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Prediction of single component adsorption isotherms on microporous adsorbents

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Abstract The adsorption of gases on microporous solids is a fundamental physical interaction which occurs in many technical processes, e.g. the heterogeneous catalysis or the purification of gases. In this context the adsorption equilibrium can determine the velocity and/or the capacity of the process. Therefore, it has to be known for designing purposes. The aim of this work has been the a priori prediction of the adsorption equilibria of arbitrary gases on microporous solids like zeolites and active carbon based only on the molecular properties of the adsorptive and the adsorbent. The adsorption isotherm is described completely from the Henry region over the transition zone to the saturation region. The quality of the model permits a first approximation of the planned process without further experimental effort.

Keywords Henry coefficient · Zeolite · Active carbon · Hamaker constant · Interaction energy · Refractive index · Adsorption isotherm · Microporous adsorbents

Abbreviations

A	Dimensionless interaction parameter
$C_{i,j}$	Interaction constant in J m^6
E	Potential energy between two molecules or atoms in J
Ha	Hamaker constant in J
He	Henry coefficient in mol/(kg Pa)
IL	Initial or Henry loading
IP	Interaction parameter
$M_{adsorptive}$	Molar mass of the adsorptive in kg/mol
N_A	Avogadro constant
Q	Quadrupole moment in Cm^2
R	Universal gas constant = 8.3143 J/(K mol)
Rm	Molar refraction in m^3/mol
S_{BET}	BET surface in m^2/kg
T	Temperature in K
T_{ads}	Adsorption temperature in K
T_b	Normal boiling temperature in K
T_c	Critical Temperature in K
e	Charge of an electron = 1.60×10^{-19} C
h	Planck's constant = 6.6256×10^{-34} J s
k	Boltzmann constant = 1.3804×10^{-23} J/K
m	Mass in kg
m_e	Mass of an electron = 9.11×10^{-31} kg
n	Loading in mol/kg
n	Refractive index
n_a	Number of atoms in the solid molecule
p	Pressure in Pa
p_{ads}	Adsorption pressure at equilibrium in Pa
p_c	Critical pressure in Pa
q	Charge in C
r	Distance in m
s	Number of electron bondings per solid atom
$s_{cations}$	Number of positive charged cations per solid atom
v_b	Molar volume at the normal boiling point in m^3/mol
v_c	Critical volume in cm^3/mol
v_{micro}	Micropore volume in m^3/kg
v_{solid}	Specific volume in m^3/kg
v_{vdW}	van der Waals volume in m^3/mol
x	Stoichiometric coefficient

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x	Reduced distance
z	Distance in m

Greek symbols

Φ	Interaction potential of an adsorptive molecule with the solid continuum in J
α	Polarisability in $(\mathrm{C}^2\,\mathrm{m}^2)/\mathrm{J}$
α'	Polarisability volume in m^3
β	London constant in $\mathrm{J\,m}^6$
β	Molar volume in $\mathrm{m}^3/\mathrm{mol}$
ε	Porosity
ε_0	Permittivity of free space $= 8.854 \times 10^{-12}$ C/(Vm)
ε_r	Relative permittivity
φ	Porosity
μ	Chemical potential in J
μ	Dipole moment in Cm (1 debye $= 3.34 \times 10^{-30}$ C m)
ν_0	Frequency of the electron in the ground state in 1/s
ρ_{app}	Apparent density in $\mathrm{kg/m}^3$
ρ_b	Bulk density in $\mathrm{kg/m}^3$
$\rho_{j,at}$	Number density of atoms in $1/\mathrm{m}^3$
σ	van der Waals diameter in m

1 Introduction

The main objective of this work has been the theoretical prediction of adsorption equilibria of single gaseous substances on microporous solids like active carbon or zeolites (e.g. MS4A, MS5A, NaX and NaY). A novel equilibrium model was derived from a differential equation considering two boundary conditions. These boundaries are the Henry coefficient for diluted gases and the saturation loading for highly pressurized gases.

The Henry coefficient which describes the adsorption isotherm of diluted gases depends on the properties of both the gaseous (adsorptive) and the solid (adsorbent) phase. However, the key parameter of the intermolecular interaction forces, the Hamaker constant, is unknown for most zeolites. Therefore, an approximated Hamaker and de Boer model for predicting the Hamaker constant of microporous solids was developed on the basis of the refractive index of the solid continuum. The refractive index was determined by the Clausius-Mosotti relationship between the relevant optical and density parameters of the solid adsorbent. For zeolitic adsorbents, the optical parameters can be derived from the polarisability of ions in the zeolite crystal.

Henry coefficients of adsorption have been a priori calculated based on gas and solid properties of the molecules. In the case of nonpolar gas–nonpolar solid, polar gas–nonpolar solid and nonpolar gas–polar solid an analytical equation was introduced to directly calculate the Henry coefficients. This approach was expanded to the fourth case of polar gas–polar solid so that the whole spectrum of possibilities is covered. A novel model for predicting the complete adsorption isotherm based only on molecular properties has been introduced. The model has been verified with own experimental and literature data.

2 Experimental techniques

2.1 Instrumentation

The adsorption equilibrium isotherms were measured at the Lehrstuhl für Technische Chemie 2 of the Technische Universität München gravimetrically in a modified SETARAM TG-DSC 111 microbalance which is able to measure differences in mass down to 10^{-6} g which is also the accuracy. The sample weight in the microbalance was applied between 13 to 22 mg in order to record precise measurement and better signal-to-noise ratio. The pressure inside the system can be reduced down to 10^{-7} mbar with a Pfeiffer turbo molecular pump and the temperatures can be applied within the range of 25 °C to 750 °C with an accuracy of 0.15 K. The high vacuum was measured with a Pfeiffer TPG 300 pressure transducer. The experiments were carried out in the pressure range from 10^{-3} to 13 mbar (0.1 Pa to 1300 Pa), measured with a BARATRON 122 A pressure transducer. The transducer has an accuracy of 0.5% of reading. For activation, the solid samples were heated in vacuum ($p < 10^{-6}$ mbar) to 500 °C with 10 K/min and held 4 h at 500 °C. After activation, the temperature was reduced to ca. 45 °C. The liquid sorbates were added in pulses to the high vacuum system in which they vaporised. After each pulse the system was equilibrated. This was monitored by observation of the sample weight and pressure. The system was regarded to be in steady state or equilibrium, when changes in any of the parameters pressure, mass or heating flux were not observed any more.

