Use of COSMO-RS for the Prediction of Adsorption Equilibria

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The novel method COSMO-RS for the calculation of thermodynamic partition equilibria based on quantum chemical calculations is applied for the first time to the correlation and prediction of adsorption equilibria. In the limit of small adsorbate concentrations, very good predictions have been achieved for adsorption equilibria of activated carbon for both the phase and the aqueous phase.

Introduction

In past years, the adsorption from the liquid phase has gained increasingly in importance. Knowledge of the adsorption equilibria is necessary for the sizing of adsorption plants, as, for example, for wastewater treatment (Sontheimer et al., 1985) or for the adsorptive removal of trace components from liquids (such as water from tetrahydrofuran (THF)). Preferentially used adsorbents are activated carbon and carbon blacks, because they are cheap and have a relatively high sorption capacity. However, the adsorption is also an important step in many applications like the crystallization, the heterogeneous catalysis, the stabilization of nanoparticles, and of redispersible agglomerates. Therefore, the elucidation of this adsorption step enables a better explanation of the processes specified above. As experimental studies of adsorption behavior are very expensive and time-consuming, predicting adsorption equilibria is tried only by the physical properties of adsorbate, adsorbent and solvent. Presently, interactions between fluid molecules can be calculated, however, due to the complex structure of solid surfaces, this is not possible to characterize them.

With the increasing performance of computers, in recent years a new strategy for the prediction of thermophysical data has emerged: For molecules in the gas-phase quantum, chemical methods, especially density functional methods (DFT), have become a reliable and efficient tool for the calculation of the molecular properties. If combined with dielectric continuum solvation methods (for reviews, see Cramer et al. (1995) and Tomasi and Persico (1994)), these methods can be used as well for the calculation of free energies and other properties of molecules in solvents. The conductor-like screening model (COSMO) presented by Klamt et al. (1993) is a highly efficient variant of these continuum solvation methods. Klamt (1995) generalized the concept of COSMO to a more realistic treatment of solvents (COSMO-RS) by a combination of molecular surface interaction energies derived from COSMO with efficient and accurate statistical thermodynamics (Klamt, 1995). Thus, COSMO-RS for the first time allows predictive calculation of vapor pressures, activity coefficients, and phase equilibria based on quantum chemical calculations. The only information that is needed for the calculation is the molecular structure of the concerned components. Basically, these calculations are suited for pure and mixed fluids of known composition, but they have been successfully applied to polymers as well. Thermophysical data of systems including fluids of chemically less well defined composition like blood, or including heterogeneous solids of unknown surface composition like the industrially used adsorbates, cannot be directly calculated. Nevertheless, there is an indirect way to treat such systems by COSMO-RS. The scope of this article is to demonstrate how COSMO-RS can be used for the prediction of solid-liquid and solid-gas equilibria involving adsorbates.

Conductor-Like Screening Model for Real Solvents

COSMO-RS is a novel theory combining the concepts of quantum theory, dielectric continuum models, surface interactions, and statistical thermodynamics. Since a full derivation of the theory of COSMO-RS is beyond the scope of this article, a short summary of the essentials will be given here. For details refer to Klamt et al. (1998) and Klamt and Eckert (2000).

COSMO-RS considers a liquid system as an ensemble of molecules of different kinds, including solvent and solute. For

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each kind of molecules X, a density functional (DFT) COSMO calculation is performed in order to get the total energy E^X_{COSMO} and the polarization (or screening) charge density (SCD) σ on its molecular surface. σ is an extremely good and local descriptor of molecular surface polarity.

For the purpose of an efficient statistical thermodynamics calculation, the liquid ensemble of molecules is now considered as an ensemble of pair-wise interacting molecular surfaces. The most important parts of the specific interaction between molecular surfaces (electrostatics (es) and hydrogen bonding (hb)) are expressed by the SCDs σ and σ' of the contacting surface pieces (Klamt et al., 1998)

$$E_{es}(\sigma,\sigma') = \frac{\alpha'}{2}(\sigma + \sigma')^2 \tag{1}$$

and

$$E_{hb}(\sigma,\sigma') = c_{hb}\min\{0,\sigma\sigma' + \sigma_{hb}^2\} \tag{2}$$

The three parameters α', c_{hb}, and σ_{hb} have been adjusted to a large number of thermodynamic data. Since all relevant interactions depend on σ, the distribution functions (histograms) $p^x(\sigma)$ are required for the statistical thermodynamics. Hydrogen bonding corresponds to a molecular surface contact of a very strongly positive polar surface region (donor) and a very strongly negative polar surface (acceptor). The extra hydrogen bonding energy (which goes beyond the electrostatic contribution that is included in the continuum solvation and the electrostatic misfit) arises from the penetration of the donor into the acceptor. This energy gain only happens if both partners are strongly polar and of opposite sign, that is, if the product of σ and σ' is more negative than a certain threshold σ_{hb}^2. This empirical functional reflects the fact that the stronger the hydrogen bonds, the more polar the two partners are (Klamt, 1998).

