Application of NIR spectroscopic method to the study of porous glasses filled with liquid crystals

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The paper focuses on NIR spectroscopic studies of the structure of surface active centers and interface interactions in novel nanocomposition materials built of nanoporous glasses (PG) and n-alkylcyanobiphenyl (nCB) liquid crystals (LC). NIR (12000–4000 cm^{-1}) spectra of bare PG with pore size ranging from 2 to 10 nm and those loaded with nCB ($n = 2, 4, 5, 8$) were investigated at room temperature for two types of PG of variable surface activity preheated to 200 °C (type I) and 600 °C (type II). The number of surface active centers for the two types of PG has been evaluated as a function of pore diameter, and the relative number of the LC molecules directly bounded to the pore active centers was estimated.

1. Introduction

In the recent years, physics of liquid crystals constrained to networks of micro- or nanopores has become an interesting field of both fundamental and applied research [1]–[5]. Such interest is connected with new unusual and unexpected properties demonstrated by confined LC which are related both to the effect of restricted geometry and to interactions of LC molecules with active centers on the pore surface of inorganic network [6]–[8]. This class of composite nanomaterials is also a promising candidate for technological applications in many fields, from information storage systems to microelectronics and photonics. Porous glasses are a potentially important family of nanoporous materials due to their large surface area and controlled pore dimension. For effective application and fundamental research in this field, it is necessary to know well the structure and composition of interfaces between the constituent parts as they have a profound effect on the fundamental properties of the composite.

Though being a bulk analysis method, infrared absorption spectroscopy is also a powerful tool in determining the structure and relative density of surface active centers

and dynamics of adsorbed molecules. It is especially useful in the case of porous materials with highly developed adsorptive surface which may be as large as 100 m^2/cm^3. However, due to strong scattering of porous materials and absorption of adsorbed atmospheric water, as well as to rather large thickness of porous samples, routine FTIR spectroscopy is often not appropriate to the quantitative analysis of porous materials. This may be avoided by using near IR (NIR) spectroscopy method. The absorption in the NIR region of the spectra ranging from 12000 to 4000 cm^{-1} is not due to fundamental vibrations of the molecules but to their high harmonics and combinations. This absorption is 10 to 1000 times less than in the middle IR region, which in some cases may be regarded as an advantage in measuring thick samples. Foundations of systematic studies of vibrational spectra of adsorbed molecules in overtone region were laid in the pioneer works of Terenin [9]. In his research of water vapour effect on the porous glass surface it was shown that vibrational spectroscopy, and in particular NIR spectroscopy, may be used both for evaluation of the structure of adsorbed molecules and characterization of surface active centers.

In numerous studies of LC confined to porous glasses mainly three problems have not yet been solved satisfactory, up to now:

– structure of surface active centers as a function of pore size and PG heat treatment,

– surface-induced order and molecular dynamics of confined LC,

– structure of near-surface layer of LC in pores of PG.

In this paper we report on the results of our research into these problems using the optical vibration spectroscopy method.

2. Experimental

Porous glasses with controlled pore diameter used in our studies were fabricated at the Institute of Technical Chemistry of Martin Luter University of Halle (Germany) from original borosilicate glasses [10]. They may be described as strongly interconnected and randomly oriented pores with rather uniform pore size distribution. Pore diameter in our glasses varied from 2 to 10 nm, and their specific surface ranged from 200 to 34.41 m^2/g, respectively. For the studies of heat treatment effect on the surface activity of our porous glasses, two types of the PG were used: the PG of the type I were subjected to heating up to 200 °C, whereas the PG of the type II were heated up to 600 °C and kept under vacuum for 5–7 hours, and then cooled down to room temperature. To obtain the nanocomposite systems, these prepared PG were dipped for 1 hour into the melt of LC and kept there for 5 hours. In our research we used LC from the family of well-known *n*-alkylcyanobiphenyles (*n*CB, *n* = 2, 4, 5, 8, 9 refers to the number of carbon atoms in the alkyl chain) (Merks, Germany, and Aldrich, USA). The length of the 5CB molecule equals to 1.7 nm and slightly varies for other homologues.

