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Infrared Spectral Studies of Various Metal Polyacrylates

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A new process for the production of high surface area, high reactivity ceramic oxide powders involves the bonding of metal cations to polymeric polyacrylate chains. This process results in the formation of a gelatinous metal polyacrylate precipitate which can be easily removed from the mother liquor, and then calcined to form a high density ceramic oxide. Using FTIR spectroscopy, the nature of the structural arrangements has been studied for metal complexes in the yttrium, lanthanum, aluminum, cerium, copper, and iron polyacrylates. Interpretation of the infrared spectra indicates that two types of metal complex formation occur in these precipitates, involving bidentate or bridging interactions. The type that is observed for a particular metal ion is dependent on its metal ion size. © 1989 Academic Press, Inc.

1. Introduction

There has been a recent trend in the ceramic community toward chemical routes of synthesis which can lead to ultrafine, high surface area powders. Such processes involve first forming intermediate organometallic materials which can then be formed into high density ceramics when they are calcined and sintered. There are several general methods used to produce these powders, which include organic gelation.

Organic gelation synthesis, which was first described by Micheli (*1*), has several advantages over other methods such as the sol-gel and the metallo organic decomposition (MOD) methods. During organic gelation synthesis, the step to prepare the precursor material (metal polyacrylate) is carried out in an aqueous environment. This reaction environment eliminates the need for toxic solvents and anhydrous atmospheres. Also, the volatility of the components in the system is minimized. Finally, the decomposition of the gelatinous precursor materials into the ceramic oxide powders occurs at low temperatures (*2*), and the resulting products are dense, single-crystal crystallites (*3*).

During organic gelation synthesis, the starting materials are dissolved into two different solutions, one containing the metal cations, and the other containing the polymeric chelating agent. By mixing these two solutions together, and controlling the pH of the resulting solution, a precipitate is formed. This precipitate, which is a precursor to the desired ceramic oxide, is the focus of this study. Using FTIR spectroscopy, the metal complex arrangements in these precursor materials (metal polyacrylates) were investigated and determined.

2. Experimental Procedures

The metal polyacrylate powders studied in this investigation were all prepared using

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organic gelation synthesis. In this process, a solution containing the desired metal cation was prepared by dissolving the related metal nitrate in distilled water. In a separate container, a quantity of the polymer was diluted using distilled water. The polymer (polyacrylic acid) possessed an average molecular weight of 5100 g/mole. Using these solutions, two different procedures (a forward strike process and a reverse strike process) were investigated to prepare the metal polyacrylates.

In the forward strike process, the polymer solution was first added to the metal ion solution, and then concentrated base (NH_4OH) was added dropwise to raise the pH. This process was used primarily for those cations where no insoluble hydroxides or related salts would precipitate as the pH was raised.

The reverse strike process was utilized in those instances when the forward strike process would cause the precipitation of metal hydroxides or related salts. In this case, the polymer solution was first buffered by addition of excess NH_4OH so that upon addition of this buffered solution, more complex formation would occur before precipitation of these compounds.

Metal cations were complexed with polyacrylate groups in each of the appropriate above-mentioned solutions, and gelatinous precipitates were formed. These precipitates were vacuum filtered, washed with distilled water, and then stored at 110°C until the FTIR spectral measurements were made. Washing was necessary to remove any soluble salts (such as NH_4NO_3) which may have been present.

The nature of the bonding and complex formation in the various precipitates was investigated on the basis of their infrared spectra which were measured with a Nicolet 60 SXR FTIR spectrometer.[1] The KBr pellet method was employed for spectral analysis, using thoroughly mixed pressed pellets containing 1.5 mg of the investigated sample in 300 mg of KBr. The measured infrared spectra possessed a resolution of 4 cm^{-1} resulting from 32 scans. Scans of spectra were collected only for polymeric materials containing one type of metal cation, which was precipitated at various pH values.

3. Results and Discussion

As discussed earlier, two different precipitation processes (the forward strike and the reverse strike processes) were used to prepare samples in this study. For metal ions such as ytttrium and lanthanum ions that did not generate insoluble hydroxides or related salts using the applied pH ranges and conditions, the forward strike process could be used. This application was possible for these metal ions because there was no need to be concerned with precipitating out the hydroxide or the related salt during the addition of the base. Aluminum-ion containing precipitates were also prepared by this method in order to compare their spectral results to those of aluminum-ion containing precipitates prepared by the reverse strike process.

