

Fourier-Transform Infrared Studies of Ionomeric Blend and Ionic Aggregation

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The ionomeric blend and the ionic aggregation studies by using a Fourier-transform infrared spectroscopy (FT-IR) are presented. Two ionomers were prepared, one is barium polyacrylate and the other is barium polystyrenesulfonate. The blend of the two ionomers of the barium salts shows intermolecular ionic interaction between the carboxylated ionomer and the sulfonated ionomer. This interaction leads to considerable differences between the spectrum of the blend and the sum of the spectra of the pure ionomers. From our results, it is shown that ionic interactions must play an important role in the compatibility of the two ionomers. In the ionic aggregation study, the bands due to asymmetric stretching mode of carboxylate anion (COO^-) in the carboxylated ionomer and the ionomer blend increase in intensity with increasing the divalent barium cations. These results indicate the formation of ion pairs. The doublet due to the asymmetric stretching modes of the carboxylate anion (COO^-) is concerned with a sort of local structure found in the ion aggregation. By considering a possible structure for multiplets in the blend, the spectral splitting and the frequency shift are well explained.

Introduction

Since compatible systems sometimes present advantages over incompatible ones, many attempts have been made to find compatible polymeric systems or to compatibilize various polymer pairs for a very long time.^{1,2} These attempts have been classified into four groups from the interactions between the pairs such as hydrogen bonds, charge transfer, van der Waals interactions, and ionic interaction.

Polyelectrolyte complexes are formed by mixing oppositely charged polyelectrolytes, *i.e.*, polyanions and polycations, where Coulomb force plays an important role. The polyelectrolyte complexes that consist of the two ionic polymers have very important properties in practice. Thus many investigations are found in the literature.^{3,4} The structure of the ionomers used in our experiment differs from that of other ion-containing macromolecules such as polyelectrolyte complexes and snake-cage resins,³ but is similar to that of ion-exchange resins. The ionomers contain only anion type of polyelectrolyte which is crosslinked by divalent counterions.

FT-IR is an excellent technique to study compatible systems. Already, a number of compatible blends have been investigated by using FT-IR.⁵⁻⁷ Miya and Iwamoto⁸ showed that chitosan not only forms a clear homogeneous blend with poly(vinyl alcohol) but also that the tensile strength of the blend is greater than the sum of the component values. Garcia⁹ reported that polystyrene/poly(vinyl methyl ether) blends can be prepared as compatible state or phase separated state depending on the solvent used. This fact reveals a strong evidence for the importance of the molecular interactions.

Recently, many of the researches have been focused on the nature of the ionic cross-links and of the states of ionic aggregation.¹⁰⁻¹⁴ In the spectral studies of both sodium and calcium ionomers, Painter *et al.*¹⁵ demonstrated that the FT-IR is potentially a powerful tool for investigating the structure of ionomers. Andreeva *et al.*¹⁶ reported that the ratio of peak intensities of the two bands due to the asymmetric stretching

mode of carboxylate ion depends upon ion concentration, the nature of cation, and temperature. Brozoski *et al.*¹⁷ reported that a pattern of bands in the asymmetric carboxylate stretching region of the spectrum varied with the nature of the cation. They reported that on the basis of the coordinating tendency of each cations, various local arrangements of the carboxylate groups are possible.

The first of the present work is the study of an ionomeric blend. The divalent barium cation plays a role as the cross-linker between poly(styrene sulfonic acid)(PSSA) and poly(acrylic acid)(PAA). From the frequency differences between the spectrum of the ionomer blend and the sum of the spectra of the two pure ionomers, it is concluded that the ionic interactions plays an important role on the compatibility of the ionomers. The second study is on the state of ionic aggregation. From the doublet due to the asymmetric stretching modes of a carboxylate anion in the carboxylated ionomer and the ionomer blend, it was possible to obtain an evidence for ionic aggregation. In order to account for the observed spectral frequency shifts and doublet splitting of the ionomer blend, a possible structure of the multiplet was postulated, and this was employed to explain all results of the FT-IR spectral studies.

