INFRARED STUDY OF THE ORIENTATION OF CHLOROBENZENE SORBED ON PYRIDINIUM-MONTMORILLONITE

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Abstract—The pyridinium-montmorillonite complex has the ability to sorb additional aromatic molecules between the layers. The neutral molecules occupy the vacant space produced by the change in orientation of the pyridinium ion from a parallel to a perpendicular position and with the N-H group directed toward the negative unit layer surface.

In favorable cases the orientation of the additional neutral molecules can be ascertained by infrared spectroscopy. Examples of this analysis are presented in the complexes of pyridinium-montmorillonite with chlorobenzene. The molecules adopt a vertical orientation but with the halogen bond axes parallel to the layers.

Layer silicates in which the exchangeable inorganic ions have been substituted by organic cations have the ability to sorb selectively additional neutral organic molecules. The process is accompanied by a separation of the silicate layers and generally with a reorientation of the organic ion. The sorption can be restricted to a single monolayer of the additional molecules or can sometimes proceed to a complete separation of the mineral layers (Jordan, 1950; Weiss, 1963).

The process can be followed by X-ray diffraction through measurement of the interlayer spacings. However, due to the nature of the material, sufficient data can seldom be collected to permit the location of the individual atoms. In many analyses the molecules are only fitted in the available space according with their dimensions. Such fit is especially uncertain in the case of heterogeneous complexes in which different kinds of molecules are present and may therefore have more than one orientation.

Infrared spectroscopy has been found highly useful in establishing the orientation of the molecules on clay-organic complexes (Serratosa, 1965 and 1966; Farmer and Mortland, 1966). This is accomplished by determining the changes in intensity of specific absorption bands as the direction of the incident infrared radiation is varied relative to strongly preferred orientated aggregates.

This paper is concerned with the analysis of the molecular orientation in complexes of pyridinium-montmorillonite with monochlorobenzene and other halogen derivatives of benzene.

Oriented films of Na-montmorillonite (Wyoming) of appropriate thickness (2–3 mg/cm$^2$) were prepared by filtering the clay suspension through a micropore filter. After drying the films were separated from the support and converted to the pyridinium form by treatment with pyridinium hydrochloride solution and successively washed with distilled water. The films were immersed in chlorobenzene for several hours. After this period the films that had become completely transparent were removed from the liquid and put in a desiccator to allow evaporation of the excess of chlorobenzene. Infrared spectra were recorded in the region 600–4000 cm$^{-1}$, for two incidence angles, 0° and 40° using a Beckman IR7 infrared spectrophotometer. Concurrently an X-ray record was obtained for the 00l diffraction sequence.

In smectites with relatively low surface charge (CEC~80 m-equiv./100 g) the pyridinium ion adopts a disposition with the plane of the molecule parallel to the silicate layers and probably hydrogen bonded to water. This orientation has been substantiated by X-ray and i.r. analysis. The measured 00l spacing is 12.5 Å, and when an oriented aggregate of the complex is analyzed by i.r., only the absorption bands corresponding to the out-of-plane vibrations (dipole moment change perpendicular to the molecular plane) increase significantly in intensity with increasing incidence angle (Fig. 1).

The pyridinium complex can sorb neutral aromatic molecules, such as benzene, with an increase of the 001 spacing to 14–6 Å (Green-Kelly, 1956). This increase and infrared evidence suggests that the benzene molecule occupies the vacant space produced by the change of orientation of the pyridinium ion from a flat to a perpendicular orientation with the N-H group directed to the negative unit layer surface (van Olphen, 1963; Farmer and Mortland, 1966).

Other neutral molecules can also be sorbed by the same mechanism. In certain cases the symmetry
of the molecule presents a favorable case for the analysis of the orientation by infrared spectroscopy.

The monohalogen derivatives of benzene, like the pyridinium ion itself, belong to the point group $C_{sv}$. The molecule possesses a two-fold axis, $(C_2)$ defined by the two mutually perpendicular planes ($\sigma_y$), one of which is the molecular plane (Fig. 2).

The molecules possess 30 normal vibrations that are classified in four symmetry classes $A_1$, $A_2$, $B_1$, and $B_2$. The $A_2$ vibrations are i.r. inactive. The changes of dipole moment associated with the other three classes are along three mutually perpendicular axes. Their i.r. spectra have been extensively studied, and Whiffen (1956) made a complete assignment of the observed frequencies to the different vibrational modes.

