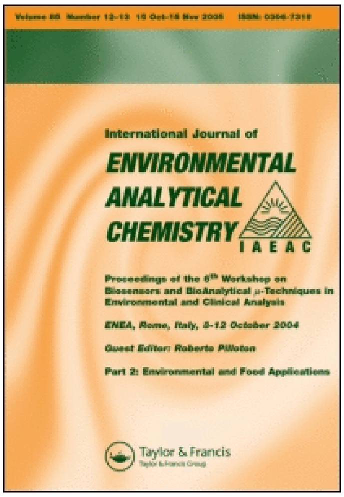

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Generator Column Determination of Water Solubilities for Saturated C_6 to C_8 Hydrocarbons

Joel Reza[a]; Arturo Trejo[a]; Luz Elena Vera-avila[b]
[a] Instituto Mexicano del Petróleo. Subdirección de Transformación Industrial. Gerencia de Investigación Aplicada de Procesos, México D. F., México [b] Departamento de Química Analítica, Facultad de Química. Universidad Nacional Autónoma de México. Coyoacán, México D.F., México

To cite this Article Reza, Joel , Trejo, Arturo and Vera-avila, Luz Elena(1999) 'Generator Column Determination of Water Solubilities for Saturated C_6 to C_8 Hydrocarbons', International Journal of Environmental Analytical Chemistry, 73: 4, 281 — 295

To link to this Article: DOI: 10.1080/03067319908032670

URL: http://dx.doi.org/10.1080/03067319908032670

Intern. J. Environ. Anal. Chem., Vol. 73(4), pp. 281-295
Reprints available directly from the publisher
Photocopying permitted by license only

GENERATOR COLUMN DETERMINATION OF WATER SOLUBILITIES FOR SATURATED C_6 TO C_8 HYDROCARBONS

JOEL REZA[a], ARTURO TREJO[a*] and LUZ ELENA VERA-AVILA[b]

[a]*Instituto Mexicano del Petróleo. Subdirección de Transformación Industrial. Gerencia de Investigación Aplicada de Procesos. Eje Lázaro Cárdenas 152. 07730, México D. F., México and* [b]*Departamento de Química Analítica. Facultad de Química. Universidad Nacional Autónoma de México. Coyoacán, 04510 México D.F., México*

(Revised 2 July 1998; In final form 11 December 1998)

Water solubilities, S_w, of C_6 to C_8 saturated hydrocarbons have been determined at 25°C by using a generator column method. The method is based on pumping water through a bed of a high-surface-area packing, coated with the studied compound. As a result of this process a saturated aqueous solution of that compound is generated, which can be analyzed by gas chromatography. Solubility data are reported for: n-hexane, n-heptane, 3-methylhexane, 2,4-dimethylpentane, n-octane, 4-methylheptane, 2,3,4-trimethylpentane and trans-1,3-dimethylcyclohexane.

Experimental S_w values determined in this work are in good agreement with reported data determined from diffusion experiments where no stirring steps are involved, and are lower than those determined from batch-stirring methods, which suggest that solutions produced by generator columns are free from emulsions. No experimental S_w data have been reported previously for 4-methylheptane and trans-1,3-dimethylcyclohexane. The uncertainty in the S_w values determined in this work ranged from ± 1.0 to ± 3.7 %.

Keywords: Water solubility; generator column; aliphatic hydrocarbons

INTRODUCTION

Environmental scientists have come to rely increasingly on physical and chemical properties of industrial chemicals in attempts to predict their environmental behavior.

Of the various parameters that affect the fate and transport of organic chemicals in the environment, water solubility, S_w, is one of the most important[1]. This parameter can affect adsorption and desorption in soils and volatility of chemi-

---

[*] Corresponding author. Fax: + 52–5–587–3967. E-mail: atrejo@www.imp.mx

cals from aquatic systems. It can also affect possible transformations by hydrolysis, photolysis, oxidation, reduction and biodegradation in water. Other specialized transport pathways, such as washout from the atmosphere by rain, are also influenced by the extent of water solubility.

Hydrocarbons are important petroleum derived substances that could be spilled into the environment from different industrial operations, therefore a knowledge of the solubilities of hydrocarbons in water is valuable to develop an understanding of the transportation and fate of hydrocarbons in the environment. Thus, for the petroleum industry experimental data on the solubilities of hydrocarbons in water are important for evaluating the impact of crude oil and oil products spills as well as to develop remediation strategies.

