Prediction of the mutual solubilities of hydrocarbons and water

with COSMO-*RS*

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Abstract

A critical collection of data for the mutual solubilities of water and hydrocarbons recently presented by Tsonopoulos is used for a careful analysis of the ability of the a priori prediction method COSMO-RS to predict the infinite dilution activity coefficients in such dissimilar systems. Although only few data of hydrocarbon-water mixtures had been used in the parameterization of COSMO-RS, the mutual solubilities of hydrocarbons (n-alkanes, 1-alkenes, alkylbenzenes, and alkylcyclohexanes) and water are quite well predicted by COSMO-*RS*. All trends of the solubilities with respect to carbon number of the hydrocarbons are very well reproduced. Some moderate deviations are observed for the temperature dependence (solvation enthalpy) of hydrocarbon solubility in water, while the temperature dependence of the water solubility in various hydrocarbons is reproduced almost within the experimental error up to temperatures of about 473 K.

The good qualitative and even satisfactory quantitative prediction of the solubilities of hydrocarbons in water proves, that COSMO-RS correctly reflects the physics of the hydrophobic solvation, i.e. the fact that the largest part of the free energy of solution of hydrocarbons in water is of entropic nature due to the re-organization of the water molecules around non-polar compounds. This is especially unexpected, because the COSMO-RS method does not take into account the 3D-geometry of solute solvent arrangements. An explanation is given, how the physics of water re-organization around non-polar surface is nevertheless described by COSMO-RS. Some ideas for further improvement of COSMO-RS regarding the mutual solubilities of hydrocarbons and water are discussed.

1. Introduction

Although important in several industrial, biological, and environmental processes, the mutual solubilities of such common compounds as hydrocarbons (HC) and water are still a field of active research, because these solubilities are so small that the accurate measurement is often restricted by experimental problems. Still a large number of contradicting and probably false experimental data can be found in new literature and even in databases. Recently, Tsonopoulos published a careful and detailed analysis of the mutual solubilities of n-alkanes, 1-alkenes, alkylbenzenes, and alkylcyclohexanes with water [1,2]. Based on a synopsis of solubility data and calorimetric data of various experimental laboratories he derived a collection of relatively simple equations which reflect the dependence of these solubilities on carbon number (CN) and temperature.

Since measurement of these solubilities is so difficult and sensitive to errors, good calculation methods for such data are desirable, especially if they provide not only numbers, but systematic understanding of the effects. While some simpler hydrocarbons can nowadays be reasonably well described by molecular modeling (molecular dynamics and especially Monte Carlo simulations), water and especially water mixtures still are a challenge for such simulation techniques despite of 30 years of active parameterization of appropriate force-fields. This is due to the extremely strong and complicated electrostatic and hydrogen-bond (HB) interactions. For a review of recent progress see ref. [3,4]. A special and unique feature caused by the extreme differences in polarity of n-alkanes and water is the hydrophobic effect, which is usually interpreted as a strong reorganization of the HB network of water around non-polar surface in order to avoid the energetically very undesirable interaction of highly polar HB donors and acceptors with non-polar partners. It is found that water tends to maintain almost the same number of hydrogen bonds per molecule in the vicinity of n-alkane molecules as it has in bulk water. As a result of this reorganization, the solvation of HC in water goes along with an extreme loss of entropy, and the free energy of solution of HC in water is almost entirely of entropic nature. This causes a solubility minimum of HC in water roughly at $T = 310$ K. Conversely, the solubility of water in HC goes along with a strong gain in entropy, because a water molecule transferred into HC is released out of the highly restricting HB network into the energetically unfavorable, but almost homogeneous and isotropic environment of the HC. Therefore almost half of the solution enthalpy of approximately 35 kJ/mole [2] of water in HC is compensated by the entropic gain, resulting in a Gibbs free energy of solution of about 18 kJ/mol.

The precedent considerations illustrate that the proper simulation of the mutual solubilities of HC and water is one of the most extreme challenges for simulation methods in fluid thermodynamics. In this article we investigate the ability of the novel, quantum-chemically based a priori prediction method COSMO-RS [5-8] to describe the above-mentioned effects qualitatively and quantitatively. After giving a short review of the COSMO-RS method in section 2, we will follow the structure of the papers of Tsonopoulos [1,2] and consider the solubility of HC in water in section 3, and that of water in HC in section 4. In section 5 final conclusions will be drawn and an outlook for further improvements of the method will be given.

2. The COSMO-RS method

COSMO-RS is a novel a priori prediction method for thermodynamic equilibria of fluids and liquid mixtures. The name is composed of "COnductor-like Screening MOdel" (COSMO) [9], which is an efficient variant of dielectric continuum salvation methods in quantum chemical programs, and its extension to "Real Solvents" (RS)[5], which is a statistical thermodynamics approach based on the results of quantum chemical COSMO calculations. Since the full description of the COSMO-RS theory is beyond the scope this article and has been given in several recent articles [7,8], we restrict ourselves here to a short introduction of the basic features required for the understanding this article.

COSMO-RS is a two step procedure. In a first step, quantum chemical calculations have to be performed for all compounds of interest. In these calculations the continuum solvation model COSMO is applied in order to simulate a virtual conductor environment for the molecule. In this environment, the solute molecule induces a polarization charge density σ on the interface of the molecule to the conductor, i.e. on the molecular surface, and these charges act back to the solute, generating a more polarized electron density than in vacuum. During the quantum chemical self-consistency algorithm the solute molecule is thus converged to its energetically optimal state in a conductor with respect to electron density and geometry. The standard quantum chemical method for COSMO-RS is density functional theory (DFT) and the DFT functional B88-PW86 [10,11] with a triple zeta valence polarized basis set (TZVP) is used throughout this study. All DFT/COSMO calculations have been performed using the quantum chemical program TURBOMOLE [12], which is very efficient for this kind of calculations. None of the calculations for the molecules considered in this study took longer than 12 hours on a single 1GHz CPU. All further details and references regarding DFT/COSMO calculations with TURBOMOLE are given in ref. [13]. Most of the DFT/COSMO calculations have been taken from the COSMO*base* database

[14] which provides pre-calculated DFT/COSMO results for about 1200 common solvents and compounds. The output of a DFT/COSMO calculation is a file providing the total energy of the molecule in its conductor environment as well as the full three-dimensional (3D) information about the polarization charge density σ on the surface of the molecule. In order to avoid a common misunderstanding, it should be noted, that these DFT/COSMO calculations only act as input for the molecular information. They are independent of the dielectric constant of the solvent and of temperature.