Experimental

Polystyrene was prepared by an anionic polymerization using *n*-BuLi as an initiator. The molecular weight ($M_w = 50,000$) of polystyrene was determined by a gel permeation chromatography (GPC) using tetrahydrofuran as an eluent. Standard polystyrene with a sharp molecular weight distribution (Pressure Chemical Co.) was used for calibration. Polystyrene was sulfonated,¹⁸ we obtained completely water-soluble poly(styrenesulfonic acid), and obtained the precipitate of the sodium salt by using sodium hydroxide. Acrylic acid was polymerized by a solution polymerization. The molecular weight ($M_w = 57,000$) was obtained by an intrinsic viscosity

measurement using an Ubbelohde type viscometer.

Poly(acrylic acid) and barium hydroxide were dissolved separately in pure water (distilled three times) in known concentrations, respectively. The barium hydroxide solution was added dropwise to the vigorously stirred poly(acrylic acid) in the equivalent of 0.2, 0.4, 0.6, 0.8 1.0. The water-insoluble precipitates produced by this procedure were filtered and dried at 25°C in a vacuum oven for over 24 hours. This sample is called the barium polyacrylate(BaPAA) ionomer. In a similar way, the barium polystyrene sulfonate(BaPSSA) ionomer was prepared. Since the reactions producing the ionomers is quantitative, the above-mentioned equivalent-ratios indicate the percentage of the ionomers in the poly(acrylic acid) or poly(styrenesulfonic acid) samples. Thus the ionomers often represented as 20 %, 40 %, 60 %, 80 % and 100 % barium polyacrylate ionomers etc..

The ionomer blend is prepared by the following procedure. Both poly(styrene sulfonic acid) and poly(acrylic acid) were dissolved in pure water in equal stoichiometric amounts. The barium hydroxide solution of known concentration is added dropwise to the vigorously stirred PSSA/PAA solution. By adjusting the amount of Ba(OH)₂ solution, one can make 20 %, 60 %, and 100 % ionomer blends. The precipitates obtained by the above-mentioned procedure was centrifuged for 3 hrs and dried at 60°C in a vacuum oven for 3 hrs.

Thin KBr pellets of barium polyacrylate, barium polystyrenesulfonate ionomers and of the ionomer blends were prepared. The KBr pellets were sufficiently thin to be within the absorbance range where the Beer-Lambert law is obeyed. Infrared spectra were obtained by a Nicolet 5-MX FT-IR spectrometer, sixty scans at a resolution of 4cm⁻¹ were signal-averaged. The spectra were transformed into absorbance units, averaged over each sample and stored on a magnetic tape. From the results, however, it appeared that the pellets thickness showed a large effect on the absorbance, so we had to look for a calibration method.

Fortunately, we knew that potassium cyanide(KCN) absorption band was not affected by the absorption band of each ionomer sample in the region 1900-1000 cm⁻¹ which is interested in our works, and showed a sharp absorption band at 2084.94 cm⁻¹ (-C≡N stretching band). So we chose this KCN as an internal standard. Thus the constant amount of KCN was added to the each ionomer sample, and the KBr pellets of these samples were prepared. Spectra are represented as absorbance (A) vs. frequency or wavenumber(σ); $A(\sigma)$ is the absorbance of the sample for frequency σ , and A^* is the absorbance of KCN at 2084.94 cm⁻¹. Spectra of KCN-containing samples $A_s(\sigma)$ were normalized by dividing it by A^* i.e.,

$$A_{s,n}(\sigma) = A_s(\sigma) / A^*$$

where the subscript n indicates the normalization.

According to the Lambert-Beer law:

$$A_s(\sigma) = \epsilon_s c_s l_s$$

$$A^* = \epsilon^* c^* l^*$$

where ϵ_s and ϵ^* are the extinction coefficient of the sample and of the KCN at 2084.94 cm⁻¹, c_s and c^* the corresponding concentrations in the pellet, and l_s and l^* are the pathlength of the light in the pellet, l_s and l^* being equal in this experiment. So $A_{s,n}(\sigma)$ is

$$A_{s,n}(\sigma) = \epsilon_s c_s l_s / \epsilon^* c^* l^*$$

$$= \epsilon_s c_s / \epsilon^* c^*$$

Thus the effect of sample thickness was removed. All spectra of our works were normalized by the this procedure.

