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Liquid Crystals

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To cite this Article Bezrodna, T. , Chashechnikova, I. , Dolgov, L. , Puchkovska, G. , Shaydyuk, Ye. , Lebovka, N. , Moraru, V. , Baran, J. and Ratajczak, H.(2005) 'Effects of montmorillonite modification on optical properties of heterogeneous nematic liquid crystal - clay mineral nanocomposites', *Liquid Crystals*, 32: 8, 1005 – 1012

To link to this Article: DOI: 10.1080/02678290500181767

URL: <http://dx.doi.org/10.1080/02678290500181767>

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Effects of montmorillonite modification on optical properties of heterogeneous nematic liquid crystal – clay mineral nanocomposites

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(Received 11 January 2005; accepted 9 April 2005)

Investigations of montmorillonite (MMT) clay mineral modification effects on electro-optical properties of nanocomposites, based on the nematic liquid crystal 4-pentyl-4'-cyanobiphenyl (5CB) and MMT have been carried out. Only the composite with MMT modified by an organic surface-active substance, dioctadecyldimethylammonium chloride, has been shown to manifest electro-optical memory effect and contrast. A polar dopant (acetone), added to the mixture, significantly increases composite homogeneity. Results of IR spectroscopy measurements lead to the conclusion, that there is a mutual influence of components on each other in organoclay systems, which appears as an alignment of near-surface layers of both the organic and inorganic components of the composite. Due to such interactions these systems show electro-optical contrast and memory effect. A composite with organophobic Na-MMT does not show these electro-optical properties, due to the absence of component interactions, as shown by IR spectroscopic data.

1. Introduction

Combined systems, consisting of a nematic liquid crystal (NLC) and a nanostructured inorganic substance, are widely used in modern technologies, such as scattering displays, windows with controlled transparency, devices for information recording and storage, etc. Because of interactions between their organic and inorganic components, these systems can exhibit properties not seen in their individual components. For example, they can be characterized by high rigidity, elasticity and uncommon electro-optical parameters. Thus such heterogeneous composites are now intensively studied by various methods. In particular, detailed investigations of electro-optical properties have been made for systems where 5CB or ZLI-4801 nematic mixture is the NLC, and pure or polymethylsiloxane-modified A-300 aerosil is used as filler [1–4]. The electro-optical parameters of these systems have been shown to depend on the physico-chemical properties and concentrations of their components; and also on the strength of interaction between the organic and inorganic components of the composite. Under certain conditions, an 'optical memory effect' is observed in the

described systems. The authors have proposed a mechanism for this phenomenon.

Natural clay minerals, which are able to exchange cations in their interplanar voids, are also used in heterogeneous systems with liquid crystals. In particular, it has been reported that the composite based on a mixture of low molar mass LCs (TFALC) with particles of modified clay, has unusual electro-optical properties [5–7]. When an electrical field was applied, a sharp increase of light transmittance was seen, and a 'memory effect' after the voltage was switched off. This effect was not found for other NLCs, probably, due to their low viscosity.

Spectroscopic methods, in particular IR spectroscopy, are very efficient for investigations of interaction processes between components of such heterogeneous systems. The formation of Si–OH... π bonds between phenyl rings of 5CB molecules and OH groups of the aerosil surface has been reported [8, 9], and hydrogen bonds have been found between CN groups of 5CB and surface hydroxyl groups of the inorganic components of the studied composites [10–12]. The effects of montmorillonite (MMT) clay mineral modified by an organic surface-active substance (SAS) on the electro-optical properties of a 5CB–MMT heterogeneous nanocomposite have been investigated in this work.

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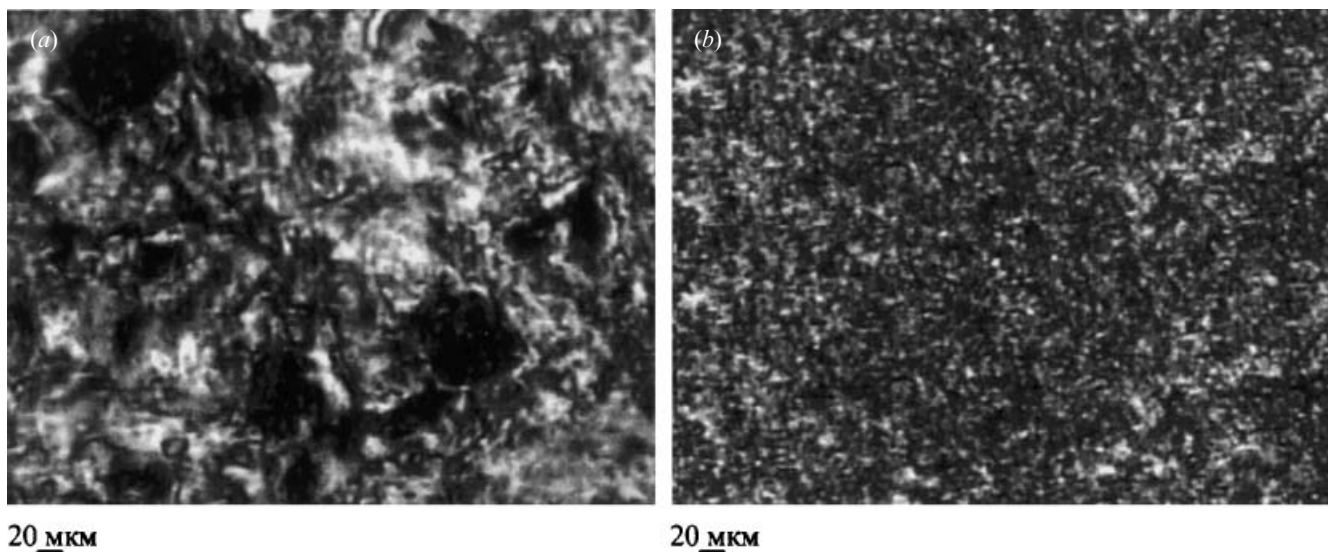


