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Aqueous Solubility and Related Thermodynamic Functions of Nonaromatic Hydrocarbons as a Function of Molecular Structure

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The aqueous solubilities of several C₈ nonaromatic hydrocarbons differing in their molecular structure (cyclooctane, cyclooctene, ethylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclohexane, 2,2-dimethylhexane, and 2,5-dimethylhexane) were studied at temperatures between 274 and 313 K using a dynamic saturation column method. The resulting experimental values had an estimated uncertainty between 5 and 10%. Their correlation as a function of temperature allowed the determination of the enthalpy and heat capacity change characterizing the dissolution process. A combination with the data on pure solutes selected from the literature made it possible to calculate Henry's law constants and the air–water partition coefficients as well as the thermodynamic functions of hydration. These different data were combined with information from the literature and analyzed with respect to the molecular structure of aqueous hydrocarbons. A simple group contribution concept was found to be useful for rationalizing the evolution of the aqueous solubility of alkanes, alkenes, cycloalkanes, and cycloalkenes.

1. Introduction

Reliable thermodynamic data on phase equilibria in aqueous systems containing hydrocarbons are highly important from both practical and theoretical points of view. This information is required by the petroleum and petrochemical industries for estimating the partition of hydrocarbons between aqueous and organic phases^{1,2} and for minimizing the presence of hazardous solutes in aqueous effluents.³ Environmental chemistry and engineering need the phase equilibrium data for modeling of the transport and fate of hydrocarbon pollutants in the environment^{4,5} and for the remediation of sites contaminated by petroleum spills.^{6,7} On a more fundamental level, thermodynamic functions of aqueous hydrocarbons are essential for the understanding of the interactions and organization in a solution containing a hydrophobic solute and water solvent.^{8,9} The determination of hydrocarbon solubility in water has a particular significance because it is the only way to access the thermodynamic properties of these systems. It is impossible to prepare at ambient conditions aqueous solutions of hydrocarbons with concentrations high enough to allow calorimetric or volumetric measurements with currently available instruments.

Besides its own practical importance, the solubility of hydrocarbons is closely linked with the limiting activity coefficients and serves, in combination with other thermodynamic data, in the determination of Henry's law constants and the air–water partition coefficients. These data are largely exploited in the calculation of vapor–liquid equilibria in aqueous systems of technological and environmental interest. In addition, Henry's law constants can be easily converted to the Gibbs energies of hydration, reflecting the Gibbs

energy difference between the standard states of infinite dilution and ideal gas. This difference is accessible by models of statistical thermodynamics and can be directly calculated by molecular simulation^{10,11} provided a realistic intermolecular potential is used. Thus, the thermodynamic functions of hydration obtained from accurate experimental data are instrumental in verifying and developing the potentials characterizing interactions between water and a highly hydrophobic solute.

A considerable amount of data are available for aromatic and basic polyaromatic hydrocarbons, which are of major environmental and health concern. On the other hand, with the exception of several *n*-alkanes, less attention has been paid to nonaromatic hydrocarbons, for which only a limited number of experimental values are available in the literature. Yet, information on compounds such as branched alkanes, alkenes, and their cyclic forms is of high interest for the understanding of the evolution of hydrophobicity with the molecular structure as well as for the development of group contribution concepts for organic compounds in general.

All solutes selected for this study contain eight carbon atoms representing thus typical liquid hydrocarbons of "average" molecular size and volatility that occur as major constituents of fuels. Their vapor pressures are high enough to be available with sufficient accuracy from conventional dynamic measurements. These vapor pressures are, however, low enough to allow one to work conveniently with the liquid solutes at near-ambient conditions and without necessity to apply a nonideality correction for the vapor phase in the calculations.

The concrete selection of compounds for this study was guided by an effort to quantify the link between the particular structural features and the changes in the thermodynamic functions related to solubility. In addition to *n*-octane studied earlier¹² and considered in this study as a "reference" compound, seven hydrocarbons were selected for which no or only fragmentary

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data were reported in the literature: cyclooctane (effect of a ring), cyclooctene (double bond in a ring), ethylcyclohexane, *cis*-1,2-dimethylcyclohexane, *trans*-1,2-dimethylcyclohexane (substitution effect in a cycloalkane ring), 2,5-dimethylhexane, and 2,2-dimethylhexane (effect of branching).

The first objective of this study was to obtain data accurate enough for rationalizing the effect of the molecular structure on solubility, represented here by the dimensionless Gibbs energy of the solution. Measurements were carried out over a limited temperature interval at near-ambient conditions, which makes it possible to determine, besides the solubility minima typical for medium molar mass hydrocarbons, the derivative properties such as the enthalpy and heat capacity changes characterizing the dissolution at 298 K. The second objective was to combine these thermodynamic functions with the vapor pressures and related thermal data on pure solutes, selected from reliable literature sources, to calculate the thermodynamic functions of hydration. In such a way, it is possible to express Henry's law constant and the air–water partition coefficient over a temperature interval extending beyond that of our experimental data. In addition, the hydration properties were used in the past repeatedly as a basis for the construction of the group contribution schemes. After the classical work of Cabani et al.,¹³ Plyasunov and Shock¹⁴ published recently a comprehensive update for hydration properties for aqueous hydrocarbons and alcohols. Thus, it was possible to compare the concepts of representing the transfer of a solute in the aqueous phase by group contributions in terms of dissolution or hydration properties. While the first concept is largely used by process engineers, the second prevails in the biochemical and geological applications.

2. Experimental Section

Materials. All of the hydrocarbon solutes studied were obtained from commercial sources: cyclooctane from Fluka, $\geq 99.5\%$ pure; cyclooctene from Fluka, $> 99.5\%$ pure; 2,5-dimethylhexane from Fluka, $> 99.0\%$ pure; 2,2-dimethylhexane from Fluka, $\sim 98\%$ pure; ethylcyclohexane from Acros, $99+\%$ pure; *trans*-1,2-dimethylcyclohexane from Fluka, $\geq 99\%$ pure; *cis*-1,2-dimethylcyclohexane from Fluka, $\sim 99\%$ pure. Distilled water and methanol (for high-performance liquid chromatography from Carlo Erba) were used as solvents and *n*-octane, *n*-nonane, and *n*-decane (from Acros 99% pure) as internal standards for the chromatographic analysis. An inert solid support (Gaz Chrom R 60/80 from Alltech) was utilized as the packing material for the saturation column. This material was coated with approximately 0.5 mass % of the examined solute by blending the support with a solution of the hydrocarbon in pentane (99.5% pure from Fluka) and by removing the solvent in a rotary evaporator. The generator columns used in this work were purged by 1000–1500 mL of water with gradually increasing flow rates from 0.1 up to 2 mL/min.

Method. The experimental technique is based on a dynamic saturation column method and was already extensively used in several versions for measurements at ambient^{15–17} and superambient conditions.^{18,19} The apparatus employed in this study was described briefly in a previous work;¹² nevertheless, we find it useful to present here a description of the experimental procedure followed in the measurements with the selected solutes.

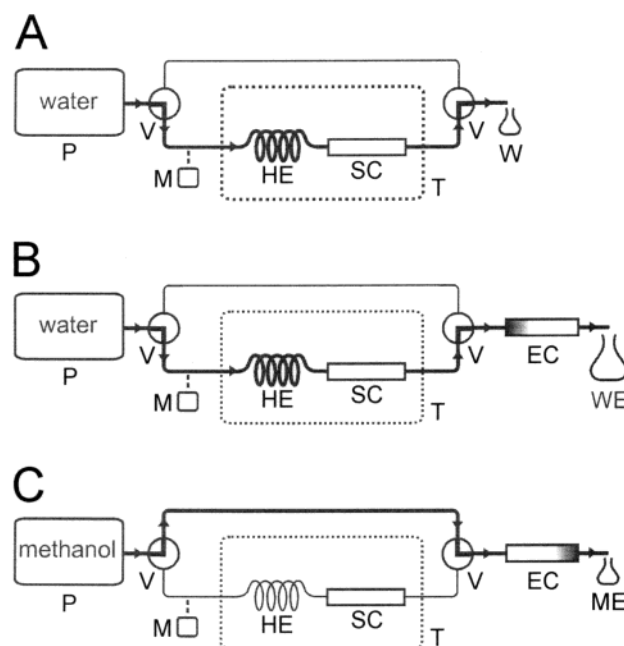


Figure 1. Schematic diagram of the saturation column apparatus: P, LLC pump delivering water or methanol; M, manometer; HE, heat-exchanging coil; SC, saturation column; EC, extractor column; V, three-way valve; T, liquid thermostat; W, waste; WE, water effluent; ME, methanolic extract.