Unfortunately, numerous conflicting water solubility values have been reported in the literature for many hydrocarbons of interest, and reliable water solubility data are lacking for others. One of the factors contributing to this situation is the lack of adequate experimental methods for determining the water solubility of highly hydrophobic organic compounds. The traditional batch-stirring or shake-flask technique, wherein excess of a solute is dissolved in an aliquot of water, and the solution is generated by mechanical shaking, suffers from several limitations, for example, it is tedious and it requires to have a highly pure test substance for the S_w determinations. It is well established[2–4] that aqueous hydrocarbon solutions can exist in colloidal or micellar form when they are prepared by mechanical means besides, volatilization to the atmosphere and adsorption of the solute onto the surfaces of transfer vessels during the generation of the saturated solution could also represent disadvantages in the shake-flask method.

In this work water solubility, at 25°C, for n-hexane, n-heptane, 3-methylhexane, 2,4-dimethylpentane, n-octane, 4-methylheptane, 2,3,4-trimethylpentane and trans-1,3-dimethyl cyclohexane have been determined by using a generator column method. No experimental S_w data have been previously reported for 4-methylheptane and trans-1,3-dimethylcyclohexane. On the other hand, for most of the other C_6 to C_8 hydrocarbons studied, the experimental S_w values reported by different authors do not show good agreement amongst them. Since, the use of improper values may lead to highly uncertain and/or faulty conclusions regarding, for example, their distribution in water and in other environmental compartments, the development and implementation of environmental policy, the development or selection of remediation technologies, model development, and the design and operation of efficient industrial processes; it was then considered of the utmost importance to carry out in this work a complete reassessment of the chosen experimental technique in order to be able to determine reliable S_w data for highly hydrophobic substances, even for previously studied compounds, but whose S_w data disagreed well outside their experimental errors.

The generator column method is based on pumping water through a constant temperature-column containing a solid support coated with the compound (the solute) being studied. When water is pumped, an aqueous solution in equilibrium with the stationary phase is generated. The solute concentration in the eluted aqueous phase is determined by solvent extraction followed by subsequent gas chromatography analysis. This method avoids several limitations inherent in the shake flask technique and provides an accurate method for determining aqueous solubilities of slightly soluble, nonionizable compounds. By varying the temperature, this technique may also be used to obtain other parameters such as enthalpies and entropies of solution that reflect the aqueous solubility behavior of highly hydrophobic substances. On the other hand by varying salinity and content of miscible organic solvents of the water that is passed through the generator column, salting-out, and solventing-out effects could be analyzed[5,6]. Even, some mixtures of sparingly soluble organic chemicals could be studied[7,8].

The development of the experimental method described in this work has been done as a part of a global research project focused on the implementation of experimental and modeling procedures for assessing the environmental fate of hydrophobic substances. In the first stages of this research project, the developed method will be helpful to measure accurate aqueous solubility data for hydrocarbons existing in crude oil, and oil related products that can be released into the environment, in order to extend or improve the previously available S_w data for such substances.

EXPERIMENTAL

Reagents

All the aliphatic hydrocarbons used in this study: n-hexane, n-heptane, 3-methylhexane, 2,4-dimethylpentane, n-octane, 4-methylheptane, 2,3,4-trimethylpentane and trans-1,3-dimethylcyclohexane, were obtained from Aldrich Chemical Co., their purities were determined by gas chromatography and found to be greater than 99.8 %. 1-octanol was also obtained from Aldrich with a stated purity of 99 %. The water used in the elution experiments was type-1 reagent water from a

Nanopure deionizer (Barnstead Thermolyne). Columns for the generation of saturated aqueous solutions of hydrocarbons were packed with 100–200 mesh Chromosorb W-HP (Chromatography Research Supplies Inc.), which was previously washed by Soxhlet extraction with acetonitrile and methanol (J. T. Baker, reagent grade). After washing, the solid support was heated for five hours in a 120 °C oven and stored in a dessicator before use.

Procedure

The experimental set up used in this work for the determination of water solubility data is shown schematically in Figure 1.

The method used was developed by considering previous works reported by May *et al.*[9]; DeVoe *et al.*[10]; Tewari *et al.*[11] and Billington *et al.* [12]; and it has been designed to circumvent many of the experimental difficulties associated with the formation of clusters or aggregates of hydrophobic molecules (micelles) in the water solutions, usually generated with the traditional shake-flask systems.