Figure 1. Nanocomposite micrographs, obtained by POM. (a) 5CB-Na-MMT, (b) 5CB-DODM-MMT; dark regions correspond to LC, light regions to clay particles.

2. Materials and experimental methods

The liquid crystal used in this work, 4-pentyl-4'-cyanobiphenyl (5CB), is in the nematic phase at room temperature, and its nematic-isotropic liquid phase transition occurs at $T=308$ K. Natural MMT, which is a layered aluminosilicate of 2:1 structural type, with an 'elastic' framework and interlayer distances d_{001} of 1.26 nm, was used as the inorganic component of the composite. It is characterized by high hydrophilicity, which impedes its dispersion in a hydrophobic organic medium, such as 5CB.

In order to increase the chemical affinity of MMT particles for 5CB molecules, and to extend the interplanar space in the mineral, the latter may be modified by hydrophobic organic substances by means of the ion-exchange of Na-type MMT with long chain alkyl(or aryl)ammonium acids. A Na-type sample (Na-MMT) was produced by the full substitution of exchange cations in purified natural bentonite (Askan deposit, Georgia) with Na ions. From X-ray diffraction (XRD) analysis, the Na-MMT obtained is characterized by d_{001} of 1.24 nm.

A cationic SAS, dioctadecyldimethylammonium chloride (DODM) (BASF, Germany) of 99.5% chemical purity was used as organic modifier. The modification was carried out by the ion-exchange interaction of Na-MMT (particle size 0.2–2 μm) with DODM aqueous solution, giving a d_{001} value of 1.91 nm for this sample (denoted as DODM-MMT).

Composites were obtained by mixing the MMT material and LC using an ultrasound disperser device

(UZDN-2T) for more efficient homogenization. In order to increase the compatibility of the two components and to obtain better swelling and structure formation of the organophilic MMT and its distribution in 5CB, acetone was added to the mixture (not more than 1%). In the case of the modified clay sample, in the presence of acetone a homogeneous dispersion is formed, and no significant sedimentation of particles occurs even after several months. The 5CB-Na-MMT sample separates into two phases even in the presence of

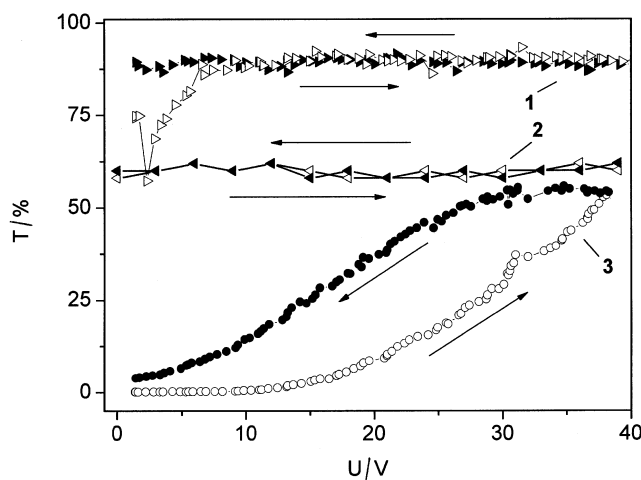


Figure 2. The dependence of light transmittance (T , %) on the value of applied voltage (U , V). 1: bulk 5CB, 2: 5CB-Na-MMT, 3: 5CB-DODM-MMT.

