An Infrared Study of Complexes of Methylmethacrylate with Cations on the Interlamellar Surfaces of Layer Silicates

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ABSTRACT. The adsorption of methylmethacrylate on layer silicates containing various interlayer cations has been studied by means of infrared spectroscopy and X-Ray. Several characteristic carbonyl bands of adsorbed methylmethacrylate appeared differently at the region of 1723~1547 cm\(^{-1}\) depending on the species of cation and the dehydration temperature.

The carbonyl stretching band shifted about 190 cm\(^{-1}\) to lower frequencies has been observed only for polyvalent cations, which has been attributed to \(\geq C = O \cdots M^+\) complex formation. The band appeared at 1703~1640 cm\(^{-1}\) is responsible for hydrogen bonding between carbonyl oxygen and cationic water or cationic hydroxyl group, and the degree of shift indicates good correlation with the polarizing power of the interlayer cations. However, the band appeared at 1723 cm\(^{-1}\) has not been correlated with the species of cation but assigned to the carbonyl stretching which reacted with the surface hydroxyl group. On the basis of interlamellar spacing, it is suggested that the molecular plane of MMA molecule is parallel to silicate layers.
form clay-organic complexes. The adsorption of organic molecules on clay surface is highly dependent on the species of surface cation, saturated at the negative charge site of clay. The nature of clay-organic complexes has long been a subject for research and studied by many workers.

Recent investigations have shown that Cu(II) ions can form complexes with benzene and its derivatives at the interlamellar cation exchange sites of layer silicate minerals. Serratos studied the orientation of pyridine molecules in clay complexes by infrared analysis and the X-ray diffraction method. Kanamaru and Vand determined the crystal structure of a 6-amino-hexanoic acid-vermiculite complex using the X-ray single crystal diffraction method. Recently, Koizumi and his coworkers studied the formation of acrylonitrile-montmorillonite complexes, and observed that the stability of the complex was directly related to the polarizing power of the interlayer cation. In the previous papers, we studied the reaction of alkyl ketone and aldehyde with layer silicate and reported a theory of the adsorption mechanism through the link formation of cationic-hydroxyl groups and $\text{C} = \text{O} - \text{M}^{3+}$ complex formation. In this work, we have investigated the magnitude of band shifts of methylmethacrylate (MMA) adsorbed on montmorillonite due to the surface water and cations at different dehydration temperatures to understand the bonding mechanism, and related the carbonyl band shifts to the properties of cations.

**EXPERIMENTAL**

The Wyoming montmorillonite obtained from Archer Daniels Midland Co. Cleveland, Ohio U.S.A. and its self-supported films saturated by one of the cations, Li$^+$, Na$^+$, Ca$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Co$^{2+}$, and Al$^{3+}$ were prepared as described in the preceding publication except the polyethylene film technique. Since copper ions reacted with the aluminum dish, clay suspensions had to be dried on a flat polyethylene film. MMA of extra pure grade as adsorbate was obtained from Kisida Kagaku Co., Japan. The sample was redistilled until no amounts of hydroquinone inhibitor were traced in its infrared absorption spectra, and kept in a refrigerator at $-15^\circ\text{C}$ to inhibit spontaneous polymerization and evaporation.

The IR spectra of adsorbents and adsorbed compounds were obtained in the range of 4000~1200 cm$^{-1}$ by a Hitachi EPI-G spectrometer equipped with a 5 x expansion unit and modified heatable gas cell with potassium bromide windows. All details of the heatable gas cell and vapor supply unit have been described elsewhere. The thin film air-dried at room temperature was mounted in a gas cell and its infrared spectrum was recorded to determine the extent of dehydration following evacuation by diffusion pump for 15 minutes.

Then it was allowed to react with the MMA vapor of about 40 torr for 3 hr and the free vapor was degassed to $10^{-4}$ torr for 30 minutes. Then, the spectroscopic measurement and the degassing for at least 1 hr at several temperatures (25, 70, 100, 140, 190, and 240$^\circ\text{C}$) were repeated to examine how the shape of absorption bands changed due to the degree of dehydration and to ascertain the adsorption mechanism. X-ray diffractograms of the film specimen used for IR measurement were taken by a Shimadzu model VD-1 X-ray diffractometer.