Wherever an insoluble hydroxide or related salt could be formed (single cation or multication system), the reverse strike process was used. The application of the reverse strike process protected against preferential precipitation of a hydroxide such as $Al(OH)_3$ or $Fe(OH)_3$ during the addition of the base, and also prevented preferential complex formation often associated with the coprecipitation of multication systems. In all investigated cases, the collected precipitates were X-ray amorphous.

It was advantageous to keep the amount of polymer added as a gelation agent to a minimum. By maintaining this control, the degree of complex formation in the materials could be more easily estimated by com-

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[1] Nicolet Analytical Instruments, Madison, WI.

paring the relative intensities of the absorption band for the protonated carboxylate groups. If too much polymer was added, the relative intensities of the related metal–carboxylate complexes would be much weaker than those of the protonated species. In this study, the metal-ion/carboxylate-group equivalent ratio was maintained at unity.

The FTIR spectrum of the starting polymer (dried polyacrylic acid) possesses a large, very broad absorption band in the 3300–2500 cm^{-1} range along with a large, fairly narrow absorption band at ca. 1710 cm^{-1}. These bands, which are characteristic of carboxylic acids, can be assigned to the O–H stretching mode, and the C=O stretching mode of the protonated carboxylate group, respectively (*4*). Comparisons of the intensities of the vibrational modes of carboxylate groups to the intensity of the latter mode will allow the determination of the extent of complex formation in the metal polyacrylate precipitates. As the protonated carboxylate groups begin to ionize, carboxylate ions are formed, giving rise to two new useful bands (*4*). Completely ionized carboxylate groups in an aqueous acetate solution possess an asymmetrical stretching mode ($\nu_a(COO^-)$) at ca. 1556 cm^{-1}, and a symmetrical stretching mode ($\nu_s(COO^-)$) at ca. 1413 cm^{-1} (*5*). The wavenumbers of the two latter bands will shift if the ionized carboxylate groups form complexes with various metal cations (*5*). The magnitude of the shifts depend upon the nature of the complex (unidentate versus bidentate versus bridging complexes) and the amount of covalent character for the metal–oxygen bond. Interpretation of such shifts observed in the spectra of gelatinous metal carboxylate materials that are investigated in this study allow determination of the nature of metal complexes formed in these materials.

Lanthanum polyacrylate powders prepared by the forward strike process were the the first series of metal–polymer materials that were spectrally investigated. The infrared spectra for four gelatinous powders of lanthanum polyacrylate which were prepared at various pHs are illustrated in Fig. 1. One may note that as the pH at which precipitation occurs increases, the relative intensity of the band at ca. 1710 cm^{-1} decreases. As previously discussed, this intensity decrease with increasing pH indicates a relative decrease in protonated carboxylate species in the materials with respect to other carboxylate species. If the organic acid groups are completely complexed or ionized, the band at 1710 cm^{-1} should completely disappear. However, a shoulder remains even at the highest preparation pH. This observation is consistent with observations of the protonated species for other polyacrylate materials prepared at higher pH.

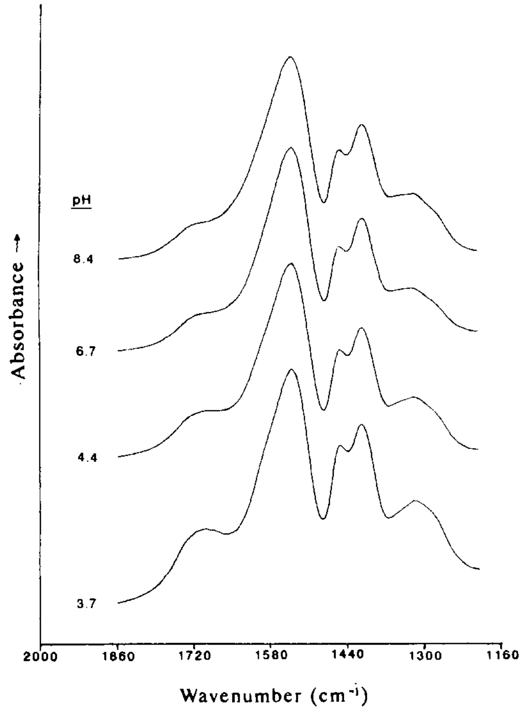

FIG. 1. IR spectra of lanthanum polyacrylates prepared at various pH values.