The principle of the technique is as follows. The water flows through a saturation column filled with a solid material of a large effective surface area, which is impregnated with the investigated hydrocarbon. The saturated aqueous solution subsequently passes through an extraction column, filled with an inverse solid phase, where the hydrocarbon is quantitatively trapped. The solute is then removed by an appropriate solvent, and the final solution is analyzed by gas chromatography.

The present apparatus and its operation are schematically represented in Figure 1. In the present arrangement, water or methanol (used as an extraction solvent for all of the solutes studied) is pumped from the stock bottles by a LLC pump (P), a Gilson pump model 306, or a Perkin-Elmer pump model 410, respectively. The saturation column (SC; 4.6 mm i.d. \times 100 mm column from Modulo-cart) is placed in a thermostatic bath (T), controlled by a proportional–integral–derivative temperature controller from Tronac Inc., model PTC-40, which maintains the stability to within ± 0.05 K in the whole temperature range of measurements.

The first step of the experimental procedure consists of the conditioning of the saturation column. To achieve this (Figure 1A), water is pumped with the LLC pump at a small flow rate (between 0.1 and 0.2 mL/min) through the saturation column and straight to the waste (W). More than 10 mL of water is normally necessary to reach steady state.

The extraction column (EC) is a 4.6 mm i.d. \times 100 mm column packed with an inverse solid phase 5 μ m C18 ODS2 from Spherisorb; exceptions were measurements for 2,2-dimethylhexane, for which a 4.6 mm i.d. \times 250 mm column packed with an inverse solid phase 5 μ m Rx-C18 from Zorbax was used. This extraction column, previously conditioned with water, is then connected to the end of the system (Figure 1B). While the hydrocarbon solute from the saturated aqueous solution is quantitatively extracted, the water effluent,

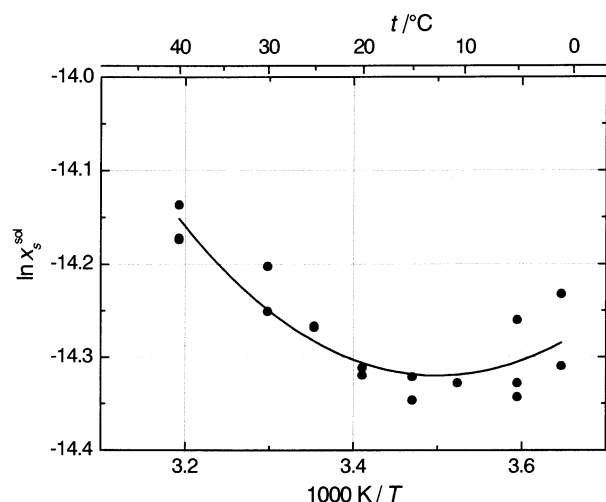


Figure 2. Aqueous solubility of ethylcyclohexane as a function of reciprocal temperature: ●, data from this work; solid line, fit to eq 1.

leaving the extraction column, is collected into a flask for gravimetric quantification (WE). The mass of water passed through the extraction column was varied according to the solute and temperature in order to keep the amount of solute extracted roughly the same. In this study the quantity of water ranged from 12 g for cyclooctene (the most soluble solute) to 200 g for 2,2-dimethylhexane and 2,5-dimethylhexane (the least soluble solutes).

After a sufficient amount of the solute is collected, the flux through the three-way valves (V) is switched as indicated and the extraction column is reversed to the back-flush mode (Figure 1C). The extraction solvent (about 10 mL of methanol was typically passed at a flow rate of 0.5 mL/min) is supplied from the LLC pump (P) and flows through the extraction column (EC) in order to completely elute the hydrocarbon solute into a weighing flask (ME). The extraction column is subsequently washed with methanol and reconditioned with water for the next measurement.

The analyses of the methanolic extract are performed using a gas chromatograph model CG14A from Shimadzu equipped with a flame ionization detector and a split/splitless injector. Chromatographic separations are accomplished with a 30 m DB-1 capillary column. The quantification of the organic compounds studied is carried out by an internal standard technique using *n*-octane, *n*-nonane, and *n*-decane for the different solutes.

3. Results

For each solute studied, multiple experimental data points were obtained in the temperature interval 274–313 K in steps of 5 K, with the list of all direct experimental values of mole fraction solubilities x_s^{sol} being presented in the Appendix (Table 6). The variation of the solubility with temperature is demonstrated, as an example, for ethylcyclohexane in Figure 2. To get representative values of the solubility, the raw experimental data were correlated as a function of temperature by the empirical equation

$$\ln x_s^{\text{sol}} = A + B/\tau + C \ln \tau \quad \tau = T/T_0, \quad T_0 = 298.15 \text{ K} \quad (1)$$

Table 1. Parameters of Equation 1 Used To Smooth the Raw Experimental Results from Table 6 along with the Standard Deviation of the Fit

compound	A	B	C	s
cyclooctane	−55.1375	41.2528	43.2804	0.033
cyclooctene	−33.3561	20.8640	23.4396	0.042
ethylcyclohexane	−53.6887	39.4055	41.1210	0.030
cis-1,2-dimethylcyclohexane	−59.7348	45.8700	46.6282	0.034
trans-1,2-dimethylcyclohexane	−58.1848	44.0938	45.2290	0.029
2,2-dimethylhexane	−104.677	89.2560	89.1497	0.029
2,5-dimethylhexane	−120.071	104.535	106.629	0.028

where $\ln x_s^{\text{sol}}$ is closely related to the solution Gibbs free energy $\Delta_{\text{sol}} G^\infty$ characterizing the dissolution process

$$\Delta_{\text{sol}} G^\infty / RT \cong -\ln x_s^{\text{sol}} \quad (2)$$

The assumptions inherent to the last relationship are presented below. The adjustable parameters *A*, *B*, and *C* are listed in Table 1 together with the standard deviation of the fit *s*, which reflects the scatter of experimental data points (on average between 3 and 4% from the fitted values of x_s^{sol}). These parameters were used for generating recommended values of the solubility for the compounds investigated in this study between 273 and 313 K, presented in Table 2 as mole fractions and mass solubilities S_w (mass of the solute in a unit volume of solvent). Also presented are Henry's law constants K_H (limiting ratio of the solutes fugacity f_s and mole fraction x_s) and the air–water partition coefficient K_{aw} (limiting ratio of the solute molarities in air c_s^{a} and in an aqueous phase c_s^{w}) using the following approximations:

$$K_H = \lim_{x_s \rightarrow 0} f_s / x_s \cong p_s^{\text{sat}} / x_s^{\text{sol}} \quad (3)$$

$$K_{\text{aw}} = \lim_{x_s \rightarrow 0} c_s^{\text{a}} / c_s^{\text{w}} \cong K_H M_w / RT \rho_w \quad (4)$$

Some assumptions have to be fulfilled to consider the above relationships as equalities: (i) the aqueous solution is regarded as infinitely dilute; i.e., Henry's law activity coefficient is unity (eqs 2–4), and the molar volume of the aqueous solution can be replaced by that of water (eq 4); (ii) the effect of water dissolved in the hydrocarbon phase on its fugacity can be neglected (eqs 2 and 3); (iii) both solute's vapor and air obey the ideal gas behavior (eqs 3 and 4). Because of low values of the solubility and of vapor pressures of the studied compounds, the first and third assumptions are fully justified. The second simplifying condition is more difficult to verify; although the solubility of water in the organic phase is at least one order of magnitude higher than that of a hydrocarbon in water, it is still low enough, with the positive deviations from Raoult's law additionally compensating for the concentration effect.