These "σ-profiles" can be easily derived from the COSMO output. Note that the σ-profiles provide a vivid picture of the molecular polarity (see Figure 1, Klamt (1995) and Klamt et al. (1998)). Furthermore, we need the σ-profile $p_S(\sigma)$ of the ensemble S. For multicomponent systems $p_S(\sigma)$ is simply calculated as a sum of the molecular σ-profiles of the concerned components X_i weighted by the mol-fractions x_i

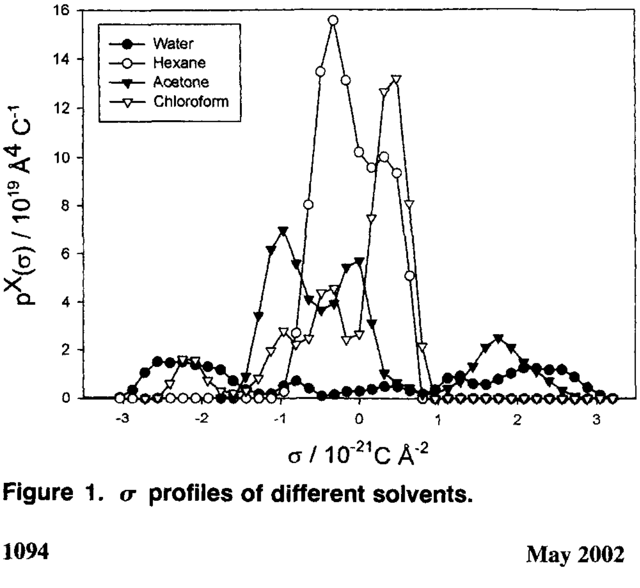

Figure 1. σ **profiles of different solvents.**

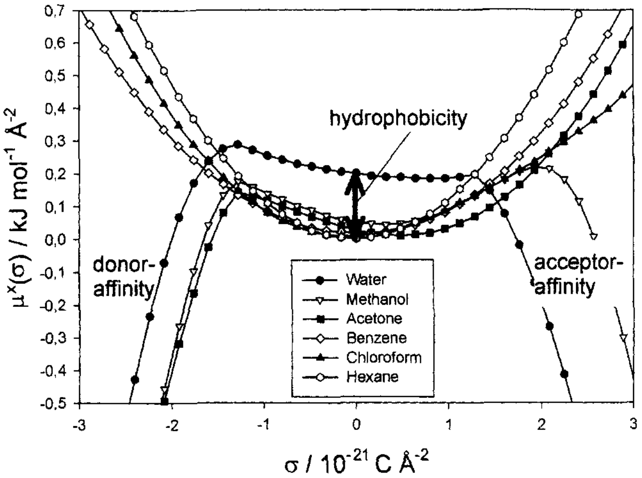

Figure 2. σ **potentials of solvents.**

$$p_S(\sigma) = \frac{\sum_i x_i p^{X_i}(\sigma)}{\sum_i x_i} \tag{3}$$

Now, the chemical potentials of the compounds in the solvent are calculated by a novel, exact, and very efficient statistical thermodynamics procedure. The first step is the iterative solution of the equation

$$\mu_S(\sigma) = -\frac{\mathrm{RT}}{a_{\mathrm{eff}}}\ln\left\{\int p_S(\sigma')\exp\left(\frac{a_{\mathrm{eff}}}{\mathrm{RT}}\left[\mu_S(\sigma') - E(\sigma,\sigma')\right]\right)d\sigma'\right\} \tag{4}$$

This implicit equation, in which a_{eff} denotes an effectively independent piece of molecular area, can be solved by iteration within milliseconds on a PC. It yields the function $\mu_S(\sigma)$ (σ-potential) which tells how much the solvent S likes the surface of polarity σ. This is a very characteristic function for each solvent. We call it the σ-potential of solvent S. Examples are given in Figure 2.