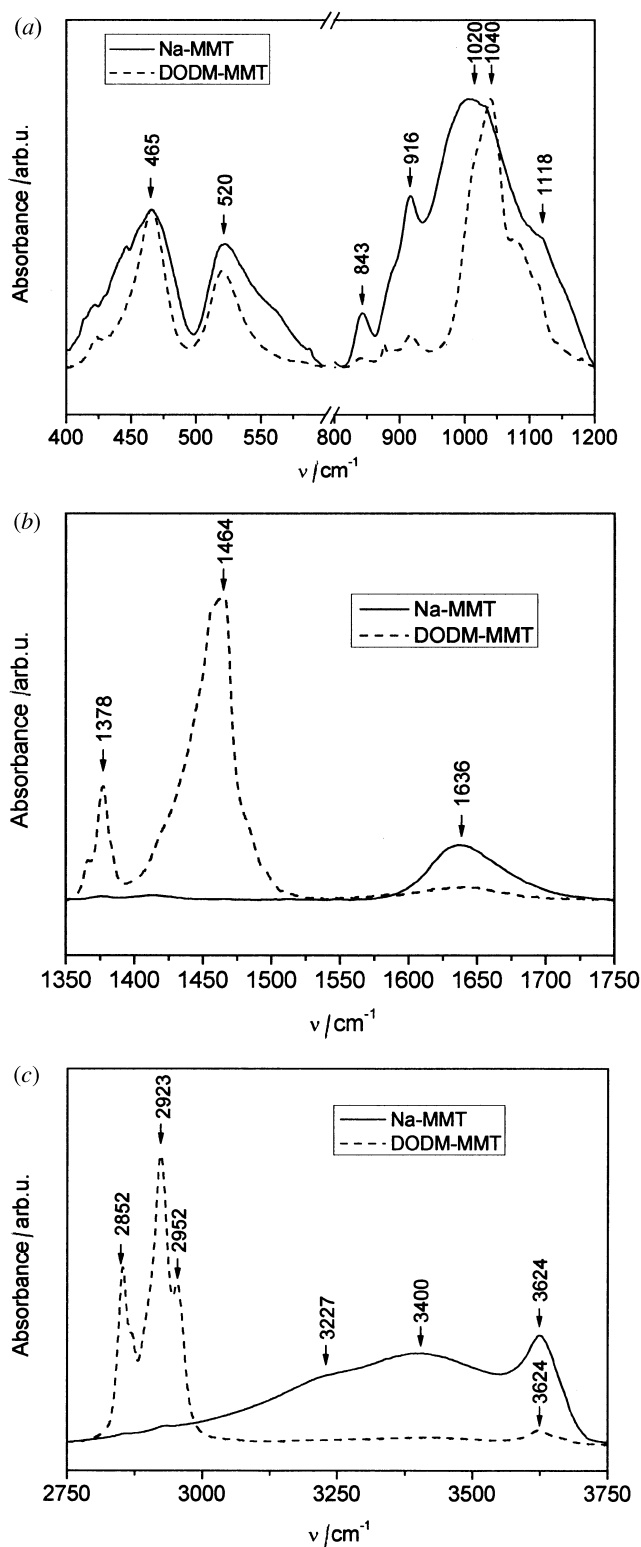


Figure 3. IR absorption spectra of Na-MMT and DODM-MMT clay minerals in the vibrational regions of (a) O–Si–O, O–Al–O, Si–O, Al–O bonds, (b) CH₂-, CH₃- and OH-groups, (c) CH bonds in CH₂-groups of the alkyl radical and OH-groups.

acetone. The different levels of composite homogeneity with the use of unmodified and organo-modified MMT are shown by polarizing optical microscopy (POM), see figure 1.

XRD analysis was performed using an X-ray diffractometer (DRON-UM1) with two Soller splits, filtered CoK_α irradiation and recording speeds of 1 and 0.5° min⁻¹ in the Bragg angle region of 3°–15°. The LC composite, previously kept at room temperature for three days, was layered onto a quartz cell and placed in the goniometer.

For electro-optical measurements, a carefully mixed sample of the composite was placed between two glass plates, whose inner surfaces were covered with a thin electroconductive film of ITO. The thickness of the sample layer was determined by the diameter of spacers located between the plates ($d=20\ \mu\text{m}$). The ends of the cell were sealed by epoxide. A helium-neon laser ($\lambda=0.63\ \mu\text{m}$) was used in these experiments; the voltage range was 0–80 V, and the current frequency $f=2\ \text{kHz}$. The dependence of the degree of light transmittance on the applied voltage was studied after preliminary exposure of samples to an alternating electric field, which led to good reproducibility of the obtained results.

