

Characterization of surface properties of carbon black and graphite

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Carbon black is used in several technical applications. Fillers in tires, black pigments in printing technology or synthetic cloth fibers are only a few examples. Because of the small particle size of carbon blacks, the surface properties have a great influence on the product property. We studied two different carbon black that show a large difference up to 20% in rolling drag when used as filler in tires. Different roughness or diverse polar groups on the surfaces are possible reasons for this.

Morphology, surface structure and chemical surface composition of carbon black are not well defined. For such systems, TGA-MS and gas adsorption are powerful tools to analyze surface properties. We use adsorption equilibria in the Henry-region that reflect the interaction of molecules with the particle surfaces. From measured Henry-coefficients and known atomic surface structure, dispersive interaction parameters of the solid, e.g. a Hamaker-constant, can be determined by inversely solving the applied adsorption model. This method can be used to characterize carbon black if the interactions of different molecules with carbon atoms are calibrated on a defined surface like graphite. From known interaction potentials of various probe molecules, structural information like surface roughness of carbon black can be determined.

1. INTRODUCTION

Interactions of particles with gaseous, liquid or solid phases are of high relevance in many industrial applications. Agglomeration, wetting of the particles with matrix polymers and dispersion technology are a few examples where surface properties of fine or nanoscaled particles are important. The underlying fundamental physical-chemical processes of adsorption and wetting can be traced back to the molecular interactions and the structure of the solid

surface. Unfortunately, most methods of surface physics can often not be applied to technical nanoparticles, since these methods need well-defined crystalline surfaces, often on a macroscopic scale. For example, the scanning tunneling microscopy (STM)-method is extremely difficult to apply in the analysis of carbon black particles with diameters of only a few nm, because a particle can be caught in the extremely strong electric field at the tip. Thus, particle scanning becomes impossible.

The use of different molecules as probes provides a powerful tool to scan particulate surface properties. Gravimetric methods or inverse gas chromatography (iGC) are two well established techniques to measure gas adsorption equilibria. To measure adsorption equilibria using gravimetric or volumetric methods is time consuming but relatively easy to perform, thus the experimental effort is comparably low because the adsorption setup can be automated.

In technical systems, the surface of the solids contains many exposed atoms and functional groups that may interact with adsorbate molecules. Surface imperfections of molecular dimensions such as dislocations, vacancies, flaws, cracks and chemical contamination may be a major source of surface heterogeneity. The heterogeneity of a sample can be scanned due to adsorption of one type of molecule over a large pressure range (for example steps in low pressure and low temperature isotherms of nitrogen) or with different molecules at similar conditions. In our approach the adsorption equilibria (Henry coefficient) of different kind of molecules derived from a plane carbon surface like graphite are compared with the Henry coefficients of carbon blacks, whose surface properties are unknown. The differences are used to gain information on polarity and roughness.

Sophisticated theories [1][2] have been developed to determine adsorption energy distribution and pore size distribution from adsorption data. From known or assumed surface structure (roughness, pores) and energetic heterogeneity, isotherms can be computed using Monte Carlo or Density Functional Theory [3]. Mostly, interaction potentials are fitted to the experimental results. Surface properties can be modeled either by mean values or by distributed ones [5]. Often, the surface structure or the interaction energy is assumed to be homogenous when solid samples are characterized. To overcome this problem, a generalized Fractal-BET-equation was suggested [4]. We use a simple but effective and physically reasonable approach to describe the adsorption equilibrium in the Henry region based on physical intrinsic parameters of the solid and the adsorbate. Here, the inversion problem is less laborious. The use of different molecules in size and interaction potential allows one to distinguish between roughness and adsorption energy. The obtained data are sampled over all particles and represent therefore mean surface properties of the particle ensemble [5].

Beside adsorption, thermogravimetric analysis (TGA) combined with mass spectroscopy (MS) provides important information about the chemical composition of solid surfaces. At ambient conditions, most surfaces are covered with water molecules. The amount of adsorbed water and the corresponding desorption temperature are a measure of water surface interaction.

2. EXPERIMENTAL

Materials. Three different carbon samples were characterized. The commercial carbon blacks CXN234 and A5741 obtained from DEGUSSA AG, Germany, and graphite EP 1005 produced by Richard Anton KG, Germany, were analyzed. The carbon content is larger than 99.6%, impurities are mainly silizium and iron (0.4%), as given by the manufacturer. The carbon blacks show quite similar properties in standard quality checks (BET- surface area and density), but product properties are significantly different when used as filler in tires.

X-ray Powder Analysis. X-ray diffraction (XRD) patterns were recovered using a Philips PW 1730/1316/19 unit to analyze the crystal structures of the carbon samples. Cu K_{α} ($\lambda = 0.15418$ nm) radiation filtered by Ni was used to record patterns in the range of $\Theta = 16$ to 80° , as shown in Figure 1.

Density. The densities of the samples were determined using a precise Helium pycnometer AccuPyc 1330, Micromeretics. The weight of the samples was measured by a Satorius microbalance MC1, accuracy 0.1 mg. It is possible to determine the density with an accuracy of better than 0.01 g/cm^3 with these instruments. Densities and BET-surface areas are given in Table 2.