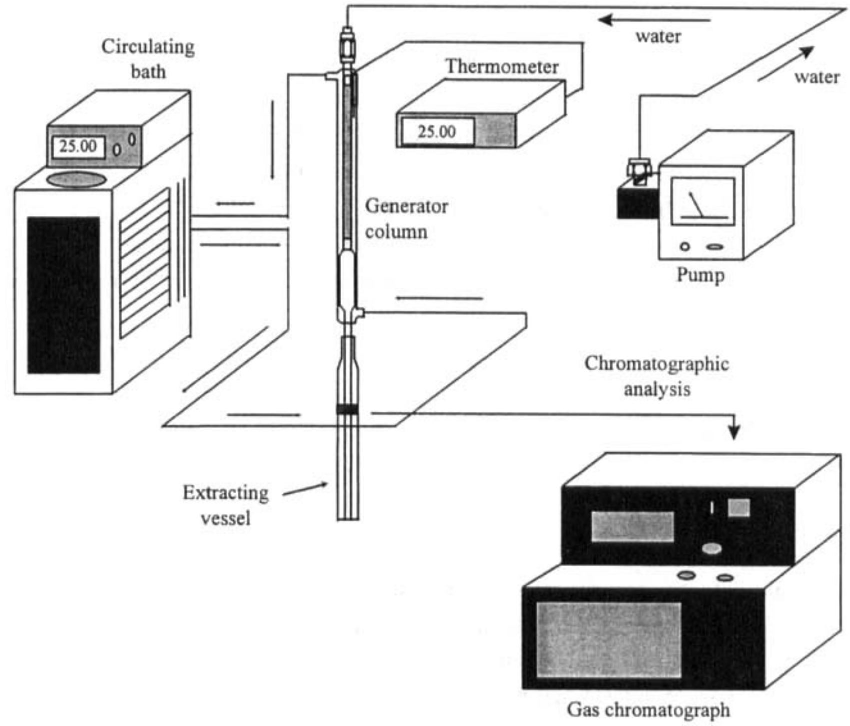

FIGURE 1 Experimental set up for the determination of water solubility data

The experimental set up was composed of two main sections: (1) a generator column for the generation of a saturated solute aqueous solution, at a given temperature, and (2) a solvent extraction-gas chromatography analysis step, for the quantification of the solute in the solution.

Columns for the generation of saturated solutions of hydrocarbons (generator columns) were prepared by packing a 30 cm × 0.6 cm o.d. Pyrex glass column joined to a short section of 3.8 cm × 0.9 cm o.d Pyrex tubing. The 0.6 cm o.d. section was hand-packed with dry and clean solid support (Chromosorb WH-P) which was held in place by two plugs of glass wool. The glass wool was previously washed by solvent extraction with acetonitrile and methanol. The column was thermostated at (25 ± 0.01) °C by pumping water from a constant temperature bath (Julabo F70) through a jacket enclosing the column. The temperature was recorded by a digital thermometer (Systemteknik S1200).

For solubility measurements, the column was coated with a pure liquid hydrocarbon by adding approximately 2 cm^3 of the liquid through the support. Saturated solutions were generated by pumping water through the column at a flow rate of 1.0 cm^3/min using a Beckman HPLC pump (model 110B). At the beginning of the experiment, the column was set up vertically up side down and a teflon outlet tube attached to the top, thus the water flow pushed a plug of the excess of the organic phase off the support. When the excess of the hydrocarbon was pushed off from the column, which was stated by visual observation, the column was inverted from its previous position to put the inlet at the top with the water flowing downward through the support, as shown in Figure 1.

In order to determine accurate experimental S_w data, it was an important task to establish the aqueous purge volume necessary to generate stable saturated solutions. This was achieved by analyzing the hydrocarbon concentration in the aqueous effluent as a function of the water volume pumped through the column. The hydrocarbon concentration in the aqueous solutions obtained at low purge volumes showed a decrease as a function of the water volume pumped through the support. However, depending on the hydrocarbon, stable saturated solutions were eluted from generator columns after an aqueous purge volume ranging between 1,500 and 6,400 cm^3. After this purge volume, the hydrocarbon concentration in the aqueous solutions became constant and was considered suitable for solubility determinations. This behavior is shown schematically in Figure 2. Table I shows the water volume necessary to achieve the equilibrium in the eluted solutions for each hydrocarbon studied.

In order to analyze the concentration of the hydrocarbon in the aqueous phase, the aqueous effluent from the generator column was collected in a cylindrical 60 cm^3 glass vessel containing about 8.5 g of a 1-octanol solution of an internal standard. The outlet of the generator column was placed such that the flowing aqueous phase was always in contact with the 1-octanol solution. Because of the large values of the octanol-water partition coefficients for aliphatic hydrocarbons[13], 1-octanol was selected as the extracting solvent.

