

Cation Motion in Anionic Fields of the Polyelectrolytic Salts of Ethylenemethacrylic Copolymers

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The far-infrared spectra of the Li^+ , Na^+ , K^+ , Cs^+ salts and acid forms of polyelectrolytic ethylenemethacrylic acid copolymers have been examined in the $800\text{--}33\text{-cm}^{-1}$ region at ambient and low temperatures. A broad band, which shifts to lower frequency as the cation mass is increased, is attributed to cation motion in anionic fields, and the appearance of a low frequency band, whose intensity is related to the cation properties, is assigned to perturbed skeletal motions of a neighboring polymer segment. Models are proposed and analyzed for the vibrational modes involving ion motion. The vibrational force constants for aggregate distortion, as calculated from the observed ion-motion frequencies, are in agreement with such constants computed here employing an ion-multipole potential energy function which does not use these experimental data. The spectral and theoretical results are considered in terms of the molecular interactions of importance in polyelectrolytes and in the physical properties of these materials.

INTRODUCTION

Among the polyelectrolytic materials whose properties are dependent upon the nature of the cation (counterion: Li^+ , Na^+ , K^+ , Cs^+), and upon the concentration of anionic sites on the polyanion are the alkali-metal salts of the copolymers formed from ethylene and methacrylic acid. These compounds, known as ionomers, thus form a series of systems in which the relationships between their properties and systematic molecular changes, such as variation of M^+ or anion-site concentration, can be investigated. Several studies attempting to correlate bulk physical properties of polyelectrolytes with stoichiometric changes have been reported.¹⁻³ Clearly, however, understanding the nature and magnitude of the specific molecular interactions in polymers and polyelectrolytes is essential to developing a microscopic theory for their physical and chemical properties. These interactions, specifically the forces acting between the cation and the polyanion(s), can be probed by studying the nature of the vibrations in which the cation takes part. To the extent that the interactions are between a cation and an anionic site, the forces are of interest in evaluating site-binding energies employed in polyelectrolyte theory.

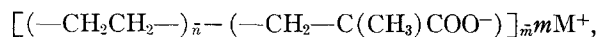
We have shown⁴ that films of several ionomers exhibit far-infrared absorption bands whose frequencies and widths depend on the cation in a manner similar to those first observed by Edgell, *et al.*⁵ in the far-infrared spectra of alkali-metal salts in solvents of low dielectric constant. These vibrational bands in solution have been interpreted as being due to motion of the cations in the potential field of their counterions, with the cation motion occurring, variously, in solvated ion pairs and higher aggregates. Based on this interpretation the nature of the forces of interaction between the cation and its neighbor ions and molecules was considered using vibrational and electrostatic models.^{6,7} In light of this, far-infrared bands due to cation motion in the potential fields of polyanion sites and poly-

ethylenic chains in the ionomers can be employed to evaluate the interaction forces involving the cation by analysis of these vibrations and by ion-multipole calculations based upon the electrostatic properties of the constituents.

In this paper we report the far-infrared spectra of the Li^+ , Na^+ , K^+ , Cs^+ ionomers of several ethylenemethacrylic acid copolymers, and the spectra of the acid copolymers themselves, at low and ambient temperatures; vibrational assignments, analysis of the spectral features involving cation-polyanion distortion; and comparison of the cation-polyanion forces evaluated from the vibrational spectra with those evaluated electrostatically.

EXPERIMENTAL

The polyelectrolytes, studied as films, are formed from the acid (unionized) form of the ethylenemethacrylic acid copolymers by fusion with $\text{M}(\text{OH})$, and have the formula



where M^+ is Li^+ , Na^+ , K^+ , Cs^+ , and \bar{n} and \bar{m} are found as follows. The average molecular weight of the copolymers is $3.0 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$, so that for samples with 7.6 or 15 wt% methacrylic acid (2.6 and 5.4 mole% acid) \bar{n} and \bar{m} are calculated to be 38 and 260, respectively, or 18 and 585, respectively. The degree of replacement of carboxylic hydrogens by M^+ was 95%–100% in the ionomer samples studied. The films were annealed carefully before measurements were made on them to relieve strain introduced in preparation and to remove residual surface water detected by differential scanning calorimetry. Since the method of polyelectrolyte salt formation is not an aqueous solution neutralization, very little bulk water is present. These experimental copolymers and their salts were prepared and kindly furnished by Dr. R. Longworth of the Plastics Department, DuPont Company, and are similar to their Surlyn ionomer resins.

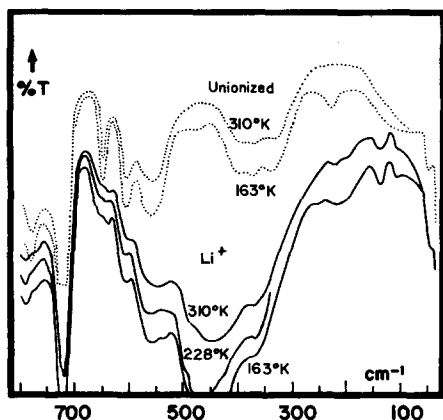


FIG. 1. The far-infrared spectra of the Li^+ salt of ethylene-methacrylic acid copolymer (7.6 mole% acid) and the corresponding unionized form of the polyelectrolyte at 310 and 163°K.