The data for the adsorption isotherms were calculated by the following method: The adsorbents were hold by a crucible in the microbalance. Its mass after activating is the blank mass m_0. The mass of the crucible with activated adsorbent is the mass m_1. After equilibrium of the injected adsorptive with the adsorbent the new absolute mass m_{i+1} was measured. So the equilibrium loading n_{i+1} of every adsorption step with its equilibrium pressure can be calculated by

$$n_{i+1} = \frac{m_{i+1} - m_1}{m_0} \frac{1}{M_{adsorptive}} \quad \text{for } i > 1 \tag{1}$$

where the masses are in kg and $M_{adsorptive}$ is the molar mass of the adsorptive in kg/mol. With (1) the equilibrium loading n in mol/kg regarding to the equilibrium pressure p in

Pa was obtained. BET surface measurements of the adsorbents were conducted with nitrogen at 77 K. The micropore volume of the adsorbents were derived from *t*-plot analysis.

2.2 Materials

The zeolites MS5A and NaX were from Grace Davison. MS5A has the trade name Sylobead®MS C 522 and NaX (13X) the trade name Sylobead®MS C 544. The adsorbent NaY was from Akzo Nobel.

3 Calculations

3.1 Refractive index of microporous solids

The refractive index is an important parameter describing the optical properties of solid materials. In general it is difficult to obtain a quantitative relation between the refractive index and the structure as well as composition of materials. It seems that the refractive index is dependent on atomic parameters like mass, radius and electric charge of the ions constituting the material (Zundu and Yidong 2004). According to classical dielectric theory, the refractive index depends on the density and on the polarisability of the atoms in a given material (Marler 1988). The polarisability of a microporous adsorbent determines its disperse properties and, thus, it is possible to calculate the *Hamaker* constant from knowledge of the refractive index (Van der Hoeven 1991). In this study the Clausius-Mosotti equation is used for further investigations because by applying this approach the refractive index of structures like aluminosilicates can be calculated a priori from knowledge of the properties of the solid. By inserting the Maxwell condition

$$\varepsilon_r = n^2 \tag{2}$$

for non ferromagnetic materials like zeolites into the Clausius-Mosotti equation the Lorenz-Lorentz relationship is obtained:

$$\frac{N_A \alpha}{3\varepsilon_0} = \frac{M}{\rho_{app}} \frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)}. \tag{3}$$

From (3) a formulation can be derived to calculate the refractive index of solids like zeolites. Therefore, either the polarisability of the adsorbent or the left side of (3) has to be known. This left side is also defined as the molar refractivity R_m. The refractive index of the solid is then

$$n = \sqrt{\frac{1 + 2\frac{R_m \rho_{app}}{M}}{1 - \frac{R_m \rho_{app}}{M}}}. \tag{4}$$

The molar refraction of a molecule with the structure $A_{xA}B_{xB}$ is

$$R_m = x_A R_{m,A} + x_B R_{m,B} \tag{5}$$

where x_A and x_B are the stoichiometrical coefficients and $R_{m,A}$ and $R_{m,B}$ the ionic molar refractions of the matters A and B, respectively. In general it is

$$R_m = \sum_i x_i R_{m,i}. \tag{6}$$

The ionic molar refractivities $R_{m,i}$ can be calculated via (3) if the ionic polarisabilities α_i are known. It is therefore

$$R_{m,i} = \frac{N_A}{3\varepsilon_0} \alpha_i. \tag{7}$$

In Table 2 the polarisability volumes $\alpha_{i'}$ and the polarisabilities α_i are shown for the interesting ions of aluminosilicates (Lide 2004–2005).

3.2 Hamaker constant of microporous solids

For the characterisation of solid materials their interaction potentials with other solids or fluids are of strong interest. One of the most important parameters for describing the disperse energies of a given system is the so-called Hamaker constant of the solid. This constant is also eminent for the calculation of adsorption equilibria of gases on energetically homogeneous and heterogeneous surfaces. Hamaker constants of organics (solids and liquids) in air have magnitudes of $(6 \pm 1) \times 10^{-20}$ J and are reported to be lower than those of inorganic salts ($(9 \pm 3) \times 10^{-20}$ J) which are again lower than those of metal oxides ($(13 \pm 4) \times 10^{-20}$ J) (Van der Hoeven 1991). Active carbon has a Hamaker constant $Ha_{ac} = 6 \times 10^{-20}$ J (Maurer 2000).

The Hamaker–de Boer microscopic approach is based on the equation

$$Ha = \pi^2 \rho_{j,at}^2 \beta \tag{8}$$

where $\rho_{j,at}$ is the number density of solid atoms in $1/\mathrm{m}^3$ and β the London constant in J m^6 (Hamaker 1937). This approach is strictly speaking valid only for monoatomic solids. If the Hamaker constant of multiatomic solids is calculated their chemical structure has to be considered. The proposed route is based on a subdivision of the solid molecule into atoms, which all have a mean concentration and polarisability. The Hamaker constant is then calculated due to these mean polarisabilities. A second assumption is that only the valence electrons of these atoms contribute to the disperse interaction potential. So the average atoms are all bonded by semi-polar bonds and only the bond-forming electrons contribute to the higher energetic waves (Van der Hoeven 1991)

Table 1 Properties of zeolites in experimental work

Adsorbent	NaY	MS5A	NaX
S_{BET} in m^2/kg	655400	464100	522000
v_{micro} in 10^{-3} m^3/kg	0.272	0.232	0.264
ρ_b in kg/m^3 (Kast 1998)	650	700	675
ε_b (Kast 1998)	0.6	0.6	0.6
ρ_{app} in kg/m^3, $\rho_{app} = \rho_b/\varepsilon_b$	1100	1166	1125
Refractive index n	1.61	1.58	1.63
Chemical structure (Kast 1998)	Na56(AlO2)56 (SiO2)106	Ca5Na2 (AlO2)12 (SiO2)12	Na86(AlO2)86 (SiO2)106
Effective pore opening in m, (Kast 1998)	10×10^{-10}	5×10^{-10}	10×10^{-10}
Van-der-Waals diameter σ_j in m	4.2×10^{-10}	3.8×10^{-10}	3.9×10^{-10}
Number density of atoms $\rho_{j,at}$ in $1/m^3$	3.28×10^{28}	3.31×10^{28}	3.72×10^{28}

