Interaction of Alkaline Earth Metal Ions with Acetic and Lactic Acid in Aqueous Solutions Studied by ^{13}C NMR Spectroscopy

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Interaction of alkaline earth metal (magnesium, calcium, strontium and barium) ions with acetic and lactic acid in aqueous media was investigated by ^{13}C NMR spectroscopy. In the acetate systems, signals whose chemical shifts were the averages of those of the free and bound acetate ions were observed. Downfield shifts of the carboxylate carbon signals with increasing metal ion concentration indicated that the acetate ion acted as a monodentate ligand coordinating to the metal ion using the carboxylate group. The metal ion concentration dependence of the peak positions of the methine and carboxylate carbon signals of the lactate ion in the lactate systems suggested that the lactate ion coordinated to a metal ion using the carboxylate and hydroxyl groups. Unique upfield shifts upon complexation in the magnesium lactate systems suggested that the lactate ion coordinated to the magnesium ion from outside the primary hydration sphere.

The present results were consistent with the isotope effects of the alkaline earth metals observed in cation exchange chromatography.

Key words: ^{13}C NMR, Alkaline Earth Metals, Acetic Acid, Lactic Acid, Isotope Effects.

1. Introduction

We have carried out a series of experiments on isotope separation of alkaline earth metals (magnesium [1], calcium [2], strontium [3] and barium [4]) by cation exchange chromatography using the chloride, acetate or lactate ion as the counterion in aqueous solutions, and observed isotope separation effects on the order of 10^{-5}–10^{-6} per unit mass difference. In the chromatographic experiments it was indicated that the behavior of the magnesium ion upon complexation with the acetate and lactate ions in aqueous media was different from that of the other alkaline earth metal ions studied, and that the acetate and lactate ions differed from each other in the coordination manner. To elucidate the observed isotope effects better and to ascertain indications given in the chromatographic experiments, we felt it necessary to conduct a solution chemical investigation of alkaline earth metal carboxylates in aqueous media. NMR and infrared (IR) spectroscopy is quite often used and seems very effective for such investigations. In this paper we report the study on interactions of alkaline earth metal ions with acetic and lactic acids in aqueous media by ^{13}C NMR spectroscopy and subsidiarily by IR spectroscopy carried out to pursue the above objectives.

2. Experimental

2.1 Preparation of Samples for ^{13}C NMR Measurements

A magnesium acetate solution for the ^{13}C NMR measurement (NMR sample solution) was prepared as follows. An aqueous solution containing magnesium and acetic acid at predetermined concentrations was prepared by dissolving required amounts of magnesium acetate and acetic acid in distilled water. Sodium hydroxide solution was then added so that the ionic strength of the solution was 0.60 M (M = mol/dm^3) [5] and the solution pH was 7.0, and the resultant solution (NMR sample solution) was subjected to the ^{13}C NMR measurement. Other sample solutions were prepared likewise.

The pH value = 7.0 of the sample solutions was chosen since, judging from the dissociation constants of acetic and lactic acids and the formation constants of complexes between alkaline earth metal ions and acetate and lactate ions [6, 7], those acids do not exist as neutral molecular species in the solutions but practically perfectly as carboxylate ions at that pH. The

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concentrations of alkaline earth metal ions were 0.0, 0.05, 0.10, 0.15 and 0.20 M.

2.2 ^{13}C *NMR Measurements*

The NMR probe unit used consisted of a 10 mm and a 5 mm o.d. glass probe. In the 5 mm o.d. probe, 1,4-dioxane, used as external reference (chemical shift $\delta = 67.8$ ppm), was dissolved in about 1 cm^3 of D_2O used as a lock. The tube was capped, inserted into the 10 mm o.d. probe and fixed to it with Teflon fixing kits. 3–4 cm^3 of an NMR sample solution was placed into the 10 mm o.d. probe.

The FT-NMR spectrometer was a JOEL JNM-GX270 operated at 67.8 MHz and 300 ± 0.5 K. The number of pulses accumulated for a measurement was $500 \sim 20{,}000$, and the repetition time was 3.9 μs. The measurements were made in the proton non-decoupling manner to avoid temperature increase of the sample solutions. A reason for this was that interactions of alkaline earth metal ions with acetate and lactate ions in aqueous media were expected to be sensitive to temperature change. In addition, preliminary ^{13}C NMR experiments showed that a change in temperature by one degree yielded $0.01 \sim 0.02$ ppm shifts in ^{13}C NMR signal positions, which were not negligible in the present measurements. Due to the present measuring manner, ^{13}C NMR signals were usually observed as multiplets. The peak position of a multiplet was determined by algebraically averaging the positions of the individual lines of the multiplet.

