

Infrared Spectra of Some Aqueous Solutions

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Abstract

A primary study of the infrared spectra of aqueous solutions concerning formic, acetic, *n*-butyric and their salts is reported. Oxalic, fumaric, malonic, succinic and tartaric acids were used as dicarboxylic ones. The aqueous solutions of them were placed between two plates made of a single crystal of silver chloride. The spectra were observed over the ranges from 4000 to 650 cm^{-1} . From the features of the positions and the shapes of the absorption bands obtained, it was noticed that (1) the band of C=O bond stretching of dimeric carboxylic acids was appeared at 1720–1680 cm^{-1} , (2) ν_a which is anti-symmetric C-O stretching band at 1570–1510 cm^{-1} and ν_s which is symmetric C-O stretching band at 1430–1390 cm^{-1} of carboxylic R-COO⁻ type were appeared strongly, but ν_s band of dicarboxylates were appeared weakly, and the band shifts at about 20–30 cm^{-1} were observed in some kinds of the carboxylic acids investigated.

Introduction

An application of the study of infrared spectra to any organic compounds leads not only the informations on the molecular structures deduced by the particular absorption bands of various active groups of the molecule, but also is widely used to identify the molecules to be analysed. Since the infrared absorption band is not affected remarkably by the neighboring molecules, the study of the molecular structures based on the vibration spectra is more advantageous for many investigators than that of the ultraviolet spectra. Moreover, it may be applicable to the study of special sorts of molecules, such as the unstable ones by matrix isolation method^{1,2}). Besides a lot of knowleges have been accumulated in the last two decades, few reports about the absorption spectra of aqueous solutions of organic and inorganic compounds have been proposed. Therefore, the observation of the infrared absorption spectra of aqueous solutions of some organic acid and their salts was made, and discussed concerning the nature of the spectra of electrolytes in here.

In the previous report³), the spectra of aqueous solutions of inorganic chemicals had been treated, and the strong and broad absorption bands of the hydrated water and the bands of each symmetry of NO₃⁻, CO₃²⁻, SO₄²⁻, NH₄⁺ had been observed.

Experimental

The same techniques for the measurements of absorption spectra as that described by a previous report³) were followed in this work. Two plates of sample container cell made of single crystal of silver chloride was also used. The aqueous solutions of organic chemicals, such as formic, fumaric, malonic, acetic, *n*-butylic, succinic, tartaric acids and their salts of

alkali, alkaline metals, were employed here. The adequate concentration of these chemicals was determined by the observations of the features of the spectral chart obtained.

Results and Discussions

In general, the vibrations between each atom which constructs a carboxyl group (C=O stretching, C-O-H bending, O-H stretching, C-OH stretching modes) absorb strongly at $3600\text{--}3500\text{ cm}^{-1}$ ($\nu_{\text{O-H}}$), $1725\text{--}1700\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$), $1320\text{--}1211\text{ cm}^{-1}$ ($\delta_{\text{C-O-H}}$), $1440\text{--}1390\text{ cm}^{-1}$ ($\nu_{\text{C-O}}$)⁴. However, most of the molecules of carboxylic acid in aqueous solution is associated with water by the hydrogen bonds through C=O carbonyl bond in the carboxyl group, so that the features of the absorption band may differ from that of pure state. Indeed, $\nu_{\text{O-H}}$ band at $2700\text{--}2500\text{ cm}^{-1}$ observed by the aqueous solution is stronger than that of free acid. $\nu_{\text{C=O}}$ band of associated acid is observed at the position which shifts about $50\text{--}70\text{ cm}^{-1}$ to the low wave number than that of free acid. Two sorts of the structures of the association of carboxylic acid may be written in Fig. 1. One of them, (a) shows a dimeric association which are most of the molecules in the vapor phase, and another (b) is a polymeric association that of in the condensed phase. The aqueous solution seems to be contained both of (a) and (b) type associations.