Table 2 Properties of ions

Ion	Polarisability volume in 10^{-30} m^3	Polarisability in 10^{-40} $(C^2\,m^2)/J$	Ionic molar refraction in 10^{-6} m^3/mol
Na^+	0.1790	0.1991	0.4515
Ca^{2+}	0.4700	0.5229	1.1857
Si^{4+}	0.0165	0.0183	0.0416
Al^{3+}	0.0520	0.0578	0.1311
K^+	0.8300	0.9235	2.0938
O^{2-}	3.8800	4.3171	9.7881

for calculating the Hamaker constant. The number density can be calculated via

$$\rho_{j,at} = n_a \frac{N_A \rho_{app}}{M} \tag{9}$$

where n_a is the number of atoms in the molecule. M denotes the relative atomic mass related to the same solid molecule with which the number of atoms is calculated (see Table 1).

In 1931 Slater and Kirkwood derived an equation for the calculation of the London constant β (Slater and Kirkwood 1931). Van-der-Hoeven modified this equation by introducing an atomic polarisability. The London constant for macro bodies like zeolites can be calculated by

$$\beta_j = \frac{3}{4}\sqrt{s}\, h \nu_0 \left(\frac{\alpha_j}{4\pi\varepsilon_0}\right)^2. \tag{10}$$

The letter s represents the number of electron bondings per atom. It is obtained simply from the summation of the single and double bond forming electrons involved in atomic bonding, divided by the number of atoms in the molecule. The parameter s is only reasonable for the calculation of the Hamaker constant and London dispersion potential, respectively. Later this potential will be introduced as the induced dipole–induced dipole interaction energy.

For example, for zeolite MS5A ($Ca_5Na_2((AlO_2)_{12}(SiO_2)_{12})$) the total number of atoms in the molecule is 79. The number of valence electrons is for calcium $5 \times 2 = 10$, for sodium $2 \times 1 = 2$, for aluminium $12 \times 3 = 36$, for silicon $12 \times 4 = 48$ and for oxygen $48 \times 6 = 288$, altogether 384 valence electrons. The number of electron bondings is then 192. It follows $s_{\mathrm{MS5A}} = 2.43$.

The polarisability α_j of the solid atoms can be calculated from the refractive index using the Lorenz-Lorentz equation. The variable ν_0 is the frequency of the electron in the ground state in 1/s.

$$\nu_0 = \frac{e}{2\pi\sqrt{m_e}} \frac{1}{\sqrt{\alpha_j}} \tag{11}$$

where e is the charge and m_e the mass of an electron. With known or calculated values of the refractive index n, the apparent density ρ_{app}, the molar mass M and the chemical structure of the solid the Hamaker constant for zeolites can be calculated. For MS5A it is $Ha_{\mathrm{MS5A}} = 7.66 \times 10^{-20}$ J (Akgün 2007).

3.3 Henry coefficient of microporous adsorbents

In the following considerations for determining the Henry coefficient one assumption is that the interactions between the adsorbate molecules are negligible. The physical cause for this is the low concentration or partial pressure of the adsorbate molecules in the Henry region, so that they do not interact with each other but only with the solid surface. A second assumption is that the solid elements do not have a permanent dipole or quadrupole moment. In equilibrium state the chemical potentials μ of the two phases of adsorptive and adsorbate are equal. The adsorptive behaves like an ideal gas in the Henry region with its low pressure. The adsorptives' chemical potential is defined as

$$\begin{aligned}\mu_{adsorptive}(T,p)\\ &= \mu_{adsorptive}(T_{ads},p_{ref}) + kT_{ads}\ln\left(\frac{p_{ads}}{p_{ref}}\right)\end{aligned} \tag{12}$$

where p_{ref} is the reference pressure, $\mu_{adsorptive}(T_{ads},p_{ref})$ the reference chemical potential of the adsorptive and k the Boltzmann constant. The second term is the correction from pressure p_{ref} to the adsorption equilibrium pressure of the gas p_{ads}. The chemical potential of the adsorbate can be expressed as

$$\begin{aligned}\mu_{adsorbate}(T,p)\\ &= \mu_{adsorbate}(T_{ads},p_{ref})\\ &\quad + kT_{ads}\ln\left(\frac{p_{ads}+dp_{adsorbate}}{p_{ref}}\right) + \sum \Phi_{gas-solid}\end{aligned} \tag{13}$$

where $\mu_{adsorbate}(T_{ads},p_{ref})$ is the reference chemical potential of the adsorbate and $dp_{adsorbate}$ is the difference pressure which acts additionally to the adsorbate layer. The second term is therefore also a correction from the reference pressure to the overall pressure of the adsorbate. The third term takes into account the sum of interactions between the adsorbate and the solid. With the equality of the chemical potentials (12) and (13) and assuming that the adsorbate behaves like an ideal gas it follows

$$\begin{aligned}kT_{ads}\ln\left(\frac{p_{ads}}{p_{ref}}\right)\\ &= kT_{ads}\ln\left(\frac{p_{ads}+\frac{\Re T_{ads}dn}{dv_{solid}}}{p_{ref}}\right) + \sum \Phi_{gas-solid}\end{aligned} \tag{14}$$

where dv_{solid} is the specific volume element of the solid. It follows with the Henry law that

$$\begin{aligned}He &= \frac{n}{p}\\ &= \frac{1}{\Re T_{ads}}\int_{v_{solid}=0}^{v_{solid}}\left[\exp\left(\frac{-\sum \Phi_{gas-solid}}{kT_{ads}}\right)-1\right]dv_{solid}.\end{aligned} \tag{15}$$

The specific volume element of the solid can be expressed with its specific surface S_{BET} and the perpendicular distance z of the gas molecules from the surface:

$$dv_{solid} = S_{BET}dz. \tag{16}$$

With (15) it follows the well known equation for the Henry coefficient expanded with the overall interaction terms:

$$He = \frac{S_{BET}}{\Re T_{ads}}\int_0^{z_{\max}}\left[\exp\left(\frac{-\sum \Phi_{gas-solid}}{kT_{ads}}\right)-1\right]dz. \tag{17}$$

The integration constant z_{max} depends on the structure of the solid. For massive solids z_{max} is infinity, for porous solids it depends on the pore volume (Mersmann et al. 2002).

