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# Structural and thermotropic peculiarities of hydrogen-bonded liquid crystals confined in mesoporous molecular sieves



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## ABSTRACT

The phase behaviour and structural organization of hydrogen-bonded liquid crystals were investigated under confinement to mesoporous molecular sieves. As such liquid crystalline compounds, 4-hexylbenzoic and 4-butylcyclohexanecarboxylic acids with different head group structure and alkyl chain length where selected and filled in the AIMCM-41 sieves. With FTIR spectroscopy it was found that some part of incorporated acid molecules, presumably located in the inner space of the AIMCM-41 pores, is in undissociated form of open dimers or chain associates and thus shows spectroscopic features characteristic to the bulk-like species. The other FTIR spectra components indicate strong interaction of the incorporated monomeric molecules with the pore surface. Two specific mechanisms are shown to be involved in molecular interactions at the interface: (1) deprotonation of monomeric acid molecules on the pore surface with formation of  $COO^-$  carboxylate ions and (2) bonding of these ions to the pore surface by a coordinated bond  $R-COO^-...Al^+$  with Lewis acid sites. Differential scanning calorimetry revealed that these near-surface processes lead to complete suppression of mesomorphic properties of the studied acids under confinement to nanopores.

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## 1. Introduction

During last two decades, behavior of condensed matter under confinement to nanoporous inorganic matrices has received considerable attention both from theoretical and experimental points of view. The academic interest is mainly associated with possibility of studying properties of organic materials in a highly dispersed state, where interfacial interactions and steric constraints play a very important role [1–3]. The reason of such interest is that the confinement drastically changes properties of many materials typical for them in the bulk state. On the other hand, these hybrid nanocomposite materials allow one to develop innovative applications in areas of optics, electronics, energy, sensorics, biology, medicine, industrial chemistry, etc. List of specific devices and materials includes elements for optical storage, fuel and solar cells, catalysts, membranes and sensors [4,5].

Among the brightest representatives of such systems studied up to date are liquid crystals (LC) confined to inorganic porous matrices [6,7]. A unique feature of LC mesophases is high sensitivity to spatial restriction of nanometer scale. As confining matrices for LCs, different porous media such as high-silica porous glasses [6,8–10], porous silicon [11–13], porous anodic oxide layers [14], Anopore membranes [15,16], aerosils [17–19], molecular sieves [20–24], etc. were applied. Depending on pore creation technology these matrices have random or regular system of pores. These studies revealed that the confinement might lead to drastic changes in thermal, optical and dielectric properties of LCs. In particular, it was found that the confinement to nanopores affects stability of LC compounds [24], leads to broadening of nematic – isotropic (N–I) phase transition and suppression of some smectic mesophases [9,25], irreversible non-linear optical response [8,26–28], ignition of excimer radiation [12,29] and slowing down of dielectric relaxation [30-32]. It has been found that these properties are shown with a pore size smaller than a certain critical value at which the surface and volume fraction of LC molecules in

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the pores become comparable. To explain these observations, such factors as spatial constraints, surface chemistry, fractality, and confining topology have been considered [33]. Yet, many physical features of confined LCs are still open questions fundamentally, such as theoretical treatment of LC mesophases under external fields induced by confinement or the mechanisms of interfacial interactions.

In most studies devoted to confined LCs was used the class of liquid crystalline cyanobiphenyls, primarily, n-pentyl-n'-cyanobiphenyl (5CB). The latter single-component substance with the nematic mesophase extended to room temperature is well studied and widely used as a model material in LC researches. Unique properties of this material in the nanopores are associated with the interfacial interaction at the pore walls, mainly via hydrogen bonding between the OH groups of the pore surface and the terminal polar CN groups and/or electrons of aromatic rings of 5CB molecules [20,21,29,34].

It seems even more interesting to investigate H-bonding of LC molecules with the pore walls for the LCs with hydroxyl and/or carbonyl groups forming hydrogen bonds of classical type. The brilliant materials of this type are so named hydrogen bonded LCs (H-LCs). In these LCs, the mesogenic properties are inherent only for supramolecules in a form of H-bonded dimers, while single molecules are non-mesogenic. The H-LCs currently attract great interest because of their unique properties and related application capabilities, such as new mesophases [35], wide temperature range blue phases [36], coordinative nanoporous organic materials [37], etc. Study of these supramolecular LCs in a confined state is doubly interesting, because effective interaction of its molecules with the pore walls should impede dimerization and thus significantly affect LC properties. About the restriction of dimerization in nanopores testify previous results obtained for the liquid crystalline cyanobiphenyls [12,24,29]. Despite these fundamental reasons and applicative potential, to the best of our knowledge, the molecular association and phase states of H-LCs confined in inorganic porous matrices were not studied. The present paper is an attempt to fill partially this gap.

For systematic research we chose two model compounds, 4-hexylbenzoic acid (4-HBA) and 4-butylcyclohexanecarboxylic acid (4-BCA) (Fig. 1), known as building blocks for commercial H-LCs. They both show a liquid crystalline nematic phase formed by H-bonded cyclic dimers.

The dimeric ring forms a central core of H-bonded complex which contains two benzene (or two cyclohexane) rings besides a dimeric one. The combination of a hard core with flexible side radicals is favourable for mesophase formation. At the same time, these two molecules have different geometry, alkyl chain length, as well as dipole moment in monomeric state. As a main confining matrix, Al-doped MCM-41 (AlMCM-41) molecular sieves with high Si/Al ratio were selected, and as subsidiary ones the undoped MCM-41 were involved. These materials are characterized by high pore volume and large surface area, as well as parallel and ideally shaped hexagonal pore structure. The high surface area accommodates a large number of binding active centres, and the hexagonal pore channels of large diameter of about 4 nm allow an easy penetration of organic molecules. The aim of the present research was to study the effect of bonding strength between the organic and inorganic components on thermotropic properties and molecular dynamics of confined H-LCs. Specifically, the structural rearrangements and thermal stability of the confined H-LC were investigated with the help of FTIR spectroscopy and differential scanning calorimetry (DSC).