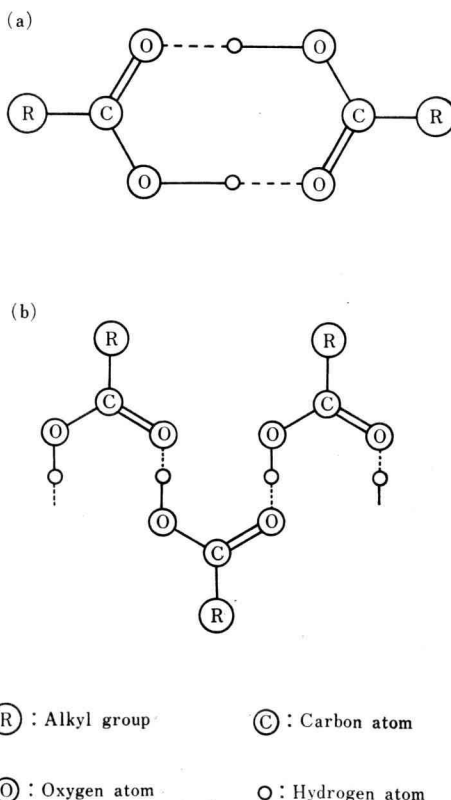


Fig. 1 Associated models of carboxylic acid.

In Fig. 2 are given the spectra of the aqueous solutions of formic, acetic, *n*-butyric acids and water itself. Several of works have been reported on the vapor state of formic⁵⁾ and acetic acids⁶⁾. The spectra of these acids are somewhat complicated because of the loss of the symmetry at the individual molecule.

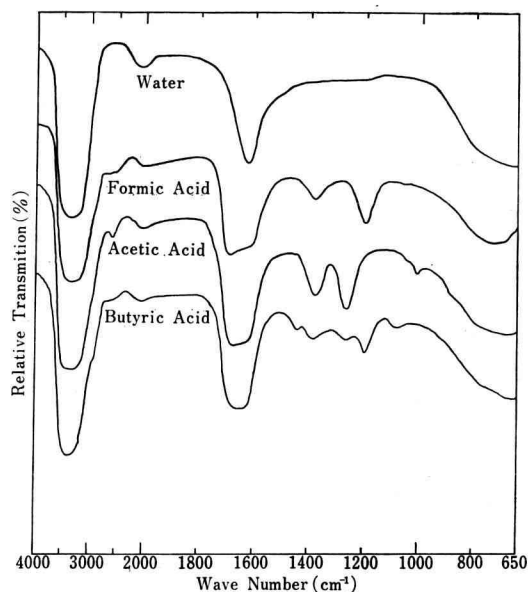


Fig. 2 Infrared spectra of various carboxylic acids.

All compounds investigated here the absorption bands of the hydrated water of the symmetric, asymmetric mode at $3550\text{--}3200\text{ cm}^{-1}$, bending mode at $1650\text{--}1600\text{ cm}^{-1}$, and wagging mode at $900\text{--}650\text{ cm}^{-1}$ are appeared strongly. A few peaks closed to them may be supposed to be merged in the broad absorption bands. The band at $900\text{--}650\text{ cm}^{-1}$ appeared in all spectra of formic, acetic, *n*-butyric acids is assigned to wagging band of the hydrated water. $\nu_{\text{O-H}}$ band at $3550\text{--}3500\text{ cm}^{-1}$ of free acid is included in the strong band at $3550\text{--}3200\text{ cm}^{-1}$ of hydrated water. The weak band of O-H stretching mode vibration of the carboxyl group is found at $3000\text{--}2500\text{ cm}^{-1}$ in comparison with the spectra of free water. The strong and broad band at $1720\text{--}1680\text{ cm}^{-1}$ is assigned to the combined band of $\nu_{\text{C=O}}$ band of the associated acid with ν_{s} band of the hydrated water. In formic and acetic acids $\nu_{\text{C-OH}}$ band at $1400\text{--}1390\text{ cm}^{-1}$ is appeared sharply. A weak band at $1400\text{--}1360\text{ cm}^{-1}$ of *n*-butyric acid is considered to be $\nu_{\text{C=O}}$ and $\nu_{\text{CH}_3(\text{s})}$ bands. $\delta_{\text{C-O-H}}$ band at $1210\text{--}1170\text{ cm}^{-1}$ of formic acid is observed, but $\delta_{\text{C-O-H}}$ band (C-O-H out of plane vibration) is included in the broad of the wagging band. The band at $1210\text{--}1170\text{ cm}^{-1}$ of acetic acid is considered to be the combination band⁷⁾ of ($\nu_{\text{C-OH}}$), ($\nu_{\text{CH}_3-\text{C}}$), ($\delta_{\text{C-O-H}}$). $\nu_{\text{C-H(as)}}$ band (C-H asymmetric mode) and $\delta_{\text{H-C-H(s)}}$ band of *n*-butyric acid is appeared at $2960\text{--}2920\text{ cm}^{-1}$ and $1460\text{--}1440\text{ cm}^{-1}$, respectively. An identification of $\delta_{\text{H-C-H(as)}}$ band (H-C-H asymmetric bending mode) have not clear, because it is very weak and

is included in wagging band at $900\text{--}650\text{ cm}^{-1}$. The weak bands at $1200\text{--}1190\text{ cm}^{-1}$ and $1090\text{--}1080\text{ cm}^{-1}$ of *n*-butyric acid seem to be the $\delta_{\text{C-O-H}}$ and $\nu_{\text{CH}_2\text{-CH}_2}$ ones.

