Quantitative Diffuse Reflectance and Diffuse Transmittance Infrared Spectroscopy of Surface-Derivatized Silica Powders

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Absolute diffuse reflectance and transmittance FT-IR spectra of optically thin layers of surface-derivatized silica powders are measured, using a photopyroelectric detector placed in direct contact with the sample. The role of inhomogeneities in the surface of the powder for quantitative diffuse reflectance and transmittance measurements is examined. It is found to be equally important and nonnegligible for both sampling methods. Diffuse transmittance is shown to be more sensitive to changes of the depth of the layer than diffuse reflectance. The effect of the pressure applied to the sample surface on the scattering coefficient of two types of silica powders of different morphologies is demonstrated. A new analytical procedure based on DRIFT spectrometry is applied to the quantitative study of the influence of the chemical environment of a cyano functional group covalently linked to the silica surface on its molar extinction coefficient.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a well-established method for qualitative analysis. Good quality spectra can be recorded using this technique without extensive sample preparation. The potential of DRIFTS for qualitative measurements was highlighted in a series of papers by Griffiths and co-workers. The capability of the method for quantitative measurements was also recognized early on. However, significant theoretical and practical problems arise when the method is applied for quantitative analysis. Indeed, a very precise sampling method is required in this case. Several hypotheses have to be put forward as well in order to derive various theories describing diffuse reflectance. It has often been found necessary in practice to fix experimental conditions to satisfy these hypotheses so that the appropriate models can be applied.

The effect of several parameters such as particle size, compression procedure, mechanical constraint applied on the powder surface, angles of incidence and collection, and reproducibility of the preparation procedure of the sample and reference mixtures have been discussed in the literature.

The most ubiquitous theory describing the diffuse reflectance phenomenon was developed by Schuster and Kubelka and Munk. In this phenomenological model of light absorption and scattering of the powder, the sample is treated as a continuum. A simplified solution of the differential Kubelka–Munk equations is generally used in the literature to relate a chromophore concentration to the intensity of the sample’s diffuse reflection:

\[ F(R_a) = \frac{(1 - R_a)^2}{2R_a} = K/S \propto c \]

In eq 1, \( R_a \) represents the ratio of the diffuse reflectance of the sample of interest to that of a selected reference sample. \( K \) designates an absorption coefficient proportional to the concentration \( c \) of the chromophore, and \( S \) is the scattering coefficient of the powder.

In such a model, the first assumption made is that the sample thickness \( d \) is large enough (\( d \to \infty \)) to allow the contribution of light transmission through the layer and the reflection from the background situated behind it to be neglected, i.e., \( R \to R_a \). The second assumption requires that both phenomenological parameters \( K \) and \( S \) are taken to be constant throughout the whole sample volume. The thickness for which the diffuse transmittance is negligible depends on the absorption and scattering coefficients of the powder. In the case of an optically thin sample, i.e., if the thickness of the layer is small compared to the optical penetration depth, or if the absorption and scattering of the light inside the sample are not sufficient, part of the incident light will travel through the whole sample and be transmitted by its back surface. Normally this transmitted light is partially
absorbed by the sample holder and partially reflected back into the sample. The real diffuse reflectance under these conditions is affected by this background reflection.

Since it is not always possible to achieve an apparent "infinite depth" using a reasonable layer thickness, in particular, in a real nondiluted system, the attempt to measure the diffuse transmittance is very interesting. This measurement provides a supplementary information channel for the determination of parameters of interest, such as the absorption and scattering coefficients. Transmittance measurements have already been performed with partially transparent self-supporting disks using an instrument equipped with an infrared microscope.\(^\text{(18,19)}\)

An original technique of diffuse transmittance infrared Fourier transform spectroscopy (DTIFTS) of loosely packed powders based on a novel photopyroelectric detector has been reported.\(^\text{(20,21)}\) In a recent paper,\(^\text{(22)}\) general hyperbolic solutions of the Kubelka–Munk equation have been adapted to the nonideality of various analyzed systems. To do this, we have taken into account light absorption by the solid substrate, specular reflection, and the possible existence of absorption and scattering coefficients profiles within the depth of the powder layer. The adapted model was applied to relate both the intensity of diffuse reflectance and the diffuse transmittance of a silica powder to the known concentration of a cyan group covalently linked to its surface.