The densities of water ρ_w were calculated using the software package STEAM distributed by NIST (the IAPWS equation of state for water²⁰). The vapor pressures p_s^{sat} necessary for calculation of Henry's constant are available for three alkylcycloalkanes and for two dimethylhexanes as constants of the Antoine equation representing the measurements performed at NBS (Willingham et al.²¹), which are generally considered as the most reliable data source. The lower temperature limits of vapor-pressure measurements vary between 320 and 323 K for alkylcyclohexanes and are near

Table 2. Aqueous Solubility S_w , Mole Fraction Solubility x_s^{sol} , Vapor Pressure p_s^{sat} , Henry's Law Constant K_H , and Air–Water Partition Coefficient K_{aw} as Functions of the Temperature for Hydrocarbons Studied in This Work^a

T (K)	S_w (g·m ⁻³)	$10^6 x_s^{\text{sol}}$	p_s^{sat} (Pa) ^b	K_H (MPa)	K_{aw}
Cyclooctane					
273.15	5.73	0.920	144	157	1.25
278.15	5.59	0.897	207	231	1.80
283.15	5.53	0.889	292	329	2.52
288.15	5.55	0.892	406	455	3.43
293.15	5.64	0.907	557	614	4.55
298.15	5.80	0.933	753	807	5.88
303.15	6.02	0.971	1010	1040	7.47
308.15	6.32	1.02	1330	1300	9.20
313.15	6.68	1.08	1730	1600	11.2
Cyclooctene					
273.15	19.9	3.26	214	65.8	0.522
278.15	20.2	3.31	299	90.3	0.704
283.15	20.7	3.38	412	122	0.931
288.15	21.3	3.48	561	161	1.21
293.15	22.0	3.61	757	210	1.55
298.15	22.9	3.76	1010	269	1.96
303.15	23.9	3.93	1340	340	2.44
308.15	25.1	4.14	1751	423	2.99
313.15	26.5	4.37	2270	521	3.64
Ethylcyclohexane					
273.15	3.92	0.630	365	579	4.59
278.15	3.82	0.613	510	833	6.49
283.15	3.77	0.605	704	1160	8.88
288.15	3.76	0.605	958	1580	11.9
293.15	3.81	0.612	1290	2100	15.6
298.15	3.89	0.626	1710	2720	19.8
303.15	4.02	0.648	2240	3450	24.8
308.15	4.19	0.677	2900	4280	30.3
313.15	4.40	0.714	3720	5210	36.4
<i>cis</i> -1,2-Dimethylcyclohexane					
273.15	6.59	1.06	424	401	3.18
278.15	6.27	1.01	590	587	4.57
283.15	6.05	0.972	809	833	6.37
288.15	5.93	0.953	1090	1150	8.66
293.15	5.90	0.949	1460	1540	11.4
298.15	5.94	0.957	1930	2010	14.7
303.15	6.06	0.977	2510	2570	18.5
308.15	6.25	1.01	3250	3210	22.7
313.15	6.51	1.05	4150	3930	27.5
<i>trans</i> -1,2-Dimethylcyclohexane					
273.15	5.10	0.818	602	736	5.84
278.15	4.87	0.782	827	1060	8.23
283.15	4.73	0.760	1120	1470	11.3
288.15	4.66	0.750	1500	2000	15.0
293.15	4.66	0.750	1980	2640	19.5
298.15	4.72	0.759	2580	3400	24.8
303.15	4.83	0.778	3340	4290	30.8
308.15	5.00	0.807	4270	5290	37.4
313.15	5.22	0.846	5410	6400	44.7
2,2-Dimethylhexane					
273.15	1.83	0.288	1100	3810	30.2
278.15	1.60	0.252	1500	5940	46.2
283.15	1.44	0.228	2010	8830	67.6
288.15	1.35	0.212	2670	12600	94.6
293.15	1.29	0.204	3500	17200	127
298.15	1.27	0.201	4540	22600	165
303.15	1.28	0.203	5830	28700	206
308.15	1.32	0.210	7400	35300	249
313.15	1.39	0.222	9310	41900	293
2,5-Dimethylhexane					
273.15	1.43	0.225	959	4260	33.8
278.15	1.27	0.200	1310	6560	51.1
283.15	1.17	0.185	1770	9590	73.4
288.15	1.12	0.177	2370	13400	101
293.15	1.11	0.175	3120	17800	132
298.15	1.13	0.179	4060	22700	165
303.15	1.19	0.188	5230	27800	200
308.15	1.28	0.203	6670	32900	232
313.15	1.41	0.225	8420	37500	262

^a Based on smoothing of the raw solubility data from Table 6 by eq 1. ^b Vapor-pressure values are from ref 21 except for cyclooctane (ref 24) and cyclooctene (ref 26). The selection of the vapor-pressure data used in calculating Henry's law constants is discussed in the text.

303 K for dimethylhexanes. The temperature range of p_s^{sat} measurements is large (in all cases over 75 K), and the data are highly accurate, permitting a reliable extrapolation toward lower temperatures. This extrapolation was, nevertheless, tested by comparing the enthalpies of vaporization calculated at 298.15 K from the vapor pressures via the Clausius–Clapeyron equation with the recommended enthalpies of vaporization resulting from the calorimetric data (of Majer and Svoboda,²² whose data were based mainly on the measurements of Osborne and Ginnings²³). The differences were, for all five compounds, less than 1%, which makes us think that the extrapolation of the vapor-pressure data does not imply an important increase of error in K_H and K_{aw} compared to the precision of the solubility measurements. In the case of cyclooctane, we have preferred the p_s^{sat} data of Anand et al.²⁴ in the temperature range between 289 and 323 K, largely overlapping with the present experiments, to the equally accurate data of Finke et al.²⁵ at temperatures above 369 K. The only values found in the literature for cyclooctene are the measurements of Lister²⁶ over the temperature range between 273 and 334 K. Their reliability is considered to be lower compared to the vapor pressures of other compounds because the data are presented in the form of a simple correlation $\ln p_s^{\text{sat}} = a + b/T$, implying a constant value of the enthalpy of vaporization over the whole temperature interval.

The literature values of aqueous solubility are compared with our data (using the parameters from Table 1) in Table 3. The temperature of minimum in solubility and the derived thermal functions $\Delta_{\text{sol}}H^\circ$ and $\Delta_{\text{sol}}C_p^\infty$ characterizing the dissolution process at 298.15 K are also given in Table 3. The thermal quantities were obtained by standard thermodynamic procedures, leading to the following relations:

$$\Delta_{\text{sol}}H^\circ = RT^2(\partial \ln x_s^{\text{sol}}/\partial T)_p = -RT(B/\tau - C) \quad (5)$$

$$\Delta_{\text{sol}}C_p^\infty = (\partial \Delta_{\text{sol}}H/\partial T)_p = RC \quad (6)$$

To get a more complete picture for the variation of the solubility of C₈ nonaromatic hydrocarbons, data for *n*-octane reported earlier¹² were also included in Table 3. The values as a function of temperature at near-ambient conditions are, however, scanty, and with the exception of 298.15 K, more measurements are needed between 273 and 298 K. Although the value at 298.15 K is in good agreement with the one recommended by Plyasunov and Shock,¹⁴ the previously reported values for *n*-octane¹² should be considered as tentative for the derivative properties.

