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Prediction of Adsorption Equilibria from Physical Properties of the Pure Components

GUDRUN SCHÜRER AND WOLFGANG PEUKERT*
Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Cauerstraße 4,
91058 Erlangen, Germany
w.peukert@lfg.uni-erlangen.de

Abstract. The prediction of adsorption energies equilibria is often based on mixed terms influenced by both the adsorptive and the adsorbent. Our aim is to predict adsorption equilibria by using physical properties of the pure components. Based on the concept of equivalent surface properties we introduce models using one or two mean parameters (Hamaker constant, mean partial charge) as well as a model which takes partial charge distributions into account. Density functional theory (DFT) calculations can be used to describe well defined and regular surfaces. However, the structure and topology of heterogeneous surfaces are generally unknown. Thus the combination of DFT-calculations with a continuum solvation model and experimental data allows the prediction of the adsorption equilibrium at infinite dilution. For activated carbon in the gas phase and in water the Henry's law coefficients obtained by this method cover a range of 7 orders of magnitude. In order to gain a better understanding of the role of heterogeneities, DFT-calculations of model surfaces like functionalized coronenes or fullerenes were performed. A good qualitative agreement with the experimentally determined results was observed.

Keywords: adsorption equilibria prediction, activated carbon, Henry's law coefficient, COSMO-RS

Introduction

Interactions between particles with gaseous, liquid or solid phases are of great interest for many applications in science and technology. The knowledge of adsorption equilibria, for example, is necessary for the sizing of adsorption plants and in various processes such as crystallization, heterogeneous catalysis, growth and stabilization of nano-particles, powder flow and biotechnology, for instance. However, the description of adsorption equilibria hardly includes the influence of the solid material. Because experimental studies of adsorption behavior are very time-consuming and expensive, our aim is to predict adsorption equilibria by using physical properties of the pure components, i.e. of the adsorbate, the adsorbent and the solvent. This is, however, only possible if the chemical composition and the physical structure of the adsorbent surface is known. In this case density functional theory (DFT) allows the prediction of the interactions based on the electronic properties of the involved molecules. DFT simulations must then be performed for each individual combination of adsorbent and adsorptive. This is hardly feasible for technical systems.

For surfaces which are chemically and structurally heterogeneous this approach cannot be applied since the atomic composition is not known exactly. In these cases, which are most interesting from an application point of view, an indirect approach is needed. First, the surface must be characterized, which is done in our case by the measurement of adsorption equilibria at infinite dilution both in the gas and in the liquid phase. Then an appropriate model for the interaction between adsorbent and adsorptive is inverted to determine surface properties of the heterogeneous surface. These models may use only one mean parameter (e.g. the Hamaker constant of the adsorbent in case of purely dispersive interactions, a mean charge for polar interactions) or

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*To whom correspondence should be addressed.

a distribution of parameters (e.g. partial charge distributions). In any case, these properties reflect the possibilities of the surface to interact. These properties also contain information due to heterogeneity. Thus, we obtain *equivalent* properties. An equivalent surface property represents a (artificial) model surface with the same interactions as the real heterogeneous surface under consideration.

Materials and Methods

The experimental data (Henry's law coefficients) in the liquid phase were measured by solid phase micro extraction coupled with a gas chromatograph (GC-SPME) (Peukert et al., 2002). Most of the experimental data in the gas phase were taken from literature, some are own measurements by a gravimetric set-up (Peukert et al., 2002). These experiments lead to accurate data but are rather time-consuming. Therefore, also dynamic chromatographic methods such as inverse gas chromatography and HPLC are employed.

The dispersive interactions of an adsorbed molecule in the gas phase with a solid surface can be modeled by using the Hamaker constant of the solid and the critical data of the molecules (Maurer et al., 2001). This approach works well for hydrocarbons up to 10 C-atoms adsorbing on activated carbon and graphite, for instance. This dispersion model can also be applied to probe dispersive interactions of polar surfaces like alumina or titania. It is also used to measure the Hamaker constant of particles as input to models for adhesion. For carbon surfaces, deviations occur for polar molecules which interact strongly with polar surface sites. This model fails with water. For relatively simple molecules like CO_2 the Hamaker approach can be extended by adding terms for polar interactions; care should be taken were polar molecules react with polar surfaces due to catalytic effects. The mean polarity of the surface can be calculated by comparing Henry coefficients of Ar and N_2. Both molecules have similar molecular diameters, polarizabilities and both possess no dipole moment. Thus, they interact preferentially by dispersive interactions. However, N_2 partly adsorbs also to polar sites due to its quadrupole moment. This leads to higher Henry coefficients (of some 10%). This difference is used to extract a mean surface charge, which in turn is used to predict the Henry coefficient of CO_2, for instance, or to learn more on structural effects.