In the present contribution we investigate some of the experimental parameters which influence quantitative diffuse transmittance and reflectance measurements. The effect of the quality of the sample surface in both sampling methods is compared. The effect of the chemical environment on the absorption coefficient of an alkyl-cyano functional group covalently linked to a surface-derivatized silica powder is studied quantitatively.

**INSTRUMENTATION AND MATERIALS**

A Bomem D.A43 Fourier transform infrared (FT-IR) spectrometer was employed to obtain the data presented in this work, in conjunction with a short 25-cm scan tube. The latter was especially designed for the slow mirror velocities inherent in the use of our slow pyroelectric detector that is employed in the diffuse transmittance measurements. A photopyroelectric detector assembly was used both as the sample holder for diffuse reflectance and as a detector for the diffuse transmittance infrared Fourier transform spectroscopy (DTIFTS) developed in our laboratory. The principle and details of the photopyroelectric detector have been reported elsewhere.\(^\text{(23,24)}\) The sample holder/detector used in this work, in conjunction with a short 25-cm scan tube. The later was especially designed for the slow mirror velocities. In a typical experiment, a diffuse reflectance spectrum is obtained at a scan speed of 0.5 cm/s, with a resolution of 4 cm\(^{-1}\), by coadding 250 scans. A diffuse transmittance spectrum is typically measured at a scan speed of 0.03 cm/s, with a resolution of 4 cm\(^{-1}\), and by coadding 75 scans. Diffuse reflectance spectra are normalized by the spectrum of a 100% reflecting semiinfinite thickness layer of dry KBr powder. Diffuse transmittance spectra are normalized by the blackbody spectrum of the empty, soot-coated PVDF sample holder/detector. In all cases, the sample compartment of the spectrometer was purged with N\(_2\) to eliminate interference absorption of atmospheric CO\(_2\) and water.

Two kinds of silica powder were employed in this work. The precipitated silica LiChrosorb Si100 (Merck, Darmstadt, Germany), characterized by a particle diameter ranging from 5 to 10 \(\mu\)m,\(^\text{(25)}\) was dried at 120 °C under vacuum before being used. The fume silica Cab-O-Sil M5 (Cabot Corp., MA) distinguishes by a primary grain diameter of 10–15 Å and a secondary particle size of the agglomerated small particles of the order of 100 Å.\(^\text{(26)}\) This nonporous powder is submitted to consecutive thermal and hydrothermal treatments to obtain a reproducible surface for chemical derivatization.\(^\text{(20,27)}\) Both silica powders are then stored and manipulated in a glovebox under a dry argon atmosphere, at a humidity level not

\(^{18}\) Fraser, D. J. J.; Griffiths, P. R. *Appl. Spectrosc.* 1990, 44, 193.

\(^{19}\) Fraser, D. J. J.; Griffiths, P. R. *Anal. Chem.* 1990, 62, 308.


The specific surface area \( S_A \) of both silica powders was determined by evaluation of the \( N_2 \) adsorption BET isotherm at 77 K. Three independent BET measurements were performed using a Sorptomatic 1900 instrument (Carlo Erba, Milan, Italy) in a relative pressure domain ranging between 0.05 and 0.23. Average values of \( S_A = 321 \pm 3 \text{ m}^2 \text{ g}^{-1} \) and \( S_A = 191 \pm 2 \text{ m}^2 \text{ g}^{-1} \) were obtained respectively for the porous LiChrosorb silica and the nonporous Cab-O-Sil.

Hydroxyl groups on the oxide surface can undergo silylation reactions with dimethylaminosilanes. LiChrosorb and Cab-O-Sil powders were chemically treated with two different reagents: (5-Cyano-3,3-dimethylpentyl)(dimethylamino)dimethylsilane (DMPCN) contains a cyano functional group with a relatively sharp characteristic infrared absorption band peaking at ca. 2247 cm\(^{-1}\). (3,3-Dimethylbutyl)(dimethylamino)dimethylsilane (DMB) has approximately the same structure as DMPCN, but does not carry a cyano chromophore. Potassium bromide (Merck, puriss p.a. grade) powder was finely ground in a Wig-L-Bug mill capsule (Crescent Manufacturing Co., Chicago, IL) and sieved. KBr particles of a diameter of 20 \( \mu \text{m} \) or less were then dried for several hours in an oven at 180 \(^\circ\)C just before being used as a reflectance standard.