#### 2. Experimental

#### 2.1. Materials

Undoped siliceous molecular sieves MCM-41 which were used as subsidiary in this research are the most studied member of this family of mesoporous materials, and their synthesis is well described (see e.g. Ref. [20] and references therein). Synthesis procedure of Al-doped MCM-41 was somewhat different as described below. To obtain mesoporous aluminosilicate molecular sieves AlMCM-41 with high Si/Al ratio, a reaction mixture of the molar ratio 16.2 SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub>: 5.4 Na<sub>2</sub>O: 13.8 CTAB: 1767 H<sub>2</sub>O was used in accordance with the method described in Ref. [38]. As an organic precursor, cetyltrimethylammonium bromide, C19H42BrN (CTAB), was used. The reaction mixture was subjected to thermal hydrolysis at 150 C during 48 h, and then the obtained product was thoroughly rinsed with water, dried in open air, and sintered at 550 °C for 6 h. The prepared nanoporous AlMCM-41 molecular sieves with Si/Al ratio as high as 7.8 and unidimensional mesoporous structure were kept in dry atmosphere in a desiccator. X-ray diffraction (XRD) and electron microscopy confirm a uniform pore



Fig. 1. Molecular structure of the studied model compounds and their associates.

structure with hexagonal pores of about 4 nm in diameter. The structure of AlMCM-41 consists of amorphous silica pierced with hexagonal channels. So, the walls of the mesopores are essentially amorphous with local atomic arrangement similar to amorphous aluminosilicates. The building blocks of AlMCM-41 walls are SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra, which are bonded together by oxygen atoms forming a series of Si-O-Si and Si-O-Al linkages. For each Si-O-Al linkage a cation is required to maintain charge neutrality. If the cation is H<sup>+</sup>, a bridged hydroxyl group, Si–(OH)–Al, is formed, which functions as a Brønsted acid site. At the same time, the offlattice aluminium ion compensating the excess of the negative charge in the lattice or acting as cation valence-bonded to the oxygen anion of the SiO<sub>4</sub> tetrahedron are associated with Lewis acid sites [38]. Due to their open porous structure allowing both the "guest" molecules incorporation into the internal crystal space and their interaction with the active centers, the sieves are suitable hosts for inclusion of large organic species.

The 4-BCA and 4-HBA materials were obtained from Sigma Aldrich (98% purity). Incorporation of 4-BCA or 4-HBA into the porous AlMCM-41 matrix was carried out from their melts (isotropic phase) by dipping the powder AlMCM-41 samples into the melted material and soaking them for 24–48 h at controlled temperature of 100–120 °C. The obtained samples were thoroughly washed with hexane to eliminate residual species on the external surface of the pores, and dried in an open air at 120 °C for 10 h. The absence of the residual species on the external pore surface was controlled with FTIR spectroscopy monitoring of the rinse solution till the disappearance of characteristic absorption bands of the LCs.

### 2.2. Thermal analysis

The thermotropic properties of the confined H-LCs were investigated with the help of a differential-scanning calorimeter from Perkin–Elmer (model DSC7) equipped with a refrigerated cooling unit CCA-7. The measurements were carried out in the temperature range of 20–150 °C, in the heating and cooling modes. The scanning rate was 8 K/min. Such slow rate enabled to detect very small temperature shifts in the heat flux curves for the samples under study. The samples were encapsulated into small-volume aluminium hermetic pans using mechanical press. In order to keep the melt peaks as narrow as possible, the masses of samples were low as 1–2 mg. The heat flux and temperature calibration was done using metal indium standard.

#### 2.3. Infrared spectroscopy

FTIR spectra (400–4000 cm<sup>-1</sup>) were measured in the 23–180 °C temperature range using Bruker IFS-88 spectrophotometer. The spectra were recorded with 1 cm<sup>-1</sup> resolution, and averaged over 64 scans. Bulk H-LC samples were prepared by depositing a small amount of powder acid between the two polished KBr windows with subsequent acid melting and further it cooling down to obtain a thin solid film. Samples of H-LC confined in the pores of MCM-41 were prepared by gentle grinding the synthesized compound with dehydrated KBr in the ratio of 1:100 with following pressing of the mixture in a die to make transparent discs. OPUS 4.2 software package was used for spectral data processing. Graphical separation of the IR spectral bands onto the components was performed with PeakFit computer program. All measurements were performed at room temperature.

## 3. Results and discussion

#### 3.1. DSC results

Differential scanning calorimetry (DSC) is used to investigate the phase transitions and physical states of H-LC loaded inside the pores of AlMCM-41. Fig. 2 shows the DSC thermograms (heating run) of bulk 4-BCA and 4-HBA compared to those loaded inside the pores of AlMCM-41 sieves. Upon cooling, both studied bulk materials undergo sequential phase transitions from isotropic to liquid crystalline (nematic) and solid crystalline phase. Within our resolution, two phase transitions can be seen in heating run for 4-HBA with corresponding temperatures: 96.2 (solid crystal I- nematic) and 116.5 °C (nematic-isotropic), and three for 4-BCA: at 30.3 (solid crystal I - solid crystal II), 50.2 (solid crystal II- nematic), and 99.6 °C (nematic-isotropic). The major enthalpy change occurs at the crystalline-to-nematic phase transition, while nematic-toisotropic phase transition enthalpy is relatively low which is typical for aliphatic compounds [39] where small conformational changes may result in structural phase transitions. The observed character and temperatures of phase transitions for bulk 4-BCA and 4-HBA are in good agreement with those known from the literature [39-42].

