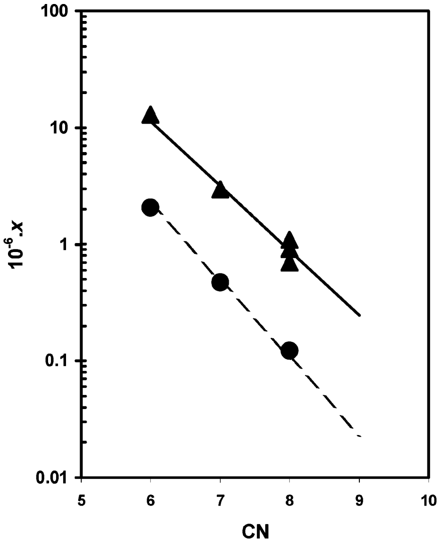

Figure 5. Mole fraction solubility of normal alkanes and alkylcyclohexanes in water at 30 °C as a function of carbon number CN: dashed line, calculated by eq 4; ●, experimental data for alkanes;[2] solid line, calculated by eq 5; ▲, this work.

ered isomer using the mixture of isomers, and $X_{\mathrm{i\ mixture}}$ is the mole fraction of cis or trans in the mixture of the 1,2-dimethylcyclohexanes. In Table 4 are reported the values of $x_{\mathrm{i\ pure}}$.

Figure 4 shows our experimental solubility values for *trans*-1,2-dimethylcyclohexane, for *cis*-1,2-dimethylcyclohexane (from the mixture), for *trans*-1,2-dimethylcyclohexane (from the mixture), the experimental value for the cis isomer from McAuliffe,[8] and the correlation proposed by Yaws et al.,[7] valid between (25 and 120) °C, expressed by eq 2. The McAuliffe experimental value is 0.96×10^{-6} at 25 °C.

The experimental data of *trans*-1,2-dimethylcyclohexane fit closely with the values of *trans*-1,2-dimethylcyclohexane from the mixture of isomers, as can been seen in Figure 4.

For these compounds, increasing temperature from 30 °C to 170 °C raises the mole fraction solubility of dimethylcyclohexanes approximately 40 times.

The solubilities of alkanes and alkylcyclohexanes in water at ambient temperature decreases steeply with increasing molar volumes, the latter being proportional to the carbon number. Thus, the variation of the mole fraction solubility of these hydrocarbons in water as function of carbon number (CN) can be given by the equations proposed by Tsonopoulos[10] and expressed by

$$\ln x_{\mathrm{hc}} = -3.9060 - 1.51894(\mathrm{CN}) \tag{4}$$

with 5 ≤ CN ≤ 9 for normal alkanes and

$$\ln x_{\mathrm{hc}} = -3.744919 - 1.27431(\mathrm{CN}) \tag{5}$$

with 6 ≤ CN ≤ 10 for alkylcyclohexanes.

Also, Figure 5 presents our measured solubilities for cyclohexane[1] (13×10^{-6} at 30°C), methylcyclohexane, ethylcyclohexane, *cis*-1,2-dimethylcyclohexane, *trans*-1,2-dimethylcyclohexane, those measured for normal alkanes (reported in our previous paper[2]) and those from eqs 4 and 5 at around 30 °C.

The values obtained in this work confirm the validity of eq 5, as already shown for the normal alkanes.

The solubility in water of alkylcyclohexanes decreases with increasing carbon number. Increasing temperature raises the mole fraction solubility of alkylcyclohexanes in water. This enhancement with respect to temperature is even more significant for solutes with very low solubilities at ambient temperature in all cases.

Conclusion

A solid-phase extraction method has been previously reported for determining the solubility in water of hexane, heptane, and octane. In this work, we have determined the solubility in water of methylcyclohexane, ethylcyclohexane, and the isomers of 1,2-dimethylcyclohexane over the temperature range of (30 to 180) °C. The results are in good agreement with literature data for methylcyclohexane and ethylcyclohexane. For the dimethylcyclohexanes, this work gave new experimental solubility data.

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