These σ-potentials describe the solvent behavior regarding electrostatics, HB-affinity, and hydrophobicity. The σ-potential is integrated in a second step over the surface of each compound X, yielding the chemical potential of X in S

$$\mu_S^X = \int p^X(\sigma)\mu_S d\sigma + \mu^X_{\mathrm{comb},\,S} \tag{5}$$

In this equation, the surface integral is evaluated as an σ-integral, making use of the σ-profile of the solute X. The combinatorial contribution $\mu^X_{\mathrm{comb},\,S}$ to μ takes into account size and shape effects of solute and solvent (Klamt and Eckert, 2000). Usually, it is small compared to the first term in Eq. 4

which results from the surface interactions. It is sufficient to consider it as a solvent specific constant, here.

As a result of this series of relatively simple steps, starting from a quantum chemical calculation for each compound, we found an expression for the chemical potential of an almost arbitrary chemical compound X in an almost arbitrary solvent S, which may be a pure compound or a mixture. This allows us to calculate any partition coefficient, as well as solubility. Based on density functional COSMO calculations, the few parameters required in COSMO-RS have been fitted to a large set of experimental data (Klamt et al., 1998), covering 215 diverse chemical compounds and the properties ΔG_{hydr}, $\log P_{\text{vapor}}$, and the aqueous partition coefficients with octanol, hexane, benzene, and ether. Note, the properties ΔG_{hydr} and $\log P_{\text{vapor}}$ involve the gas phase, which requires a small addendum to the steps given above that is not of interest here. However, since the logarithmic aqueous solubility is the difference of $\Delta G_{\text{hydr}}/RT$ and $\ln P_{\text{vapor}}$, aqueous solubility was implicitly taken into account in the parameterization of COSMO-RS. The initial COSMO-RS parameterization yielded a rms-error of 0.3 log-units for the diverse partition and solubility properties of small and medium sized molecules. The error has been reduced in recent parameterizations to about 0.23 log-units.

Extension of COSMO-RS to Complex Solutions and Adsorbates

As shown in the previous section, COSMO-RS is a reliable method for the *a priori* prediction of thermophysical data and phase equilibria of pure fluids and liquid mixtures of well-defined composition. Nevertheless, there are several thermodynamic equilibria of industrial importance which involve one or more phases, which are either chemically less defined or are disordered, but are not really liquid, or both. Examples of such systems are physiological phases like blood, brain, or special tissue (Klamt et al. 2001a,c) structurally sophisticated polymers, and solid adsorbents, like soil (Klamt, 2001b) or activated carbon. Since no surface composition function $p_S(\sigma)$ is available in such phases, the σ-potential $\mu_S(\sigma)$ of the phase S and the chemical potentials $\mu_S{}^X$ of solutes X in these phases cannot be directly calculated by COSMO-RS. However, an indirect treatment of such phases by COSMO-RS is enabled by the following extension:

Consideration of a large number of different solvents led to the finding (see as well Figure 2) that σ-potentials can be described very well by a Taylor-like of the form

$$\mu_S(\sigma) \cong \sum_{i=-2}^{m} c_S^i f_i(\sigma) \tag{6}$$

with

$$f_i(\sigma) = \sigma^i \quad \text{for} \quad i \geq 0 \tag{7}$$

and

$$f_{-2/-1}(\sigma) = f_{\text{acc/don}}(\sigma) \cong \begin{cases} 0 & \text{if } \pm\sigma < \sigma_{hb} \\ \mp\sigma + \sigma_{hb} & \text{if } \pm\sigma > \sigma_{hb} \end{cases} \tag{8}$$

The highest order of the polynomial contributions (Eq. 7) required for a sufficient description of σ-potentials typically is $m = 3$. The hydrogen bonding contributions expressed by Eq. 8 are necessary to describe the acceptor and donor behavior of solvent. As can be seen in Figure 2, this behavior corresponds to a linear descent in the σ-potentials starting from some threshold σ_{hb}. The functions $f_{\text{acc}}(\sigma)$ and $f_{\text{don}}(\sigma)$ are well capable of describing just these features of the σ-potentials. Using this Taylor expansion, we may characterize each solvent (at fixed temperature, usually room temperature) by the set of σ-coefficients c_S^i. Obviously, any difference between the σ-potentials of two solvents is of the same kind of expansion, with coefficients $c_{S,S'}^i$ being just the difference of the coefficients of the two solvents. Partition coefficients are connected with the pseudo-chemical potentials by the equation