2.3 *Measurements of IR Spectra*

The IR spectrum of each NMR sample solution was taken by the attenuated total reflection method. The used Perkin Elmer FTIR1650 spectrometer was equipped with a cell for solution samples whose windows were made of ZnSe (Spectra Tech Inc. ATR-H-1403).

3. Results and Discussion

3.1 *Alkaline Earth Metal-Acetic Acid Systems*

In any combination of alkaline earth metal and acetic acid only two signals were observed. As an example the spectrum of the calcium acetate solution with the calcium ion concentration of 0.2 M is shown in Figure 1. The ^{13}C NMR signal at around $\delta = 182$ ppm, observed as a quartet, is assigned to the carboxylate carbon ($\underline{C}OO^-$) of the acetate ion, and the quartet at about $\delta = 24$ ppm to the methyl carbon ($\underline{C}H_3$). Based on the values of the dissociation constant of acetic acid and the complex formation constant of the calcium ion with the acetate ion [6, 7], the chemical forms of acetic acid expected for the solution are; 25% as the acetate ion coordinating to the calcium ion (bound acetate ion), 75% as the free non-coordinating acetate ion (free acetate ion) and 0% as the neutral molecular acetic acid. Considering the very weak interaction between the calcium and acetate ions, observation of only two signals means that the interchange between the bound and free acetate ions is fast on the ^{13}C NMR time scale, and hence single signals of the methyl and carboxylate carbons are observed whose chemical shifts are the averages of those of the bound and free acetate ions weighted by their respective amounts. This is in contrast with the strong interaction of a metal ion with the acetate ion; for instance, distinct signals corresponding to the bound and free acetate ions were observed for the uranyl acetate system [8].

The weak coordination of the acetate ion to the calcium ion is also evidenced in the IRspectra. It is well established that the coordination mode of a carboxylate ion to a metal ion can be understood by the difference in the vibrational frequency of the asymmetric and symmetric COO^- vibrational modes of the bound carboxylate ion, relative to that of the free carboxylate ion [9]. Figure 2 shows the IR spectra of the calcium acetate solutions with varying ion concentrations in the frequency range of 1300–1700 cm^{-1} (asymmetric and symmetric COO^- frequency region). As is seen, no appreciable change in the spectra is observed; no distinct adsorption peaks corresponding to the bound and free acetate ions are observed. This IR result is consistent with the ^{13}C NMR results above.

Similar features as for the calcium acetate system were also found for the other alkaline earth metal acetate systems examined.

In Figs. 3 a and 3 b, we plotted the chemical shifts of the methyl carbons (Fig. 3 a) and the carboxylate carbons (Fig. 3 b) against the concentrations of the alkaline earth metal ions examined. A higher concentration corresponds to a larger percentage of the bound acetate ions. The change in chemical shift with increasing metal ion concentration is much larger for the carboxylate carbon signal than for the methyl car-

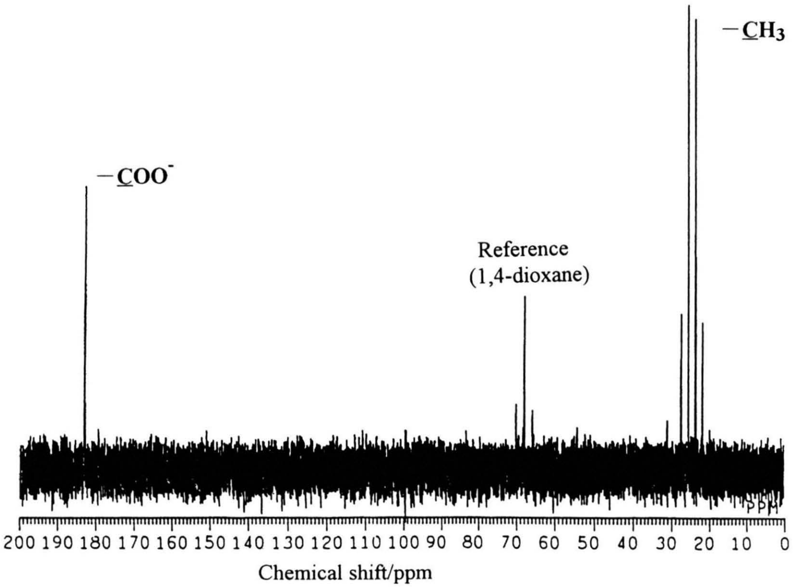

Fig. 1. The ^{13}C NMR spectrum obtained for an aqueous solution with calcium and acetic acid concentrations of 0.20 mol/dm^3 and 0.40 mol/dm^3, respectively. pH = 7.0, ionic strength 0.6 mol/dm^3. 1,4-dioxane was used as the external reference.