The present measurements could be compared with the literature values for cyclooctane and *cis*-1,2-dimethylcyclohexane at 298.15 K, where the experimental data of McAuliffe²⁷ are available. In addition, it was possible to make comparisons at temperatures above 298 K using the data from higher temperature measurements.^{28,29} The reproducibility of our solubility measurements and the reasonable agreement with the literature sources suggest that our data have an overall uncertainty between 5 and 10% in the temperature interval studied as well as in moderate extrapolation. The error in K_H and K_{aw} obtained from eqs 3 and 4 will not be significantly higher, with the exception of cyclooctene, where the accuracy of vapor-pressure data is uncertain (see above). The uncertainties in the deriva-

Table 3. Aqueous Solubility and Derived Thermal Properties at 298.15 K Calculated from Equations 1, 5, and 6

compound	$10^6 X_s^{\text{sol}}$		$\Delta_{\text{sol}} H^\circ$ (kJ·mol ⁻¹)	$\Delta_{\text{sol}} C_p^\circ$ (kJ·K ⁻¹ ·mol ⁻¹)	T_{min} (K)
	this work	lit.			
cyclooctane	0.933	1.27 ²⁷	5.0 ± 0.7	0.36 ± 0.09	284 ± 2
cyclooctene	3.76		6.4 ± 0.8	0.19 ± 0.10	(265 ± 15) ^a
ethylcyclohexane	0.627		4.3 ± 0.5	0.34 ± 0.07	286 ± 2
	0.702 ^b	1.10 ²⁸			
	0.650 ^c	0.699 ²⁹			
<i>cis</i> -1,2-dimethylcyclohexane	0.956	0.960 ²⁷	2.2 ± 0.4	0.38 ± 0.05	292 ± 1
<i>trans</i> -1,2-dimethylcyclohexane	0.759		2.8 ± 0.5	0.38 ± 0.07	291 ± 1
	0.779 ^c	0.800 ²⁹			
2,2-dimethylhexane	0.201		-0.3 ± 0.5	0.74 ± 0.07	299 ± 1
2,5-dimethylhexane	0.179		5.2 ± 0.5	0.89 ± 0.08	292.3 ± 0.4
<i>n</i> -octane	0.129 ^d	0.133 ¹⁴	2.3 ± 0.8	0.62 ± 0.11	294 ± 2

^a Highly uncertain value of little physical significance. ^b At 311.65 K. ^c At 303.45 K. ^d Value based on our earlier data from ref 12 obtained using parameters $A = -89.7855$, $B = 73.9215$, and $C = 74.8574$ in eq 1.

Table 4. Vapor Pressures and Thermodynamic Properties of Hydration at 298.15 K Calculated from Equations 7–9

compound	p_s^{sat} (Pa)	$\Delta_{\text{hyd}} G^\circ$ (kJ·mol ⁻¹)	$\Delta_{\text{hyd}} H^\circ$ (kJ·mol ⁻¹)	$\Delta_{\text{hyd}} C_p^\circ$ (kJ·K ⁻¹ ·mol ⁻¹)
cyclooctane	753	22.30	-38.7	0.43
cyclooctene	1004	19.56	-35.6	0.30
ethylcyclohexane	1705	25.31	-36.3	0.39
<i>cis</i> -1,2-dimethylcyclohexane	1927	24.57	-37.5	0.44
<i>trans</i> -1,2-dimethylcyclohexane	2584	25.87	-35.6	0.43
2,2-dimethylhexane	4542	30.56	-37.7	0.80
2,5-dimethylhexane	4058	30.57	-32.7	0.95
<i>n</i> -octane ^a	1872 ^b	29.46	-38.9	0.69

^a Based on the earlier experimental solubility data of Sarraute et al.¹² ^b Vapor-pressure value obtained from the correlation of Růžicka and Majer.³²

tive properties are taken as the standard deviations calculated by error propagation from the parameter variance–covariance matrix of the solubility data fit by eq 1. The present values of $\Delta_{\text{sol}} H^\circ$ and $\Delta_{\text{sol}} C_p^\circ$ are not highly accurate but yet meaningful thanks to the precision of the measurements and to the sufficiently large temperature range covered.

Hydration properties were obtained at 298.15 K by combining $\Delta_{\text{sol}} X^\circ$ with the residual properties $\Delta_{\text{res}} X^\circ$, expressing the difference between the thermodynamic functions of a pure hydrocarbon in the liquid and an ideal gas at $p^\circ = 100\,000$ Pa (see Table 4). The following equations are valid:

$$\Delta_{\text{hyd}} G^\circ = RT \ln(K_H/p^\circ) \cong \Delta_{\text{sol}} G^\circ + RT \ln(p_s^{\text{sat}}/p^\circ) \quad (7)$$

$$\Delta_{\text{hyd}} H^\circ = \Delta_{\text{sol}} H^\circ - \Delta_{\text{vap}} H^\circ \quad (8)$$

$$\Delta_{\text{hyd}} C_p^\circ = \Delta_{\text{sol}} C_p^\circ - \Delta_{\text{vap}} C_p^\circ \quad (9)$$

While the latter two relationships are exact, eq 7 becomes equality only when the saturated vapor of the solute behaves like an ideal gas. The vaporization properties were obtained in most cases from independent thermal data on pure solutes. The recommended values²² of $\Delta_{\text{vap}} H^\circ$ calculated from calorimetric enthalpies of vaporization were used for all alkanes and alkylcyclohexanes. For cyclooctane and cyclooctene, where no direct calorimetric data are available, the vaporization enthalpies derived from the saturated vapor pressures via the Clausius–Clapeyron equation were used. The heat capacity difference $\Delta_{\text{vap}} C_p^\circ$ was calculated from the liquid and ideal gas heat capacities found in representative compilations of evaluated data.^{31,32}

Because of the direct link between Henry's law constant and the thermodynamic properties of hydra-

tion, it is possible to use the values of the hydration properties at 298.15 K for calculating K_H at superambient conditions semiquantitatively up to at least 373 K:

$$\ln(K_H/p^\circ) = \Delta_{\text{hyd}} G^\circ/RT = \Delta_{\text{hyd}} G_{T_0}^\circ/RT_0 - \int_{T_0}^T [\Delta_{\text{hyd}} H_{T_0}^\circ + \Delta_{\text{hyd}} C_p^\circ(T - T_0)]/(RT^2) dT \quad (10)$$

This is an alternative to the direct determination of K_H from eq 1, which is useful in the case when the vapor pressures are not available or are of low accuracy. The possibility of predicting Henry's law constant, and hence also the air–water partition coefficient, as a function of temperature is useful for the removal of hydrocarbons from aqueous effluents by air stripping, which is often carried out at moderately elevated temperatures.