The far-infrared absorption spectra ($33\text{--}800\text{ cm}^{-1}$) of 0.05–0.20 mm thick annealed films were measured with a Beckman IR-11 spectrometer at ambient and low (163°K) temperatures by placing them in a variable temperature cell (RIIC) without windows, but with a 25 liter·min $^{-1}$ stream of dry argon or dry nitrogen passing into the evacuation ports and out the window ports. Using this arrangement good optical transmission was obtained with no condensation on the films at low temperature. The temperature was held constant, and measured at the film mounting block with an iron-constantan thermocouple, throughout each spectral measurement. Each spectrum was repeated several times with reproducibility of 1% T . The spectra were run with a resolution of $\approx 1\text{ cm}^{-1}$, and were calibrated using the CO_2 and H_2O vapor spectra.^{8,9}

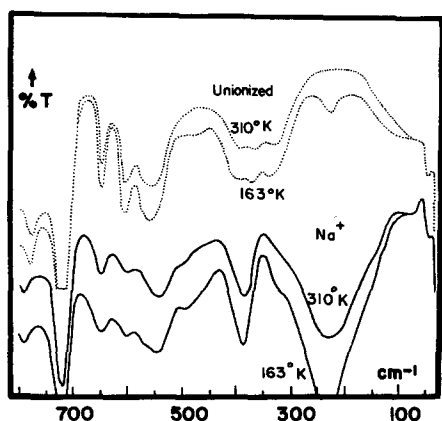


FIG. 2. The far-infrared spectra of the Na^+ salt of ethylene-methacrylic acid copolymer (7.6 mole% acid) and the corresponding unionized form of the polyelectrolyte at 310 and 163°K.

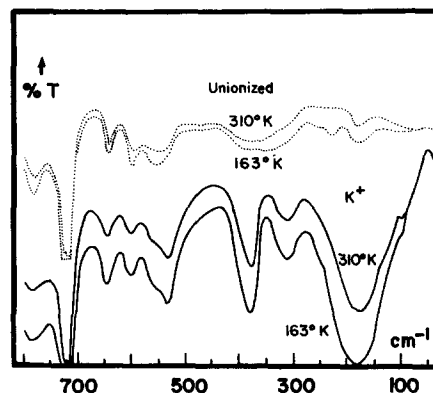


FIG. 3. The far-infrared spectra of the K^+ salt of ethylene-methacrylic acid copolymer (15 mole % acid) and the corresponding unionized form of the polyelectrolyte at 310 and 163°K.

SPECTRAL RESULTS

The far-infrared spectra of these polyelectrolyte salts, shown in Figs. 1–4, each contain a dominant feature in the region below 600 cm^{-1} which is not present in the acid form of the copolymer. This feature is a broad, well-defined band which shifts from $450 \pm 5\text{ cm}^{-1}$ for the Li^+ ionomer to $230 \pm 5\text{ cm}^{-1}$ for Na^+ , $180 \pm 3\text{ cm}^{-1}$ for K^+ and $135 \pm 3\text{ cm}^{-1}$ for Cs^+ . These principal bands, whose frequency variation is roughly accounted for by the change in mass of the cation, if the vibrational reduced mass is taken as approximately that of the anionic field in the copolymer. The shoulder at $485 \pm 3\text{ cm}^{-1}$ on the main Li^+ band, which is centered at 450 cm^{-1} , in Fig. 1 is attributed to the same motion of the $^6\text{Li}^+$ isotope. Again assuming the vibrational reduced mass

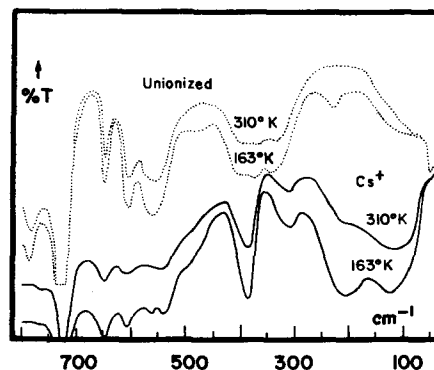


FIG. 4. The far-infrared spectra of the Cs^+ salt of ethylene-methacrylic acid copolymer (7.6 mole % acid) and the corresponding unionized form of the polyelectrolyte at 310 and 163°K.

for the 450-cm^{-1} band to be that of ${}^7\text{Li}^+$, we expect such a shoulder at $\omega' = (7/6)^{1/2}\omega = 486\text{ cm}^{-1}$.

In addition to the cation motion bands assigned, the spectra clearly show the occurrence of several types of perturbations on the polyanion itself. The analysis of these features is helpful in understanding the role of the cation and the nature of its surroundings.

There are two types of perturbation of the polyanion evident from the spectra, of which the first is that of those vibrational modes associated with and approximately localized on the COO^- group, and the second is that of the polymer backbone deformations. Evidence of the first is seen in the shift of the 785-cm^{-1} band of the acid form of the copolymer, which is associated with O-C-O bending motions,¹⁰ by about 10 cm^{-1} to higher frequencies in the salts. The perturbation of the COO^- by the alkali-metal ion is also seen by the changes in the 645-cm^{-1} band, assigned to a COO wag, which is shifted to slightly higher frequencies in the ionomers and is split in the case of the Li^+ salt.

The 560-cm^{-1} band of the acid form is split into two bands (Figs. 1-4) in the ionomer spectra together with a weak shoulder at $\approx 500\text{ cm}^{-1}$. Although we cannot assign this feature unambiguously at present, we note that polymeric esters with a pendant COOR group have bands in this region which are assigned to a bend of the C-O-R linkage with respect to the C-C=O grouping and are both frequency and intensity sensitive to mechanical coupling with the R group. However, vibrations containing large C-C-C wagging-motion components¹¹ are also expected to have frequencies in this region. Thus, in neutron diffraction studies^{12,13} of polyethylene a band was observed at $550 \pm 50\text{ cm}^{-1}$ which corresponds to the coupled skeletal deformation and skeletal stretching motion, calculated as ν_5 by Tasumi, Shimanouchi, and Muyazawa (TSM)¹⁴ and Lin and Koenig (LK).¹⁵ The purely C-C-C skeletal deformation mode, which the above theories predict to be inactive for crystalline, unbranched polyethylene, could well be perturbed into activity in the copolymer containing $-\text{COOH}$, and split by interactions of M^+ with the anion sites on the polyanion.