The i.r. spectrum of chlorobenzene sorbed on pyridinium-montmorillonite is similar to that of liquid chlorobenzene, Fig. 1. The main absorptions 687, 702, 745, 1446, 1477, and 1583 cm$^{-1}$ are easily recognized. The identification of other bands is more doubtful, either because they are weak or fall close to an absorption of the pyridinium ion or of the silicate substrate.

After the sorption of chlorobenzene, several changes are observed in the spectrum of the pyridinium ion. The pattern of bands between 2800–3200 cm$^{-1}$ disappears, and the 3270 cm$^{-1}$ band shifts to a higher frequency (3285 cm$^{-1}$). These absorptions have been assigned to N–H stretching vibrations in pyridinium salts. The two bands between 1600–1700 cm$^{-1}$ become sharper and well resolved. In the region between 1200–1700 there is a general shift to lower wave numbers of about 400 cm$^{-1}$ in the $B_2$ absorption bands of chlorobenzene. The diagram in the lower right corner illustrates the symmetry elements of both molecules (point group $C_{sv}$) and the directions of the dipole moment change for each vibration class.
10 cm⁻¹ (Table 1). The new positions are similar to the positions shown by pyridinium ions when adsorbed in highly charged smectites in which it is known that the ions adopt an almost vertical position.

The orientation studies indicate that, after the sorption of chlorobenzene, the pyridinium ion adopt also a nearly vertical orientation with the N—H group directed to the surface oxygens. The disappearance of the adsorptions between 2800–3200 cm⁻¹ and the shift of the 3270 cm⁻¹ band to higher frequency, 3285 cm⁻¹, indicates that the hydrogen bond is weaker in the perpendicular position. This fact can also explain some of the other shifts observed; for example, the 1553 cm⁻¹ band which corresponds to a vibration in which N—H bending is involved, moves to lower frequency, 1545 cm⁻¹, as expected, when the hydrogen bond is weaker. The observed displacements, therefore, may not be necessarily related to the interaction of the pyridinium and chlorobenzene molecules.

Figure 2 shows the infrared spectra of the pyridinium-montmorillonite-chlorobenzene complex for two angles of incidence 0° and 40°, in the region between 1300 and 1700 cm⁻¹. This region is completely free of silicate absorptions and the bands arising from the organic species are well-defined, of strong intensity and unequivocally assigned. Significant increases in intensity, of the order of two times, are observed for the bands at 1302, 1446, 1487 and 1635 cm⁻¹, when the incidence angle is varied from 0° to 40°. The intensities of the rest of the bands remain practically unchanged.

The bands at 1487 and 1635 cm⁻¹ correspond to vibrations of symmetry class A₁ of the pyridinium ion (dipole moment change along the C₂ axis). The increase in intensity with the inclination indicates that the pyridinium ions have a nearly vertical disposition with the C₂ axis at a large angle to the silicate layers and with the N—H groups directed to these layers. A less marked intensity increase with the inclination is also observed for the 3285 cm⁻¹ band (N—H stretching).

The bands at 1302, observed only for inclined incidence, and 1446 cm⁻¹ have been assigned to vibrations of symmetry class B₁ (oscillating dipole moment in the plane of the molecule but perpendicular to the C₂ axis) of the chlorobenzene molecules. The changes in intensity with the inclination indicate that these molecules are also disposed with their planes nearly normal to the silicate layers but with the C₂ axis parallel to them, i.e. with the chlorine atoms situated midway between the negative oxygen surfaces of the silicate sheets.

The bands that do not change with the inclination correspond to vibrations of symmetry class B₂ of the pyridinium ion or symmetry class A₁ of the chlorobenzene molecule, and are indicated in Fig. 2.

The measured 001 spacing for the chlorobenzene-pyridinium complexes is 15·0 Å (8 orders observed), Fig. 4. The interlayer clearance is only about 5·8 Å.

<table>
<thead>
<tr>
<th>Pyridinium-montmorillonite</th>
<th>Pyridinium-montmorillonite-chlorobenzene</th>
<th>Symmetry class</th>
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<tbody>
<tr>
<td>Pyridinium</td>
<td>Chlorobenzene</td>
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<tr>
<td>677</td>
<td>675</td>
<td>B₂</td>
</tr>
<tr>
<td>748</td>
<td>—</td>
<td>A₁</td>
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<tr>
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<tr>
<td>3200–3285</td>
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<td>3020–3020</td>
<td></td>
<td>(C—H)</td>
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Table 1. Observed frequencies (cm⁻¹) for pyridinium and chlorobenzene in the complexes
not sufficient to accommodate the molecules in either of the completely vertical positions unless a keying mechanism takes place. This is more unlikely for the observed orientation of the chlorobenzene, and probably indicates that the molecules are slightly tilted from the vertical.

