Predicting Adsorption of Organic Chemicals at the Air−Water Interface

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The sorption capacity of the air−water interface for organic chemicals can easily be much larger than the bulk water or bulk air phase of small water droplets or air bubbles in water, respectively. Therefore, adsorption constants must be known in addition to the bulk air/water partition constants to assess the transport capacity of such small droplets or bubbles. Here the quantum-chemical-based software COSMO*therm* is tested for its ability to predict air−water adsorption constants for a diverse set of more than 200 organic compounds. To this end, the free energies of adsorption that are received as model output are converted into adsorption constants based on a reference state of adsorption that is derived here. This approach can be shown to predict adsorption constants with a root-mean-square error of 0.6 log units for K values ranging over seven orders of magnitude. In addition, the model's ability to predict enthalpies of adsorption is demonstrated.

1. Introduction

The adsorption equilibrium of organic chemicals at the water surface is of interest for technical applications as well as for environmental issues. Small water droplets as they exist in fog or in technical applications can carry as many or more chemicals at their surface than in their bulk phase.[1−3] The same is true for small gas bubbles in water.[2−4] In both cases, the transport of chemicals can be correctly assessed only if the equilibrium adsorption constant at the water surface is known in addition to the bulk air−water partition coefficient. The efficiency of reactions that occur at the water surface, for example, on aerosols, also depends on these adsorption constants.[5] The experimental determination of such constants is rather tedious, and the number of chemicals for which these equilibrium adsorption constants have already been measured is rather small. Therefore, a model that can successfully predict this adsorption process would be very valuable. In an earlier work, we calibrated a linear solvation energy relationship (LSER) for this sorption process based on experimental data for 60 organic chemicals.[6] This model uses experimentally determined molecular descriptors that characterize the ability of a chemical to undergo various interactions with surrounding phases. This model suffers from two drawbacks: (i) it was calibrated for rather simple chemicals with no more than one functional group. In cases where molecules possess several functional groups that cannot all interact with the water surface because of conformational constraints, this model cannot be expected to work well because the utilized chemical descriptors represent the interactions of all functional groups; (ii) the required LSER compound descriptors are publicly available for only ∼1500 compounds. Kelly et al.[7] have presented two semiempirical models based on a set of calibration data similar to that used in the LSER model. The models by Kelly et al. require only the molecular structure of the adsorbates as model input; however, no comprehensive validation of these models with reliable independent data and for more complex compounds is available. Vacha et al.[5] have presented some molecular dynamics simulation for adsorption at the air−water interface for three PAHs and found good agreement with experimental values for two of them; however, these data are by far too few to judge on the general quality of this modeling approach.

The goal of this work was to check whether the commercial software COSMO*therm* can be used for predicting the equilibrium adsorption of organic chemicals to the water surface. This validation is done with a much larger and more diverse experimental data set than has been used in previous works. COSMO*therm* is a quantum-chemistry-based method that has been successfully used before for calculating bulk phase equilibrium partitioning including various environmental partition problems.[8−11] Version C2.1 release 01.08 (COSMO*logic* GmbH & Co. KG: Leverkusen, Germany, 2008) also offers the prediction of the free energy gain of a molecule at a surface or an interface. If an appropriate standard state of adsorption can be identified (see below), then these adsorption free energies can be converted into adsorption constants.

2. Model Predictions

2.1. Model. The COSMO*therm* software is based on the COSMO-RS theory (details of which are given elsewhere).[12,13] The COSMO*therm* method requires the computation of each molecule that is involved in the partition system by the quantum chemical "conductor-like screening model" (COSMO).[14,15] To create all relevant conformers of a molecule, the module COSMOconf 2.1 was used. COSMO calculations were done with TURBOMOLE 5.10 (TURBOMOLE, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989−2007, TURBOMOLE GmbH, www.turbomole.com). Using these COSMO files as an input, COSMO*therm* then calculates adsorption free energies according to the following concept: The chemical potential of the adsorbate is calculated for various positions (i.e., various distances of the adsorbate center from the interface) and various orientations. Taking into account the free energy difference between different conformations of an adsorbate, the search for an optimal association of the molecule at the surface can be extended to conformationally flexible molecules. On the basis of these data, the total free energy of adsorption is then calculated using

