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Impedance Spectroscopic Measurements of Pure Gas Adsorption Equilibria on Zeolites

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Abstract. Physisorption equilibria of gases on inert porous solids like activated carbon or molecular sieves can be characterized by measuring the (frequency dependent) capacitance of a capacitor filled with a sample adsorbent. This quantity strongly depends not only on the physico-chemical structure of the empty adsorbent in vacuum, but also on the permanent or induced dipole moments of the molecules adsorbed and of the fluid phase. Consequently, it should be possible to determine the excess mass being adsorbed on the internal surface of a highly porous solid by measurements of the dielectric constant. The aim of this work is to show for various pure gases and adsorbents that the change of the capacitance of an adsorption system depends on the adsorbed mass. Therefore, this effect can be used to characterize porous solids and their adsorbates and, for example, to check the state or the quality of industrial adsorbents during a process on site if calibration measurements have been taken (Staudt et al., 1994, 1998).

Keywords: impedance spectroscopy, uptake curve, adsorption, polarization of adsorbate, dielectric properties of adsorbed phases

Introduction

The state of a dielectric medium is changed in an electric field, due to the shifting of the electric charges in the solid. The resulting dipoles are fixed in the electrical field (Böttcher, 1973; Fröhlich, 1990; Jackson, 1975). Non-polar molecules like N_2, Ar, CH_4 do not have a permanent dipole moment. However, they are polarized in an external electric field. The resulting so-called induced dipole moment is usually small, leading to a dielectric permittivity $\varepsilon_r \cong 1$. Polar molecules like CO, H_2O, H_2S etc. exhibit permanent dipole moments which due to thermal motion are orientated at random. However, in an external electric field they will be oriented in the direction of the field, thus increasing the dielectric capacity of a capacitor. The dielectric constant ε is defined by the ratio of the electric capacity of the capacitor with medium C_M to the same capacity of the capacitor in vacuum C_V i.e., $\varepsilon = C_M/C_V$.

In an alternating electrical field both induced and permanent dipoles are forced to oscillate with the same frequency as the field. In case of resonance oscillation the capacity of the capacitor increases considerably and a resonance frequency can be determined.

Microporous activated carbons (AC) are materials which exhibit a rather complicated and almost chaotic structure of graphite planes (Stöckli, 1990). The highly disorganized structure depends on the production process and the treatment during thermal or chemical activation. Because of their basic graphite structure AC possess quasi free electrons. Therefore AC are weak electrical conductors. Most of the zeolites are electrical insulators with very strong crystal forces. Their behaviour in an electrical field can be described by the Debye theory for dielectric materials (Böttcher, 1973; Fröhlich, 1990).

If the capacitor is filled with gas only (N_2: 12, 3 MPa, CO: 13, 5 MPa, $T = 298$ K) there occurs a small shift of the capacity spectrum compared to the vacuum capacity spectrum (Staudt et al., 1995), indicating that the gases' dielectric permittivity even at high pressures is nearly equal to 1.

