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Invited Review

Mutual Solubilities of Water and Alkanes*

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Summary. The evaluation of mutual solubility data for systems water with *n*-alkanes, isoalkanes, and cycloalkanes along the three phase line is reported and a formula for the prediction of solubility of alkanes in water is developed. Then a cubic equation of state with an added term, which accounts for hydrogen bonding is used for correlation of liquid–liquid equilibrium data and for prediction of solubility of water in hydrocarbons using alkane in water solubility data. Comparison of the predicted and experimental solubilities is performed using all accessible experimental data. With this approach it is possible to predict the solubilities of water in alkanes with good accuracy over the temperature range up to about 20 K below critical temperature. Solubility of alkanes in water can also be calculated using experimental data for solubility of water in alkanes but results of these calculations are more sensitive to experimental errors of the data.

Keywords. Hydrogen bonding; Equation of state; Mutual solubilities; Alkanes; Water.

Introduction

Solubility phenomena, particularly the dissolving of solids and liquids in water to form aqueous solutions, have been observed since ancient times. However, only since the rise of the modern molecular theory of matter in the eighteenth century, there has been a basis for distinguishing the essentially physical processes of solubility from chemical reactions. Prior to that time the nature of solubility was a matter of speculation [1]. Today solubility phenomena are studied as part of the broader topic of phase equilibria. The solubilities considered are primarily liquid–liquid equilibria (LLE), and, more rarely, vapor–liquid equilibria (VLE) or solid–liquid equilibria (SLE).

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* Dedicated to Prof. Dr. H. Gamsjäger on the occasion of his 70th birthday anniversary

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In the modern world reliably precise and accurate information about chemical solubility is essential to a wide variety of human activities. From the theoretical perspective solubility data can be interpreted to provide understanding of molecular properties and the nature of the liquid state, especially for water, a uniquely complex and important liquid [2]. Solubility data also find important application in a number of applied branches of chemical science. For instance, in medicinal chemistry and pharmacology knowledge of the aqueous solubility of drugs and their metabolites guides the development of dosage regimes. In chemical engineering knowledge of the solubility of water in various petrochemicals (*e.g.*, benzene, phenol, *etc.*) is essential for the prevention of the formation of separate aqueous phases ("free water") which, especially at elevated temperatures, can corrode process equipment and interfere with desired reactions. In environmental chemistry knowledge of the water solubility of potentially polluting substances is necessary for the design of equipment and processes to keep discharges within permitted and acceptable levels. Many other examples could be cited in which knowledge of solubility contributes in important ways to technical advances which avoid harm and improve our quality of life. Given the importance and wide applicability of solubility data, it is not surprising that many thousands of experimental determinations of solubility have been reported in the primary chemical literature.

To address the needs for the compilation and critical evaluation of experimental solubility determinations, the International Union of Pure and Applied Chemistry organized the Solubility Data Project [3], which has assembled an international group of solubility experts who are preparing compilations and evaluations of published solubility data. The results of this project have appeared as the Solubility Data Series, an ongoing collection of printed volumes and, more recently in co-operation with the US National Institute of Standards and Technology, as an internet-accessible database. The Solubility Data Series has included several volumes dealing with binary systems containing water and hydrocarbons [4, 5], alcohols [6, 7], esters [8, 9], halogenated ethanes and ethenes [10], halogented aliphatic hydrocarbons [11], and ternary systems of hydrocarbons, alcohols, and water [12].

The Solubility Data Project is strongly focused on the critical evaluation of experimentally determined solubility data for well-defined individual chemical systems. For some systems fitting or smoothing equations are provided which allow the interpolation of solubility for conditions (usually temperatures) at which direct measured data are not available. However, extrapolation and prediction of solubility beyond the ranges of conditions studied or for analogous or homologous systems is beyond the scope of the project.

The solubility of hydrocarbons in water is a mutual process giving rise to a water-rich phase containing a small fraction of dissolved hydrocarbon and a hydrocarbon-rich phase containing a small fraction of dissolved water. A large body of experimental data [4, 5] shows that the solubility of hydrocarbons in water is highly dependent on the identity of the hydrocarbon with larger molecules being less soluble, but that the solubility of water in hydrocarbons is much less strongly influenced by the identity of the hydrocarbon. For all systems mutual solubility is favored by the entropy of mixing but must overcome the enthalpy required to disrupt the hydrogen bonding of liquid water. When a molecule of hydrocarbon is dissolved in water, the number of hydrogen bonds broken and distorted depends very much on the size of the cavity in the water needed to accommodate the hydrocarbon molecule and, hence, on the size and shape of that hydrocarbon. But when water is dissolved in a hydrocarbon the number of water–water hydrogen bonds broken is always two (at least at low temperatures, where solubility of water is small). The solubility of water in hydrocarbons is not identical because hydrocarbons, depending on their polarizability, engage in weak but variable van der Waals interactions with water. These considerations imply that equations which accurately predict the solubility of hydrocarbons in water will take quite different forms from equations which predict the solubility of water in hydrocarbons.

This work deals with liquid–liquid equilibria (LLE) in mixtures of water with *n*-alkanes, cycloalkanes, and isoalkanes. Solubility of these alkanes in water is very low over the whole temperature range from 273 K to the critical temperature of the solubility. Even near three-phase critical temperatures, the mole fraction of the alkane is usually below 0.001. The solubility of various alkanes in water varies widely. *Tsonopoulos* [13] has examined the solubilities of hydrocarbons in water for homologous series of alkanes, alkyl cyclohexanes, 1-alkenes, and alkyl benzenes. Within each homologous series the regularity of changes in solubility with increasing alkyl chain length suggests that estimation of solubility for longer chain lengths by extrapolation is reasonable. Comparison of solubilities among homologous series at a given number of carbon atoms provides insights into the nature of the solubilization phenomena for both hydrocarbons dispersed in water and water dispersed in hydrocarbons.

The solubility of water in hydrocarbons is at least two orders of magnitude higher than solubility of the hydrocarbons in water. At low temperatures the solubility of water depends weakly on the type of alkane. The solubility increases very rapidly with increasing temperature and reaches a relatively high value at the three-phase critical end point.

The solubility of water in hydrocarbons is often described with empirical equations [14, 15]. The cited equations contain four empirical constants for each mixture. Another approach uses a *van der Waals* type equation of state (EoS) as, for example, the modification of *Redlich–Kwong* equation proposed by *Zudkevitch* and *Joffe* [16]. This equation was successfully applied to the solubility of water in hydrocarbons. A similar approach was used by *Tsonopoulos* and *Wilson* [15]. They were able to correlate the data with a single temperature-independent binary parameter. However, this simple EoS fails for the water-rich phase. Other modifications of the cubic EoS proposed in the literature use local compositions or density dependent mixing rules. In general, they fail to describe even qualitatively the solubility of hydrocarbons in water. Several unconventional mixing rules were proposed for water systems, but with limited success [17]. Another approach is to use equations which account for hydrogen bonding and other anisotropic interactions. *Economou* and *Tsonopoulos* [17] calculated LLE in water plus hydrocarbon systems using the equations APACT [18, 19] and SAFT [20]. They tested several models of hydrogen bonding for water as well as different mixing rules and found that "None of these theories provide quantitative estimate of the *n*-alkane solubility in water nor do they predict the *n*-alkane solubility minimum" [17].