**RESULT AND DISCUSSION**

**Infrared Spectra.** Infrared absorption spectra of MMA vapor and of a MMA-Montmorillonite (Mont) complex in the range of 4000~1200 cm$^{-1}$ are illustrated in Fig. 1 together with that of
Ni$^{2+}$-Mont. Absorption bands appearing in the region below 1200 cm$^{-1}$ have been omitted since they were interfered by the silicate skeletal vibration. The absorption maxima of the adsorbed MMA are summarized in Table 1, together with those of vapor MMA. The assignments have been carried out by several authors. The observed bands for adsorbed MMA are similar to those of vapor MMA except the shifts of carbonyl stretching frequency due to adsorption as shown in Fig. 1.

Vapor MMA exhibits the absorption at 1749 cm$^{-1}$, which is assigned to the C=O stretching vibration, while in adsorbed MMA the band shifts to 172 as a shoulder and 1679 cm$^{-1}$. The magnitude of the shifts varied according to the kind of cations and degree of dehydration. The resulting carbonyl frequency shift has provided the evidence that the adsorption took place through carbonyl oxygen instead of other sites of molecules. The band appeared at about 1650 cm$^{-1}$ has been assigned to the $>\text{C}=\text{C}<$ stretching vibration though it has been obscured by the absorption due to the deformation vibration of the adsorbed water. Adsorbed MMA also exhibited bands at 1454, 1440, 1403, and 1379 cm$^{-1}$, those being attributed to the CH$_3$ and CH$_2$ deformation vibration. Nagai$^{14}$ referred that the spectra of MMA in a gas state exhibited bands in 1330~1308 cm$^{-1}$ region and the frequencies of these bands were about 50 cm$^{-1}$ higher than those of

![Infrared spectra of (A) vapor MMA, (B) air-dried Ni$^{2+}$-Mont, and (C) MMA-Ni$^{2+}$-Mont complex at 20°C.](image)

**Table 1.** Infrared absorption frequencies of vapor MMA and MMA adsorbed on Ni$^{2+}$-Mont at room temperature.

<table>
<thead>
<tr>
<th>Vapor MMA frequencies, cm$^{-1}$</th>
<th>Adsorbed-MMA frequencies, cm$^{-1}$</th>
<th>Tentative assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2990</td>
<td>2985</td>
<td>$\nu$(CH$_3$) $\nu$(CH$_2$)</td>
</tr>
<tr>
<td>2960</td>
<td>2955</td>
<td>$\nu$(CH$_3$) $\nu$(CH)$_2$</td>
</tr>
<tr>
<td>2850</td>
<td>2850</td>
<td>Combination band associated with ester CH$_3$ group</td>
</tr>
<tr>
<td>1749</td>
<td>1722</td>
<td>$\nu$(C-O)</td>
</tr>
<tr>
<td>1640</td>
<td>1632</td>
<td>$\nu$(C=O)</td>
</tr>
<tr>
<td>1463</td>
<td>1454</td>
<td>$\delta$(as-CH)$_3$</td>
</tr>
<tr>
<td>1447</td>
<td>1440</td>
<td>$\delta$(as-CH$_2$)</td>
</tr>
<tr>
<td>1405</td>
<td>1403</td>
<td>$\delta$(as-CH/O)</td>
</tr>
<tr>
<td>1381</td>
<td>1379</td>
<td>$\delta$(as-CH$_2$)</td>
</tr>
<tr>
<td>1332</td>
<td>1345</td>
<td>$\nu$(C-O)</td>
</tr>
<tr>
<td>1313</td>
<td>1302</td>
<td>$\nu$(C-C)</td>
</tr>
<tr>
<td>1206</td>
<td>1219</td>
<td>Skeletal stretching</td>
</tr>
</tbody>
</table>

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the corresponding polymer bands. In this work two bands at 1332 and 1313 cm\(^{-1}\) and two bands at 1345 and 1302 cm\(^{-1}\) have been observed, respectively, in the vapor and the adsorbed states which are related to C—C—O stretching vibrations as indicated in Table 1. Besides, skeletal vibration band at 1206 cm\(^{-1}\) in vapor state also shifted to 1219 cm\(^{-1}\) in the adsorbed state.

