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# DENSITY OF ADSORBED SURFACE SPECIES FOR CYANOPHENYL ALKYL BENZOATES CONFINED TO AEROSIL A380: DEVELOPMENT OF THE EVALUATING ALGORITHM FOR ATTACHMENT BY TWO TYPES OF BONDS

Stefan FRUNZA[1], Ligia FRUNZA[1,2], Constantin Paul GANEA[1], Irina ZGURA[1], Andreas SCHÖNHALS[3]

*We found previously how to estimate the density of the adsorbed surface species in the case of the molecules interacting to the oxide support surface by one type of bond. Here this algorithm is developed for the case of the molecules which can be bonded to the support surface by two types of bonds. The adsorption assumptions are similar to those considered in the case of only one type of bond. The calculation is exemplified for some composites of cyanophenyl alkylbenzoates (CPnBs) (n is the number of carbon atoms in the alkyl chain) interacting with Aerosil A380. The interaction takes place by hydrogen bonding between the –OH groups or the support and the functional groups of the CPnB molecules. The estimated values of the total surface density of CPnBs agree well with those found for the composites containing related but simpler molecules.*

**Keywords**: surface species, adsorption by two types of bonds, density of surface species, infrared spectroscopy, thermogravimetric analysis.

## 1. Introduction

Confinement in the voids of different dimensionalities, mostly of oxides supports, received much attention due to the intense worldwide research within the last three decades (see e.g. a few relevant books and reviews [1-5]). Continuous importance of these studies comes from the properties and the applications of porous media supports and from the confined small molecules like liquid crystals (LCs) as well. Molecular mobility in confinement followed up by several methods as nuclear magnetic resonance (NMR) or dielectric spectroscopy reflects many types of interactions ([6,7]) between the two components of the composites. Beside these relaxation methods, a surface layers of rod-like cyanophenyl derivatives have been already observed by different other

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[1] PhD., National Institute of Materials Physics (INCDFM), 077125 Magurele, Romania

[2] Corresponding author, e-mail: lfrunza@infim.ro .

[3] Professor, Bundesanstalt für Materialforschung und prüfung (BAM), 12205 Berlin, Germany

experimental techniques which give quantitative information as thermogravimetric analysis (TGA), infrared, Raman or ultraviolet-visible spectroscopy and ellipsometry, photon correlation spectroscopy, quasi-elastic neutron scattering, electron scattering and electron energy loss spectroscopy, neutron and X-ray scattering, (synchrotron) X-ray diffraction, Brewster angle microscopy, autocorrelation spectroscopy, the second-harmonic and/or sum-frequency generation, near edge X-ray absorption fine structure spectroscopy etc ([8-11]). Moreover, the interaction of the electrode surface with molecules confined in the liquid crystal cells was studied as well (for example see [12-19]).

In a recent work, some features of the surface layer of cyanophenyl derivatives, mostly cyanobiphenyls (CBs) adsorbed on (confined to the surface of) oxide particles were reported [20]: Thus, the density of the surface species $n_a$ was introduced and its values were estimated from quantitative data obtained by Fourier transform infrared spectroscopy (FTIR) coupled with thermogravimetric analysis. It was then found that similar interaction of the probe molecules with the hosts/supports may appear. Moreover, data measured for surface species of some phenyl compounds with ester instead of cyan groups was also taken into consideration [20] to estimate the density of the corresponding surface species: It was shown that the density is similar leading to the conclusion that the ester molecule forms a small angle with the normal of the surface as the cyan containing molecules arrange on the same supports.

It would be interesting to compare the interaction between the oxide supports and CB molecules with that of the molecules which might develop two types of bonds on these supports: we have thus chosen the molecules of the homologous series of cyanophenyl alkyl benzoates (CPnBs). The members of this series can form liquid crystalline phases as it is known for long time [21-25]. From the application point of view, these compounds are used in matrix-addressing driving systems containing CPnBs as such or their derivatives [26-30]. Nevertheless, they were investigated mostly from the point of view of synthesis and of the liquid crystalline properties.