The polarization charge density σ is a good local descriptor of the molecular surface polarity. In the second step of COSMO-RS, the statistical thermodynamics of the molecular interactions, this polarization charge density is used for the quantification of the interaction energy of pair-wise interacting surface segments with regard to the most important molecular interaction modes, i.e. electrostatics and hydrogen bonding. The less specific van der Waals (vdW) interactions or dispersive interactions are taken into account in a more approximate way by element specific dispersion coefficients. Because these cancel out in liquid-liquid equilibria, the dispersive interactions are of no importance for the purpose of this paper. Thus the quantum chemical information about the polarization charge densities σ plays the key role for the evaluation of the molecular interactions in the liquid phase, and it replaces the empirical interaction parameters usually used in chemical engineering models like UNIQUAC [15] and UNIFAC [16]. As a prerequisite for an efficient statistical thermodynamics treatment, the 3D distribution of the polarization charges σ on the surface of each molecule X is converted into a surface composition function (σ-profiles), i.e. a histogram $p^X(\sigma)$, which gives the relative amount of surface with polarity σ on the surface of the molecule. Such σ-profiles provide detailed information about the molecular polarity distribution [5,6], but they do no longer provide geometric 3D information. Some representative σ-profiles of molecules considered in this study are given in figure 1. It can be seen, that n-alkanes and alkyl chains give a relatively narrow double peaks in the vicinity of $\sigma = 0$, resulting from the slightly positive and negative screening charges σ on the carbon atoms and hydrogens, respectively. No major difference is apparent between hexane and cyclohexane, apart from a small difference in the peak height, arising from the smaller surface area of the latter compound. The π-orbitals of the sp^2-carbon atoms produce a shoulder in the σ-profile of hexane. Benzene, and phenyl rings in general, show a broader double peak due to the larger polarity of the π-face and the hydrogen atoms. In contrast to the hydrocarbons, the water molecule has an extremely broad σ-profile, which is dominated by two quite symmetric peaks. The peak at large positive σ-values results from the oxygen lone-pairs,

and that at strongly negative σ-values originates from the two polar hydrogens. Only a small part of surface area of water is located in the intermediate σ-region.

The statistical thermodynamics itself is done using a coupled set of non-linear equations for the activity coefficients of the surface segments. This new method, which was recently published separately under the name COSMOSPACE (COSMO Segment Activity Coefficient Equations) [17], was specially developed for the COSMO-RS method [5]. It provides an exact solution for independently pair-wise interacting surface segments and thereby has a more realistic behavior, especially at infinite dilution, than the traditional chemical engineering methods, e.g. UNIQUAC, which make additional approximations. The temperature dependence of COSMO-RS predictions thus results mainly from the explicit appearance of the temperature in the statistical thermodynamics procedure. In hydrogen bonded systems an intrinsic temperature dependence of the hydrogen bond energy term[7] also contributes to the temperature dependence of activity coefficients and solubilities.

For this paper it is important to understand, that the COSMO-RS recasts the original statistical thermodynamics problem of a large number of interacting molecules in 3D space into the much simpler to solve problem of the statistical thermodynamics of effectively independently pair-wise interacting surface segments. Although thus disregarding all 3D constraints, COSMO-RS nevertheless performs a statistical thermodynamic calculation and hence yields enthalpic and entropic information for the system. In this paper it will be shown that despite of the severe simplification COSMO-RS is able to describe subtle effects like the hydrophobic effect, which are usually considered in a terminology of molecular 3D geometry rearrangements. It is important to note, that the chemical potentials arising from the COSMOSPACE thermodynamics do not only represent the enthalpic electrostatic and hydrogen bonding interactions, but also include entropic information arising from the number of favorable segment pairings that can be formed in a mixture. They also include the contribution which is often called cavity formation (free) energy, because the free energy required for the release of a surface segment from the interactions with the bulk solvent is explicitly accounted for the chemical potentials.

All COSMO-RS calculations of this paper are performed using the COSMO*therm* program [18], which provides an efficient and flexible implementation of the COSMO-RS method. The total CPU time spent for the over 1000 COSMO*therm* calculations required for this paper took only about 2 min on a 900 MHz laptop computer. The latest parameterization BP_TZVP_C12_0102 is used. In such parameterization the very few global parameters (~15) of the COSMO-RS method are optimized based on a set of about 1000 thermodynamic data, mainly

partition coefficients and vapor pressures [for details see ref. 6], in combination with DFT/COSMO calculations of a certain quantum chemical method. Such parameterization may be considered as the equivalent of a specific force-field in MD/MC simulations, but it has much less adjusted constants than typical force fields, since only global and element specific constants are required in COSMO-RS. Detailed values of the parameterization used in this are given in Appendix A.