NIR spectra of independent components (PG and *n*CB) and nanocomposites PG + *n*CB were measured in the range 4000–10000 cm^{-1} with Cary-5E (Varian)

UV-VIS-NIR spectrophotometer. Spectral slit width was 2–4 cm^{-1}. All measurements were carried out at room temperature.

3. Results and discussion

FTIR spectra in the middle IR of the our nanocomposites and their independent components were studied earlier [11], [12]. The spectra showed strong absorption in the regions of OH stretching vibrations (3000–4000 cm^{-1}) and vibrations of silica framework (2000–400 cm^{-1}), thus making impossible their quantitative analysis. Therefore, measurements in the NIR region are needed.

Firstly, we studied NIR spectra of independent components of our nanocomposite systems, *i.e*, PG and LC. Figure 1 (dashed line) gives an example of NIR spectra of PG with pore diameter 4 nm. NIR spectra for all studied PG are very similar and consist of a few absorption bands of low intensity. The assignment of the NIR bands is a difficult problem due to lack of structure-spectral correlations in overtone region. The assignment of the bands observed in NIR spectra of our PG to overtones and combination tones was made on the basis of the literature data [13], [14]. According to these works, the absorption bands observed in NIR spectra of porous glass originate from overtones and combinations of vibrations of surface hydroxyl groups and adsorbed water. The bands centered at 4528 and 4450 cm^{-1} are assigned to combination tones of stretching and out-of-plane twisting vibrations of Si-OH groups, whereas the bands centered at 7123 and 6864 cm^{-1} are related to first overtones of OH stretching
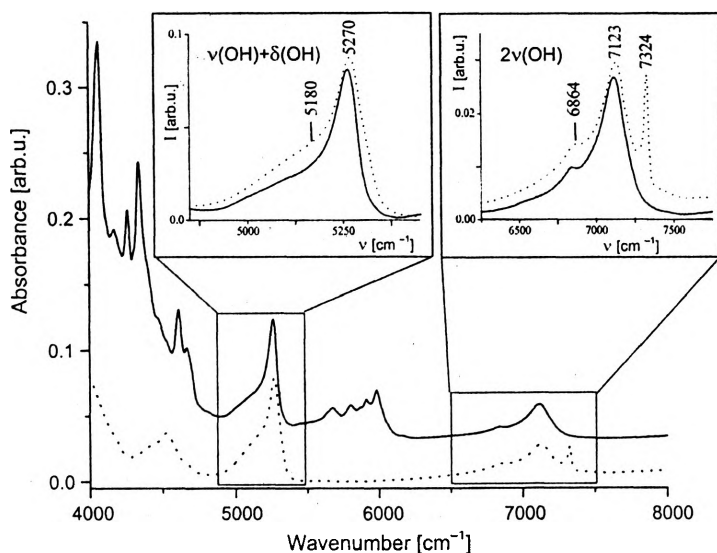

Fig. 1. NIR absorption spectra of PG (type II) with pore diameter 4 nm (PG4) (dashed line) and nanocomposite system PG +5CB (solid line). The inserts show fragments of the spectra in the regions of the first overtone 2ν(OH) and combination tone ν(OH) + δ(OH) of OH stretching and bending vibrations of adsorbed water molecules and Si-OH groups.

vibration, and those at 5183 and 5272 cm^{-1} – to combination of OH stretching and bending vibrations of adsorbed water molecules. Our assignment complies well with the results of temperature dependent studies of water vapor adsorption and desorption on silica gel surface [14]. As it follows from these studies, the first pair of bands completely disappears only at the temperature above 700 °C. More narrow 7123 and 5272 cm^{-1} bands which appear at the first stage of adsorption process, are related to overtone and combination tone of OH stretching vibrations of isolated adsorbed water molecules. At further stages of adsorption, the bands centered at 5183 and 6864 cm^{-1} appear in the spectra, which are therefore assigned to adsorbed water molecules connected by hydrogen bonds in branched network close in its behavior to capillary condensed water. The Table shows the frequencies of NIR absorption bands observed in the spectra of PG and their assignment to overtones and combinations of fundamental vibrations of the PG.