Low Temperature Nitrogen Adsorption. Low temperature nitrogen adsorption isotherms were measured at 77.4 K using a fully automated volumetric sorption analyzer Nova 2000, Quantachrome. BET surface area was determined by standard 10-Point analysis.

TGA-Analysis. For an interpretation of the adsorption experiments in the Henry-region and the determined adsorbent-adsorbate-interaction, a chemical analysis of strong and specific bound surface groups is essential. TG, DTA and MS analysis were performed in the laboratory of Prof. Knözinger, Physikalische Chemie, LMU, München. A Netsch system for simultaneous thermoanalysis, STA 409C, was used. The TGA was connected by a heated capillary with a high vacuum system (6×10^{-7} mbar) with integrated quadrupole-mass-spectrometer Balzer, QME 125. Reference material and sample crucibles made of alumina were heated to burn off impurities at 1200°C for 2 h before use. All

TGA-MS measurements were performed in a pure nitrogen environment (Linde, 5.0) at a flow rate of 25 ml/min. Buoyancy effects were corrected. Weight losses of the carbon black samples were measured over a temperature range from 30 to 723 °C at a furnace-heating rate of 10 K/min. The graphite was analyzed in a range from 40 to 1127 °C at a furnace-heating rate of 5 K/min. Results are given in Figure 4, Figure 5 and Figure 6, respectively.

Adsorption in the Henry-region. Single component adsorption equilibria in the Henry-region were measured by a gravimetric method. The amount of adsorbed gas or vapour was determined from the variation of the sample weight due to rising pressure in a sealed volume. To correct buoyancy effects, the sample volume was determined by the Helium method.

Essential part of the adsorption setup is a Satorius Ultramicro Balance (Satorius GmbH, Type 7014, Göttingen, Germany), an accuracy of +/- 1µg can be obtained in the measuring range of 0 to 100 mg. The upper housing temperature is kept constant at 302 K. Isotherms were measured in a pressure range from smaller than 0.5 mbar up to 3 bar.

For sample preparation, the upper balance housing is flushed over night with helium for 12 h while the lower housing containing the sample is heated to 250 °C for desorption. After that, the pressure is reduced to 50 mbar using a turbo molecular pump and a throttled valve. Then the temperature of the lower housing is hold constant at 20 °C. After 15 minutes, the housing is evacuated for 2 h to a pressure smaller than 10^{-4} mbar using an turbo molecular pump. The pressure is measured by two MKS membrane pressure gauges (1-5000 mbar and 10^{-4} - 2 mbar). Depending on the individual component, the increase in weight was carefully recorded until equilibrium was reached. Several probe molecules were used to characterize surface properties of the three different solid systems. The gases were obtained from Messer Griesheim GmbH, Germany. Table 1 shows some properties of the probe molecules.

3. RESULTS AND DISCUSSION

XRD. The analyzed graphite shows a main peak at 26.35 ° (0.338 nm) and another peak at 54.4° (0.1685 nm). The latter peak is not observed for the carbon black, and the main peak is shifted to 24.25° (0.367 nm) and also broadened due to the small crystallite size. This indicates a lower density of the carbon black samples and the absence of the hexagonal and the layered crystal structure of graphite.

Tab. 1. Properties of the used gaseous probe molecules

gas	$T_c / p_c^{0.5}$ K bar ^{-0.5}	polarizability 10^{-30} m ³	dipole moment $1D=3.33 \times 10^{-30}$ cm	quadrupole moment $\text{cm}^2 \times 10^{40}$
Ar (4.6)	21.7	1.63	0	0
Kr (4.0)	28.4	2.5	0	0
CH ₄ (5.0)	28.2	2.6	0	n. a.
C ₃ H ₈ (3.6)	57.1	5.5*	0	n. a.
C ₄ H ₁₀ (3.6)	68.0	7.36*	0	n. a.
N ₂ (5.0)	21.8	1.77	0	4.7
CO ₂ (4.6)	35.6	2.911	0	13.4

* Calculated from group-polarizability

n.a. not available.

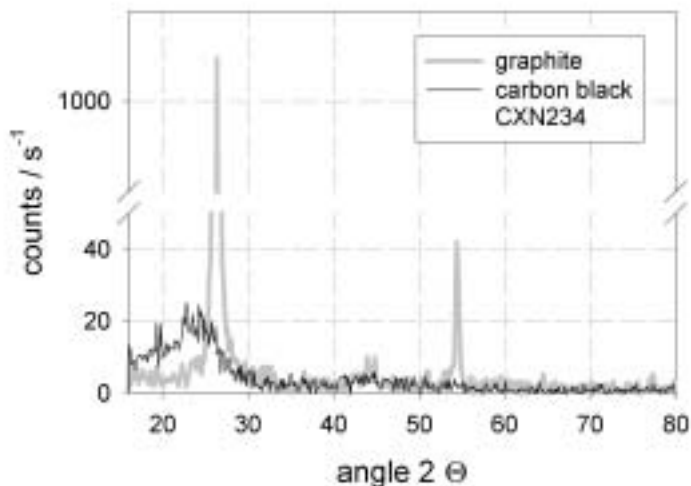


Fig. 1. XRD patterns for graphite and the carbon black CXN234 (A5741 is similar). The main peak of graphite is found at 26.35 ° (0.338 nm) and another peak occur at 54.4° (0.1685 nm). This peak is not observed for the carbon black, and the main peak is shifted to 24.25° (0.367 nm)

Figure 2 shows nitrogen isotherms of carbon black CXN234 at $T=77.4$ K. The isotherm of A5741 looks quite similar. The resulting pore volume distribution indicate that the pore volume of the particles is below 0.5% of the solid volume. Therefore, it is reasonable to assume that the particles are essentially nonporous since the small pore volume is at least partly due to interstitial voids between the adhering particles in the sample.