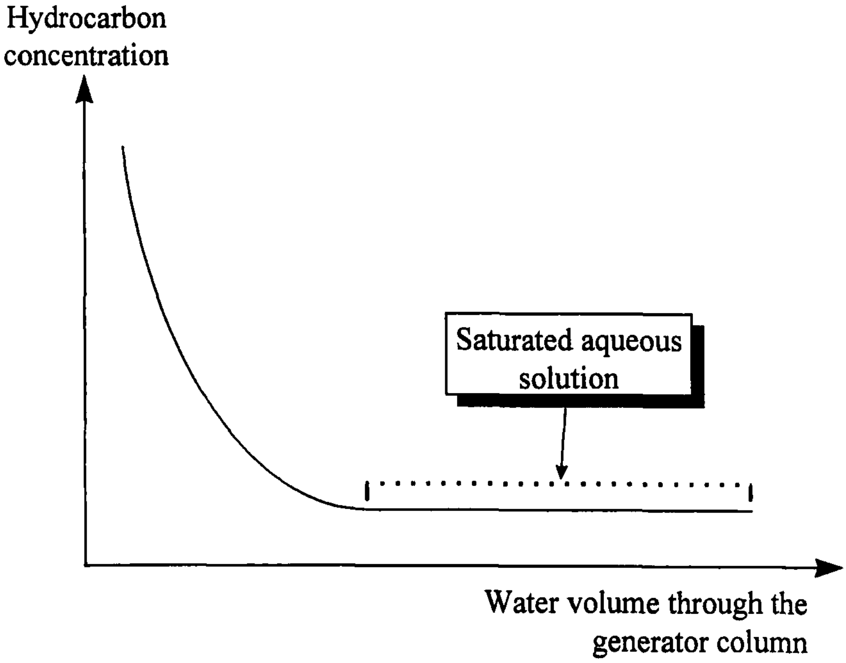

FIGURE 2 Determination of the saturation volume during experimental S_w determinations

After the aqueous phase was collected (about 50 cm^3), the collecting vessel was capped with a borosilicate glass stopper and the quantity of aqueous phase was determined by weighing. The extraction solvent and the aqueous phase were equilibrated by rotating the collecting vessel at a rate of about three revolutions per minute during thirty minutes. After a two hours settling time, a small amount of the organic solvent was injected into the gas chromatograph and the hydrocarbon concentration was determined from a calibration curve.

TABLE I Volume of water eluted through the column to generate saturated solutions of the studied hydrocarbons

Hydrocarbon	*Volume (cm^3)*
n-Hexane	1,500
n-Heptane	2,100
2,4-Dimethylpentane	3,600
n-Octane	3,750
3-Methylhexane	5,150
4-Methylheptane	5,600
2,3,4-Trimethylpentane	6,400
trans-1,3-Dimethylcyclohexane	6,050

The quantification of the studied hydrocarbons was carried out by an internal standard technique. Except for n-octane and 2,4-dimethylpentane, all the studied hydrocarbons were quantified by using n-hexane as internal standard (IS), the quantification of 2,4-dimethylpentane was accomplished by employing n-octane as IS (evidently 2,4-dimethylpentane was the internal standard in n-octane analysis). n-Hexane was quantified by using n-heptane as IS.

In order to determine the error in the calculated concentrations from the generated calibration curves, the equation proposed by Miller and Miller[14] was employed. In this equation, the estimated standard deviation, S_{x0}, of a calculated concentration x_0, from a calibration curve, is given by

$$S_{x_o} = \frac{S_{y/x}}{b}\left[\frac{1}{m} + \frac{1}{n} + \frac{(y_o - \bar{y})^2}{b^2 \sum_i (x_i - \bar{x})^2}\right]^{1/2} \qquad (1)$$

where the statistic $S_{y/x}$ is given by:

$$S_{y/x} = \left[\frac{\sum_i (y_i - \hat{y}_i)^2}{n-2}\right]^{1/2} \qquad (2)$$

and the y_i values are the chromatographic signals corresponding to the several individual hydrocarbon concentrations (x_i-values) considered for constructing the calibration curve. The $\hat{y}_i$ values represent the calculated y-values from the regression equation; **n** is the number of calibration points on the calibration curve, **b** represents the slope of the curve; $\mathbf{y}_0$ is the experimental value of **y** from which the concentration value $\mathbf{x}_0$ (actually the water solubility, S_w) was determined; m is the number of independent measurements of $\mathbf{y}_0$ carried out to obtain a final value of $\mathbf{x}_0$, and $\bar{x}$ and $\bar{y}$ are the mean of the $\mathbf{x}_i$ and $\mathbf{y}_i$values, respectively.

The confidence limits for the determined concentrations of the studied hydrocarbons in the aqueous solutions were calculated as $x_0 \pm t_{\alpha/2(n-2)}\ S_{X_0}$, where $t_{\alpha/2(n-2)}$ is the **t** of Student with (n-2) degrees of freedom and a confidence level (α) of 95%.