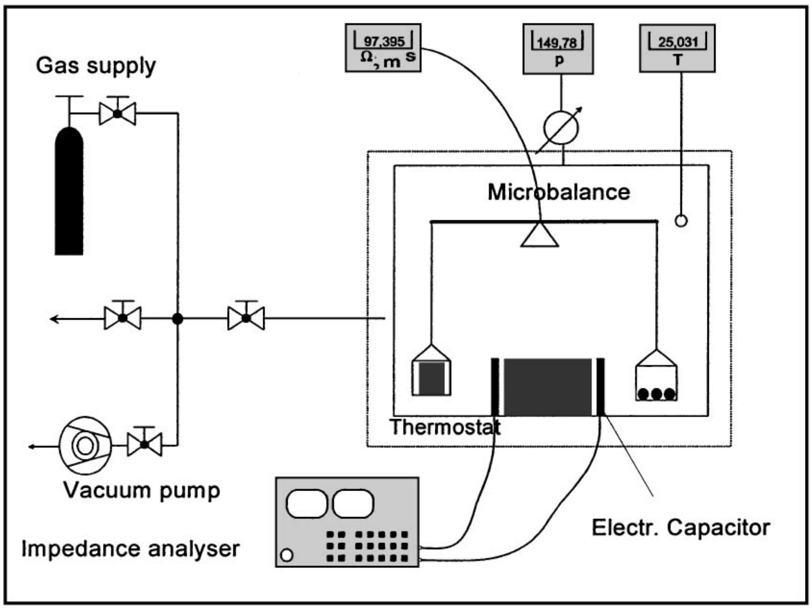

Figure 1. Experimental setup for dielectric and gravimetric measurements of adsorption equilibria.

Characterization of Porous Solids

Experimental

The experimental setup for electric and gravimetric measurements (Staudt et al., 1994, 1995) of adsorption equilibria is sketched in Fig. 1. It mainly consists of a microbalance (Sartorius, M 25D-P) and an impedance analyzer (HP, 4192 A) with a capacitor in the adsorption vessel. After providing the microbalance and the capacitor with (physico-chemical identical) adsorbent and after evacuating the whole system measurements are started by measuring the impedance spectrum of the unloaded sample. Using the impedance analyser HP 4192A this can be done within a frequency range from 5 Hz to 13 MHz. Opening the valve connecting the gas supply and the adsorption vessel adsorption occurs. In equilibrium the pressure p, the temperature T of the adsorptive and the weight G of the loaded adsorbent at the microbalance are registrated. The impedance spectrum is also measured.

Theory

Molecules with permanent (CO, H_2O) or induced (N_2, Ar, CH_4) dipole moments will be oriented in the direction of an applied electrical field. Thus the capacitance of a capacitor increases leading to an increase of the dielectric constant ε_s. Debye derived for the static electric field a relation between the molar polarization P_M of the molecules and the static dielectric constant ε_s (Böttcher, 1973; Fröhlich, 1990; Jackson, 1975):

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{n\,P_M}{V_C}, \quad \text{(SI-system)}. \tag{1a}$$

with

$$P_M = \frac{N_A}{3\,\varepsilon_0}\left(\alpha + \frac{\mu^2}{3\,k_B\,T}\right) \tag{1b}$$

Here V_C is the volume of the capacitor and n is the amount of molecules with molar polarization P_M needed for the static dielectric permittivity ε_s at temperature T. The molar polarization indicates the strength of interaction between the applied electric field and the molecules with dipole μ and polarizability α. Here ε_0 indicates the general dielectric constant, N_A Avogadro's number and k_B Boltzmann's constant.

In an alternating electric field ($\vec{E}(\omega) = \vec{E}_0 \cdot \cos(\omega t)$) both induced and permanent dipoles are forced to oscillate with the same frequency $\nu = \omega/2\pi$ as the field. In 1912, Debye developed a macroscopic theory for the frequency dependence of the complex dielectric constant $\varepsilon = \varepsilon' + i\varepsilon'' (\varepsilon^* = \varepsilon' - i\varepsilon'')$.

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_\mathrm{s} - \varepsilon_\infty}{1 + \omega^2 \tau^2} \tag{2a}$$

$$\varepsilon''(\omega) = \frac{(\varepsilon_\mathrm{s} - \varepsilon_\infty)\,\omega\tau}{1 + \omega^2 \tau^2} \tag{2b}$$

This theory was generalized by Cole and Cole in 1941 (Böttcher, 1973; Fröhlich, 1990).

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_\mathrm{s} - \varepsilon_\infty}{1 + i(\omega\tau)^{1-k}} \tag{3}$$

If an adsorbent is placed between the plates of a capacitor, there will be a change in the electric capacitance, when gas is adsorbed. From this capacity change the change of the complex dielectric constant ε can be calculated. The change of the dielectric constant of an adsorbent/adsorbate system in an alternating electric field can be described by the theory of Cole and Cole (Eq. (3)). Fitting the parameters of this model to the measured frequency dependent dielectric constant will lead to a numerical value for the static dielectric constant ε_s.