**Effect of Dehydration.** The Mont film air-dried at room temperature holds much adsorbed water, whose absorption bands occur broadly at 3600—3200 cm\(^{-1}\) for stretching vibration and 1630 cm\(^{-1}\) for deformation vibration respectively as shown in Fig. 1. When this air-dried film is exposed to MMA vapor, a number of shifted bands are observed along with those of adsorbed water as illustrated in Fig. 1 and 2. The most prominent perturbations in IR spectra due to the adsorption have always been noticed in the range from 1723 to 1547 cm\(^{-1}\). As illustrated in Fig. 2 and 3, a large amount of shift due to the adsorption begin to occur accordingly as the film is exposed to MMA at room temperature and dehydrated at a higher temperature.

The intensity of the water band in the range of 3600—3200 cm\(^{-1}\) diminished gradually according to the elevation of the dehydration temperature. The frequency shift of carbonyl stretching vibration varied from 27 to 189 cm\(^{-1}\) depending on the species of cation, extent of dehydration, and dehydration temperature.

The A band in Fig. 2 and 3 always appears as a shoulder or as a sharp independent band at 1723 cm\(^{-1}\) within ±1cm\(^{-1}\) variation. Since the independent nature of the band exhibits no correlation with the species of cation, we have assigned this band to the carbonyl band adsorbed on the surface hydroxyl group as >C=O—HO—Si (surface hydroxyl).

![Infrared spectra of MMA adsorbed on Co\(^{3+}\)-Mont at various dehydration temperature.](image)

*Fig. 2. Infrared spectra of MMA adsorbed on Co\(^{3+}\)-Mont at various dehydration temperature.*
The B band appears as a relatively broad intense band covering the range of shifts from 46 to 109 cm$^{-1}$ and shows appreciable variation in its frequency and shape according to the species of cation as well as dehydration temperature. By pumping off the adsorbate vapor from the gas cell at an elevated temperature, the B band shifts to lower frequencies and simultaneously the intensity of the band is reduced, as indicated in Table 2 and Fig. 2. Similar spectra have been observed with other cation-Mont except Na$^+$- and K$^+$-Mont. This result supports both the resonance theory reported previously$^{11}$ and the fact that the B band is related to the species of interlayer cation. Namely, at low dehydration temperature, it involves the linking of MMA to an exchangeable metal cation through a water bridge bonding as $\text{H} \cdots \text{C}=\text{O} \cdots \text{O} \cdots \text{M}^+$. This kind of bond has been demonstrated for Mont complexes with pyridine, benzoic acid, nitrobenzene, and amides by other authors$^{17-19}$. On the other hand in a reasonably dehydrated condition, the equilibrium between the adsorbed water and cationic hydroxyl formation being established, which involves link formation of the cationic hydroxyl group as $\text{H} \cdots \text{C}=\text{O} \cdots \text{O} \cdots \text{M}^+(\text{aq})$.

However, in the case of Na$^+$- and K$^+$-Mont, the position of B band persists as shown in Table 2. It is considered that Na$^+$- and K$^+$-Mont are holding a small amount of water in comparison with other cation-Mont, and the adsorbents may preferentially link through cationic hydroxyl group rather than a water bridge.

*Fig. 3. Infrared carbonyl band of MMA adsorbed at various dehydration temperature.*
bond with MMA at an even low dehydration temperature.

The >C=O stretching absorption band (C band) which appeared at 1640 cm⁻¹ in vapor state is observed at about 1533 cm⁻¹ and interfered by the deformation band of adsorbed water at low dehydration temperature. However, the band is shifted gradually to lower frequencies as the dehydration temperature is elevated as shown in Fig. 2. This has been attributed to the result that the >C=O double bond is weakened by the stronger carbonyl interaction with adsorbent at a higher dehydration temperature. Table 2 indicates that these phenomena occur more prominently in the case of polyvalent cation and higher dehydration temperature than monovalent cation and lower dehydration temperature.