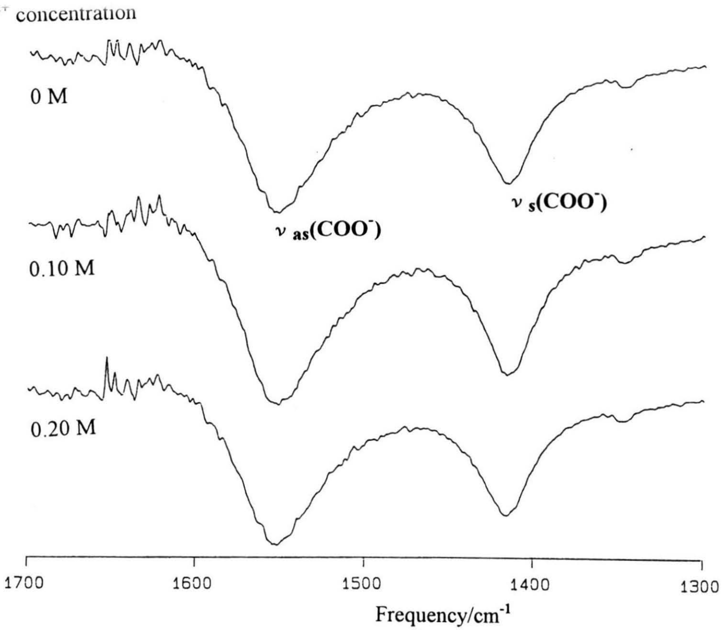

Fig. 2. The IR spectra in the symmetric and asymmetric COO$^-$ frequency region of aqueous solutions of the calcium acetate system with varying calcium ion concentration.

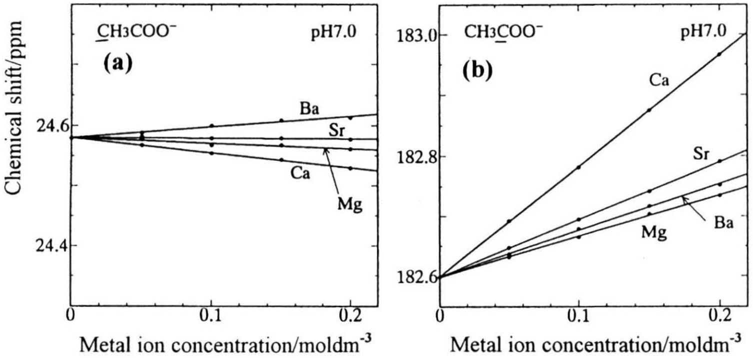

Fig. 3. Plots of chemical shifts of (a) the methyl carbon signal and (b) the carboxylate carbon signal of the acetate ion in the acetate systems against alkaline earth metal ion concentrations.

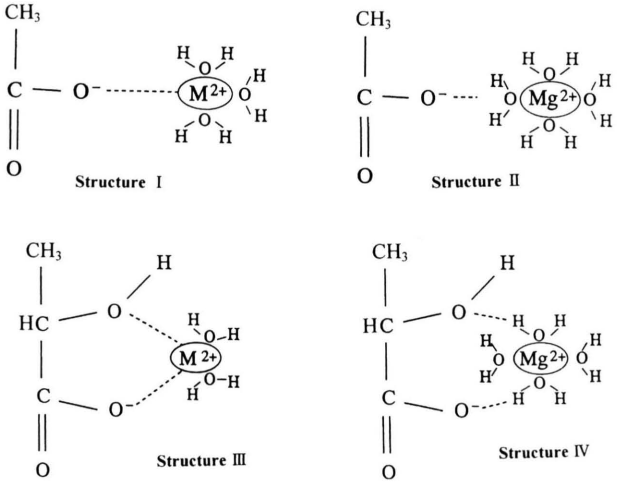

Fig. 4. Schematic drawings of possible structures of alkaline earth metal acetate and lactate complexes in aqueous solutions.

bon signal in any alkaline earth metal acetate system examined, suggesting that the acetate ion coordinates to metal ions using its carboxylate group, as is usually the case.

