

PhD. Theses

GAS AND SOLUTION ADSORPTION PROPERTIES OF
SILICA SORBENTS

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1. Introduction

Exact knowledge of the adsorption processes at solid/liquid interfaces is of primary importance both in basic research and industrial applications. Calculation of most important parameters like the surface density of the liquid components and the thickness of the adsorbed layer – determining the thermodynamic properties, colloidal stability and structure of suspensions – is only possible on the basis of the well known actual surface area and pore structure of the solids giving place for the adsorption of the liquid components. It is known, that for adsorbents like swelling clay minerals or sol-gel derived amorphous solids the specific surface area and pore size distribution can vary with an order of magnitude depending on the method used for determination. The generally used specific surface area determination method, the standard BET method (BET-analysis of N₂ adsorption at 77K), does not always reflect the real surface area or pore size distribution. In addition, application of the BET method for microporous adsorbents is restricted. Improvements and modifications of the BET analysis methods of the popularly applied N₂ adsorption isotherms at 77 K can be found in the literature but there are examples of different other experimental approaches too. These methods are all aimed at better and more accurate surface area and porosity determination.

Adsorption of ionic surfactants at solid/liquid interfaces and more closely, the mechanism of the adsorption had attracted increasing attention since the mid 90s. The scientific interest is mainly rooted in coming up and fast development of supramolecular chemistry (investigation of self-assembling processes) and scanning probe microscopy (SPM) techniques. One of the main strategies of the synthesis of new functional materials in nanotechnology and biotechnology is based on self-assembly of amphiphiles. New SPM techniques helped to clear up the ordering properties of surfactants and other amphiphiles at flat solid surfaces and as a result threw new light upon the adsorption mechanisms. In the case of solids which do not have macroscopically flat surface such as nanoparticles or nanoporous materials investigation of interfacial exchange processes can provide additional information on the adsorption mechanism. For example, in adsorption of ionic surfactants on oxide type surfaces proton exchange occurs thus, measuring the pH change during adsorption is a useful additional tool in mechanistic investigations.

In the first part of my thesis work I investigated the possibility of obtaining reliable specific surface area and porosity data for four silica

adsorbents with widely different pore structure properties, Aerosil 200, a precipitated silica, Stöber silica and silica gel. I analysed the adsorption and desorption isotherms of N_2 at 77K by using the BET method and the Tóth method. These results were compared subsequently with data from other experimental surface area determination and pore structure investigation methods, analysis of high temperature N_2 adsorption isotherms (according to Bond and Spencer), liquid mixture adsorption isotherms (according to Schay-Nagy) and small angle X-ray scattering curves. The purpose of these investigations was to find the most appropriate and relevant specific surface area of these solids for applications in solid/liquid adsorption experiments. The results allow to conclude about the influence of porosity on the applicability of the analysis results of N_2 adsorption isotherms measured at 77 K by either the BET or other (like the Tóth) analysis methods.

In the second part I investigated the solid/liquid interfacial equilibria of cationic surfactant dodecylpyridinium chloride solutions of varying pH and ionic strength on the above silica surfaces. The applied experimental methods (adsorption measurements, potentiometric acid-base titrations, electrokinetic and rheological experiments) together with interfacial ionic speciation model calculations allow getting more insight into the adsorption mechanism of dodecylpyridinium cation at charged silica surfaces. Fitting the charge-potential curves using the 2pK/triple layer electrostatic model the equilibrium constants of the surfactant adsorption can be calculated and subsequently used to separate the electrostatic part from the total adsorption isotherm. The effect of the structure of the adsorbents on the surfactant adsorption equilibria and on the adsorption mechanism was investigated by comparative analysis of the surfactant adsorption on different silica surfaces.

II. Methods

I measured N_2 adsorption isotherms for specific surface area determination in a Gemini 2375 Surface Area Analyzer. I used differential interferometry to determine equilibrium molar fractions of the liquid mixture components to calculate liquid mixture adsorption excess isotherms. Small angle X-ray scattering curves were measured in an apparatus equipped with a Philips PW 1830 generator, a Kratky camera and position sensitive detector. The measured experimental data were analyzed as follows: N_2

adsorption isotherms by the method of Tóth and the method of Bond and Spencer, the liquid mixture excess isotherms by the Schay-Nagy extrapolation method, the SAXS curves by the method of Degovics and Glatter, and the method of Porod.