When Co⁺⁺-Mont is exposed to MMA vapor at room temperature, adsorbed MMA exhibits bands at 1452, 1439, 1403, and 1379 cm⁻¹, respectively, corresponding to E, F, G, and H band in Fig. 2. H. Nagai assigned these bands to methyl and methylene deformation vibrations. These bands are shifted to the higher frequencies as the dehydration temperature is elevated. The fact that the positive displacement of these deformation bands is accompanied by the slight displacement of the C=H stretching vibration band to lower frequency as shown in Fig. 2 has provided the information for the hydrogen bonding through the methylene hydrogen with surface oxygen so as to be lying parallel to the surface. These trends are always similar to other adsorbents.

Role of Cations. As previously illustrated,
The magnitude of the B band shift is different according to the species of cation and dehydration temperature: It is of great interest to relate the band shift with the properties of cations.

The B band exhibits a systematic shift toward the lower frequency with respect to that of vapor MMA and a good correlation between the magnitude of the shift and the polarizing power of interlayer cations as shown in Fig. 5. However, in the case of Al3+-Mont, an extraordinary deviation from the linearity is noticed (Table 3 and Fig. 4). For a better understanding of the interaction between Al3+-Mont and MMA, some additional factors must be taken into account. Polarizing power (Z/R) is defined as a ratio of the charge of the cation (Z) to its ionic radius (R), and is directly related to the strength of the electrostatic field around the cation. Since no information is available on the size of these ions at Mont interface, Pauling's crystal radii have been used. Carbonyl frequency shifts (B band) at 20 and 240°C are listed in Table 3 together with the polarizing power of the interlayer cations. There is a similar relation between them at different dehydration temperatures. These results suggest that bridge bonded water and cationic hydroxyl groups of higher polarizing power are able to interact more powerfully with the carbonyl oxygen of MMA.

Several carbonyl split bands as shown in Fig. 2, 3, and 4 indicate the existence of many different adsorption sites on the adsorbent. Careful study of the bands leads us to divide these adsorption sites correlated with the extent of carbonyl band shifts into two classes: one on which the carbonyl bands shifted about 46~48 cm⁻¹ and the other on which negative shift exceeded 189 cm⁻¹.

The 1st group occurs predominantly with K⁺, Na⁺, and Li⁺ Mont, whereas the second group, as shown in Fig. 4, prevails for the adsorption of MMA on Ca²⁺, Cu²⁺, Cu²⁺, Ni²⁺, and Al³⁺ Mont. One of the most prominent piece of evidence to support the fact that the 2nd group forms >C=O-M⁺ type complex with MMA is the color observed with the 2nd group adsorbent. This is also supported by the fact that the intensity of the perturbed carbonyl D band in Fig. 3 and 4 increased gradually with the sample dehydrated at elevated temperature, by which direct contact of the substrate with cations should be promoted. From the analysis of Fig. 2 and 3, it becomes certain that the intensities of carbonyl D bands increases gradually at the expense of carbonyl str.

Table 3. Infrared frequency shifts of carbonyl stretching vibrations and the polarizing power of the interlayer cation.

<table>
<thead>
<tr>
<th>Interlayer Cation</th>
<th>Ionic radius(R), Å</th>
<th>Charge(Z)</th>
<th>Polarizing Power(Z/R)</th>
<th>Carbonyl band shift(Δv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20⁰(cm⁻¹)</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.33</td>
<td>+1</td>
<td>0.75</td>
<td>46</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.95</td>
<td>+1</td>
<td>1.05</td>
<td>49</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.60</td>
<td>+1</td>
<td>1.67</td>
<td>55</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.89</td>
<td>+2</td>
<td>2.02</td>
<td>67</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.72</td>
<td>+2</td>
<td>2.78</td>
<td>74</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.72</td>
<td>+2</td>
<td>2.78</td>
<td>69</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.69</td>
<td>+2</td>
<td>2.90</td>
<td>70</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.50</td>
<td>+3</td>
<td>6.00</td>
<td>71</td>
</tr>
</tbody>
</table>

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Infrared shifted carbonyl bands of MMA adsorbed on cation-Mont dehydrated and degassed to $10^{-4}$ torr at 240°C.