As is seen in Fig. 3, the chemical shifts of the carboxylate carbons show monotonous downfield shifts with increasing metal ion concentration, irrespective of the kind of metal, showing that the electron densities on the carboxylate carbons decrease with increasing metal ion concentrations. This is best understood by assuming that part of the electron cloud on the carboxylate carbon is attracted by the metal ion through the metal ion-carboxylate group interaction. It is difficult to infer the coordination mode of the acetate ion to the alkaline earth metal ions only from the present ^{13}C NMR and IR results. Considering the very weak interactions between the alkaline earth metal ions and the acetate ion, however, the most probable mode is the one in which the acetate ion acts as a monodentate ligand coordinating to a cation using the single bonded oxygen of the carboxylate group as shown in Fig. 4 (Structure I).

The order of the value of the complex formation constant between the alkaline earth metal ion and the acetate ion is

$$\mathrm{Mg^{2+}-COO^-} > \mathrm{Ca^{2+}-COO^-} > \mathrm{Sr^{2+}-COO^-} > \mathrm{Ba^{2+}-COO^-}$$

[6, 7]. Contrary to this sequence, the order of the deviation of the chemical shift of the carboxylate carbon signal at a given metal ion concentration from that at 0 M concentration is

$$\mathrm{Ca^{2+}-COO^-} > \mathrm{Sr^{2+}-COO^-} > \mathrm{Ba^{2+}-COO^-} > \mathrm{Mg^{2+}-COO^-}.$$

Magnesium is not at the right place expected from the complex formation constant values. This magnesium anomaly is best understood by assuming that the magnesium ion behaves as if it were larger than the barium ion, probably due to the effect of hydration (cf.: Fig. 4, Structure II). That is, in the coordination to a magnesium ion, the acetate ion does not replace a water molecule hydrating the magnesium ion but interacts with it from outside the primary hydration sphere around it.

As for the coordination manner of the acetate ion to the alkaline earth metal ions other than the magnesium ion, two manners seem possible. Either the carboxylate group interacts with an alkaline earth metal ion from outside the primary hydration sphere as in the case of the magnesium ion, or the acetate ion directly coordinates to a cation in the primary hydration sphere without the liberation of hydrating water molecule. The hydration number in the primary hydration sphere is six for the magnesium and calcium ions. Slightly larger numbers are reported for the strontium and barium ions [10]. A simple solid geometric calculation using the radii of the alkaline earth metal ions and the oxide ion suggests that, while the primary hydration sphere of the magnesium ion accommodates only six water molecules, those of the calcium, strontium and barium ions accommodate at least eight. That is, it seems possible to add a ligand in the primary hydration spheres of calcium, strontium and barium ions without the liberation of a hydrating water molecule. A molecular orbital calculation [11] also supports this. In any case, it seems quite unlikely that the acetate ion directly coordinates to an alkaline earth metal ion with the liberation of a hydrating water molecule from the primary hydration sphere.

3.2 *Alkaline Earth Metal-Lactic Acid Systems*

In every ^{13}C NMR spectrum taken, three signals corresponding to the methyl carbon ($\underline{\mathrm{C}}\mathrm{H_3}$), the methine carbon ($\underline{\mathrm{C}}\mathrm{H(OH)}$) and the carboxylate carbon ($\underline{\mathrm{C}}\mathrm{OO^-}$) were observed at around $\delta = 21$ ppm as quartet-doublets, at about 70 ppm as doublet-quartets and at around 183 ppm as triplets, respectively. As in the case of the acetate systems, no distinct signals corresponding to bound and free lactate ions were observed for any of the methyl, methine and carboxylate carbons, due to the fast interchange between the two states of the lactate ion. Also, no appreciable change in the IR spectra in the asymmetric and symmetric $\mathrm{COO^-}$ frequency region with the change in the metal ion concentration was observed in any system.

