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SAXS studies of porous materials coated by organic layer

Abstract

The aim of the present investigation was to determine the relationship between the small angle X-ray intensities and structural information on coating films. Thus, the SAXS intensities scattered by different porous materials (silica gel, porous glasses) coated with an organic-compound (aliphatic alcohols and $\text{Si}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$) layer were analysed. The results obtained show that SAXS intensities are very sensitive to the loading of samples. Both positive and negative deviations from the Porod law were observed. The former were caused by thermal density fluctuations within the organic phase; the latter were related to the existence of a transition layer (a layer of organic compounds) on the surface of the porous material.

Thickness is the most important value which characterises the coating. The Ruland-Vonk and Ciccarello-Benedetti methods can be used to determine the thickness of the transition layer from the direct analysis of slit-smear intensity data. The thickness values of the transition layer obtained correspond with the theoretically anticipated thickness of organic-compound layers on the surface.

Key words: SAXS, transition layer thickness

1. Introduction

In recent years the small angle X-ray scattering method (SAXS) has been used more and more frequently in investigating the profile of electron density changes on the phase boundary [1-13]. This is why it can be and is used in characterising the organic properties of films on porous materials. The deposition of such a film undoubtedly changes the profile of electron density changes on the phase boundary (i.e. the porous material skeleton), which also cause changes in the small angle scattering values.

Coating processes have recently become more and more important from a practical and theoretical point of view. Consequently, it appears useful to find simple and non-destructive techniques that allow the physical characterisation of the deposited films.

Silica gels and controlled porous glasses (CPG) belong to the most popular siliceous materials used as supports for coating processes. The most popular coated silicas are reversed-phase silicas, a class of materials used in chromatography. This class of materials includes RP-2, RP-8, and RP-18, in which the pore surfaces of silica gels are fully derived with ethyl, octyl, or octadecyl chains.

There are also many other systems in which a transition layer occurs on the phase boundary (understood as the

change in electron density) and which can be successfully investigated using the SAXS method.

The aim of the following investigations was to determine the relationships between the small angle X-ray intensities and the parameters characterising the film deposited on porous materials.

2. Theory

The intensity of SAXS for complex, disordered and porous systems can often be described by the power law scattering equation:

$$I(q) = I_0 q^{-\alpha} \quad (1)$$

where I_0 , α are constants and

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (2\theta \text{ is the scattering angle,}$$

λ is the X-ray wavelength).

For many materials which are characterised by the possession of the diffuse phase boundary caused by, for example, the presence of an organic layer, the α -coefficient is greater than 4. This means that the existence of a diffuse phase boundary causes a depletion of the SAX scattering resulting in a negative slope for the Porod plot ($I(q) \times q^4$ vs q for the point-collimated system or $I(q) \times q^3$ vs q for the slit-collimated system). Hence, this effect is referred to as the negative deviation from the Porod law.

For the majority of solid organic substances the Porod plot, especially at the end of the Porod curve, does not reach a constant value. This behaviour can be caused by the existence of thermal or other density fluctuations (on the small scale of several Å). The presence of density fluctuations results in the enhancement of scattering at the end of the scat-

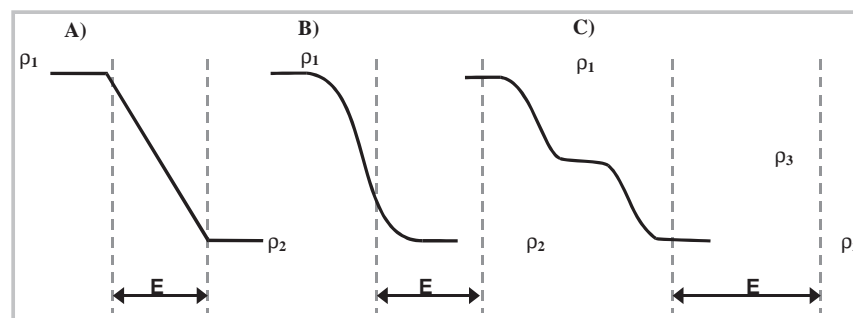


Figure 1. Schematic diagram of materials with different electron density distribution; ρ_1 - electron density of solid skeleton, ρ_2 - electron density of medium in pores (air), ρ_3 - electron density of organic layer, E - thickness of transition layer.

tering curves, giving the Porod plot a positive slope. For this reason, this effect is known as the positive deviation from the Porod law.