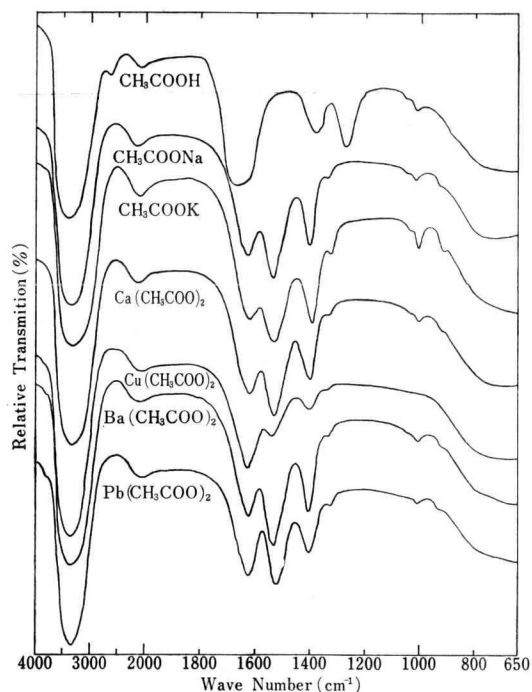


Fig. 3 Infrared spectra of various acetates.

Fig. 3 shows the spectra of aqueous acetic acid and aqueous solutions of its various metal acetates (of Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Cu^{2+} , Pb^{2+}). The strong bands at 1540 cm^{-1} and 1390 cm^{-1} which are appeared in all acetates (illustrated in Fig. 3) are considered to be that of the ionized R-COO^- group of the carboxylate. The ionized carboxyl group may be resonated bands between two C=O groups, and absorbs at $1420\text{--}1390\text{ cm}^{-1}$ ($\nu_{\text{C-O(s)}}$) and $1610\text{--}1550\text{ cm}^{-1}$ ($\nu_{\text{C-O(a)}}$). $\nu_{\text{C-O(a)}}$ at $1570\text{--}1520\text{ cm}^{-1}$ and $\nu_{\text{C=O(s)}}$ bands at $1430\text{--}1390\text{ cm}^{-1}$ are also observed. Concerning the assignment of the $\nu_{\text{C-O(a)}}$ band of acetate, it is shifted to the lower wave number.

The spectra of various dicarboxylic acid are given in Fig. 4. $\nu_{\text{C-O}}$ band of dicarboxylic acids is also appeared at same the position ($1720\text{--}1680\text{ cm}^{-1}$) of carboxylic acid. The dicarboxylic acids associated by intermolecular hydrogen bond with water show the weak band at $2700\text{--}2500\text{ cm}^{-1}$ ($\nu_{\text{O-H}}$) and the strong band at $1720\text{--}1680\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$). The strong band at $1720\text{--}1690\text{ cm}^{-1}$ of oxalic, malonic, tartaric acids is assigned to the band of $\nu_{\text{C=O}}$ band of carboxyl group. $\nu_{\text{C=O}}$ band of succinic acid is obscure because of getting no adequate concentration, but the weak band which is found at $1720\text{--}1680\text{ cm}^{-1}$ in comparison with spectra of free water is considered to be $\nu_{\text{C-O}}$ band. $\nu_{\text{O-H}}$ band at 2700--

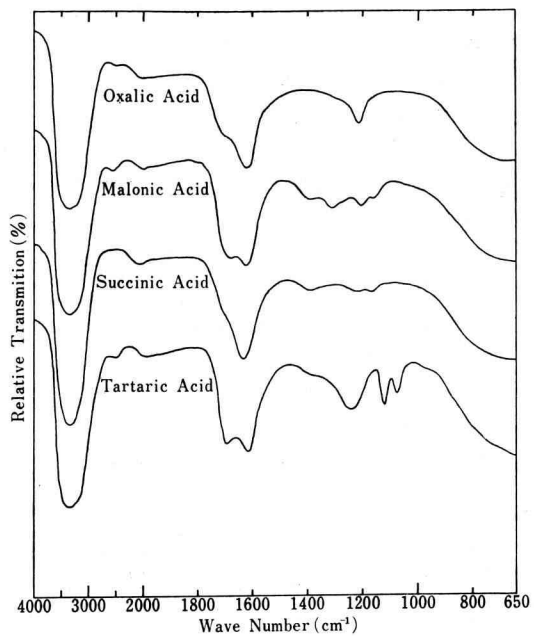


Fig. 4 Infrared spectra of various dicarboxylic acids.