Results and Discussion

(a) The compatibility of ionomers. Figure 1 shows the FT-IR spectra of barium polyacrylate (20 %, 40 %, 60 %, 80 %, and 100 %) in the region 1900-1456cm⁻¹. The carbonyl (C=O) stretching frequency occurs at 1701.3cm⁻¹. Also, the absorption due to the asymmetric stretching mode of the carboxylate ion(COO⁻) occurs at 1554.7cm⁻¹ and at 1547.0cm⁻¹. The symmetric stretching mode of the carboxylate ion(COO⁻) occur at 1410.1cm⁻¹ which is not shown in Figure 1 but in Figure 2.

Macknight *et al.*¹⁹ have studied the infrared spectrum of the ethylene-methacrylic acid copolymers and their sodium salts system, and found that quantitatively the intensity of the band of carbonyl mode(1700 cm⁻¹) decreases while that of the bands of asymmetric stretching mode of COO⁻(1560 cm⁻¹) increases with increasing sodium equivalent ratios. From Figure 1, we found a similar phenomenon that the intensity of the band of carbonyl (C=O) mode(1701.3cm⁻¹) decreases while that of the bands of asymmetric stretching mode of COO⁻(1554.7cm⁻¹, 1547.0cm⁻¹) increases with increasing barium

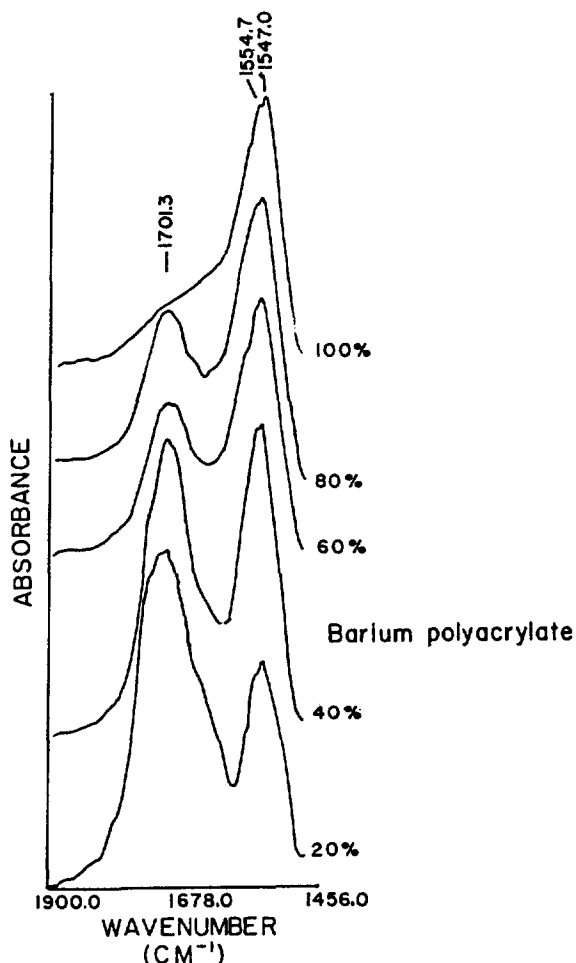


Figure 1. FT-IR spectra of carboxylated ionomers (20%, 40%, 60%, 80%, and 100%) in the region 1900-1456cm⁻¹.