The purpose of this work was to analyze experimental data in order to develop methods of correlation, verification and prediction of LLE in mixtures of hydrocarbons and water. First, minimum solubilities of alkanes in water were investigated and a predictive equation was developed. Next, an equation for the prediction of the solubilities of the hydrocarbons in water over the temperature range from 273.15 K to the three-phase critical end point was developed. Finally, a new method based on a cubic equation of state appended with a term which accounts for hydrogen bonding was used to predict the solubility of water in *n*-alkanes, cycloalkanes and isoalkanes.

Results and Discussion

Minimum of Alkanes Solubility Curve

The solubility of alkanes in water goes through a minimum at which the heat of solution ($\Delta_{\mathrm{sln}}h_i$) is zero. The relation between solubility and the heat of solution is given by Eq. (1) where x_i is the mole fraction of *i*th alkane in water and $\Delta_{\mathrm{sln}}h_i$ is the difference between the partial enthalpy of the *i*th hydrocarbon at infinite dilution and the molar enthalpy of the pure hydrocarbon.

$$[\partial \ln x_i/\partial(1/T)]_P \cong -\Delta_{\mathrm{sln}}h_i/R \qquad (1)$$

The heat of solution includes two effects: a positive heat of cavity formation and a negative heat of hydrophobic interaction between the hydrocarbon and water. These two effects cancel each other at T_{m}, the temperature at which $\Delta_{\mathrm{sln}}h_i = 0$, which according to Eq. (1) corresponds to the minimum solubility of the hydrocarbon in water. *Tsonopoulos* [13] investigated the mole fraction of hydrocarbons at $T = 298$ K, which practically corresponds to solubility at the minimum, $x_i(T_{\mathrm{m}})$. Within each homologous series (alkanes, alkyl cyclohexanes, 1-alkenes, and alkyl benzenes) he found a linear dependence between $\log(x_i(T_{\mathrm{m}}))$ and the number of carbon atoms of the corresponding hydrocarbon.

In this work the separate linear dependences on solubility for *n*-alkanes, cycloalkanes and isoalkanes are reduced to one linear function, shown in Fig. 1, in which the number of carbon atoms is replaced by excluded volume used in equations of state of *van der Waals* type. This approach results from assumption that the solubility of alkanes is related to the effect of cavity formation, which in turn is proportional to the excluded volume (b_i) of the *i*th alkane. Here b_i is defined by Eq. (2) where T_{c} and P_{c} are critical parameters of the *i*th alkane.

$$b_i = 0.08664\,\mathrm{R}(T_{\mathrm{c}}/P_{\mathrm{c}})_i \qquad (2)$$

This definition corresponds to *Redlich–Kwong* EoS used later on this paper.

Decimal logarithms are used, in all the figures presented in this paper, to allow easier estimation of the solubilities placed in the plot. The dependence of $\log x_i(T_{\mathrm{m}})$ on b_i, shown in Fig. 1, contains points corresponding to the three series of alkanes investigated in this paper. Each point represents an average value of $\log x_i(T_{\mathrm{m}})$ for the *i*th alkane/water system in the range 293–313 K. In this temperature region the change of the solubility due to temperature is negligible compared to experimental errors. At the same time this region usually contains many experimental points (see, for example, Fig. 3).

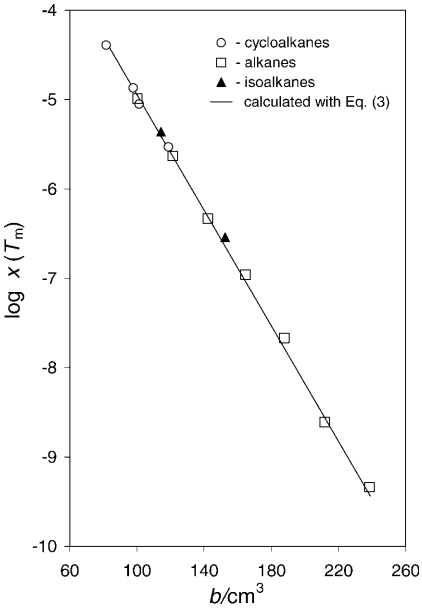

Fig. 1. The dependence of log x (T_m) on excluded volume b as defined by Eq. (3)

In order to remove outlying points the following procedure was applied. At first, arithmetic mean of $\log x_i(T_m)$ was calculated using all the experimental points reported for a given mixture within the temperature interval 293–313 K. After then standard deviation was calculated. The points which differ from the arithmetic mean more than double value of the standard deviation were removed from the further calculations. Then the data were examined once more using the same procedure but with corrected arithmetic mean and standard deviation. The procedure was repeated until no outlying points were found. All together 84 experimental points for thirteen mixtures were investigated. Fourteen experimental points were rejected by the procedure described above.

Regression of the points shown in Fig. 1 yields a straight line described by Eq. (3) where b_i in cm^3 was calculated according to Eq. (2).

$$\ln x_i(T_m) = -4.03 - 0.0735\, b_i \tag{3}$$

As is shown by the plot no systematic deviations from linearity are observed. In order to estimate accuracy of $\ln x_i(T_m)$ calculated with Eq. (3) its standard deviation was calculated from scattering of points shown in Fig. 1. This standard deviation is equal to 0.036. It should be noted, however, that Eq. (3) must not be extrapolated to higher n-alkanes. The experimental data for dodecane and higher n-alkanes suggest significantly weaker b_i dependence. According to *Tsonopoulos* [22], "This change has been attributed to the formation of micelles. The formation of such colloidal suspensions can, indeed, raise significantly the apparent non-equilibrium solubility, but this could also result from a transition of the $C_{11}+$ normal alkanes to a collapsed conformation, which would reduce contact of the alkane with water, and would, thus, make their solubility in water higher...".

Equation (3) is useful for identification of outlying experimental data not only at T_m, but also at other temperatures, because experimental points at other temperatures should lie on a curve going through the minimum predicted with Eq. (3). This feature is very useful in cases where two contradicting sets of points are reported for the same system.