3.3.1 Henry coefficient of energetic homogeneous adsorbents

A special case of (17) is the adsorption of arbitrary gases on energetic homogeneous adsorbents like silicalite-1. For this case Maurer derived the potential function for the interaction energy $\Phi_{indind}(Z)$ which depends on the critical properties of the adsorptive and the solid properties of the adsorbent. The Henry coefficient reduces in this case to:

$$He = \frac{S_{BET}}{\Re T_{ads}}\int_0^{z_{\max}}\left[\exp\left(\frac{-\Phi_{indind}(z)}{kT_{ads}}\right)-1\right]dz. \tag{18}$$

It is referred to the literature for the derivation of the interaction energy $\Phi_{indind}(z)$ (Maurer 2000; Mersmann et al. 2005). For consistency the main formulars shall be mentioned in this work with

$$\phi_{indind}(z) = -\frac{4\pi C_{i,j}\rho_{j,app}}{3(\sigma_{i,j}+z)^3} \tag{19}$$

where $C_{i,j}$ is an interaction constant between the adsorbate molecule and the solid atoms, $\sigma_{i,j}$ the minimum contact distance between the adsorption participants and $\rho_{j,app}$ the apparent density of the solid. The minimum distance $\sigma_{i,j}$ is calculated by the arithmetic mean of the van-der-Waals diameters of the adsorbate and the solid molecules with

$$\sigma_{i,j} = \frac{1}{2}(\sigma_{i,i}+\sigma_{j,j}). \tag{20}$$

Maurer derived the van-der-Waals diameter of the adsorptive from its critical properties. It is

$$\sigma_{i,i} = \sqrt[3]{\frac{3kT_c}{16\pi p_c}} \tag{21}$$

where T_c and p_c are the critical temperature and critical pressure, respectively. The van-der-Waals diameter of the solid can be found in the literature (Akgün 2007; Maurer 2000).

The interaction constant itself can be formulated as

$$C_{i,j}=\frac{9\Re\sigma_{i,j}^3}{16\rho_i N_A}\sqrt{\frac{2Ha_j}{\pi^3\sigma_{j,j}^3}}\,\frac{T_c}{\sqrt{p_c}} \tag{22}$$

where Ha_j is the Hamaker constant of the solid.

It is now possible to formulate a dimensionless function for the Henry curve considering only London dispersion forces (Hamaker dominant). It is based on the advancement of the Henry function formulated by (18) in the case of energetic homogeneous adsorbents. Equation (18) can be rearranged to

$$\frac{He\Re T_{ads}}{S_{BET}\sigma_{i,j}}=\int_0^{\frac{z_{\max}}{\sigma_{i,j}}}\left[\exp\left(\frac{3}{4(1+(\frac{z}{\sigma_{i,j}}))^3}\sqrt{\frac{2Ha_j}{\pi\sigma_{j,j}^3 p_c}}\,\frac{T_c}{T_{ads}}\right)-1\right]d\left(\frac{z}{\sigma_{i,j}}\right). \tag{23}$$

Both sides of (23) are now dimensionless. The left side is defined by Mersmann et al. as the dimensionless Initial or Henry Loading IL with

$$IL\equiv\frac{He\Re T_{ads}}{S_{BET}\sigma_{i,j}} \tag{24}$$

which is mainly a function of the Interaction Parameter IP or $A_{indind}\equiv 3/4IP$ with

$$IP\equiv\frac{T_c}{T_{ads}}\sqrt{\frac{2Ha_j}{\pi\sigma_{j,j}^3 p_c}}=\frac{4}{3}A_{indind} \tag{25}$$

(see (49)) and the variable

$$x\equiv\frac{z}{\sigma_{i,j}}. \tag{26}$$

The dimensionless Henry function can then be expressed as

$$IL=\int_0^{x_{\max}}\left[\exp\left(\frac{3}{4\,(1+x)^3}IP\right)-1\right]dx. \tag{27}$$

This integral cannot be solved analytically but only numerically. Therefore the numerical values are approximated by the function

$$IL=\exp(p_1 IP^{p_2}) \tag{28}$$

where p_1 and p_2 are parameters adjusted to the real numerical values of the integral (27). The adjustment was performed by the numerical software Maple. For the two cases the parameter values $p_1=0.3312917$ and $p_2=1.1803227$ for $x_{\max}=0.9$ and $p_1=0.3312936$ and $p_2=1.1803211$ for $x_{\max}=2.0$ were obtained. The two parameter sets do not differ significantly. For this work the second set was chosen. In Fig. 1 the exponential function (28) with the second set is shown and compared with the numerical values. The regression curve goes through the thermodynamic consistent point (0/1) (Mersmann et al. 2002). This function does not cover only the adsorption behaviour of energetic homogeneous adsorbents like silicalite-1 but also the case of non-polar adsorbents paired with energetic heterogeneous adsorbents like zeolites. This is a very new aspect derived for the first time in this work.

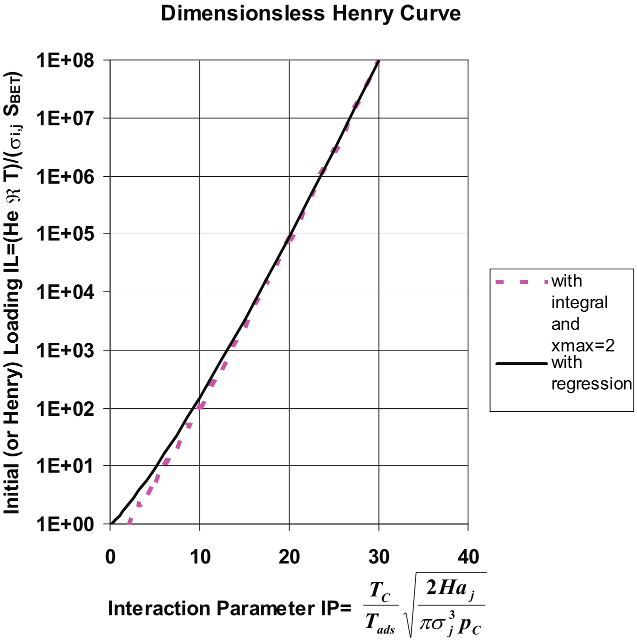


Fig. 1 Dimensionless Henry curve

3.3.2 *Henry coefficient of energetic heterogeneous adsorbents*

In order to calculate the Henry coefficient for the adsorption of polar gases on energetic heterogeneous adsorbents like zeolites it is necessary to take into account all the possible interaction potentials between the adsorbate and the solid atoms (see (17)). In this section analytical functions for those potentials are derived.