By examining the wavenumber shifts for the bands for $\nu_a(COO^-)$ and $\nu_s(COO^-)$, one can determine the nature of complex formation between the metal cations and the carboxylate ions (5). In the case of lanthanum polyacrylate materials, their spectra show a shift of ν_a to lower wavenumbers (1543 cm^{-1}), and a shift of ν_s to higher wavenumbers (1454 cm^{-1}) with respect to those of the protonated carboxylate species. In the case of a related rare earth acetate $[Er(O_2CCH_3)_3(H_2O)_4]$ where bidentitate complexes occur, similar vibrational band shifts were noted (5, 6). Therefore, it is reasonable to assume that lanthanum ions form similar bidentate complexes with carboxylate groups in the polyacrylate material.

A similar spectral trend is noted for the carboxylate stretching modes of yttrium polyacrylates prepared at various pH by the forward strike process (see Table I). Again, the relative intensity of the band at ca. 1710 cm^{-1} decreases as the preparation pH increases, indicating a decrease in the relative concentration of protonated carboxylate groups. Also, the wavenumber shift for ν_a (1552 cm^{-1}) and ν_s (1457 cm^{-1}) indicates that yttrium ions form bidentate complexes with carboxylate groups similar to those involving lanthanum ions.

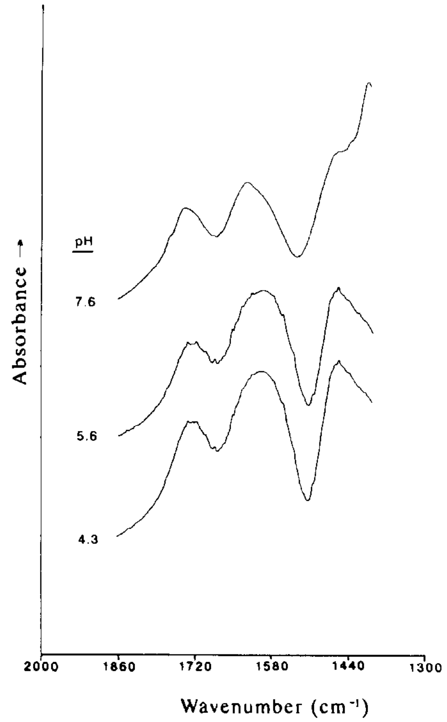

FIG. 2. IR spectra of aluminum polyacrylates prepared at various pH values by a forward strike.

Analysis of infrared spectra for aluminum polyacrylates (see Fig. 2) prepared by the forward strike method indicates that the same level of complex formation for aluminum ions was not attainable as noted earlier for yttrium and lanthanum ions. The higher relative intensities for the absorption band at ca. 1710 cm^{-1} for the aluminum-containing precipi-

TABLE I

IONIC RADII (8), WAVENUMBERS (cm^{-1}), AND COMPLEX STRUCTURES FOR THE STUDIED CATIONS

Ion	Radius (Å)	ν_a	ν_s	Complex structure
Ba^{2+}	1.34	1540	1456	Bidentate
Sr^{2+}	1.12	1551	1454	Bidentate
Ce^{3+}	1.034	1543	1454	Bidentate
La^{3+}	1.016	1543	1454	Bidentate
Bi^{3+}	0.96	1550	1450	Bidentate
Y^{3+}	0.893	1552	1457	Bidentate
Cu^{2+}	0.72	1559, 1616	1454	Bridging/Bidentate
Fe^{3+} (low pH)	0.64	1541, 1589	1454	Bridging/Bidentate
Al^{3+}	0.51	1599	1458	Bridging

tates prepared at higher pH values indicates that there is significantly less complex formation involving aluminum ions at these pH values than is noted with yttrium and lanthanum ions. This difference in trend for complex formation in aluminum polyacrylates prepared by a forward strike process can be explained on the basis of the low solubility of aluminum hydroxide. Weefers and Misra (*7*) noted that whenever the pH of a solution containing aluminum ions is increased above 3.5, $Al(OH)_3$ readily precipitates. The solubility of this hydroxide is so low at higher preparation pH values that aluminum hydroxide mainly forms rather than aluminum ions complexing into the polyacrylate phase. Therefore, the infrared band for the protonated carboxylate groups will be relatively stronger for aluminum-containing solutions. However, it is possible to decrease the amount of protonated carboxylate groups and increase the amount of complexed species by using the reverse strike method. Figure 3 illustrates the infrared spectra for various aluminum polyacrylate materials prepared by the reverse strike method. As one may note, the relative band intensity for protonated carboxylate groups decreases considerably over the investigated pH range in contrast to that for samples prepared by the forward strike process.