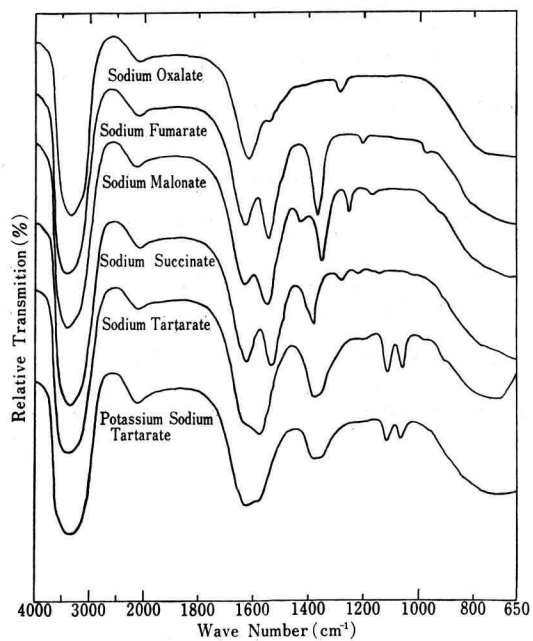


Fig. 5 Infrared spectra of various dicarboxylates.

2500 cm^{-1} is also observed in all compounds illustrated in Fig. 4 except succinic acid. The hydrated water bands (ν_s , ν_{as} , δ_s and wagging bands) are also shown at 3550–3200 cm^{-1} , 1650–1600 cm^{-1} , 900–650 cm^{-1} , respectively. δ_{C-O-H} band at 1220–1200 cm^{-1} of oxalic acid is found, but δ_{C-O-H} and ν_{C-O} bands may be included in the strong and broad bands of hydrated water. ν_{C-C} band is not resolved over the ranges of this experiment. ν_{C-OH} at 1220–1200 cm^{-1} and δ_{-CH_2-} bands at 1320–1300 cm^{-1} of malonic acid are observed. The weak bands at 1430–1380 cm^{-1} and 1170–1150 cm^{-1} are also considered to be the bands of ν_{C-CH_2} and δ_{H-C-H} bands, respectively. The bands at 1240–1210 cm^{-1} and 1410–1390 cm^{-1} of succinic acid seem to be the bands which is due to ν_{C-OH} and ν_{C-CH_2} bands. Tartaric acid shows the combination bands of δ_{CO-O-H} and δ_{CH-O-H} at 1270–1230 cm^{-1} .

Fig. 5 shows the spectra of various dicarboxylates.

$\nu_{C-O(a)}$ band at 1570–1510 cm^{-1} of R-COO⁻ group is also observed by the spectra of oxalate, fumarate, malonate, succinate in water, but that of tartarate is appeared at 1600–1560 cm^{-1} . It seems that the C-O asymmetric vibration is influenced by the strong polarity of CHOH group. $\nu_{C-O(s)}$ band is appeared weakly at 1410–1330 cm^{-1} in the spectra of dicarboxylic acid (sodium fumarate at 1390–1340 cm^{-1} , sodium malonate at 1370–1300 cm^{-1} , sodium succinate at 1400–1370 cm^{-1} and tartarate at 1410–1360 cm^{-1}). The other bands characterizing these acids in water could not be obtained here.

Nomenclatures

- $\nu_{C-O's}$: the frequency of the C-O stretching vibration.
 $\nu_{C-O(a)'s}$: the frequency of the anti-symmetric C-O stretching vibration.
 $\nu_{C-O(as)'s}$: the frequency of the asymmetric C-O stretching vibration.
 $\nu_{C-O-H's}$: the frequency of the C-O-H stretching vibration.
 δ_s : the frequency of the symmetric bending vibration.
 δ_{as} : the frequency of the asymmetric bending vibration.

References

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