Assuming that the adsorption-system is a homogeneous mixture of porous solid, adsorbate and adsorptive the dielectric behaviour can be described by the so-called Debye equation for mixtures (Böttcher, 1973; Fröhlich, 1990):

$$\frac{\varepsilon_\mathrm{s} - 1}{\varepsilon_\mathrm{s} + 2} = \sum_i \frac{n_i P_{\mathrm{M},i}}{V_\mathrm{C}}, \tag{4}$$

$$P_{\mathrm{M},i} = \frac{N_\mathrm{A}}{3\,\varepsilon_0}\left(\alpha_i + \frac{\mu_i^2}{3\,k_\mathrm{B}\,T}\right) \tag{5}$$

$$i = \begin{cases} f & \text{gaseous adsorptive} \\ s & \text{sorbens} \\ a & \text{adsorbate} \end{cases}$$

Doing the same measurements and calculation for the empty adsorbent in vacuum we get via Eq. (4) the reduced polarization Π^S of the porous solid with

$$\Pi^\mathrm{S} = \frac{n_\mathrm{s} P_\mathrm{Ms}}{V_\mathrm{C}}. \tag{6}$$

If the dipole moment μ_i and the polarizability α_i $(i = f, a)$ of the adsorptive and the adsorbate are known, the number of molecules in the capacitor, i.e., the excess amount adsorbed can be calculated.

The experimental results of gravimetric or volumetric measurements of adsorption equilibria only allow to calculate the so-called reduced mass

$$\Omega = m - \rho^\mathrm{f} V^\mathrm{as}. \tag{7}$$

This has been emphasized in recent years by Keller et al. (1992, 1998) and Staudt et al. (1992). These types of measurements only deliver the difference between the net mass adsorbed m, and the buoyancy related volume V^as of the adsorbent/adsorbate system multiplied by the density of the (fluid) adsorptive ρ^f. Combining impedance spectroscopic measurements with gravimetric or volumetric measurements of adsorption equilibria it is possible to calculate the excess amount adsorbed if the molar polarization of the adsorbed phase and/or the volume of the porous solid is known (Eqs. (4) and (5)). Normally the molar polarization of the adsorbed phase is unknown but on principle can be approximated by its “low pressure value”, i.e., its value which is experimentally determined by simultaneous gravimetric and impedance spectroscopic measurements of adsorption equilibria at low pressures (cp. Fig. 5).

Results and Discussion

Figure 2 shows typical impedance spectra of H_2S adsorbed on MS 13X (UOP) for different pressures in the frequency range 1 kHz $< \nu <$ 100 kHz. The spectra show a capacity decrease with increasing frequency (so-called normal dispersion). With increasing pressure, i.e., increasing amount adsorbed, the electric capacity of the capacitor increases. The reason for this behaviour is the increase of the number of adsorbed molecules with a permanent dipole. The analysis of these impedance spectra can lead to a frequency, at which the electric capacity changes considerably with the amount adsorbed. This frequency is a proper frequency to determine breakthrough curves or to check the state of the porous solid during technical adsorption processes (Staudt et al., 1998).

Experimental results of dielectric and gravimetric measurements of adsorption equilibria of pure gases are plotted in Fig. 3. It shows the capacitance change versus the excess amount of adsorbed for N_2, CH_4 and CO on pellets TP AC-20 Engelhard) and of CO on MS 5A at 298 K. In the case of nonpolar adsorbates (N_2 and CH_4) we observe a steep increase of the capacitance at very low coverage and a nearly linear change of the