This work presents the results concerning the interaction between the surface of oxide supports and the molecules of the CPnB homologous series. TGA and FTIR techniques were used to study this interaction in composites with Aerosil A380 (2D confinement). Since the data on the composites containing the members with n=4…6 carbon atoms were presented elsewhere [31-33], new measurements were especially performed for samples containing the molecules with n=2, 3 and 7 carbon atoms in the alkyl chain finalizing the information on the CPnB series. The composites studied have a rather high content of aerosil since in this case the surface layer of adsorbed molecules can be investigated in detail, independently of the bulk [34]. The degree of loading the composites with the probe molecules of CPnB was estimated and the involvement of different parts of these molecules in the interaction with the aerosil surface was proved. We focused on obtaining the surface density of the adsorbed CPnB molecules (further called also “bonded to the aerosil surface”). The algorithm estimating the density of the surface species $n_a$ previously introduced [20] was here developed for the case of interaction by two types of bonds with the support surface. The properties of the aerosil composites of the whole CPnB series were used to test this algorithm.

## 2. Experimental details

### *2.1. Samples*

The data were obtained either by new measurements, or by reconsidering the results already appeared. The probe molecules CPnB (with n=2,3,7) were commercial products from La Roche and Nemoptic (purity +98%) and were used as received. The other members of this series (with n=4,5,6) were already investigated both in the bulk and in the composites [31,33].

The chemical structure of CPnBs is schematically shown in Fig. 1, where *n* is the number of carbon atoms in the alkyl chain. CPnB molecules have two main polar units (functional groups): carboxylate (or ester, -COO-) and cyan (-CN) group: These groups possess a dipole moment of 2.5 and respectively ~5.83 D. Computer simulations [35] have shown that the ester part and the benzoyl moiety are coplanar. In earlier works [31,33] we considered the total dipole moment to be oriented along the long molecular axis, but in fact its direction defines a given angle with this axis. The total dipole moment exhibits a relatively weak but discernible dependence on the conformation [36].

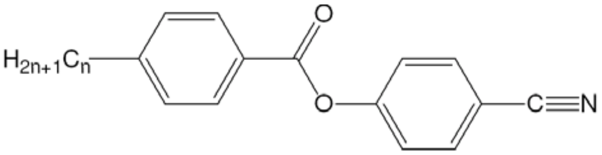


Fig. 1. Chemical structure of cyanophenyl alkyl benzoates.

The composites to be studied were prepared from the CPnB molecules and Aerosil A380 (from Degussa-Hüls). The later consists in silica nanoparticles of ~7 nm diameter, covered by hydroxyl (OH) groups ensuring hydrophilic properties. These OH groups can be lost or re-acquired by the dehydroxylation/hydroxylation processes that take place by raising the temperature or by contact with water vapors. The BET specific surface area of Aerosil A380 is 380 $m^2/g$. The composite preparation is described in detail for related systems (see [31,33,37,38]). In short, the aerosil powder is dried and degassed in a vacuum chamber at 500K, for 24 h. A solution of CPnB in carbon tetrachloride is prepared, considering the intended weight ratio aerosil/CPnB. The degassed powder was added gradually to the CPnB solution under continuous stirring. Special attention was paid to the complete solvent evaporation at 348K for 20 h. The composite samples were labeled CPnB/A380($\Theta_S$) using the liquid crystal acronym, the aerosil support and when relevant, the loading degree “$\Theta_S$” (the weight ratio aerosil/CPnB, see below).

### *2.2. Investigation methods*

The samples either in the bulk or composite state were characterized by several techniques (some were specific for LC containing materials) [39] but it was beyond the aim of this work to discuss in detail all of them: The results presented here were obtained by two classical and accessible techniques suited to the study quantitatively the surface layers and the interactions inside them

Thermal analysis was applied to check the phase transition temperature(s) of the CPnBs in the bulk but especially to estimate the loading degree of the composites. The evaluation of the later is based on the different thermal behavior of the composite components [40]. Thermogravimetry (TG) and parallel differential thermal analysis (DTA) measurements were carried out on a Perkin-Elmer Diamond TG-DTA apparatus from room temperature up to 1100K with a rate of 10K/min (or lower, when necessary) in dry air.