RESULTS AND DISCUSSION
Importance of Surface Homogeneity for Diffuse Reflectance and Transmittance Measurements. The morphology of the top surface of a sample is an important parameter for the reproducibility of diffuse reflectance measurements. The optical or geometrical irregularities at the surface affect the global reflectance and transmittance more than an identical mechanical perturbation in the bulk or at the bottom of the sample. To evaluate the uncertainty introduced in the quantitative measurements due to the macroscopic surface imperfections, the spectra are recorded for a sample of derivatized Cab-O-Sil, the surface of which is deliberately deteriorated. The powdered sample placed in the photopyroelectric detector sample holder is submitted to mechanical vibrations of about 100 Hz until a homogeneous 3-mm layer with a horizontal and regular looking surface is attained. The creation of small holes (ca. 10 per \( \text{cm}^2 \), 0.2 mm in diameter, and 0.2 mm deep) using a needle leads to a decrease of the measured reflectance by about 20–30%. At the same time, diffuse transmittance intensity increases by approximately the same proportion. Such an observation shows that the two analytical channels are optically reproducible surfaces essentially independent of the operator. However in the case of the transmittance measurements, this method cannot be employed with the present experimental configuration. Even a small pressure transmitted to the bottom of the powder is sufficient to modify the sensitive PVDF element, which is also known to display strong piezoelectric properties. This problem prevents the comparison of the sample transmittance intensity with the one corresponding to the empty blackened detector.

The homogenization of thin powdered samples by mechanical vibration is an alternative for the leveling of their surface. The variation recorded for eight independent reflectance and transmittance measurements of a 300-\( \mu \text{m} \)-thick layer of a mixture of treated Cab-O-Sil powders is about 6% in both cases. The reproducibility for this preparation method thus appears to be somewhat poorer than that obtained by the pressure application technique used for thicker samples.
Table 1. Normalized Diffuse Reflectance and Transmittance of KBr Powder Layers of Various thicknesses a

<table>
<thead>
<tr>
<th>d (cm)</th>
<th>( R/R_\infty )</th>
<th>( T/T_\infty )</th>
<th>( R/R_\infty + T/T_\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0 &lt; d1 &lt; 0.3</td>
<td>0.55 ± 0.03</td>
<td>0.42 ± 0.02</td>
<td>0.97 ± 0.05</td>
</tr>
<tr>
<td>0 &lt; d2 &lt; 0.3</td>
<td>0.90 ± 0.05</td>
<td>0.13 ± 0.01</td>
<td>1.03 ± 0.06</td>
</tr>
<tr>
<td>0.3</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

a The uncertainties on diffuse reflectance and transmittance measurements are estimated at about ±6 and ±5%, respectively.

Normalization of Diffuse Reflectance and Diffuse Transmittance Measurements. The transmittance, \( T \), normalized by the signal obtained with the empty detector is considered to be absolute. The problem is more complex for diffuse reflectance. Only a collection system including an integrating sphere could give an exact indication about the absolute reflectance value \( R \). A quantitative measurement hence implies the normalization of the spectra by using a reference. The choice of this reference is particularly important. The alkali halide salts are well-known for their excellent transmittance in the mid-infrared domain. A thick, totally opaque layer of KBr powder finely ground and carefully dehydrated should display in principle, in the absence of any absorbance, a diffuse reflectance equal to unity. For thinner, partially transparent layers, the conservation of energy implies \( R + T = 1 \).

In Table 1, the quantitative results obtained for two thin layers of a KBr powder with a particle diameter of less than 20 \( \mu \)m are presented. The values are all taken at \( \tilde{\nu} = 2247 \text{ cm}^{-1} \), the wavenumber corresponding to the -C≡N chromophore absorption maximum. The high scattering power of KBr implies a total opacity for a thickness of the layer larger than 2 mm. The reflectance of a 3-mm-thick layer can therefore be used for the normalization of the measurements. The sum of diffuse reflectance and transmittance values reported in Table 1, taking into account the uncertainties, tends to unity, indicating that absolute diffuse reflectance and diffuse transmittance are effectively measured.

Higher Sensitivity of Diffuse Transmittance Channel. In Figure 1, we show as an example two raw spectra obtained by diffuse reflectance FT-IR measurements of both Cab-O-Sil silica powders, treated up to surface saturation by the aminosilanes DMB and DMP-CN, respectively. The narrow and well-defined peak centered at \( \tilde{\nu} = 2247 \text{ cm}^{-1} \) is easily distinguishable and is characteristic of the nitrile function of the DMP-CN substituent.

