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INFLUENCE OF CONFINEMENT ON THE PHASE TRANSITION AND SPECTRAL CHARACTERISTICS OF NEMATIC LIQUID CRYSTALS

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Abstract

The results of nematic liquid crystal – isotropic liquid phase transition study by the method of differential scanning calorimetry for inclusion compounds – mesoporous aluminosilicate molecular sieves of MCM-41 type (including Cu-exchanged samples) with encapsulated in inner-crystalline space nematic liquid crystal (5CB), as well as IR spectroscopic data for such compounds were represented. It was shown, that the 5CB molecules are able to interact with the active centers in the MCM-41 channels forming strong enough bonds of –C≡N···H–O– type. The relative amount of 5CB molecules interacting with the walls of channels and those retaining ‘liquid crystalline’ state in binary systems of molecular sieves MCM-41 and CuMCM-41 was estimated. This conclusion was confirmed by the data obtained from differential scanning calorimetry measurements.

Keywords: 5CB liquid crystal, differential scanning calorimetry, IR spectroscopy, mesoporous aluminosilicate molecular sieves of MCM-41 type, nematic liquid crystal – isotropic liquid phase transition

Introduction

In recent years great attention has been devoted to the study of intermolecular interactions and physical properties of different heterogeneous liquid crystal systems due to their wide application in electronic devices. It was established, that liquid crystals in confined volume have physical properties which are not observed for bulk samples.

The investigation of such systems is also useful for establishing the interaction mechanism of liquid crystal (LC) and surface active centers. Molecular sieves filled with liquid crystals may be regarded as one of such heterogeneous systems [1]. The IR spectroscopy method proves to be rather sensitive to identification of local surrounding and changes in intermolecular interactions, and is known to be a powerful

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tool for studying the processes of interaction between LC molecules and surface of meso-channels of the sieves.

The 4-pentyl-4’-cyanobiphenyl (5CB) is a nematic liquid crystal (NLC) in the temperature range from 22.5 to 35°C. The structure and spectral features of 5CB have been studied in details previously [2–4].

The MCM-41 type molecular sieves have unidimensional mesoporous structure with regular arrangement of hexagonal channels of 40 Å diameter and about 25 Å ‘free’ space diameter [1]. Both the sieve composition and the physical properties of the compounds included in the sieves are well reproducible. Due to its open porous structure which allows both the ‘guest’ incorporation into internal crystal space and its interaction with active centers, the sieves are suitable for inclusion of large organic molecules [1].

This work is devoted to study of possibility of inclusion of the 5CB molecules into the internal crystal space of MCM-41 type aluminosilicate mesoporous molecular sieves; possible mechanism of interaction between the 5CB molecules and active centers located on the internal surface of such mesoporous molecular sieves; and phase transition LC-isotropic liquid (IL) in the binary system by differential scanning calorimetry (DSC) method.

Experimental

The MCM-41 type mesoporous aluminosilicate molecular sieves Si,Al-MCM-41 (hereinafter referred to as MCM) studied in this work were manufactured in presence of cetyltrimethylammonium bromide $C_{16}H_{33}N(CH_3)_3Br$, the reagent mixture composition was $16.2SiO_2$:Al_2O_3:$5.4Na_2O$:$13.8C_{16}H_{33}N(CH_3)_3Br$: $1767H_2O$. The aluminum sulfate was used as a source of Al supply, which provided the incorporation of total Al into the MCM-41 framework in the tetrahedral coordination [5]. The hydrothermal synthesis was carried out at 150°C during 48 h. According to chemical analysis results, the SiO_2:Al_2O_3 ratio in the final compound was 15.65 (near to one of reaction mixture). According to the nitrogen absorption data (ASAP 2000 ‘Micromerites’ device, 77.2 K, activation temperature 573 K), ‘free’ space value of the sieves amounts to 1.16 $cm^3\ g^{-1}$, and their specific surface area is equal to 851 $m^2\ g^{-1}$. The pore diameter distribution (estimated by Kelvin equation) shows one broad peak at about 25 Å (width is about 2 Å).