There are two approaches to the analysis of the SAXS effect from porous materials with a transition layer. The first is based on Ruland's and Vonk's work; they analysed the SAXS effect from polymer lamellar structures [14, 15, 16]. The other approach was developed by Ciccariello's team [11-13].

It is well known that the amplitude of scattered X-rays is proportional to the Fourier transformation of the auto-convolution of the electron-density profile, $\rho(r)$, so that:

$$I_{\text{obs}}(q) = F\{\Delta\rho_{\text{obs}}^{*2}\} \quad (2)$$

where F - three-dimensional Fourier transform, $\Delta\rho_{\text{obs}}$ - the difference between the local electron density and the average, and $*2$ stands for auto-convolution.

According to Ruland [14], for a system with diffuse interface boundaries (transition layer E), the electron-density profile (see fig.1) may be represented by a convolution between an ideal electron-density profile with sharp boundaries $\rho(r)$, and a smoothing function $h(r)$, given as

$$\Delta\rho_{\text{obs}}(r) = \Delta\rho(r) * h(r) \quad (3)$$

where r is the distance along an arbitrary vector inside the scattering volume. The Fourier transform of a convolution product in real space is equivalent to the product of the Fourier transforms in reciprocal space,

$$I_{\text{obs}}(q) = F\{\Delta\rho^{*2}(r)\}F\{h^{*2}(r)\} \quad (4)$$

and

$$\lim_{q \rightarrow \infty} [I_{\text{obs}}(q)] = I_p(q)H^2(q) \quad (5)$$

where $I_p(q)$ is the Porod-law intensity and $H^2(q)$ is the Fourier transform of the autocorrelation of the smoothing function. The term $H^2(q)$ represents the negative deviations from the Porod law caused by the diffuse interface.

For coated porous materials, the thermal density fluctuations in coatings can exist, which results in positive deviations from the Porod law. Thus, the scattering intensity becomes:

$$\lim_{q \rightarrow \infty} [I_{\text{obs}}(q)] = I_p(q)H^2(q) + I_B(q) \quad (6)$$

where

$I_B(q)$ is the scattering due to electron density fluctuations within the coating.

So far, two different electron density profiles presented in Figs. 1A and 1B have been discussed by Ruland and Vonk. For the majority of coated porous materials, the electron density profile has somewhat of a step character, but for coated porous materials, where the transition layer is much smaller than the diameter of pores, a simplification can be assumed. The smoothing functions for the cases presented in Figs.1A and 1B are as follows, respectively:

$$H(q) = e^{-\frac{1}{2}E^2q^2} \quad (7)$$

$$H(q) = \frac{\sin \frac{Eq}{2}}{\frac{Eq}{2}} \quad (8)$$

For both cases, the expansion of the smoothing function into power series and the truncation of the series after the second term for slit-collimated data results in

$$\tilde{I}(q) \cdot q = c \left(\frac{1}{q^2} - \frac{E^2}{6} \right) \quad (9)$$

c - constant

This means that the plot $\tilde{I}(q) \cdot q$ vs $\frac{1}{q^2}$ should be a straight line; from this relation the E values may be calculated [10].

In several works [11-13] Benedetti and Ciccariello presented a very interesting procedure which allows the determination of not only the thickness but also the electron density of the transition layer.

They assumed that, within the range of q attainable in SAXS measurements, coated materials can be considered as isotropic three-phase systems, with each phase having a uniform electron density. The three phases correspond to the skeleton (bulk) of porous material, the voids (pores) characterised by the electron density of the air (equal ≈ 0), and the phase formed by the molecules anchored on the support surface. The latter phase is characterised by constant thickness, depending mainly on the length of coating molecules, as well as by constant electron density. They also assumed that the thickness of a coating layer is independent of the support loading. This means that the procedure can yield realistic results only in investigations of materials with significant coating close to 100% because, as has been proved [10], the number of deposited molecules determines their ar-

rangement of the adsorbent surface and, by that token, the thickness of the coating layer.