For interpretation of these results, it is worth to compare them with similar results for LC 5CB. According to [43], the isotropic-tonematic phase transition in 5CB confined in nanopores is severely weakened and broadened; its character changes from a strong first



Fig. 2. DSC thermograms (heating run) of 4-HBA (a) and 4-BCA (b) in the bulk and under confinement to AIMCM-41. The insets show expanded plots for the confined samples. The arrows indicate corresponding nematic-to-isotropic transition points of bulk 4-HBA and 4-BCA.

order transition in bulk to continuous glassy-like transition. This effect was explained by spatial restrictions hindering molecular ordering of dipole—dipole dimeric 5CB molecules inside the pores. By contrast to 5CB case, no sign of phase transition to crystalline, liquid crystalline or glassy state can be seen for either 4-HBA or 4-BCA confined in mesoporous AlMCM-41 matrices (Fig. 2a, b, insets). In other words, the confinement even stronger influences the phase behavior of H-LC. This may be caused by the fact that, together with spatial constraints, strong molecular interaction between the incorporated molecules and the AlMCM-41 surface active centers impedes molecular dimerization which is an absolutely necessary condition for mesomorphic properties of these compounds. To prove this suggestion, we further investigated interfacial interaction and molecular structure of the confined H-LCs by FTIR transmission spectroscopy.

## 3.2. FTIR spectroscopy

The spectra of the H-LC/AlMCM-41 composites are rather complicated since they contain the absorption bands due to both the organic component and AlMCM-41. Therefore, we consider first the spectra of the individual components.

## 3.2.1. Mesoporous AlMCM-41 molecular sieves

The assignment of the IR spectra of these porous samples was earlier reported by Frunza et al. [22–24,44] and Puchkovska et al. [20,21,45] as well as Handke et al. [46] based on handbooks of A.V. Kiselvov [47] and K. Nakamoto [48]. The bands in the region below 1500 cm<sup>-1</sup> correspond to vibrations of the framework-forming AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra: strong absorption band centered at 1075 cm<sup>-1</sup> is associated with SiO<sub>4</sub> v<sub>3</sub>(F<sub>2</sub>) stretching vibration, the shoulder at 951 cm<sup>-1</sup> is due to  $\rho(OH)$  bending of adsorbed water, the bands at 801 and 459  $\text{cm}^{-1}$  correspond to SiO<sub>4</sub> (A) stretching and SiO<sub>4</sub> (E) bending vibration, respectively, while the shoulder at 570 cm<sup>-1</sup> is assigned to the combination of SiO<sub>4</sub> (F<sub>2</sub>) and AlO<sub>4</sub> (A<sub>1</sub>) modes. It worth mentioning that according to [38] in the spectra of AlMCM-41, compared with those of undoped MCM-41, no essential changes are observed in the region of framework vibration  $(1700-400 \text{ cm}^{-1})$ , which confirms that the Al<sup>+</sup> cations on the MCM-41 pore surface do not have any impact on its framework structure. Mesoporous structure of AlMCM-41 tends to adsorb water vapours from the air, so the strong asymmetrically shaped broad band centered at 3420 cm<sup>-1</sup> is due to OH stretching vibrations of surface silanols and adsorbed water molecules which indicate that the silica framework is hydrophilic. The stretching vibration of water molecules at around 3420 cm<sup>-1</sup> is associated with bending vibration of water molecules at around 1640 cm<sup>-1</sup> having a characteristic and fixed integrated peak intensity ratio of 1:6. As follows from curve fitting of the broad OH stretching band centered at 3420 cm<sup>-1</sup> [20,21] it is separated at least into four components with peak positions at 2970, 3240, 3420, and 3640 cm<sup>-1</sup>. Moreover, the large width of the OH stretching band indicates inhomogeneity and the presence of a broad distribution of different hydroxyls. The proportion of various components varies with temperature indicating the differences in the binding energies of structurally different hydroxyls on the AlMCM-41 surface. Upon heating up to 200 °C in air, AlMCM-41 shows the dehydration process of the pore surface - the intensity of the bands centered at 3240 and 3420 cm<sup>-1</sup> assigned to OH stretching vibrations of physisorbed water, drastically decreases at elevated temperatures. When AlMCM-41 samples are heated up to 170 °C, the emergence of the absorption bands centered at 3690 and 3640 cm<sup>-1</sup> is observed, which are assigned to stretching vibrations of hydrogenbonded bridging Al-OH...O and Si-OH...O groups. As the treatment temperature is raised above 400 °C, the small narrow absorption peak at 3760 cm<sup>-1</sup> can be seen which is ascribed to the fundamental stretching vibrations of the "free" terminal Si–OH silanol groups. However, it is obvious that the temperature of 200 °C is not enough to completely remove physisorbed water coverage from the AlMCM-41 surface. It should be mentioned though that the applied surface pre-treatment improves AlMCM-41 activity, since it facilitates binding of incorporated organic molecules to active surface sites. The transparency region of AlMCM-41 molecular sieves ranges from 1500 to 3000 cm<sup>-1</sup> so they are suitable matrices for FTIR monitoring of spectral changes in main characteristic bands of the incorporated compounds.

#### 3.2.2. Bulk samples of 4-HBA

4-HBA and 4-BCA are typical representatives of liquid crystal materials formed via hydrogen bonding within the dimer molecules. Because of this, crystal structure and IR absorption features of these compounds as well as their close homologues in a bulk state have been intensively studied both experimentally and theoretically [49–52]. It was reported [52] that in the crystalline state, the 4-HBA and 4-BCA molecules are arranged in cyclic dimers by hydrogen bonding, and only their dimeric form is observed. In Ref. [42] it was found that in the nematic phase, the non-hydrogenbonded monomeric molecules could appear, their amount increases with a temperature. This is consistent with the finding of [26,53,54] that only the presence of a conveniently large proportion of closed cyclic dimers of trans-isomer of H-bonded carboxylic acid molecules allows the nematic mesophase to be established.