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statistical thermodynamics. For adsorption to surfaces, an artificial vacuum phase is suggested to be used as a placeholder for the gas phase in the current version of COSMO*therm* C2.1 0108. The disadvantage of this approach is that an optimization of the gas-phase energies of the adsorbates is missing. Indeed, the results thus calculated did not show any reasonable correlation with experimental data. To overcome this shortcoming, one can calculate the vacuum/gas phase partitioning with COSMO*therm* in an additional step and combine these data to the surface/vacuum adsorption constants by applying a thermodynamic cycle, thus yielding the desired surface/gas phase adsorption constants. This latter approach is the one that is further evaluated here. It must be noted that a bug in the conformer treatment of the adsorption subroutine was found and removed by the provider of the software (COSMOlogic) during the beginning of this work. Therefore, adsorption calculations should be done only with COSMO*therm* versions released later than 01.08.

2.2. Standard State of Adsorption. COSMO*therm* calculations provide only free energies of adsorption, which then have to be converted to adsorption constants by the user. Free energies of bulk phase partitioning can be converted into equilibrium partition constants according to eq 1 if an appropriate standard state is known.

where ΔG_{12} is the free energy of transfer between phases 1

$$\Delta G_{12} = -RT \ln K_{12} \qquad (1)$$

and 2, R is the gas constant, T is absolute temperature, and K_{12} is the bulk phase partition constant between 1 and 2. Interestingly, even for partitioning between two bulk phases, there is an ongoing debate of whether the standard state has to be chosen such that K_{12} is based on units of mol/mol or mol/volume.[16−18]

To set up an equation analogue to eq 1 for adsorption processes, a standard state of adsorption has to be found. This problem is equivalent to defining a thickness τ for the surface layer in which the molecules are defined as being adsorbed. With this thickness, τ, the relationship between the free energy of adsorption, ΔG_{ads}, and the adsorption constant, K_{ads} (in [(mol/m^2)/(mol/m^3)]), becomes[19]

$$\Delta G_{\mathrm{ads}} = -RT \ln(K_{\mathrm{ads}}/\tau) \qquad (2)$$

In the literature, one finds two different standard states of adsorption to be used. Kemball and Rideal arbitrarily used a thickness of 6×10^{-10} m as the standard state.[19] To avoid such an arbitrary decision, de Boer[20] made the plausible assumption that under standard state conditions (i.e., $\Delta G_{\mathrm{ads}} = 0$), the average distance between the molecules in the surface layer should be the same as their mutual distance in the gas phase under standard conditions. This corresponds to a thickness of 33×10^{-10} m. Depending on which of the two standard states is used, predictions for log K_{ads} will differ systematically by 0.8 log units, and it remains unclear which one if any of the suggested standard states is appropriate. One possible way of dealing with this problem is to simply treat τ as a fitting parameter when eventually comparing calculated ΔG_{ads} with experimental log K_{ads} values. However, this is unsatisfying because it would remain unclear whether the fitting parameter also makes up for some systematic errors in the calculated ΔG_{ads} values. Therefore, it appeared to be desirable to identify the correct standard state of adsorption directly from experimental data. This can be done as follows:

The thickness, τ, that represents the most suitable standard state of adsorption can be calculated from eq 2 if one or more pairs of data of ln K_{ads} and the respective ΔG_{ads} values are known. The problem is that these ΔG_{ads} values cannot directly be measured for adsorption at infinite dilution. However, for alkanes there is another way of receiving unambiguous ΔG_{ads} values. There is quite a number of adsorption constants on various surfaces for compounds that differ by one or several CH_2 increments (alkanes, alkylbenzenes). These data allow us to derive ΔG_{ads} values for the methylene increment (CH_2) on the respective surface irrespective of the correct standard state (because τ cancels out in this equation)

$$\Delta G_{\mathrm{CH_2}} = -RT \ln(K_{\mathrm{C}_{n+1}}/\tau) - (-RT \ln(K_{\mathrm{C}_n}/\tau)) \qquad (3)$$

where $K_{\mathrm{C}_{n+1}}$ and K_{C_n} denote the adsorption constants for two consecutive members of a homologous series of compounds having n and $(n + 1)$ carbon atoms in their molecules. Such methylene increments, $\Delta G_{\mathrm{CH_2}}$, are constant for a given surface. (See Table S1 of the Supporting Information.) Therefore, it should be possible to determine the free energy of transfer of a molecule consisting (almost) only of methylene increments such as *n*-nonane as being 9 times the free energy of a methylene increment. This procedure yields an unambiguous value of ΔG_{12} for the adsorption of *n*-nonane on the specific surface and can be entered into eq 2 together with the experimental adsorption constant of *n*-nonane on that surface to yield a value for τ. Table 1 shows the averaged $\Delta G_{\mathrm{CH_2}}$ values extracted from experimental adsorption data of alkanes and alkylbenzenes on various surfaces, the corresponding $\Delta G_{\mathrm{nonane}} = 9\Delta G_{\mathrm{CH_2}}$ values, and the measured adsorption constants, log K_{nonane}. The thickness τ representing the standard state of adsorption that follows from these data is given in the last row. The average $\tau = 7.3 \times 10^{-10}$ m is close to the value of Kemball and Rideal. The standard deviation of the average value is rather small (s.d. = 3.4×10^{-10} m), as it should be if τ is indeed a constant with general validity. It must be noted, though, that only aqueous surfaces have been used here either as neat water or in form of a multilayered water film on top of a mineral surface. Whereas this standard state should work for adsorption on a neat water surface, it still remains to be tested whether it is also valid for surfaces that are devoid of water.

3. Results and Discussion

3.1. Adsorption Constants. Experimental data for adsorption at the interface between air and neat water (defined as $K_{\mathrm{ads}} = (c_{\mathrm{interface}}\ (\mathrm{mol/m^2}))/(c_{\mathrm{air}}\ (\mathrm{mol/m^3}))$) are limited to a set of 79 compounds. This set includes various functional groups, but the experimental values cover a range of only three orders of magnitude, and all compounds are rather simple in that they are only monofunctional. A more comprehensive validation becomes possible if adsorption data on quartz at 90% relative humidity are used. At 90% relative humidity, the quartz surface is covered with an adsorbed water film that is between 5 and 10 molecular layers thick and that has sorption properties that are very similar to those of neat water.[21] For these conditions, a set of 192 chemicals, among them various bifunctional molecules covering a range of more than seven orders of magnitude in K_{ads} (defined as $K_{\mathrm{ads}} = (c_{\mathrm{interface}}\ (\mathrm{mol/m^2}))/(c_{\mathrm{air}}\ (\mathrm{mol/m^3}))$), is available.[8,22,23]

Figure 1 shows that the agreement between experimental and predicted values is excellent for the neat water surface at 15 °C. (Data are provided in Table S2 in the Supporting Informa-