I measured the pH- and ionic strength-dependence of the surface charge density by using automated acid-base titration equipment with a Dosimat 665 autoburette, homemade potentiometer, a Radelkis combined glass electrode and specifically designed controlling software. The titration curves were evaluated using the linear transformation method and the H^+ and OH^- concentrations were calculated from the titrations of background electrolyte using the linear relation between the actual ion concentration and electrochemical activity of the corresponding ions. The titrations were performed both in the absence and presence of dodecylpyridinium chloride. The equilibrium distribution of all the ions present in the systems was calculated with the help of MINTEQA2 solution speciation software. I measured the electrokinetic potentials with a Malvern Zetasizer dynamic light scattering instrument.

The surfactant adsorption isotherms were measured in static conditions. The equilibrium DPCI concentrations were determined spectrophotometrically using an Uvikon 930 UV-VIS spectrometer. I measured the equilibrium flow curves of the dense silica/surfactant/electrolyte suspensions to examine the rheological properties, in a Rheotest 2 rheometer. The flow curves were evaluated according to the Bingham model.

III. New scientific results

1. I established based on the comparative evaluation of the gas adsorption experiments that the internal surface area of Stöber silica is not accessible for N_2 at 77 K thus, by this method only about 5 % of the total specific surface area can be assessed. I found that there are several other appropriate methods to determine the real specific surface area of Stöber silica, such as adsorption of N_2 at 253 K, microcalorimetric enthalpy of wetting, liquid mixture adsorption and small angle X-ray scattering (SAXS).
2. Analysis of the N_2 adsorption isotherms measured at 77 K applying the Tóth methods the and appropriate modifications to the BET method lead to an increased specific surface area value approximately

by 30 %. This higher value is still very low for Stöber silica compared with the results from other experiments. The Tóth analysis method of $N_2/77K$ can be successfully applied to adsorbents with mesoporous, microporous or non-porous structure (precipitated silica, silica gel and Aerosil 200).

3. Stöber silica has a complex pore structure. Micropore, mesopore and macropore domains can equally be found in its structure, which is the consequence of the pore-fractal character of this adsorbent.
4. The surface charge density of the silica adsorbents prepared by different synthesis methods proved to be very similar when calculated on the basis of the real specific surface area values obtained by the non-BET methods.
5. The adsorption of dodecylpyridinium chloride on silica adsorbents is independent of the ionic strength at the cip point. This state corresponds to the complete monolayer coverage regarding surfactant adsorption and to maximum charge density regarding proton desorption. The equilibrium surfactant concentration in this point coincides for the investigated adsorbents meaning that the adsorption on the chemically identical surfaces (with the same type of surface dissociating groups) is determined by the interfacial association properties of the surfactant.
6. The amount of the surfactant adsorbed in the cip depends on the silica structure. For the non-porous Aerosil 200 it corresponds with the surface charge density (at $pH=9$ and $I=0.1 M$), but for the mesoporous precipitated silica it is only about half and for the micro- and mesoporous Stöber silica only about one hundredth of the surface charge density. Consequently, in the case of the two porous adsorbents only the corresponding fraction of the total surface area is accessible for surfactant adsorption.

7. The adsorption mechanism can be investigated in the case of the Aerosil 200/DPCI system, while the porous structure of the precipitated silica and Stöber silica excludes this possibility. Comparing the results from surfactant adsorption, potentiometric surface charge determination, electrokinetic and rheological experiments the following adsorption mechanism was assumed: electrostatically driven adsorption in head-on orientation with surface ion-pair formation up to $0.03 \mu\text{mol}/\text{m}^2$ surface coverage. With increasing surface coverage the adsorption occurs both in head-on orientation via electrostatic interaction and tail-on orientation via hydrophobic interaction between the carbon chains of the surfactant in the adsorbed state. Adsorption in tail-on orientation includes adsorption of counter ions, which is responsible for the charge imbalance within the plane of shear. In the cip point, the surface charge density reaches the maximum value and the surfactant adsorption corresponds with complete monolayer coverage.

8. The surfactant adsorption isotherm can be decomposed to separate the electrostatic part from non-electrostatic (principally hydrophobic) part with the help of electrostatic modeling of the potentiometric acid-base titration experiments in the presence of the surfactant. The electrostatic component includes the specific interaction potential as well, which is apparent from the values of the surface complexation constants. The surfactant complexation constant is about four orders of magnitude larger than that of the cation of the indifferent background electrolyte.

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