Because of the form of the confidence limits, the determination of a concentration from a calibration experiment in chromatographic studies will give the most precise results when the measured instrument signal corresponds to a point close to the centroid of the regression curve[14]. Inspection of equation 1 confirms that as y_0 approaches $\bar{y}$, the third term inside the bracket approaches zero, and S_{X_0} thus approaches a minimum value. On the other hand by increasing m and n, the first and second terms in equation 1 could also be reduced and therefore S_{X_0} is reduced too.

Thus, by considering these approaches the confidence limits of the calibration curves for the studied hydrocarbons were improved (i.e. narrowed) by constructing the calibration curves in narrower concentration intervals (usually setting the limits of the interval between ± 45 % around the expected water solubility concentration), and evidently setting the expected water solubility concentration as the center of the concentration interval. On the other hand n was fixed in 7 and m ranged between 6 and 7. Additionally, the random errors associated with the other steps of the experimental procedure were also estimated[15]. Quadratic addition of all the random errors yielded the uncertainty for the experimental determinations of S_w data.

The gas chromatograph used in this work was a Tremetrics model 541 fitted with a flame ionization detector, utilizing a 50 cm × 1/8 inch stainless steel column packed with 5% of a polydimethylsiloxane (OV-101) on Chromosorb G-HP, 100–120 mesh. The temperature of the oven was initially maintained at 40°C for 7 min, then the oven temperature was increased to 110°C, at 15°C/min and kept there for 10 min to remove all the relatively high boiling 1-octanol. The temperature was then lowered to 40°C and after stabilization the next sample was analyzed. Nitrogen was used as carrier gas. The temperature of the injection port and the detector were kept at 220 °C and 260 °C, respectively.

TABLE II Aqueous solubilities, S_w, of saturated hydrocarbons in water, at 25°C

Sw (g/m³)				
n-Hexane	*n-Heptane*	*n-Octane*	*Experimental Method /Temperature control*	*Reference*
9.5 ± 1.3	2.93 ± 0.20	0.66 ± 0.06	SF† / ± 1.5°C	McAuliffe[18,19]
12.4 ± 0.2	3.37 ± 0.13	0.85 ± 0.03	SF†-PEWS‡ / ± 0.01°C	Polack and Lu[20]
9.47 ± 0.20	2.24 ± 0.04	0.431 ± 0.012	PEWS‡ / ± 1°C	Price[22]
12.3 ± 0.4	—	—	SF† /—	Aqua-Yuen *et al.*[21]
12.30 ± 0.12	3.57 ± 0.04	1.10 ± 0.01	GC§ / ± 0.1°C,	Tewari et al.[11]
9.40 ± 0.97	**2.23 ± 0.03**	**0.465 ± 0.004**	**GC§ / ± 0.01°C,**	**This work**
Sw (g/m³)				
3-Methylhexane	*2,4-Dimethylpentane*	*2,3,4-Trimethylpentane*	*Experimental Method/Temperature control*	*Reference*
—	3.62 ± 0.10	—	SF† / ± 1.5°C	McAuliffe[18]
—	4.06 ± 0.29	—	SF† / ± 1.5°C	McAuliffe[19]
4.95 ± 0.20	5.50 ± 0.09	2.30 ± 0.09	SF†-PEWS‡ / ± 0.01°C	Polack and Lu[20]
2.64 ± 0.08	4.41 ± 0.05	1.36 ± 0.03	PEWS‡ / ± 1°C	Price[22]
2.66 ± 0.05	**2.45 ± 0.02**	**1.32 ± 0.04**	**GC§ / ± 0.01°C,**	**This work**

† Shake-Flask ; ‡ Phase Equilibrium With no Stirring ; § Generator Column.

RESULTS AND DISCUSSION

The experimentally determined water solubility data for the studied hydrocarbons are given in Tables II and III. The S_w values were obtained by employing two or three independent columns, and determining two or three separated values on each column. The determinations on each column were carried out at several water elution volumes above the saturation purge volume (see Table I). Thus, the experimental data in Tables II and III are the average of four to nine independent and highly consistent measurements.

TABLE III Aqueous solubilities, S_w, of aliphatic hydrocarbons in water, at 25°C determined in this work. No experimental data have been previously reported for these substances

Hydrocarbon	*$S_w (g/m^3)$*
4-Methylheptane	**0.836 ± 0.016**
trans-1,3-Dimethylcyclohexane	**3.20 ± 0.04**

When the purge volumes shown in Table I were reached, the concentration of each pure hydrocarbon in the aqueous effluent became constant, even varying the flow rate between 0.2 and 1.5 cm^3/min. The hydrocarbon concentration of the solutions was also constant through large volumes of aqueous purge ranging between 500 and 2,700 cm^3 above the saturation volume.