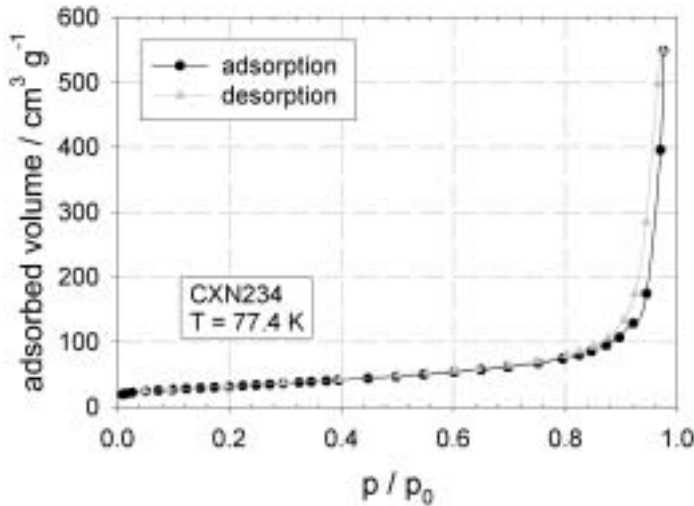


Fig. 2. Nitrogen adsorption isotherms of carbon black CXN234, measured at 77.4 K

Tab. 2. BET-surface area, density and fractal dimension of graphite, the carbon blacks CXN234 and A5741

	A5741	CXN234	graphite
BET-surface area /m ² g ⁻¹	117.65 +/- 1,7	110.7 +/- 0,6	22.52 +/- 0,32
density / g cm ⁻³	1.9914 +/- 0,007	1.9688 +/- 0,004	2.319 +/- 0.0032
Mean particle diameter /nm	25.61	27.53	114.9
fractal dimension	2.61	2.65	2.45

Fractal Dimension. Since the surfaces of carbon black is not smooth, fractal dimension analysis provides an easy method to get information about the roughness of the surface. The fractal dimension D covers a range between 2 (ideal smooth) and 3 (surface so rough that it essentially occupies all available volume).

The Neimark-Kiselev [6] method has gained popularity because only one single adsorption isotherm in the multilayer region is required for the calculation of the fractal dimension D .

$$S_{inter} = K(r_{curv})^{2-D} \quad (1)$$

S_{inter} denotes the adsorbate - vapor interface area, which is calculated by the Kiselev equation $S_{inter} = (RT/\gamma) \int_n^{n_{max}} \ln(p_0/p) dn$, and r_{curv} denotes the mean radius of the curvature of the adsorbate - vapor interface, which can be

calculated by the Kelvin equation. The plot of $\log [S_{\text{inter}}]$ versus $\log [r_{\text{curv}}]$ yields a straight line, as shown in Figure 3. In the range p/p_0 from 0.008 to 0.21 a fractal dimension of 2.65 for the CXN234, 2.61 for the A5741 and 2.45 for the graphite is found. These results indicate an increased roughness of the CXN234 carbon black sample.

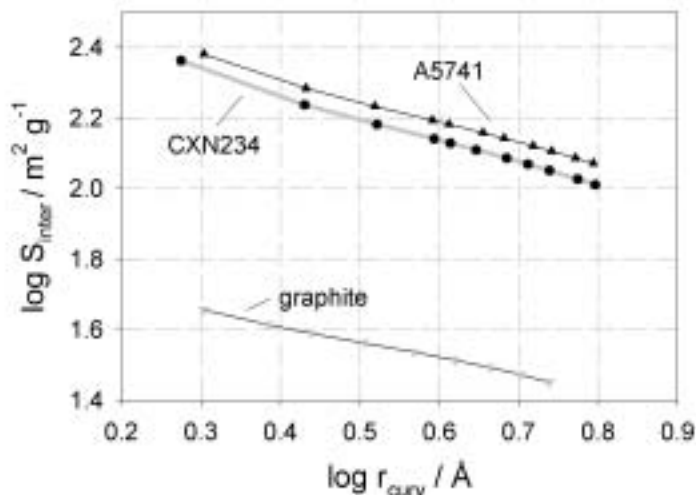


Fig. 3. Plots of the logarithm of the adsorbate-vapor interface area S_{inter} versus the logarithm of the mean radius of curvature of the adsorbate-vapor interface r_{curv} to obtain the fractal dimension D of the three samples using the Neimark-Kiselev-method

TGA. The surface of graphite is assumed to be essentially nonpolar. Thus it is expected that only a relatively small amount of water is adsorbed on the surface at ambient conditions. This was confirmed by the TGA-measurement, as shown in Figure 4.