Since this paper is specially dealing with water-hydrocarbon solubilities, it is necessary to consider the amount of information about such data used during the parameterization in order to value the predictive power of the COSMO-RS method. No special solubility data are contained in the parameterization data set, but some information about the room-temperature water solubility of HC is contained in the hexane-water and benzene-water partition coefficients. The combination of room-temperature Henry's law constants and vapor pressures also provides some information about HC solubilities in water. The temperature dependence of the surface interaction (free) energies, especially of the vdW and the HB contributions [7], is fitted to pure compound vapor pressures and hence does not contain information about the special systems under consideration. No data for the solubility of water in any solvent is used in the general parameterization, but a special surface scaling parameter has been introduced for water in COSMOtherm release 1.2 in order to overcome the notorious problem with solute properties of water [6,7]. This downscaling factor of 0.6 has been adjusted to various room-temperature infinite dilution activity coefficients of water. It appears to be a good cure for the original systematic overestimation of such water activity coefficients. Unfortunately it is a purely empirical correction for the special compound water, lacking any theoretical justification. Summarizing, some indirect information about mutual HC-water solubilities has been used during the parameterization, but in a very dilute manner amongst much more data of various functionalized and more polar compounds.

3. Prediction of hydrocarbon solubility in water

Following the analysis of Tsonopoulos [1,2], HC of the classes n-alkane, 1-alkene, alkylbenzene, and n-alkylcyclohexane are considered in this study, generally with carbon numbers CN = 6 to 10. In some diagrams CNs 3 to 5 are also considered for n-alkanes and n-alkenes. All experimental data mentioned in the following sections is taken from refs. [1,2]. Solubilities are shown as $\Delta G_{HC} = RT \ln(x_{HC})$ of solution in order to simplify a decomposition with respect to enthalpy and entropy. For numerical convenience, all calculations of ΔG_{HC} are done at infinite solution. By some test calculations we proved that errors arising from the infinite dilution approximation are only about 1% compared to a fully consistent treatment of the low mutual solubilities or water

and hydrocarbon. Only stretched (all-trans) conformations of the alkyl chains are considered, because the σ-profiles of alkyl chains are almost insensitive with respect to conformation. Really folded conformations, which would have less accessible surface, are of no statistical relevance.

Figure 2 shows the CN-dependence of the ΔG of solution of HC in water at T = 298 K. The predicted values for alkanes, alkenes, and alkylcyclohexanes are only about 5%, i.e. 2 kJ/mol, low, corresponding to an overestimation of HC solubility by about a factor 2. The predicted relative solubilities of these compounds are in almost exact agreement with experiment. For alkylbenzenes the predicted and experimental solubilities appear to coincide perfectly. The experimental values of ΔG for alkanes increase by 3.8 kJ/mol with each added carbon atom, while COSMO-RS gets a slightly smaller slope of 3.5 kJ/mol. Interestingly, due to this small difference the experimental and calculated curves would coincide at CN = 0. For alkenes the slopes are very similar to those discussed for alkanes, and for alkylbenzenes the COSMO-RS predictions also show a very small underestimation of the slope. For alkylcyclohexanes the experiments suggest the smallest increase with CN (3.2 kJ/mol) while the slope predicted by COSMO-RS is close to that of the other HC (3.6 kJ/mol), and hence in this case the two curves appear to cross at about CN = 14. Since at large CNs alkanes and alkenes should become more and more similar, a similar slope for these compounds classes as suggested by COSMO-RS appears to be more plausible than the exceptionally small slope reported from experiments.

Using the relation $\Delta H_{HC} = RT^2\, d(\ln x_{HC})/dT$ given in ref. [1] the enthalpies of solution have been calculated by numerical differentiation of COSMO-RS results. Fig. 3 shows an apparent disagreement with experimental values of ΔH_{HC}. While the experimental values are in the range of ±2 kJ/mol and show almost no dependence on CN, the calculated enthalpies of solution are in the range of 8 kJ/mol with a positive CN slope of about 0.7 kJ/mol. Interestingly, the experimental and calculated curves would again coincide at about CN = 0. Although the experimental enthalpies are subject to some uncertainty [1,2], the discrepancy of about 8 kJ/mol is most likely due to shortcomings of COSMO-RS. Nevertheless, the model correctly reflects the unusual feature, that only a small part of the large free energies of solution of HC in water is due to enthalpy, while the largest part is of entropic nature. While the experimental finding is that almost 100% of ΔG_{HC} at 298K is entropic, COSMO-RS predicts a portion of 80% for $T\Delta S_{HC}$. While usually the large entropy loss of HC during solution in water is addressed to the rearrangement of water molecules around the non-polar surface, in COSMO-RS this large entropy loss is caused by the fact, that only the small amount of weakly polar surface of water is available as

partners for the HC surface segments for enthalpic reasons. Thus COSMO-RS also finds the fact that the strongly polar surface regions avoid to make contacts with HC as the reason for the entropy loss of HC solution in water, only using a slightly different picture.

Table 1 shows the experimental heat capacities of solution and the results of COSMO-RS, which are derived by numerical differentiation of ΔH_{HC} with respect to T. The calculated heat capacities are in general about a factor 2 smaller than those reported by Tsonopoulos. Dividing the calculated values of ΔH_{HC} by the calculated heat capacities leads to extrapolated solubility minima for HC in water. These are also shown in Table 1. They are almost independent of CN, with the exception of alkylbenzene, where a clear CN trend is apparent. All calculated values of T_{min} are in the range of 247 K to 263 K. They are in average about 40K lower than the observed solubility minima.

Figure 4 shows the calculated temperature dependencies of the solubility of HC in water for benzene (fig. 4a), cyclohexane (4b) and 1-hexene (fig 4c). The calculated lines have been shifted in order to allow a better comparison of the curves. Above room temperature the temperature dependency is reasonably well reproduced by COSMO-RS, but below 298 K the calculated and experimental curves considerably disagree due to the lower temperature minimum predicted by COSMO-RS.

4. Prediction of water solubility in hydrocarbons

Figure 5 gives a comparison of the calculated values of the free Gibbs energy of solution of water in HC (ΔG_W) with the analytic functions, which Tsonopoulos proposed as reasonable fit of the experimental data.