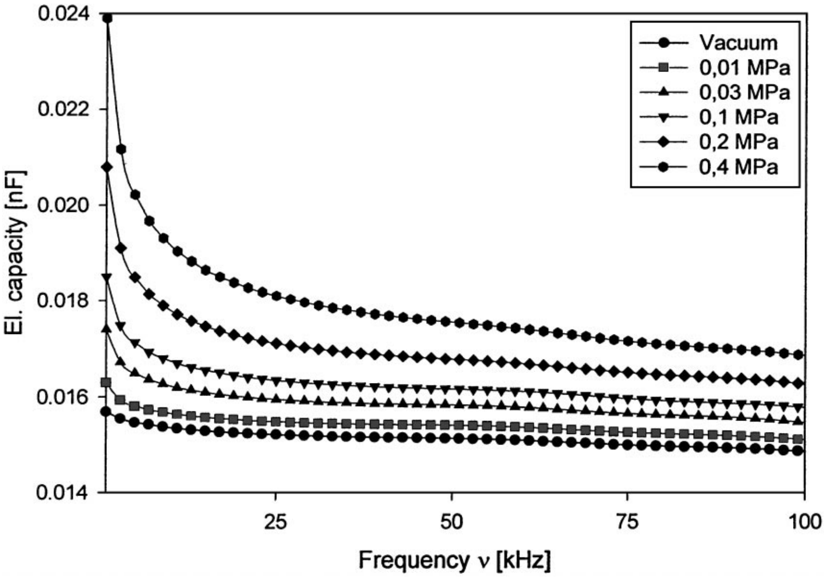

Figure 2. Impedance spectra of H_2S on MS 13X (UOP) at $T = 298$ K for different pressures.

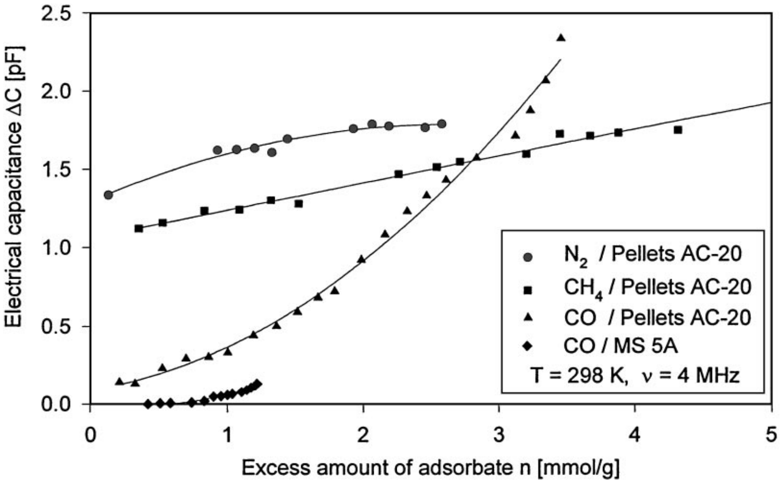

Figure 3. Change of the capacitance versus excess amount adsorbed for N_2, CH_4 and CO on pellets TP AC-20 and for CO on TP AC-20 and MS 5A at 298 K and $\nu = 4$ MHz.

capacitance at higher coverage (Young et al., 1962; Channen et al., 1955). The slope in the capacitance versus the amount of adsorbate plot seems to decrease with increasing coverage. In both cases the polar adsorbate CO reveals an increase with the square of the coverage i.e., amount of adsorbate. This behaviour sets up a remarkable difference between polar and non polar adsorbates. If CO is adsorbed on TP AC-20 the capacitance change is very large compared to that occurring during adsorption of CO on MS 5A. This can be explained by the higher adsorption capacity of TP AC-20 for CO and the higher sensitivity of the microdisperse activated carbon included in TP AC-20 on the alternating electrical field at 4 MHz.

Normally, the dipole moment μ and the polarizability α of free molecules are known from literature and the molar polarization $P_{\mathrm{M,f}}$ of free molecules can be calculated by Eq. (1b). But the molare polarization $P_{\mathrm{M,Ad}}$ of the adsorbed phase is unknown and no data or models (μ_{Ad}, α_{Ad} for adsorbed H_2S or CO on MS 13X)