For samples which show a memory effect, on increasing the applied voltage U , the light transmittance T (%) increases; on reducing U , partial transparency remains, yielding a memory parameter M defined as [13]:

$$M = \frac{T_m - T_o}{T_{\text{sat}} - T_o} \times 100\% \quad (1)$$

where T_o is the initial light transmittance, T_m the residual transmittance and T_{sat} is the maximum transmittance at U_{sat} . For the application of heterogeneous nanocomposites to information display devices, the system must have a large difference between T_{sat} in the electric field and T_o , i.e. a large contrast value K , which is defined as

$$K = T_{\text{sat}}/T_o. \quad (2)$$

IR absorption measurements were carried out at room temperature in the spectral range 400–4000 cm⁻¹ on a Bruker IFS-88 spectrometer with a spectral resolution of 1 cm⁻¹ and 64 scanings for each spectrum. Samples of clay minerals for IR spectral experiments were prepared as emulsions in vaseline or fluorinated vaseline oils. Samples of heterogeneous suspensions were placed directly between KBr cell windows.

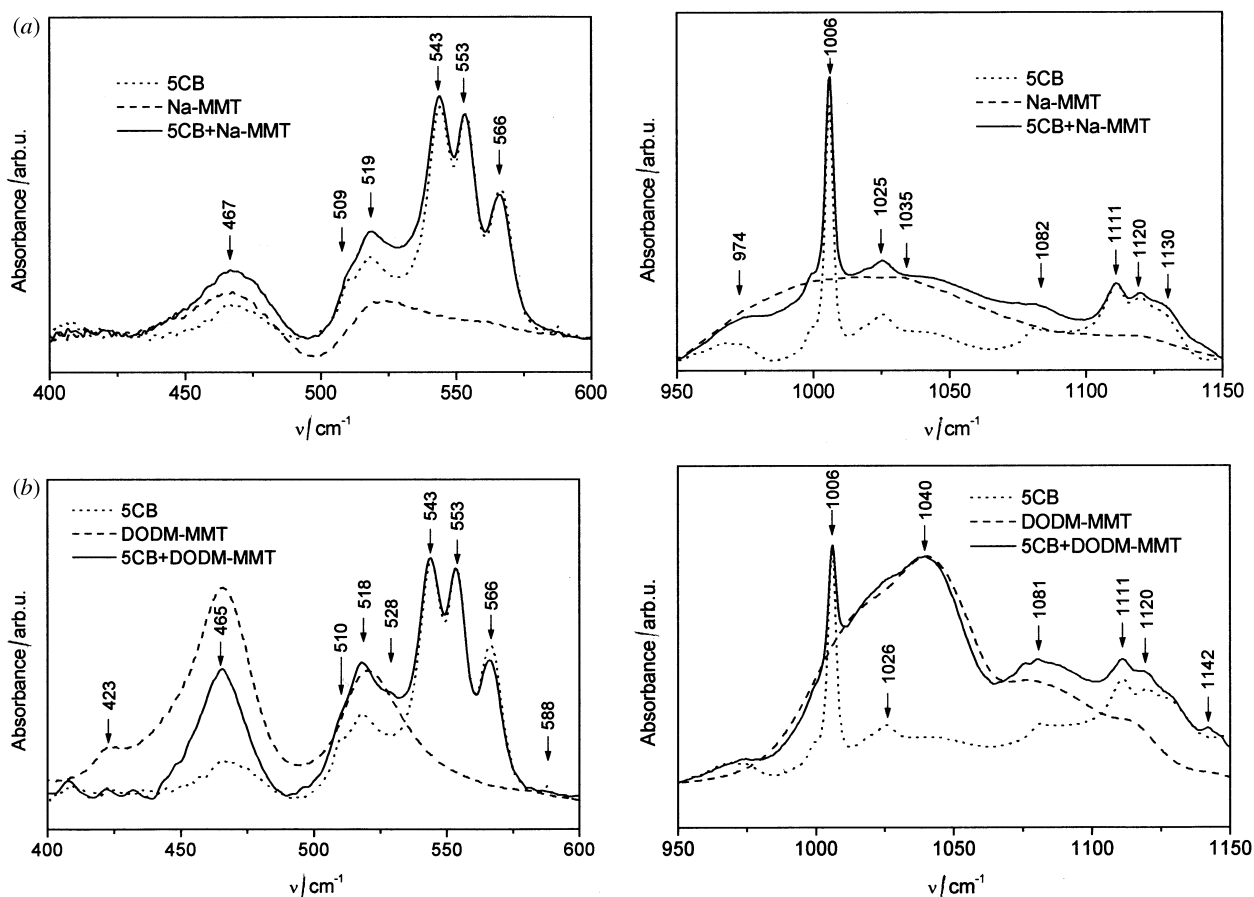


Figure 4. IR absorption spectra of composites in the vibrational regions of O–Si–O, O–Al–O, Si–O, Al–O bonds of clay minerals: (a) 5CB–Na–MMT, (b) 5CB–DODM–MMT.