T a b l e. Hydroxyl absorption bands in the NIR spectra of porous glass and their assignment to fundamental vibrations, overtones and combinations of surface hydroxyl groups and adsorbed water.

v [cm^{-1}]	$\Delta v_{1/2}$ [cm^{-1}]	Anharmonicity shift χ [cm^{-1}]	Assignment
7324	31	80	$2v(OH)$ (free)
7123	166	55	$2v(OH)$
6864	182	24	$2v(OH)$
5272	76	−28	$v(OH) + \delta(OH)$
5183	203	−102	$v(OH) + \delta(OH)$
4643	66		$v(OH) + v_3(Si–O–Si)$
4579	57		$v(OH) + v_3(Si–O–Si)$
4528	71		$v(OH) + \delta(Si–OH)$
4450	139		$v(OH) + \delta(Si–OH)$
3840	60		$Q(C{\equiv}N) + Q(C{=}C)$

To study the pore size effect on the structure of surface active centers of our PG, we compare NIR spectra of PG of variable pore size in the regions of the first overtone and combination tone of fundamental vibrations of hydroxyl groups (Fig. 2). As one can see from the spectra, relative intensity of 7324 cm^{-1} band, as compared to the OH absorption bands of adsorbed water molecules with peak positions at 7123 and 6864 cm^{-1}, decreases when pore size increases from 2 to 10 nm. However, it is worth mentioning that in the spectra of porous glasses with pore diameter 2 nm the intensity of 7324 cm^{-1} band is lower as compared to less dense silica. This suggests that under severe confinement the distance between surface hydroxyls becomes less than 3 Å, which results in the formation of hydrogen bonds between these groups thus decreasing the number of isolated OH groups. At the same time, relative intensity of the bands centered at 5183 and 6864 cm^{-1}, which are assigned respectively to the first overtone and combination tone of adsorbed water vibrations, increases in the spectra of PG with larger pore diameter. This confirms the fact that small pore size prevents water
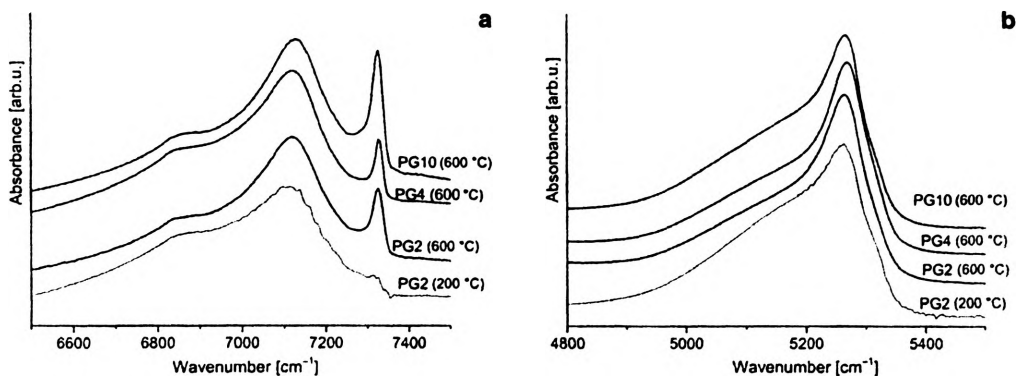
Fig. 2. Fragments of NIR absorption spectra of PG preheated to 200 °C (type I) and 600 °C (type II) with pore diameter 2, 4 and 10 nm in the region of first overtone (a) and combination (b) of OH stretching and bending vibrations of adsorbed water and Si-OH groups (all spectra were normalized by the bands 5272 and 7123 cm^{-1}, respectively).

penetration into the pores. In addition, in the spectra of porous glasses with large pore diameter, the A_{5183}/A_{5272} ratio of integral intensities of combination bands of adsorbed water increases. That is consistent with easier water adsorption in PG with larger pore diameter, which results in an increase in the amount of hydrogen-bonded adsorbed water.