Solubility Curve for Alkanes in Water

Gill et al. [23] have measured the heat of solution of hydrocarbons in water as a function of temperature. The measurements were made over a narrow temperature range, but they suggest that the heat of solution ($\Delta_{\mathrm{sln}}h_i$) is a linear function of temperature, which implies that heat capacity of solution ($\Delta_{\mathrm{sln}}C_{\mathrm{P},i}$) is constant. In this case $\Delta_{\mathrm{sln}}h_i$ can be written as Eq. (4).

$$\Delta_{\mathrm{sln}}h_i = \Delta_{\mathrm{sln}}C_{\mathrm{P},i}(T - T_{\mathrm{m}}) \tag{4}$$

Integration of Eq. (1) with $\Delta_{\mathrm{sln}}h_i$ as expressed by Eq. (4) yields Eq. (5) where $x_i(T)$ denotes the mole fraction of the *i*th alkane in a saturated mixture at temperature T.

$$\ln x_i(T) = \ln x_i(T_{\mathrm{m}}) + (\Delta_{\mathrm{sln}}C_{\mathrm{P},i}/\mathrm{R})[\ln(T/T_{\mathrm{m}}) + T_{\mathrm{m}}/T - 1] \tag{5}$$

It is not certain over what range Eq. (4) is justified, but the resulting Eq. (5) is commonly used for the description of solubility of hydrocarbons in water. *Economou et al.* [24] claim that Eq. (5) is very satisfactory up to the three phase critical temperature ($T_{3\mathrm{c}}$). In this work Eq. (5) was used for correlation and verification of literature data for solubility of alkanes in water. At the beginning the data were correlated with Eq. (5) using two adjustable parameters, T_{m} and $\Delta_{\mathrm{sln}}C_{\mathrm{P},i}/\mathrm{R}$. The third parameter, $\ln x_i(T_{\mathrm{m}})$, was obtained from Eq. (3). It was found that the adjusted value of T_{m} is sensitive to errors of the data. Even if the verified data were used, the adjusted values of T_{m} seem to be randomly scattered. For *n*-alkanes the following values of T_{m} were obtained: pentane (306 K), hexane (309 K), heptane (310 K), octane (300 K), and nonane (320 K). These adjusted values of T_{m} can be varied by about 10 K without affecting significantly the quality of the correlation. In this situation arbitrary value $T_{\mathrm{m}} = 308$ K was adopted for *n*-alkanes and isoalkanes. For a cyclohexane/water mixture the calorimetric measurements of *Gill* yield $T_{\mathrm{m}} = 298$ K. This temperature works well for all cycloalkanes investigated in this work and was thus, adopted for all cycloalkane/water mixtures.

At the next stage of this investigation, the solubilities of alkanes were correlated with $\ln x_i(T_{\mathrm{m}})$, obtained from Eq. (3), and the fixed values of T_{m}. This leaves ($\Delta_{\mathrm{sln}}C_{\mathrm{P},i}/\mathrm{R}$) as the only adjustable parameter in Eq. (5). The values of this parameter were obtained for five cycloalkane/water mixtures and for mixtures of water with *n*-alkanes from pentane to decane. These values are plotted in Fig. 2. Other systems investigated in this paper are not indicated in Fig. 2, because corresponding data are measured only in the vicinity of minimum of the solubility curve.

The approximating line shown in Fig. 2 is described by Eq. (6).

$$\Delta_{\mathrm{sln}}C_{\mathrm{P},i}/\mathrm{R} = 0.376\, b_i \tag{6}$$

Average standard deviation of the calculated $\Delta_{\mathrm{sln}}C_{\mathrm{P},i}/\mathrm{R}$ estimated from scattering of white points in Fig. 2 is equal 0.7, but it should be noted that the assumed values of T_{m} influence to some extent the adjusted values of the heat capacity. Nevertheless, Fig. 2 is very useful, because it helps to avoid systematic errors occurring

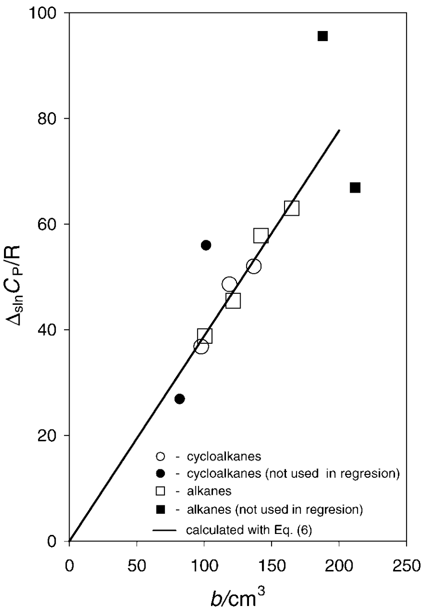

Fig. 2. The dependence of $\Delta_{\rm sln}C_{\rm P}/{\rm R}$ on excluded volume b. The points representing values of $\Delta_{\rm sln}C_{\rm P}/{\rm R}$ were adjusted by means of Eq. (5) to solubility data

in data corresponding to black points. Taking into account Eqs. (3) and (6) one can write Eq. (5) as shown in Eq. (7) where b_i is expressed in cm^3.

$$\ln x_i(T) = -4.03 + b_i\{(0.376[\ln(T/T_{\rm m}) + T_{\rm m}/T - 1] - 0.0735\} \qquad (7)$$

In view of the uncertainty of the available data Eq. (7) is entirely adequate to represent the temperature dependence of solubility of the alkanes. If more data become available, this equation will probably need to be updated but at the present state it represents a better approximation of the existing experimental data than individually adjusted curves, which are more likely to fit systematic errors of the data for a given system. This is exemplified in Fig. 3, which contains experimental points for the solubility of *n*-octane in water and the curve determined with Eq. (7). It appears that the calculated curve is too low and this is supported by the fact that Price's point at 298 K is certainly too low, what suggests that other Price's points may also be too low. But if Price's data are omitted and Eq. (5) is adjusted to data of *Heidman et al.*, then one obtains $T_{\rm m} = 281.5$ K and $\Delta_{\rm sln}C_{\rm P}/{\rm R} = 49.2$. But these values are not consistent with regularities observed in the homologous series of alkane/water mixtures discussed above and it is not reasonable to ignore these regularities and reject Price's data in order to obtain a nice approximation. The curve calculated with Eq. (7) is more justified. Moreover, the calculated curve is consistent with corresponding solubility of water in octane shown in Fig. 4, but this point will be discussed in a subsequent part of this paper. One must rather assume that the observed discrepancy between some experimental points and the curve shown in Fig. 3 indicates error of these experimental points.

Equation (7) has been applied to calculate solubilities of hydrocarbons in water for all available data. Results are presented in Table 1.