In addition to being in the field of anionic sites on the polyanion, the cations are expected to be proximate to polyethylenic portions of one or more polyanions. In this event, we expect ion-multipole forces to cause perturbation of the backbone deformations. The direct interaction of the cation and hydrocarbon backbone is best detected in the 200-cm^{-1} region where TSM and LK predict a second mode (often identified as ν_9) corresponding to a torsional motion of the C-C-C skeleton, which is sensitive to the magnitudes of intermolecular interactions. The neutron scattering experiments of Safford *et al.*^{12,13} have resulted in the observation of this band. Although it is not predicted to be infrared or Raman active, an unassigned feature has been observed at 228 cm^{-1} in the Raman spectrum of crystalline polyethylene.¹⁶ For polymethacrylic acid¹⁰

and the acid forms of the presently investigated ethylenemethacrylic acid copolymers at ambient temperature no infrared band is observed in this region. However, at low (163°K) temperature, at which the motion of the polymer is restricted, a band is observed for the copolymers at 225 cm^{-1} (Fig. 5). This band is observed at both ambient and low temperatures (with enhanced intensity) in the alkali-metal salts of the copolymer. It is clearly observed in the case of the Li^+ and Cs^+ ionomers (Figs. 1 and 4), while in the Na^+ and K^+ salts it is seen as asymmetry on the low and high frequency sides, respectively, of the cation motion bands. We interpret this observation to indicate that the cation places a restraint on the motion of the polyethylenic portion of the backbone and perturbs this inactive band into activity. The band is most intense when the cation is Cs^+ , which has the smallest cation motion amplitude but highest polarizability. In addition to these observations, the 600-cm^{-1} band in the acid copolymer is shifted to $605\text{--}610\text{ cm}^{-1}$ upon ionomer formation. A similar shift of a 595 (588)- cm^{-1} Raman band in polyacrylic acid to 603 (610) cm^{-1} in its sodium salt has been assigned^{17,18} to perturbation of a C-C-C bending motion.

There are, of course, certain features associated with the polyanion that are relatively insensitive to the presence of the cation. In all of the spectra the strong 725-cm^{-1} absorption is due to a doublet (720 and 730 cm^{-1}) characteristic of a methylene rocking-twisting motion in higher paraffins.^{11,19-25} The 720-cm^{-1} band contains components of both crystalline (out-of-phase CH_2 rocking of the two chains in the crystalline phase analog of the unit cell) and amorphous polyethylene (CH_2 rocking of chain segments in *trans* configuration and associated²⁶ with sequences of more than four *trans* bonds). The 730-cm^{-1} band is assigned to CH_2 in-phase rocking modes for the two chains in the unit cell of crystalline polyethylene. These assignments

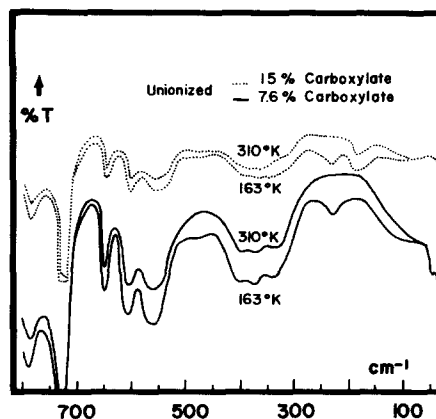


FIG. 5. The far-infrared spectra of unionized ethylenemethacrylic acid copolymers with 7.6 and 15 mole % carboxylic acid at 310 and 163°K .

are possible by analogy since the long ($\bar{n}=18-38$) polyethylenic segments can exist in both amorphous and crystalline regions.²⁷ The complex band envelope with inflections and relative maxima at ≈ 400 , 370 and 335 cm^{-1} for the acid form of the polymer appears rather as two bands at 370–380 cm^{-1} and 305–315 cm^{-1} in the ionomers, as is best seen in the spectra of the K^+ and Cs^+ salts in Figs. 3 and 4. In the acid form of the polyelectrolyte these two C–C–C bending and twisting modes, together with the out-of-plane deformation²⁸ of hydrogen-bonded carboxylate groups, which is not possible in the ionomers, give rise to the broad envelope. The spectra of the two acidic form copolymers (7.6% and 15%), shown in Fig. 5, are identical except for a band in that with 15% carboxylic acid at ≈ 180 cm^{-1} which is associated with the greater number of hydrogen bonds present in that case.²⁹

VIBRATIONAL ANALYSIS MODELS AND INTERIONIC FORCES

Our interpretation of the spectra of the ionized and acid forms of the copolymer lead us to the following conclusions. First, for each alkali-metal ionomer there is a vibrational band which is assigned to cation motion under the influence of anionic fields within the polymer. The large bandwidth ($\nu_{1/2} \approx 50-100$ cm^{-1}) of the cation motion band indicates that there may be several environments for the cation, that differ somewhat in the forces exerted on it, and that the vibrations of the resulting assemblies are probably quite anharmonic. The intensification and narrowing of these bands, which occur near $hc\omega = kT$ at $T = 300^\circ\text{K}$, are as generally expected at low temperature. Second, the presence of the alkali-metal ion perturbs the vibrational motion of the COO^- groups. And third, the motion of the polyethylenic backbone is restricted by the presence of the cation.

The force resisting the observed vibration involving cation motion is of immediate interest as a measure of the cation–polyanion interaction. Clearly the frequency of this mode depends upon this force, which can be calculated if the form of the vibration is known. In the present case determining the form of the vibration involves postulating models for the vibrating assemblies and specifying an assumed coordinate for the infrared active mode. On the basis of our spectral interpretation and on reported studies of these ionomers, we postulate several models to describe the principal features of the vibrating assemblies. From electron microscopic,³⁰ dielectric,³¹ mechanical,^{32,33} near infrared,^{27,34} x-ray,^{30,35} and NMR³⁶ studies it appears likely that the M^+ and COO^- ions form ionic domains within the hydrocarbon matrix of the polyethylenic backbone portion in which the anion sites are incorporated. These ionic domains are analogous to ion aggregates formed in nonaqueous electrolyte systems which we have studied³⁷ in the past, but the ionomers provide a less ambiguous system in