TABLE 1: Values for the Average Experimental Free Energy of Adsorption of a CH_2 Increment on Various Surfaces, the Standard Deviation, the Experimental Adsorption Constants, and the Resulting τ According to Equation 2 (All Values for 15°C)

		average ΔG_{CH_2} J/mol	s.d.	$9\Delta G_{CH_2}$ kJ/mol	log K_{ads} (m) *n*-nonane	τ (m)	ref
quartz	45% rh	−2884	388	−25.95	−4.30	9.89×10^{-10}	22
quartz	70% rh	−2844	280	−25.59	−4.81	3.53×10^{-10}	22
quartz	90% rh	−2622	265	−23.60	−5.32	2.52×10^{-10}	22
water		−2176	187	−19.58	−5.72	5.39×10^{-10}	6
bentonite	45% rh	−2736	430	−24.62	−4.54	9.92×10^{-10}	24
bentonite	60% rh	−2553	420	−22.97	−5.02	6.49×10^{-10}	24
bentonite	80% rh	−2540	200	−22.86	−5.42	2.71×10^{-10}	24
$CaCO_3$	40% rh	−2445	190	−22.01	−5.24	5.93×10^{-10}	22
$CaCO_3$	70% rh	−2262	140	−20.36	−5.43	7.58×10^{-10}	22
$CaCO_3$	90% rh	−2168	225	−19.51	−5.59	7.40×10^{-10}	22
kaolinite	45% rh	−2696	188	−24.26	−4.83	5.90×10^{-10}	24
kaolinite	60% rh	−2600	305	−23.40	−5.09	4.60×10^{-10}	24
kaolinite	80% rh	−2330	697	−20.97	−5.31	7.66×10^{-10}	24
$(NH_4)_2SO_4$	20% rh	−2708	101	−24.37	−4.41	1.48×10^{-09}	24
$(NH_4)_2SO_4$	40% rh	−2682	263	−24.14	−4.57	1.13×10^{-09}	24
$(NH_4)_2SO_4$	60% rh	−2596	115	−23.37	−4.61	1.41×10^{-09}	24
Al_2O_3	40% rh	−2318	137	−20.87	−5.35	7.37×10^{-10}	22
Al_2O_3	70% rh	−2241	189	−20.17	−5.58	5.75×10^{-10}	22
Al_2O_3	90% rh	−2169	174	−19.52	−5.75	5.07×10^{-10}	22
					average	7.3×10^{-10}	
					s.d.	3.4×10^{-10}	

tion.) The rmse is 0.32 log units. However, this promising result cannot yet be taken as representative for the overall performance of COSMO*therm* on predicting air/water surface adsorption because of the rather small number and range of validation data.

For the quartz surface at 15 °C and 90% rh, the overall performance is also good, although the scatter is larger now (rmse = 0.63 log units). Three outliers had been anticipated beforehand and are not shown in Figure 2, but data are presented in Table S3 in the Supporting Information: diethylamine and pyridine are likely protonated under the experimental conditions in the adsorbed state so that a prediction for the neutral species is meaningless. Dimethylsulfoxide is known to be poorly presented in DFT calculations, as performed here with Turbomole for the required COSMO files. For all other compounds, the results are shown in Figure 2. There is one significant outlier (1,2-naphtoquinone) with a deviation of >3 log units between predicted and experimental value for which no explanation can be given. A failure of the calculations in only this single case appears to be unlikely because a quantum-chemical-based model like COSMO*therm* is expected to be quite robust. Therefore, an error in the experimental value appears to be more likely.

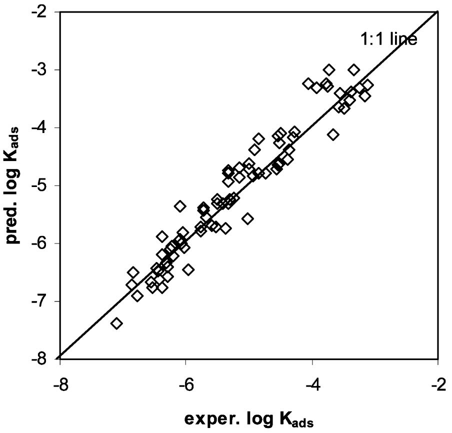

Figure 1. Experimental values for adsorption at the air/water interface at 15 °C plotted versus values calculated with COSMO*therm* based on the standard state of adsorption derived here.