Here we carry out the FTIR spectroscopy studies of 4-HBA and 4-BCA bulk samples in different phases in order to elucidate temperature behavior of spectral parameters of characteristic absorption bands, to monitor changes in hydrogen bonds system and variation of the amount of different conformers in different phases. The frequencies of the IR absorption bands and their assignment to the vibrations of corresponding groups of 4-HBA and 4-BCA were obtained on the basis of available literature data [49–51,47,48,55]. The peak positions of main IR absorption bands of the bulk 4-HBA and 4-BCA corresponding to the transmission windows of AIMCM-41 as well as their assignment to vibrations of functional groups are given in Table 1. Since both 4-HBA and 4-BCA belong to the same class of mesogenic carboxylic acids and their molecular dynamic behavior is very similar, we describe here in detail only the results obtained for 4-HBA compound and mention just specific features for 4-BCA.

Fig. 3 shows the room temperature FTIR absorption spectra of bulk 4-HBA and those of 4-HBA/AlMCM-41 sample. Major absorption bands of bulk 4-HBA are also presented in its spectra in the confined state, which confirms fairly good incorporation of the 4-HBA molecules into the AlMCM-41 pores. The FTIR spectra of bulk 4-HBA in crystalline state show strong absorption band at 1694 cm<sup>-1</sup> due to the carbonyl stretching v(C=O) mode of dimeric molecules (Fig. 3a). The dimeric form of 4-HBA molecules is manifested as a characteristic broad absorption band of hydrogen bond v(OH) stretching vibrations appearing as a broad absorption band spreading between 2400 and 3200 cm<sup>-1</sup> with its center of gravity at ~2900 cm<sup>-1</sup> (Fig. 3b). The H-bond enthalpy inside the 4-HBA dimers was estimated from the frequency shift of the v(OH) band and was found equal to ~5 kcal/mol [56].

Some other bands characteristic of 4-HBA, can be clearly identified such as: the peaks centered at 3072 and 3010 cm<sup>-1</sup> due to aromatic CH stretching vibrations; those at 2955, 2925, 2872 and 2855 cm<sup>-1</sup> due to CH<sub>3</sub> and CH<sub>2</sub> asymmetrical and symmetrical stretch; at 1611, 1576 and 1514 cm<sup>-1</sup>, to C...C ring vibrations; at 1466, 1457, and 1425 cm<sup>-1</sup>, to the coupled vibrations of CH<sub>2</sub> banding and ring vibrations; at 1379 cm<sup>-1</sup> to CH<sub>2</sub> wagging; at 1321 and 1293 cm<sup>-1</sup>, to coupled CH bending and CC ring vibrations. It

## Table 1

Main IR absorption band frequencies and their assignment to molecular vibrations of 4-HBA and 4-BCA in the bulk and the state of confinement in AlMCM-41 molecular sieves (T = 25 °C).

4-HBA			
Bulk 4-HBA (crystalline phase)		4-HBA/AIMCM-41	
Wavenumber, cm <sup>-1</sup>	Assignment [49-51]	Wavenumber, cm <sup>-1</sup>	Assignment [48,50]
1293 s	ν(C-O)		
1321 s	$\delta_s(CH_3)$		
1379 w	(CH <sub>2</sub> ) wagging	1379 w	
1425 s	δ(COH)	1440 s	$v_{s}(COO^{-})$
		1448 sh	
1457 m	ρ(CH <sub>2</sub> )		
1466 m	$\delta_{as}(CH_3)$		
1514 w	ν(C <u></u> C)	1515 w	ν(C <u></u> C)
	_	1560 s	$v_{as}(\overline{COO^{-}})$
1576 s	$\beta(CH) + \nu(CC)$	1575 sh	$\beta(CH) + \nu(CC)$
		1602 s	v(CC)
1611 s	ν(C <u></u> C)	1611 s	$v(C_{\underline{u}}C)$
		1628 sh	
		1640 m	$\delta(OH)$ (H <sub>2</sub> O adsorbed on AlMCM-41)
1658 sh	ν(C==0)		
1694 vs	ν(C==0)	1698 m	v(C=0) bulk-like open dimers
		1745 w	v(C=O) bulk-like monomers
2554 m			
2600 sh	FR with $v(OH)$		
2674 m			
2855 s	$v_{s}(CH_{2})$	2859 s	$v_s(CH_2)$
2872 s	$v_{s}(CH_{3})$	2872 s	$v_{s}(CH_{3})$
2900 sb	v(OH) cyclic dimers		
2925 vs	$v_{as}(CH_2)$	2929 s	$v_{as}(CH_2)$
2955 s	$v_{as}(CH_3)$	2955 s	$v_{as}(CH_3)$
3010 w	ν( <u></u> CH)	3050 mb	v(OH) open dimers
3072 w	ν( <u></u> CH)		
		3240 sb	v(OH) adsorbed water in AlMCM-41
		3420 sb	v(OH) capillary water in AlMCM-41
		3630 s	v(OH) surface hydroxyls AlMCM-41
		3690 w	Al-OH, Si-OH

4-BCA				
Bulk 4-BCA (crystalline phase)		4-BCA/AIMCM-41		
Wavenumber, cm <sup>-1</sup>	Assignment [47,50]	Wavenumber, cm <sup>-1</sup>	Assignment [48,55]	
1377 w	γ(CCC), β(CCH)			
1419 m	δ(HCH)			
1450 m	$\beta$ (COH), $\nu$ (C $-$ O)	1452 w		
		1460 s	v <sub>s</sub> (COO <sup>-</sup> )	
1466 m	β(HCH)	1468 m	β(HCH)	
		1573 s	$v_{as}(COO^{-})$	
		1630 m	$\delta(OH)$ (H <sub>2</sub> O adsorbed on AlMCM-41)	
1700 vs	v(C=0) (cyclic dimers)	1699 w	v(C=0) (cyclic dimers)	
		1710 m	v(C=0) (open dimers)	
		1741 w	v(C=0) (monomers)	
2650 mb	FR with $v(OH)$			
2852 vs	$v_{s}(CH_{2})$	2855 m	$v_{s}(CH_{2})$	
2872 vs	$v_{s}(CH_{3})$	2872 s	$v_s(CH_3)$	
2923 vs	$v_{as}(CH_2)$	2932 m	$v_{as}(CH_2)$	
2956 vs	$v_{as}(CH_3)$	2959 m	$v_{as}(CH_3)$	
3100 mb	v(OH) cyclic dimers	3100 vw	v(OH) cyclic dimers	
		3240 sb	v(OH) in adsorbed water on AIMCM-41	
		3420 sb	v(OH) capillary water on AIMCM-41	
		3640 s	v(OH) surface hydroxyls on AlMCM-41	
		3690 w	Al-OH, Si-OH	