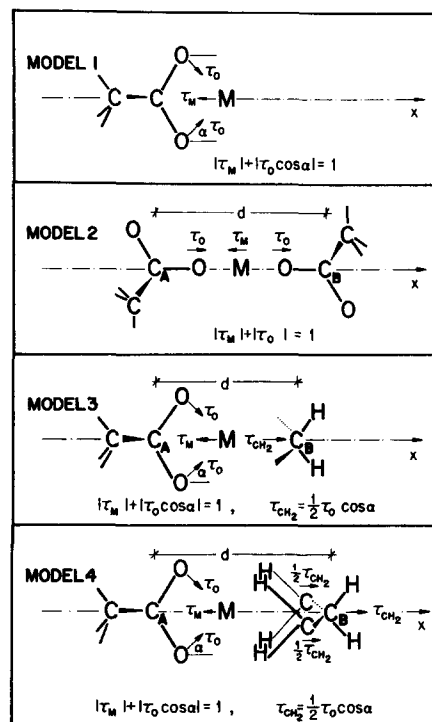


FIG. 6. Models postulated for the vibrating aggregate in the ionic copolymer, and their assumed ion motion vibrational mode.

which to study the ionic forces since the complicating factor of ion solvation is not present. In each model we require that an infrared active mode involving motion of the cation occur at a COO^- site, and then consider various models for the remainder of the vibrating aggregate.

The first model (Model 1; Fig. 6) is of a cation associated with one COO^- site, which completely dominates the forces interacting with the cation. The second model (Model 2; Fig. 6), that of the cation in the field of two equivalent COO^- sites, is based upon the postulates of ion clustering in domains and the near-infrared data,^{27,34} evidencing hydrogen bond “dimerization” between two carboxylate sites. Since there is spectral evidence, as discussed in the previous section, that the presence and motion of the cation perturbs skeletal modes of the polyethylenic backbone, two models (Models 3 and 4; Fig. 6) are proposed in which the cation is the field of both a COO^- site and a paraffinic chain fragment.

For each model we can compute the net force constant, K_i^{net} , resisting displacement along the infrared active vibrational mode of the aggregate taken to represent the cation motion. It is normalized by requiring unit change in the cation–carboxylate oxygen separation at the vibrational extremum. By specifying the assumed *form* (only the relative displacements are given by the models) of the normal mode, the vibrational kinetic energy and the observed frequency can be

TABLE I. Force elements, $K_{\text{obs}}^{\text{net}}$, calculated from experimental data.^a

Cation	Model 1		Model 2		Model 3		Model 4	
	Υ^{red}	$K_{\text{obs}}^{\text{net}}$	Υ^{red}	$K_{\text{obs}}^{\text{net}}$	Υ^{red}	$K_{\text{obs}}^{\text{net}}$	Υ^{red}	$K_{\text{obs}}^{\text{net}}$
Li ⁺	6.10	0.73	5.74	0.69	6.11	0.73	6.11	0.73
Na ⁺	14.90	0.47	13.38	0.42	15.18	0.47	15.32	0.48
K ⁺	19.45	0.37	17.58	0.32	20.18	0.39	20.57	0.39
Cs ⁺	28.90	0.31	25.79	0.28	30.93	0.33	32.99	0.34

^a Units of $K_{\text{obs}}^{\text{net}}$ entries; 10^8 dyn/cm.

employed to compute K_i^{net} . In applying the models for the forms of the assumed eigenvectors, the normalization condition is ($|\tau_M| + |\tau_0 \cos\alpha| = 1$). Here α (Fig. 5) is determined by requiring $\angle\text{OCO}$ to be 120° and $r(\text{C-O})$ to be 1.27 \AA , both known, and positioning the cation along the x axis such that its sphere, of ionic radius r_{M^+} , is tangent to the oxygen spheres of radius $r_0 = 1.4 \text{ \AA}$, the van der Waals radius. The reduced mass is not very sensitive to the precise value of α , but some such choice is required to compute the x component of the oxygen displacement relative to that of M^+ .

The kinetic energy T can be expressed, following Edgell,^{38,6} as

$$T = \frac{1}{2} \sum_n m_n \dot{\mathbf{p}}_n \cdot \dot{\mathbf{p}}_n = \frac{1}{2} \sum_{i,j} \Upsilon_{ij} \dot{R}_i \cdot \dot{R}_j, \quad (1)$$

where

$$\Upsilon_{ij} = \sum_n m_n \tau_{ni} \cdot \tau_{nj} \quad (2)$$

and \mathbf{p}_n is the displacement of atom n whose mass is m_n , while R_i is the i th normal coordinate whose form is given by the vectors τ_{ni} . For one vibrational mode, assumed to be the i th normal mode, we write the reduced mass, Υ_i^{red} ,

$$\Upsilon_i^{\text{red}} = \sum_n m_n \tau_{ni} \cdot \tau_{ni}. \quad (3)$$

Thus, Υ_i^{red} is computed from the τ_{ni} that result from the model geometry, necessary momentum conservation constraints and the normalization constraint imposed. Now the vibrational potential energy can be expressed, in terms of the force constants $V_{k,l}$ for the internal coordinate changes Δr , as

$$V = \frac{1}{2} \sum_{k,l} V_{k,l} \Delta r_k \Delta r_l = \frac{1}{2} \sum_{i,j} K_{ij}^{\text{net}} R_i \cdot R_j. \quad (4)$$

Let $\bar{\Delta} \bar{r}_{ki}$ be the relative change in the k th internal coordinate for the given relative atomic displacements τ_{ni} for the mode i . Then we have the "reduced force constant"

$$K_i^{\text{net}} = \sum_{k,l} V_{k,l} \bar{\Delta} \bar{r}_{ki} \bar{\Delta} \bar{r}_{li}. \quad (5)$$

Thus, the equation of motion for the i th normal mode is

$$K_i^{\text{net}} = 4\pi^2 c^2 \omega_i^2 \Upsilon_i^{\text{red}}, \quad (6)$$

which allows calculation of K_i^{net} , since ω_i is the wave-

number (cm^{-1}) of the i th mode. Clearly each model has a unique K_i^{net} , since the model affects Υ_i^{net} . The values of K_i^{net} are designated $K_{\text{obs}}^{\text{net}}$, to indicate their calculation from spectral data, and are listed along with Υ^{red} in Table I for each model and each cation-polyelectrolyte system.