FTIR spectroscopy was employed to identify species resulting from the interaction of the functional (polar) groups with the surface of the aerosil particles. IR absorption spectra were collected with a Perkin Elmer Spectrum BX apparatus in the range 400–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and accumulating 128 scans at room temperature. The samples were prepared as self-supported pellets or were embedded in KBr matrices. The spectra were analyzed by the decomposition of the characteristic peaks fitting Gaussian profiles (see one example in a related case [41]).

### *2.3. Evaluating the density of adsorbed surface species*

In the case of the molecules with a single functional group able to interact with the surface of the oxide supports, the procedure to evaluate the density of (adsorbed) surface species was established previously [20] using simple basic laws/rules of thermogravimetry and (IR) spectroscopy (see also [42]).

In this subsection we remind the main features of this procedure.

The following assumptions were made:

- the dispersion of the probe compound is uniform in all the voids/pores;
- all voids have the same filling degree;
- the density of the probe molecule is close to 1: $\rho_{ptobe}$~1g/cm$^3$.

The amount of probe molecule in 1g of dried composite [43] (loading degree) was firstly determined by thermogravimetry.

A ratio $k$ is defined by the mass of adsorbed molecules $m_{ads}$, to the mass of free molecules $m_f$.

$$m_{ads}/m_f = k \tag{1}$$

For the same values of the absorptivities, the ratio of the mass of the species responsible for the absorption peaks would correspond to the ratio of the two areas of the IR bands (of un- and bonded molecules), the area being proportional to the number of molecules. Furthermore, we have

$$m_{ads} + m_f = \Theta_S V_p \rho_{probe} \tag{2}$$

where $V_p$ is the volume of the pores in 1g of the host and $\Theta_S$ is the filling degree. The mass of the adsorbed molecules can be further expressed as

$$m_{ads} = (k/(k+1))\Theta_S V_p \rho_{probe} \tag{3}$$

The surface density of adsorbed molecules or the density of surface species $n_a$ is then

$$n_a = (m_{ads}/M_{probe}) N_A / S \tag{4}$$

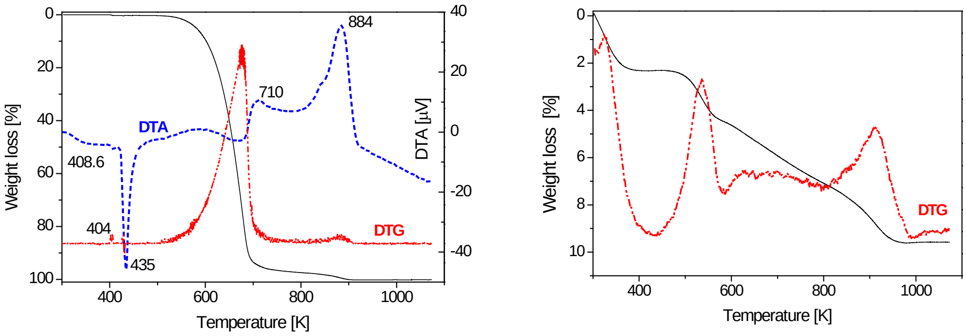
where $N_A$ is the Avogadro's number, $M_{probe}$ is the molecular mass of the considered probe molecule and $S$ is the surface area (in $m^2$) of 1 g of the confining host. Then the estimation of the density $n_a$ of probe molecules bonded to the surface is straightforward according to the eq. (4) because all the parameters are known or can be determined from experiments.

This calculation was developed in the Section of the Results to be applied in the case of a probe compound which can interact with the surface of oxide support by two types of bonds (see below).

## 3. Results and discussions

### *3.1. Thermal analysis*

Representative thermal behavior of CP3B as bulk and in composites is given in Figs. 2 (a and b). The DTA curve of the bulk shows the expected phase transition from crystalline-to-isotropic state, since this member of the series has a monotropic behavior (the compound melts from the crystalline to isotropic state and undergoes a transition isotropic-to-nematic only during cooling). The first step in the weight loss curve up to ca 400K is due to the water evaporation; therefore, in order to determine the amount of the loaded probe only the weight loss taking place in the temperature interval between 400 and 800K was considered. TG data have proven in addition that the investigated CPnB materials are thermally stable (at least) up to ca. 430K. For higher temperatures, a remarkable weight loss is observed which is mostly due to decomposition of the CPnB molecules [31,33].