Table 2 shows a comparison of experimental and calculated values of the solvation enthalpies of water in HC. For alkanes and alkylbenzenes the calculated data are in excellent agreement with the experimental values, while for alkenes ΔG_W is underestimated by about 1kJ/mol and for alkylcyclohexanes it is underestimated by 0.5 kJ/mol. In all cases the slope and even the curvature of ΔG_W is in good agreement with experiment. Tsonopoulos reports a single value for each class of HC, which is independent of CN. The calculated solvation enthalpies are about 10% - 20% higher than the experimental results. While they are almost independent of CN for alkanes and alkylcyclohexanes, we find a significant increase of ΔH_W with increasing CN for alkylbenzenes

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and alkenes. This increase appears to be physically very plausible, because the alkylbenzene and alkene solvents become more and more similar to alkane in the limit of large CN. Hence we would expect that the ΔH_W also increases towards the value of alkanes in this limit. From this consideration the constant values reported in ref. 2 appear somewhat questionable.

Despite the small deviations between calculated and experimental data, it is most important to note that COSMO-RS correctly reproduces the unusual fact that for water in HC ΔH_W is about twice as large as ΔG_W. This implies that there is a large negative entropic contribution $T\Delta S_W$ to ΔG_W that compensates half of the large positive solvation enthalpy. The physical origin of this entropy is obvious. When a water molecule is transferred from the strongly restrictive hydrogen bond network of water into the almost isotropic environment of n-alkanes, it has to pay a lot of the favorable interaction energy in water, but it gains a considerable amount of entropy from the loss of the orientation constraints. In the picture of COSMO-RS this means that water in water can arrange very favorable pairings of surfaces of almost complementary strong polarity and thus it can gain a lot of interaction enthalpy, while water in n-alkanes faces a large amount of almost non-polar surface, causing a big loss of enthalpy but releasing almost any pairing constraints, because all pairings are equally unfavorable. Thus we conclude that COSMO-RS well captures the unusual physics of water solubility in HC as it did for the opposite situation of HC in water.

Since the heat capacities reported by Tsonopoulos have a considerable uncertainty, we compare the full temperature dependence of the water solubility in HC for four examples in figures 6 a-d. In general the slope of the experimental curves (full lines) is well reproduced by COSMO-RS (dashed curves) up to about 473 K. At higher temperatures the COSMO-RS results show a stronger curvature than experimentally observed. The larger errors at temperatures above 473 K may be due to the increasing importance of density changes by the appearance of vacancies at high temperatures, which are presently not taken into account in the COSMO-RS model.

5. Conclusions and Outlook

The mutual solubilities of HC and water calculated by the quantum chemically based *a priori* prediction method COSMO-RS have been systematically compared with experimental data carefully collected by Tsonopoulos. In general a good qualitative and quantitative agreement has been found in absolute values as well as regarding the dependence on CN and temperature.

Some differences have been observed in the temperature dependencies of HC solubility in water below 298 K and of water solubility in HC above 473 K. The former may be overcome by improvements of the hydrogen bond temperature dependence in future COSMO-RS parameterizations, while the latter may be addressed to the neglect of vacancy effects in the present formulation of the COSMO-RS model. The small errors in the CN dependence of the n-alkane and n-alkene solubilities in water (see fig. 1) probably can be addressed to a favorable arrangement of pure chain liquids, which is presently not taken into account in COSMO-RS. A concept for inclusion of such shape effects is available and will be implemented soon. Thus there is a chance for further improvement in this regard, too.

The most important finding of the comparison given in this article is that COSMO-RS is able to correctly describe the unusual physics of the mutual solubilities of HC and water. The solvation of HC in water goes along with an extreme loss of entropy, so that the almost the entire large solvation Gibbs energy of HC in water is of entropic nature at 298K, leading to a solubility minimum. COSMO-RS correctly predicts such unusual minimum, even though at slightly low temperatures. The entropy loss, which is usually addressed to a special arrangement of water molecules around non-polar surface, in COSMO-RS is caused by the fact, that only the very few less polar surface segments of water molecules can make energetically acceptable pairs with non-polar HC surface. Conversely, the solvation of water in HC goes along with a large entropy gain that compensates half of the large enthalpy loss of a water molecule which is transferred from water to the non-polar environment of HC. COSMO-RS gives a good description of this effect too, because the highly polar surface segments of water make very specific selections of favorable partners in water, while they are facing a large amount of equally unfavorable non-polar surface in HC. The ability of COSMO-RS to predict both converse effects demonstrates that the underlying model of pair-wise interacting surface segments gives a different, but surprisingly equivalent description of the physics of molecular arrangements in liquids than the usual picture of three dimensionally coordinated molecules in space, as it is used in Monte Carlo or molecular dynamics simulations.

6. List of symbols

HC	hydrocarbon
CN	carbon number
ΔG_{HC}	Gibbs energy of solvation of HC in water
ΔG_w	Gibbs energy of solvation of water in HC

ΔH_{HC} enthalpy of solvation of HC in water

ΔH_w enthalpy of solvation of water in HC

ΔS_{HC} entropy of solvation of HC in water

ΔS_w entropy of solvation of water in HC

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Appendix A: Details of COSMO-RS parameterization

For the calculation presented in this paper the COSMOtherm program has been used. The a parameterization BP-TZVP-C1.2-01.02 was used. For the results of the present paper the following numerical parameter values are relevant:

α' = misfit energy constant including average polarizability correction = 6614 kJ/mol $Å^2$

f_{corr} = correlation correction factor in misfit energy constant = 2.79

σ_{HB} = threshold for hydrogen bonding = 0.0083 e/$Å^2$

c_{HB} = coefficient for hydrogen bonding = 31516 kJ/mol $Å^2$

a_{eff} = effective contact size = 6.12 Å

As mentioned above, a scaling factor of 0.62 was used for all surface segments of water molecules.