A layer thickness of 1.3 mm is not sufficient to ensure the complete opacity of a Cab-O-Sil sample. The light intensity transmitted in a diffuse way can in consequence be measured by the photopyroelectric detector. The measured signals are normalized by the spectrum of the soot layer covering the PVDF film placed in the empty container yielding the absolute transmittance of the scattering layer.

Mixtures in different proportions of Cab-O-Sil powders, treated respectively by DMB and DMP-CN, are prepared. The absolute diffuse reflectance and transmittance are measured for different concentrations of the cyano group at \( \tilde{\nu} = 2247 \text{ cm}^{-1} \) and corrected for light absorption by the oxide substrate, as well as for the Fresnel reflection. The general hyperbolic solutions of the Kubelka-Munk equation allow the considerations of diffuse reflectance and diffuse transmittance of the sample simultaneously. These solutions are adjusted for both sets of experimental data using a modified Marquardt nonlinear least-squares fitting procedure. Results are reported in ref 22. An excellent correlation between the respective transmittance and reflectance measurements is obtained, and the scattering coefficient value at \( \tilde{\nu} = 2247 \text{ cm}^{-1} \) is determined. In such a case, the absorption coefficient \( K \) as well as the scattering coefficient \( S \) can be determined simultaneously. Moreover, it was observed that the transmittance channel is more sensitive to concentration variations, therefore this channel can be used advantageously for analysis.

In Figure 2a, we report the reflectance of a LiChrosorb powder derivatized by DMB as a function of the depth of the scattering layer. Results show that the reflectance at the absorption maximum of the CN group does not vary between 1 and 3 mm. No transmittance can be measured for layers

The results are presented in Figure 3 and Table 2. The absolute density has been determined by weighing the sample holder. Nevertheless, as the maximum compaction is achieved already is submitted for a second time to a mechanical pressure. A same amount of the powder is poured on the top of this first layer and compressed in the same way. Thus, the first sublayer of powders are compression using a cylindrical piston penetrating inside the sample holder. A known pressure is applied by a dynamometric press and maintained for 1 min. the sample holder volume is compressed using a cylindrical piston and a porous morphology, the scattering coefficient increases beyond which the reflectance no longer increases does not to change beyond 300 μm depth. Figure 2c shows that the phenomenon is completely different for the transmittance measurements. There is a very important decrease of transmittance from T = 0.44 at 0.3 mm to about one-tenth of this value at 3.3 mm. As the reflectance is not affected, such a variation is due to the absorption of the treated silica. This observation shows the higher sensitivity of the transmittance measurements to the absorption of the sample.

A similar conclusion has been drawn from the computer model simulations for the case of a new discontinuous multilayer theory. The transmittance in that case is more sensitive than the reflectance to the number of the particle layers. These observations indicate the necessity of a reconsideration of the total opacity criterion generally used in the literature. Indeed, the fact that there exists a depth beyond which the reflectance no longer increases does not necessary imply the absence of any transmitted light through thicker layers.

Effect of Application of Pressure on Scattering Coefficient of Powder. The application of a mechanical pressure on the surface of the powder can not ascertain a homogeneous density in the depth of the layer. This method is usually employed to level the powder surface and to obtain reproducible surfaces for reflectance measurements. In a recent paper, we have shown that the variation of the scattering coefficient with the depth of the layer can dramatically influence the reflectance value of the layer without necessarily affecting the mean value of this coefficient. In order to separate the effects of applied pressure from those of the apparition of inhomogeneities of the optical properties, such as absorption and scattering coefficients, samples constituted of mixtures of Cab-O-Sil powder with different concentrations of the CN group on their surfaces have been prepared in a particular way: An amount of the powder corresponding to about one tenth of the sample holder volume is compressed using a cylindrical piston penetrating inside the sample holder. A known pressure is applied by a dynamometric press and maintained for 1 min. A same amount of the powder is poured on the top of this first layer and compressed in the same way. Thus, the first sublayer is submitted for a second time to a mechanical pressure. Nevertheless, as the maximum compaction is achieved already at the first compression, the density does not change anymore. This operation is repeated until a 3-mm depth sample constituted of 10 superimposed sublayers is made. Each sublayer is thin enough to consider that absorption and scattering coefficients K and S are effectively constant within the depth of the whole sample.