The Cu-containing Si,Al-MCM-41 formula – Cu-Si,Al-MCM-41 (hereinafter referred to as CuMCM) – studied in this work was manufactured by means of ionic exchange in 10^{-2} mol l^{-1} water solution of copper acetate $Cu(CH_3COO)_2$ of air-free specimen at the ratio of solid to liquid phases of 1:100.

The 5CB-MCM and 5CB-CuMCM heterogeneous systems were manufactured by mixing 50 mg of molecular sieve with 200 μl of 5CB in the nematic phase. Then the mixture was rinsed with the hexane in order to eliminate the residual LC remaining out the channels.

The IR absorption spectra of 5CB, MCM, CuMCM and their heterogeneous binary systems were measured at room temperature in 400–4000 cm^{-1} spectral range using UR-20 (Carl Zeiss, Jena) and FTIR Nicolet ‘Avatar’ 360 spectrophotometers (spectral slit width was 2–4 cm^{-1}; suspension in Nujol or pellet with KBr).

DSC measurement were carried out with a Perkin Elmer DSC7 using sealed pans at heating rates 20 and 8 K min^{-1} in temperature range from –180 to 180°C.

The graphical separation of the IR bands onto the components was performed with the use of PEAKFIT computer program.

Fragments of IR spectra and DSC diagrams of studied samples are presented in Figs 1 and 2.

Results and discussion

IR spectra

The IR absorption spectra of alkylcyanbiphenyls in different phases have been studied earlier [3–4]. In the present work, IR spectra of 5CB LC were measured in spectral region of fundamental vibrations. The assignment of the IR bands to normal vibrations of various structural groups were carried out using literature data on similar formulas [3, 6, 7]. In the LC and IL phases the 5CB, alike those of the other members of the nCB and nOCB homologous series (*n* is the number of carbon atoms in alkyl or alkoxy chains), are arranged in dimers by dipole-dipole interactions [8–9]. Isolated molecules (monomers) of these compounds exist only in diluted solutions in neutral solvents giving the characteristic parameters of the Q(C≡N) absorption band: ν_{max}=2228 cm^{-1}, and $\Delta\nu_{1/2}$=5 cm^{-1}.

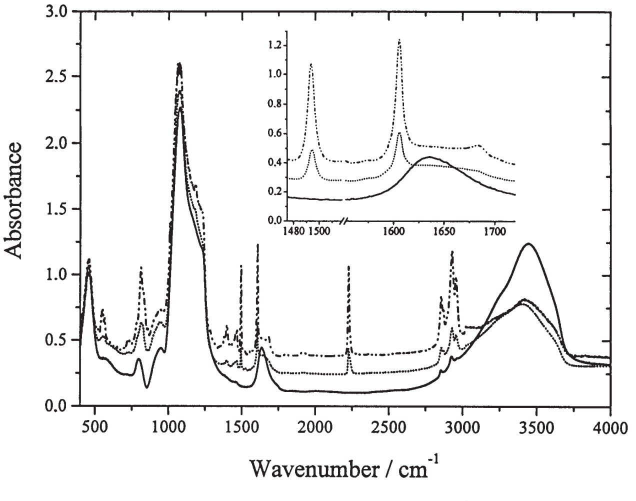

Fig. 1 IR spectra of studied samples (region 4000–400 cm^{-1}). All spectra were normalized to the peak intensity of $\nu_3(F_2)$ band (1075 cm^{-1}) and were displaced an amount 0.25 along the y-axis. Insert: enhanced fragment of these spectra in the range of Q(C$\overset{-}{\underline{\quad}}$C) vibrations