$$kT \ln K_{S,S'}^X = \left[\mu_{S'}^X - \mu_S^X \right] \tag{9}$$

If the σ-potential of the solvents and the σ-profile of the solute are known, the pseudo chemical potentials μ_S^X and $\mu_{S'}^X$ of the component X in the solutes S and S' can be calculated with Eq. 5. Using Eq. 6 for $\mu_S(\sigma)$, we thus find that any partition coefficient between two solvents S and S' should be expressible in the form

$$\begin{aligned} \ln K_{S,S'}^X &= \frac{1}{kT}\left[c_{S,S'} + \int p^X(\sigma)(\mu_{S'}(\sigma) + \mu_S(\sigma))\,d\sigma \right] \\ &\cong \tilde{c}_{S,S'} + \int p^X(\sigma) \sum_{i=-2}^{m} \tilde{c}_{S,S'}^i f_i(\sigma)\,d\sigma = \tilde{c}_{S,S'}^i M_i^X \end{aligned} \tag{10}$$

where the combinatorial contributions have been subsumed in $\tilde{c}_{S,S'}$ and the σ-moments M_i^X of the solute X are defined by

$$M_i^X = \int p^X(\sigma) f_i(\sigma)\,d\sigma \tag{11}$$

Thus, with Eqs. 6 and 10, the σ-potentials of any solvent (or solid) can be approximately calculated by using the linear regression of the partition coefficients of different solutes with their σ-moments. Equation 11 implies that any logarithmic partition coefficient can be represented as a linear combination of σ-moments. As a consequence, the set of σ-moments M_i^X, $i = 0,2,3$, complemented by the hydrogen bond moments M_{acc}^X $(= M_{-2}^X)$ and M_{don}^X $(= M_{-1}^X)$ should be a very good and almost complete set of molecular descriptors for a linear regression analysis of any partition problem. Note that the first moment M_1^X usually is of no importance, because it is just the negative of the total charge of the molecule. Hence, for neutral compounds M_1^X trivially vanishes. By definition of the σ-profiles, the zero-th moment M_0^X is identical with the molecular surface. The second moment is an excellent measure of the overall polarity of the solute, and the third moment is a measure of the asymmetry of the sigma profile. The hydrogen bond moments are quantitative measure of the acceptor and donor capacities of the compound X, respectively.

Application to adsorption equilibria

In the first step, we just consider adsorption from dilute aqueous solutions because in the very low concentration range one can assume the interactions between the adsorbed molecules are very small due to their spatial distance, and the change of composite sigma profiles can be neglected. On heterogeneous adsorbents like activated carbon with energetically different adsorption sites, the energetically higher sites will first be occupied and with increasing concentration, and the energetically lower sites will be used step by step. Thus, a curved shape of the isotherm is expected. Nevertheless—in the scope of precision—in the very low concentration range, a linear increase of the adsorbed amount n^X with increasing concentration c^X can be detected (see Figure 3)

$$n^X = H^X \cdot c^X \tag{12}$$

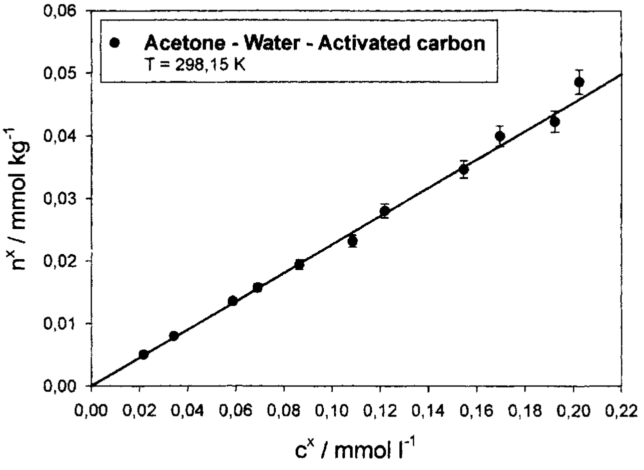

Figure 3. Adsorption isotherm of acetone from aqueous solution on activated carbon.

$T = 298.15$ K; assumed standard error = 10%.

Thus, the adsorption can be described with one parameter H^X. Analogous to the adsorption from gaseous phase, this parameter is sometimes called averaged Henry's Law coefficient.