A continuous increase of weight loss occurs at temperatures higher than 580 °C. This weight loss is accompanied by an increase in CO_2 in the gas phase and an increase in the DTA-signal. The reason might be the beginning oxidation of the sample. Impurities in the nitrogen or desorption of OH-groups of the furnace wall are possible sources for oxygen.

The weight loss of 0.15% up to temperatures of 150°C can be attributed to coordinately bound water. From the specific surface area of 22.5 m^2/g the number of water molecules results in 40 per nm^2 . For desorption of this water, a temperature of 250 °C was chosen before adsorption isotherms in the Henry region were performed. The main peak of desorbed water occurs at a temperature of 70°C.

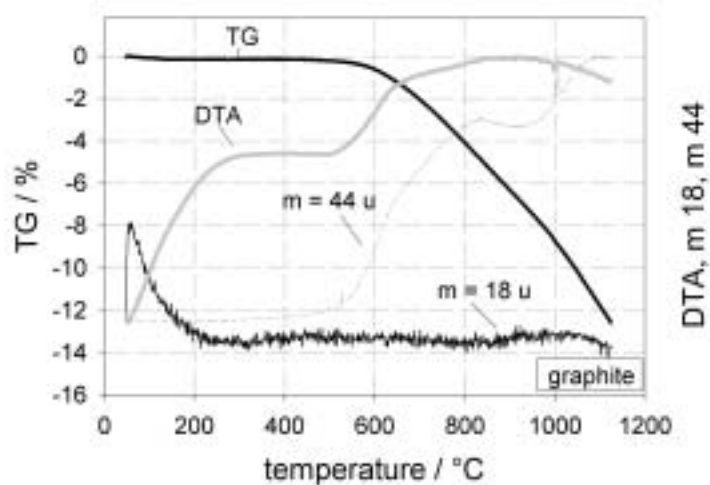


Fig. 4. TGA signals of graphite as a function of temperature measured in N_2 (5.0). DTA and mass spectra signals of $m = 18$ u and $m = 44$ u are plotted in arbitrary units

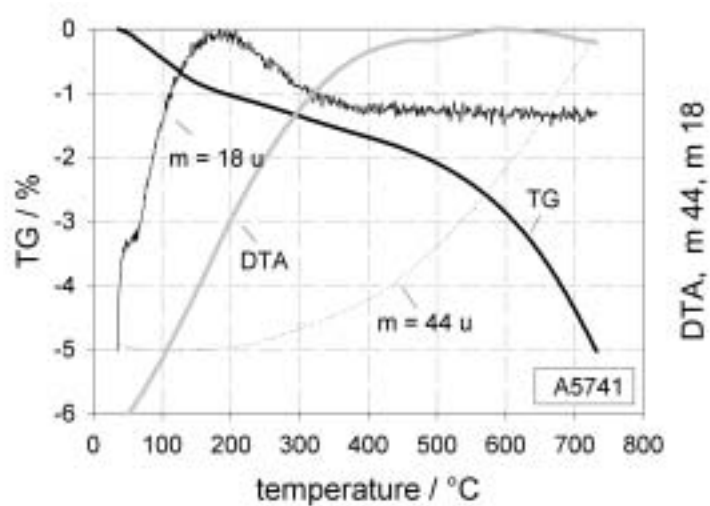


Fig. 5. TGA signals of the carbon black A5741 as a function of temperature measured in N_2 (5.0). DTA and mass spectra signals of $m = 18$ u and $m = 44$ u are plotted in arbitrary units

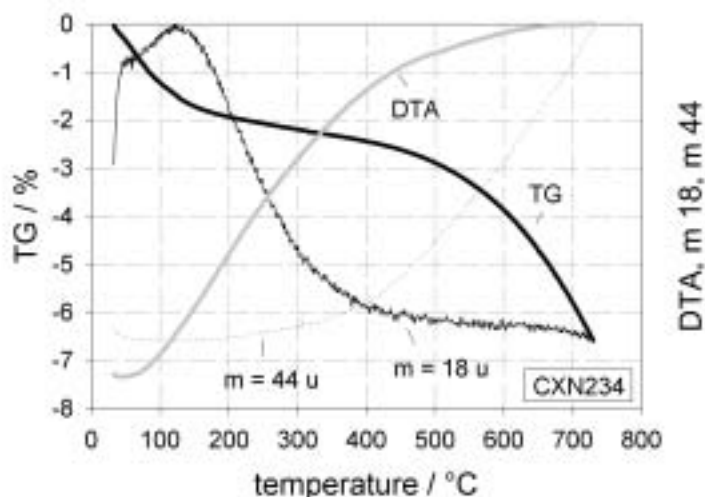


Fig. 6. TGA signals of the carbon black CXN234 as a function of temperature measured in N_2 (5.0). DTA and mass spectra signals of $m = 18$ u and $m = 44$ u are plotted in arbitrary units