Figure 2 also shows the heat treatment effect on surface activity of PG. As it was expected, spectra of the PG of type II, which were heated up to 600 °C, are characterized by higher intensity of 7324 cm^{-1} absorption band and, therefore, by larger amount of isolated surface hydroxyl groups. Therefore, we can conclude that heating up to as much as 600 °C is not sufficient for the removal of adsorbed water from the inner surface of pores. Moreover, the ratios A_{5183}/A_{5272} and A_{6864}/A_{7123} in the spectra of PG2 (type I) are respectively 2.5 and 2 times larger than in the spectra of PG2 (type II). At the same time, the intensity of absorption bands of adsorbed water is lower in the spectra of PG (type II) regardless the pore diameter. This suggests that, if the heat treatment temperature is not high enough, a fairly large amount of adsorbed water remains on the pore surface.

In NIR spectra of composite systems (Fig. 1, solid line), new bands originating from the vibrations of nCB molecules are observed in the regions 5600–6000 cm^{-1} and 3800–5000 cm^{-1} (see the Table). According to the suggested mechanism of nCB adsorption on the PG surface *via* hydrogen bonds CN···OH–Si [12], the most significant changes in the spectra of the composite system are expected in the absorption bands of surface hydroxyls of PG and cyanogroup of nCB. In addition to earlier made qualitative assessments [15], it is now possible to provide some quantitative estimates of the interface interactions in the composite systems using NIR spectroscopy. In the NIR spectra of the composite systems (Fig. 1) we observed disappearance of the first overtone of stretching vibrations of isolated OH groups at 7324 cm^{-1}, and some changes in the shape of 2v(OH) and combination tone

ν(OH) + δ(OH) of OH vibrations of adsorbed water. After loading of PG with nCB molecules, relative intensity of low-frequency components (5183 and 6864 cm^{-1}) of these bands originating from vibrations of absorbed water decreases, as if LC molecules penetrating into the pores pulled out of them water molecules weakly bounded to the pore surface.
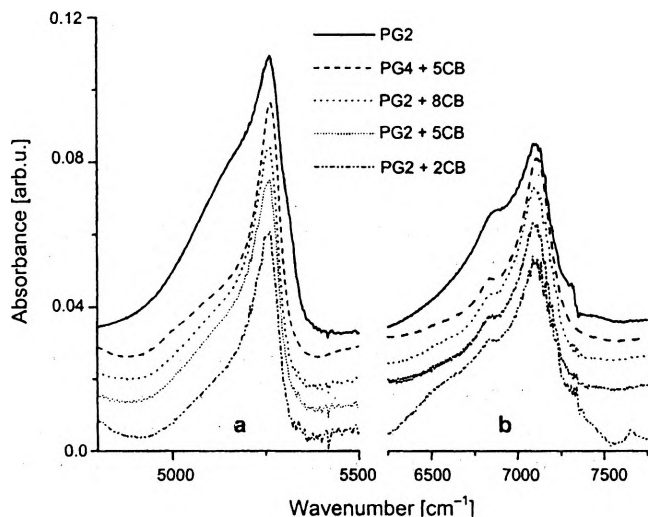

Fig. 3. Fragments of NIR spectra of PG (type I) and nanocomposite systems PG + 2CB, PG + 5CB and PG + 8CB in the region of first overtone (a) and combination tone (b) of OH stretching vibrations of adsorbed water and Si–OH groups.
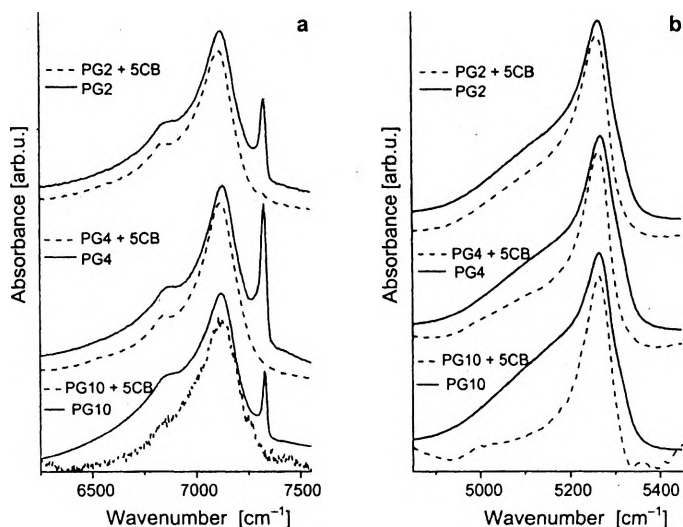