Three different series of reflectance measurements have been done this way by application of increasing pressures of 5.89 × 10^6, 1.18 × 10^7, and 1.05 × 10^8 Pa. In each case, the density has been determined by weighing the sample holder. The results are presented in Figure 3 and Table 2. The absolute reflectance corrected for the Fresnel reflection increases with increasing pressure up to 1.18 × 10^7 Pa and decreases by a further increase of pressure up to 1.05 × 10^8 Pa. For each family of the results, the hyperbolic model of Kubelka is used with success, and one can extract the scattering coefficient S without introduction of any absorption or scattering coefficient profile in the depth of the layer.

For the smallest pressure, there is an increase of the compaction density of 40%. By application of further pressures, one obtains a density up to two times higher than the 'natural' density of the powder. The changes in the scattering coefficient follow the variations in the reflectance values. For Cab-O-Sil which is a fluffy powder, this is related to an increase of the number of the scattering centers by unit of volume in the first compaction phase. In a second phase, the number of the interfaces and thus the scattering coefficient decreases.

Griffiths et al. reported an important decrease of the scattering coefficient following application of a pressure on their model systems constituted of dispersed caffeine in potassium chloride. The KCl powder, as well as KBr employed usually as a diluant, is a compact powder formed by angular particles. A pressure of 6 × 10^7-1.0 Pa can just rearrange the position of the particles, which will tend to be aligned. Here, in the second phase of the compression of Cab-O-Sil powder, a similar behavior is hence observed.

A similar series of experiments has been carried out with the samples of LiChrosorb (Figure 4). Results are reported in Table 3. For LiChrosorb powder, which has a higher density and a porous morphology, the scattering coefficient increases.

![Figure 3. Absolute diffuse reflectance of mixtures in various proportions of both Cab-O-Sil powders treated up to surface coverage by DMB and DMP-CN aminosilanes, respectively. The samples are stacks of 10 thin layers, each of which was compressed under a pressure of (a) 58.9 × 10^6, (b) 117.7 × 10^6, and (c) 1054.5 × 10^6 Pa. Solid curves display the best fit of parameters in Kubelka's equation to the experimental results.](image-url)

Table 2. Results of Fitting of Scattering Coefficient S in Kubelka's Model to Experimental Data of Figure 3

<table>
<thead>
<tr>
<th>pressure (10^6 Pa)</th>
<th>ρ (g/L)</th>
<th>S (cm^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~0</td>
<td>130</td>
<td>1.25</td>
</tr>
<tr>
<td>58.9</td>
<td>170</td>
<td>1.30</td>
</tr>
<tr>
<td>117.7</td>
<td>220</td>
<td>1.65</td>
</tr>
<tr>
<td>1054.5</td>
<td>260</td>
<td>1.47</td>
</tr>
</tbody>
</table>

* The mean value in the absence of an applied pressure has been established for the experimental results reported in ref 22, where profiles of scattering and absorption coefficients were taken into account.
In this case, the environment of the cyano group is expected to depend on the relative rate of coverage of silica by the DMP-CN substituent and on the nature of the other molecules adsorbed on the same surface.

Figure 5 shows four different diffuse reflectance spectra of the LiChrosorb powder, which is partially covered with various concentrations of DMP-CN substituents. C, H, and N elementary analyses allow determination in each case of the surface coverage by the siloxy groups. The large IR absorption of hydroxyl groups on the silica surface results in a strongly varying baseline. Quantitative diffuse reflectance analysis of the cyano group is thus impossible in this case. The maximum absorption peak of the cyano group for a total surface coverage is positioned at 2247 cm⁻¹. For the smaller fractions of DMP-CN, one can observe a logical decrease of the band intensity together with a blue shift of the peak. At a quarter of the surface covered with DMP-CN substituents, the maximum of the absorption peak is shifted by 13 cm⁻¹ as compared to the completely covered surface. This shift to higher energies may be attributed to the formation of hydrogen bonds CN=OH between the cyano and hydroxyl groups in their environment. Such an effect has been reported for the aliphatic nitrile groups in a protic solvent. Once the silylation reaction is completed with the two aminosilanes simultaneously and saturation of the silica surface is attained, the hydroxyl groups are mostly eliminated, and the above-mentioned effect is no longer expected. The variation of the molar fraction of the DMP-CN substituents balanced by that of the DMB substituents does not give rise to any shift of the absorption maximum of the nitrile group, which remains at $\tilde{\nu} = 2247$ cm⁻¹.