For polar components like water the use of DFT-methods is more appropriate. In combination with a continuum solvation model and statistical thermodynamics this approach allows the calculation of partition coefficients between various compounds. The DFT-calculations were performed using the program packages Gaussian 98 (Frisch et al., 2001) and Dmol^3 (Delley, 2000), respectively, including the Conductor-Like Screening Model (COSMO) (Klamt, 1995). The basic idea behind continuum solvation models is to describe solvent effects by placing the solute in a cavity surrounded by a dielectric continuum. The charge distribution of the solute polarizes the dielectric medium which is described by the generation of screening charges on the cavity surface. Unlike other continuum models, COSMO allows geometry optimization within the continuum and thus gives a good description of the electrostatic interactions at the cavity surface.

The Conductor-Like Screening Model for Real Solvents (COSMO-RS) uses the screening charge distribution obtained with the COSMO-method to calculate thermodynamic properties. The ensemble of interacting molecules is considered as an ensemble of pair-wise interacting surface patches with a screening charge density σ. The frequency profile of the occurrence of a certain charge density, the so-called σ-profile, is characteristic for the molecule in question. From the σ-profile the σ-potentials μ can be derived, which describe the affinity of the system, that is the ensemble of surface patches, to a surface of the polarity σ. The σ-potentials are the key to the chemical potential and thus to various thermodynamic properties. Beside the electrostatic interaction contribution, hydrogen bonding and van der Waals terms are taken into account.

The COSMO-RS-method was developed originally for molecules in solvents and is now extended to macroscopic particles interacting with molecules in the fluid phase. However, for this method the knowledge of the chemical structure of the components is required. For heterogeneous solid surfaces like that of activated carbon or nanoparticles this is not the case. Nevertheless, the approach can be used to create a model for the property prediction by calibrating the system to experimental data. The σ-potentials can be expanded to a Taylor-series (Eq. (1)). The σ-moments $M_i(\sigma)$ represent physical information like the charge, the surface area or hydrogen donor and acceptor terms. For the generation of a model for the prediction of Henry's law coefficients the σ-moments of the orders to $i = 2$

are sufficient.

$$\mu_s(\sigma) = \sum_{i=-2}^{m} c_s^i M_i(\sigma) \qquad (1)$$

The linear regression of the equation for the solute molecules to experimentally determined Henry's law coefficients leads to a model for the prediction of a solid with an unknown structure. Furthermore, it is possible to derive the σ-profile from the σ-moment regression using the projection onto convex sets (POCS) method. This is the only appropriate approach for heterogeneous surfaces of unknown composition.

To construct a link between ideal and heterogeneous surfaces, we start from well-defined model surfaces like functionalized coronenes or fullerenes which can be treated by (electronic) density functional theory (DFT). The extension to extended pores (e.g. carbon nanotubes) or crystalline surfaces using periodic boundary conditions is under development. The comparison between the indirect approach with inversion technique and the direct DFT-approach will open new insights into the possibility to describe heterogeneity and its influence on adsorption by means of equivalent surface properties.

Results and Discussion

Figure 1 shows the σ-profiles of water, benzene, wet and dry activated carbon. As the σ-profile is the charge distribution frequency of the screening surface, a positive charge in the σ-profile corresponds to a negative charge on the molecule. The σ-profiles give a vivid picture of the molecular polarity and a good description of the solutional behavior of chemical compounds. A detailed discussion of σ-profiles is given in reference (Klamt and Eckert, 2000).