In Fig. 5a, 5b, and 5c, we plotted the chemical shifts of the methyl carbon signal (Fig. 5a), the methine carbon signal (Fig. 5b), and the carboxylate carbon signal (Fig. 5c) of the lactate ion against the concentrations of alkaline earth metal ions. As is seen, all the chemical shifts except that of the methine carbon signal in the magnesium lactate system show monotonous downfield or upfield shifts with increasing metal ion concentrations, and the behavior of the magnesium lactate system differs from those of the other alkaline earth metal lactate systems.

In the calcium, strontium and barium lactate systems, all the signals shift downfield with increasing

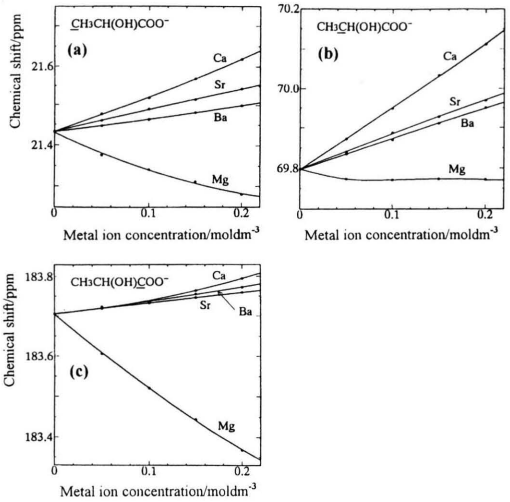

Fig. 5. Plots of chemical shifts of (a) the methyl carbon signal, (b) the methine carbon signal and (c) the carboxylate carbon signal of the lactate ion in the lactate systems against alkaline earth metal ion concentrations.

metal ion concentrations. The trend in the concentration dependence of the three kinds of carbon signal indicates that the electron densities of the carbons in the free lactate ion are higher than those of the corresponding carbons in the bound lactate ion, as in the cases of metal acetate systems above. The deviation of the chemical shift of the methine carbon signal at any metal ion concentration from that at 0 M concentration is larger than that of the carboxylate carbon signal for any of the three lactate systems. This suggests that the lactate ion coordinates to the alkaline earth metal ions using both the carboxylate group and the hydroxyl group to form a five member ring as is shown in Fig. 4 (Structure III). The hydroxyl group is expected to coordinate to a metal ion without dissociation of its proton under the present experimental conditions. In fact, no value of the dissociation constant of the hydroxyl group of the lactic acid is given in the literature. The interaction of the hydroxyl group with the alkaline earth metal ion is thus the one utilizing a lone electron pair of the hydroxyl oxygen. Then, the most reasonable explanation of the results of the calcium, strontium and barium lactate systems shown in Fig. 5 is as follows. The alkaline earth metal ion attracts electron clouds of the single-bounded carboxylate ($C(=O)\underline{O}^-$) and hydroxyl oxygens, which causes a decrease in the electron density of all the carbons of the lactate ion, resulting in downfield shifts of their signals with increasing metal ion concentration. The decrease of the electron density of the carboxylate carbon upon the complexation is smaller than that of the methine carbon, probably because the decrease of the electron density of the carboxylate carbon is partially compensated by the influx of the electron cloud from the double-bonded oxygen of the carboxylate group ($C(=\underline{O})O^-$).

Contrary to the calcium, strontium and barium lactate systems, in the magnesium lactate system the signals of the carbons of the lactate ion showed upfield shifts upon complexation. Also, it is characteristic of the magnesium lactate system that, while the metal ion concentration dependence of the methine carbon signals is larger than that of the carboxylate carbon signals in the other systems, the metal ion concentration dependence of the carboxylate carbon signal is by far the largest among the three kinds of carbon, and that of the methine carbon signal is very slight in the magnesium lactate system.

Generally the ^{13}C NMR signal of the carboxylate carbon (and probably the hydroxyl carbon, too) of a carboxylate ion seems to show a downfield shift upon complexation with a metal ion by reason of the attraction of electron clouds of the oxygens of the carboxylate and hydroxyl groups by the metal ion, and consequently those of the carboxylate and methine carbons. This general explanation can be applied to the present calcium, strontium and barium acetate and lactate systems as shown above. Experimental facts that do not obey this generality were found in the case of downfield shifts of carboxylic carbons of carboxylic acids upon dissociation ($COOH$ to COO^-), the decisive explanation for which has not yet been established [12]. The upfield shift of the carboxylate carbon signal upon complexation in the present magnesium lactate system can be understood by referring to the behavior of carboxylic carbon signals of carboxylic acids upon dissociation. The magnesium ion does not interact directly with the carboxylate group (and maybe the hydroxyl group, either) of the lactate ion but indirectly through a hydrating water, as schematically shown in Fig. 4 (Structure IV). The carboxylate group of the bound lactate ion interacts apparently with the hydrogen of a hydrating water. This situation is similar to the situation in which a carboxylate ion interacts with a proton to form a neutral carboxylic acid.