4. Discussion

Once both $\Delta_{\text{sol}} X^\circ$ and $\Delta_{\text{hyd}} X^\circ$ are determined, it is possible to examine how the structure of hydrocarbons affects the different thermodynamic properties characterizing the dissolution and the hydration processes. For the thermal properties, obtained from the temperature derivatives of measured solubility data and therefore of limited accuracy, only a qualitative interpretation can be given. As seen from Table 3, all of the examined solutes exhibit low values of the enthalpy of solution (the experimental temperature range includes the minimum in solubility), indicating that the process of dissolution is entropy-controlled. The enthalpies of hydration (Table 4) are negative and much larger in absolute value because they reflect mainly the energetic effect of pure solute condensation. As far as the heat capacity is concerned, it varies considerably with structure and, unlike for enthalpies, the contribution of the dissolution property is here generally more important than that of

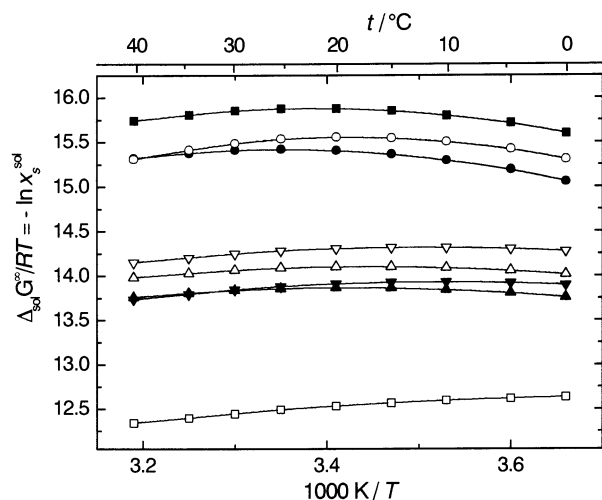


Figure 3. Dimensionless Gibbs energy change (eq 2) characterizing dissolution as a function of reciprocal temperature based on smoothing of the raw solubility data from Table 6 by eq 1: ▼, cyclooctane; □, cyclooctene; ▽, ethylcyclohexane; ▲, *cis*-1,2-dimethylcyclohexane; △, *trans*-1,2-dimethylcyclohexane; ●, 2,2-dimethylhexane; ○, 2,5-dimethylhexane; ■, *n*-octane.¹²

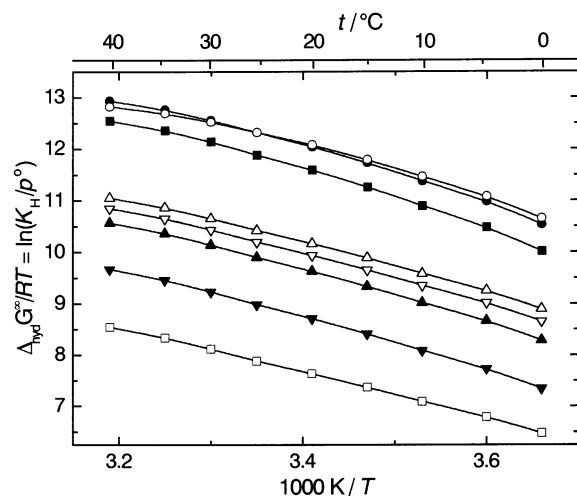


Figure 4. Dimensionless Gibbs energy of hydration (eq 7) as a function of the reciprocal temperature based on the fitted solubility data and literature vapor pressures: ▼, cyclooctane; □, cyclooctene; ▽, ethylcyclohexane; ▲, *cis*-1,2-dimethylcyclohexane; △, *trans*-1,2-dimethylcyclohexane; ●, 2,2-dimethylhexane; ○, 2,5-dimethylhexane; ■, *n*-octane.¹²

the residual property. The largest values for the heat capacities are observed for the open-chain alkanes, both for the dissolution and for the hydration, with the introduction of the ring and of the double bond diminishing them significantly.

The following discussion is centered on the Gibbs energies, which were determined with a considerably better accuracy than the thermal properties and thus allowed a more detailed analysis. The temperature dependence of both $\Delta_{\text{sol}}G^\circ/RT$ and $\Delta_{\text{hyd}}G^\circ/RT$ for the investigated solutes including *n*-octane is depicted in Figures 3 and 4, respectively. The flat maximum observed for most of the solutes in Figure 3 reflects a minimum in solubility (see Table 3). If *n*-octane is taken as the reference, it is observed that cyclooctane exhibits a larger solubility (effect of a ring) and that the presence of a double bond (cyclooctene) makes the aqueous solubility further increase. The effect of substitution in the cyclohexane ring can also be verified: ethylcyclo-

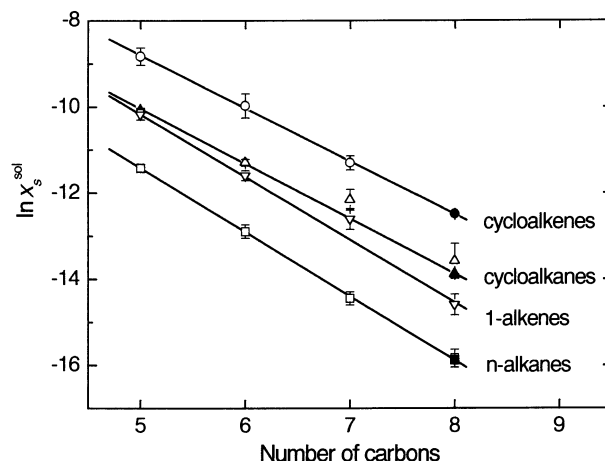


Figure 5. Molecular structure effects on the aqueous solubility of C₅–C₈ hydrocarbons at $T = 298.15$ K: □, *n*-alkanes; ▽, 1-alkenes; △, cycloalkanes; ○, cycloalkenes from ref 14; ▲, cyclooctane; ●, cyclooctene from this work; ■, *n*-octane from our earlier work.¹² Solid lines are weighted linear fits. Error bars correspond to uncertainties as estimated in ref 14 and this work for respective data.

hexane is less soluble than the two isomers of 1,2-dimethylcyclohexane, with the *cis* isomer being distinctly more soluble than the *trans* isomer. Finally, the branching of the aliphatic chain makes the aqueous solubility increase, as can be corroborated by comparison of the *n*-octane values with those for the dimethylhexanes.

The Gibbs energy of hydration is an increasing function of temperature in the interval of our measurements where its temperature variation is mainly controlled by the enthalpy of vaporization. The comparison of the curves in Figures 3 and 4 suggests that the evolution of volatility from an aqueous solution (directly related to Henry's law constant and hence to $\Delta_{\text{hyd}}G^\circ/RT$) is qualitatively linked with the solubility: the more hydrophobic C₈ solutes have generally higher values of K_H . A closer examination reveals that the effect of the molecular structure on x_s^{sol} and K_H is not analogous. Although a similar difference in behavior for the dissolution and hydration properties is observed between the group of three alkanes and three alkylcyclohexanes, the order within these two homologous groups is different. Cyclooctane has values for $\Delta_{\text{sol}}G^\circ/RT$ similar to those of alkylcyclohexanes, but it exhibits a distinct behavior for $\Delta_{\text{hyd}}G^\circ/RT$. The effect of the double bond is analogous for both properties.

To employ for our further consideration the potential of literature data, mostly available at 298.15 K, we will adhere in the following to this reference temperature. Figure 5 shows the consistency between the present measurements for C₈ hydrocarbons and the literature values for hydrocarbons with a lower number of carbon atoms. By inspection of Figure 5, some effects of the structure on the solubility of nonaromatic hydrocarbons can be well identified: from C₅ to C₈, the values of $\ln x_s^{\text{sol}}$ at 298.15 K for four nonaromatic hydrocarbon series (*n*-alkanes, cycloalkanes, 1-alkenes, and cycloalkenes) decrease linearly with the number of carbon atoms, n_C , with the slopes being different for cyclic and open-chain structures independently of the presence of the double bond. In other words, the effects of increasing the open-chain length or the ring size are constant but numerically different, with the same slopes being

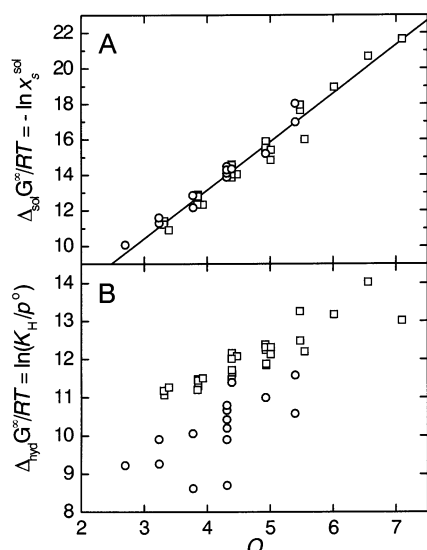


Figure 6. Dimensionless Gibbs energy of solution (panel A) and of hydration (panel B) of the saturated hydrocarbons versus the normalized van der Waals molecular surface area Q . \square , alkanes; \circ , cycloalkanes.

preserved when the double bond is introduced into the open chain and in the cyclic structure.