With

$$\mu_{S1}^X = \mu_0^X + kT \ln \gamma_{S1}^X \tag{13}$$

$$\mu_{S2}^X = \mu_0^X + kT \ln \gamma_{S2}^X \tag{14}$$

and

$$\frac{X_{S1}^X}{X_{S2}^X} = \frac{\gamma_{S2}^X}{\gamma_{S1}^X} \tag{15}$$

the equation for the calculation of H^X follows

$$H^X = \frac{n^X}{c^X} = \frac{\tilde{M}_{S1}\,\rho_{S1}}{\tilde{M}_{S2}} \frac{X_{S2}^X}{X_{S1}^X} = \frac{\tilde{M}_{S1}\,\rho_{S1}}{\tilde{M}_{S2}} \frac{\gamma_{S1}^X}{\gamma_{S2}^X}$$

$$= \frac{\tilde{M}_{S1}\,\rho_{S1}}{\tilde{M}_{S2}} \exp\left(\frac{\mu_{S1}^{X_i} - \mu_{S2}^{X_i}}{kT} \right) \tag{16}$$

γ_{S1}^X and γ_{S2}^X are the activity coefficients, $\tilde{M}_{S1}$ and $\tilde{M}_{S2}$ are the molecular masses of the solvent and the adsorbent, and ρ_{S1} is the density of the solvent. Thus, besides the previously mentioned molecular parameters, only the charge frequency distributions from solvent, adsorbent, and adsorptive $p^{S1}(\sigma)$, $p^{S2}(\sigma)$, and $p^X(\sigma)$ are necessary for the prediction of H^X.

Table 1. Adsorption from Gaseous Phase: Experimental Data ($T = 300$ K, Adsorbent: Activated Carbon) and Sigma Moments of Components X

Adsorptive	$\log \frac{H_i\,(\text{exp.})}{[\text{m}^3/\text{kg}\cdot\text{Pa}]}$	$\log \frac{H_i\,(\text{Th.})}{[\text{m}^3/\text{kg}\cdot\text{Pa}]}$	M_0^X [Å^2]	M_2^X [10^{-38}C^2/Å^4]	M_{acc}^X [10^{-19}C]	M_{don}^X [10^{-19} C]
Acetone	−0.69	−1.23	102.6792	122.98	4.48	0.00
Benzene	0.25	−0.17	123.6773	73.30	0.00	0.00
Carbondioxide	−4.17	−3.98	66.1657	55.89	0.00	0.00
Carbonmonoxide	−5.25	−4.88	57.8705	17.24	0.00	0.00
Dichloromethane	−1.74	−1.66	98.4893	84.33	0.00	0.00
Diethylether	−0.40	0.13	130.349	80.69	4.22	0.00
Ethane	−3.65	−3.70	77.1878	12.01	0.00	0.00
Ethene	−3.56	−3.74	72.2284	40.79	0.00	0.00
Ethylene	−3.82	−3.47	68.6006	93.66	0.00	0.00
H_2S	−3.69	−3.88	62.4876	85.14	0.17	0.15
Hydrogen	−6.43	−6.94	27.3222	5.27	0.00	0.00
Methane	−4.82	−5.07	55.6966	12.22	0.00	0.00
Methanol	−2.17	−2.05	66.3616	137.55	6.77	3.43
Nitrogen	−5.43	−5.11	54.7439	14.22	0.00	0.00
Propane	−2.56	−2.41	97.3749	13.99	0.00	0.00
Propene	−2.43	−2.57	90.3286	43.66	0.00	0.00
Trichloroethene	0.34	0.05	130.9097	47.74	0.00	0.00
Trifluormethane	−3.52	−2.97	80.2262	68.68	0.00	0.00
Water	−1.87	−1.93	43.0598	193.29	9.23	6.18

Standard deviation: *0,377*

Even with the increasing performance of modern computers, it is still not possible to calculate the charge distribution of energetically heterogeneous solid surfaces p^{S2} *a priori*. This is mainly caused by the unknown composition and structure of heterogeneous solids. Therefore, one must characterize the solid with the help of experimental data.

Correlation with the sigma-moments

The infinite dilution adsorption coefficients H^X can be considered as partition coefficients of the adsorbates between the "absorbents phase" and a reference phase. Hence, we expect they can be described by a σ-moment regression, as described in the previous section. In this section we will discuss the use of this COSMO-RS σ-moment approach to two sets of adsorption coefficients, one being for the adsorption from gas phase to activated carbon, and the other for adsorption from water to activated carbon. Most of the experimental data sets, covering 19 and 24 compounds, respectively, have been collected from literature (Baldauf and Zimmer, 1986; Chatzopoulos and Varma, 1993; Urano et al., 1982; Juang et al., 1996; Miyahara and Okazaki, 1992; Radke and Prausnitz, 1972; Sakoda et al., 1986; Fukuchi and Arai, 1989), some of them are data from our own measurements. Experimental and theoretical data are given in Tables 1 and 2. Due to the lack of experimental data, we have included both results from our own measurements as well as results from literature on different active carbon materials. We are aware that activated carbon is heterogeneous due to impurities and different conditioning prior to measurements. Nevertheless, we can show that Henry coefficients both in the gas and in the liquid phase can be predicted surprisingly well by our model. Currently, measurements are carried out with specific activated carbon and other materials which will allow us to distinguish between individual solids and will further improve our predictions. This article introduces the new method and proves its applicability on the basis of the existing experimental data.