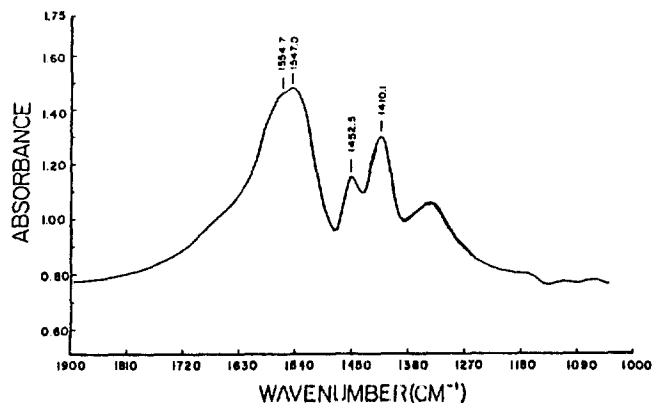


Figure 2. Completely neutralized carboxylated ionomer in the region 1900–1000 cm^{-1} .

equivalent ratios. This indicates that the ion pair, $\text{COO}^-\text{Ba}^{++}\text{OOC}^-$, forms increasingly with the barium equivalent ratios. That is, the formation of the ion pairs depends on the concentration of carboxylate anions and the divalent barium cation which play a role of cross-linker between two carboxylate anions.

Figure 2 shows the spectrum of completely neutralized carboxylated ionomer. The band of carbonyl($\text{C}=\text{O}$) stretching mode disappears completely and the two bands due to asymmetric stretching mode of the carboxylate ion (COO^-) appear besides the bands due to CH bending (1452.5 cm^{-1}) and COO^- symmetric stretching (1410.1 cm^{-1}). From infrared study of calcium salts of an ethylene-methacrylic acid copolymer, Painter *et al.*¹⁵ had assigned the doublet splitting at 1515 and 1548 cm^{-1} to the characteristic of an interaction which could well occur between the modes of COO^- groups in calcium carboxylate dimers. Thus we looked upon the doublet band of asymmetric stretching mode of COO^- (1554.7 cm^{-1} , 1547.0 cm^{-1}) in our system as an analogue described above.

Figure 3 shows the FT-IR spectra of barium polystyrene sulfonate (20%, 40%, 60%, 80%, and 100%) in the region 1567–1345 cm^{-1} . The stretching absorption due to aromatic double bond($\text{C}=\text{C}$) occur at 1442.8 cm^{-1} and 1402.3 cm^{-1} . These bands were shifted to lower frequencies by inductive effect of sulfonate anion(SO_3^-) more than ordinary aromatic double bond stretching band. One notes from Figure 3 that the bands at 1442.8 cm^{-1} and 1402.3 cm^{-1} increase in intensity with increasing the barium equivalent ratios. This is due to the intensity increase of the stretching mode of the aromatic double bond($\text{C}=\text{C}$), because of the increase in ion pairs, $-\text{SO}_3^-\text{Ba}^{++}_3\text{O S}-$, with increasing barium equivalent ratios.

Figure 4 shows the FT-IR spectra of the ionomer blend of PAA and PSSA according to equivalent ratios (20%, 60%, and 100%) in the region 1900–1000 cm^{-1} . The absorption due to the asymmetric stretching mode of the carboxylate ion (COO^-) in the blend occur at 1564.5 cm^{-1} and 1552.8 cm^{-1} , which shows an increase in intensity with increasing the barium salts. The stretching absorption due to aromatic double bond ($\text{C}=\text{C}$) occur at 1454.4 cm^{-1} and 1410.1 cm^{-1} , and the bands increase in intensity with increasing the barium salts as well. From these increase in intensity, it is explained that the formation of ion pairs in the blend increases with increasing the barium salts.

In Figure 5, A and B show the FT-IR spectra of the barium polyacrylate(BaPPA) (100%) ionomer and of the barium polystyrenesulfonate(BaPSSA) (100%) ionomer, respective-