However, further assumptions for the Benedetti-Ciccariello procedure are required. The support must have a sufficiently large pores (more than $\geq 50\text{\AA}$) for the Porod plateau to become observable, while the average pore size must be considerably larger than the length of coating molecules.

3. Experimental

All SAXS measurements were performed on a slit-collimated Kratky camera using filtered Cu radiation. A proportional counter and a pulse-height analyser were used to measure the scattered intensity. The investigated samples were placed in a cuvette of 1mm thickness with windows covered by plastic foil.

The porous glass used for these investigations has pores of 400\AA diameter. Figures 2 and 3 present the volume size distribution and the Porod plot for this glass. The porous glass was covered with a thin layer of high aliphatic alcohol: octadecanol, heptadecanol, hexadecanol, and dodecanol. The procedure used for the preparation was as follows: 10 ml CH_2Cl_2 containing an adequate amount of alcohol was added to 1g of porous glass. The suspension was stirred; subsequently the evaporation of the CH_2Cl_2 at room temperature occurred.

In the following sections of this paper, the amount of alcohol will be indicated as a % degree of coverage of the glass surface. It was assumed that one alcohol molecule takes up 21\AA^2 of the glass surface when alcohol molecules form a 'brush' (monolayer) with the maximum density.

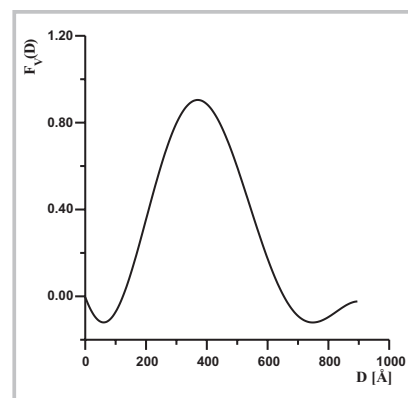


Figure 2. The volume size distribution $F_v(D)$ for pure CPG glass.

The samples which had been previously analysed by Benedetti and Ciccariello [11] were investigated. This particularly concerns the RP-18 sample, as well as a number of silica gel samples with the increasing amount of $\text{Si}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$ (in Benedetti and Ciccariello, marked as $\text{SiO}_2\text{-00}$, $\text{SiO}_2\text{-01}$, $\text{SiO}_2\text{-05}$, $\text{SiO}_2\text{-1}$, $\text{SiO}_2\text{-5}$).

4. Results

Fig. 4 shows parts of the Porod plots for glass samples coated with different amounts of hexadecanol; Fig. 5 shows the Ruland plots for two example samples. The Porod curves presented in Fig. 4 clearly show negative deviations from the Porod law; an increase in the coverage by alcohol molecules causes an increase in the negative slope of the Porod curve.

Also, for other investigated samples containing octadecanol, heptadecanol and dodecanol, an increase in the negative deviation of the curves was observed, accompanying an increase in the coverage.

The Ruland plots shown in Fig. 5 clearly manifest an almost ideally rectilinear run within a relatively significant range of the $1/q^2$ values. A similar rectilinear run of the Ruland plot was observed for all investigated samples. Accordingly, using equation (9), the thickness of a transition layer (E) for all investigated samples was calculated; the E values can be treated as the thickness of an alcohol layer. Table 1 shows the obtained values of the thickness of the transition layer E for the samples of glass covered with increasing amounts of hexadecanol. Generally, the thickness of an alcohol film deposited on the

carrier surface depends on the alcohol molecule length as well as on the degree of coverage.