Pumping of the saturated aqueous solutions through the glass wool plugs fitted on both ends of the column does not alter the concentration of the generated solutions because the plugs are saturated with the hydrocarbons of interest during the column conditioning process and became therefore an integral part of the solution generating system from the beginning[9].

When spectroscopic techniques are used to analyze the solute dissolved in the aqueous phase, the presence of dissolved impurities which contribute to the signal of the solute reduces the accuracy of the method to determine S_w data. The method presented in this work comprises a chromatographic step which is capable of separating the signals produced by impurities from the signal produced by the analyte of interest and therefore the use of this technique can also relax the purity requirement for the individual hydrocarbons.

The uncertainty in the S_w values reported in this work was assessed[14,15] by a whole error analysis which included both the operational as well as the chromatographic steps of the method. The error analysis showed that the precision of the method was strongly affected by the uncertainties related with the chromatographic analysis step. However, as it has been established, through a proper selection of the calibration curve range, the number of points in the curve and the number of repeated injections of the sample, it was possible to reduce the global error of this step. The random errors that were associated with the operational and chromatographic steps of the method have been estimated to vary between 0.5 – 0.7 %, and 1.0 – 3.0 %, respectively. Quadratic addition of these random errors yields an uncertainty of 1.0 – 3.7 % for the developed method.

Table II shows a comparison between the water solubilities, at 25°C, of several saturated hydrocarbons, as determined in this work, with some of the best literature values[16,17]. The experimental method employed to determine the previously reported S_w values, as well as the temperature control used in such determinations are also given. Table III gives experimental data of S_w obtained in this work for 4-methylheptane and trans-1,3-dimethylcyclohexane. No experimental S_w data have been previously reported for these substances.

Despite the relatively large number of studies on the water solubility of linear and branched-chain paraffin hydrocarbons, most of the previously reported S_w data are only in partial agreement (see Table II). Such disagreement can be ascribed to the experimental technique used in each work. On the one hand, it should be considered that the extremely low solubility of these hydrocarbons presents a daunting experimental problem and, if no proper analytical techniques are used to analyze aqueous solutions, the accuracy and precision of the S_w results is reduced. On the other hand, the chosen method for the preparation of the saturated aqueous solution of the hydrophobic substance can also diminish the reliability of the experimental S_w values.

Of the hydrocarbons studied in this work, McAuliffe[18,19] has reported experimental S_w values for n-hexane, n-heptane, 2,4-dimethylpentane and n-octane; and Aqua-Yuen *et al.*[21] have determined experimental solubility data for n-hexane. All the above mentioned data were determined by employing a shake-flask method. The data reported by Price[22] include S_w values for n-hexane, n-heptane, 3-methylhexane, 2,4-dimethylpentane, n-octane, and 2,3,4-trimethylpentane and were obtained by using a method where the saturated aqueous solution was generated by putting in contact the water and the hydrocarbon phases with no stirring or shaking (phase equilibrium with no stirring, PEWS) during long periods of time.

Polack and Lu[20] have determined water solubility data for n-hexane, n-heptane, 3-methylhexane, 2,4-dimethylpentane, n-octane and 2,3,4-trimethylpentane by using both a shake-flask as well as a PEWS method. These authors established that an excellent agreement was obtained between the results of the two methods. However, their experimental S_w values are higher than those reported by Price[22]. Finally, although the results reported by Tewari *et al.*[11] for n-hexane, n-heptane and n-octane, were obtained by a generator column technique, they are also higher than those of Price. In all the above mentioned methods the aqueous phase analysis was accomplished by gas chromatography.

It is quite clear from table II that most of the experimental S_w data for n-hexane, n-heptane, 3-methylhexane, 2,4-dimethylpentane, n-octane, and 2,3,4-trimethylpentane; previously reported by different authors, and determined from apparently equally good studies disagree well outside their experimental errors. Hence, we conclude that most of the previous sets of measurements do not show good accuracy, particularly those obtained with unreliable techniques.

As shown in Table II, the experimental S_w values determined in this work for the three linear alkanes studied are in good agreement with those reported by Price[22]. The S_w value for n-hexane is also in good agreement with that reported by McAuliffe[18,19], but it is lower than the reported by Aqua-Yuen *et al.*[21]. However, the S_w data for the three above mentioned hydrocarbons are lower than those determined by Polack and Lu[20]. The solubility data for n-heptane and n-octane reported by McAuliffe *et al.*[18,19] are also larger that those determined in this work.