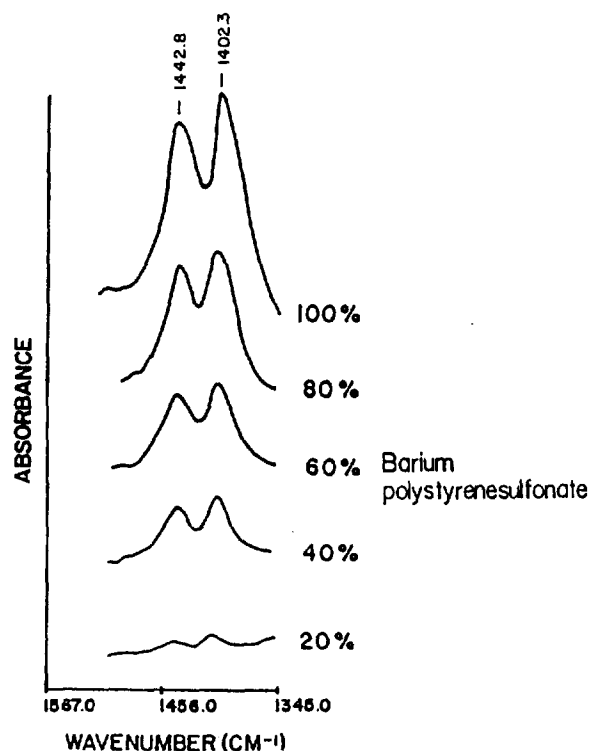


Figure 3. FT-IR spectra of sulfonated ionomers (20%, 40%, 60%, 80%, and 100%) of PSSA in the region 1547–1345 cm^{-1} .

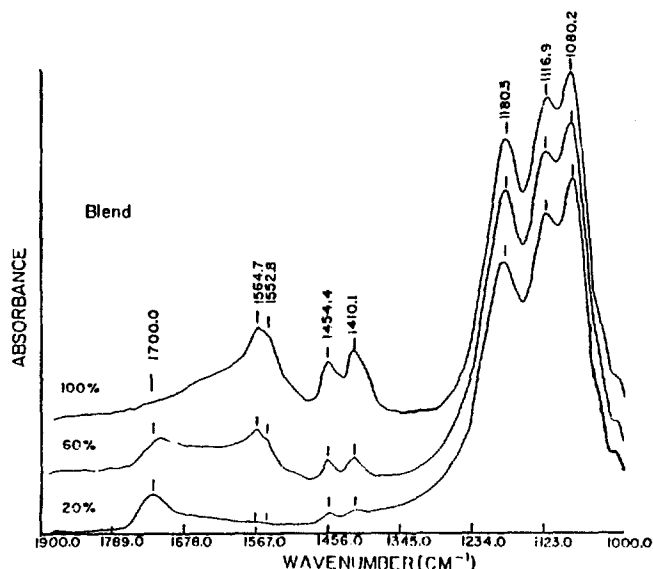


Figure 4. FT-IR spectra of ionomer (20%, 60% and 100%) blends of PAA and PSSA in the region 1900–1000 cm^{-1} .

ly, and the addition of two spectra is represented in C; the blend of the BaPAA and BaPSSA (100%) is shown in D. The frequencies of the asymmetric stretching carboxylate anion are shifted from 1554.7 cm^{-1} 1547.0 cm^{-1} to 1564.7 cm^{-1} and 1552.8 cm^{-1} , respectively. By the way the 1452.5 cm^{-1} due to the absorption of CH_2 and 1410.0 cm^{-1} due to the symmetric stretching of COO^- are not shifted so much with increasing the barium salts in polyacrylic acid, and their intensity is small as compared with that of the stretching band of aromatic double bond($\text{C}=\text{C}$) (See Figure 5 A and B). Thus we can consider that the shifting from 1442.8 cm^{-1} and 1402.3 cm^{-1} to