Note: v - stretching;  $\delta_{\gamma}$ ,  $\beta$ -in-plane bending;  $\rho -$  out-of-plane bending; subscript "s"-symmetric, "as"-asymmetric vibrations; designation of intensity: s-strong, vs-very strong, m-medium, w-weak, sh-shoulder, b-broad; FR- Fermi resonance.

should be mentioned that most of these vibrations cannot be truly described as a single vibrational mode belonging to a certain functional group, since they generally are combinations of several normal modes.

Temperature-dependent FTIR spectra of the bulk samples were measured in the wide temperature range covering the phase transition temperatures. From the changes of spectral parameters of characteristic IR absorption bands, a conclusion about the changes in the molecular conformation and hydrogen bond transformation in different phases could be made. As an example, Fig. 4 shows the variation of carbonyl stretching v(C=O) vibration modes of bulk 4-BCA as a function of temperature. When temperature increases, the peak position of v(C=O) band moves to higher wavenumbers, and an additional absorption maximum can be seen on its high-frequency slope when approaching the isotropization temperature. We performed spectral deconvolution of this band



**Fig. 3.** Fragments of FTIR transmission spectra of bulk 4-HBA and 4-HBA/AIMCM-41 confined system in the regions of carbonyl stretching (a) and OH stretching (b) vibrations. The 4-HBA spectra were normalized by CH stretching vibrations band at 2855 cm<sup>-1</sup> and magnified for convenience. The 4-HBA/AIMCM-41 spectra were normalized by SiO<sub>4</sub>  $v_3(F_2)$  stretching vibration band of AIMCM-41 at 1075 cm<sup>-1</sup>.



**Fig. 4.** Temperature dependence of v(C=O) carbonyl stretching vibration mode in FTIR spectra of bulk 4-BCA.

using the PeakFit software package, and Fig. 5 shows the variation of peak positions of the components. As seen from Fig. 5(a), in the crystalline state (below 51.6 °C), only one component is observed centred at 1703 cm<sup>-1</sup>, which originates from the hydrogen-bonded molecular dimeric form. However, once the temperature increases, the position of this band gradually shifts to higher wavenumbers (1710 cm<sup>-1</sup>) while approaching the nematic-to-isotropic phase transition point, T<sub>c</sub>. Since the frequency of carbonyl stretching band involved in hydrogen bonding increases when the H-bond enthalpy decreases [57], this observation suggests that H-bonding within the dimeric LC molecules became weaker when the temperature increases. As it was shown in Ref. [42], the enthalpy of the H-bonds decreases by 10-20% with temperature increasing. This is accompanied with changes in the dimeric ring dynamics, which leads to dissociation of H-bonded dimeric molecules, and gives rise to the formation of different types of molecular associates with lower Hbond strength. These could be H-bonded open dimers or linear polymeric chains. With temperature approaching the melting point  $T_{\rm c}$ , another high-frequency component could be seen on the carbonyl stretching band at about 1745 cm<sup>-1</sup> that corresponds to monomeric non-hydrogen-bonded 4-BCA molecules. The intensity of this band increases upon heating; an abrupt increase has been



**Fig. 5.** Peak position of v(C=0) carbonyl stretching (a) and  $\rho(OH)$  out-of-plane bending (b) vibration bands in FTIR spectra of bulk 4-BCA as a function of temperature. The square and circle symbols in (a) show the changes in position of v(C=0) band respectively for dimeric (cyclic and open) and monomeric 4-BCA molecules. The dotted lines indicate the C–N and N–I transition points.

observed at the melting point where the monomeric species dominate.

At the same time, the position of  $\rho(OH)$  out-of-plane bending vibrations band centred at 950 cm<sup>-1</sup> (Fig. 5b) shifts to the lowfrequency side of the spectrum, which confirms that the enthalpy of H-bonding decreases at the phase transition. This makes the dimeric ring less stable and increases the probability of gradual formation of open associates and monomers when temperature is approaching the nematic-to-isotropic phase transition point.

## 3.2.3. 4-HBA/AlMCM-41 samples

To analyse the mechanisms of molecular interactions at organic-inorganic interface in 4-HBA/AIMCM-41 composite, we select the regions of structure-sensitive vibrations of 4-HBA molecule: carbonyl (1400–1750 cm<sup>-1</sup>) and OH (2800-3800 cm<sup>-1</sup>) stretching vibrations regions. The carboxylic acid groups are known to be capable of subsequent bonding with the oxide surface either by physisorption with hydroxyls or chemisorption due to formation of a coordinatively bonded carboxylate [47]. As seen in Fig. 3, significant changes of some absorption bands are observed upon 4-HBA confinement into the mesopores of AlMCM-41. In particular, v(C=O) stretching band of 4-HBA centered at 1694  $cm^{-1}$  becomes broaden and weaken, its peak position being shifted to higher wavenumbers by  $4 \text{ cm}^{-1}$  compared to that of the bulk. Curve fitting with PeakFit software has been performed for the carbonyl stretching region for 4-HBA in the bulk and confined in AlMCM-41 pores. The results are shown in Table 1. As seen from the Table 1, in the confined 4-HBA/AIMCM-41 system, the broad weak v(C=0)band can be separated (using decomposition of this complex band into Gaussian curves with PeackFit application) into two components centered at 1698 and 1745 cm<sup>-1</sup>. The peak position of the component at 1698 cm<sup>-1</sup> is by 5 cm<sup>-1</sup> higher than that for C=O stretching in the bulk 4-HBA, suggesting a weaker hydrogen bonding. It could be assumed that this band is due to an insignificant amount of undissociated 4-HBA molecules with different types of dimer conformation (open dimers or chain-like associates) which, according to DSC results (Fig. 2), are not able to form a liquid crystalline nematic phase inside the AlMCM-41 matrix. The carbonyl band centered at 1745 cm<sup>-1</sup> is ascribed to free nonhydrogen-bonded C=O group of monomeric 4-HBA molecules, which also exist in the inner space of AIMCM-41 pores.