3.3 Correspondence of the Present ^{13}C NMR Results to the Isotope Effects Observed in Ion Exchange Systems

The present ^{13}C NMR spectroscopic results help to understand the isotope effects of alkaline earth metals observed in ion exchange chromatographic separation systems with chloride, acetate or lactate ion as the counterion [1–4]. The essence of the observed isotope effects is summarized and some relations between the ^{13}C NMR and chromatographic results are discussed below.

1) For any alkaline earth metal studied, the heavier isotopes were fractionated into the solution phase [1–4]. Based on a theory of isotope distribution between two phases [13], this is equivalent to state that the value of the heavier isotope-to-lighter isotope reduced partition function ratio (RPFR) [14] of a chemical species is larger in the solution phase than in the ion exchanger phase.

2) The magnitudes of isotope separation effects of the calcium, strontium and barium acetate systems [2–4], in which certain percentage of metal ions formed complexes with acetate ions both in the external solution and ion exchanger phases, were larger than or equivalent to those of the metal chloride systems in which complexations between metal and chloride ions were negligible. This means that the sum of the forces acting on the metal ion is larger in the complex form than in the simply hydrated form [14], and seems more compatible with the inference that the acetate ion coordinates to a metal ion in the primary hydration sphere without the liberation of a hydrating water molecule than the one that the acetate ion coordinates to the metal ion from outside the primary hydration sphere (cf.: Fig. 4, Structure I).

3) Contrary to the other acetate systems examined, the isotope separation effect of the magnesium acetate system was smaller than that of the magnesium chloride system [1], showing that the sum of the forces acting on the simply hydrated magnesium ion is larger than that acting on the ligand coordinated magnesium ion. This situation can be realized if the ligand coordination from outside the primary hydration sphere around the magnesium ion disturbs the interaction between the magnesium ion and hydrating waters in the primary hydration sphere, which results in weakening the bonding between the magnesium ion and hydrating waters.

4) The isotope separation effect of any of the alkaline earth metal lactate systems examined is larger than or equivalent to that of the metal chloride system, which means that sum of the forces acting on a metal ion is larger in the complex form than in the simply hydrated form as in the cases of the calcium, strontium and barium acetate systems. In any lactate system, the coordination of the lactate ion, using both the carboxylate and hydroxyl groups and the formation of a ring structure is expected to increase the sum of the forces acting on the metal ion, which results in a larger isotope effect than that in the metal chloride systems.

4. Conclusion

The major findings of the present ^{13}C NMR spectroscopic study are as follows:

1) No distinct ^{13}C NMR signals corresponding to free and bound acetate ions were observed for the methyl and carboxylate carbons in the aqueous magnesium, calcium, strontium and barium acetate systems. The metal ion concentration dependence of the ^{13}C NMR signal positions of the methyl and carboxylate carbons of the acetate ion and IR spectra of the sample solutions in any system suggested that the acetate ion worked as a monodentate ligand (Fig. 4, Structure I). It was also indicated that the acetate ion coordinated to the magnesium ion from outside the primary hydration sphere around the magnesium ion (Fig. 4, Structure II).

2) Similarly to the acetate systems, no distinct ^{13}C NMR signals corresponding to free and bound lactate ions were observed for either of the methyl, methine and carboxylate carbons in any of the aqueous alkaline earth metal lactate systems. The metal ion concentration dependence of the ^{13}C NMR signal positions of the methine and carboxylate carbons of the lactate ion in any system suggested that the lactate ion coordinated to the metal ion using both the carboxylate group and the hydroxyl group without dissociation of the hydroxyl proton (Fig. 4, Structure III). The unique upfield shift of the carboxylate carbon of the lactate ion upon compelxation with the magnesium ion indicated that the lactate ion coordinated to the magnesium ion from outside the primary hydration sphere of the magnesium ion (Fig. 4, Structure IV).

3) The present ^{13}C NMR spectroscopic results are consistent with the isotope effects of the alkaline earth metals observed in cation exchange chromatography.

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