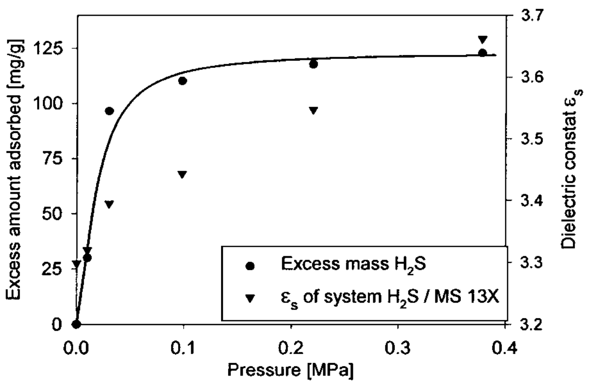

Figure 4. Adsorption isotherm and dielectric constant ε_s of H_2S on MS 13X at 298 K.

are available in literature. The dielectric-gravimetric experiment delivers only the reduced mass Ω (Eq. (6)) and the static dielectric constant ε_s (Eq. (4)) with the 3 unknown quantities adsorbed mass m (adsorbed amount n), volume V^{as} of the porous solid and the molar polarization $P_{M,Ad}$ of the adsorbed phase. No direct measurements of the amount adsorbed are possible yet except in case where the molar polarizability either from literature or molecular modeling is explicitly known. Therefore a model or assumptions for the volume of adsorbent or for the molar polarization should be introduced to calculate the excess amount adsorbed. Figure 4 shows the change of the static dielectric constant ε_s with the pressure of the adsorptive for the system H_2S on MS 13X at 298 K. The numerical values for the static dielectric constant ε_s are the results of a correlation of the Cole-Cole model (Eq. (3)) to the measured frequency dependent dielectric constant. The dielectric constant increases. This is caused by the increase of both adsorption and pressure (or density) of the adsorptive phase of H_2S molecules. The system CO on MS 13X shows a similar dielectric behaviour. The excess mass adsorbed is calculated from the microbalance signal Ω (Eq. (6)) using the so-called He-volume for the buoyancy correction. The adsorption isotherm is of type I and can be fitted by a Langmuir isotherm.

Figure 5 shows again the adsorption isotherm of H_2S on MS 13X at 298 K calculated from the gravimetric experiment using the He-volume for the buoyancy correction. If the amount adsorbed is known, the molar polarization $P_{M,Ad}$ of the adsorbed phase can be calculated by Eq. (4). Figure 5 also shows the molar polarization of adsorbed H_2S as a function of pressure, i.e., the amount adsorbed and the molar polarization $P_{M,f}$ of free H_2S molecules in the gas phase. At low pressures (i.e., low coverages) the molar polarization of the adsorbed phase is smaller than the molar polarization of free molecules. This indicates strong binding forces between the surface of the adsorbent and adsorbed molecules so that the influence of the applied electric field on the adsorbed molecules is small (i.e., orientation and/or polarization). With increasing load the molar polarization of adsorbed molecules increases which can be explained by an increase of the interaction electric field—adsorbate caused by weaker binding forces. This behaviour represents the dependence on the heat of adsorption from amount adsorbed. Again the system CO/MS 13X shows similar results.

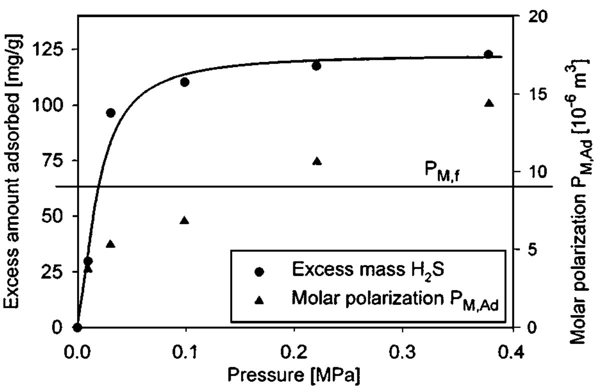

Figure 5. Adsorption isotherm and molar polarization $P_{M,Ad}$ of H_2S on MS 13X at 298 K, $P_{M,f}$ is molar polarization of H_2S in adsorptive phase.