3.3.2.1 Induced dipole gas–electrical charge solid interaction (indcha) The potential energy E_{indcha} between two molecules or atoms, of which one is polarisible and the other one possesses an electrical charge, can be described by (Hirschfelder et al. 1964)

$$E_{indcha}(r)=-\frac{1}{2}\frac{\alpha_i q_j^2}{r^4\,(4\pi\varepsilon_0\varepsilon_r)^2} \tag{29}$$

where α_i is the polarisability of the gas molecule in $(\mathrm{C}^2\,\mathrm{m}^2)/\mathrm{J}$, q_j the effective charge of the atom of the solid in C, ε_0 the permittivity of free space $=8.854\times$

10^{-12} C/(V m), ε_r the relative permittivity of the adsorbent and r the distance between the centre of the molecules in m. For calculation of the relative permittivity of microporous adsorbents the porosity of the solid has to be taken into account. It is assumed that

$$\varepsilon_r = \varphi \cdot 1 + (1-\varphi) \cdot n^2 \tag{30}$$

where φ is the porosity and n the refractive index of the solid. From a summation of all pair potentials it follows the interaction potential of the gas molecule with the whole solid continuum. In general it is (Israelachvili 1991)

$$\Phi = \int_{\sigma}^{\infty} E(r)\rho_{j,at} 4\pi r^2 dr. \tag{31}$$

In this work the following general description of the interaction potentials was chosen:

$$\Phi = \int_{\sigma_{i,j}+z}^{\infty} E(r)\rho_{j,at} 4\pi r^2 dr. \tag{32}$$

The lower integration limit of (31) was substituted by $(\sigma_{i,j} + z)$ because the minimum distance between the molecules is $\sigma_{i,j}$, also known as the minimum van-der-Waals contact distance.

The average number of positive charged cations $s_{cations}$ per solid atom is introduced as

$$s_{cations} = \frac{n_c}{n_a} \tag{33}$$

where n_c is the number of positive charges and n_a the number of atoms in the solid molecule. It follows for the effective charge that

$$q_j = s_{cations} e. \tag{34}$$

The reduced interaction energy Φ_{indcha} is then due to the above equations

$$\frac{\Phi_{indcha}(x)}{kT_{ads}} = -\frac{1}{8}\frac{\alpha_i s_{cations}^2 e^2 \rho_{j,at}}{\pi\varepsilon_0^2\varepsilon_r^2(kT_{ads})} \times \frac{1}{\sigma_{i,j}}\frac{1}{(x+1)}. \tag{35}$$

The dimensionless interaction parameter for the actual case is then defined as

$$A_{indcha} = \frac{\alpha_i s_{cations}^2 e^2 \rho_{j,at}}{8\pi\varepsilon_0^2\varepsilon_r^2 (kT_{ads})\sigma_{i,j}}. \tag{36}$$

3.3.2.2 Permanent dipole gas–induced dipole solid interaction (dipind) Gas molecules can have a permanent dipole when the centers of different charge of the molecule do not coincide in one point. For example, trifluormethane CHF_3 has a dipole moment of 1.6 debye or 5.344×10^{-30} C m. Permanent dipoles induce a dipole in the attraction partner if this partner is polarisible. The potential attraction energy between two molecules is (Israelachvili 1991):

$$E_{dipind}(r) = -\frac{\mu_i^2\alpha_j}{r^6(4\pi\varepsilon_0\varepsilon_r)^2} \tag{37}$$

where μ_i is the dipole moment of the gas molecule in Cm. In the following it is assumed that the solid atoms are induced from the polar gas molecules but do not have a permanent dipole themselves. The reduced interaction energy of one polar gas molecule with the whole solid continuum is therefore

$$\frac{\Phi_{dipind}(x)}{kT_{ads}} = -\frac{\mu_i^2\alpha_j\rho_{j,at}}{12\cdot\pi\varepsilon_0^2\varepsilon_r^2 kT_{ads}}\frac{1}{\sigma_{i,j}^3}\frac{1}{(1+x)^3}. \tag{38}$$

The dimensionless interaction parameter A_{dipind} is then

$$A_{dipind} = \frac{\mu_i^2\alpha_j\rho_{j,at}}{12\cdot\pi\varepsilon_0^2\varepsilon_r^2(kT_{ads})\sigma_{i,j}^3}. \tag{39}$$

3.3.2.3 Permanent dipole gas–electrical charge solid interaction (dipcha) This interaction type is dominant for highly polar adsorptives like trifluormethane (CHF_3), ammonia (NH_3) and methanol (CH_3OH). The potential attractive energy of a permanent dipole with a charged atom is quantified (Hirschfelder et al. 1964) with

$$E_{dipcha}(r) = -\frac{1}{3kT_{ads}}\frac{\mu_i^2 q_j^2}{r^4(4\pi\varepsilon_0\varepsilon_r)^2} \tag{40}$$

with already known parameters. The summation of the potential energy over the whole solid yields after integration and dividing by the energy unit (kT_{ads}) and introducing the dimensionless variable x:

$$\frac{\Phi_{dipcha}(x)}{kT_{ads}} = -\frac{\mu_i^2 s_{cations}^2 e^2\rho_{j,at}}{12\cdot\pi\varepsilon_0^2\varepsilon_r^2(kT_{ads})^2} \times \frac{1}{\sigma_{i,j}}\frac{1}{(1+x)}. \tag{41}$$

Then the dimensionless interaction parameter A_{dipcha} can be defined as

$$A_{dipcha} = \frac{\mu_i^2 s_{cations}^2 e^2\rho_{j,at}}{12\cdot\pi\varepsilon_0^2\varepsilon_r^2(kT_{ads})^2\sigma_{i,j}}. \tag{42}$$

3.3.2.4 Quadrupole moment gas–induced dipole solid interaction (quadind) The quadrupole moment Q_i is a fundamental property for the description of the molecular charge distribution. In the theory of electricity there are two signs of electric charge. The net total charge is the monopole moment. If there are charges of two signs separated, then there exists a dipole moment along the line connecting the charges. If there are charges of both signs, but separated in a more complicated way, an electric quadrupole may be present. The quadrupole moment gives an indication of the derivation of the charge distribution of the adsorptive from spherical symmetry.