Starting with Version C1.2, the COSMO*therm* program includes a new generic expression for the combinatorial contribution to the chemical potential. The new combinatorial contribution $\mu^{Xi}_{C,S}$ results from the derivation of the combinatorial free energy expression $G_{C,S}$:

$$G_{C,S} = \lambda_0 \sum_i x_i \ln r_i - \lambda_1 \ln\left[\sum_i x_i r_i\right] - \lambda_2 \ln\left[\sum_i x_i q_i\right] \tag{A1}$$

where the volume parameters r_i and the surface parameters q_i are taken from the taken the COSMO cavities.

The corresponding parameters are $\lambda_0 = 0.096$, $\lambda_0 = 0.22$, and $\lambda_2 = -0.004$.

The COSMO radii used are $R_H = 1.3$ Å, , $R_C = 1.72$ Å, and $R_O = 1.72$ Å.

All other parameters are not relevant, because no gas phase properties are calculated in this article.

Figure Captions

Figure 1: σ-profiles of water and C_6-hydrocarbons

Fig. 2: Experimental (full lines) and calculated (dashed lines) free energies of solution of HC in water (298 K).

Fig. 3: Experimental (full lines) and calculated (dashed lines) enthalpies of solution of HC in water (298 K).

Figure 4: Comparison of calculated (solid) and experimental HC solubility in water as a function of temperature. The dashed lines show two fits of experimental data according to Tsonopoulos [1,2]. COSMO-RS values are shifted for better comparability.

Figure 5: Comparison of calculated and experimental water solubility in HC (298 K) as a function of CN

Figure 6: Comparison of calculated (dashed) and experimental water solubility in hydrocarbons as a function of temperature: a) n-decane; b) butylbenzene; c) butylcyclohexane; d) 1-decene. The full lines show fits of experimental data according to Tsonopoulos [1,2].

Table Captions

Table 1: Calculated heat capacities of solution and extrapolated temperatures of solubility minimum