(a) (b)

Fig. 2. TG (solid line), DTA (dotted line) DTG (dash dotted line) curves of (a) bulk CP3B and (b) CP3B/A380. The curves were measured with a heating rate of 10K/min. Endothermal effects in DTA curve are in the up direction.

In the case of the composites, TG measurements give the CPnB content and allow to estimate the interactions between the CPnB guest molecules and surface of the silica particles [34,40]. The loading degree $\Theta_S$ of the samples is given in Table 1. Besides, an equivalent surface layer thickness is estimated assuming a density of the CPnB layer of ca. 1 g/cm$^3$ and the aerosil BET surface area of 380 m$^2$/g.

The hydration level of the composites is low, confirming that the voids are filled with probe molecules, while the water adsorbed onto the external surface is negligible. By this way one can easily estimate the amount of the probe molecules in the composite.

*Table 1.*

**Loading degree $\Theta_S$ and estimated layer thickness for selected composites**

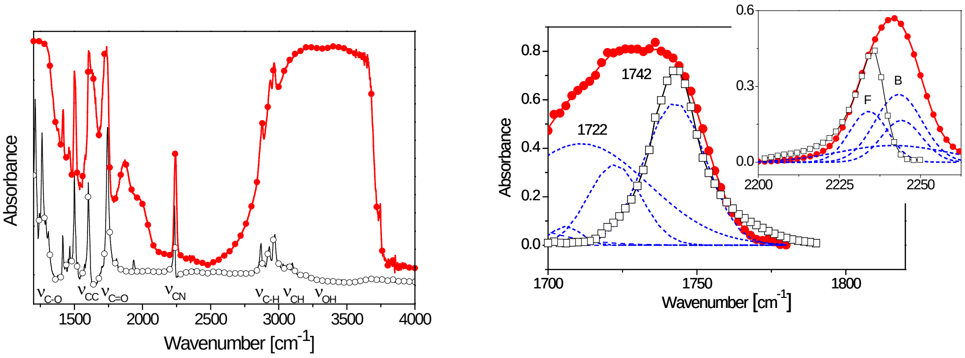
| Sample | Loading degree $\Theta_S$ | Equivalent thickness /nm | Ref. |
|---|---|---|---|
| CP2B/A380(10) | 10.03 | 0.26 | This work |
| CP3B/A380(9) | 8.95 | 0.29 | This work |
| CP4B/A380(11.2) | 11.21 | 0.23 | [31,33] |
| CP5B/A380(11.3) | 11.33 | 0.23 | [31,33] |
| CP6B/A380(13.1) | 13.14 | 0.20 | [31,33] |
| CP7B/A380(10.6) | 10.59 | 0.25 | This work |

The number of molecules in the surface layer can be estimated by considering the close size of the molecules of the CB and CPnB series and assuming a perpendicular anchoring of the cyan groups at the hydrophilic silica surfaces [20,31,33,41]. Thus, approx. 1 (up to 1.5) molecule(s) was/were expected to exist in the composites for the case of the highest surface area; the area decreases by agglomeration of the particles and the equivalent thickness might increase.

On the other part, DTG curves of the composites have rather similar temperature dependence, allowing the comparison of the sample behavior. The observed curve asymmetry can be due to the contribution of several adsorbed species. The first main DTG peak shifts to lower temperature compared to the corresponding bulk due to the interaction of the CPnB molecules with the aerosil surface, as discussed [41] for CPnBs with n=4-6. For example, this shift is larger than 30K in the case of CP7B/A380(6) compared to bulk CP7B. It is also assumed that not only the cyan but also the carbonyl group interacts with the surface [41].

### 3.2. FTIR Spectroscopy

Representative IR spectra of CP3B bulk and its composite are shown in Fig. 3a, the main assignments of the peaks are also given in accordance with the literature data for related compounds [29,44,45]: These spectra show strong IR absorptions which are similar to those of the CPnBs with n=4-6 discussed elsewhere (see [31,41] and refs. cited therein) and with that of CP7B [29].