For gases with strong quadrupole moments like CO_2 or C_2H_4 the previous potential phenomena are not sufficient to describe their great adsorption effect in the Henry region particularly because their permanent dipole is small or even zero in the case of benzene or C_2H_4. The cause is that the quadrupole moment can also induce a dipole moment on the solid atoms or can interact with electrical charges of the adsorbent. For two molecules of which one has a quadrupole moment and the other is polarisible the potential energy is (Hirschfelder et al. 1964)

$$E_{quadind}(r) = -\frac{3}{2}\frac{Q_i^2\alpha_j}{(4\pi\varepsilon_0\varepsilon_r)^2 r^8} \tag{43}$$

where Q_i is the quadrupole moment of the adsorptive in $\mathrm{C\,m^2}$. It follows for the reduced interaction potential

$$\frac{\Phi_{quadind}(x)}{kT_{ads}} = -\frac{3}{40}\frac{Q_i^2\alpha_j\rho_{j,at}}{\pi\varepsilon_0^2\varepsilon_r^2 kT_{ads}} \times\frac{1}{\sigma_{i,j}^5}\frac{1}{(1+x)^5}. \tag{44}$$

The dimensionless interaction parameter $A_{quadind}$ can then be directly specified as

$$A_{quadind} = \frac{3}{40}\frac{Q_i^2\alpha_j\rho_{j,at}}{\pi\varepsilon_0^2\varepsilon_r^2(kT_{ads})\sigma_{i,j}^5}. \tag{45}$$

3.3.2.5 Quadrupole moment gas–electrical charge solid interaction (quadcha) This potential is in the same order of magnitude as the permanent dipole–electrical charge interaction. The potential energy between two molecules with a quadrupole moment and an electrical charge is (Israelachvili 1991)

$$E_{quadcha}(r) = -\frac{1}{20kT_{ads}}\frac{Q_i^2 q_j^2}{(4\pi\varepsilon_0\varepsilon_r)^2 r^6}. \tag{46}$$

It follows for the reduced interaction potential

$$\frac{\Phi_{quadcha}(x)}{kT_{ads}} = -\frac{1}{240}\frac{Q_i^2 s_{cations}^2 e^2\rho_{j,at}}{\pi\varepsilon_0^2\varepsilon_r^2(kT_{ads})^2} \times\frac{1}{\sigma_{i,j}^3}\frac{1}{(1+x)^3}. \tag{47}$$

The dimensionless interaction parameter $A_{quadcha}$ is then

$$A_{quadcha} = \frac{Q_i^2 s_{cations}^2 e^2\rho_{j,at}}{240\pi\varepsilon_0^2\varepsilon_r^2(kT_{ads})^2\sigma_{i,j}^3}. \tag{48}$$

3.3.3 The general Henry equation

Inserting the interaction parameters into (17) leads to the general Henry equation:

$$\begin{aligned} He = {} & \frac{S_{BET}\sigma_{i,j}}{\Re T_{ads}} \\ & \times\int_0^{z_{\max}}\left[\exp\left(\frac{A_{dipcha}+A_{indcha}}{(1+x)} \right.\right. \\ & + \frac{A_{indind}+A_{dipind}+A_{quadcha}}{(1+x)^2} \\ & \left.\left. + \frac{A_{quadind}}{(1+x)^3}\right) - 1\right]dz. \end{aligned} \tag{49}$$

3.4 A priori adsorption isotherm model

In this section a new model will be introduced which enables the prediction of isotherms of Type I of the IUPAC classification from the Henry to the saturation region for Hamaker dominant adsorption pairs and for systems where the adsorptive is polar and the adsorbent is heterogeneous with respect to energy. The idea of the presented new model is that any isotherm of type I has two boundary conditions for the two variables loading n and pressure p. The first boundary condition is that in the Henry region the loading and the equilibrium pressure have a constant ratio, equal to the Henry coefficient. The second boundary condition is that in the saturation region the slope of the curve $n = f(p)$ becomes zero. With a differential equation for the variables in the intermediate range it is possible to calculate the whole adsorption isotherm mathematically.

The maximum loading n_∞ for $p \to \infty$ is given when the micropore volume of the adsorbent is completely filled with adsorbate which has the molar volume $\beta(T)$:

$$n_\infty = \frac{v_{micro}\rho_{adsorb}}{M_i} = \frac{v_{mciro}}{\beta(T)}. \tag{50}$$

It is further assumed that in the transition range between the Henry and the saturation region the Hamaker energy is dominant in comparison to other possible potentials. According to Braun (2004) and Hirschfelder et al. (1964) Hamaker potentials are long-range interactions. For the first layer of adsorbate molecules on the solid surface the electrostatic potentials have to be taken into account as done for the calculating of the Henry coefficient. In the second layer the Hamaker energy is dominant because of its long-range attraction compared to the electrostatic forces. These and further ideas discussed in (Akgün 2007; Mersmann and Akgün 2008) lead to the following differential equation:

$$\frac{d(\ln n)}{d(\ln p)} = \frac{dn}{dp}\frac{p}{n}$$

$$= \frac{1}{1 + C\frac{T_c}{T_{ads}}(\frac{Ha_j}{\sigma_j^3 p_c})^{3/2}(\frac{n/n_\infty}{1-n/n_\infty})}. \tag{51}$$

The constant $C = 0.55 \times 10^{-3}$ is based on many experimental results. The calculation of the adsorbate density, especially in the supercritical region, is afflicted with uncertainties because the physical state of an adsorbed molecule cannot be described definitely. In this work, the ratio of molar mass of the adsorbate and adsorbate density is calculated by the molar volume of the adsorbate $\beta(T)$ which depends on the adsorption temperature T_{ads}. The molar volume is inter- and extrapolated between the molar volume of the adsorptive molecule at the normal boiling point v_b and the van-der-Waals volume v_{vdW} (Sievers 1993). It is

$$\frac{M_i}{\rho_{adsorb}} = \beta(T_{ads}) = v_b + \left(\frac{T_{ads} - T_b}{T_c - T_b}\right)(v_{vdW} - v_b) \tag{52}$$

where T_b is the normal boiling temperature of the adsorptive. T_b and the normal molar volume of the adsorptive v_b are tabulated for many cases in the literature (Read et al. 1988). For any other case the normal molar volume in $\mathrm{m}^3/\mathrm{mol}$ can be calculated by the following equation (Sievers 1993):

$$v_b = 0.285 \times 10^{-6} \times v_c^{1.048} \tag{53}$$

where v_c is the critical volume of the adsorptive in $\mathrm{cm}^3/\mathrm{mol}$.