In attempts to rationalize the above-mentioned behavior, we made use of the now widely accepted observation that the thermodynamic functions of solution of hydrophobic solutes in water are directly proportional to the solute molecular size.^{33,34} Let us focus on the class of saturated hydrocarbons for which, because of their chemical homogeneity, the interaction with solvent water can be considered uniform throughout the entire class and hence the molecular size of the solute should become the only decisive descriptor in the quantitative structure–property relationship (QSPR). Indeed, such a correlation generally works, as can be seen in Figure 6A, where the dimensionless Gibbs energy of the solution is plotted versus the normalized van der Waals molecular surface area.³⁵ The data represented are based on critically assessed literature information¹⁴ completed by the present data and covering 42 C_5 – C_{12} saturated hydrocarbons. Among the three molecular size descriptors we considered (LeBas volume,³⁶ van der Waals molecular volume,³⁵ and van der Waals molecular surface area³⁵), the area parameter was preferred because it gave a better correlation. It can be noted in Figure 6A that the solubility of both the open-chain hydrocarbons and the cyclic compounds follows the same trend with the solute size, with each cluster of points seen comprising open-chain hydrocarbons with a given n_C and cyclics with $n_C + 1$. As seen from Figure 6B, an analogous correlation for the Gibbs energy of hydration fails particularly because of a very poor representation of cyclic compounds. Despite the success in accounting consistently for the effect of n_C on the aqueous solubility of various types of saturated hydrocarbons, the general correlation in Figure 6A is not very accurate. In addition, it totally fails in accounting for less pronounced effects of the structure on solubility such as those of open-chain branching and isomeric ring substitution. Improvement of this QSPR can still be expected through the adoption of a better molecular size descriptor like the solvent-accessible surface area^{37,38} of the solute molecule obtainable from molecular mechanics calculations. Values of this more

Table 5. Numerical Values of the Group/Structure Contributions to $\ln x_s^{\text{sol}}$ at 298.15 K Together with the Indication of the Route of Their Evaluation

group/ structure	contribution to $\ln x_s^{\text{sol}}$	based on data for
CH_3	−3.471	(nC_5 , nC_6 , nC_7 , nC_8) ^{a,b}
CH_2	−1.493	(nC_5 , nC_6 , nC_7 , nC_8) ^{a,b}
CH	0.667	2,5-dimethylhexane ^a
C	2.942	2,2-dimethylhexane ^a
$[=]$ ^c	−2.832	1-octene
cycle	−3.843	(cyC_5 , cyC_6 , cyC_7 , cyC_8) ^{a,b}
$cyCH_2$	−1.232	(cyC_5 , cyC_6 , cyC_7 , cyC_8) ^{a,b}
$cyCH$	0.684	ethylcyclohexane ^a
cyC	2.936	1,1,3-trimethylcyclopentane
$cy[=]$ ^d	−2.625	cyclooctene ^a

^a A solubility value determined in this or our earlier¹² work was used. ^b Linear fit of $\ln x_s^{\text{sol}}$ vs n_C . ^c Double bond in an open chain. ^d Double bond in a cycle.

sophisticated parameter are, however, not available for the majority of substances of our concern.

With the aim rationalizing, at least at a basic level, the effects of the structure on the aqueous solubility of nonaromatic hydrocarbons in a more detailed manner than QSPR, we have decided to make use of a simple group contribution scheme. Rather than developing a comprehensive solubility estimation method using a large training data set, we have opted for an inverse strategy. Our aim was to demonstrate that the effects of the molecular structure on the aqueous solubility of nonaromatic hydrocarbons can be quantitatively captured by only a small set of accurate solubility data for characteristic substances. Group contributions determined on the basis of this limited experimental information are then able to provide a realistic prediction for a variety of nonaromatic hydrocarbons of medium molar mass. We applied a simple first-order group contribution scheme, which, in general, ignores nearest-neighbor and steric hindrance effects, and assumed that

$$\ln x_s^{\text{sol}} = \sum_i n_i (\ln x_s^{\text{sol}})_i \quad (11)$$

where $(\ln x_s^{\text{sol}})_i$ stands for the contribution of group i and n_i is the number of its occurrences in the solute molecule, with the summation being over all groups. Considering the validity of eq 2, these contributions have a direct relation to the Gibbs free energy characterizing the dissolution process. Besides the contributions of the groups alone, contributions of some major structural features (ring and double bond) were also considered explicitly. The contributions are listed in Table 5 together with the indication of the route of their evaluation. To determine the values of the contributions, we proceeded in a stepwise manner: the values of basic contributions for n -alkanes (CH_3 and CH_2) and cycloalkanes ($cyCH_2$ and ring) were evaluated first by fitting straight lines to the experimental $\ln x_s^{\text{sol}}$ data for C_5 – C_8 hydrocarbons of the respective series, with any other contribution then being obtained from a single solubility datum for a selected characteristic compound. For determining the contributions, we employed our new solubility data in combination with a limited number of literature values. For this purpose, we adopted the critically assessed information based on a recent comprehensive compilation of literature data presented by Plyasunov and Shock.¹⁴ They focused their effort on the establishment of representative and comprehensive thermodynamic functions of hydration but also report

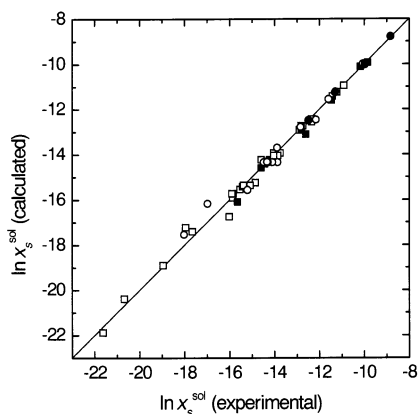


Figure 7. Aqueous solubility of nonaromatic hydrocarbons. Experimental values versus those predicted from the group contributions: \square , alkanes; \blacksquare , alkenes; \circ , cycloalkanes; \bullet , cycloalkenes.

the residual (vaporization) thermodynamic functions, allowing one to get back to the Gibbs free energy of dissolution and hence to the solubilities. The data available from this source updated by a few results published recently^{16,38} were used to test the performance of the contribution scheme. The calculated and experimental solubility values are graphically compared in Figure 7 and given numerically in the Appendix (Table 7), where the group construction considered for each substance and the literature source of each experimental value are also listed. The comparison shows that the group contribution analysis we carried out is capable of portraying the effects of structure on the aqueous solubility of nonaromatic hydrocarbons. As seen from Figure 7, the largest deviations are encountered for the lowest solubilities corresponding to hydrocarbons with the number of carbon atoms of 10 and more. Such a situation is understandable: solubility data for the higher hydrocarbons are scarce and less reliable, and the group contribution prediction here was an extrapolation based on data for hydrocarbons having from 5 to 8 carbon atoms. In summary, the 10 group/structure contributions in Table 5 based only on 14 solubility values reproduce $\ln x_s^{\text{sol}}$ of 53 aliphatic, cyclic, and unsaturated hydrocarbons with 5–12 carbon atoms, which spans over almost 13 units (i.e., more than 5 orders of magnitude of x_s^{sol}), with a root-mean standard deviation (RMSD) of 0.27 (i.e., about 30% in x_s^{sol}). This level of error approaches the realistic estimate of uncertainty of many aqueous solubility data for hydrocarbons reported in the literature and favorably compares with the performance of the recently published group contribution scheme of Plyasunov and Shock.¹⁴ Their scheme uses a similar type of group contribution but developed for hydration properties and predicts $\Delta_{\text{hyd}}G^\circ/RT$ at 298.15 K for the same test data set with a RMSD of 0.37. The group contribution scheme established by us for dissolution properties appears to perform better especially for cyclic hydrocarbons, both saturated and unsaturated, although Plyasunov and Shock optimized their group contributions on an extensive database comprising the majority of data from the present testing data set. Our scheme is not, however, able to describe well isomeric ring substitutions and other situations where second-order effects of neighbor groups can play an important role. As demonstrated on cis and trans forms of 1,2-dimethylcyclohexane examined experimentally in this work, the proximity group