Table 2: Experimental [1,2] and calculated solvation enthalpies for water in HC at T = 298 K
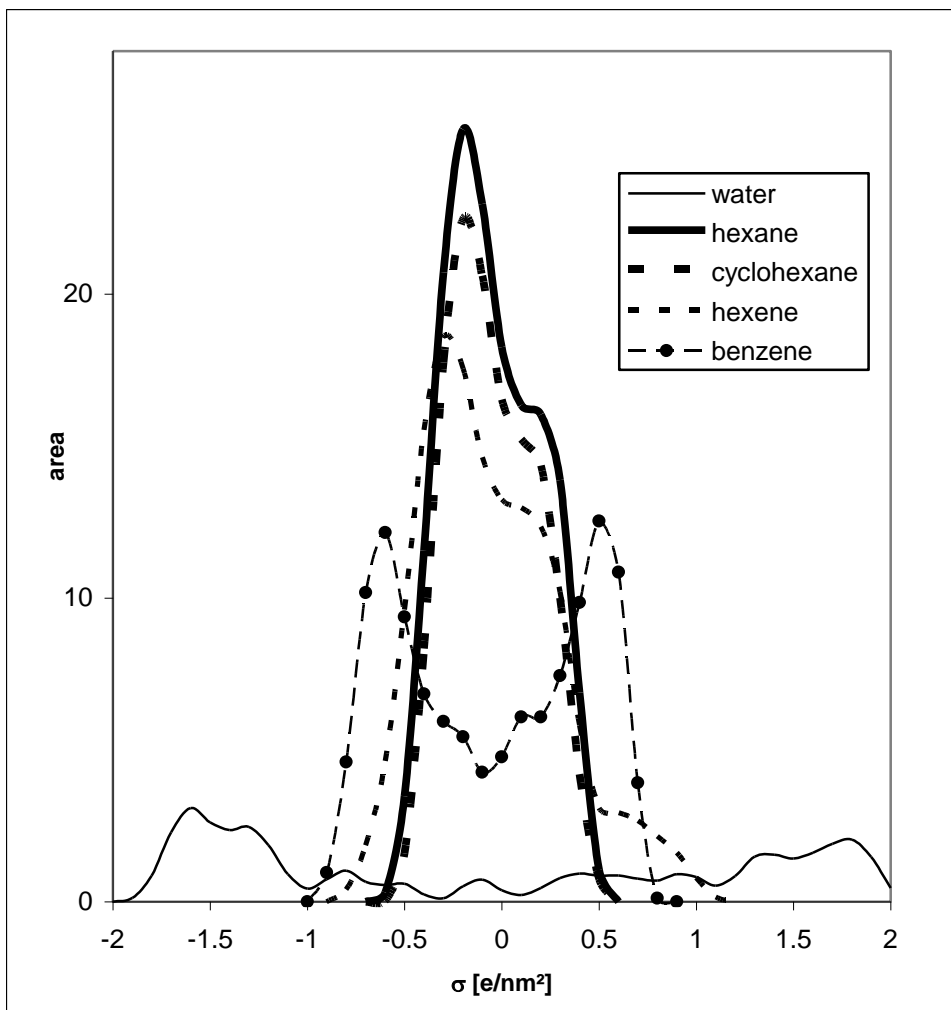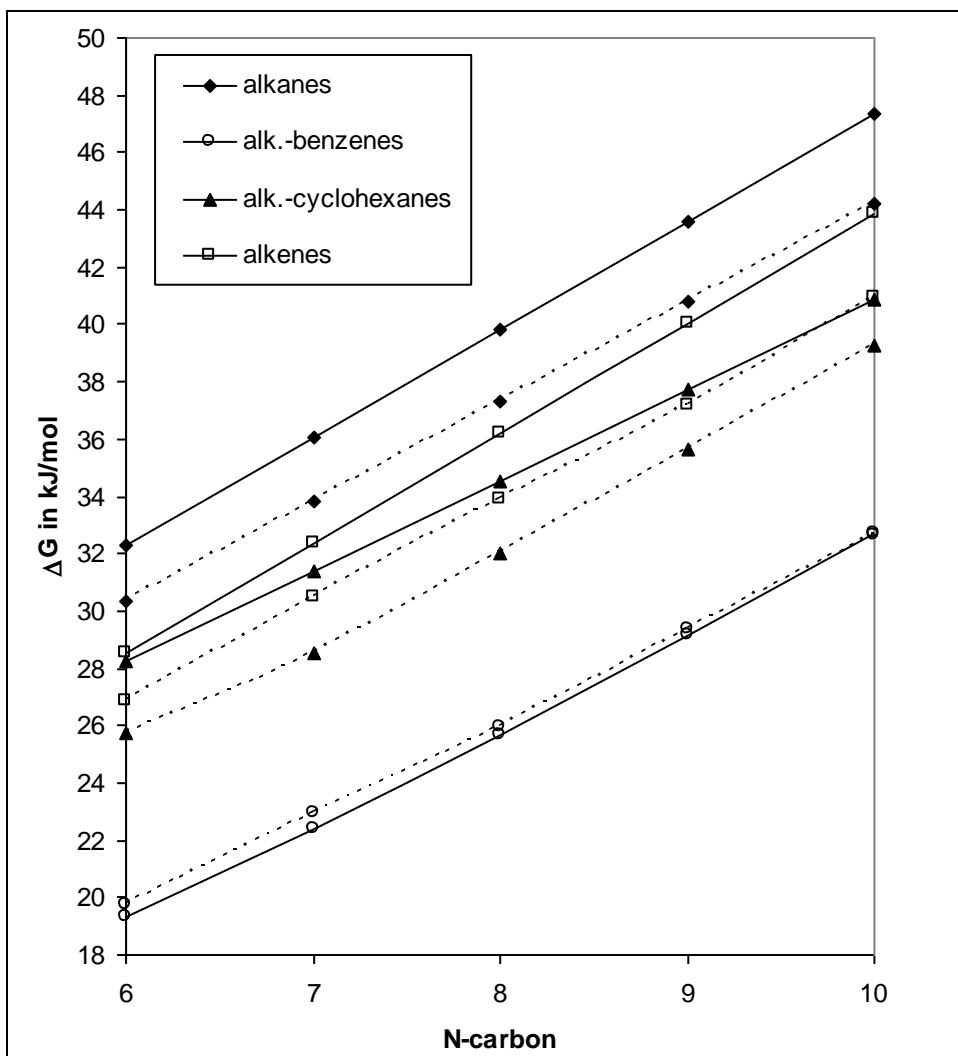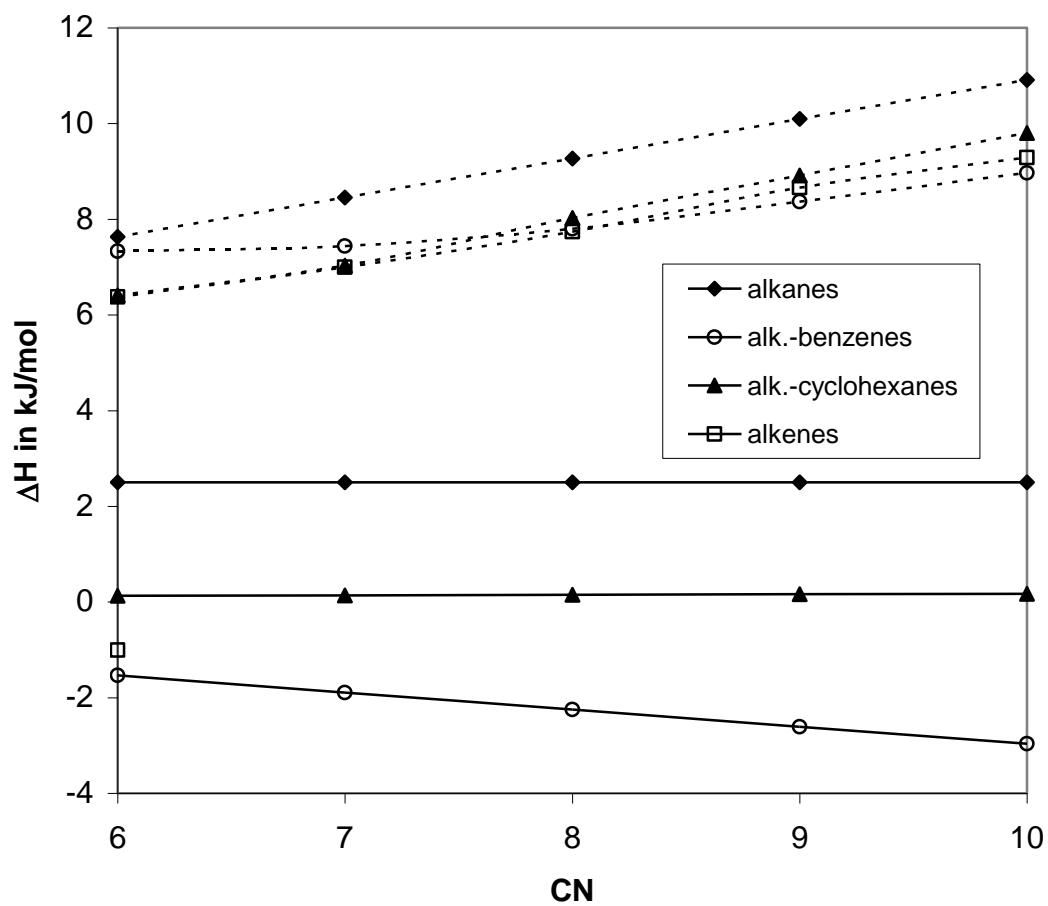
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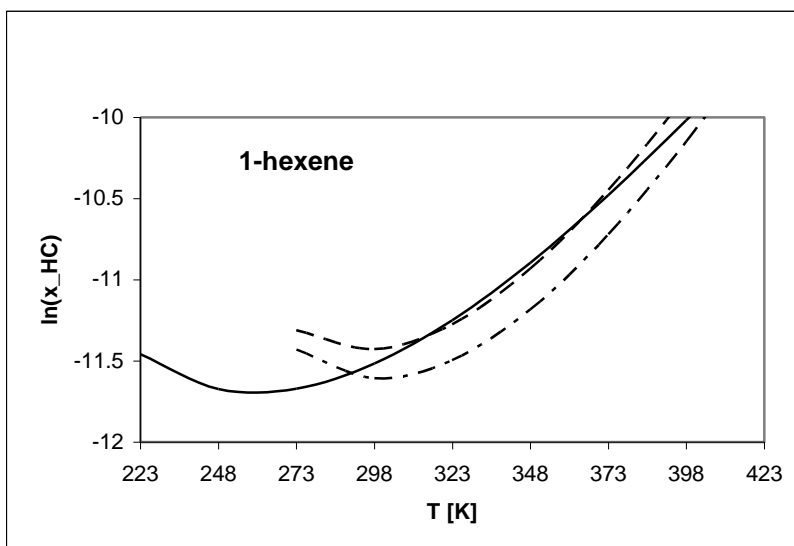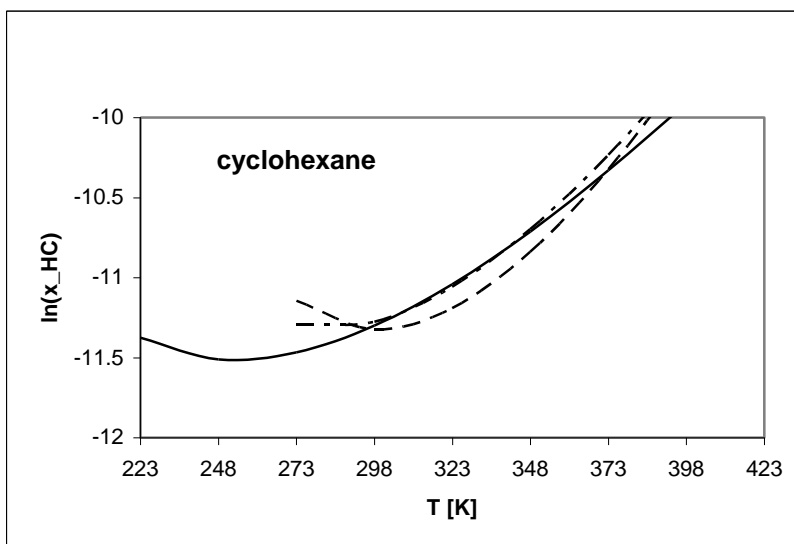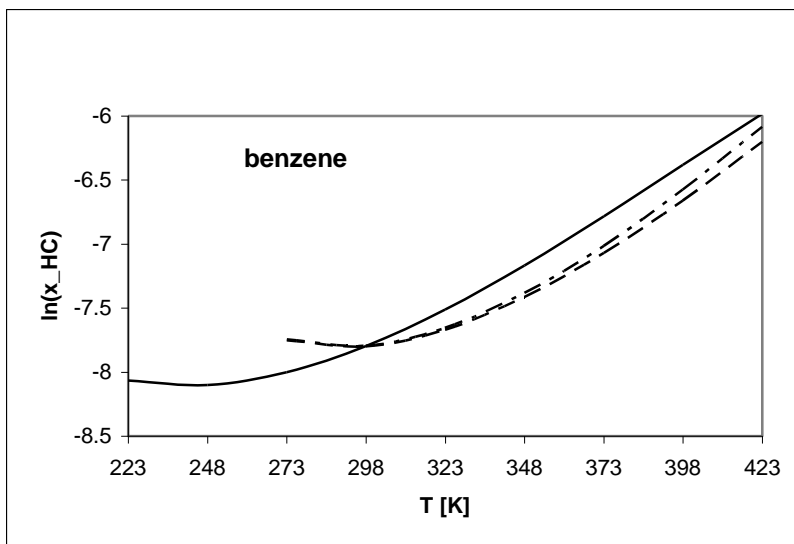
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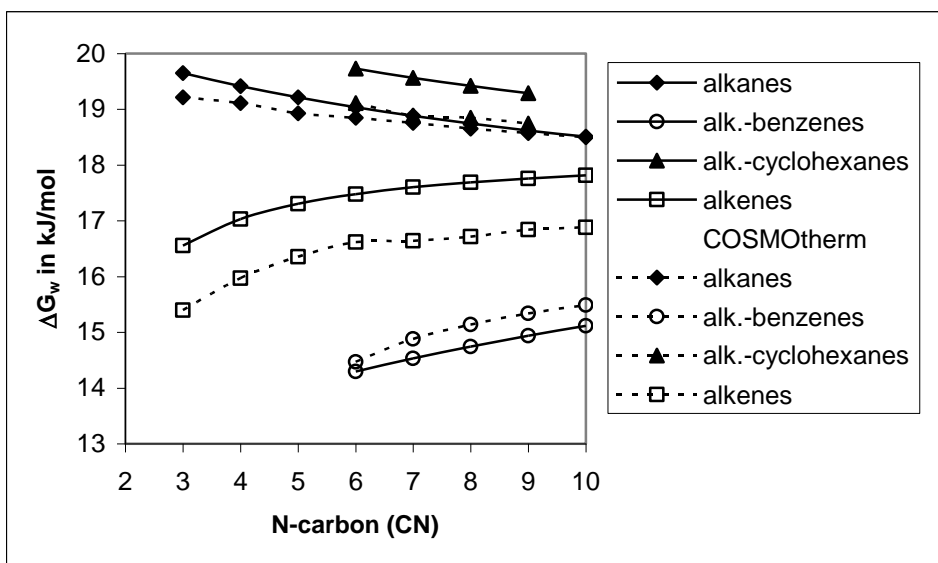
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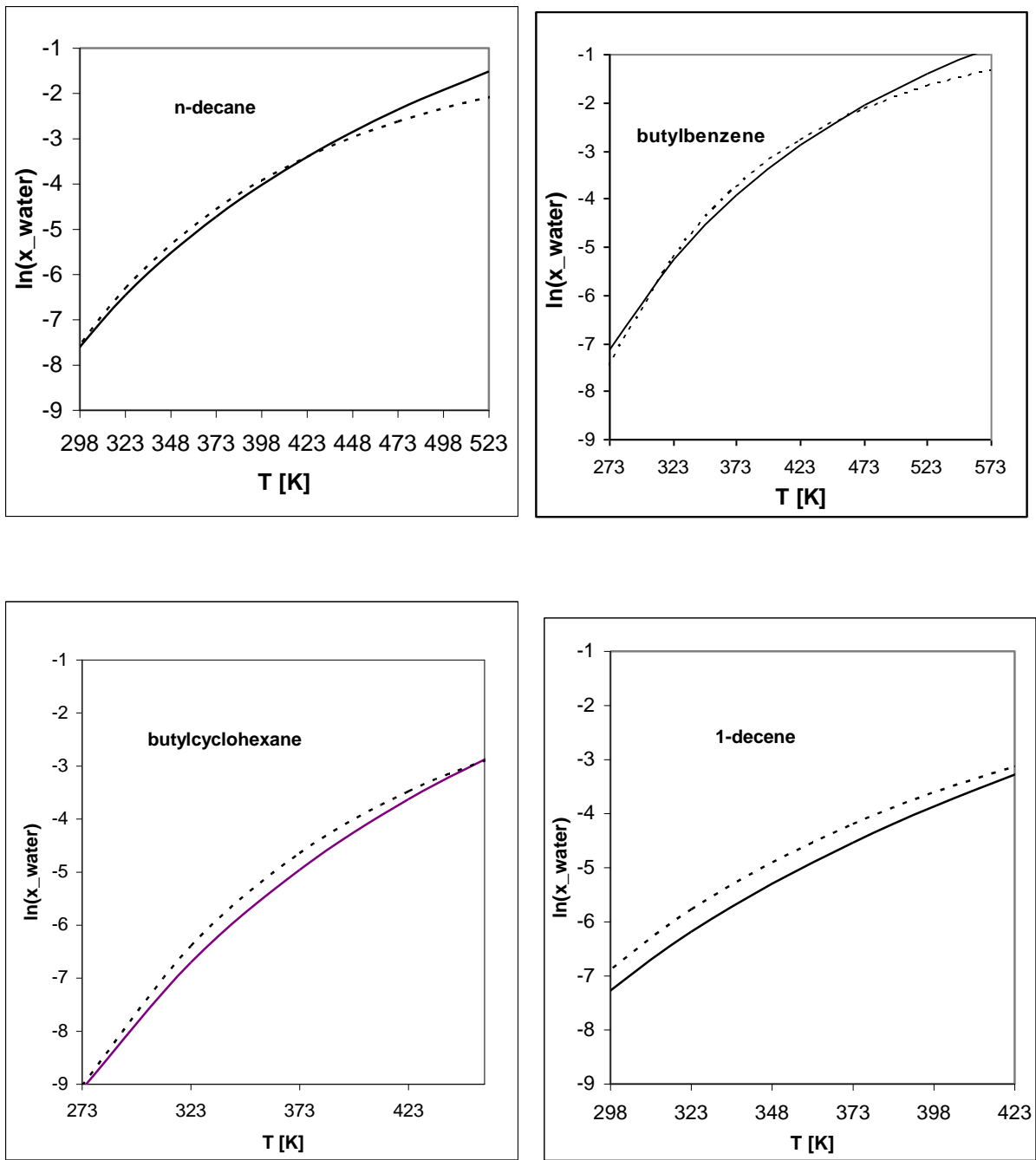