As shown in the Figure 5 and Figure 6, the weight loss of the carbon black CXN234 is significantly larger than the weight loss of the carbon black A5741. As seen from the water peak at 150 °C, the weight loss can mainly be attributed to a larger amount of adsorbed water. Compared with graphite, this higher temperature indicates a stronger adsorption energy of water on the carbon blacks. The amount of water on the CXN234 is approximately two times larger than on A5741. Compared with the graphite, the carbon blacks are covered by thicker water layers. Using a surface area of 117 m^2/g and 110 m^2/g and weight loss of 1 and 2%, respectively, a number of water molecules of 335 and 670 per nm^2 can be calculated (40 on the graphite) on the A5741 and the CXN234, respectively. The water may not be distributed uniformly on the surface but may be located around specific sites or concentrated in hydrophobic voids. The behavior at temperatures above 600 °C (significant and continuous weight loss with an increase in DTA and $m = 44$ u signal) is similar at all carbon samples.

These TGA-MS analysis indicate that on carbon black polar groups are present, to which water can be bound. It seems that on the CXN234 more or stronger polar groups are present than on the carbon black A5741. At temperatures larger than 600 °C, the surface of carbon solids changes even in pure nitrogen. Due to the increase of $m = 44$ u signal and the exothermic DTA signal, the carbon systems are oxidized. Thus, the preparatory desorption temperature of 250 °C was chosen before adsorption isotherms were measured in the Henry region, in order to remove the water. It is safely assumed that the carbon surface does not change at this temperature.

Gas-solid interaction in the Henry-region. Measuring isotherms in the sub-monolayer region provide information on the type and the strength of interaction of a gas molecule with a surface because lateral interactions can be neglected. If the surface is energetically heterogeneous, the adsorption on the energetically highest sites is dominating at low pressures. Depending on energy- and number distribution of the adsorption sites, steps or a nonlinear adsorption isotherm may be measured in the sub-monolayer region. However, the measured Henry-isotherms of argon and nitrogen on the carbon samples are strictly linear. As shown in Figure 7, the scaled amount of adsorbed argon is largest on the carbon black CXN234 followed by A5741 and lowest on graphite. Henry-coefficients scaled by the BET-surface area are a measure of the gas solid interaction potential $\varphi_{i,s}$.

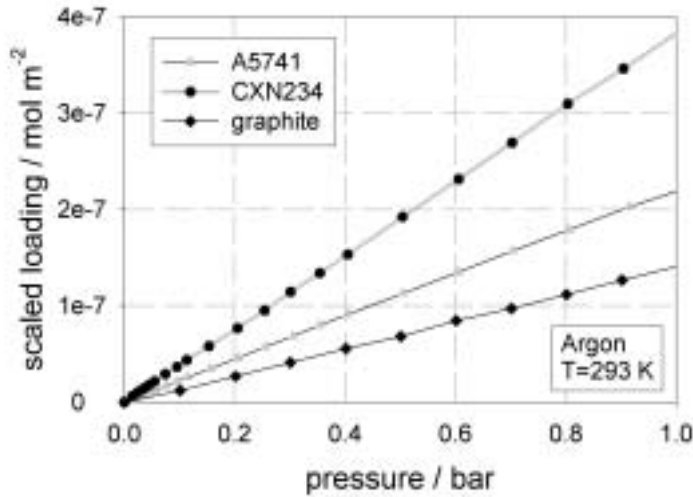


Fig. 7. Adsorption isotherms of Argon measured at T=293 K. For comparability, the isotherms were scaled by the BET surface area (n / S_{BET})

The relation between the scaled Henry coefficients $H_{i,s}^S$ and the interaction potential $\varphi_{i,s}$ of a molecule i with the solid s can be quantified by the well-known equation derived by Pierotti and Thomas (7):

$$H_{i,s}^S = \frac{H_{i,s}}{S_{BET}} = \frac{1}{N_A kT} \int_{z_{min}}^{z_{max}} \left[\exp\left\{-\frac{\varphi_{i,s}(z)}{kT}\right\} - 1 \right] dz \quad (2)$$

where z is the distance of the molecule from the solid surface, T the temperature, k the Boltzmann factor, N_A the Avogadro constant and S_{BET} the BET surface area. Assuming additivity of van der Waals forces, the interaction

potential $\varphi_{i,s}$ depends on the molecular interaction parameter $C_{i,s}$ of a gas molecule with an atom of the solid, as well as on the particle density and the crystal structure of the solid. Steele [8] calculated the interaction $\varphi_{i,s}$ of gases for a graphite surface using a Lennard-Jones type pair potential. The parameters of Lennard-Jones potentials are often unknown. Maurer et al. [9] used a Sutherland potential $\varphi \propto C_{i,s}/z^6$ to calculate the interaction of a molecule with a solid. The dispersive molecular interaction parameter $C_{i,s}$ between gas i and solid s can be derived from the Hamaker - constant of the solid according to

$$A = A_{s,s} = \pi^2 \rho_s^2 C_{s,s} \quad (3)$$

From the well-known mixing rules of Bertholet [10], Mauer et al. [9] introduced the following expression for the gas solid interaction:

$$A = 32\pi^3 d_s^3 \left(\frac{16\rho_s C_{i,s}}{9k(d_i + d_s)^3} \cdot \frac{\sqrt{p_c}}{T_c} \right)^2 \quad (4)$$

d_i and d_s are the molecular van der Waals-diameters of the gas and of the solid molecule and T_c and p_c are the critical data of the gas, respectively. The term $T_c/p_c^{0.5}$ is a measure of the van der Waals interaction parameter of the gaseous components. It is important to note that the parameter $C_{i,s}$ can be calculate a priori by eq. (4), without any empirical correlation. Only intrinsic physical data of the adsorbent and the adsorbate are necessary to describe the adsorption in the Henry region of molecules which interact only via van der Waals interactions like Argon and simple hydrocarbons. The critical data are available for most gases. The Hamaker-constant of the adsorbent can be derived from Lifshitz-theory [9]. Deduced from the Steele summation method, the interaction potential $\varphi_{i,s}$ for a molecule at distance z of a flat surface interacting via the Sutherland potential is given by [11]

$$\varphi_{i,s}(z) = \sum_{g=0}^{\infty} \left(- \frac{\pi \rho_{s,2D} C_{i,s}}{2(d_{i,s} + g\Delta + z)^4} \right) \quad (5)$$

where g is the number of the layer, Δ the distance between two layers and $\rho_{s,2D}$ the two dimensional density of a layer. The values $\Delta = 0.336$ nm and $\rho_{s,2D} = 3.813 \times 10^{-9}$ m⁻² were used for graphite. To calculate the interaction potential $\varphi_{i,s}$ an assumption has to be made on the geometrical structure of the solid near the surface. If pores or kinks exist, a significant increase in the surface potential is expected because the molecules adsorbed in corner sites or

in pores experience stronger interaction. In these cases, an increase of the measured Henry-coefficient is expected.

The dispersive interactions decline rapidly with the distance z . Therefore molecular adsorption is very sensitive to surface properties. Fortunately, the sum in eq. (5) is highly convergent because of the rapid decline of the atomic interactions. From a measured Henry coefficient and with known critical temperature T_c and critical pressure p_c of the adsorptives under the assumption of an ideal graphite surface, the Hamaker constant of the solid or a surface energy can be derived by inverting eq. (2).

The great advantage of this approach is that only pure material properties of solid and of the adsorbate are used. Deviations will occur if polar interaction become important and if the structure of solid, e.g. due kinks and pores have to be included. As shown in the following, the polarity of the interacting partners leads to an additional term in the interaction potential (see eq. (7)). A shift of $T_c / p_c^{0.5}$ may become important when the van der Waals equation of state, which only includes dispersive forces, deviates strongly from the T-p-behavior of the pure component. This issue will not be covered in this paper and is subject of further investigation.

If quadrupole interaction are important, the interaction potential $\varphi_{i,s}$ can be calculated by

$$\varphi_{i,s}^{tot} = \varphi_{i,s}^{vdW} + \varphi_{i,s}^{quad} = \sum_{g=0}^{\infty} \left(-\frac{\pi \rho_{S,2D} C_{i,s}}{2(d_{i,s} + g\Delta + z)^4} \right) - \frac{1}{2} \cdot Q \cdot \frac{\partial E}{\partial z} \quad (6)$$

were Q denotes the quadrupole moment of the adsorbate. In the Henry region, molecules with quadrupole moment will adsorb preferable on charged sites. If the density of these charged sites is low, it is reasonable to assume that site-site interactions can be neglected and only the interaction of the molecule with one charged site is taken into account. Therefore, gradient of the electric field can be calculated using the Coulomb law $E \propto q/z^2$.

$$\varphi_{i,s}^{tot} = \sum_{g=0}^{\infty} \left(-\frac{\pi \rho_{S,2D} C_{i,s}}{2(d_{i,s} + g\Delta + z)^4} \right) - \frac{Q \cdot q}{4\pi \epsilon_0 z^3} \quad (7)$$

The charge q of an adsorption site is usually unknown. But from experimentally determined Henry coefficients of molecules with and without a quadrupole moment like argon and nitrogen, a mean charge q can be calculated using eq. (7) and inversely solving eq. (2).

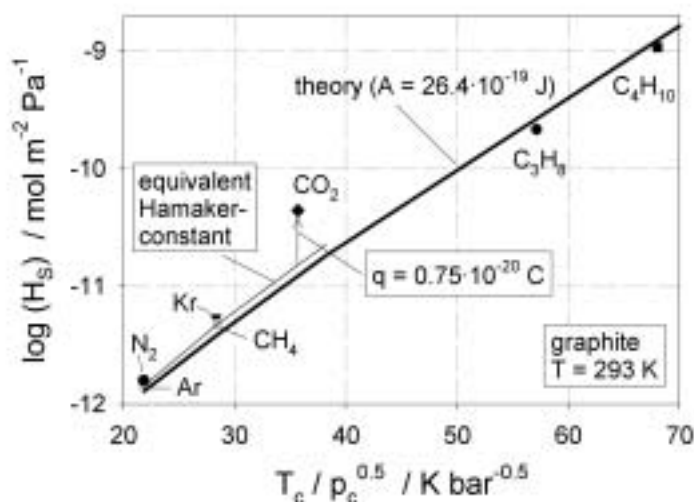


Fig. 8. Henry-coefficients of various gases on graphite, measured at 293 K. The adsorption of various nonpolar molecules can be satisfactorily described by the theory using only van der Waals interactions and a Hamaker-constant of 26.4×10^{-19} J