Fig. 4. Fragments of NIR absorption spectra of composite systems 5CB+PG (type II) with pore diameter 2, 4 and 10 nm in the region of first overtone (a) and combination tone (b) of OH stretching vibrations of adsorbed water and Si–OH groups.
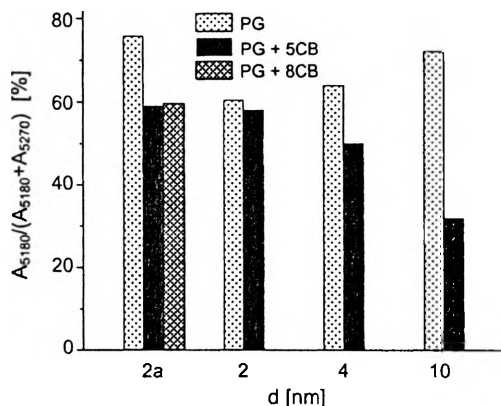
Fig. 5. Relative intensity of low-frequency component of $\nu(OH) + \delta(OH)$ combination band in the spectra of PG (type II) and composite systems PG + nCB originating from absorption of adsorbed water molecules as a function of pore diameter and alkyl chain length.

Similar changes were observed in all studies of the composite systems, the effect observed being dependent on the pore diameter and thermal treatment of the samples (Fig. 3). If the pore diameter increases, the intensities of the low-frequency components of $2\nu(OH)$ and $\nu(OH) + \delta(OH)$ bands in the spectra of composite systems decrease, and completely vanish if pore diameter is larger than 10 nm. At the same time, little changes are observed in the case of composite systems with pore diameter 2 nm (Fig. 4). Using graphic separation of $\nu(OH) + \delta(OH)$ combination band with Peakfit computer program we could evaluate relative intensity of its low-frequency component originating from absorption of adsorbed water molecules in the spectra of PG (type II) and composite systems PG + nCB as a function of pore diameter and alkyl chain length. As one can see from the diagram (Fig. 5), if the size of voids increases, larger number of LC molecules can directly contact the pore surface replacing adsorbed water molecules, while in small pores steric restrictions prevent near-surface self -organization of the LC molecules. This effect is consistent with the proposed mechanism of LC adsorption on the pore surface *via* hydrogen bonding to surface hydroxyl groups, and does not depend on the length of the LC molecule.

Significant changes were also observed in the NIR bands related to vibrations of nCB molecules. In NIR absorption spectra of nCB loaded into PG, $Q(C\equiv N) + Q(C\dot{-}C)$ combination band of cyanogroup vibrations centered at 3840 cm^{-1} is blue-shifted, broadened and asymmetric (Fig. 6). Graphic separation of this band with Peakfit computer program showed that this band consists of two components. Spectral parameters for the first component are the same as those observed in the spectra of bulk nCB (peak position 3831 cm^{-1}, full width at half-maximum (FWHM) 16 cm^{-1}) for $Q(C\equiv N) + Q(C\dot{-}C)$ band in LC phase. The second component with peak position 3847 cm^{-1} and FWHM equal to 12 cm^{-1} may be attributed to nCB molecules adsorbed on surface active centers. Figure 7 shows relative intensity of the blue-shifted component of $Q(C\equiv N) + Q(C\dot{-}C)$ combination band in the spectra of composite
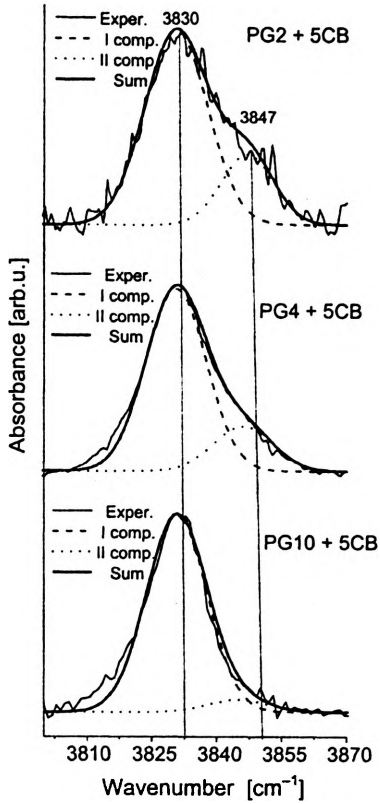
Fig. 6. Fragments of NIR absorption spectra of 5CB and hybrid systems 5CB+PG with pore diameter 2, 4, and 10 nm in the region of $Q(C \equiv N) + Q(C \dots C)$ combination band and its graphic separation.
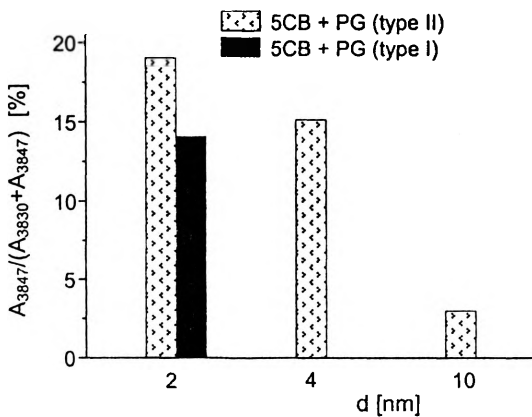