The σ-profiles for wet and dry activated carbon show high values in the low and non-polar region. As quantum chemical calculations of polyaromatic molecules lead to a peak in this region, too, it can be interpreted as the contribution from the carbon atoms. The broad σ-profile of dry activated carbon shows small values in the polar region with $\sigma < -0.0088$ e/Å^2 and $\sigma > 0.0088$ e/Å^2, too. Thus, dry activated carbon can build hydrogen bonds as well. This agrees with the well-known finding, that the surface properties of dry activated carbon is significantly influenced by oxygenated groups and pre-adsorbed water on the surface. The peak of wet activated carbon in the region around $\sigma = 0.02$ e/Å^2 shows that wet activated carbon has a high H-donor-affinity. The position of the large peak in the low negative region confirms the finding that wet activated also has a low H-acceptor-affinity.

The number and kind of probe molecules is very important for the quality of the solid surface characterization. Five parameters are determined in the regression and thus at least five adsorptive molecules have to be used. Additionally, the set of probe molecules has to cover all kinds of interactions the solid can build, i.e. the set of probe molecules must probe all possible types of interactions to receive a good picture of the solid surface properties.

Using these descriptors the Henry's law coefficients of adsorption on activated carbon can be calculated. Therefore the experimental determination of the Henry's law coefficients of 5 to 7 clever chosen

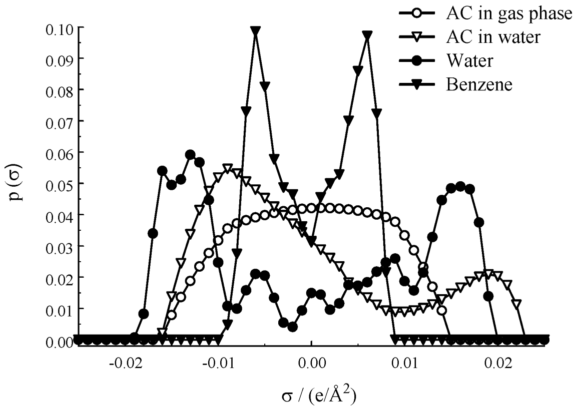

Figure 1. σ-Profile of dry and wet activated carbon, water and benzene.

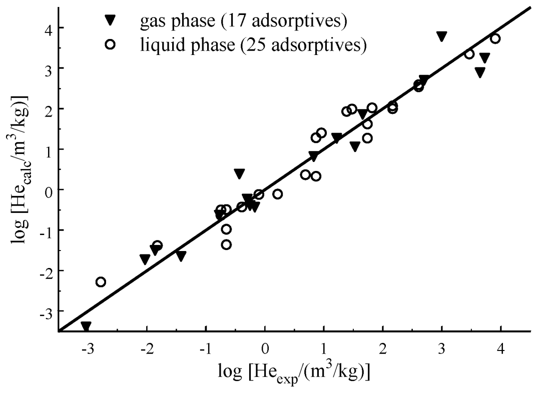

Figure 2. Correlation of experimental adsorption data from gaseous and liquid phase with data calculated from the σ-moments.

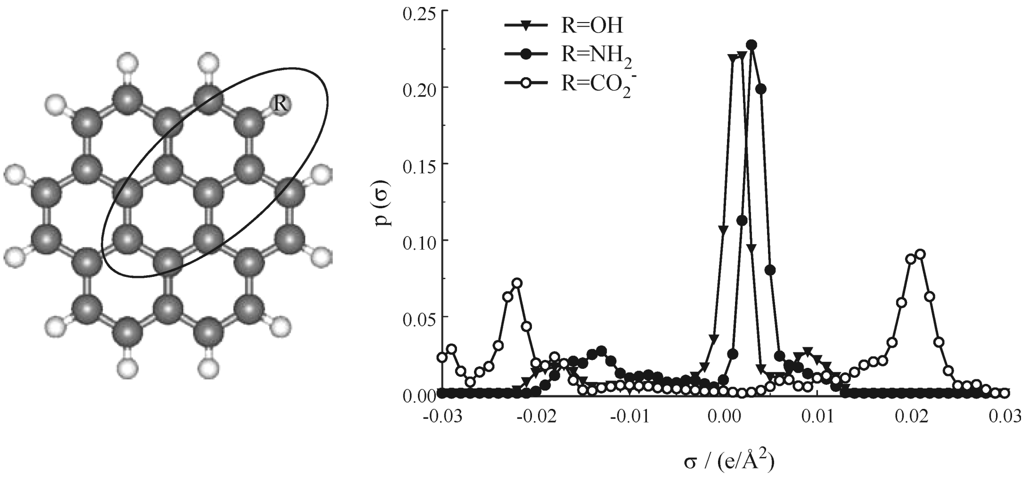

Figure 3. Quantum chemical calculation of model surfaces (Coronene).