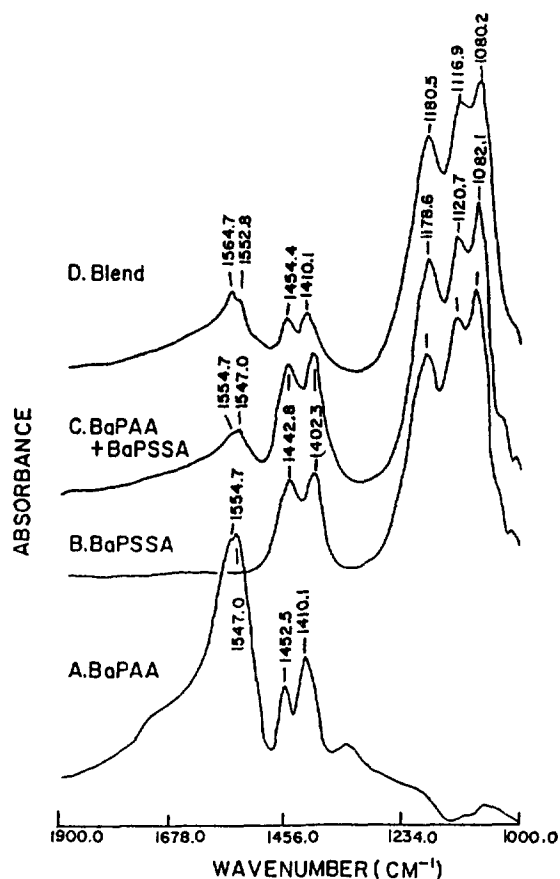


Figure 5. FT-IR spectra of barium ionomers.

A. Barium polyacrylate (BaPAA) ionomer, (magnified five times). B. Barium polystyrenesulfonate (BaPSSA) ionomer. C. The addition of A and B. D. The blend of BaPAA and BaPSSA.

1454.4cm^{-1} and 1410.1cm^{-1} , respectively, is mainly due to that of the stretching band of aromatic double bond ($\text{C}=\text{C}$). We also note that the frequencies of the asymmetric stretching mode of the sulfonate anion (SO_3^-) is shifted from 1178.6cm^{-1} and 1120.7cm^{-1} to 1180.5cm^{-1} and 1116.9cm^{-1} , respectively, and that the band of the symmetric stretching mode of the sulfonate anion is shifted from 1082.1cm^{-1} to 1080.2cm^{-1} .

From these frequency shifts, it is concluded that there must be a distinct ionic interaction between the carboxylated ionomer and the sulfonated ionomer. This interaction leads to considerable differences between the spectra of the ionomer blend and the sum of the spectra of the pure ionomers. From these FT-IR spectra of ionomers, we can show that ionic interactions must play an important role in the compatibility of the two ionomers. That is, the divalent barium cation play a role as a crosslinker between the sulfonate anion and the carboxylate anion, and the frequency shift are caused by the inductive effect of the sulfonate anion which is more electron withdrawing than the carboxylate anion. From these results, it is concluded that the two ionomers are compatible.

(b) The Ionic Aggregation of Ionomers. Ionic species tend to aggregate in low dielectric media, and so ion aggregation is expected in our ionomers. As shown in Figure 1, the increase of spectral intensity of polyacrylate ionomer with the divalent barium cation ratio shows the existence of ionic aggregation. That is, as ion pairs increase, the spectral intensity increases. As shown in Figure 2, the absorption due to

carbonyl ($\text{C}=\text{O}$) stretching vibration (1701.3cm^{-1}) is absent in completely neutralized ionomer whereas it still appears in Figure 1, and only the absorptions due to the asymmetric stretching of carboxylate ion (COO^-) appear with other bands. Therefore, the doublet that appeared at 1554.7cm^{-1} and 1547.0cm^{-1} is concerned with some sort of local structure found in ionic aggregations. Brozowski *et al.*¹⁷ reported that bands in the asymmetric carboxylate stretching region of the spectrum vary with the nature of the cations, and they postulated that the alkaline earth metal (Mg, Ca, Sr and Ba) ionomers have tendencies to build octahedral structure of a coordination number of 6.

In contrast to the planar carboxylate anion, the sulfonate anion is tetrahedral,^{20,21} as shown in Figure 6. Lafelar and Weiss²² reported that in sulfonated ionomer the anion packing is independent of the cation from the small angle X-ray experiments, and that the divalent cation shares faces between two antiparallel layers of hexagonally packed anions. From our results of FT-IR studies, it is concluded that one Ba^{++} ion and two sulfonate anions in the sulfonated ionomers make an octahedron. The geometry belongs to the symmetric group D_3 . The three asymmetric stretching modes are distributed among the A_2 and E species. Both of these modes are infrared active. As a result, the two asymmetric stretching modes of sulfonate anion occur at 1178.6cm^{-1} and 1120.7cm^{-1} .