For a small degree of coverage, it can be assumed that the alcohol molecules lie on the glass surface, which explains the rather small thickness of the transition layer (see table 1), and consequently the insignificant negative deviation from the Porod law. A rise in the degree of coverage causes the alcohol molecules to 'rise' (see Fig. 6), which extends the transition layer (alcohol layer) and increases the negative slope of the Porod curve. A further increase in the degree of coverage causes further erection of alcohol chains until the molecules form a 'brush' of alcohol chains on the glass surface (Fig. 6).

The data in Table 1 shows a clear increase in the thickness of the layer accompanying an increase in the amount of alcohol. Similar changes in the thickness of the transition layer caused by an increase in the degree of coverage for other investigated alcohols were also observed.

Table 1. Thickness of transition layer (E) for investigated samples porous glass coated with hexadecanol

Sample	Thickness E [Å]
A+10%	10.1
A+30%	14.1
A+50%	16.6
A+75%	19.8
A+100%	20.6

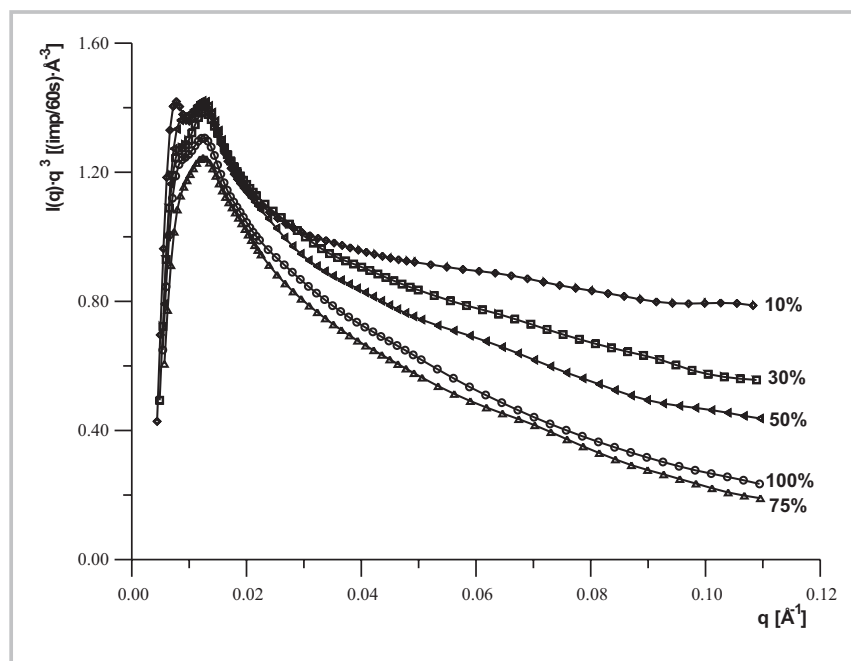


Figure 4. Porod plots for porous glass coated with hexadecanol.

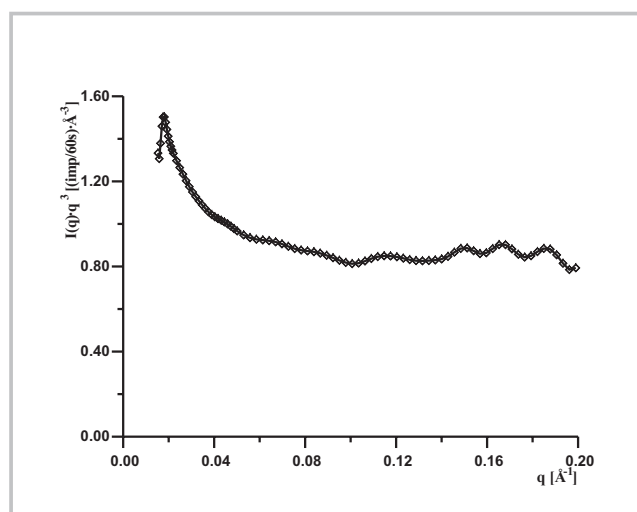


Figure 3. Porod plot for pure CPG glass.