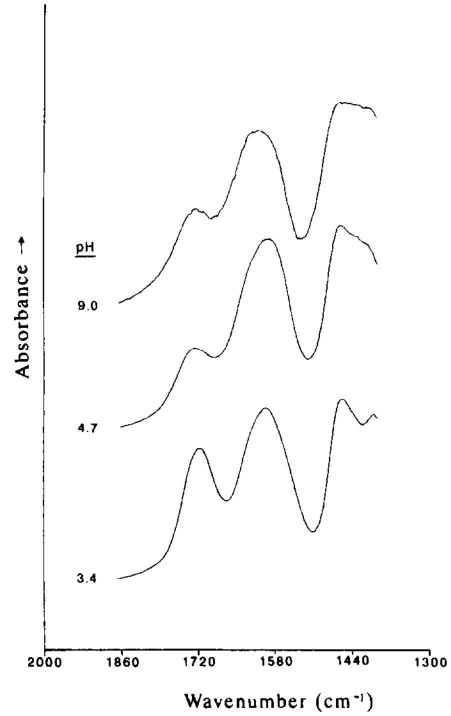

FIG. 3. IR spectra of aluminum polyacrylates prepared at various pH values by a reverse strike.

For aluminum polyacrylate materials, the shifts in the bands for ν_a (1599 cm^{-1}) and ν_s (1458 cm^{-1}) seem to indicate that bridging complexes rather than bidentate complexes are formed between aluminum ions and carboxylate groups. The wavenumbers of both of these bands shift to wavenumbers higher than those noted for the ionized carboxylate group. Similar trends have been noted for related acetate compounds, $[Cr_3(O_2CCH_3)_6O(H_2O)_3]Cl\ 6H_2O$ and $[Rh(O_2CCH_3)_2(H_2O)]_2$, whose X-ray diffraction data clearly indicate that they possess bridging complexes (*6*). Such bridging structural units involve different cations being bonded to each oxygen in the carboxylate group.

Using the reverse strike process with cerium ions, a high degree of complex formation is obtained at high preparation pH (see Fig. 4). A relatively large amount of protonated carboxylate groups exists in the material prepared at low pH, due to the low initial amount of ionization in the polymer chain. For the sample prepared at higher pH, more extensive ionization occurs in the initial polymer units in the solution, allowing more extensive complex formation to take place. The FTIR spectra reflect this difference in the intensity relations between the various infrared bands for the complexed carboxylates and the protonated carboxylates. In the case of cerium polyacrylate, the shift in the wavenumbers for ν_a (1543 cm^{-1}) and ν_s (1454

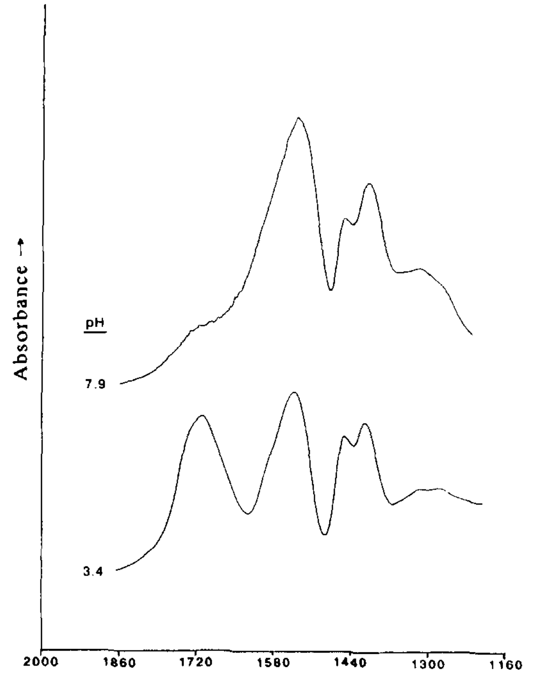

FIG. 4. IR spectra of cerium polyacrylates prepared at various pH values.

cm^{-1}) indicates that the complexes which are formed between the polymer's carboxylate groups and the cerium ions are similar to those for yttrium and lanthanum ions (bidentate type).