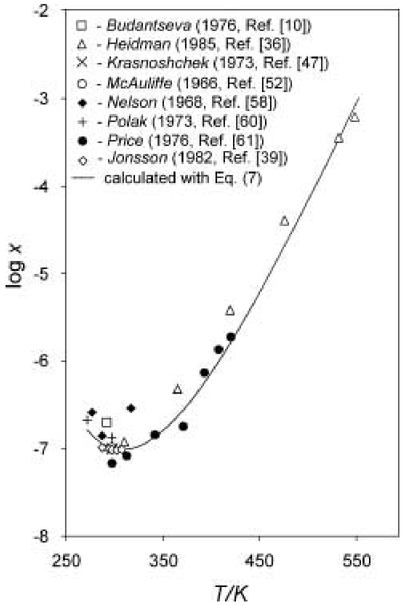

Fig. 3. Solubility of *n*-octane in water

Table 1. The experimental x_{exp} and calculated (Eq. (7)) x_{cal} solubility of hydrocarbons in water

Substance	T/K	x_{cal}	x_{exp}
Cyclopentane	298.15	4.4E – 05	4.0E – 05 [25], 4.1E – 05 [26]
	313.25	4.5E – 05	4.2E – 05 [26]
	328.85	5.0E – 05	4.6E – 05 [26]
	372.25	8.7E – 05	7.6E – 05 [26]
	391.15	1.2E – 04	9.6E – 05 [26]
	410.45	1.8E – 04	1.6E – 04 [26]
	426.25	2.5E – 04	2.0E – 04 [26]
Pentane	273.15	1.5E – 05	1.6E – 05 [27]
	277.15	1.4E – 05	1.0E – 05 [28]
	283.15	1.3E – 05	1.1E – 05 [28]
	289.15	1.2E – 05	9.0E – 05 [29]
	293.15	1.2E – 05	9.8E – 06 [28], 1.7E – 04 [30], 2.7E – 05 [31]
	298.15	1.1E – 05	9.6E – 06 [25], 9.9E – 06 [26], 1.2E – 05 [27] 1.0E – 05 [28], 1.2E – 05 [32]
	303.15	1.1E – 05	1.0E – 05 [28]
	310.95	1.1E – 05	3.9E – 05 [31]
	313.25	1.1E – 05	9.9E – 06 [26]
	328.85	1.2E – 05	1.0E – 05 [26]
	344.55	1.4E – 05	6.4E – 05 [31]
	372.25	2.1E – 05	1.7E – 05 [26]
	394.45	3.2E – 05	2.7E – 05 [26]
	410.45	4.6E – 05	5.0E – 05 [26]
	422.65	6.2E – 05	7.4E – 05 [26]

(*continued*)

Table 1 (*continued*)

Substance	T/K	x_{cal}	x_{exp}
Cyclohexane	289.15	1.4E – 05	1.3E – 05 [33]
	296.65	1.3E – 05	1.1E – 05 [34]
	298.15	1.3E – 05	1.2E – 05 [35], 1.2E – 05 [36], 1.7E – 05 [37]
	313.15	1.4E – 05	1.6E – 05 [15]
	373.15	3.1E – 05	3.8E – 05 [15]
	422.04	9.6E – 05	1.0E – 04 [15]
	423.15	9.9E – 05	1.3E – 04 [15]
	473.15	4.0E – 04	3.9E – 04 [15]
	482.21	5.3E – 04	4.9E – 04 [15]
Methylcyclopentane	298.15	1.0E – 05	9.0E – 06 [25], 8.9E – 06 [26]
	334.65	1.3E – 05	4.9E – 05 [38]
	419.15	7.4E – 05	3.3E – 04 [38]
	457.15	2.2E – 04	9.8E – 04 [38]
	487.15	5.4E – 04	3.2E – 03 [38]
2,2-Dimethylbutane	273.15	5.7E – 06	8.2E – 06 [27]
	298.15	4.1E – 06	3.8E – 06 [25], 4.4E – 06 [26], 5.0E – 06 [27]
Hexane	273.15	3.5E – 06	3.4E – 06 [27]
	277.15	3.2E – 06	3.4E – 06 [28]
	287.15	2.7E – 06	3.2E – 06 [28]
	288.15	2.7E – 06	2.2E – 06 [39]
	288.65	2.7E – 06	2.9E – 05 [29]
	289.15	2.6E – 06	7.5E – 06 [33]
	293.15	2.5E – 06	2.9E – 05 [30], 2.1E – 06 [39], 3.0E – 06 [40]
	298.15	2.4E – 06	2.0E – 06 [25], 2.0E – 06 [26], 2.6E – 06 [27] 3.8E – 06 [28], 3.4E – 06 [32], 2.5E – 06 [35] 2.5E – 05 [37], 2.1E – 06 [39], 2.6E – 06 [41] 2.8E – 06 [42], 3.3E – 05 [43]
	303.15	2.4E – 06	2.1E – 06 [39]
	308.15	2.4E – 06	2.7E – 06 [28], 2.1E – 06 [39]
	310.93	2.4E – 06	2.4E – 05 [15], 8.3E – 04 [44]
	313.25	2.4E – 06	2.1E – 06 [26]
	318.15	2.4E – 06	4.6E – 06 [28]
	328.15	2.6E – 06	4.4E – 06 [28]
	328.85	2.6E – 06	2.8E – 06 [26]
	342.85	3.0E – 06	3.2E – 06 [26]
	366.48	4.5E – 06	5.7E – 05 [15]
	367.55	4.6E – 06	5.3E – 05 [15]
	372.25	5.1E – 06	4.7E – 06 [26]
	373.15	5.2E – 06	6.2E – 05 [15]
	387.55	7.3E – 06	6.1E – 06 [26]
	394.45	8.6E – 06	7.9E – 06 [26]
	410.45	1.3E – 05	1.2E – 05 [26]
	422.04	1.9E – 05	2.7E – 04 [15]
	423.15	1.9E – 05	3.4E – 04 [15]
	424.95	2.0E – 05	2.3E – 05 [26]
	473.15	9.8E – 05	1.8E – 03 [15]

(*continued*)

Table 1 (*continued*)

Substance	T/K	x_{cal}	x_{exp}
Methylcyclohexane	298.15	2.9E – 06	2.6E – 06 [25], 2.9E – 06 [26]
	313.25	3.0E – 06	3.3E – 06 [26]
	328.85	3.5E – 06	3.5E – 06 [26]
	372.25	7.8E – 06	6.2E – 06 [26]
	393.15	1.3E – 05	1.5E – 05 [26]
	410.45	2.2E – 05	2.6E – 05 [26]
	422.65	3.2E – 05	4.5E – 05 [26]
Heptane	273.15	7.9E – 07	7.9E – 07 [27]
	277.45	7.1E – 07	3.5E – 07 [28]
	286.65	6.0E – 07	3.6E – 07 [28]
	288.15	5.9E – 07	4.8E – 07 [39]
	288.65	5.8E – 07	9.0E – 06 [29]
	289.15	5.8E – 07	1.8E – 06 [33]
	293.15	5.5E – 07	1.1E – 05 [30], 4.6E – 07 [39], 3.0E – 06 [40]
	298.15	5.3E – 07	5.3E – 07 [25], 4.0E – 07 [26], 6.0E – 07 [27] 3.8E – 07 [28], 4.5E – 07 [39], 5.0E – 07 [42]
	303.15	5.2E – 07	4.5E – 07 [39]
	308.15	5.1E – 07	4.1E – 07 [28], 4.5E – 07 [39]
	311.00	5.0E – 07	2.0E – 04 [45]
	313.15	5.1E – 07	1.0E – 05 [40]
	313.25	5.1E – 07	5.0E – 07 [26]
	318.15	5.2E – 07	4.3E – 07 [28]
	328.85	5.7E – 07	5.6E – 07 [26]
	344.65	7.0E – 07	1.8E – 05 [46]
	372.25	1.3E – 06	1.0E – 06 [26]
	381.15	1.6E – 06	2.9E – 05 [46]
	391.15	2.1E – 06	2.0E – 06 [26]
	409.75	3.8E – 06	4.9E – 06 [26]
	423.55	6.1E – 06	7.9E – 06 [26]
	454.15	1.9E – 05	1.1E – 04 [46]
	460.15	2.4E – 05	1.2E – 04 [46]
Ethylcyclohexane	311.50	7.8E – 07	1.1E – 06 [14]
	352.15	1.4E – 06	7.7E – 06 [38]
	367.60	2.1E – 06	2.4E – 06 [14]
	415.65	9.6E – 06	6.4E – 05 [38]
	423.40	1.3E – 05	2.0E – 05 [14]
	449.15	3.4E – 05	2.2E – 04 [38]
	479.50	1.2E – 04	1.2E – 04 [14]
	486.15	1.5E – 04	1.0E – 03 [38]
	536.10	1.3E – 03	1.2E – 03 [14]
	552.80	2.7E – 03	2.4E – 03 [14]
2,2,4-Trimethylpentane	273.15	3.9E – 07	3.9E – 07 [27]
	293.15	2.6E – 07	3.0E – 07 [40]
	298.15	2.5E – 07	3.8E – 07 [25], 1.8E – 07 [26], 3.2E – 07 [27]
Octane	273.15	1.6E – 07	2.1E – 07 [27]
	278.15	1.4E – 07	2.6E – 07 [28]