Figure 6 shows the so-called Cole-Cole plot for the system H_2S on MS 13X at 298 K (Böttcher, 1973; Fröhlich, 1990). This representation is obtained by plotting the experimental values of $\varepsilon''(\omega)$ against those of $\varepsilon'(\omega)$. In case of an ideal single relaxation mechanism in the adsorbent/adsorbate molecular system

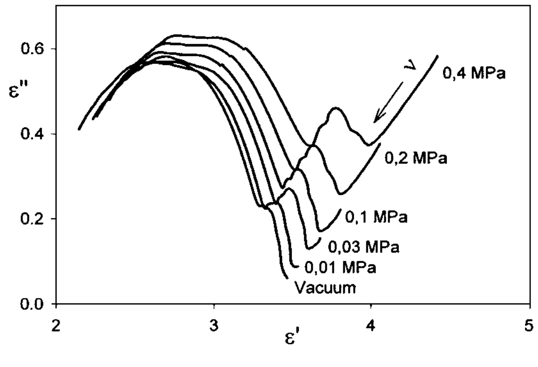

Figure 6. Cole-Cole-plot for the system H_2S on MS 13X at 298 K.

with relaxation time τ, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are given by Eqs. (2a) and (2b) and the points $(\varepsilon', \varepsilon'')$ lie on a semicircle with the center on the ε' axis and intersecting this axis at $\varepsilon' = \varepsilon_s$ and $\varepsilon' = \varepsilon_\infty$. If there are several relaxation mechanisms with various relaxation times of considerably different magnitudes a distribution function should be introduced. We observe in the case of an unloaded adsorbent an asymmetric semicircle with a small structure at low frequencies. With increasing load two additional structures (relaxation phenomena) appear in the low frequency region. This can be an effect of different adsorption sites available for H_2S molecules in the MS 13X. We observed a similar behaviour for the system CO on MS 13X. These results will be discussed in more detail by comparison with respective curves referring to the bulk liquid and/or solid state elsewhere.

An uptake curve for the system H_2S on MS 13X is shown in Fig. 7 for $p = 10$ kPa. IA marks the uptake curve measured with an impedance analyser at $\nu = 250$ kHz and MB the curve measured simultaneously with a microbalance (Staudt et al., 1998). The microbalance shows no significant change after 10 min, i.e., the mass adsorbed is constant. But the impedance analyser observes a change in the adsorbed phase and registers an adsorption equilibrium after one hour. First the impedance analyser observes a sharp increase to a maximum and then a weak decrease of the electric capacity. This increase of the electrical capacity is proportional to the number of adsorbed molecules, i.e., the number of dipoles in the capacitor. The decrease can be explained by diffusion and orientation processes of adsorbed molecules. Adsorbed molecules diffuse in pores or on inner surfaces of porous solids to their adsorption places where they will be arranged in the surface potential. This leads to a partial neutralization of dipoles and hence to a decrease of the electric capacity of the capacitor filled with porous solid. We observe this behavior in case of systems containing strong dipoles. All experiments show that the impedance spectroscopy is much more sensitive than the gravimetric or volumetric method. Therefore it can by used to characterize adsorption equilibria, diffusion and relaxation processes of adsorbed molecules in porous solids.

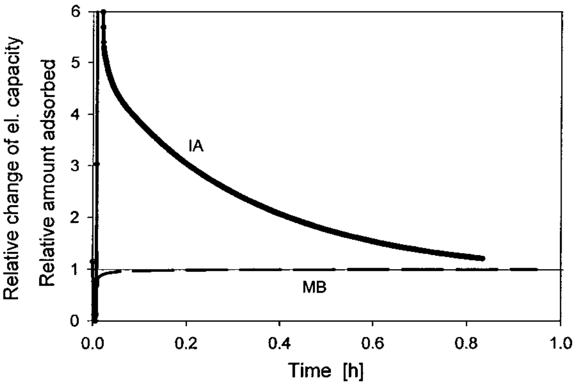

Figure 7. Relative uptake curve of H_2S on MS 13X at 298 K and $p = 10$ kPa; MB: measured with microbalance; IA: measured with impedance analyser at $\nu = 250$ kHz.