It is evident that the generator column method gives lower S_w values than those determined from aqueous saturated solutions prepared by a batch stirring-contact (shake-flask) method.

In aqueous solutions of hydrophobic substances generated from a batch stirring-contact technique, depending on the conditions of agitation, micellar aggregates could be formed in different concentrations and sizes, the concentration of such aggregates changes with time after formation, and therefore the concentration of the hydrophobic substance present in the aqueous solution could be expected to be somewhat arbitrary[4].

Thus, the results reported in this work could suggest that solutions produced by generator columns are free of emulsions in the effluent stream, and therefore the water solubility determinations could be more accurate. In their experimental determinations of S_w data for polynuclear aromatic hydrocarbons (PAH) Billington *et al.*[12] have also found that regardless of the chromatographic method (either gas chromatography or liquid chromatography) used to analyze aqueous solutions, the generator column method gives commonly S_w values lower than those determined from aqueous solutions prepared by shake-flask techniques. The water solubility values for PAH determined by the generator column method could be from 1 to 96 %, lower than those determined by the shake-flask technique.

On the other hand, Coates *et al.*[4] have established that the problem of hydrocarbon aggregates in water could be overcome by long-term equilibration experiments where a small quantity of n-alkane is layered carefully with no mixing, onto the water surface. Apparently, without agitation, aggregates are not formed and with long equilibrium times a true solution result through diffusion. Thus, the agreement with the reported data by Price[22] seems to be reasonable by considering that this author generates the hydrocarbon aqueous solutions with no stirring, thus minimizing the emulsions formation.

Table II shows that the S_w data for n-hexane, n-heptane, and n-octane reported by Tewari *et al.*[11] are higher than those determined in this work, even though the generator column method was used in both works. The origin of this disagreement could lie on the water volume pumped through the column, previous to the sampling and analysis steps. As it has been indicated, in order to determine reliable S_w data, it is crucial to make sure that aqueous solutions are perfectly saturated with the hydrophobic compound at the given temperature. In this work all the S_w values were determined by sampling the aqueous phase until the saturation was established as indicated by constant concentration of the hydrophobic substance in the aqueous phase (see Figure 2). No aqueous purge volumes are reported by Tewari *et al.*[11] during their S_w determinations. Billington *et al.*[12] have also found differences up to 76 % between their PAH experimental S_w values and those reported by May *et al.*[23] even when both set of data were determined by employing generator column methods.

Regarding the branched hydrocarbons, Table II shows that the previously reported S_w values for 3-methylhexane, 2,3,4-trimethylpentane and 2,4-dimethylpentane are also in poor agreement amongst them. Even, for 2,3,4-trimethylpentane it has been established by IUPAC[17] that in the absence of other independent studies it is not possible to prefer any of the reported values.

The S_w data determined in this work for 3-methylhexane and 2,3,4-trimethylpentane compare satisfactorily with those reported by Price[22], and are lower than those reported by Polack and Lu[20]. As mentioned, experimental values by Polack and Lu[20] unlike values by Price[22] were determined by a shake-flask technique. It is supposed that in the method by Price the problem of hydrocarbon aggregates formation could be overcome, and therefore his experimental values for 3-methylhexane and 2,3,4-trimethylpentane show a good agreement with the values reported in this work. Finally, the experimental S_w value for 2,4-dimethylpentane determined in this work is lower than all the previous reported values. The value determined in this work was obtained by employing three independent columns, and determining two or three separated values on each column. The error of the individual determinations lay into the average error of the global method.

Additionally, Table III gives experimental data of S_w, at 25°C, determined in this work for 4-methylheptane and trans-1,3-dimethylcyclohexane. So far as it is known to the authors, experimental water solubility data have not been reported for these hydrocarbons.

Some studies have indicated[19] that for homologous series of hydrocarbons, the logarithm of the solubility in water is a linear function of the hydrocarbon molar volume, and that for paraffins, branching increases its water solubility; on the other hand, for a given carbon number, ring formation increases water solubility. In a general way the hydrocarbons studied in this work follow such behavior even though water solubility for 2,4,-dimethylpentane is lower than the S_w value for 3-methylhexane.

CONCLUSIONS

A generator column method has been used to determine experimental water solubility data for saturated C_6 to C_8 hydrocarbons. Because of its characteristics, the experimental technique provides a reliable method for determining water solubility of sparingly soluble organic compounds because avoids the formation of emulsions in the aqueous solutions, and therefore the concentration of the hydrophobic compound in those solutions become constant at a given temperature. The reported method also includes a chromatographic step of analysis which is able of separating the signals produced by impurities from the signal produced by the compound of interest and therefore does not require the use of ultra pure substances. An error analysis allows to identify and diminish the global error of the method. The uncertainty in most of the S_w values reported in this work ranged from ± 1.0 to ± 3.7 %.