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	heat capacities of solution [kJ/mol/K]				min. solubility temperatures [K]			
		alkyl-	alkylcyclo-			alkyl-	alkylcyclo-	
CN	alkanes	benzenes	hexanes	alkenes	alkanes	benzenes	hexanes	alkenes
6	0.178	0.143	0.149	0.175	255.2	247.0	255.0	261.7
7	0.201	0.166	0.169	0.201	256.1	253.4	256.6	263.4
8	0.224	0.188	0.191	0.225	256.8	256.7	256.0	263.7
9	0.247	0.212	0.214	0.245	257.3	258.7	256.6	262.8
10	0.270	0.236	0.238	0.271	257.8	260.1	256.4	263.8

Table 1: calculated heat capacities of solution and extrapolated temperatures of solubility minimum

CN	alkanes	alkyl-benzenes	alkylcyclo-hexanes	alkenes
ΔH [kJ/mol] exp.				
all CN	34.000	24.000	34.000	31.000
ΔH [kJ/mol] calc.				
3	38.198			30.038
4	38.356			31.713
5	38.211			32.268
6	38.347	30.890		33.012
7	38.371	31.502	38.666	33.249
8	38.363	31.934	38.466	33.554
9	38.378	32.330	38.581	33.957
10	38.380	32.658	38.575	34.132

Table 2: Experimental [1,2] and calculated solvation enthalpies for water in HC at T = 298 K