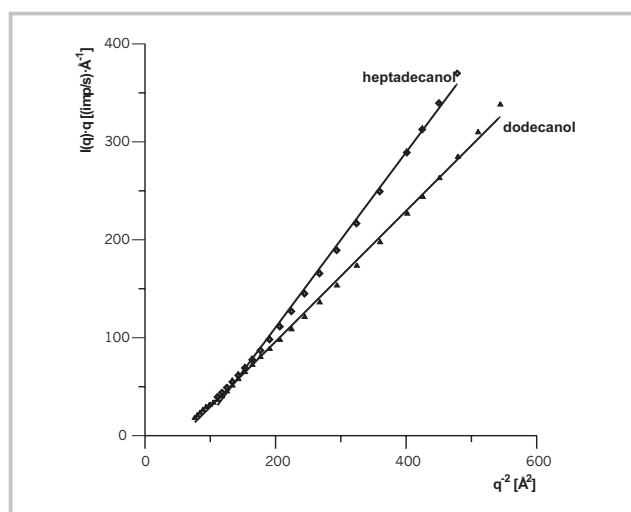


Figure 5. Ruland plots for porous glass coated with dodecanol and heptadecanol (degree of coverage was equal to 100% for both samples).

Table 2 contains the thickness of alcohol layer for 100% degree of coverage as well as theoretical lengths of carbon chains. As can be observed, there is good agreement between the theoretical length of chain and the values obtained by the Ruland-Vonk equation. The results presented in Tables 1 and 2 as well as in Figs. 4 and 5 strongly suggest that the thickness of an alcohol layer can be reliably determined by means of the Ruland-Vonk relation (9). The usefulness of the Ruland-Vonk equation was additionally confirmed in the analysis of SAXS data presented in paper [11].

Table 2. Theoretical length of the alcohol molecule chain and thickness of transition layer E for porous glass with the 100% degree of coverage

aliphatic alcohol	theoretical length of chain [Å]	thickness of transition layer [Å]
C ₁₈ H ₃₇ OH	23.6	22.1
C ₁₇ H ₃₅ OH	22.3	20.3
C ₁₆ H ₃₃ OH	21.0	20.2
C ₁₂ H ₂₅ OH	15.7	14.0

Table 3. Thickness of transition layer (E) obtained by Benedetti, Ciccariello [11] and the Ruland-Vonk equation (9).

SAMPLE	E [Å]	
	Benedetti, Ciccariello	Ruland-Vonk
RP-18	16.5	18
SiO ₂ -00	16.8	2.2
SiO ₂ -01	13.0	4.3
SiO ₂ -05	11.8	6.2
SiO ₂ -1	11.7	13.9
SiO ₂ -5	11.1	15.6

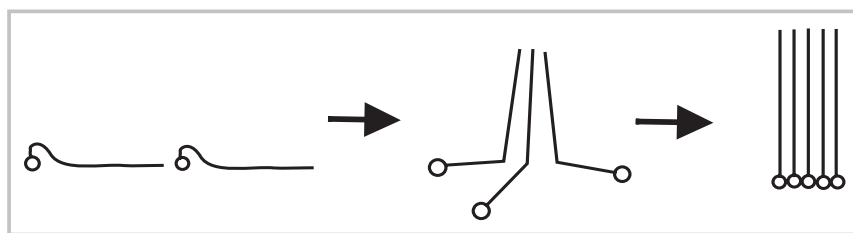


Figure 6. Suggested models for the orientation of alcohol molecules on porous glass.

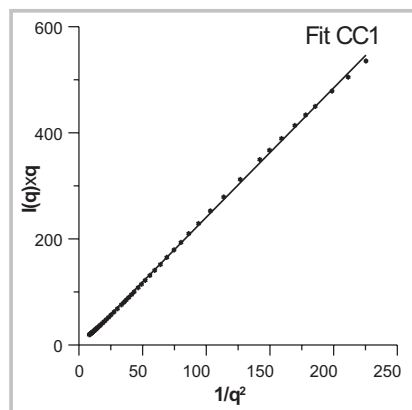


Figure 7. Ruland plot for pure silica gel (SiO₂).