The generator column method has been used to determine new accurate data of water solubility, at 25°C, for two hydrocarbons no previously studied. The method has also been employed to generate new accurate data of water solubility, at 25°C, for six hydrocarbons studied previously by several authors but whose data disagreed well outside their reported experimental errors. A complete assessment of all the attributes, internal consistency and error analysis of the method has also been carried out.

The obtained results will be useful to develop estimation techniques for modeling the environmental fate of hydrophobic substances.

Acknowledgements

Financial support for this work was provided by a grant from "Fondo de Apoyo a Proyectos de Investigación en Colaboración con Instituciones de Educación Superior (FIES)", of the Instituto Mexicano del Petróleo, under research project FIES-95F-141-II.

References

[1] W. J. Lyman, In: *Handbook of Chemical Property Estimation Methods* (W. J. Lyman, W. F. Reehl and D. H. Rosenblatt, eds. American Chemical Society, Washington, DC, 1990), Chap. 2, pp. 2.1 – 2.52.

[2] E. Peake and G. W. Hodgson, *J. Am. Oil Chem. Soc.*, **43,** 215–222, (1966).

[3] E. Peake and G. W. Hodgson, *J. Am. Oil Chem. Soc.*, **44,** 696–702 (1967).

[4] M. Coates, D. W. Connell and D. M. Barron, *Environ. Sci. Technol.*, **19,** 628–632 (1985).

[5] C-S. Hong and H. Qiao, *Chemosphere*, **31,** 4549–4557 (1995).

[6] G. T. Coyle, T. C. Harmon and I. H. Suffet, *Environ. Sci. Technol.*, **31,** 384–389 (1997).

[7] W. Y. Shiu, A. Maijanen, A. L. Y. Ng and D. Mackay, *Environ. Toxicol. Chem.*, **7**, 125–137 (1988).

[8] A. G. van Haelst, Q. Zhao, F. W. M. van der Wielen and H. A. J. Govers, *Chemosphere*, **33,** 257–264 (1996).

[9] W. E. May, S. P. Wasik and D. H. Freeman. *Anal. Chem.*, **50,** 175–179 (1978).

[10] H. DeVoe, M. M. Miller and S. P. Wasik, *J. Res. Nat. Bur. Stand.*, **86,** 361–366 (1981).

[11] Y. B. Tewari, M. M. Miller, S. P. Wasik and D. E. Martire, *J. Chem. Eng. Data*, **27,** 451–454 (1982).

[12] J. W. Billington, G-L. Huang, F. Szeto, W. Y. Shiu and D. Mackay, *Environ. Toxicol. Chem.*, **7,** 117–124 (1988).

[13] J. Sangster, *J. Phys. Chem. Ref. Data*, **18,** 1111–1229 (1989).

[14] J. C. Miller and J. N. Miller, Statistics for Analytical Chemistry (Ellis Horwood, Chichester, 1988) 2nd ed., Chap. 5, pp. 101–115.

[15] J. R. Taylor, An Introduction to Error Analysis (University Science Books, Mill Valley, CA. 1982), Chaps. 1–5, pp. 1–137.

[16] IUPAC, *Solubility Data Series. Hydrocarbons with water and sea water. Hydrocarbons C_5 to C_7*, (D. G. Shaw, ed. Pergamon Press, Oxford. 1989) Volume 37, Part I, pp. 314–323, 469–475, 481–517.

[17] IUPAC, *Solubility Data Series. Hydrocarbons with water and sea water. Hydrocarbons C_8 to C_{36}*, (D. G. Shaw, ed. Pergamon Press, Oxford. 1989) Volume 38, Part II, pp. 126–130, 135–160.

[18] C. McAuliffe, *Nature*. **200,** 1092–1093 (1963).

[19] C. McAuliffe, *J. Phys. Chem.*, **70,** 1267–1275 (1966).

[20] J. Polak and B. C-Y. Lu, *Can. J. Chem.*, **51,** 4018–4023 (1973).

[21] M. Aquan-Yuen, D. Mackay and W. Y. Shiu, *J. Chem. Eng. Data*, **24,** 30–34 (1979).

[22] L. C. Price, *Am. Assoc. Petr. Geol. Bull.*, **60,** 213–244 (1976).

[23] W. E. May, S. P. Wasik and D. H. Freeman. *Anal. Chem.*, **50,** 997–1000 (1978).