As a first step, we calculated the seven σ-moments for each adsorbate, corresponding to $i = -2, \ldots, 4$ in Eqs. 11 and 12 (see Tables 1 and 2). This was done using the program COSMOtherm-3.0 (Klamt, 1998), based on DFT-COSMO calculations from TURBOMOLE (Ahlrichs et al., 1989) using a TZVP-basis set and the BP-functional (Schäfer et al., 2000). Typical calculation times for the small molecules considered in this study are 30 min. on an INTEL-PII-600 MHz computer.

In the case of the adsorption from the gas phase, we first performed a direct σ-moment regression, yielding the equation

$$\log\left(H^X_{\text{gas}}\right) = -8.6658 + 0.0629 \cdot M_0^X + 0.00876 \cdot M_2^X + 0.372 \cdot M^X_{\text{don}} \quad (17)$$

It turned out the third and higher moments, as well as the acceptor moment were not significant. The results are shown in Figure 4.

In the case of wet adsorption from water to AC we had experimental data for a broader range of compounds available. In a first σ-moment regression pyridine was clearly detected as an outlier. We therefore left it out in the final regression, yielding

Table 2. Adsorption from Aqueous Phase: Experimental Data (T = 300 K, Adsorbent: Activated Carbon) and Sigma Moments of Components X

Adsorptive	$\log \frac{H_i(\text{exp.})}{\text{m}^3/\text{kg}}$	$\log \frac{H_i(\text{Th.})}{\text{m}^3/\text{kg}}$	M_0^X [Å^2]	M_2^X [10^{-38} C^2/Å^4]	M^X_{acc} [10^{-19} C]	M^X_{don} [10^{-19} C]
Acetic Acid	−0.65	−1.11	92.26	184.80	3.16	6.14
Aniline	0.87	0.69	134.93	164.13	1.91	1.79
Benzoic Acid	0.96	1.56	152.86	195.94	2.18	6.42
1-Butanol	0.87	0.30	128.36	136.05	6.44	2.95
Butanone	0.22	0.17	120.65	118.29	4.45	0.00
Butyric Acid	0.69	0.68	130.91	178.99	3.03	5.94
o-Cresole	2.17	2.12	148.66	159.87	0.88	5.56
p-Cresole	2.17	2.03	149.96	164.11	1.33	5.61
Cis-1,2-Dichloroethene	1.74	1.44	111.66	68.97	0.00	0.00
Ethanol	−1.82	−1.49	88.27	134.79	6.70	2.92
Methanol	−2.78	−2.42	67.56	136.54	6.83	3.11
Nitrobenzene	1.39	1.85	149.38	134.69	0.38	0.00
1-Octanol	3.91	3.80	208.71	141.85	5.99	3.03
Phenol	1.74	1.26	131.12	165.18	1.11	5.83
1-Propanol	−0.74	−0.56	108.34	134.43	6.46	2.95
2-Propanol	−0.74	−0.75	106.44	131.99	6.70	2.24
Propanone	−0.30	−0.70	102.68	122.98	4.47	0.00
Propionic Acid	−0.65	−0.21	110.82	179.07	3.11	5.96
Propionitrile	−0.39	−0.27	102.28	120.93	2.10	0.00
Pyridine	−0.10	−0.19	116.98	120.21	5.43	0.00
Tetrachloroethene	3.47	3.76	147.45	27.16	0.00	0.00
Toluene	2.61	2.65	140.57	71.77	0.00	0.00
Trichloroethene	2.61	2.66	130.91	47.75	0.00	0.00
Trichloromethane	1.82	1.70	117.53	68.77	0.00	0.00