The chlorobenzene-pyridinium complex is relatively stable and decomposes only very slowly when left in the atmosphere. The shifts in frequency of the absorption bands of pyridinium depending on its orientation permit one to follow the desorption process. Figure 3 shows the i.r. spectrum of the complex after 48 hr in the atmosphere. Bands corresponding to the flat and vertical position of the pyridinium ion have been indicated.

![Infrared spectrum of the partially decomposed pyridinium-montmorillonite-chlorobenzene complex in the 1750-1300 cm⁻¹ region, for two incidence angles. The absorption bands corresponding to the flat and vertical position of the pyridinium ion have been indicated.](image)

Fig. 3. Infrared spectrum of the partially decomposed pyridinium-montmorillonite-chlorobenzene complex in the 1750-1300 cm⁻¹ region, for two incidence angles. The absorption bands corresponding to the flat and vertical position of the pyridinium ion have been indicated.

corresponding to the flat and vertical position of the pyridinium ion are observed in the doublets at 1553–1540 cm⁻¹ and at 1492–1487 cm⁻¹. The 1487 band corresponding to the ions disposed vertically shows intense dichroism; the 1492 cm⁻¹ is not sensitive to the inclination as it corresponds to a flat orientation. The X-ray pattern (Fig. 4c) indicates a mixed-layer structure of 12.5 Å and 15.0 Å species. At the illustrated stage the diffraction effects of some remaining 15 Å complex are superimposed on those of the mixed-layer system.

Other halogen derivatives of benzene, the fluoro-, bromo-, and iodo-, and p-dichloro-benzene (point group—D₂h) are also adsorbed by the pyridinium-montmorillonite and the molecules adopt a similar orientation although the complexes are not as stable as in the case of chlorobenzene.

![X-ray diffraction patterns of, (a) pyridinium-montmorillonite, (b) pyridinium-montmorillonite-chlorobenzene and (c) pyridinium-montmorillonite-chlorobenzene partially decomposed. The small peak at 2θ = 22° is attributed to an impurity of opal.](image)

Fig. 4. X-ray diffraction patterns of, (a) pyridinium-montmorillonite, (b) pyridinium-montmorillonite-chlorobenzene and (c) pyridinium-montmorillonite-chlorobenzene partially decomposed. The small peak at 2θ = 22° is attributed to an impurity of opal.

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**REFERENCES**


Résumé — Le complexe pyridinium-montmorillonite peut absorber des molécules aromatiques supplémentaires entre les feuilles. Les molécules neutres occupent l’espace vide produit par le changement d’orientation de l’ion pyridinium à partir d’une position parallèle à une position perpendiculaire et avec le groupe N-H dirigé vers la surface de le feuillet de l-élément négatif.

Dans des cas favorables, l'orientation des molécules neutres supplémentaires peut être définies par spectroscopie. Des exemples de cette analyse sont présentés dans les complexes de pyridinium-montmorillonite avec du chlorobenzène. Les molécules adoptent une orientation verticale mais avec les axes du lien halogéné parallèle aux feuilles.

Kurzreferat — Der Pyridinium-Montmorillonit-Komplex hat die Fähigkeit zusätzliche aromatische Moleküle zwischen den Schichten aufzunehmen. Die neutralen Moleküle besetzen die durch die Veränderung der Orientierung des Pyridinium-Ions aus einer parallelen in eine senkrechte Lage leergebliebenen Räume, wobei die N-H Gruppe der negativen Schichtoberfläche zugewandt ist.


Резюме — Пирдин-монтмориллонитовый комплекс обладает способностью сорбирования между слоями дополнительных ароматических молекул. Нейтральные молекулы занимают пустое пространство, образованное изменением ориентации иона пирдиния с параллельно в перпендикулярное положение и с группой N–H, направленной к поверхности отрицательного слоя.

В благоприятных условиях ориентация добавочных нейтральных молекул определяется инфракрасной спектроскопией. Примеры этого анализа представлены в пирдин-монтмориллонитовых комплексах с хлорбензолом. Молекулы принимают вертикальную ориентацию, но с осями галогенных связей, которые параллельны со слоями.