The two new strong absorption bands centered at 1560 and 1440 cm<sup>-1</sup> are seen in the FTIR spectra of 4-HBA/AIMCM-41 system. These bands are characteristic of ionized carbonyl group [57] and therefore suggest deprotonation of the 4-HBA molecules inside the AIMCM-41 pores. Usually, a broad band in the 1560-1570 cm<sup>-1</sup> region is assigned to the asymmetric carboxylate stretching vibration  $v_{as}(COO^{-})$ . The asymmetrically shaped band in the 1440–1460 cm<sup>-1</sup> region is due to the corresponding symmetric carboxylate stretching vibration  $v_s(COO^-)$ . This confirms the deprotonation of carboxylic acid group of monomeric 4-HBA molecules on the AlMCM-41 pore surface, with 4-HBA being further chemisorbed as coordinatively bonded carboxylate. This assignment is in agreement with other works on chemisorption of carboxylic acids on metal oxide surfaces [58–61]. The peak separation value  $\delta = v_{as}(COO^{-}) - v_s(COO^{-})$  is known [47,48,57] to determine the coordination type of the carboxylate. Three main types of coordination are distinguished, such as bridging bidentate, chelating bidentate, and monodentate, each giving a characteristic peak separation. The  $\delta$  values obtained for 4-HBA (120 cm<sup>-1</sup>) indicate a bidentate coordination for the carboxylate ion to aluminium cation on the AlMCM-41 pore surface (Fig. 6). Summarizing, the following possible interaction mechanisms of the carboxylic acid molecules with AIMCM-41 surface active centers could be proposed. At the first stage, the H-LC dimers dissociate in confined volume due to



Fig. 6. Schematic representation of possible mechanism of a carboxylic acid adsorption on Al-MCM-41 surface.

spatial restrictions and interaction with surface hydroxyl coverage, and then the carboxyl group of the acid loses the hydrogen atom bound to the hydroxyl oxygen, so that the hydroxyl oxygen becomes negatively charged, and the carboxylate ion ( $COO^-$ ) is formed. At the second stage, the carboxylate ion is involved in coordinated bond R– $COO^-$ ...Al<sup>+</sup> with Lewis acid sites.

Benzene ring breathing v(C...C) vibration bands of 4-HBA at 1611 and 1576 cm<sup>-1</sup> also markedly vanish and broaden upon confinement. In addition, two new bands shifted to lower wavenumbers emerge at 1602 and 1575 cm<sup>-1</sup>. This suggests that significant changes occur in charge distribution in the benzene ring electronic system due to molecular interaction with the MCM-41 pore surface. In the region of 1425–1466 cm<sup>-1</sup>, the intensity of CH bending modes markedly dropped upon confinement, though their peak positions can hardly been distinguished since they are superimposed with carboxylate stretching vibration v<sub>s</sub>(COO<sup>-</sup>) at 1440 cm<sup>-1</sup>. The spectral changes observed in this spectral range indicate that confinement has a significant effect on conformational structure of the incorporated LC molecules suggesting the formation of new molecular conformations with different geometry and local environment.

Notable changes are also observed in the region of OH stretching vibrations (Fig. 3b). As seen, no broad absorption is observed in the range of 2500–3000 cm<sup>-1</sup> caused by OH stretching vibrations in 4-HBA dimeric molecules, which proves that major part of 4-HBA molecules in AIMCM-41 is in a monomeric state. In addition, the shape of OH stretching vibrations band of AlMCM-41 is changed upon incorporation of 4-HBA. In particular, the intensity of the component at ~3200 cm<sup>-1</sup> decreases as compared to that of bare AlMCM-41 indicating that chemisorbed 4-HBA molecules could displace some hydroxyls from the pore surface while forming coordinative bonds with AlMCM-41 active sites. This is also confirmed by the appearance of hydrogen-bonded Si-OH and Al–OH stretching vibrations band at 3690  $\text{cm}^{-1}$  (Fig. 3b). The intensity of the component centered at 3420  $\text{cm}^{-1}$  slightly increases due to additional water molecules generated from the acid deprotonation process. The subtle new OH stretching bands centered between 3000 and 3100 cm<sup>-1</sup> are indicative of the presence of some amount of different types of dimer conformations of 4-HBA molecules (kinds of open dimers or chain associates) with weaker hydrogen bonds.