Standard deviation: 0,347

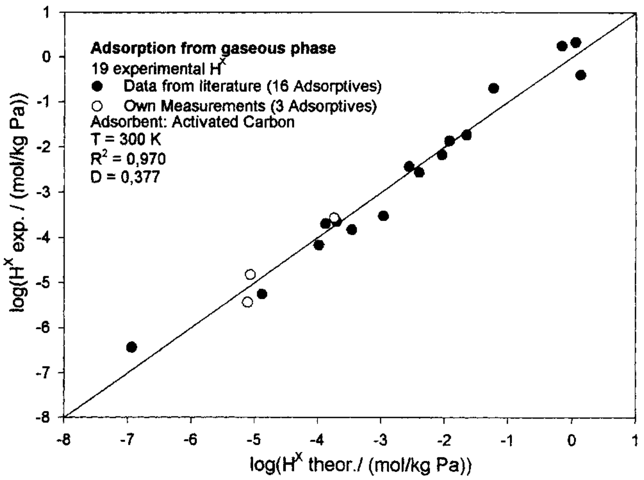

Figure 4. Correlation of adsorption data from gaseous phase with sigma moments.

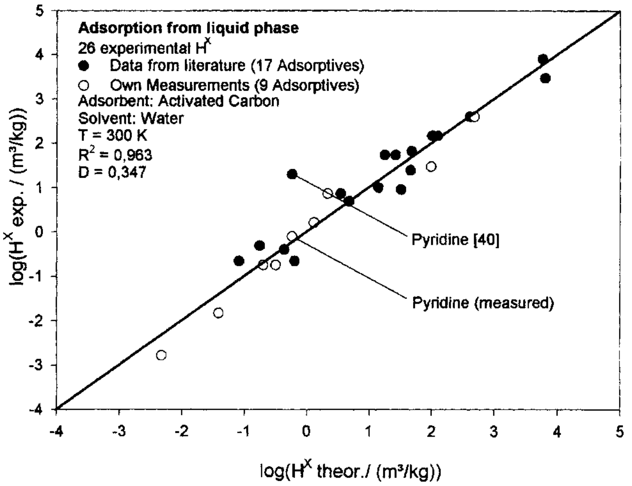

Figure 5. Correlation of adsorption data from aqueous phase with sigma moments.

$$\log\left(H_{\text{water}}^{X}\right) = -2.217 + 0.0438 \cdot M_0^X - 0.0179 \cdot M_2^X - 0.174 \cdot M_{\text{acc}}^X + 0.152 \cdot M_{\text{don}}^X \quad (18)$$

Again, the addition of third and higher moments did not significantly improve the fit. The standard deviation of 0.35 log-units, which correspond to an error of a factor 2.3 for the adsorption constants, is still safely within the experimental error because the data were taken from literature. Also, the experimental conditions (type of activated carbon, pretreatment of the activated carbon, temperature, equilibration time, and so on) of different data vary and the quality of the correlation can be increased by the use of a data basis that is taken with constant experimental conditions. For example, the deviation of pyridine was about 4.3 times the standard deviation, and, thus, an experimental error was highly likely, since pyridine usually is well described by COSMO-RS regarding other properties. Therefore, we did our own measurement on pyridine, yielding to $\log(H^{\text{Pyridine}}) = -0.096$, which corresponds to an error of a factor 0.28 times the standard deviation. The results are shown in Figure 5.

Physical interpretation

The regression parameters of the σ-moments include information about the difference of the interactions of the two involved phases, that is, of gas phase and dry activated carbon in the first case, and about aqueous phase and wet activated carbon in the second case. (Note, that $\ln(H^X)$ is related to free energy by the factor 1/RT, which is 1/2.5 kJ/mol at room temperature.)

Since $M_0{}^X$ is the molecular area (in Å²), the coefficient of this moment takes into account all surface proportional interactions, which may be dispersion (or van der Waals) energies, cavitation energies, and various smaller contributions. The value of 0.0629 Å^{-2} in the gas-phase equation corresponds to 0.36 kJ/mol/Å². The main contribution here is the dispersion energy, which is zero in the gas phase and about −0.25 kJ/mol/Å² in condensed phases. (Note that the adsorbate phase contributes with a negative sign. Hence, we get a positive coefficient.) For the case of adsorption from water, the dispersive energy contributions are almost identical in both phases, but the pure aqueous phase is known to have a high positive cavitation energy of about 0.2 kJ/mol/Å². This matches quite well with the coefficient of $0.0438\text{Å}^{-2} = 0.25$ kJ/mol/Å².