(a) (b)

Fig. 3. (a) FTIR spectra at room temperature for bulk CP3B (in KBr; empty symbols) and for its composite CP3B/A380 (as self-supported pellet; filled symbols). Details of the cyan/ester stretching peak (as experimental points) and the decomposition into Gaussians (dashed lines) for these samples are given in part (b). The line through the points is the sum of the Gaussian components.

The following discussion regards the peaks of the bulk materials and their change by adsorption upon aerosil surface. For the quantitative analysis, the most suitable vibrations for discussion are the stretching modes of the carbonyl/ester and cyan groups for the organic material and the OH stretching of the aerosil. In the case of bulk material, the spectra show the presence of monomers and antiparallel dimers [46] as well as free non interacting carbonyl/ester groups (at ca. 1740 $\mathrm{cm}^{-1}$) and interacting groups (at 1730 $\mathrm{cm}^{-1}$) [41]. The spectra of the composites depend on the interaction of the molecules with the aerosil surface by formation of hydrogen bonds. The existence of such bonds was already put in evidence in the case of 4-n-alkyl-cyanobiphenyl (CB) molecules adsorbed on aerosil, embedded in molecular sieves (see ref. [47] and citations herein) or dispersed in polymeric films (e.g. [48]). The intensity of the stretching of OH aerosil surface groups (not shown here) increases strongly (see Fig. 3a) in composites as compared with the pure aerosil, due to the H-bonding of the CPnB molecules. Figure 3b gives the components of cyan and ester peaks; free (F) and bonded-to-the-surface (B) species appear in the cyan part of the spectra.

Thus IR spectra have indicated the interaction of both cyan and ester groups with the surface OH groups.

### 3.3. Density of surface species attached by two types of bonds

The interaction of CPnB molecules with the silica supports can be assumed to take place by the cyan head group as in the case of CB composites. However, there are several bonding types of these molecules to the support surface as follows:

- molecules bonded only by cyan group with surface density $n_s^1$.
- molecules bonded only by carboxylate group, with surface density $n_s^2$.
- molecules bonded by cyan group (either only by cyan group or by cyan and additionally, by carboxylate groups), with surface density $n_a^1$.
- molecules bonded by carboxylate group (either only by carboxylate group or by cyan and carboxylate groups), with surface density $n_a^2$.
- molecules bonded simultaneously by cyan and carboxylate groups, with surface density $n_d$.

Surface density $n_a^1$ is then given by

$$n_a^1 = \frac{m_{ads}^1 N_A}{M_{probe}} \times \frac{1}{S} \tag{5}$$

where $m_{ads}^1$ is the mass of the molecules adsorbed by cyan part. The density of surface species $n_a^1$ can be estimated using eq. (5) as it was shown for the case of attachment by only one type of bonds [20]. This formula can be transformed as follows:

$$n_a^1 = \frac{N_A}{M_{probe}} \times \frac{1}{S \times r} \times k_1/(k_1+1) \tag{6}$$

where $r = 1/\Theta_s$ is the inverse of the loading degree, $k_1$ is the ratio defined by the mass of adsorbed molecules $m_{ads}^1$ to the mass of the free (non bonded by cyan group) molecules $m_f^1$ which is estimated from the FTIR measurements

$$m_{ads}^1 / m_f^1 = k_1 \tag{7}$$

In a similar manner, molecules interacting by the carboxylate (ester) group are characterized by $n_a^2$, $m_{ads}^2$, $m_f^2$ (non bonded by ester group), $k_2$ using analogues definitions. Under these conditions the fraction of molecules bonded *via* -CN as $k_1/(k_1+1)$ and the fraction of molecules bonded *via* -COO- as $k_2/(k_2+1)$ can be defined. The high values of the estimated loading degree for the investigated samples allow to ignore the amount of CPnB molecules non bonded to the surface so that the total surface density

$$n_t = n_s^1 + n_s^2 + n_d$$

is given by

$$n_t = \frac{N_A}{M_{probe}} \times \frac{1}{S \times r} \tag{8}$$

The values of the total surface densities $n_t$ of CPnB molecules bonded to the aerosil particles agree well with those found for the composites with cyanobiphenyl molecules having the same alkyl tail [20].