Technical Application

Measurements of Breakthrough Curves

The experimental setup to determine the breakthrough curves by the impedance spectroscopic method and by a classic gas concentration detector is sketched in Fig. 8. It mainly consists of an adsorption column filled with porous solid, an impedance analyser (HP, 4192 A) with a capacitor in the adsorption column and a TCD (thermal conductivity detector, Perkin Elmer, Germany) to detect concentrations at the end of the column. The capacitor can be filled with porous solid and is installed at ca. 2/3 of the column length. The electrical capacity of the capacitor filled with porous solid can be measured at a fixed frequency ν as a function of time. The electrical capacity of the capacitor is changed if the mass transport zone enters the capacitor and adsorption occurs. This leads to a breakthrough curve measured in the adsorption column and the state of the porous solid during the adsorption and the regeneration process can be controlled.

One difficulty in this procedure is the knowledge of the frequency ν which should be used in the dynamic experiment. This frequency can be determined by measuring so-called impedance spectra of the same adsorption system. [1, 2, 9, 10] (cp. Fig. 2).

Results

Two breakthrough curves of CO with carrier gas He on AC Norit R1 Extra are sketched in Fig. 9. IA represent the breakthrough curve measured with the impedance analyser in the column and TCD the curve measured at the end of the column with a concentration detector. The impedance analyser detects the mass transfer

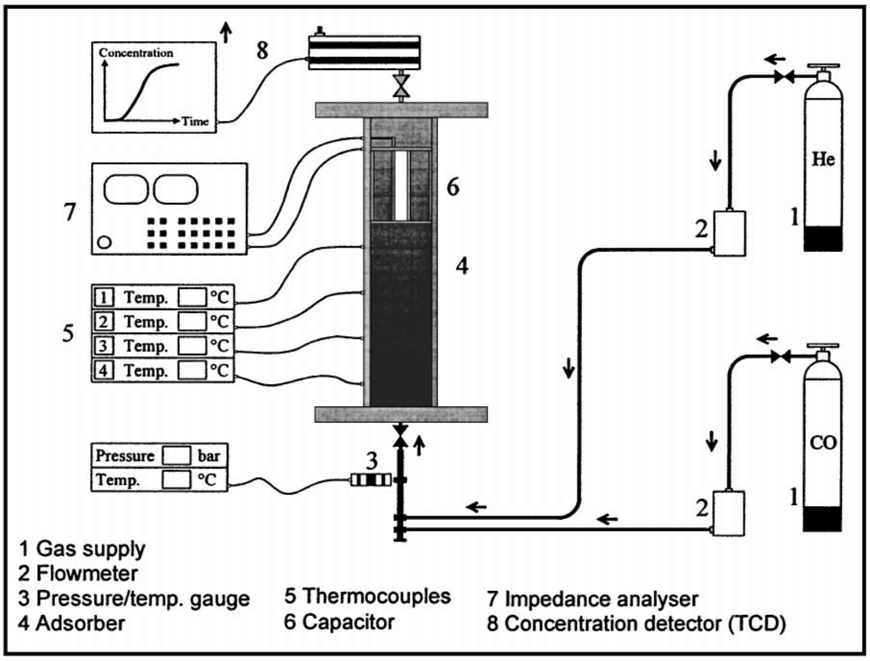

Figure 8. Experimental setup for impedance spectroscopic measurements of breakthrough curves.