The overall IR absorption spectra of the molecular sieves filled with 5CB are shown in Fig. 1. The bands related to vibrations of the alumosilicate framework of the sieve do not change either their shape or position (SiO_4 $\nu_3(F_2)$ stretching vibration at 1075 cm^{-1}, SiO_4 $\nu_1(A)$ stretching vibration at 795 cm^{-1}, SiO_4 (E) bending vibrations at 457 cm^{-1}, combination of $\delta(SiO_4)(F_2)+\nu_1(AlOH_4)$ (A_1) at 615 cm^{-1}, others [10–11]). One can see only some variation in intensity and shape of the ν(OH) stretching band (ν_{max}=3375 cm^{-1} for MCM system, whereas for CuMCM, ν_{max}=3460 cm^{-1}). Graphical decomposition of this band enables one to isolate at least four bands with peak positions 3600, 3420, 3240 and 2970 cm^{-1}. The corresponding H-bond enthalpy has been estimated and appeared to be equal to ca 3, 5, 6.6 and 8.8 kcal mol^{-1}. Relative intensity of last two bands is 1.3–1.5 times larger as compared to that of corresponding bands of unfilled MCM-41. This presumably may correspond to formation of a system with more strong hydrogen bonds between the hydroxyl groups of the framework and 5CB molecules incorporated into channels. It should be noted that, as compared to the spectra of MCM, the integral intensity of ν(OH) and δ(OH) bands of hydroxyls of molecular sieve is approximately two times less in the spectra of MCM+5CB system, and approximately 3 times less in those of CuMCM+5CB one (Fig. 1).

Spectra of the samples shown in Fig. 1 are reduced to the intensity of the $\nu_3(SiO_4)$ band with peak position at 1075 cm^{-1}. As it is seen from the Fig. 1, the intensity of all absorption bands of 5CB incorporated into the MCM is approximately 3–4 times less than that in the CuMCM system. This indicates a lesser quantity of LC molecules penetrating into the channels.

Practically, all the bands of 5CB incorporated into the channels retain their shape and position. This concerns also the bands related to benzene rings stretching vibrations (Fig. 1, insert), plane bending vibrations $\beta(C\overset{\cdots}{=}C{-}H)$ and $\gamma(C\overset{\cdots}{=}C\overset{\cdots}{=}C)$ with peak positions 856, 812, 565, 554 cm^{-1} and some other bands. At the same time, in the spectra of 5CB+MCM system, the $\rho(C\overset{\cdots}{=}C{-}H)$ out-of-plane vibration band moves from its position at ν=829 cm^{-1} to the lower frequencies by 5 cm^{-1}. To the contrary, the band at ν=543 moves to the higher frequency of 547 cm^{-1}. This band is associated with bending vibrations ρ(C–H) and γ(C–C≡N) [12–13].

The most significant changes are observed in the region of Q(C≡N) vibration (Table). It is known, that the dipole moment of the C≡N bond is equal to 4.05 D [12–13]. Corresponding Q(C≡N) stretching vibration band is very sensitive to variation of local surrounding and intermolecular interactions, probably due to conjugated π–electron system localized on cyan biphenyl core of 5CB molecule. The incorporation of 5CB into the MCM channels results in the displacement of the peak position of the band towards the higher frequencies and the band broadening. Graphical decomposition of this band to the components has shown that, in the case of MCM, the band consists of two bands. By its position and the half-width the first one is the same as that in the nematic phase of NLC 5CB, whereas the second one represents a new band with higher frequency and of twice larger half-width (Table).

Table Spectral parameters of the Q(C≡N) IR absorption bands; ν_I and ν_{II} – peak positions (cm^{-1}) of I and II components, respectively; $\Delta\nu_{1/2}$ – bandwidth, *S* – normalized integral intensity

Studied sample	ν_I/ cm^{-1}	$\Delta\nu_{1/2I}$/ cm^{-1}	S_I/ %	ν_{II}/ cm^{-1}	$\Delta\nu_{1/2II}$/ cm^{-1}	S_{II}/ cm^{-1}
R–C≡N (4.2 K)	2235	4.9	100			
5CB (in solution, 300 K)	2228	5	100			
5 CB (LC)	2226	13	100			
5CB+MCM	2226	12	18	2238	25	82
5CB+CuMCM	2226	14	53	2236	22	47

It can be supposed that appearance of such a new band may be due to specific interaction of 5CB molecules with the channel active centers of the kind of –C≡N····H–O–Al(Si) hydrogen bond. This is confirmed by changes in the absorption spectra observed in the region of ν(OH) and by displacement of γ(C–C≡N) band. The enthalpy of this new H-bonds, as it was mentioned earlier, is equal to ca –6 –8 kcal mol^{-1}, which is much more as compared to the energy of dipole-dipole interaction taking place in LC state during the process of 5CB dimers formation. As it is seen from the Table, the new component is more intensive in the system with MCM. Comparing integral intensities of these bands, one can estimate the number of 5CB molecules retaining the LC state and those interacting with active centers. In the case of system with MCM the last number is approximately 2 times larger. It is clear that existence of the active centers, namely the hydroxyl groups, can result in dimers dissociation and 5CB molecules 'anchoring' to the walls of the channels through flexible H-bond bridges. Therefore such molecules can form different angles with channel walls, which may result in the spread of the H-bond enthalpy and inhomogeneous broadening of second component of Q(C≡N) band comprising up to 23 cm^{-1} (the band width in LC state is equal ca 13 cm^{-1}).