3. Results and discussion

3.1. Electro-optical properties of composites

Figure 2 shows the dependence of the light transmittance T on applied voltage for the systems studied. Curve 1, for pure 5CB in the nematic phase, has a high light transmittance ($T=90\%$), which is independent of applied voltage. The 5CB–Na–MMT (acetone) composite in its initial state is characterized with lower transparency ($T=60\%$) due to light scattering by the suspended solid mineral particles. With increase in applied voltage (up to 80 V) there is no change in transmittance, as in the case of pure 5CB. With voltage decrease T does not change, i.e. the system is reversible ($M=0$, $K=1$) (figure 2, curve 2). This shows the absence of interaction between the components of the system, due to the surface hydrophilicity of unmodified MMT. The heterogeneity of this composite is also seen from its photomicrograph, figure 1(a). In addition, this material has relatively high electroconductivity

($3.5 \times 10^{-4} \text{ ohm}^{-1}$), compared, for example, with that of the 5CB–TiO₂ system ($8 \times 10^{-7} \text{ ohm}^{-1}$); this probably results from the partial transfer of sodium ions into the liquid phase, providing the system with conductivity.

The modification of Na–MMT with the hydrophobic organic salt results in a sharp increase in the affinity of the organoclay for the liquid crystal and to changes in the electro-optical properties of the 5CB–MMT heterosystem. In the absence of an electric field, 5CB–DODM–MMT transmits practically no light; for $\lambda=0.63 \mu\text{m}$, $T=0.1\text{--}0.2\%$. However, when a voltage is applied, the light transmittance increases and reaches a maximum ($T_{\text{sat}}=56\%$) at $U=38 \text{ V}$. At higher voltages the nematic–isotropic liquid phase transition takes place due to ohmic heating. On decreasing the voltage, the transmitting state remains, and a small memory effect is observed; $M=7\%$, with a high contrast value $K=300\text{--}400$ (figure 2, curve 3).

The effect of organic modification of MMT on the electro-optical properties of 5CB–MMT heterocomposite,

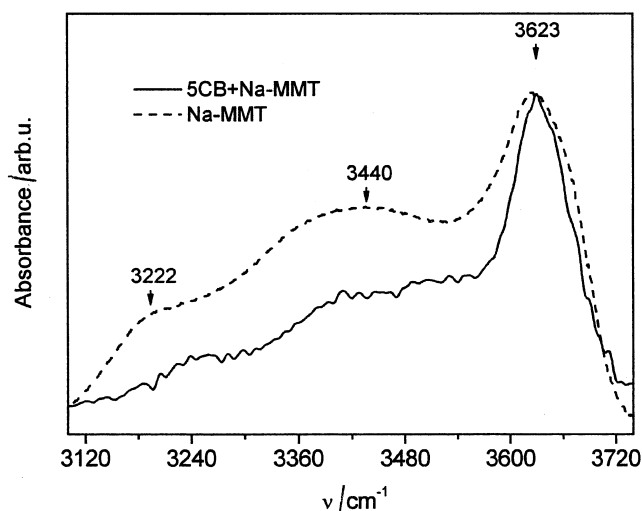


Figure 5. Sections of IR absorption spectra for Na-MMT in the region of OH stretching vibrations of physically adsorbed water and inner-surface OH groups; before (dashed curve) and after (solid curve, obtained by subtracting the 5CB spectrum from the spectrum of the 5CB–Na-MMT composite) dispersion of the mineral in 5CB.

is probably due to interaction between the components of the system. In fact, from XRD investigations, interplanar distances in DODM-MMT increase from 1.91 nm in the dry state to 1.97 nm after its immersion in 5CB. In other words, LC molecules probably penetrate the interplanar voids of the clay, leading to its swelling. The type and strength of component interactions in the composites were investigated by IR spectroscopy.

3.2. IR spectroscopic investigations

Figure 3 presents sections of IR spectra for pure samples of the clay minerals Na-MMT and DODM-MMT, recorded in vaseline oil in the spectral range $400\text{--}3750\text{ cm}^{-1}$. Bands in the regions $450\text{--}550$ and $800\text{--}1150\text{ cm}^{-1}$, figure 3(a), correspond to deformation and stretching vibrations of O–Si–O and O–Al–O bonds in the crystal framework of the aluminosilicate, and agree with literature data [13, 14]. As can be seen from the figure, when the mineral is modified, the peak positions of the 465 and 520 cm^{-1} bands do not shift, while a complex band at 1020 cm^{-1} in the spectrum of Na-MMT changes shape and shifts to 1040 cm^{-1} in the spectrum of DODM-MMT. The spectral widths of all these bands are significantly narrower in the organoclay than in Na-MMT. These spectral changes probably show some reconstruction of the aluminosilicate nanolayers, when large organic molecules are incorporated in the mineral, accompanied with changes of Si–O and Al–O bond lengths.

Spectral bands in the regions of deformation ($\sim 1636\text{ cm}^{-1}$), figure 3(b), and stretching vibrations of structural hydroxyl groups and physisorbed water ($3200\text{--}3500\text{ cm}^{-1}$), figure 3(c), are observed in the spectra of the mineral samples studied. However, in the case of the organo-modified clay these bands are much weaker than those for Na-MMT, which shows a low hydration level of the organoclay surface.