3.2. Adsorption Enthalpies and Entropies. In a next validation step, the performance of COSMO*therm* in predicting the temperature dependence of the water surface−air adsorption equilibrium was tested. Similar to all other gas-phase partition processes, water surface−air adsorption exhibits a substantial temperature dependence. For 91 of the 192 compounds shown in Figure 2, experimental enthalpies of adsorption were available and could be used for evaluation. The results in Figure 3 show reasonable good agreement between experimental and predicted enthalpies of adsorption, ΔH_{ads} (data provided in Table S4 in the Supporting Information). Therefore, COSMOtherm should be able to predict good adsorption constants for the water surface not only at 15 °C but also at other environmentally relevant temperatures. The enthalpy data together with the free energies derived from the adsorption constants eventually also allowed a comparison of experimental and predicted entropies of adsorption (calculated as $\Delta S_{ads} = (-\Delta G_{ads} - \Delta H_{ads})/T$). The agreement is in the same range as that for the other thermodynamic data (data provided in Table S5 in the Supporting Information.).

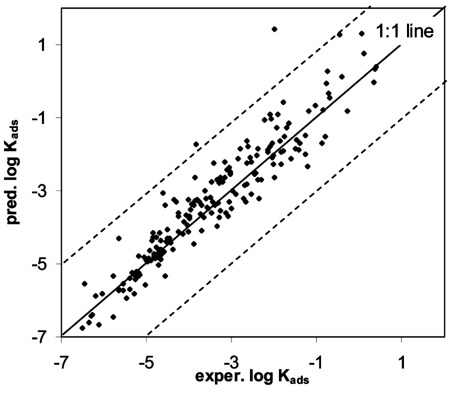

Figure 2. Experimental values for adsorption at the air/water interface on quartz at 90% relative humidity and 15 °C plotted versus values calculated with COSMO*therm* based on the standard state of adsorption derived here.

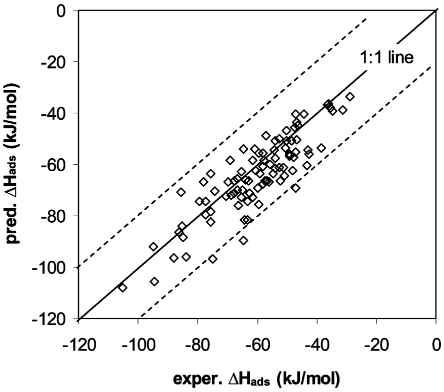

Figure 3. Experimental enthalpies of adsorption measured between 15 and 55 °C plotted versus predicted values.

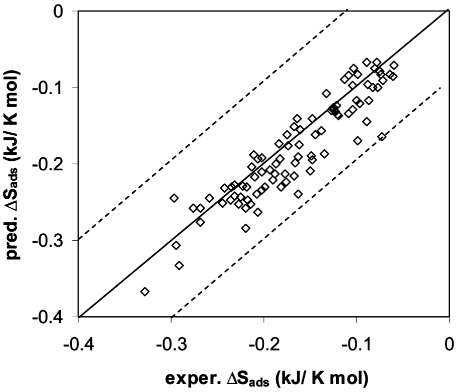

Figure 4. Experimental entropies of adsorption measured at 15 °C plotted versus predicted values.

4. Conclusions

COSMO*therm* model results for the free energy of adsorption in combination with the standard state of a sorption derived here has shown good performance in predicting equilibrium adsorption constants at the air−water interface for more than 200 organic compounds with K values ranging over seven orders of magnitude. No other model has been validated successfully for such a large and diverse data set. As another advantage compared with other models, the approach presented here did not use any kind of calibration. Therefore, one may expect that the modeling presented here has a very wide applicability domain beyond the type of chemicals that were represented in the evaluation data set. Some further implications arise from the fact that this good performance was achieved without any calibration: (1) The predictions exhibit very little systematic deviation (bias) when compared with the experimental values. This gives further support to the standard state of adsorption that was identified in this work. (2) The information about the energetically most favorable orientation and position of the adsorbates in the interface, which is offered by COSMO*therm* as an additional model output, is likely to be sound. (See the Supporting Information for examples.) This information may be relevant for mechanistic studies such as chemical reactions that occur at the surface.[5]