CALCULATION OF INTERACTION FORCES

The potential energy and nature of the interactions within polyelectrolytes, and especially those corresponding to "site binding," are of great interest in a variety of systems. These have eluded detailed evaluation largely because there have been no experimental data with which direct comparisons can be made.

In the present case, however, the values of $K_{\text{obs}}^{\text{net}}$ form the basis for such comparisons. Thus, we may evaluate the potential energy of the ion-atom aggregates, represented by the vibrational models, as a function of the vibrational normal coordinate and from it obtain the equivalent $K_{\text{calc}}^{\text{net}}$ from $(d^2U/dR^2)|_{R_0}$. The problems with such an approach are that an adequate potential function must be found, and that the spatial arrangement of the atoms surrounding the cation must be determined. The latter can be determined by energy minimization criteria because bond distances and angles are known for the covalently bound atoms of the surrounding polymer fragments and the separation of the fragments is made the only independent variable.

The basis for selection of a potential function is the assertion that the dominant attractive interactions are electrostatic. This reduces the problem to assuming pairwise additivity, formulating the attractive potential as basically a multipole function, and of employing a valid repulsive potential. The Born-Mayer repulsive potential, $A_{ij} \exp(-r_{ij}/\rho)$ where A_{ij} and ρ depend, in general, upon the pair of interacting atoms, has been widely used in calculations on gaseous ion clusters³⁹⁻⁴¹ and ionic lattices⁴² with satisfactory results that have encouraged theoretical studies to determine its quantum mechanical origin. Thus, Hafemeister and Zahrt⁴³ calculated the summation of the electrostatic energy between effective nuclear charges and the exchange charges for alkali halides and hydrides, using ionic SCF wavefunctions, and showed that it very closely fits the

TABLE II. Values of parameters employed in potential energy calculations.

Atom (X)	Z (Calc 1)	Z (Calc 2)	Z (Calc 3, 4)	α (10^{24} cm ³)	A_{ij} (10^{-3} eV)			C_{ij} (10^{60} erg·cm ⁶)		
					X-O	X-C	X-H	X-O	X-C	X-H
Li ⁺	+1.0	+1.0	+1.0	0.03	0.8	1.3	0.8	2.0	1.4	0.33
Na ⁺	+1.0	+1.0	+1.0	0.188	2.45	3.5	1.5	11.2	7.85	1.85
K ⁺	+1.0	+1.0	+1.0	0.887	6.2	8.7	3.8	48.0	33.75	7.78
Cs ⁺	+1.0	+1.0	+1.0	2.545	14.0	17.5	8.3	129.0	90.00	21.27
C (in -CH ₂ -)	0.0	-0.12	-0.12	2.0	9.5	13.0	5.7	a	a	a
H (in -CH ₂ -)	0.0	+0.06	+0.06	0.666	4.5	5.7	...	a	a	a
C (in COO ⁻)	0.0	0.0	-0.2	2.0	9.5	13.0	5.7	a	a	a
O (in COO ⁻)	-0.5	-0.5	-0.4	3.2	7.5	9.5	4.5	a	a	a

^a The van der Waals interaction term is negligible for such interactions.

form of the Born-Mayer repulsive potential and that ρ does, indeed, derive from the radial dependence of these repulsive-electrostatic interactions. Reddington⁴⁴ has found that expanding the Born-Mayer repulsive potential does not significantly improve its accuracy for ions of similar size.

On this basis we have modified the Rittner potential³⁹

$$U = -\frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} + A \exp(-r/\rho) - \frac{C}{r^6} + \frac{h\nu_0}{2} + \frac{h\nu_0}{\exp(h\nu_0/kT) - 1} - \frac{1}{2}(kT), \quad (7)$$

which was employed to calculate bond energies and dipole moments of gaseous alkali halides^{39,40} and matrix isolated alkali oxides,⁴⁵ for use in the case of the ionic copolymers. A modified Rittner potential has been successfully employed by Risen⁶ and Edgell *et al.*⁷ to treat solvated ion aggregate interactions in solution in computing $K_{\text{calc}}^{\text{net}}$ for comparison with $K_{\text{obs}}^{\text{net}}$ for vibrational ion motion in solution. French and Wood⁴⁶ found that if M^+ salts of $B(C_6H_5)_4^-$ are assumed to form pseudodiatom ion pairs, the Rittner potential does not adequately describe the potential energy of ion-pair formation, but this is not unexpected in light of the oversimplification such a treatment entails. They did find reasonable agreement between observed force constants and those calculated using an inverse 1-4-7-18 power potential to which *ad hoc* additions were made to obtain specific cation dependence, but this potential is designed for use in treating nonionic pseudospherical molecules.

The potential function we have employed is of the form $U = U(\text{Coulomb}) + U(\text{charge-induced dipole}) + U(\text{van der Waals}) + U(\text{repulsion})$, where the first three terms can be formulated upon specification of the interactions to be included and evaluated upon specification of the required parameters. The detailed

expression for this potential is

$$U = U_1 = \sum_i (z_i z_j / r_{ij}) - \sum_i [(\alpha_i z_j^2 + \alpha_j z_i^2) / 2r_{ij}^4] - \sum_i (C_{ij} / r_{ij}^6) + \sum_i A_{ij} \exp(-r_{ij} / \rho), \quad (8)$$

where j indexes the cation and i the surrounding atoms.