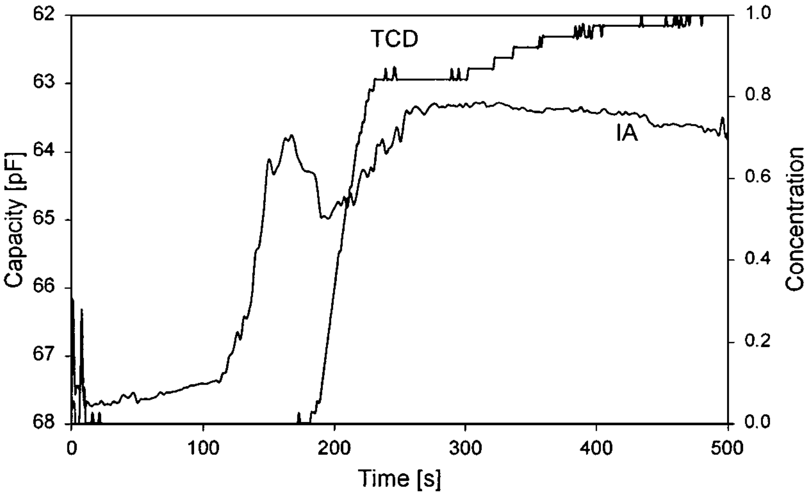

Figure 9. Breakthrough curves of CO on AC Norit R1 Extra with He as carrier gas at $T = 295$ K and $p = 0.102$ MPa; TCD: data measured with concentration detector; IA: data measured with impedance analyser at $\nu = 10$ MHz.

zone after ca. 130 s. The breakthrough is registered by the TCD after ca. 190 s. The capacitor is installed at 2/3 of the column length which explains the difference in the breakthrough times. The IA-breakthrough curve shows the same behaviour as the uptake curve in Fig. 5. After reaching a maximum the signal of the impedance analyser decreases and increases again to a constant value which characterises the equilibrium. This behaviour can be explained by the same physical phenomena as in the case of uptake curves. All breakthrough curves measured with the TCD can be fitted very well by simple analytical isothermal models (Kast, 1988).

Table 1. Excess mass adsorbed determined from breakthrough curves, measured by TCD and Impedance analyser (IA), $T = 295$ K, $p \equiv 0.11$ MPa.

		Mass adsorbed (mg/g)	
Gas	Porous solid	TCD	IA
	Carrier gas: He		
CO	Norit R1 Extra	14.64	15.81
CO	MS 5A	2.692	2.667
CO	MS 13X	5.019	4.656
CO	DAY	5.351	5.033
CO	Envisorb b+	4.479	4.583
CO_2	MS 13X	52.455	49.291
	Carrier gas: N_2		
CO_2	Envisorb b+	6.367	6.079

Also these models can describe the IA-breakthrough curves.

Conclusion

The electric capacitance of a capacitor filled with a porous solid and exerted to a gaseous sorptive depends on the amount of gas adsorbed! The dielectric behaviour of zeolites with their adsorbates can be described by Debye's theory of dielectrics. The so-called Cole-Cole plot of the system H_2S on MS 13X shows different relaxation phenomena which are probably due to different adsorption sites and energies of these molecules. By a combination of gravimetric and dielectric measurements the excess amount adsorbed and the molar polarization of the adsorbed phase can be determined. The molar polarization of adsorbed H_2S and CO on MS 13X molecules increases with increasing coverage caused by a decrease of binding forces between the surface and the adsorbate. Impedance spectroscopy measurements are also much more sensitive to the internal state of the adsorbed phase than volumetric or gravimetric measurements. Exerting for example zeolite MS 13X to H_2S at 298 K and 10 kPa, a diffusion/orientation process of the adsorbed molecules to their final positions within the adsorbate could be observed. This process is “invisible” for gravimetric measurements as has been depicted in Fig. 7.

The impedance spectroscopy is a new method to investigate breakthrough curves in adsorption columns and to check the state of porous solids during an adsorption or regeneration process online.

Nomenclature

C	electric capacity	F
n	amount adsorbed	mmol/g
N_A	Avogadro's number	$6.02214 \cdot 10^{23}$ mol^{-1}
k_B	Boltzmann's constant	$1.38066 \cdot 10^{-21}$ J/K
k	constant	1
P	molar polarization	m^3/mol
p	pressure	Pa
t	time	s
T	temperature	K
V	volume	m^3
α	polarizability	(C^2 m^2)/J
ε	dielectric constant	1
ε_0	general dielectric constant	$8.854 \cdot 10^{-12}$ C^2/(J m)
μ	dipole moment	C m
ν	frequency	s^{-1}
ρ	density	kg/m^3
τ	relaxation time	s
Ω	reduced mass	mg/g
ω	circular frequency	s^{-1}

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