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Ionomers

Comments on the Effect of Cation, Type on Ionomer Properties

Shriram Bagrodia and Garth L. Wilkes

Department of Chemical Engineering and Polymer Materials and Interfaces Laboratory,
Virginia Polytechic Institute and State University Blacksburg, VA 24061-6496, USA

ABSTRACT

One of the important parameters that affects the properties of metal-neutralized ionomers is the nature of the cation used for neutralization. It is suggested that the electronic configuration of the cation, which in turn governs its degree of covalent character, is a very important parameter in determining many of the differences in the physical and rheological properties of a series of sulfonated polyisobutylene-ionomers neutralized with Ca^{++}, K^{+} or Zn^{++}. Similar considerations may also apply to other ionomers of different backbones and possibly to other cations of transition metals.

Theory and Discussion

Ionomers derive their unique properties due to coulombic interactions between the ionic moieties (1). An important parameter that affects these interactions is the type of the metal cation used to neutralize the precursor acid. Various researchers have studied the effect of metal cation type on the properties of many different ionomers (2-6). Eisenberg proposed and demonstrated that the ionic potential (q/a, charge to ion size ratio) is an important parameter, and has rationalized the behavior of ethyl acrylate-acrylic acid copolymers neutralized with various cations and other ionomer systems on the basis of this concept.

The energy, E, of coulombic attraction between two charged particles is proportional to the product of their charge, and inversely proportional to the distance between them. Specifically,

$$E = - (Z^{+} Z^{-}) q^{2}/ 4\pi \varepsilon_{0} R \qquad (1)$$

where Z^{+} and Z^{-} is the charge of the cation and anion respectively, ε_{0} is the dielectric constant of the medium, r is the distance between the two charged centers and q is the electrostatic charge.

Thus, the higher the q/a ratio of a cation, the more strongly it will be attracted by a given anion. In fact this concept works well for cations within the same group of the periodic table, as demonstrated by Eisenberg. However, we believe that the q/a ratio by itself is often insufficient to account for the observed behavior in various other ionomer systems neutralized with cations belonging to different groups in the periodic table. For example Lundberg et al. have also studied the effect of cation type on the flow and physical properties of sulfonated EPDM materials. They observed that the behavior of Hg^{++} and Ca^{++} neutralized ionomers was drastically different, although their ionic radii differ by only 2 pm (the respective radii are Hg^{++} 102 pm and Ca^{++} 100 pm. They also observed that the melt viscosity at elevated temperatures of sulfonated EPDM polymers when neutralized with zinc acetate is much lower than those neutralized by Na(IA), Mg(IIA), Ca(IIA) etc. They tentatively explained this behavior in terms of a combination of the following two phenomena. The plasticization of the ionic associations by zinc acetate at elevated temperatures and through the conversion of disulfonates SO_3 - Zn - SO_3 to less strongly associating monosulfonates (SO_3- Zn - OOC-CH_3 at high zinc acetate concentration. (This latter effect in principal should only be operative when excess neutralizing agent has been added, otherwise the acetate ion should not be present. That is it should have been released after proton addition to give acetic acid.) These explanations indirectly reflect that because of the more covalent character of zinc, the viscosity of Zn^{++} neutralized material is low.

Clearly then there are other factors besides the ionic potential (q/a) that affect the association character of the final ionomers. It has also been observed by Lundberg et al. that Zn^{++} neutralized sulfonated EPDM have the lowest melt viscosity at higher temperatures as compared to the same polymer neutralized with other cations such as Na(1A), Mg(IIA), Ca(IIA), Co(VIII), Li(IA), Ba(IIA), Pb(IVA), etc. However, Zn^{++} neutralized EPDM's have comparable if not better, tensile strength than those neutralized with many of the other cations listed above. Similar behavior has been observed by us for sulfonated polyisobutylene ionomers neutralized with either zinc acetate, potassium or calcuim hydroxide (7-9).

In line with the explanation offered by Lundberg et al. we propose that besides the coulombic effects, an additional important parameter that deserves consideration is the ionic/covalent character of the cation. Specifically, the bivalent zinc cation is more "covalent" than the corresponding bivalent calcium, magnesium, or barium cation. Hence, at elevated temperatures the coulombic interactions in the case of Zn^{++} neutralized ionomers are weaker than with Ca^{++}, or the other bivalent ions which are more ionic in character. We believe this will also help explain the lower melt viscosity at elevated temperatures in the case of the former.

There are various factors which indirectly support the more covalent character of Zn^{++} relative to Ca^{++}, K^{+} and Ba^{++}. Specifically, zinc compounds have lower decomposition energies than the corresponding calcium and potassium compounds. For example, the decomposition energy of potassium, calcium and zinc sulfate is 164, 95 and 66 kcal/g mol, respectively. Zinc compounds also have lower melting points than corresponding calcium or potassium compounds. For example, zinc sulfate melts at 600°C while the melting point of potassium sulfate and calcuim sulfate is 1069°C and 1450°C respectively. The higher melting points are more typical of ionic crystals, whereas those of covalent crystals are generally lower. Thus, we believe that the covalent character of the cation, which in turn is governed by its electronic configuration, is a very important parameter in influencing the properties of ionomers (10). With the introduction of the $3d^{10}$ level electrons in the zinc atom, which poorly shield the nucleus , zinc is more polarizable and hence zinc compounds are more covalent. For example, Hg^{++} and Ca^{++} have the same charge and nearly the same ionic radii, but the Hg compounds are more covalent than the corresponding calcium compounds. The electronic configuration of Ca is [Ar] $4s^2$ devoid of "d" shell electrons while for mercury it is [Xe] $4f^{14}$, $5d^{10}$, $6s^2$. Thus, the electronic configuration, which in turn influences the covalent character of atoms, also appears to be a very important parameter affecting the behavior of metal-neutralized ionomers.

Pearson has used polarizability of an atom as a criterion for defining "hard" and "soft" acids and bases. He defines a soft base as one in which the valence electrons are easily distorted, polarized, or removed. A hard base has the opposite properties i.e., it holds on to its valence electrons much more tightly. Likewise, a hard acid is defined as one of small size, high positive charge and with no valence electrons that are easily distorted or removed. Strictly speaking it is the acceptor atom of the acid which has these properties. In conclusion, a soft acid is one in which the acceptor atom is of large size, small or zero positive charge, or has several valence electrons which are easily distorted.

Also according to the concept of hard and soft acids, Pearson (9) has shown that the Zn^{++} is on the border line of hard and soft acids, while both K^+ and Ca^{++} are very hard acids. Since the sulfonic (SO_3) group is a hard base, it associates more strongly with Ca^{++} and K^+ than with Zn^{++}. This also helps explain the lower melt viscosities and softening temperatures of zinc neutralized PIB ionomers than the corresponding calcium or potassium based ionomers studied by the authors (7-9). Thus, we believe that more emphasis must be paid to the electronic configuration and/or the degree of covalent character of the cation used for neutralization of an ionomer in that it influences significantly the physical and rheological properties of both the solid and melt states. It is also speculated that similar condiderations should likely apply to other ionomers of different backbone structures. In addition, it is anticipated that other cations of transition metal origin may also display similar results.

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