Table 6. Raw Experimental Values of Mole Fraction Solubilities in Water As Determined in This Work

T (K)	$10^6 x_s^{\text{sol}}$	T (K)	$10^6 x_s^{\text{sol}}$	T (K)	$10^6 x_s^{\text{sol}}$
Cyclooctane					
274.15	0.887	288.15	0.881	308.15	1.04
274.15	0.944	293.15	0.974	308.15	1.03
278.15	0.890	298.15	0.938	313.15	1.08
278.15	0.873	298.15	0.887	313.15	1.10
283.15	0.890	303.15	0.950		
283.15	0.923	303.15	0.936		
Cyclooctene					
274.15	3.33	288.15	3.37	303.15	3.73
274.15	3.29	293.15	3.58	308.15	4.45
278.15	3.33	298.15	3.86	308.15	4.04
278.15	3.20	298.15	4.02	308.15	4.39
283.15	3.47	298.15	3.73	313.15	4.46
283.15	3.34	303.15	3.78	313.15	4.05
288.15	3.42				
Ethylcyclohexane					
274.15	0.610	288.15	0.603	303.15	0.647
274.15	0.659	288.15	0.588	303.15	0.679
278.15	0.641	293.15	0.604	313.15	0.699
278.15	0.590	293.15	0.609	313.15	0.725
278.15	0.599	298.15	0.636	313.15	0.700
283.75	0.599	298.15	0.637		
cis-1,2-Dimethylcyclohexane					
274.15	1.06	288.15	0.925	298.15	0.963
274.15	1.07	288.15	1.00	303.15	0.993
274.15	1.03	288.15	0.986	308.15	1.04
278.15	0.992	293.15	0.956	308.15	0.965
278.15	1.00	293.15	0.911	313.15	1.05
278.15	0.975	293.15	0.959	313.15	1.04
283.75	0.988	298.15	0.943	313.15	1.09
283.75	0.969	298.15	0.941		
trans-1,2-Dimethylcyclohexane					
274.15	0.784	288.05	0.755	303.15	0.814
274.15	0.824	288.05	0.756	303.15	0.767
278.15	0.792	293.15	0.738	308.15	0.781
278.15	0.774	293.15	0.757	308.15	0.780
278.15	0.786	293.15	0.733	313.15	0.852
283.75	0.725	293.15	0.774	313.15	0.875
283.75	0.797	298.15	0.744		
2,2-Dimethylhexane					
274.55	0.272	288.05	0.214	308.05	0.209
274.35	0.269	297.95	0.192	308.05	0.210
278.05	0.269	297.95	0.197	312.95	0.229
278.25	0.252	303.05	0.208	312.95	0.217
283.15	0.228	303.15	0.208	313.15	0.226
288.05	0.211				
2,5-Dimethylhexane					
275.15	0.213	282.85	0.182	308.15	0.199
275.15	0.219	288.15	0.181	308.15	0.207
278.15	0.203	288.15	0.176	313.05	0.227
278.15	0.189	297.95	0.181	313.05	0.214
278.15	0.208	303.15	0.188	313.05	0.230
282.85	0.181	303.15	0.190		

influencing can lead to a considerable increase of the aqueous solubility (decrease of the Gibbs energies of solution and hydration). For the sake of a better predictive performance in this respect, an extra correction (pseudogroup) could be introduced to correct for proximity neighbor effects of ring substituents. Although adopted by Plyasunov and Shock for the description of hydration properties, no such correction was considered in the present scheme in order to preserve its first-order character.

Being substantiated by their good predictive performance, the contributions listed in Table 5 can be employed to elucidate various general effects of the molecular structure on the solubility of nonaromatic hydrocarbons:

Table 7. Comparison of the Experimental and Calculated Solubility at 298.15 K by the Group Contribution Scheme