So, the observed changes in spectral parameters of characteristic FTIR absorption bands of 4-HBA/AlMCM-41 composites (Fig. 3) give evidence of effective interaction between the acid molecules and active sites on the AlMCM-41 pore surface. First, this clearly indicates that upon confinement to AlMCM-41 channels the dimeric nature of the 4-HBA is broken, and it prefers to exist in a monomeric form. Moreover, with FTIR spectroscopy it was possible to

identify the bulk-like undissociated LC molecules inside the pores, which were in form of open dimers or chain associates. Next, the appearance of two new absorption bands at 1560 and 1440 cm<sup>-1</sup> is attributed to symmetric and asymmetric stretching vibrations of ionized COO<sup>-</sup> carbonyl group, which are generally observed, e.g. in the IR absorption spectra of carboxylic acid salts. It means that upon interaction with AlMCM-41 surface, the monomeric 4-HBA molecule dissociates losing the hydrogen from the hydroxyl group, so that the hydroxyl oxygen becomes negatively charged, and the carboxylate ion (COO<sup>-</sup>) is formed. This carboxylate ion then is able to link to the AlMCM-41 pore surface by forming a coordinated bond R-COO<sup>-</sup>...Al<sup>+</sup> with Lewis acid sites.

### 3.2.4. 4-BCA/AlMCM-41 samples

The reason of involving second acid in this research is twofold. On the one hand, we wanted to clarify how general are the regularities received for 4-HBA. On the other hand, it was interesting to clarify how changes in molecular structure influence properties of these compounds in the confined state. According to Fig. 1, 4-BCA has different geometry and length of alkyl tail comparing with 4-HBA. Also, the 4-BCA molecular cyclic dimers are more flexible and essentially non-planar. This may influence efficiency of incorporation in nanopores, interfacial interaction and other properties.

Fig. 7 depicts room temperature FTIR absorption spectra of 4-BCA before and after nanoconfinement to AlMCM-41 matrix. Table 1 shows main IR absorption bands and their assignment to molecular vibrations for pure and confined 4-BCA in the transmission window of AlMCM-41 molecular sieves. The infrared absorption bands and their assignment for bulk 4-BCA are given according to [55]. Because of close proximity of the C–C bonds force constants in cyclic and linear alkanes, the most of vibrational modes of 4-BCA molecule cannot be described as single form of normal vibrations. Instead, they all are represented as mixture of different types of vibrational modes. Among the major absorption bands of 4-BCA are strong absorption band of carbonyl stretching vibrations centered at 1700 cm<sup>-1</sup>, those at 2956, 2923, 2872, and 2852 cm<sup>-1</sup> due to CH<sub>3</sub> and CH<sub>2</sub> asymmetrical and symmetrical stretching vibrations.

A broad absorption band centered at 3100 cm<sup>-1</sup> is assigned to v(O-H) stretching mode of medium-strong hydrogen bond inside 4-BCA cyclic dimers. Some other characteristic bands of 4-BCA can be identified such as the peaks at 1450 and 1377 cm<sup>-1</sup> due to CH<sub>3</sub>

bending as well as at 1419 and 948 cm<sup>-1</sup> due to in-plane and outof-plane OH bending vibrations. Major absorption bands of bulk 4-BCA are present in the FTIR spectra of the composite 4-BCA/ AlMCM-41 system, which indicates the incorporation of the 4-BCA molecules into the AlMCM-41 pores. However, total amount of incorporated 4-BCA molecules, as evidenced from the intensity of characteristic IR absorption bands of CH stretching vibrations at ~2855 and 2932 cm<sup>-1</sup> (Fig. 7b), is much less compared to that of 4-HBA/ALMCM-41 system (Fig. 3b).

In general, changes in the shape and intensity of OH stretching vibrations bands of 4-BCA molecules due to their chemisorption on the AlMCM-41 pore surface are less pronounced than those for 4-HBA, which is in accordance with lower adsorptive capacity of 4-BCA molecules. Hydroxyl coverage of AlMCM-41 pore surface characterized with v(O-H) stretching vibrations of absorbed water molecules (Table 1) is only slightly perturbed by 4-BCA adsorption due to insignificant amount of chemisorbed species (Fig. 7b).

Fig. 7a shows a fragment of 4-BCA FTIR absorption spectra in the region of carbonyl stretching vibrations. As seen from the Table 1 and Fig. 7a, in the confined state, similarly to the discussed above 4-HBA, a single strong carbonyl stretching band of bulk 4-BCA centered at 1700 cm<sup>-1</sup> is vanished and instead a weak broad band is seen with asymmetric contour and its center of gravity at 1699 cm<sup>-1</sup>, where three main components centered at 1699, 1710, and 1741 cm<sup>-1</sup> (assigned to minor fraction of bulk-like cyclic dimers, open associates, and small number of free monomers, respectively) could be separated using decomposition of this complex band into Gaussian curves. At the same time, the emergence of two new bands at 1573 and 1460  $\text{cm}^{-1}$  is observed in the FTIR spectra of confined 4-BCA similar to those found for 4-HBA. Such changes in carbonyl absorption features suggest similar mechanisms of molecular interactions with active centers on the pore surface for both compounds, i.e. partial ionization of C=O group during the acid adsorption onto the AlMCM-41 silica surface so that the COO<sup>-</sup> carboxylate ion is formed which is further coordinated to aluminium cations on the AIMCM-41 pore surface. It worth mentioning that changes observed in the region of OH stretching vibrations of 4-BCA molecules upon their incorporation into the AlMCM-41 pores (Fig. 7b) suggest that some changes in the hydrogen bonding system also occur. Like in the case of 4-HBA, no band of OH stretching vibrations of hydrogen-bonded 4-BCA molecular dimers is observed at  $3100 \text{ cm}^{-1}$ , which confirms that major



**Fig. 7.** FTIR spectra of bulk 4-BCA and 4-BCA/AlMCM-41 confined system in the regions of carbonyl stretching (a) and OH stretching (b) vibrations. The 4-BCA spectra were normalized by CH stretching vibrations band at 2855 cm<sup>-1</sup> and magnified for convenience. The 4-BCA/AlMCM-41 spectra were normalized by SiO<sub>4</sub>  $\nu_3(F_2)$  stretching vibration band of AlMCM-41 at 1075 cm<sup>-1</sup>.

part of adsorbed 4-BCA molecules in the pores of AIMCM-41 is in a monomeric form. So, the analysis of the observed changes in the IR spectra of the both studied model compounds, 4-HBA and 4-BCA mesogenes, indicates that due to interaction with AIMCM-41 pore active centers, the major part of the H-bonded molecules dissociates forming deprotonated carboxylate ion COO<sup>-</sup> which is able to link to the pore surface by forming a coordinated bond R–COO<sup>-</sup>... Al<sup>+</sup> with surface active centers.