With the definition

$$B = C\frac{T_c}{T_{ads}}\left(\frac{Ha_j}{\sigma_j^3 p_c}\right)^{3/2} \tag{54}$$

(51) can be integrated to the adsorption isotherm

$$p = \frac{n}{He}\left(\frac{1}{1 - \frac{n}{n_\infty}}\right)^B \tag{55}$$

if the integration constant is understood as the Henry coefficient.

4 Results

In order to test the validity and the accuracy of the new model the Henry coefficients were calculated for several adsorption cases of gases on zeolites and compared with values from own experiments and literature in the ranges $23\ \mathrm{K} < T_{ads} < 623\ \mathrm{K}$ and $1\ \mathrm{Pa} < p < 10^7\ \mathrm{Pa}$. As example Figs. 2 and 3 show Henry coefficients of zeolite MS4A with the adsorptives ammonia, carbon dioxide, carbon monoxide, methane, propane, hexane, helium, nitrogen, oxygen and benzene on zeolite MS4A. In Fig. 2 the theoretical Henry coefficients were calculated on basis of the induced dipole-induced dipole potential only.

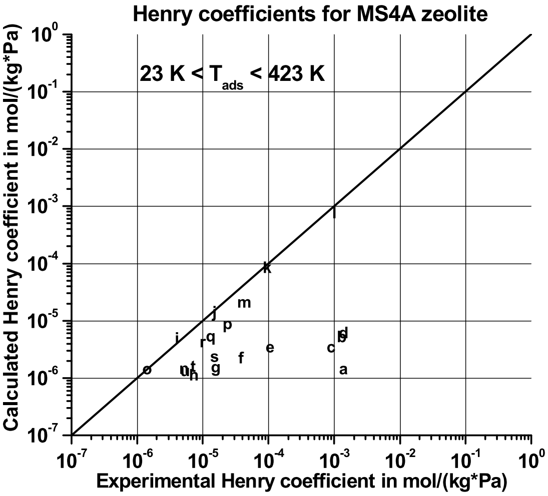


Fig. 2 Henry coefficient prediction based only on induced dipole–induced dipole interactions

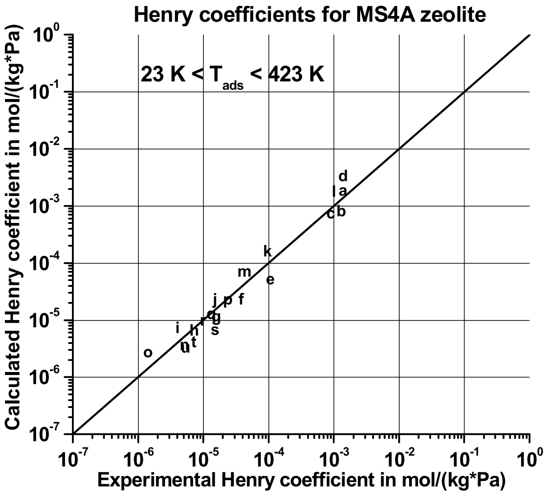


Fig. 3 Henry coefficient prediction based on all interactions

In Fig. 3 all potentials are taken into account as described previously.

The prediction works very well as can be seen in Figs. 2 and 3. The tested adsorptives cover different types of molecules with different polar properties. Noble gases like helium have no dipole moment, no quadrupole moment and small polarisabilities. Alkanes like methane, propane and hexane have no dipole moment, small quadrupole moments and intermediate polarisabilities. Carbon monoxide and carbon dioxide have small and medium dipole moments, respectively, large quadrupole moments and small polarisabilities. $\mathrm{NH_3}$ has a relative big dipole moment of 1.5 debye, a big quadrupole moment of $8.67 \times 10^{-40}\ \mathrm{C\,m^2}$ but only a small polarisability of $3.13 \times 10^{-40}\ \mathrm{C^2\,m^2/J}$.

In Fig. 4 the prediction of isotherms for active carbon coal is shown. It is assumed that activated carbon is not

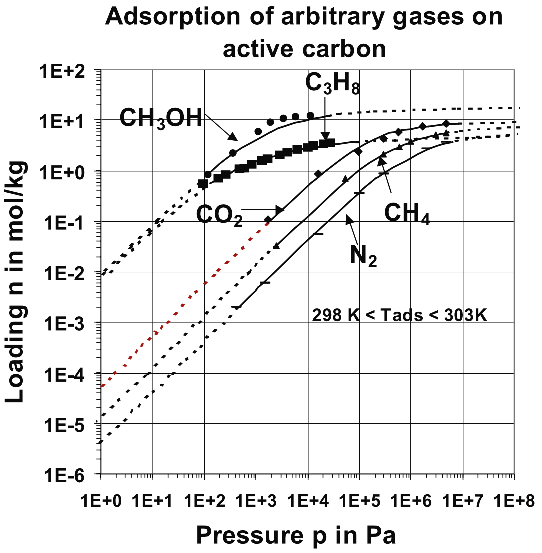


Fig. 4 Experimental and predicted adsorption isotherms of active carbon coal. Experimental data are for nitrogen (303.15 K, –), methane (303.15 K, ▲), carbon dioxide (303.15 K, ♦), propane (298 K, ■) and methanol (298.15 K, •), –, - - calculated

charged electrically ($q_j = 0$) with the consequence that the interactions indcha, dipcha and quadcha are zero. A comparison of calculated loadings with experimental data has shown that the equilibrium of arbitrary gases on active carbon is mostly dominated by the inind-interaction. The dipind- and quadind-interactions play a minor role. Therefore, activated carbon can be considered to be energetically homogeneous to a certain degree.