Supporting Information Available: Methylene increments, ΔG_{CH_2}, extracted from adsorption constants of homologue compounds on various water covered surfaces; values for experimental and predicted adsorption constants for a neat water surface at 15 °C; values for experimental and predicted adsorption constants on quartz at 90% relative humidity and 15 °C; values for experimental and predicted enthalpies of adsorption on a water surface; values for experimental and predicted entropies of adsorption on a water surface at 15 °C for selected compounds; and preferred orientation of the adsorbates in the air−water interface as predicted by COSMO*therm*. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Valsaraj, K. T. *Chemosphere* **1988**, *17*, 875.
(2) Valsaraj, K. T. *Chemosphere* **1988**, *17*, 2049.
(3) Hoff, J. T.; Gillham, R.; Mackay, D.; Shiu, W. Y. *Environ. Sci. Technol.* **1993**, *27*, 2174.
(4) Shunthirasingham, C.; Lei, Y. D.; Wania, F. *Environ. Sci. Technol.* **2007**, *41*, 3807.
(5) Vacha, R.; Jungwirth, P.; Chen, B. H.; Valsaraj, K. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4461.
(6) Roth, C. M.; Goss, K.-U.; Schwarzenbach, R. P. *J. Colloid Interface Sci.* **2002**, *252*, 21.
(7) Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2004**, *108*, 12882.
(8) Goss, K.-U.; Arp, H. P. H.; Bronner, G.; Niederer, C. *Environ. Toxicol. Chem.* **2009**, *28*, 52.
(9) Niederer, C.; Goss, K.-U. *Environ. Sci. Technol.* **2007**, *41*, 3646.
(10) Arp, H. P.; Niederer, C.; Goss, K.-U. *Environ. Sci. Technol.* **2006**, *40*, 7298.
(11) Arp, H. P. H.; Goss, K.-U. *Environ. Sci. Technol.* **2009**, *43*, 1923–1929.
(12) Eckert, F.; Klamt, A. *AIChE Journal* **2002**, *48*, 369.
(13) Klamt, A.; Eckert, F. *Fluid Phase Equilib.* **2000**, *172*, 43.
(14) Schäfer, A.; Klamt, A.; Sattel, D.; Lohrenz, J. C. W.; Eckert, F. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2187.
(15) Klamt, A.; Schüürrmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799.
(16) Goss, K.-U. *J. Phys. Chem. B* **2003**, *107*, 14025.
(17) Vitha, M. F.; Carr, P. W. *J. Phys. Chem. B* **2000**, *104*, 5343.
(18) Sharp, K. A.; Kumar, S.; Rossky, P. J.; Friedman, R. A.; Honig, B. *J. Phys. Chem.* **1996**, *100*, 14166.
(19) Kemball, C.; Rideal, E. K. *Proc. R. Soc. London, Ser. A* **1946**, *187*, 53.
(20) de Boer, J. H. *The Dynamic Character of Adsorption*, 2nd ed.; Clarendon Press: Oxford, U.K., 1968.
(21) Goss, K.-U. *Crit. Rev. Environ. Sci. Technol.* **2004**, *34*, 339.
(22) Goss, K.-U.; Schwarzenbach, R. P. *J. Colloid Interface Sci.* **2002**, *252*, 31.
(23) Arp, H. P.; Goss, K.-U.; Schwarzenbach, R. P. *Environ. Toxicol. Chem.* **2006**, *25*, 45.
(24) Goss, K.-U.; Buschmann, J.; Schwarzenbach, R. P. *Environ. Toxicol. Chem.* **2003**, *22*, 2667.

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