The second moment is a measure for electrostatic interactions, as the dielectric energy, which is the difference of the gas-phase energy and the COSMO-energy, that is, the energy of a solute X in a conductor, can be calculated as the energy of the solute solvated in vacuum. Since the vacuum "has only nonpolar (and nonpolarizable) surface," the COSMO-RS misfit energy in this case is just the surface integral of σ^2 over the surface of the solute. However, this is just identical to the second moment. The validity of this relation is shown in the diagram given in Klamt et al. (1998). The positive coefficient in the first equation results from the fact that the condensed phase (the adsorbate) is very well able to make favorable electrostatic interactions with the adsorbate, while there is no electrostatic interaction in the gas phase. On the other hand, the negative coefficient in the second case expresses the fact that pure water makes even better electrostatic interactions than active carbon.

The coefficient of the hydrogen-bond donor moment M_{don}^X expresses the ability of the phases to interact with donors, that is, to act as an acceptor. Hence, the large positive coefficients in the both equations correspond to the fact that activated carbon has a lot of acceptor capacity due to the oxygenated sites on the surface.

Finally, the coefficient of the acceptor moment expresses donor capacity of the phases. In agreement with our expectation, there is no significant donor capacity in activated carbon in the gas phase and, hence, the corresponding coefficient vanishes in the respective regression. In the liquid phase Franz et al. (2000) detected the formation of water clusters around hydrophilic oxygen groups and ions on the surface of activated carbons. The equilibrium of donors and acceptors of the pure water is thereby disturbed. As we expected, wet activated carbon has a lower donor capacity than pure water, which leads to the negative contribution of the acceptor moment in Eq. 18.

Summary and Outlook

It was shown that the extension of COSMO-RS to the adsorption from gas phase and from the aqueous solution is a promising way for the prediction of adsorption equilibria. The presented prediction method is based on σ-moments, which are directly derived from the polarization charge distributions from *ab initio* calculations. This method is presently restricted to very dilute solutions. The characteristics of the solvent (or gas phase) and of the adsorbing solid are contained in the regression parameters. These parameters can be interpreted in a physically founded way.

As a next step, we will try to make use of the information about the adsorbing solid, covered in the regression parameters, in order to derive an approximate σ-profile p_{S2}^{X} of the solid. With the knowledge of that σ-profile, we should be able to extend the method to finite adsorbate concentrations using the standard COSMO-RS equations.

Notation

a_{eff} = contact area, $\mathrm{\AA}^2$
c = equilibrium concentration, $\mathrm{mol \cdot L^{-1}}$
c_S^i = regression parameter of the ith moment, $\mathrm{\AA}^{-2+2i} \cdot C^{-i}$
c_{hb} = strength coefficient of the hydrogen bonding, $\mathrm{kJ \cdot mol^{-1}}$
E = energy, kJ
$f_i(\sigma)$ = profile-function of the ith moment, $C/\mathrm{\AA}^{2i}$
G = enthalpy, kJ
$\mathrm{H_{gas}}$ = Henry's Law coefficient for adsorption from gaseous phase, $\mathrm{mol \cdot Pa^{-1} \cdot kg^{-1}}$
$\mathrm{H_{water}}$ = Henry's Law coefficient for adsorption from aqueous phase, $\mathrm{m^3 \cdot kg^{-1}}$
k = Boltzmann constant, $\mathrm{J \cdot K^{-1}}$
K = equilibrium constant
n = mass-related amount of adsorbate, $\mathrm{mol \cdot kg^{-1}}$
M_i = ith σ-moment, $\mathrm{C}^i \cdot \mathrm{\AA}^{2-2i}$
M = molecular mass, $\mathrm{kg \cdot mol^{-1}}$
$p(\sigma)$ = frequency distribution of charge (Sigma Profile), $\mathrm{\AA}^4 \cdot C^{-1}$
R = general gas constant, $\mathrm{kJ \cdot mol^{-1}} \cdot T^{-1}$
T = temperature, K
α' = misfit energy coefficient, $\mathrm{kJ \cdot mol^{-1} \cdot \AA^{-2}}$
$\mu_S(\sigma)$ = Sigma potential, $\mathrm{kJ \cdot mol^{-1} \cdot \AA^{-2}}$
μ^X = chemical potential, $\mathrm{kJ \cdot mol^{-1}}$
ρ = density, $\mathrm{kg \cdot m^{-3}}$
σ, σ' = charge, $C \cdot \mathrm{\AA}^{-2}$

Indices

acc = acceptor term
comb = combinatorial term
don = donor term
es = electrostatics term
hb = hydrogen bonding term
hydr = hydration
S = solvent

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Manuscript received Feb. 1, 2001, and revision received Nov. 12, 2001.