Difference in behavior of the Q(C≡N) band in MCM and CuMCM, namely, in the integral intensity ratio and respective number of the H-bonded 5CB molecules, are caused by existence of exchangeable cations Cu^{2+}, each of them blocking at least two hydroxyl groups on the surface of channels. In such case channels are filled mainly with 5CB dimers in LC state with the long axes of molecules directed along the channel axis. In heterogeneous system with MCM, most of 5CB molecules, which have penetrated into channels, are connected to walls and are arranged perpendicular to the channel axis, which fact, unlike to systems with CuMCM mentioned earlier, prevents further filling of channels.

Calorimetric studies

As it was mentioned above, 5CB undergoes following first order phase transitions SC (solid crystal) – NLC at 22.5°C (T_{SN}) and NLC – IL at 35°C (T_{NI}).

We have performed calorimetric measurements in the temperature range 20–70°C in the MCM+5CB and CuMCM+5CB systems (Fig. 2) in heating and cooling mode.

As it can be seen from Fig. 2, in the case of MCM+5CB system no sharp peaks were observed near temperatures of phase transitions in 5CB. In the case of CuMCM+5CB system (Fig. 2b) both under heating and cooling broadened peaks were observed at the temperatures of 36.9 and 33.3°C, respectively, instead of sharp peak observed in pure 5CB [14]. This fact confirms our previous conclusions that in the CuMCM+5CB system the greater amount of 5CB molecules is present in the form of dimers in LC state.

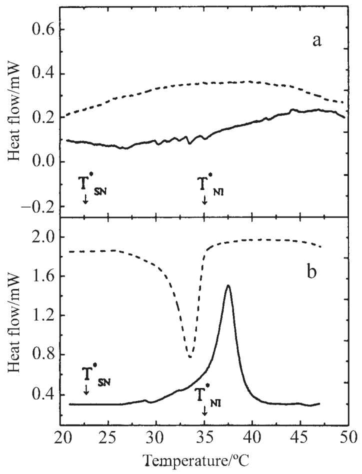

Fig. 2 DSC curves of 5CB+MCM (a) and 5CB+CuMCM (b) system. Solid line is heating and dotted line is cooling process. T^*_{SN} and T^*_{NI} are temperatures of the SC-NLC and NLC-IL phase transition of pure bulk 5CB

It should be noted, that NLC–SC phase transition was not observed in DSC curves of both systems, so one can suppose that most of 5CD dimeric molecules in the CuMCM channels are in the LC state close to the vitreous one, whereas in the MCM channels most of the 5CB molecules are arranged chaotically and are connected with channel walls through H-bonds.

Conclusions

Nematic liquid crystals can be incorporated into the internal space of uniformly mesoporous molecular sieves of MCM type. Molecules of liquid crystal interact with active centers on the internal surface of MCM channels.

According to results of DSC measurements, 5CB included in MCM-41 matrix does not participate in any phase transitions, whereas its mesomorphic behavior in Cu-MCM-41 matrix differ from that exhibited in bulk state. This may be explained by specific interactions between the LC molecules and active centers located on the pore surface.

The interaction of LC with active centers of matrix is confirmed not only by the appearance of new IR band in the region of Q(C≡N) vibrations but also by the change in ratio of the number of LC molecules interacting and not interacting with the active centers when some part of these centers is blocked with Cu^{2+} cations. Data obtained also indicate the localization of the Cu^{2+} cations near active centers. 5CB dimeric molecules not washed out from MCM inner-crystalline space by hexane, including that which do not interact with active centers, give an evidence for remaining dipole-dipole interactions which are characteristic for LC phase.

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