(*continued*)

Table 1 (*continued*)

Substance	T/K	x_{cal}	x_{exp}
	288.15	1.1E – 07	1.4E – 07 [28], 1.0E – 07 [39]
	293.15	1.1E – 07	1.0E – 07 [39], 2.0E – 07 [40]
	298.15	1.0E – 07	1.0E – 07 [25], 6.8E – 08 [26], 1.3E – 07 [27] 1.0E – 07 [39], 1.0E – 07 [42]
	303.15	9.8E – 08	1.0E – 07 [39]
	308.15	9.8E – 08	1.0E – 07 [39]
	310.90	9.8E – 08	1.2E – 07 [14]
	313.25	9.8E – 08	8.3E – 08 [26]
	318.15	1.0E – 07	2.9E – 07 [28]
	342.85	1.4E – 07	1.4E – 07 [26]
	366.50	2.3E – 07	4.8E – 07 [14]
	372.25	2.8E – 07	1.8E – 07 [26]
	394.45	5.6E – 07	7.3E – 07 [26]
	409.75	9.9E – 07	1.3E – 06 [26]
	422.00	1.6E – 06	3.8E – 06 [14]
	422.65	1.7E – 06	1.9E – 06 [26]
	479.50	2.1E – 05	4.0E – 05 [14]
	536.10	3.4E – 04	3.5E – 04 [14]
	552.80	7.8E – 04	6.0E – 04 [14]
Nonane	288.15	2.1E – 08	4.0E – 08 [39]
	293.15	2.0E – 08	3.8E – 08 [39]
	298.15	1.9E – 08	1.7E – 08 [26], 1.0E – 08 [42], 3.1E – 08 [47]
	342.85	2.6E – 08	4.3E – 08 [26]
	372.25	5.8E – 08	5.9E – 08 [26]
	394.45	1.3E – 07	2.4E – 07 [26]
	409.75	2.5E – 07	7.1E – 07 [26]
Decane	298.15	3.2E – 09	1.1E – 09 [42], 6.6E – 09 [47], 2.0E – 09 [48] 2.5E – 09 [49]
Undecane	298.15	4.6E – 10	4.1E – 10 [42], 5.1E – 10 [47]
Dodecane	298.15	6.0E – 11	8.9E – 10 [49], 4.0E – 10 [50]

Analysis of the data gathered in Table 1 shows that about half of the data are of high quality.

Solubility of Water in Alkanes

Solubility of water in hydrocarbons at low temperatures can be described by Eq. (8) where γ_w denotes the activity coefficient of water standardized in respect to infinite dilution, *e.g.* $\gamma_w = 1$, when concentration of water is sufficiently low. Δh_w denotes the change in enthalpy when one mole of water is transferred to the infinitely diluted solution.

$$[\partial \ln(x_w\gamma_w)/\partial(1/T)]_P \cong -\Delta_{\mathrm{sln}}h_w/\mathrm{R}, \tag{8}$$

The infinite dilution of water causes complete breaking of the hydrogen bonds between water molecules and their replacement by much weaker *van der Waals* interactions between water and hydrocarbon molecules. Therefore $\Delta_{\mathrm{sln}}h_{\mathrm{w}}$ depends mainly on the enthalpy of the hydrogen bonds and is weakly dependent on the alkane. $\Delta_{\mathrm{sln}}h_{\mathrm{w}}$ is much higher than the heat of solution in Eq. (1). Consequently, solubility of water increases very rapidly with increasing temperature. The solubility curves of water in alkanes appear simpler than those for the solubility of alkanes in water. $\Delta_{\mathrm{sln}}h_{\mathrm{w}}$ is always positive and depends weakly on temperature. Hence a solubility curve has no minimum and $\ln x_{\mathrm{w}}$ plotted *vs.* $1/T$ shows rather small curvature. Yet our efforts to develop a general equation for prediction of water solubility over a wide temperature range were not as satisfactory as for the solubility of alkanes in water, which is well described by Eq. (7). In this situation we decided to exploit phase equilibrium between coexisting liquid phases. Concentration of water rich phase can be predicted with Eq. (7), hence, concentration of the second phase can be calculated provided that an adequate method of LLE correlation is available. Some attempts described in literature and mentioned in the introduction are not successful. In this work a method of phase correlation developed by *Góral* [51] is used. This equation of state correlation (EoSC) method is based on the *Redlich–Kwong* equation of state (RK EoS) appended with a term which accounts for hydrogen bonding. This EoSC was successfully used for correlation and prediction of VLE and LLE in hydrogen bond forming binary and multicomponent systems [51], for correlation and verification of selected VLE data for alcohols and hydrocarbons [52–54], and for simultaneous correlation and prediction of VLE and LLE data in a hydrogen bonding quaternary system [55].

The calculations of the phase equilibria are performed using general constraints described in Eqs. (9a) and (9b) where ${\mu_i}^{(1)}, {\mu_i}^{(2)}, {\mu_{\mathrm{w}}}^{(1)}$ and ${\mu_{\mathrm{w}}}^{(2)}$ are the chemical potentials of hydrocarbon and water in the coexisting phases calculated with EoSC.

$$ {\mu_i}^{(1)}(x_i, \Theta) = {\mu_i}^{(2)}(x_{\mathrm{w}}, \Theta) \tag{9a} $$

$$ {\mu_{\mathrm{w}}}^{(1)}(x_i, \Theta) = {\mu_{\mathrm{w}}}^{(2)}(x_{\mathrm{w}}, \Theta) \tag{9b} $$

They depend on concentration and on one adjustable parameter Θ defined by Eq. (13). Because mole fraction of alkane (x_i) in the water rich phase is known from Eq. (7), then two unknown quantities, mole fraction of water (x_{w}) in the second phase and the binary parameter Θ, can be found by solving Eqs. (9a) and (9b).