The reverse strike process was applied to form iron polyacrylates in order to prevent the formation of iron hydroxides at the higher preparation pH values. For all final solutions possessing the investigated preparation pH values (ranging from 2.35 to 6.54), the observed infrared band at ca. 1710 cm^{-1} is intense (Fig. 5), indicating that a large amount of protonated carboxylate remains in these materials. The relative intensity of this band is not observed to change with change in preparation pH, as was noted earlier for the aluminum polyacrylates. The spectral data seem to indicate that two different types of complexes, whose relative concentrations are changing as a function of preparation pH, are occurring in these materials at the same time. As is illustrated in Fig. 5, the band for $\nu_s(\mathrm{COO^-})$ appears at 1454 cm^{-1}. However, two bands appear for $\nu_a(\mathrm{COO^-})$ at both 1589 and 1541 cm^{-1}, due to the possible formation of bridging complexes and bidentate complexes, respectively. As the preparation pH is increased, the relative intensities of the two latter bands indicate primarily bridging complexes at low pH, and totally bidentate complexes at high pH. The ability for this metal complex system to possess two types of complex formation has been reported earlier in the literature (5). In this laboratory, similar behavior was also observed for copper polyacrylates. The spectral data for the latter system were consistent with those observed for bidentate complexes in $\mathrm{Cu(O_2CCH_3)(Ph_3P)_2}$ and

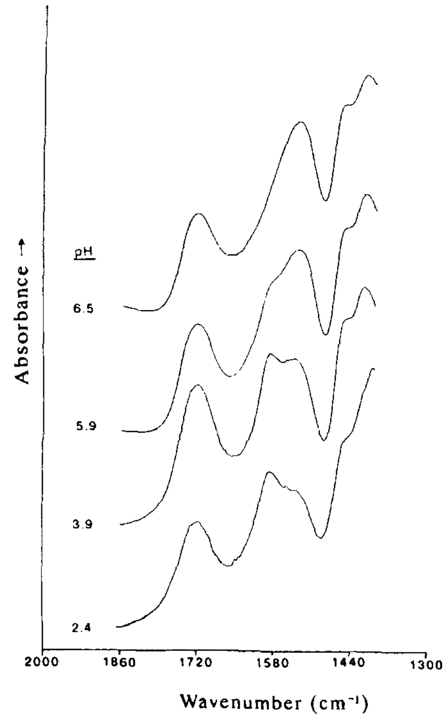

FIG. 5. IR spectra of iron (III) polyacrylates prepared at various pH values.

bridging complexes in $[Cu(O_2CCH_3)_2(H_2O)]_2$ (*6*).

The nature of complex formation in the investigated metal polyacrylates seems to be related to the effective size of the cationic species in solution. Table I lists the reported (*8*) ionic radii along with the types of metal complexes observed for various investigated metal ions. When the ionic (or covalent) radius drops for the investigated series below that of Y^{+3}-ions (0.893 Å), a mixture of the two types of complexes may be observed. In some cases, a mixture may be due to the formation of metal–hydroxide complexed cationic species at higher pH values which should possess a larger resulting ionic radius than that of the host metal ion with respect to bonding to other ions such as carboxylate groups. For the investigated metal polyacrylates, metal cations with larger ionic radii would form bidentate complexes due to the low degree of strain energy associated with a bidentate-complexed ligand and a large ion. The substitution of a small metal ion for a large metal cation would cause larger structural deformation upon formation of a bidentate complex, straining the O–C–O bond angle of the carboxylate group. In contrast, a bridged complex would possess a less strained or a more stable complex structure with these metal cations. In the case of aluminum ions (ionic radius = 0.51 Å), a bridging complex seems to occur both at high and low preparation pHs.

4. Conclusions

The structural configurations of the complexes formed in several different metal polyacrylates were determined using FTIR spectroscopy. These polyacrylates are of interest because they are precursors for high performance ceramic powders.

The degree of complex formation in the polyacrylate can be controlled by varying the precipitation pH. While in most cases full complex formation would be desired, there may be cases where incomplete formation may be desired. This investigation indicates that the degree of complex formation in these materials can be monitored using FTIR spectroscopy.

The differences between the forward strike process and the reverse strike process were discussed for those metal cations that possess soluble or insoluble hydroxides and related salts in the investigated preparation pH ranges. This study noted that the reverse strike method generated a higher degree of complex formation between the metal cations and the carboxylate groups in the polymer in cases where insoluble nonpolyacrylate precipitates could also be formed.

Finally, the effect of the ionic radius of a metal cation on the nature of the complex that is formed with carboxylate groups of polyacrylates was investigated. As the ion size of the metal cation decreased, the structural arrangement for the complex changed from a bidentate configuration to a bridging configuration. In the case of iron and copper ions, mixtures of the two types of complexes were noted. Variations in these mixtures' compositions with preparation pH were probably caused by possible variations in the effective ionic radii for such metal cations upon changing the pH.

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