Figure 5 shows the adsorption of nonpolar adsorptives on zeolites NaX, NaY and MS5A. The new model is very successful also in predicting adsorption isotherms in the case of nonpolar gases and energetic heterogeneous adsorbents. It has to be mentioned that the success of the model depends strongly on reliable data of the Hamaker energy, the BET surface and the micropore volume of the adsorbent.

Figures 6 and 7 show the adsorption of permanent dipole dominant adsorptives and of quadrupole dominant adsorptives respectively. Methanol and ammonia are adsorptives with strong dipole moments but rather small polarisabilities. Furthermore the quadrupole moment of ammonia is very high. Especially methanol is an adsorptive which offers the possibility to test the validity of the model. The adsorptives ethene and carbon dioxide are characterised by strong quadrupole moments but zero (ethene) or moderate (carbon dioxide) dipole moments and rather moderate polarisabilites.

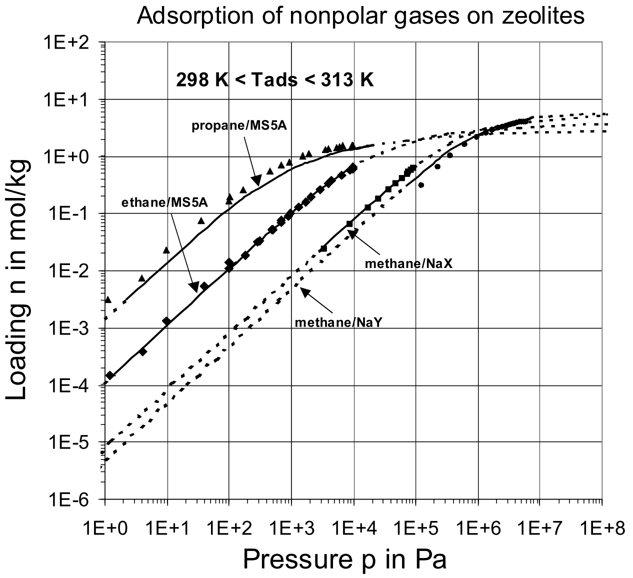


Fig. 5 Experimental and predicted adsorption isotherms of zeolites. Experimental data are for methane/NaY (298 K, •), methane/NaX (304.5 K, ■), ethane/MS5A (313 K, ♦) and propane/MS5A (313 K, ▲). –, - - calculated

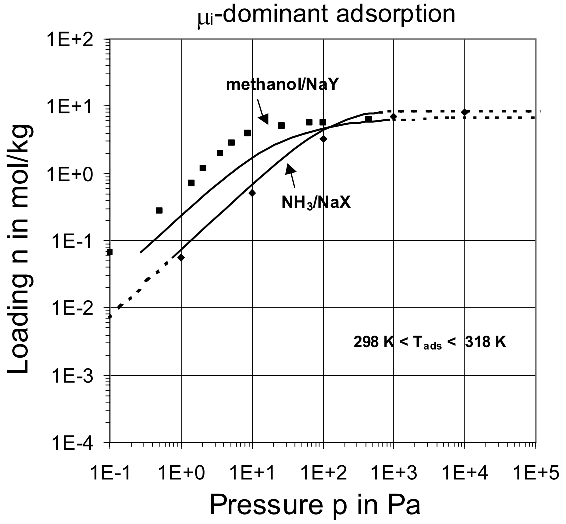


Fig. 6 Adsorption of methanol on NaY (318 K, ■) and ammonia on NaX (298 K, ♦). –, - - calculated

5 Conclusions

The main objective of this work is the theoretical prediction of adsorption equilibria of single gaseous substances on microporous solids like active carbon or zeolites (e.g. MS4A, MS5A, NaX and NaY). A novel equilibrium model was derived from a differential equation considering two boundary conditions. These boundaries are the Henry coefficient for low pressure gases and the saturation loading for highly pressurized gases.

The Henry coefficient which describes the adsorption isotherm of gases for $p \to 0$ depends on the properties of both the gaseous (adsorptive) and the solid (adsorbent) phase. However, the key parameter of the intermolecular in-

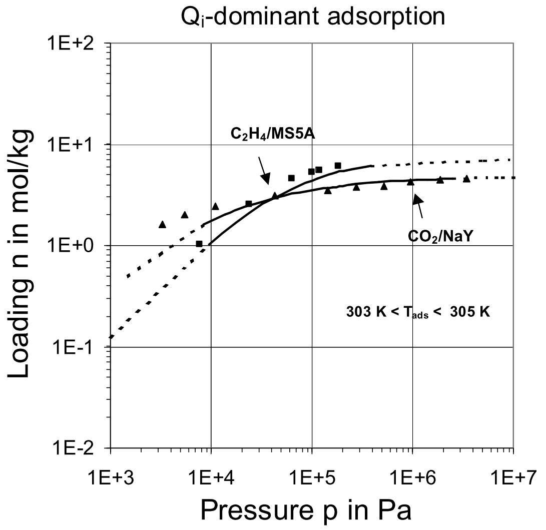
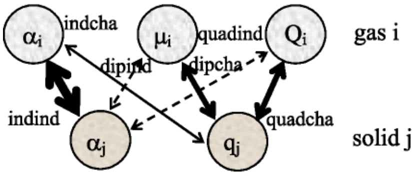


Fig. 7 Adsorption of ethene on MS5A at 303 K and the adsorption of carbon dioxide on NaY at 305 K. –, - - calculated

teraction forces, the Hamaker constant, is unknown for most zeolites. In Sect. 3, an approximated Hamaker and de Boer model for predicting the Hamaker constant of microporous solids is developed on the basis of the refractive index.

An important result of this work is the finding that the adsorption of unpolar as well as polar gases on energetical heterogeneous adsorbents is controlled by the Hamaker constant. Therefore, the dominant mechanism is the induced dipole–induced dipole interaction. The adsorption of polar gases on energetical heterogeneous adsorbents depends mainly on four interaction energies.

The adsorption isotherm model for all cases was developed by integrating the fundamental differential equation under consideration of the boundary conditions, The novel model fits the isotherms very well beginning at the Henry region and ending at the saturation region. It was shown that the induced dipole–induced dipole interaction is always eminent. For polar gases additionally the permanent dipole–charge and/or the quadrupole moment–charge interaction have to be taken into account. All other induced dipole interactions have minimal impact and can be neglected.



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