Fig. 7. Relative intensity of the blue-shifted component of $Q(C \equiv N) + Q(C \dots C)$ combination band in the spectra of composite system 5CB + PG as a function of pore diameter and thermal treatment.

system 5CB + PG, which is proportional to the number of 5CB molecules absorbed on the pore surface and is a function of pore diameter and thermal treatment. As one can see from this figure, the relative amount of nCB molecules adsorbed on the pore surface decreases if pore diameter increases. In the case of PG with pore diameter 4 and 10 nm, steric hindrances are practically absent, and nCB molecules are able to interact freely with active centers on the pore surface (the free OH absorption band completely disappears in corresponding spectra). At the same time, the increase in the pore size results in the increase of the bulk part of LC molecules inside the pores, which determines the shape of $Q(C\equiv N) + Q(C\dot{\cdot}C)$ combination band and relative intensity of its components. Similar behaviour is observed for composite systems with other nCB homologues [15]. One can also a see significant difference in the ratio of the intensities of the two components of $Q(C\equiv N) + Q(C\dot{\cdot}C)$ combination band depending on the level of pore surface dehydration. In the case of weakly dehydrated PG samples, which are characterized by a small number of free OH groups, the intensity of the blue -shifted component of $Q(C\equiv N) + Q(C\dot{\cdot}C)$ combination band originating from vibrations of 5CB molecules directly contacting the pore surface is lower. This is consistent with our suggestion about the formation of hydrogen bonds between nCB molecules and free OH groups on the pore surface. As it follows from Fig. 7, if the pore size is more than 10 nm, the effect of bulk nCB molecules inside the channels dominates over the absorption of near-surface molecules.

4. Conclusions

This work can be summarized as follows:

1. NIR spectra of nanocomposite systems nCB + PG can be well correlated with their structure.

2. Free OH groups on the surface of nanoporous glasses play a role of surface active centers for adsorption of alkylcyanobiphenyles. Adsorbed water molecules deactivate part of them forming hydrogen bonds. The surface activity of PG with pore diameter more than 2 nm depends mainly on the heat treatment conditions, and not on the pore diameter, whereas in smaller pores the distance between surface hydroxyls may become less than 3 Å, which may favor hydrogen bonds formation between these groups, thus decreasing the number of isolated OH groups or surface active centers.

3. Incorporation of nCB molecules into the pores of PG is accompanied with the partial removal of adsorbed water molecules from the pore surface; at the same time, some part of nCB molecules bonded in dimers by dipole–dipole interactions dissociate into monomers which interact with surface active centers via hydrogen bonds $-C\equiv N\cdots H-O-Si$.

4. Relative amount of nCB molecules directly contacting pore walls decreases if pore diameter increases due to the increase of the bulk part of LC molecules inside the pores regardless the alkyl chain length of nCB molecules.

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