For the ion-atom aggregate represented by each model, the potential function U was formulated, each species assigned its fundamental properties, Z (charge) and α (polarizability), and each pair was assigned its parametric values, A_{ij} (pre-exponential repulsive constant) and C_{ij} (van der Waals constant). Then U was evaluated at n points ($n > 100$) along R , the assumed vibrational coordinate, by holding all atoms except the cation fixed and evaluating U at n cation positions. This was repeated for m ($m \approx 10^3$) arrangements of the surrounding atoms (polymer fragments) which differ by translation of those groups relative to one another along the direction of cation motion. Thus, expressing the internal coordinate of cation displacement as x and the separation of the groups of surrounding atoms as d (see Fig. 6), we require the aggregate geometry and cation position for which $(\partial^2 U / \partial d \partial x) = 0$. We evaluate $K_{\text{calc}}^{\text{net}}$ from $(\partial^2 U / \partial x^2)$ at that position by numerically fitting $U(x)$ to a parabola about the minimum, employing in the fitting 11-20 points with a grid such that the range in U spanned is $\approx hc\omega(\text{exptl})/2$. The numerical evaluation for each cation-polyelectrolyte model was based on $(m \times n) \approx 1 \times 10^6$ values of U .

These calculations have been carried out on four levels which correspond to those on which interpretations are commonly based. In the first three calculations the accuracy of estimation of parameters is successively improved, but all interactions are between the cation and the atoms of the surrounding polyanion fragments, so the position of the cation and the separation of the surrounding (field) atoms are determined only by these interactions. These three calculations are labeled Calc 1-3 in Table II, which gives the values of the parameters used, and in Tables III and IV, which give

TABLE III. Results of calculations of potential energy and force elements ($K_{\text{calc}}^{\text{net}}$).^a

Model	Cation	Calculation 1		Calculation 2		Calculation 3		Calculation 4	
		$U(\text{min})$	$K_{\text{calc}}^{\text{net}}$	$U(\text{min})$	$K_{\text{calc}}^{\text{net}}$	$U(\text{min})$	$K_{\text{calc}}^{\text{net}}$	$U(\text{min})$	$K_{\text{calc}}^{\text{net}}$
1	Li ⁺	-104.67	1.28	-104.67	1.28	-101.89	1.27	-101.89	1.27
1	Na ⁺	-80.33	0.85	-80.33	0.85	-78.23	0.80	-78.23	0.80
1	K ⁺	-69.94	0.65	-69.94	0.65	-68.17	0.63	-68.17	0.63
1	Cs ⁺	-64.36	0.58	-64.36	0.58	-62.76	0.54	-62.76	0.54
2	Li ⁺	-169.47	2.20	-169.47	2.20	-163.33	2.07	-125.04	1.54
2	Na ⁺	-132.21	1.37	-132.21	1.37	-128.53	1.30	-97.25	0.98
2	K ⁺	-116.28	1.03	-116.28	1.03	-113.50	0.99	-85.45	0.74
2	Cs ⁺	-106.54	0.85	-106.54	0.85	-104.25	0.82	-78.33	0.60
3	Li ⁺	-105.82	1.34	-114.11	1.43	-111.95	1.38	-106.66	1.31
3	Na ⁺	-81.00	0.86	-88.08	0.91	-86.51	0.91	-82.18	0.84
3	K ⁺	-70.38	0.67	-76.65	0.72	-75.36	0.71	-71.52	0.66
3	Cs ⁺	-64.76	0.56	-70.44	0.60	-69.28	0.61	-65.74	0.58
4	Li ⁺	-109.17	1.35	-106.19	1.29
4	Na ⁺	-84.38	0.88	-81.66	0.87
4	K ⁺	-73.37	0.68	-70.83	0.67
4	Cs ⁺	-67.51	0.59	-65.09	0.58

^a The units for $U(\text{min})$ are 10^{-13} erg/cation aggregate, for $K_{\text{calc}}^{\text{net}}$ are mdyne/Å or 10^3 dyn/cm; and for CAGE(C-C), which gives the separation

of the carbon atoms designating the positions of the surrounding polymer fragments, the units are angstroms.

the results. The primary estimation in Calculation 1 is that the charge on each oxygen atom in the $-\text{COO}^-$ group is -0.5 and that on $-\text{CH}_2-$ groups is zero. The charge distribution in Calc 2 was improved in the commonly used manner of employing bond moments; in this case using the C-H bond moment of 0.3 D with

$r(\text{C-H})$ of 1.09 \AA to estimate the $-\text{CH}_2-$ charge distribution. The charge distribution of Calculation 3 is that found in quantum mechanical calculations on related systems. Thus, the charge distribution for the $-\text{COO}^-$ group is obtained from the computed electron density map for HCOO^- ⁴⁷ and that for $(-\text{CH}_2)^*$ is

TABLE IV. Calculated aggregate geometry.^a

Model	Cation	Calculation 1		Calculation 2		Calculation 3		Calculation 4	
		X(M ⁺)	d	X(M ⁺)	d	X(M ⁺)	d	X(M ⁺)	d
1	Li ⁺	2.57	...	2.57	...	2.57	...	2.57	...
1	Na ⁺	3.23	...	3.23	...	3.25	...	3.25	...
1	K ⁺	3.68	...	3.68	...	3.69	...	3.69	...
1	Cs ⁺	4.01	...	4.01	...	4.03	...	4.03	...
2	Li ⁺	3.27	6.54	3.27	6.54	3.30	6.60	3.38	6.75
2	Na ⁺	3.93	7.86	3.93	7.86	3.95	7.70	4.02	8.04
2	K ⁺	4.35	8.70	4.35	8.70	4.38	8.76	4.45	8.89
2	Cs ⁺	4.69	9.38	4.69	9.38	4.71	9.41	4.79	9.57
3	Li ⁺	2.57	5.89	2.56	5.52	2.58	5.52	2.58	5.62
3	Na ⁺	3.23	7.11	3.24	6.70	3.24	6.68	3.26	6.80
3	K ⁺	3.68	8.01	3.68	7.56	3.69	7.54	3.70	7.66
3	Cs ⁺	4.01	8.66	4.02	8.20	4.02	8.18	4.03	8.28
4	Li ⁺	2.58	7.04	2.59	7.10
4	Na ⁺	3.25	8.12	3.25	8.16
4	K ⁺	3.70	9.02	3.69	9.10
4	Cs ⁺	4.03	9.72	4.03	9.80