In the EoSC method chemical potential is separated into physical and chemical contributions. To calculate the physical contribution the RK EoS was used. This yields Eq. (10) for change of the chemical potential of the kth component with respect to the standard state defined as a perfect gas at 1 kPa at the same temperature where V is the molar volume determined with the RK EoS at temperature T, pressure P and mole fraction x_k using parameters b and a calculated with the classical mixing rules outlined in Eqs. (11) and (12) where a_{ij} is related to the binary adjustable parameter Θ_{ij} by Eq. (13).

$$ \Delta\mu_k = RT\ \ln[x_k RT/(V-b)] - (na/b)'\ \ln(1+b/V) + (b_k/b)(PV-RT) \tag{10} $$

$$ b = x_i b_i + x_j b_j \tag{11} $$

$$a = x_i{}^2 a_{ii} + 2x_i x_j a_{ij} + x_j{}^2 a_{jj} \tag{12}$$

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - \Theta_{ij}). \tag{13}$$

$(na/b)'$ in Eq. (10) denotes the differential of the expression in parenthesis where n is the total number of moles and a and b are expressed by Eqs. (11) and (12). Differentiation is performed with respect to the number of moles of the kth component. Eq. (10) is also applicable for pure components provided that the following constraints are used: $x_k = 1$, $a = a_{kk}$, $b = b_k$. In this method the equation of state of the pure hydrogen bonding component is not modified. Pure water is treated in the same way as a hydrocarbon using effective a_{kk}, b_k-parameters.

The excluded volume, b_k, of a pure substance is assumed to be temperature independent and is calculated from the relevant critical parameters T_c and P_c using standard formula for RK EoS given previously (see Eq. (2)).

The energetic parameter, a_{kk}, of alkanes was calculated from Eq. (14) given by *Soave* [56] where $a_{kk}(T_c)$ at critical temperature (T_c) is calculated using Eq. (15).

$$a_{kk}(T) = a_{kk}(T_c)\{1 - m_k[(T/T_c)^{0.5} - 1)]\}^2 \tag{14}$$

$$a_{kk}(T_c) = 0.42747(T_c{}^2/P_c)_k \tag{15}$$

The parameter m in Eq. (14) was determined from a_{kk} adjusted to saturated vapor pressure of the pure compound, P_k^0, at $T = 0.7T_c$. The adjustment of a_{kk} was done in the following way: liquid and vapor molar volumes at P_k^0 were calculated from the RK EoS using a starting value of a_{kk}. The calculated volumes were introduced into Eq. (10) to calculate chemical potentials of the pure component in the liquid and vapor phases. At equilibrium the chemical potentials in both phases must be equal. If not, an improved value of a_{kk} was used in the next iteration. After a satisfactory value of a_{kk} was obtained it was used for calculation of the coefficient m *via* Eq. (14).

For water Eq. (14) was modified as shown in Eq. (16).

$$a_{ww}(T) = a_{ww}(T_c)\{1 - 0.699[(T/T_c)^{0.74} - 1]\}^2 \tag{16}$$

In mixtures Eq. (10) is supplemented with the chemical term $F^E_{k,\mathrm{chem}}$ which accounts for the change in hydrogen bonding in the mixture with respect to the pure component. This gives Eq. (17) where $F_{k,\mathrm{chem}}$ and $F^0_{k,\mathrm{chem}}$ correspond to the kth hydrogen bonding substance in the mixture and in the pure state, respectively.

$$F^E_{k,\mathrm{chem}} = F_{k,\mathrm{chem}} - F^0_{k,\mathrm{chem}} + \Delta_k \tag{17}$$

The expression for $F_{k,\mathrm{chem}}$ is outlined in Eq. (18) where β_k is the fraction of free, non-hydrogen bonded molecules of the bonding substance (here water) at chemical equilibrium with hydrogen bonded clusters.

$$F_{k,\mathrm{chem}} = \mathrm{R}T \ln \beta_k - (V_k - b_k)P_{\mathrm{chem}} \tag{18}$$

P_{chem} is the change of vapor pressure due to hydrogen bonding. Both β_k and P_{chem} depend on the hydrogen bonding model. To use Eq. (18) one must determine the dependence of β_k and P_{chem} on concentration. This task seems to be prohibitively complicated in multicomponent mixtures of hydrogen bonding substances or in mixtures of water, which contain a complicated variety of clusters described by equilibrium conditions and stoichiometric constraints. The resulting set of equations must be solved in order to calculate β_k and P_{chem}. The methods presented in literature are designed for special cases or use approximate solutions. Quite recently general formulas were described by *Góral* [57]. These formulas applied to the systems investigated here (water and non-hydrogen bonding second components) reduce to Eqs. (19) and (20) where X is a fraction of free hydrogen atoms of water (not engaged in hydrogen bonds).

$$\beta_k = X^4, \tag{19}$$

$$P_{\text{chem}} = (X - 1)C, \tag{20}$$

C depends on the mole fraction of water (x_{w}) and alkane (x_i) as shown in Eq. (21) in which V_{w} and V_i are molar volumes of pure water and the ith alkane.

$$C = 2\,\mathrm{R}Tx_{\text{w}}/[x_{\text{w}}(V_{\text{w}} - b_{\text{w}}) + x_i(V_i - b_i)], \tag{21}$$

They are calculated with the RK EoS under the vapor pressure of the mixture. b_{w} and b_i are excluded volumes used in RK EoS. X, is calculated by solving Eq. (22) where K is the equilibrium constant of self-association of water.

$$X = 1/(1 + KXC), \tag{22}$$

For pure water $F^0_{k,\text{chem}}$ is calculated with the same equations as $F_{k,\text{chem}}$, but using the constraint $x_k = 1$. For hydrocarbons $F^0_{k,\text{chem}}$ is zero by definition. The term Δ_k in Eq. (17) is a small correction, which does not contain any adjustable parameters and was defined by *Góral* [51].