Fig. 4. Linear relationship between carbonyl frequency shift of MMA and polarizing power of interlayer cations.

\[ \text{Fig. 5.} \quad \text{Linear relationship between carbonyl frequency shift of MMA and polarizing power of interlayer cations.} \]

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Mont-MMA complex from the lar to the main complex. The study indicates that the intensities of the MMA bands do not essentially change but those due to adsorbed water decrease. Because the interlamellar spacings are below 4,1Å under dehydration at 240°C, it is suggested that the intercalated MMA molecules coordinate to cation in such a way that the molecular plane of the MMA molecule is parallel to silicate layers.

### Table 4. Interlamellar spacing* of cation-Mon and Mont-MMA complex(Å).

<table>
<thead>
<tr>
<th></th>
<th>K⁺⁺</th>
<th>Na⁺⁺</th>
<th>Li⁺⁺</th>
<th>Ca²⁺⁺</th>
<th>Cu²⁺⁺</th>
<th>Co²⁺⁺</th>
<th>Ni²⁺⁺</th>
<th>Al³⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cation mont</strong></td>
<td>2.3</td>
<td>2.8</td>
<td>3.7</td>
<td>5.1</td>
<td>5.9</td>
<td>5.2</td>
<td>5.2</td>
<td>4.9</td>
</tr>
<tr>
<td><strong>Mont-MMA complex at 25°C</strong></td>
<td>3.2</td>
<td>3.5</td>
<td>4.7</td>
<td>4.4</td>
<td>5.6</td>
<td>5.4</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td><strong>Mont-MMA complex at 240°C</strong></td>
<td>2.5</td>
<td>2.6</td>
<td>3.0</td>
<td>4.4</td>
<td>2.7</td>
<td>3.0</td>
<td>3.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

* Calculation based on 9.6 Å as a non-expanded interlayer spacing of Mon.

\[
\begin{align*}
\text{C}=\text{O} \cdots \text{H} - \text{O} & \cdots \text{M}^{n+}+ \rightarrow \\
& \text{H}^+ \\
& \text{O} \\
\text{intermediate dehydration state} \\
\text{C}=\text{O} \cdots \text{H} - \text{O} & \cdots \text{M}^{(n-1)+} \rightleftharpoons \\
& \text{H}^+ \\
& \text{O} \\
\text{C}=\text{O} \cdots \text{H} - \text{O} & \cdots \text{M}^+ \rightleftharpoons \\
& \text{H} \\
& \text{O} \\
\text{C}=\text{O} \cdots \text{M}^+ & + \text{H}_2\text{O} \\
& \text{O} \\
\text{higher dehydration state}
\end{align*}
\]

Interlamellar Spacing. The thickness of the covering around cations can be measured by X-ray diffraction study. Interlamellar spacings of the samples prepared under various conditions are listed in Table 3. Values of these spacings of cation-Mon can be classified into two main groups. K⁺⁺, Na⁺⁺, and Li⁺⁺-Mont belong to the 1st group whose interlamellar spacings are from 2.3 to 3.7Å, while Ca²⁺⁺, Cu²⁺⁺, Co²⁺⁺, Ni²⁺⁺, and Al³⁺⁺-Mont belong to the 2nd group whose interlamellar spacings are from 4.9 to 5.9Å. This means that adsorbents of the 1st group hold a monolayer of water and those of the 2nd group hold a double layer of water in the air dried state.

As listed in Table 4, the interlamellar spacing of MMA complexes at room temperature decreases to the extent of 0.7~2.4 Å under dehydration at 240°C. The decrease of the interlamellar spacing is attributed to the removal of retained water instead of MMA adsorbed, because the infrared study indicates that the intensities of the MMA bands do not essentially change but those due to adsorbed water decrease. Because the interlamellar spacings are below 4.1Å under dehydration at 240°C, it is suggested that the intercalated MMA molecules coordinate to cation in such a way that the molecular plane of the MMA molecule is parallel to silicate layers.

### REFERENCES

赤外線分光法に応用層状酸化物層間表面上の陽イオン methylmethacrylate 錯物