adsorptives is sufficient to allow the prediction of other adsorptives (with the same solvent and adsorbent). The correlation between predicted and measured coefficients is presented in Fig. 2. This correlation shows that this strategy represents a promising way for the calculation of adsorption equilibria and that this model allows a reasonable prediction of Henry's law coefficients both in the gas and liquid phase. The results cover Henry coefficients over 7 orders of magnitude. The mean standard deviation is 0.38 log-units in the liquids phase and 0.49 log-units in the gas phase. This agreement is quite reasonable taking into account that parts of the data especially in the gas phase are taken from literature (and thus refer also to other solids).

Direct DFT-COSMO calculations of model surfaces like functionalized coronenes or fullerenes give us a picture of the influence of different heterogeneities. Further on, the σ-profiles of the model surfaces help us to verify the experimentally determined results. A reasonable qualitative agreement was observed (see Figs. 3 and 4 as examples), taking into account the simplicity of these model surfaces.

The σ-profiles of the functionalized fullerenes shown in Fig. 4 are normalized to unity. Although the functional hydroxy-groups have a far less contribution to the molecular surface than the carbon atoms, it is evident that they have a significant effect to the adsorption behavior. However, the huge peak at about $\sigma = 0$ suggests that for systems with large non-polar regions the van der Waals-contribution is crucial. The DFT-COSMO-approach gives a good description of polar interactions, but strongly underestimates the van der Waals-contributions. On the other hand, the method of Maurer is appropriate especially for non-polar interactions. It is straightforward to combine both methods by correcting the van der Waals-terms in COSMO using the critical data and the Hamaker constant for the components according to Maurer's method. Beside corrections for non-polar interactions, it is crucial to include periodic boundary conditions in order to model larger and more realistic model surfaces like graphite, crystal surfaces or carbon nanotubes. This will allow us to quantify the influence of chemical and structural heterogeneity based on a quantum chemical method.

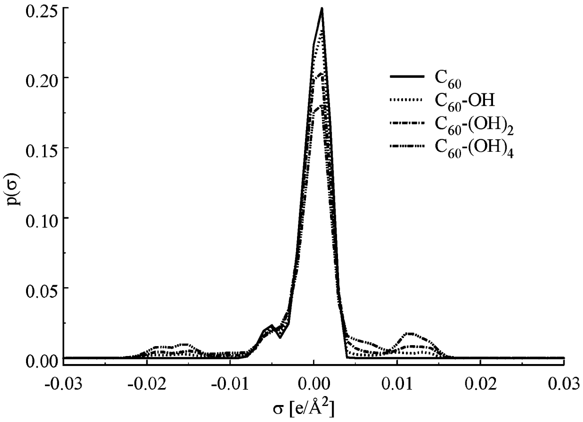

Figure 4. σ-Profiles of functionalized Buckminster-fullerenes.

Conclusion

It could be shown that adsorption equilibria at infinite solution both in the gas and in aqueous phase can be described by properties of the pure components. In the gas phase dispersive interactions can be described by the Hamaker constant of the solid and the critical data of the adsorptives both for nonpolar and polar surfaces. The effect of polarity can be included by a mean partial charge. For the adsorption of water in the gas phase and the adsorption in water on activated carbon a more detailed model was employed. The extension of a continuum solvation model is used to describe solid surfaces as a set of patches carrying a partial charge. The characterization of solid surfaces requires only a small set of clever chosen adsorptives with well-known properties. The method is suitable for a good quantitative prediction of adsorption equilibria at infinite dilution. We are also a step further on the way to predict adsorption equilibria with pure compound information without the usage of experimental adsorption data. Together with periodic boundary conditions this is a promising approach to gain insight into adsorption phenomena on the molecular level.

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