^a Units are angstroms.

obtained from the work of Phillips and Sandrock.⁴⁸ In the fourth calculation, labeled Calculation 4, all electrostatic interactions, except those between atoms covalently bound in the same polyanion fragment, were included and the data used in Calculation 3 were employed. The potential function, thus, takes the form

$$U = U_1 + \sum_{k,l} (z_k z_l / r_{kl}) - \sum_{k,l} [(\alpha_k z_l^2 + \alpha_l z_k^2) / 2r_{kl}^4] + \sum_{k,l} A_{k,l} \exp(-r_{kl}/\rho), \quad (9)$$

where k and l index atoms on polymer fragments containing C_A and C_B , respectively, and $i = k + l$ [Eq. (8)]. Clearly, Calculation 4 should give the best results, but, since other work is done at the various levels treated here, it is interesting to see how the results change as the approach is made more comprehensive.

Evaluation of the Potential Energy

The parameters employed in the evaluation of U for each model are important features of the calculation not only because of the sensitivity of the results to these values, but also because the parameters do *not* include data from the experiments conducted. In all calculations, described above, the charge on the alkali metal cation was $+1.0$, and the charge distribution over the field atoms were as discussed above in differentiating the levels of calculation. The cation polarizabilities were taken as given by Pauling⁴⁹ or Fajans⁵⁰ and are listed in Table II. The polarizabilities of H, C, and O as listed in Table II, are necessarily only estimates since these atoms are bound in the polymer and are not free atoms. The value for H is experimentally accepted,⁵¹ and those for C and O are taken from the table of Dalgarno⁵² for C and O⁻. The van der Waals term is evaluated using the C_{ij} parameters of Table II, which were estimated using the approximate relation

$$C_{ij} \approx \frac{3}{2} [\epsilon_i \epsilon_j \alpha_i \alpha_j / (\epsilon_i + \epsilon_j)] \quad (10)$$

employed by Mayer⁵³ to calculate C_{MX} coefficients for alkali-metal ion-halide pairs from polarizabilities, ionization potentials and electron affinities. These values have been used extensively.³⁸⁻⁴⁰ We have accepted the assumption of White *et al.*⁴⁵ that $C_{LiCl} \approx C_{LiO}$ and used $C_{MO} \approx C_{MCl}$ (M: alkali metal) and approximated the carbon-cation constants as $C_{MC} = \frac{1}{2}(C_{MF} + C_{MCl})$. Cation-hydrogen coefficients were estimated via the above formula using the first ionization potential of hydrogen and the second ionization potentials of the alkali metals⁵⁴ to approximate ϵ_M .

The repulsion term is the sum of the $A_{ij} \exp(-r_{ij}/\rho)$ terms, with the A_{ij} 's and ρ 's evaluated as follows. In the treatments of alkali halide, and oxide data using the Rittner potential the values of A_{ij} and ρ are usually determined, using the experimental data, from the first and second derivatives of the total energy; $(dU/dR)|_{R_0=0}$ and $(d^2U/dR^2)|_{R_0=k}$. Here the force constant, k , and the equilibrium internuclear distance,

R_0 , are based on experimental information. From such studies on many molecules,^{38-41,45,55-57} and from the theoretical works of Hafemeister and Zahrt⁴³ and Dick and Overhauser⁵⁸ it is clear that the values found for ρ for alkali halides fall in the range 0.35 ± 0.10 Å, and that excepting the iodides most fall in the range of 0.35 ± 0.05 Å. In view of this approximate constancy, and in order to avoid inclusion of our experimental data in the calculation as far as possible, we have taken the value of ρ for NaCl of 0.325 Å for all repulsive interactions. Similarly, Berkowitz took $\rho = 0.338$ Å, the average of the mean crystalline ρ and mean gaseous ρ values available.⁵⁹ However, examination of the same works on the gaseous halides and matrix isolated oxides shows that A_{ij} varies exponentially with $(r_i + r_j)$, where r 's are the ionic radii. A plot of A_{ij} vs $(r_i + r_j)$ results in a smooth curve,⁶ as expected from the relationship of the Born-Mayer to the Huggins⁶⁰ potential. In our calculations, the values of A_{ij} were obtained directly from this plot and are given, along with all of the data employed, in Table II.

Calculation Results

The results of the calculations for the total energy at its minimum [$U(\min)$], the equilibrium configuration {position of the cation [$X(M^+)$], and separation of surrounding groups (d)}, and the value of K_{calc}^{net} are given in Tables III and IV. Since the calculations are not dependent upon any data from the experiments we have reported here, they can be compared to equivalent experimental results, as follows.

On all four levels of calculation the cation-aggregate total potential energy is negative in each model for each cation, and falls in the range of -0.63×10^{-11} erg/cation aggregate for $[-COO^- - Cs^+]$ in Model 1 to -1.69×10^{-11} erg/cation aggregate for $[-COO^- - Li^+ - OOC^-]$ in Model 2. Generally the magnitude of U is in the order $Li^+ > Na^+ > K^+ > Cs^+$ in all models in all calculations. As expected, the magnitudes of U in Model 2, in which the cation aggregate consists in $[-COO^- - M^+ - OOC^-]$, are greater than in Models 1, 3, and 4, in which only one anionic site is present. The magnitudes of U for a given cation in Models 1, 3, and 4 differ by 10% or less, with the presumably more realistic of these (3 and 4) being of greater magnitude (lower total potential energy). The total potential energies can be usefully compared to the alkali halides containing the same cation. On a molecular basis they are expected to be similar to those found for gas phase M^+X^- monomers, and the magnitude of U for Avogadro's number of cation aggregates is expected to be lower than for a gram formula of MX. Indeed, for the Na^+ -aggregate in models 1, 3, or 4 we calculate U to be $-8.0 \pm 0.2 \times 10^{-12}$ ergs/cation-aggregate, while the experimentally derived value for NaCl (g) is -8.9×10^{-12} ergs/molecule³⁸; and, on a molar basis U is -115 kcal/6.023 $\times 10^{23}$ Na^+ aggregates compared to U of