In addition, spectra of both samples of studied minerals, figure 3(c), contain bands in the region $3600\text{--}3700\text{ cm}^{-1}$, which correspond to the stretching vibrations of inner-surface OH groups, located inside the aluminosilicate crystalline structure. It should be noted that the frequency of this band, 3623 cm^{-1} for Na-MMT, agrees with literature data for this type of smectite [14].

DODM-MMT spectra also contain bands corresponding to vibrations of the modifier C–H alkyl radicals (spectral regions $1350\text{--}1550$ and $2750\text{--}3000\text{ cm}^{-1}$), figures 3(b,c). The intense band at 1464 cm^{-1} is assigned to deformation (scissors) vibrations of CH_2 and CH_3 groups, and bands at 2852 and 2923 cm^{-1} correspond to the symmetrical and unsymmetrical stretching vibrations of C–H in CH_2 groups of the alkyl radical.

Figures 4–7 present sections of IR spectra in the regions where the characteristic bands of inorganic and organic components of the heterosystems are observed. In order to show the mutual influence of components in the mixture, each figure contains normalized spectra of bulk 5CB, the clay mineral sample, and the composite consisting of these components. Figures marked as (a) show data for the 5CB–Na-MMT system, while figures (b) apply to the 5CB–DODM-MMT system.

In figure 4(a), in the Na-MMT spectrum, bands in the regions $400\text{--}600$ and $950\text{--}1150\text{ cm}^{-1}$, are due to O–Si–O, Si–O, O–Al–O and Al–O bond vibrations. These bands change neither their peak positions, nor spectral widths after this mineral is dispersed in liquid crystal. This shows the absence of influence of 5CB molecules on the mineral structure. The intensity of bands in the region $3100\text{--}3500\text{ cm}^{-1}$, resulting from adsorbed water in the unmodified MMT, decreases significantly when the mineral is in contact with LC. This is probably due to the partial removal of H_2O molecules from the mineral surface by 5CB molecules (figure 5). The corresponding OH group deformation band at 1645 cm^{-1} practically disappears in the spectrum of the 5CB–Na-MMT composite. In the spectra of heterosystems based on the modified clay, figure 4(b), there is some narrowing, of the 465 , 543 , 553 and 1040 cm^{-1} bands, while their peak positions remain the same. This observation indicates the