#### 3.2.5. 4-HBA/MCM-41 samples

To bring additional arguments for the conclusion about formation of  $R-COO^-...AI^+$  bonds at the interface, we additionally investigated the composites consisting of H-LC confined to molecular sieve without Al dopant. If our conclusion is correct, no new bands related to ionized carbonyl groups of H-LC should arise in these samples. As a sieve of this type we used siliceous molecular sieve MCM-41 with a mean pore radius of about 4.6 nm. H-LC 4-HBA was selected for confinement because of its larger adsorptive capacity.

The carbonyl region of the FTIR spectra of investigated composites and their components is depicted in Fig. 8. As can be seen, unlike the previous case of AlMCM-41 confining matrix, no new bands related to ionized carbonyl group arise in the spectra of 4-HBA/MCM-41 composite. Also, unlike the previous case, the carbonyl band of bulk 4-HBA molecules in dimeric state centered at 1695 cm<sup>-1</sup> is just slightly lowered. This means that much smaller part of dimers is broken due to weaker interaction with the pore walls. These facts suggest that dominating mechanism of interfacial interaction in case of MCM-41 matrix is different from coordination bonding.

To shed light on this mechanism, consider other features of the spectrum of 4-HBA in MCM-41 sieves (Fig. 8). It is evident that in the pores the mentioned carbonyl band centered at 1695 cm<sup>-1</sup> is broaden and shifted towards higher frequencies by 6 cm<sup>-1</sup>. The overall shape of this bond becomes complicated suggesting that there are different states of C=O groups in the pores. Decomposition of this complex band into Gaussian curves (not shown here) yields three components centered at 1675, 1695, and 1741 cm<sup>-1</sup>. According to [62–64], these components can be attributed to the



**Fig. 8.** FTIR spectra of 4-HBA/MCM-41 composite system in the region of carbonyl stretching vibrations compared to those of 4-HBA and bare MCM-41. The 4-HBA spectra (of the bulk and confined one) were normalized by CH stretching vibrations band at 2852 cm<sup>-1</sup>, and then the confined 4-HBA spectra were magnified for convenience.

following states of C=O groups: (1) hydrogen-bonded with silanol groups on the pore surface, (2) in the bulk-like dimers, and (3) in monomers of 4-HBA, respectively. Arising of the first component suggests that the hydrogen bonding of the type -Si-OH...O=C is the mechanism determining interfacial interaction in the 4-HBA/MCM-41 samples.

Analysis of spectral features in the range of 2900–3700 cm<sup>-1</sup> corresponding to OH groups stretching vibrations may specify other types of hydrogen bonds at the interface. Correct interpretation of these spectra requires a very thorough treatment of the molecular sieves to remove water adsorbed in the pores. Precise assignment of this spectral range left beyond the scope of this work.

Thus, the results for the 4-HBA/MCM-41 composites supports the conclusion that the metal cations on MCM-41 pore surface initiate ionization of carbonyl groups of H-LCs opening way for formation of coordinated bonds between these groups and Lewis acid sites at the surface of metal-doped siliceous molecular sieves. If these cations are absent, hydrogen bonding is a prevailing mechanism of interfacial interaction.

## 4. Conclusions

In this study, the 4-HBA and 4-BCA carboxylic acids with different head group structure and alkyl chain length where selected as representatives of hydrogen-bonded LCs, i.e. the LCs having mesomorphic properties due to dimerization of their molecules via hydrogen bonding. The peculiarities of structural organization and interfacial interaction of these compounds are studied under their confinement to nanoporous AlMCM-41 molecular sieves and compared with their properties in the bulk state. The hydrogen-bonded LCs are shown to be easily incorporated into this porous material.

With DSC measurements it is shown that thermal properties of the H-LC are radically changed by confinement to AlMCM-41. In contrast to conventional nematic LCs in nanoporous media [9,25], no any traces of crystallization or mesophase formation is observed. Instead, H-LCs incorporated in nanopores behave as amorphous materials in a wide temperature range of 10-120 °C covering crystal, nematic and isotropic phases of these materials in the bulk state. This happens due to the fact that the dimerization is strongly restricted in the pores due to limited space and interaction with the pore walls. As shown by FTIR spectroscopy, upon confinement into AlMCM-41 porous matrix, the majority of molecular hydrogen bonds are broken, reflecting decay of molecular dimers. At the same time, FTIR spectroscopy detected some amount of the bulk-like undissociated LC molecules. These molecules, presumably located in the inner space of the pores, were in the form of open dimers or chain associates. The DSC results suggest that the amount of these dimers was well below the level needed for formation of LC mesophases.

The appeared monomeric acid molecules at the interfaces strongly interacted with the pore surface. The active sites on AlMCM-41 pore walls, or Lewis acid sites associated with Al<sup>+</sup> cations, are found to be capable of deprotonation of the carboxylic acid groups of H-LC molecules, resulting in the formation of carboxylate ions. FTIR results indicate that most of the loaded monomeric molecules of both 4-HBA and 4-BCA are chemisorbed to the surface of AlMCM-41 by coordination bond R-COO<sup>-</sup>...Al<sup>+</sup> in a bidentate way to aluminium cation on the AlMCM-41 pore surface. This finding is well supported by the fact that the intensive characteristic bands of the mentioned coordinated bonds are completely absent if the studied acids are filled into Si-MCM-41 molecular sieves having no Al<sup>+</sup> cations. Our next efforts will be aimed at ascertaining the impact of the H-LC terminal group structure on the coordination bonds strength.

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