The surface densities of different species bonded to the surface, either only by the cyan group ($n_s^1$), by the ester group ($n_s^2$) or bonded simultaneously by both groups ($n_d$) are given by the following expressions:

$$n_s^1 = n_a^1 - n_d$$

$$n_s^2 = n_a^2 - n_d$$

$$n_d = n_a^1 + n_a^2 - n_t$$

Table 2 collects the data referring to the densities of the molecules differently bonded to the surface in the investigated composite systems.

*Table 2.*

**Density of the adsorbed surface species (in molec.nm$^{-2}$) for the CPnB composite samples**

| Surface species / Sample | Fraction of molecules bonded *via* CN | Fraction of molecules bonded *via* COO | $n_a^1$ | $n_a^2$ | $n_s^1$ | $n_s^2$ | $n_d$ | $n_t$ | $\frac{n_d}{n_t}$ | Reference of exper. data |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | |
| CP2B/A380 | 0.48 | 0.64 | 0.34 | 0.45 | 0.25 | 0.36 | 0.09 | 0.70 | 0.13 | This work |
| CP3B/A380 | 0.60 | 0.67 | 0.45 | 0.50 | 0.25 | 0.30 | 0.20 | 0.75 | 0.27 | This work |
| CP4B/A380 | 0.75 | 0.79 | 0.41 | 0.38 | 0.23 | 0.20 | 0.18 | 0.65 | 0.27 | [31,33] |
| CP5B/A380 | 0.69 | 0.73 | 0.34 | 0.39 | 0.18 | 9.23 | 0.11 | 0.52 | 0.31 | [31,33] |
| CP6B/A380 | 0.68 | 0.75 | 0.36 | 0.37 | 0.09 | 0.06 | 0.20 | 0.30 | 0.39 | [31,33] |
| CP7B/A380 | 0.56 | 0.81 | 0.27 | 0.38 | 0.09 | 0.20 | 0.18 | 0.47 | 0.39 | This work |
| | | | | | | | | | | |
| 2CB/A380 | 0.93 | - | 0.86 | - | 0.86 | - | - | 0.86 | - | [20] |
| 3CB/A380 | 0.98 | - | 0.86 | - | 0.86 | - | - | 0.86 | - | [20] |
| 4CB/A380 | 0.91 | - | 0.82 | - | 0.82 | - | - | 0.82 | - | [20] |
| 5CB/A380 | 0.68 | - | 0.58 | - | 0.58 | - | - | 0.58 | - | [20] |
| 6CB/A380 | 0.79 | - | 0.52 | - | 0.52 | - | - | 0.52 | - | [20] |
| 7CB/A380 | 0.80 | - | 0.48 | - | 0.48 | - | - | 0.48 | - | [20] |

One can observe from Table 2 that the sum of the numbers giving the fractions of the total LC molecules bonded at the silica surface by -COO- or -CN groups from the total of LC molecules in the composite is greater than 1. This can only take place when some molecules are bonded to the surface simultaneously by both groups. The ratio $n_d / n_a$ seems to vary inversely to the variation of the dielectric strength of the series members in composites [39]: We have then supposed that the contribution the dipole moments of the functional groups is diminished by the bonding of these groups to the silica surface.

## 4. Conclusions

The density of the surface species attached by two types of bonds was developed here as a characteristic of the confined systems. Its values were estimated by quantitative FTIR investigations coupled with thermogravimetric measurements. Thermogravimetric analysis gives the amount of the probe molecules adsorbed on the oxide particles. Data of infrared spectroscopy deliver information on the interaction strength with the oxide surface and the type of bonding to the surface.

Attaching the CPnB molecules to the surface of aerosil particles by each of the functional groups CN- and -COO- and even simultaneously by these two groups was proven. In particular when the loading degree is very high (a small amount of CPnB in composites) one can consider that all molecules are bonded directly to the surface. The surface density of every kind of bonded species was then estimated. The results were thus obtained in accordance to the results already reported for single bonding for CBs.

Some properties of the surface layer in composites containing cyanophenyl alkyl benzoates as probe molecules and silica oxide (nano)particles were discussed in connection with their interfacial interaction. Since this interaction was elucidated it might be used to model different other interfacial phenomena.

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