The experimentally determined Henry coefficients of various probe molecules are compared with results calculated by the theoretical model. The adsorption equilibria in the Henry region of N_2 , Ar, CH_4 , Kr, C_4H_8 and C_4H_{10} are estimated quite reasonably by using eq. (5), that includes only van der Waals interactions, and a mean Hamaker constant of 26.5×10^{-20} J, which can be derived from Lifshitz-theory. CO_2 has a large quadrupole - moment. If the oxygen is bound to the carbon surface, the symmetry of the molecule is broken and an additional quadrupole bond can form. This results in a larger interaction of CO_2 than expected by eq. (5). At a more detailed view, the van der Waals interactions of Ar and CH_4 are slightly larger than derived from the model for a plane surface. An equivalent Hamaker constant can be derived from Ar and CH_4 by inverting eq. (2). This equivalent Hamaker constant includes structural effects, that slightly increase the van der Waals interaction of argon on graphite, e.g. by kink sites that always exist in technical systems. The physical meaning of an equivalent Hamaker constant is the following: it quantifies the interaction energy between a hypothetical adsorbed carbon atom and a nonideal, e.g. rough graphite particle under the assumption that the unknown rough graphite surface is described by a well defined model system, i.e. by an ideally smooth graphite surface. The equivalent Hamaker constant is larger than the reference value for the ideal surface because the adsorbed atom interacts with more atoms of the bulk phase. Since the complete structural characterization of technical surfaces in general is beyond scope, the only manageable way to circumvent this obstacle is the introduction of equivalent properties. The determined equivalent

Hamaker-constant is 20% larger than that of ideal graphite. Furthermore, the Henry-coefficient of N_2 is larger than that of Ar because of the quadrupole moment of N_2 . Fortunately, the van der Waals interaction parameter $T_c/p_c^{0.5}$ of Ar and N_2 is nearly the same for both molecules. From the deviation of the Ar and N_2 Henry-coefficient using eq. (7), a mean charge of 0.75×10^{-20} C can be calculated. If the equivalent Hamaker-constant derived from the small molecules Ar and CH_4 is used to calculate the Henry-coefficient of CO_2 , a value of $4.9 \times 10^{-11} \text{ mol m}^{-2} \text{ Pa}^{-1}$ is obtained, that is very close to the experimental value of $4.45 \times 10^{-11} \text{ mol m}^{-2} \text{ Pa}^{-1}$. These results show that our simplified method is quite sufficient to describe the adsorption of various gases on graphite. Only available intrinsic physical data of adsorbate and adsorbent are necessary to describe van der Waals and quadrupole interactions. Using this approach, an adsorbent can be characterized by measuring only the adsorption isotherms of nitrogen and argon.

If the surface structure is not known, which is usually true in the case of carbon black, the deviation between calculated and measured Henry-coefficients of Argon indicates qualitatively the amount of carbon atoms are interacting with the probe molecule. This again can be considered as an equivalent Hamaker-constant. For a quantitative description, additional sums have to be introduced in eq. (5) to describe the van der Waals interaction, e.g. at kinks properly. This is of course, only possible for known surface structure.

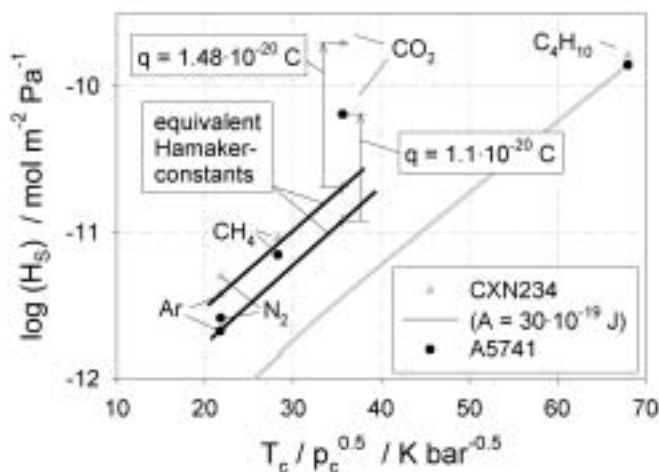


Fig. 9. Scaled Henry-coefficients of various gases on carbon black CXN234 and A5741, measured at 20°C . Because of surface roughness, the adsorption of molecules with different size can not be described by the model of a plane surface.