Figure 6 shows the absolute diffuse reflectance at $\tilde{\nu} = 2247$ cm⁻¹ for the LiChrosorb powder submitted to a reaction with a mixture of both aminosilanes DMB and DMP-CN. The phenomenological absorption coefficient is calculated knowing

![Graph](image-url)

**Table 3. Results of Fitting of Scattering Coefficient $S$ in Kubelka’s Model to Experimental Data of Figure 4**

<table>
<thead>
<tr>
<th>Pressure (10⁵ Pa)</th>
<th>Density (g/L)</th>
<th>Scattering Coefficient $S$ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~0</td>
<td>350-370</td>
<td>26.5</td>
</tr>
<tr>
<td>58.9</td>
<td>480</td>
<td>48.1</td>
</tr>
<tr>
<td>117.7</td>
<td>500</td>
<td>49.2</td>
</tr>
<tr>
<td>1054.5</td>
<td>500</td>
<td>47.0</td>
</tr>
</tbody>
</table>

*The mean value in the absence of any applied pressure is reported for comparison.
the molar fraction of DMP-CN and the molar extinction coefficient \( \epsilon = 27 \text{ L mol}^{-1} \text{ cm}^{-1} \) determined previously for the CN chromophore. The optical absorption of the silica powder itself has also been taken into account. A quantitative model derived from the hyperbolic solutions of Kubelka for the differential equations of Kubelka–Munk developed in a recent paper is applied to the experimental results. The best Marquardt least-squares adjustment of the results gives a scattering coefficient of \( S = 39.7 \text{ cm}^{-1} \), which is larger than \( S = 26.2 \text{ cm}^{-1} \) obtained for mixtures of two powders treated up to saturation of their surfaces by both aminosilanes respectively. A first hypothesis put forward to explain this difference is a change in the morphology of the powders used in both cases. No difference is observed in the density of the two powders, nor is any change in the morphology of the grains noticed under the electron microscope. The two groups of results reported in Figure 6 and the two theoretical fits show a good coincidence of the two extreme points \( y(B) = 0 \) and \( y(B) = 1 \) where the samples must effectively be nondiscernible. This observation suggests identical scattering coefficients for both sets of samples equal to \( S = 26.2 \text{ cm}^{-1} \).

In these conditions, only an error on the evaluation of the \( K_{tot} \) coefficients can explain the difference observed between the scattering coefficients in the two sets of experiments. The molar extinction coefficient of the chromophore can indeed be a function of its molar fraction on the silica mixed treated surface. If this is the case, \( K_{tot} \), which has been calculated using \( \epsilon = 27 \text{ L mol}^{-1} \text{ cm}^{-1} \), is not correct for the various concentrations, and the difference observed between the two curves is due to the error in the determination of \( K_{tot} \).

The two curves in Figure 6 can be superimposed by identifying at equal reflectance the absorption coefficient to that calculated for the mixture of the powders. Once the real absorption coefficients \( K \) are determined, one can obtain the molar extinction coefficient corresponding to each fraction \( y(B) \) by using the linear relation

\[
K = 2 \ln (10) \epsilon \rho c_m
\]

where \( \epsilon \) is the chromophore molar extinction coefficient (L mol\(^{-1}\) cm\(^{-1}\)), \( \rho \) is the solid density (g L\(^{-1}\)), and \( c_m \) is the mass concentration of the substituent carrying the CN group (mol g\(^{-1}\)):

\[
c_m(B) = \frac{y(B) \Gamma_{tot}}{S_A + \Gamma_{tot} \nu(B) M_A + [1 - y(B)] M_A - \delta}
\]

The results of this operation are presented in Figure 7. For a complete surface coverage of silica by DMP-CN substituents, an extinction coefficient of \( \epsilon = 27 \text{ L mol}^{-1} \text{ cm}^{-1} \) is found. This value tends in a linear way to \( \epsilon = 20 \text{ L mol}^{-1} \text{ cm}^{-1} \), as the molar fraction of the chromophore tends to zero. This phenomena is the result of a change of the environment of the cyano group. For \( y(B) = 1 \), this implies an important interaction between vicinate nitrile groups. An inductive effect of the nitrogen electronegative group on the electrodiffluent carbon of the neighbor group tends to improve the polarization of the triple bond under its mesomer form \(-\text{C}^+==\text{N}^-\), which is characterized by a higher absorption. Diluted in the nonpolar DMB substituent, the chromophore extinction coefficient approaches that of capronitrile in solution in n-dodecane (\( \epsilon = 20 \text{ L mol}^{-1} \text{ cm}^{-1} \)).

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