RAMAN SPECTROSCOPIC STUDY OF ORGANO-MONTMORILLONITES

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Abstract: A detailed observation about the ordering conformation of hexadecyltrimethylammonium (HDTMA) ions confined within the montmorillonite interlayer in different concentration surfactant modified organo-montmorillonites has been obtained by Raman spectroscopic study.

Raman spectroscopy has been proven to be an ideal method to investigate the ordering conformation of surfactant intercalated in an inorganic layered host [1-3]. Although there are few Raman studies on organoclays, based on previous studies on various materials at various temperatures [4-7], it is assured that Raman spectroscopy is a powerful probe for the microstructural environment of organic within organoclays. So in this paper, the ordering conformation of surfactant molecules in organoclay prepared at various concentrations has been investigated using Raman spectroscopy and such a study is very important to understand the detailed conformation of surfactant in the organoclays.

Raman spectroscopy in the C-H stretching modes has been extensively used to characterize amine chain conformation [2]. Figure 1 shows the Raman spectra of HDTMA surfactant recorded at room and liquid nitrogen temperature and that of HDTMA modified montmorillonite. The two bands are sensitive to the ordering conformation of amine chains confined within the montmorillonite interlayer, as indicated by the changes of frequencies, relative intensities and width of the bands [1,2,8,9].

Many studies show that with the increase of the concentration of surfactant, the arrangement of surfactant in the clay interlayer will vary from lateral-monolayer, lateral-bilayer, paraffin-type monolayer and last to paraffin-type bilayer. In this study, the ordering conformation depends strongly on the concentration of the confined amine. In the sample with low amine concentration, the amine ions are parallel to the interlayer and individually separated [3]. The interaction among amine molecules is very weak. This dilution effect causes the formation of gauche conformers. However, with the increase of the amine concentration, increased interchain interaction and restriction of the room for the movement of the amine tail will be resulted. This will lead to the increase of the number of the ordered conformers which are reflected by the wavenumber shift to lower wavenumber and the decrease of the band width. For the paraffin-type model of the amine chains, there is a relative high packing density. This means the room for movement of the tail of amine chain is limited and the confined amine chains adopt an essentially all-trans conformation. Therefore, there will be no dramatic change of the wavenumber of the bands as demonstrated in the present study. It shows that both wavenumber and band width of antisymmetric and symmetric stretching modes are sensitive to the ordering conformation of the inserted organic surfactant cation. In addition, comparing with that of symmetric stretching mode, the wavenumber of the antisymmetric stretching mode is more sensitive to the mobility of the tail of amine chain.

In this study, the effect of temperature is also considered. At room temperature, the conformational ordering is more easily to be effected by the packing density in the lateral model

than in the paraffin-type model. However, when at liquid nitrogen temperature, the positions of antisymmetric and symmetric stretching modes are independent of the surfactant concentration and the band width of symmetric stretching mode is sensitive to the ordering conformation of organic. Upon heating the organo-montmorillonites, both the position of the antisymmetric and symmetric stretching bands shift to higher wavenumbers, indicating the decrease of conformational ordering.

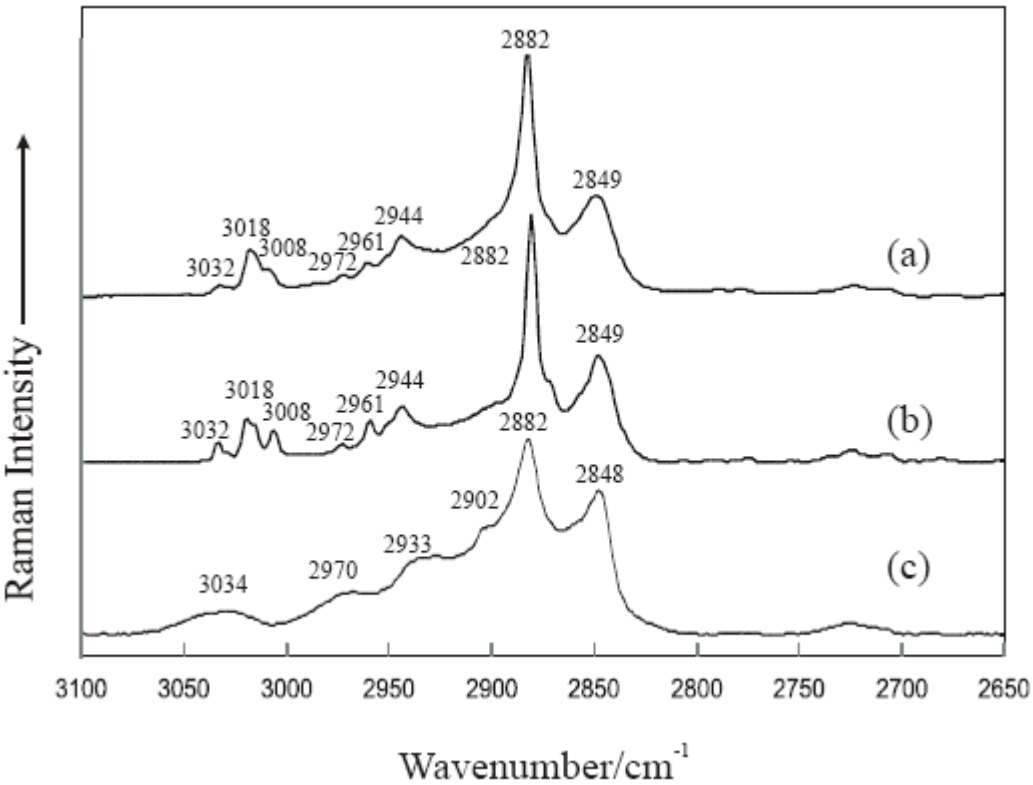

Figure 1 (a): Crystalline HDTMA at room temperature
(b): HDTMA at liquid nitrogen temperature
(c): HM5.0CEC (cation exchange capacity) organoclay

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