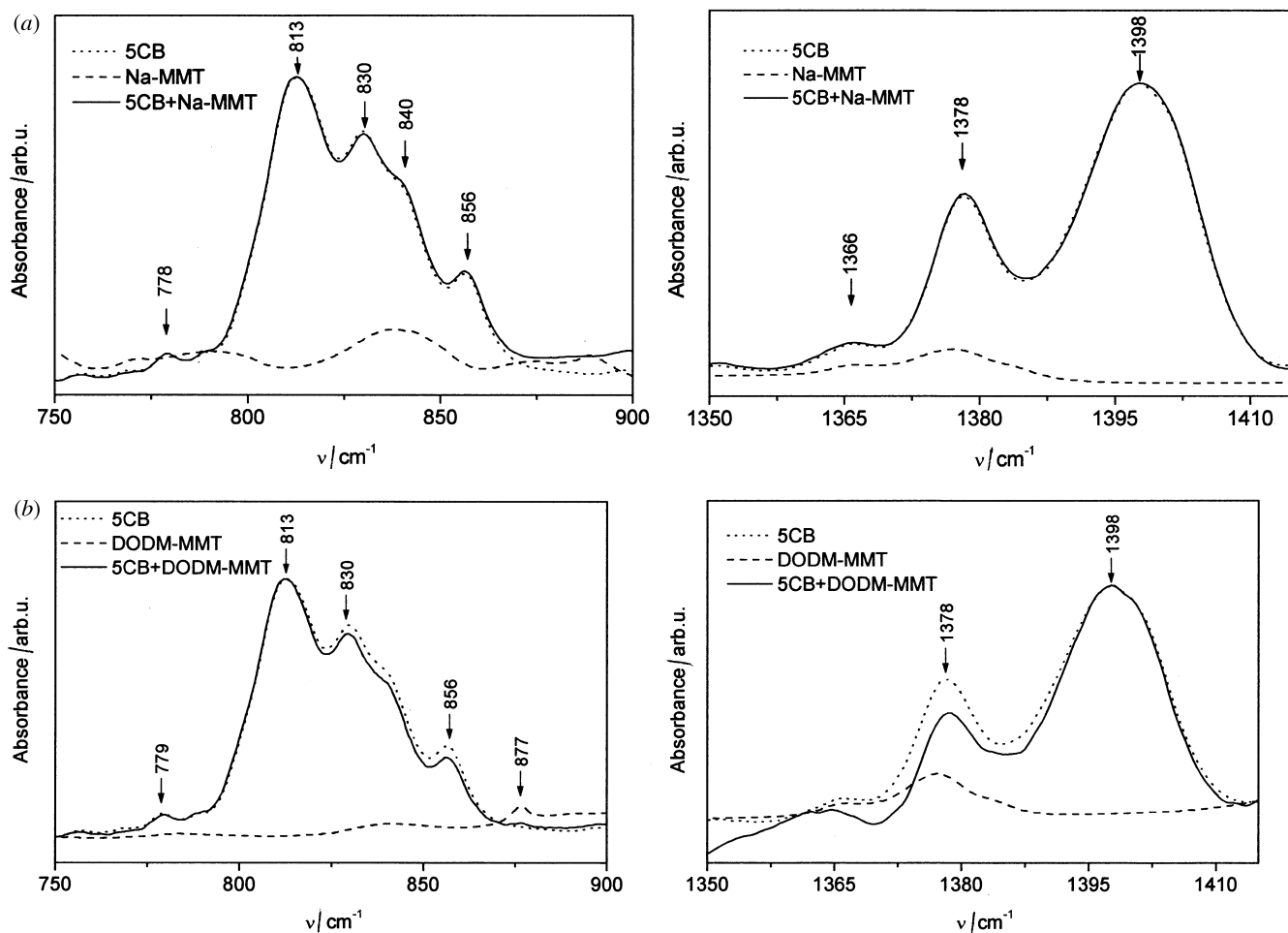


Figure 6. IR absorption spectra of nanocomposites in the region of 5CB alkyl chain vibrations: (a) 5CB–Na–MMT, (b) 5CB–DODM–MMT.

alignment of near-surface layers of organoclay lamellae under the influence of 5CB molecules.

The 5CB spectrum also changes when the LC interacts with the organoclay, in contrast to the case of the composite with Na–MMT. As shown in figure 6(a), in the IR spectrum of 5CB filled with Na–MMT, absorption bands at 750–900 and 1350–1410 cm^{-1} (corresponding to deformation vibrations of 5CB–C–CN– and C–H alkyl chain bonds [15]), retain their same peak positions and relative intensities. For this heterosystem the 830, 1492 and 1606 cm^{-1} bands, corresponding to in-plane and out-of-plane deformation of C–H and stretching C–C vibrations of phenyl rings, respectively, and also the CN bond 2226 cm^{-1} band, also retain their spectral parameters, figure 7(a).

As has been mentioned before, the modification of clay minerals by organic substances leads not only to the increasing of d_{001} , but also increases their affinity for

liquid crystals. It should be noted that the length of 5CB dipole–dipole-bonded dimer in the bulk nematic phase and isotropic liquid is approximately 2.2 nm [10], which is comparable with the interplanar distance (1.97 nm) of DODM–MMT in the heterocomposite. This allows LC molecules to penetrate into the interplanar voids of organoclay particles, leading to changes in the 5CB IR spectra in this heterogeneous system. According to figures 6(b) and 7(b), in the spectra of the 5CB–DODM–MMT system the peak positions of bands at 830, 1494, 1606 and 2226 cm^{-1} , corresponding to vibrations of 5CB molecules (see above), do not change in comparison with those of bulk 5CB, but the spectral widths of these bands decrease. The fact that the peak position of the CN band is the same in the bulk nematic phase and the heterosystem, indicates the presence of 5CB dimers inside the organoclay; in the case of 5CB monomer this band is at 2229 cm^{-1} [10].