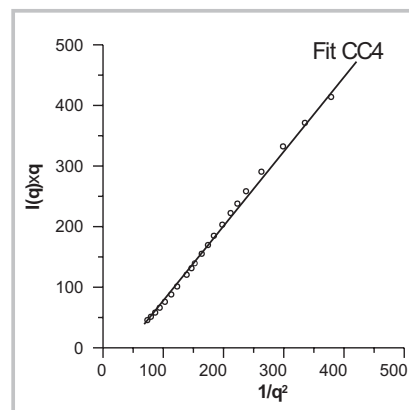


Figure 8. Ruland plot for silica gel covered by Si(CH₂)₂P(C₆H₅)₂ (SiO₂-05).

Figs. 7 and 8 present two exemplary Ruland plots for samples which were investigated by Benedetti and Ciccariello [11]. The curves in Figures 7 and 8 clearly manifest an almost ideally rectilinear run within a relatively significant range of $1/q^2$ values. It must also be noted that the remaining curves analysed also manifested the rectilinear run.

Table 3 shows the thickness of the transition layer obtained by the Ruland-Vonk equation (9) and by the Benedetti and Ciccariello procedure [11]. The first line contains values obtained for RP-18;

a rather good agreement between the values estimated using the two methods can be observed. The following five lines demonstrate the results obtained for silica gel covered with an increasing amount of Si(CH₂)₂P(C₆H₅)₂. The E values obtained using the Benedetti-Ciccariello procedure for pure silica gel (16.8Å) are so large that it is difficult to explain what kind of species on the silica gel surface can form a transition layer of such thickness.

The analysis of the further data in column 2 shows that an increase in loading causes a decrease in the E value. The values of E obtained from the Ruland-Vonk relation (see the third column of Table 3) are more logical. For pure silica gel, the value of the transition layer is small (2.2 Å), and it increases with an increase in loading. Moreover, the length of the coating molecule (Si(CH₂)₂P(C₆H₅)₂) estimated on the basis of its chemical structure is 9Å.

Considering this, it can be stated that the E value obtained for the SiO₂-5 sample (in this sample, the degree of coverage equals almost 100%) using the Benedetti and Ciccariello procedure is more realistic than that obtained using the Ruland-Vonk equation. The data in Table 3 demonstrates the thesis from [11], stating that the Benedetti and Ciccariello procedure yields results with a high error margin for samples with small coverage, but appears to be more precise for the sample with the 100% coverage. On the other hand, the high values for SiO₂-1 and SiO₂-5 samples obtained using the Ruland-Vonk equation can be explained by the incompatibility of the profiles of electron density of Si(CH₂)₂P(C₆H₅)₂ coverage assumed in equation (9) (see Fig. 8). The Si(CH₂)₂P(C₆H₅)₂ molecule contains a 'heavy atom' phosphor containing as many as 15 electrons, which makes it hard to assume that changes in the electron density are compatible with any profile shown in Fig. 1.

5. Conclusions

The results presented show that the SAXS scattering is undoubtedly very sensitive to the presence of a transition layer (in context of electron density changes) on the surface of the porous materials. The deposit of an organic layer on silica gel or porous glass results in the creation of a transition layer on their surface understood as the changes in electron density. That is

why the SAXS method can yield interesting data concerning coated materials. The determination of the thickness of a coating film appears to be particularly desirable. The above investigation has shown that the thickness of a coating film can be reliably determined by means of the Ruland-Vonk equation (9). For selected samples, the comparison of results obtained using the Ruland-Vonk relation and the Benedetti-Ciccariello procedure have been performed (Table 3). It has been determined that for materials with 100% coverage (e.g. RP-18, SiO₂-5) both methods yield comparable results, with the thickness value obtained using the Benedetti-Ciccariello procedure being closer to the theoretical film thickness. For small degrees of coverage, the Ruland-Vonk procedure yields reliable results, which is not the case with the Benedetti-Ciccariello procedure (samples SiO₂-00, SiO₂-01, SiO₂-05).

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