The experimentally determined Henry coefficients shown in Figure 9 can not be described by the simple model according to eq. (5). For the theoretically

calculated line in Figure 10 the measured density $\rho_{S, 3D}$ of 1.97 g cm^{-3} or $9.88 \times 10^{28} \text{ m}^{-3}$ was used. From the XRD data it is known that the layered graphite structure does not exist in the carbon blacks. Thus, a mean two dimensional density $\rho_{S, 2D}$ of $2.138 \times 10^{19} \text{ m}^{-3}$ was calculated from $\rho_{S, 2D} = (\rho_{S, 3D})^{2/3}$. Because the Henry coefficients of C_4H_{10} of both carbon blacks are similar, this molecule was used to calculate a Hamaker-constant. A value of $30 \times 10^{-19} \text{ J}$ can be derived by inverting eq. (2) and eq. (5). Smaller molecules like Ar and CH_4 can adsorb at vacancy sites, where the van der Waals interaction is larger. The deviations observed for these probe molecules from the model for plane surfaces is a qualitative measure of surface roughness, because they interact only via nonspecific van der Waals interactions. At kinks and in pores, the interaction potential is increased, because more carbon atoms interact with the adsorbate. This increased surface potential can again be described by an equivalent Hamaker-constant. For small molecules like Argon, the equivalent Hamaker-constant is 2.82 times larger than for C_4H_{10} for A5741 and 3.63 times larger for CXN234. This indicates that only small molecules can adsorb at vacancy sites and that the carbon black CXN234 is rougher than A5741. An extension of the used model may include information on roughness, so that the equivalent Hamaker-constant can be calculated from the intrinsic Hamaker-constant for the plane surface and the structural information such as roughness, kink density etc.

Beside this structural deviation, which are described by an equivalent Hamaker-constant, the polar properties of the carbon blacks are different. Using the deviation of the experimental Henry-coefficients of argon and nitrogen, a mean charge of $1.1 \times 10^{-20} \text{ C}$ and $1.48 \times 10^{-20} \text{ C}$ can be calculated on the carbon black A5741 and CXN234, respectively. The assumed increased polarity of CXN234 compared with A5741 from the TGA-MS results are confirmed and can be quantified. If the equivalent Hamaker-constant derived from Argon adsorption isotherm and the charges of $1.1 \times 10^{-20} \text{ C}$ and $1.48 \times 10^{-20} \text{ C}$ are used, respectively, Henry-coefficients of $6.49 \times 10^{-11} \text{ mol Pa}^{-1} \text{ m}^{-2}$ and $1.81 \times 10^{-10} \text{ mol Pa}^{-1} \text{ m}^{-2}$ can be calculated for CO_2 , again in very good agreement with the experimentally determined values given in Table 3.

To summarize, the analyzed carbon blacks that show a similar behavior in low temperature nitrogen adsorption can be clearly distinguished by adsorption in the Henry region. Because of larger Henry coefficients of argon and a lower Henry-coefficient of C_4H_{10} , the number of interacting carbon atoms with those molecules is increased or decreased, respectively, when the rough carbon blacks are compared with graphite. The increase of adsorption at these sites, e.g. by kinks or vacancies, can be qualitatively attributed to an increased roughness. Roughness, e.g. due to kinks or vacancies, is larger for the carbon black CXN234 than for A5741. Beside structural differences, the mean charge

calculated from CO₂ and N₂ adsorption is larger for CXN234, thus it is more polar.

Tab. 3. Measured Henry-coefficients of the carbon black A5741 and CXN234

H _S / mol Pa ⁻¹ m ⁻²	A5741	CXN234	deviation
Ar	2,12×10 ⁻¹²	3,76×10 ⁻¹²	1.77
N ₂	2,59×10 ⁻¹²	4,99×10 ⁻¹²	1.92
CH ₄	7,04×10 ⁻¹²	9,17×10 ⁻¹²	1.30
C ₄ H ₁₀	1,39×10 ⁻¹⁰	1,617×10 ⁻¹⁰	1.15
CO ₂	6.44×10 ⁻¹¹	1.96×10 ⁻¹⁰	3.04

4. CONCLUSION

This study discusses the use of experimentally determined Henry-coefficients of small molecules combined with statistical modeling to analyze surface roughness and polarity of solid carbon systems. By an approach using only intrinsic physical data of the pure interacting partners, the adsorption of nonpolar molecules on graphite can be described by the equation derived by Maurer. Thus graphite is used as model system. Polar molecules like CO₂ are properly described, if quadrupole interactions are included. Polarity expressed as a mean charge of adsorption sites can be detected, if corresponding molecules, e.g. nitrogen or CO₂, are used as probes. It was shown that adsorption in the Henry region is very sensitive to analyze the surface properties. Structural variations effect a huge increase of the interaction potential of small molecules like Argon. These structural variation can be described by an equivalent Hamaker-constant. Compared with a plane surface, a larger equivalent Hamaker-constant is observed when more carbon atoms interact with the probe molecule. Two industrial carbon blacks which show similar behavior at low temperature nitrogen adsorption can be distinguished clearly by our approach. Because of the larger Henry-coefficient of CO₂, the surface of the carbon black CXN234 has stronger or more polar groups and because of the larger Henry of Ar and CH₄ the surface is rougher than the surface of the carbon black A5741. These conclusions from Henry-adsorption are confirmed by TGA-MS results, the amount of desorbed water is two times larger on the CXN234 than on the A5741. Moreover, the fractal dimension of the CXN234 is larger than of the A5741.

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