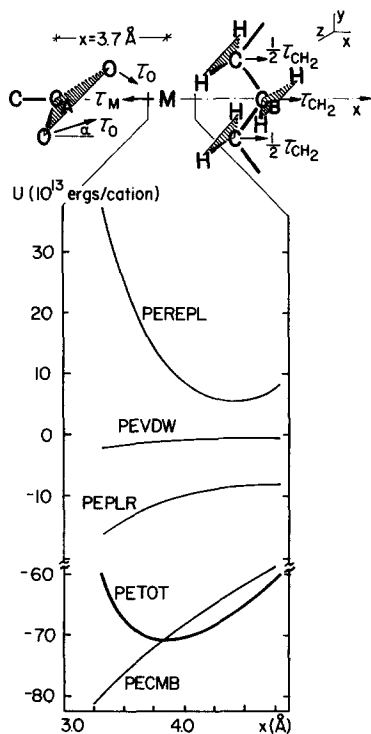


Fig. 7. The calculated geometry and mode of vibration for a typical case of Model 4, Calculation 4 ($M=K^+$), drawn to scale, plus the contributions to the total potential energy (PTOT) as a function of cation position for $d=9.1$ Å. PECMB, PEREPL, PEPLR, and PEVDW are the Coulombic, repulsive, ion-induced dipole and van der Waals terms, respectively.

–183 kcal/mole for the lattice energy of NaCl. In Fig. 7 we have drawn the equilibrium geometry calculated for K^+ in Model 4, Calculation 4, and have shown below the behavior of the total potential energy function and the contributions from its components in the region about the cation equilibrium position for that geometry.

Similarly, the calculated equilibrium configurations, in terms of the cation–anion site spacings and the spacings between anion site and second polymer fragment with the cation between them, can be considered. The locations on the x axis of the cation and the carbon (C_B) defining the position of the second polymer fragment are given in Table IV, and the resultant geometry for a typical case is shown in Fig. 7. The separations calculated are reasonable, and consistent with the spectral interpretations, but cannot be further evaluated because there are no useful experimental data available with which to compare them.

The values of K_{calc}^{net} provide the most useful test of the application of this potential function to site binding because of the values of K_{obs}^{net} obtained above, and because of their sensitivity to the repulsive as well as attractive terms in the function. The most

striking features of the comparisons between K_{obs}^{net} (Table I) and K_{calc}^{net} (Table III) are that they are of quite similar magnitude and are in the same order. Thus, in Model 1 the values of K_{obs}^{net} are $Li^+(0.73) > Na^+(0.47) > K^+(0.37) > Cs^+(0.31)$, while those of K_{calc}^{net} are $Li^+(1.27) > Na^+(0.80) > K^+(0.63) > Cs^+(0.54)$ (all in 10^6 dyn/cm). Similar comparisons obtain for the other models, with K_{calc}^{net} taken from Calculation 4, the most complete application of the potential function to this problem. The extent of agreement between K_{calc}^{net} and K_{obs}^{net} , while not complete, is rather great within the context of these models.

DISCUSSION

The ionic copolymers are polyelectrolytes of a special type, having the property that polyanion site-unsolvated cation interactions are found, and they are materials whose physical properties are cation and site-concentration dependent. Thus, it is of interest to note how the results of this study relate to these properties.

In developing theories of polyelectrolyte behavior it is necessary to deal with the short range interactions which are responsible for determining the effective size of the counterion (in solution usually a solvated cation), and those interactions between a polyanion site and a counterion as occur, for example, in a cell model of a localized counterion distribution. The systems studied here permit isolation of one type of interaction, that of a polyanion site with a simple cation in an aggregate in which solvation does not occur. The spectra are consistent with the formation of stable site-bound pairs which vibrate at frequencies such that a vibrational quantum is roughly equal to kT , at room temperature, for $M^+=Na^+, K^+, Cs^+$. The force required to cause displacement from the equilibrium pair configuration as evaluated from the spectral data agrees well with that calculated using a Rittner-type interionic potential function. On this basis we may conclude that site binding forces calculated in this manner will be of the correct order of magnitude. Moreover, it is clear that the forces between fully solvated cations and polyanion sites will be lower than those found here; and that the force constant for dissociation displacement from the equilibrium configuration will be on the order of 1×10^4 dyn/cm or less. Of potential interest, however, is the expectation from these results and our ionic solution studies that an aggregate (cell model) consisting of polyanion site–cation–solvent ($A^-M^+S_x; x \approx 2$) will vibrate at frequencies near 6×10^{12} Hz (200 cm^{-1}).

The physical properties of the ionomers, as materials, are primarily anion-site concentration dependent. Although the properties of metal ion copolymers are significantly different from those of the analogous acid forms, the cation dependence appears primarily in the magnitude and temperature dependence of relaxation processes. Two relaxation processes (α and β) are

associated with introduction of the metal cations.³¹ The α process, observed as dielectric loss and NMR relaxation, has been assigned to motions within the ionic domains, and the β process, observed as mechanical relaxation, has been attributed to "microbrownian segmental" motion of hydrocarbon fragments. The vibrational model found most appropriate in this study is Model 4, in which the cation is in the field of both a carboxylate site and a hydrocarbon fragment, and in which both cation motion relative to the polyanion site and cation-perturbed vibrational distortion of the adjacent hydrocarbon fragment are involved in the aggregate vibration. Such an aggregate may provide a molecular basis for interpreting the cation-dependent relaxation and rheological data, since both ionic sites, alone or in clusters, and neighboring hydrocarbons are involved as they would be within and on the periphery of ionic domains.

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