Equations (19)–(22) are valid for the continuous association model in which each hydrogen bonded cluster of water molecules possessing unshared electron pairs or non-hydrogen bonded hydrogen atoms can grow by hydrogen bonding to adjacent molecules of water. The kind and concentration of the hydrogen bonded clusters depends on the chemical equilibrium in the mixture. It is assumed that formation of each hydrogen bond in water is described by the same association constant K. In this work the temperature dependence of K was obtained by integration of the *van't Hoff* equation which yields Eq. (23) where $T_0 = 303.15$ is a reference temperature, ΔH^0 is the molar enthalpy of hydrogen bond formation at T_0 and ΔC_{p} is the corresponding heat capacity.

$$K = K_0 \exp[(-\Delta H^0/\mathrm{R})(1/T - 1/T_0)]\, \exp\{(-\Delta C_{\text{p}}/\mathrm{R})[T_0/T - 1 + \ln(T/T_0)]\} \tag{23}$$

The following values of these quantities were adopted:

$$(-\Delta H^0/\mathrm{R}) = 2200\,\mathrm{K} \tag{24a}$$

$$(-\Delta C_{\text{p}}/\mathrm{R}) = 3 \tag{24b}$$

ΔH^0 was estimated from Δh_{w}, used in Eq. (8). Contribution of *van der Waals* interactions to Δh_{w} is relatively small and dilution of one mole of water is accompanied by breaking two moles of hydrogen bonds, hence, one can assume:

$$(-\Delta H^0/\mathrm{R}) \approx (-\Delta_{\mathrm{sln}} h_{\mathrm{w}}/\mathrm{R})/2 \tag{25}$$

Calorimetric measurements of *Nilsson* [58] gave $(-\Delta_{\mathrm{sln}} h_{\mathrm{w}}/\mathrm{R})/2 = 2100\,\mathrm{K}$, which agrees with solubility data yielding $(-\Delta_{\mathrm{sln}} h_{\mathrm{w}}/\mathrm{R})/2 = 2200$. But it is more difficult to estimate $(-\Delta C_{\mathrm{p}}/\mathrm{R})$ in Eq. (23). Small contribution of *van der Waals* interactions to $\Delta_{\mathrm{sln}} h_{\mathrm{w}}$ can produce significant contribution to the heat capacity of solution, $\Delta_{\mathrm{sln}} C_{\mathrm{p,w}}$, whereas heat capacity of the hydrogen bond formation should be rather small. Hence, validity of Eq. (25) does not imply that the corresponding heat capacities are equal. Moreover $\Delta_{\mathrm{sln}} C_{\mathrm{p,w}}$ determined from solubility data is increased by the assumption that γ_{w} in Eq. (8) can be omitted. In this situation $(-\Delta C_{\mathrm{p}}/\mathrm{R})$ in Eq. (23) was treated as adjustable parameter which should be nearly to zero as is suggested by *Nilsson's* [58] calorimetric measurements. The third numerical parameter in Eq. (23) $(K_0 = 0.100\,\mathrm{Mpa}^{-1})$ was determined by adjusting to the LLE data. Eq. (23) with the same numerical values of these three parameters was used in all LLE calculations.

The excluded volume of water (b_{w}) used in the chemical part (Eqs. (18) and (21)) is shifted with respect to b_{w} calculated with Eq. (13) and used in the physical part. This shift $\Delta b_{\mathrm{w}} = -6.5\,\mathrm{cm}^3$ is used in all mixtures of water. For hydrocarbons $\Delta b_i = 0$.

As was mentioned in the introduction it is possible to describe solubility of water with a cubic EoS without any association term but such equations are not able to describe simultaneously the both coexisting liquid phases. These methods are simpler, but they are limited to correlation of water solubility in hydrocarbons only.

The results of calculations described in this paper are the predicted values (as a function of temperature) of water solubility in the investigated *n*-alkanes, cycloalkanes and isoalkanes. The input information is solubility of the alkane in water, calculated with Eq. (7). This was explained previously (see Eqs. (9a) and (9b)). Solubility of water in hydrocarbon was used only at the beginning of this investigation to fix the four parameters used in the model of water (K_0, ΔH^0, ΔC_{p}, and Δb). These parameters were constant for all the investigated mixtures. These calculations can be used for prediction or for testing consistency between solubility data reported for the both coexisting liquid phases. An example is given in Fig. 4, where the approximating line is predicted from the curve shown in Fig. 3.

Similar results are observed for all other mixtures of alkanes and water available in literature. The predicted solubility curves of water in hydrocarbons have been calculated for all investigated water/alkane systems. The experimental and the predicted data are presented in Table 2.

We conclude that by using the EoSC and data yielded by Eq. (7) it is possible to predict the solubilities of water in alkanes with good accuracy over the temperature range up to about 20 K below $T_{3\mathrm{c}}$. The calculation can be also performed in the inverse direction. Solubility of alkanes in water can be calculated using experimental data of solubility of water in alkanes. This possibility was not used because solubility of alkanes can be simply calculated with Eq. (7). Moreover, these calculations are more sensitive to experimental errors of data.

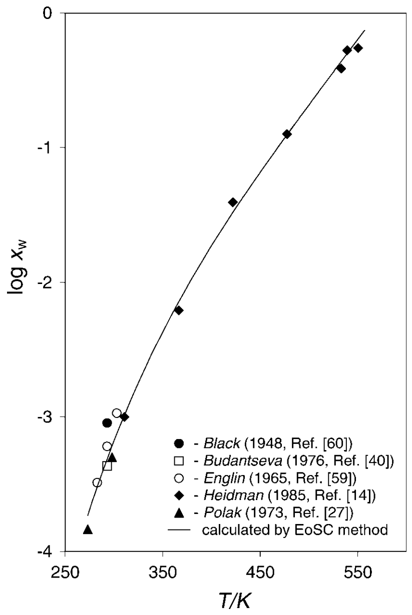

Fig. 4. Solubility of water in *n*-octane

Table 2. The experimental x_{exp} and calculated x_{cal} solubility of water in hydrocarbons

Substance	T/K	x_{cal}	x_{exp}
Cyclopentane	273.15	1.0E – 04	1.8E – 04 [59]
	283.15	2.0E – 04	3.4E – 04 [59]
	293.15	3.0E – 04	5.5E – 04 [59]
	303.15	5.0E – 04	9.7E – 04 [59]
	313.15	8.0E – 04	1.5E – 03 [59]
Pentane	273.15	2.0E – 04	1.0E – 04 [27]
	278.65	2.0E – 04	1.4E – 04 [60]
	288.15	4.0E – 04	2.5E – 04 [60]
	297.95	6.0E – 04	4.8E – 04 [60]
	298.15	6.0E – 04	4.0E – 04 [27]
Cyclohexane	283.15	2.0E – 04	1.6E – 04 [61]
	288.15	3.0E – 04	2.0E – 04 [61], 2.8E – 04 [62]
	293.15	3.0E – 04	2.8E – 04 [61]
	298.15	4.0E – 04	3.3E – 04 [61], 3.5E – 04 [62], 2.6E – 04 [63] 3.2E – 04 [64], 3.3E – 04 [65]
	303.15	5.0E – 04	4.5E – 04 [61], 4.1E – 04 [62]
	308.15	6.0E – 04	5.3E – 04 [61]
	313.15	8.0E – 04	8.9E – 04 [15], 6.1E – 04 [61]
	373.15	6.8E – 03	4.4E – 03 [15]
	423.15	3.1E – 02	2.0E – 02 [15]
	473.15	1.2E – 01	7.9E – 02 [15]

(*continued*)

Table 2 (*continued*)