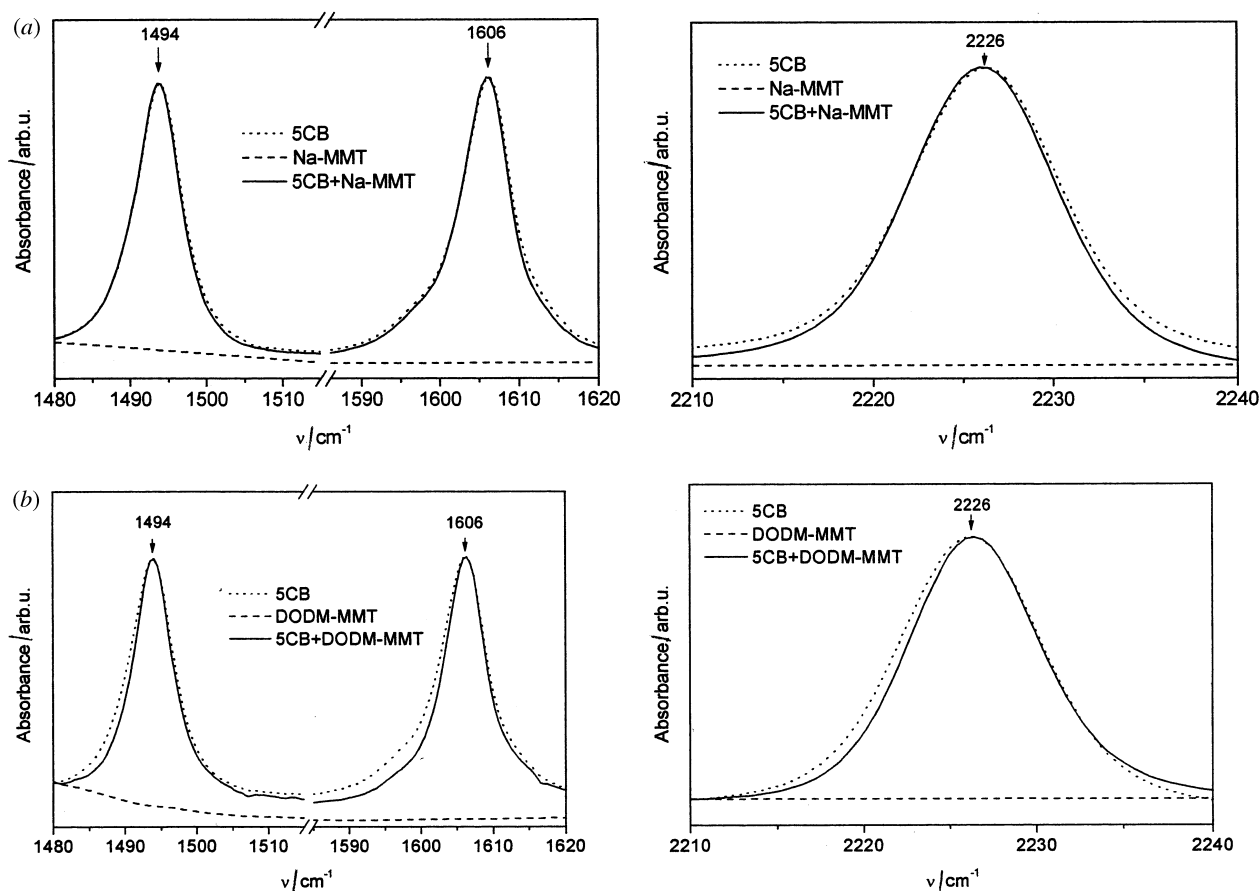


Figure 7. IR absorption spectra of nanocomposites in the region of 5CB phenyl ring C–C bond and CN group vibrations: (a) 5CB–Na–MMT, (b) 5CB–DODM–MMT.

The narrowing of spectral bands, is probably the result of stronger hindering of reorientation of 5CB molecules along their X and Y axes, when these molecules contact the inner surface of the organo-modified clay. In other words, some alignment of LC layers near the surface of organoclay particles is observed.

Thus, our IR spectroscopic investigations have shown that in the heterogeneous nanosystem based on 5CB and organo-modified MMT, a mutual influence of its components occurs, which appears as an alignment of near-surface layers of both organic and inorganic compounds. Due to this interaction, when a voltage is applied to the sample, MMT particles and LC molecules are oriented along the electric field, which results in a significant increase in light transmittance of the system; a so-called ‘contrast’ is observed. Due to the regulating effect of the mutual influence of 5CB domains and organoclay particles, the system remains

partially transparent and when the electric field is removed, a small memory effect is observed. In the composite with unmodified MMT no such electro-optical properties are observed; because interactions between the components in this heterosystem are absent.

4. Conclusions

The liquid crystal 5CB has been assumed to penetrate the interplanar voids of the organoclay in 5CB–DODM–MMT nanocomposite, which results in the increase of d_{001} from 1.91 to 1.97 nm and in considerable swelling of the clay lamellae. The 5CB nevertheless retains its dimer state.

The electro-optical properties of nanocomposites based on 5CB and MMT clay mineral have been investigated, in relation to the surface treatment method of the latter. A significant contrast ($K=300\text{--}400$) and

small electro-optical memory effect ($M=7\%$) were shown only by the nanocomposite with MMT modified by dioctadecyldimethylammonium chloride.

By means of IR spectroscopy, the mutual influence of LC molecules and mineral particles was revealed in the nanocomposite based on LC (5CB) and organoclay, which appears as an alignment of near-surface layers of both composite components. Due to this (van der Waals) interaction, the system becomes transparent under the influence of an electric field and retains this state when the voltage is removed. In other words, the system shows a contrast and a small memory effect. In the case of the 5CB–Na–MMT system no such electro-optical effects are observed, because of the absence of component interactions, due to the organophobicity of unmodified MMT particles.

Acknowledgments

This work was carried out with financial support of the National Academy of Science Ukraine under the ‘Nanophysics and nanoelectronics’ program (NVC 89-297-23 project).

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