n_C	compound	group construction	ref	$\ln x_s^{\text{sol}}(\text{exp})$	$\ln x_s^{\text{sol}}(\text{calc})$	$\Delta \ln x_s^{\text{sol}}$
Alkanes						
5	<i>n</i> -pentane	2CH ₃ + 3CH ₂	14	-11.419 ^a	-11.421	0.002
5	2-methylbutane	3CH ₃ + CH ₂ + CH	14	-11.230	-11.239	0.009
5	2,2-dimethylpropane	4CH ₃ + C	14	-10.913	-10.942	0.029
6	<i>n</i> -hexane	2CH ₃ + 4CH ₂	14	-12.896 ^a	-12.914	0.018
6	2-methylpentane	3CH ₃ + 2CH ₂ + CH	14	-12.738	-12.732	-0.006
6	3-methylpentane	3CH ₃ + 2CH ₂ + CH	14	-12.811	-12.732	-0.079
6	2,2-dimethylbutane	4CH ₃ + CH ₂ + C	14	-12.343	-12.435	0.092
6	2,3-dimethylbutane	4CH ₃ + 2CH	14	-12.351	-12.550	0.199
7	<i>n</i> -heptane	2CH ₃ + 5CH ₂	14	-14.441 ^a	-14.407	-0.034
7	2-methylhexane	3CH ₃ + 3CH ₂ + CH	14	-14.594	-14.225	-0.369
7	3-methylhexane	3CH ₃ + 3CH ₂ + CH	14	-14.219	-14.225	0.006
7	3,3-dimethylpentane	4CH ₃ + 2CH ₂ + C	14	-13.751	-13.928	0.177
7	2,2-dimethylpentane	4CH ₃ + 2CH ₂ + C	14	-14.037	-13.928	-0.109
7	2,3-dimethylpentane	4CH ₃ + CH ₂ + 2CH	14	-13.860	-14.043	0.183
7	2,4-dimethylpentane	4CH ₃ + CH ₂ + 2CH	14	-14.037	-14.043	0.006
8	<i>n</i> -octane	2CH ₃ + 6CH ₂	12	-15.863 ^a	-15.900	0.037
8	4-methylheptane	3CH ₃ + 4CH ₂ + CH	16	-15.839	-15.718	-0.121
8	3-methylheptane	3CH ₃ + 4CH ₂ + CH	14	-15.893	-15.718	-0.175
8	2,5-dimethylhexane	4CH ₃ + 2CH ₂ + 2CH	this work	-15.536 ^a	-15.536	0
8	2,2-dimethylhexane	4CH ₃ + 3CH ₂ + C	this work	-15.421 ^a	-15.421	0
8	2,2,4-trimethylpentane	5CH ₃ + CH ₂ + CH + C	14	-14.848	-15.239	0.391
8	2,3,4-trimethylpentane	5CH ₃ + 3CH	16	-15.381	-15.354	-0.027
8	2,3,4-trimethylpentane	5CH ₃ + 3CH	14	-15.078	-15.354	0.276
9	<i>n</i> -nonane	2CH ₃ + 7CH ₂	14	-17.656	-17.393	-0.263
9	4-methyloctane	3CH ₃ + 5CH ₂ + CH	14	-17.955	-17.211	-0.744
9	2,2,5-trimethylhexane	5CH ₃ + 2CH ₂ + CH + C	14	-16.014	-16.732	0.718
10	<i>n</i> -decane	2CH ₃ + 8CH ₂	38	-18.958	-18.886	-0.072
11	<i>n</i> -undecane	2CH ₃ + 9CH ₂	38	-20.684	-20.379	-0.305
12	<i>n</i> -dodecane	2CH ₃ + 10CH ₂	14	-21.634	-21.872	0.238
					RMSD	0.252
Alkenes						
5	1-pentene	CH ₃ + 3CH ₂ + CH + [=]	14	-10.177	-10.115	-0.062
5	2-pentene	2CH ₃ + CH ₂ + 2CH + [=]	14	-9.862	-9.933	0.071
6	1-hexene	CH ₃ + 4CH ₂ + CH + [=]	14	-11.471	-11.608	0.137
7	1-heptene	CH ₃ + 5CH ₂ + CH + [=]	14	-12.605	-13.101	0.496
7	2-heptene	2CH ₃ + 3CH ₂ + 2CH + [=]	14	-12.803	-12.919	0.116
8	1-octene	CH ₃ + 6CH ₂ + CH + [=]	14	-14.594 ^a	-14.594	0
9	1-nonene	CH ₃ + 7CH ₂ + CH + [=]	14	-15.647	-16.087	0.440
					RMSD	0.262
Cycloalkanes						
5	cyclopentane	5cyCH ₂ + cycle	14	-10.068 ^a	-10.003	-0.065
6	cyclohexane	6cyCH ₂ + cycle	14	-11.290 ^a	-11.235	-0.055
6	methylcyclopentane	CH ₃ + 4cyCH ₂ + cyCH + cycle	14	-11.593	-11.558	-0.035
7	cycloheptane	7cyCH ₂ + cycle	14	-12.157 ^a	-12.467	0.310
7	methylcyclohexane	CH ₃ + 5cyCH ₂ + cyCH + cycle	14	-12.839	-12.790	-0.049
8	cyclooctane	8cyCH ₂ + cycle	this work	-13.885 ^a	-13.699	-0.186
8	ethylcyclohexane	CH ₃ + CH ₂ + 5cyCH ₂ + cyCH + cycle	this work	-14.283 ^a	-14.283	0
8	<i>cis</i> -1,2-dimethylcyclohexane	2CH ₃ + 4cyCH ₂ + 2cyCH + cycle	this work	-13.860	-14.345	0.485
8	<i>trans</i> -1,2-dimethylcyclohexane	2CH ₃ + 4cyCH ₂ + 2cyCH + cycle	this work	-14.091	-14.345	0.254
8	<i>trans</i> -1,3-dimethylcyclohexane	2CH ₃ + 4cyCH ₂ + 2cyCH + cycle	16	-14.479	-14.345	-0.134
8	<i>trans</i> -1,4-dimethylcyclohexane	2CH ₃ + 4cyCH ₂ + 2cyCH + cycle	14	-14.288	-14.345	0.057
8	1,1,3-trimethylcyclopentane	3CH ₃ + 3cyCH ₂ + cyCH + CH + cycle	14	-14.332 ^a	-14.332	0
9	1,1,3-trimethylcyclohexane	3CH ₃ + 4cyCH ₂ + cyCH + CH + cycle	14	-15.199	-15.564	0.365
10	cyclodecane	10cyCH ₂ + cycle	38	-16.971	-16.163	-0.808
10	pentylcyclopentane	CH ₃ + 4CH ₂ + 4cyCH ₂ + cyCH + cycle	14	-18.015	-17.530	-0.485
					RMSD	0.315
Cycloalkenes						
5	cyclopentene	3cyCH ₂ + 2cyCH + cycle + cy[=]	14	-8.829	-8.796	-0.033
6	cyclohexene	4cyCH ₂ + 2cyCH + cycle + cy[=]	14	-9.975	-10.028	0.053
7	cycloheptene	5cyCH ₂ + 2cyCH + cycle + cy[=]	14	-11.302	-11.260	-0.042
8	cyclooctene	6cyCH ₂ + 2cyCH + cycle + cy[=]	this work	-12.492 ^a	-12.492	0
					RMSD	0.038
					total RMSD:	0.268

^a Used to evaluate the group contributions.

(i) The simple branching of the linear aliphatic chain, which corresponds to the substitution of 2CH₂ by 1CH + 1CH₃, is accompanied by a moderate increase of the solubility of $\Delta \ln x_s^{\text{sol}} = (\ln x_s^{\text{sol}})_{\text{CH}} + (\ln x_s^{\text{sol}})_{\text{CH}_3} - 2(\ln x_s^{\text{sol}})_{\text{CH}_2} = 0.182$.

(ii) Branching the linear aliphatic chain twice on the same carbon atom (quaternary carbon), which corre-

sponds to the substitution of 3CH₂ by 1C + 2CH₃, leads to a solubility increase of $\Delta \ln x_s^{\text{sol}} = 0.479$, i.e., to a more pronounced increase than what would be caused by single branching on two different carbon atoms.

(iii) The effect of transforming the linear alkane chain in a ring structure depends on the number of carbon atoms involved. One can look at it as composed of a ring

closure, corresponding to the substitution of 2CH_3 by $2\text{cyCH}_2 + 1\text{cycle}$, and a change of the nature of each of the $n_{\text{C}} - 2$ methylene groups involved, from that of the linear nature (CH_2) to that of the cyclic nature (cyCH_2). Both of these substitutions affect the solubility positively, with $\Delta \ln x_{\text{s}}^{\text{sol}}$ being 0.635 for the ring closure and 0.261 for the change of the nature of each of the $n_{\text{C}} - 2$ methylene groups.

(iv) The contributions of CH and C groups have values similar to respectively the contributions of their cyclic counterparts, cyCH and cyC , although all were evaluated independently. This remarkable finding means that, independently whether in the open chain or in the cycle, the branching (the presence of CH or C) affects the aqueous solubility of nonaromatic hydrocarbons to the same extent. As a consequence, this suggests that for both the open-chain and the cyclic hydrocarbons the identical CH and C groups could probably be considered in future developments.

(v) The introduction of a double bond at the end of the linear chain to form 1-alkene from n -alkane, which corresponds to the substitution of $1\text{CH}_3 + 1\text{CH}_2$ by $1\text{CH}_2 + 1\text{CH} + [=]$, is accompanied with a major increase of the solubility, with $\Delta \ln x_{\text{s}}^{\text{sol}}$ being 1.306. Still a greater increase of the solubility ($\Delta \ln x_{\text{s}}^{\text{sol}} = 1.488$) should be expected according to the scheme when the double bond is introduced at another position in the chain, but the limited experimental information is rather inconclusive in supporting such a prediction (see Table 7 in the Appendix).

(vi) The introduction of a double bond into the ring structure has a similar but weaker effect than its introduction into the linear aliphatic chain. It is represented by the substitution of 2cyCH_2 by $2\text{cyCH} + \text{cy}[=]$, with $\Delta \ln x_{\text{s}}^{\text{sol}}$ being 1.207.

5. Conclusion

This work has shown that the solubility data determined with an accuracy better than 10% can serve as a basis for building up empirical schemes for rationalizing the effect of the molecular structure on the solubilization of organic hydrophobic solutes in water. In addition, the availability of such data over a moderate temperature interval (30–40 K) at near-ambient conditions allows the estimation of the thermal derivative properties at 298.15 K, completing a picture of the dissolution process. A combination of these data with vapor pressures, available for many organic compounds with good accuracy, opens a way toward coefficients expressing the volatility of a hydrocarbon from its aqueous solution as a function temperature, which is of high relevance for environmental issues, and toward thermodynamic functions of hydration, which are of interest for theoretically quantifying hydrophobic interactions.

We have further demonstrated that a valid group contribution scheme can be built on the level of the solubility function (dimensionless Gibbs energy of solution characterizing a dissolution process). The group contribution approaches formulated for hydration properties, though considered, in general, as better founded from the theoretical point of view, do not seem to present any particular advantage when used at one temperature or in a limited temperature interval. From the engineering point of view, the possibility of adopting a simple empirical model to the function directly linked

with experimental data of high practical value, such as solubility, is certainly a great advantage.

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Appendix

See Tables 6 and 7.

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