Also, the frequencies (1554.7cm^{-1} , 1547.0cm^{-1}) of the asymmetric stretching of carboxylate anion in the carboxylated ionomer are shifted to higher frequencies (1564.7cm^{-1} , 1552.8cm^{-1}) in the ionomer blend. The frequencies (1120.7cm^{-1} , 1082.0cm^{-1}) of sulfonate anion in the sulfonated

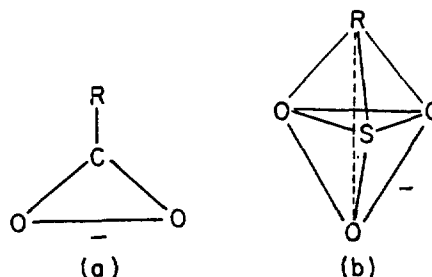


Figure 6. Geometry of carboxylate anion (a), sulfonate anion (b).

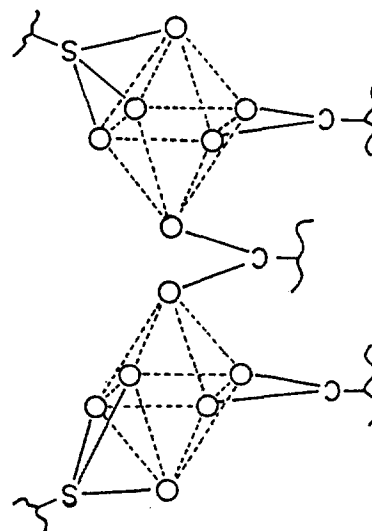


Figure 7. A possible structure of ionic multiplets in ionomer blend.

ionomer are shifted to lower frequencies (1116.9cm⁻¹, 1080.2cm⁻¹) in the ionomer blend.

We consider the possible local structure for multiplet in order to account for the observed two bands of asymmetric stretching carboxylate anion and the frequency shifts in the ionomer blend. We postulate that Figure 7 shows the possible structure for the ionomer blend. One carboxylate anion is connected with the two ionic pairs (octahedral structure). That is, one oxygen ion of the carboxylate ion constitutes an ionic multiplet with sulfonate ion (octahedral structure) and the other oxygen forms another ionic multiplet. By considering the possible local structure for the multiplet, it is concluded that the frequency shift is caused by the inductive effect of sulfonate ion, and that the multiplet structure is a reasonable one. But, as to the ionic aggregation, more works have to be done to justify our postulation.

Conclusion

From this work, the following items are concluded. (1) Ionic interaction leads to considerable frequency shifts between the spectrum of the blend and the sum of the spectra of the pure ionomers. In view of these results, the barium cation binds the carboxylate anion and sulfonate anion intermolecularly and compatibilize the blend. (2) By considering the possible local structure of the blend, it is concluded that the frequency shift is caused by the inductive effect of the sulfonate ion, and that the local structure also well explains the spectral splittings. **Acknowledgements.** We acknowledge the Korea Research Center for Theoretical Physics and Chemistry for a partial support of this work. One of the authors, (J.I. Sohn) is indebted to the Korea Science and Engineering Foundation for the research grant awarded to him.

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Study of Diffusion-controlled Processes. Solution of the Smoluchowski Equation with a Step Potential

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The Smoluchowski equation with a step potential is solved in one-dimensional case and three-dimensional case with spherical symmetry. Exact analytic expressions for the solution and the remaining probability are obtained in one-dimensional case for the reflecting boundary condition and the long time behavior of the remaining probability is compared with the earlier work. In three-dimensional case, only the long time behavior is evaluated. More general case with the radiation boundary condition is also investigated and the results are shown to approach correct limits of the reflecting boundary condition.

Introduction

Recently, study of diffusion-controlled processes has been

very active in order to investigate various chemical phenomena occurring in solution^{1,2}. The quantity of interest in these processes is the coordinate and time dependent probability distribution function which satisfies the diffusion equation.