Substance	T/K	x_{cal}	x_{exp}
Methylcyclopentane	283.15	2.0E – 04	3.4E – 04 [59]
	293.15	4.0E – 04	6.1E – 04 [59]
	303.15	6.0E – 04	9.6E – 04 [59]
2,2-Dimethylbutane	273.15	2.0E – 04	1.5E – 04 [27]
	298.15	7.0E – 04	4.0E – 04 [27]
Hexane	273.15	2.0E – 04	1.3E – 04 [27]
	293.15	5.0E – 04	3.7E – 04 [40], 4.8E – 04 [59], 5.3E – 04 [60] 4.6E – 04 [66], 7.9E – 04 [67]
	298.15	6.0E – 04	4.3E – 04 [27], 4.8E – 04 [68], 5.1E – 04 [69]
	303.00	8.0E – 04	2.4E – 04 [70]
	303.15	8.0E – 04	8.6E – 04 [59]
	310.93	1.1E – 03	9.5E – 03 [44]
	313.15	1.2E – 03	1.2E – 03 [15], 1.5E – 03 [59]
	354.82	5.9E – 03	6.7E – 03 [71]
	366.48	9.0E – 03	1.0E – 02 [71]
	367.55	9.3E – 03	5.9E – 03 [15]
	373.15	1.1E – 02	7.1E – 03 [15]
	379.26	1.4E – 02	1.5E – 02 [71]
	394.26	2.3E – 02	2.3E – 02 [71]
	400.37	2.8E – 02	2.7E – 02 [71]
	417.59	4.8E – 02	4.2E – 02 [71]
	422.04	5.5E – 02	4.7E – 02 [71]
	423.15	5.6E – 02	3.1E – 02 [15]
	431.48	7.2E – 02	5.8E – 02 [71]
	442.59	1.0E – 01	7.3E – 02 [71]
	449.82	1.2E – 01	8.4E – 02 [71]
	452.59	1.3E – 01	9.0E – 02 [71]
	460.37	1.6E – 01	1.0E – 01 [71]
	468.15	2.0E – 01	1.3E – 01 [71]
	473.15	2.2E – 01	1.1E – 01 [15]
	477.59	2.5E – 01	1.4E – 01 [71]
Methylcyclohexane	283.15	2.0E – 04	3.3E – 04 [59]
	293.15	4.0E – 04	6.3E – 04 [59]
	303.15	6.0E – 04	9.8E – 04 [59]
Heptane	273.15	2.0E – 04	1.5E – 04 [27], 1.5E – 04 [59]
	283.15	3.0E – 04	3.0E – 04 [59], 4.3E – 04 [60]
	293.15	5.0E – 04	5.0E – 04 [40], 5.3E – 04 [59], 7.6E – 04 [60]
	295.65	5.0E – 04	3.2E – 04 [72]
	296.15	6.0E – 04	7.7E – 04 [67]
	298.15	6.0E – 04	4.6E – 04 [27], 8.4E – 04 [60], 5.1E – 04 [73] 6.7E – 04 [74]
	303.15	8.0E – 04	9.6E – 04 [59]
	311.00	1.0E – 03	6.6E – 03 [45]
	313.15	1.1E – 03	7.0E – 04 [40], 1.7E – 03 [59], 8.7E – 04 [74]
	323.15	1.7E – 03	2.7E – 03 [59]

(*continued*)

Table 2 (*continued*)

Substance	T/K	x_{cal}	x_{exp}
Ethylcyclohexane	310.90	8.0E – 04	8.1E – 04 [14]
	367.60	6.1E – 03	6.5E – 03 [14]
	423.40	3.1E – 02	3.0E – 02 [14]
	479.50	1.3E – 01	1.1E – 01 [14]
	536.10	3.5E – 01	2.9E – 01 [14]
	552.80	4.5E – 01	4.1E – 01 [14]
	561.40	5.1E – 01	6.0E – 01 [14]
2,2,4-Trimethylpentane	271.65	2.0E – 04	7.0E – 05 [75]
	273.15	2.0E – 04	1.5E – 04 [27], 2.0E – 04 [59]
	283.15	3.0E – 04	3.7E – 04 [59], 2.3E – 04 [75]
	293.15	5.0E – 04	4.4E – 04 [40], 7.3E – 04 [59] 3.5E – 04 [75]
	298.15	7.0E – 04	5.1E – 04 [27]
	303.15	8.0E – 04	1.3E – 03 [59]
	313.15	1.3E – 03	2.1E – 03 [59], 5.1E – 04 [75]
	323.15	1.9E – 03	3.4E – 03 [59]
Octane	273.15	2.0E – 04	1.5E – 04 [27]
	283.15	3.0E – 04	3.2E – 04 [59]
	293.15	5.0E – 04	4.3E – 04 [40], 6.0E – 04 [59], 9.0E – 04 [60]
	298.15	6.0E – 04	5.0E – 04 [27]
	303.15	8.0E – 04	1.1E – 03 [59]
	310.90	1.0E – 03	1.0E – 03 [14]
	366.50	7.7E – 03	6.2E – 03 [14]
	422.00	4.0E – 02	3.9E – 02 [14]
	477.60	1.7E – 01	1.3E – 01 [14]
	533.10	3.3E – 01	3.9E – 01 [14]
	539.10	3.6E – 01	5.3E – 01 [14]
	550.40	4.3E – 01	5.5E – 01 [14]
Nonane	298.15	6.0E – 04	5.6E – 04 [73]
	303.00	8.0E – 04	3.2E – 04 [70]
Decane	293.15	5.0E – 04	2.3E – 03 [76]
	298.15	6.0E – 04	5.7E – 04 [73]
	313.15	1.1E – 03	1.1E – 03 [73]
	423.15	3.7E – 02	2.8E – 02 [77]
	473.15	1.2E – 01	9.5E – 02 [77]
	498.15	2.2E – 01	1.6E – 01 [77]
	523.15	4.2E – 01	2.5E – 01 [77]
	548.15	4.2E – 01	4.0E – 01 [77]
	558.15	4.8E – 01	5.0E – 01 [77]
	563.15	5.2E – 01	6.1E – 01 [77]
Undecane	298.15	6.0E – 04	6.0E – 04 [73]
	313.15	1.2E – 03	1.1E – 03 [73]
Dodecane	298.15	6.0E – 04	6.1E – 04 [73]
	313.15	1.2E – 03	1.2E – 03 [73]
Tridecane	298.15	7.0E – 04	6.1E – 04 [73]
	313.15	1.2E – 03	1.3E – 03 [73]

(*continued*)

Table 2 (*continued*)

Substance	T/K	x_{cal}	x_{exp}
Tetradecane	313.15	1.2E – 03	1.3E – 05 [73]
Hexadecane	293.15	6.0E – 04	8.7E – 04 [59]
	298.15	7.0E – 04	6.8E – 04 [73]
	303.15	9.0E – 04	1.5E – 03 [59]
	313.15	1.3E – 03	2.6E – 03 [59], 1.3E – 03 [73]
	323.15	1.9E – 03	4.2E – 03 [59]

Summarizing the presented investigations we conclude that Eq. (7) in conjunction with EoSC allows to calculate solubility of alkanes in water as well as solubility of water in alkanes. To apply the presented equations no experimental solubility data is necessary. As was discussed previously this method of prediction must not be applied to $C_{11}+$ normal alkanes.

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