

Rheological properties of ethylene ionomer neutralized with binary metal cation

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Abstract

The roles of ionic bonding in molten ethylene ionomers without ionic aggregates were rheologically characterized in linear regions under shear. We have measured melt viscosities of ethylene-methacrylic acid (EMAA) ionomers by means of dynamic shear experiment. The samples used in this study were binary mixtures selected from Na, Mg and Zn salts of EMAA (MAA = 5.4 mol%). The dynamic shear properties revealed that the time–material superposition is applicable to these ionomer blends in a temperature range from 140 to 200 °C. It was also found that these binary mixtures unexpectedly give decreases of zero shear viscosities obtained from a time–material superposition, if the cations were selected from different metal groups such as alkali, alkaline earth and transition metals. This behavior can be explained by the acid-cation exchange mechanism.

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1. Introduction

Ionomers are polymers including a small amount of metal ionic salt groups. Above all, poly(ethylene-*co*-methacrylic acid) (EMAA) is the most widely used base polymer for metal cation ionomers in the industrial applications. Structural and mechanical properties of ethylene ionomer have been extensively investigated in both solid and melt states. Ionic metal cations tend to form ionic aggregates in the hydrophobic polymer matrix [1–5]. It has been investigated by the dielectric and dynamic mechanical relaxation studies that a microphase separation of ionic aggregates and the hydrocarbon matrix takes place depending on the neutralization degree. Hirasawa et al. and Tachino et al. indicated that ionic aggregates are formed at a degree of neutralization more than 35% in the following two systems, EMAA-Na and EMAA-Mg ionomers [6,7]. They also reported that ionic aggregates are formed at a degree of neutralization more than 80% in EMAA-Zn ionomer. It has been reported that physical properties of ionomers depend

on the kinds of cations due to the difference in their ionic strength and on the number of carboxyl groups associated with a single cation. For example, ionomers including alkaline and/or alkaline earth metal and those including transition metals exhibit different physical properties. The metal cation dependent characteristics of ionomers are essential to mechanical and rheological properties in solid and melt states.

Recently, binary mixtures of ethylene ionomers neutralized with different metal cations have been used in industrial applications. Up to now, it is known that blending of ethylene ionomers makes the properties of moisture absorption and mechanical properties such as stiffness and yield strength improve [8–10]. However, there are a few systematic studies that focus on these properties of blend ionomers [11,12]. Tachino et al. demonstrated the importance of ionic aggregates of ethylene ionomers neutralized with binary metal cations. They reported that distinct changes take place in case that conjugated binary metal ions are formed in ionic aggregates.

On the other hand, very few studies on melt rheological properties of blend ionomers have been carried out. Tachino et al. and Permenter et al. have studied that the logarithm of

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melt index (MI) linearly increases with increase in EMAA-30Na content in the mixture of EMAA-60Zn and EMAA-30Na [11,12]. However, in their experiments an elimination of absorbed water into the ionomer sample was not paid attention. As Nishioka et al. have already reported that melt viscosities of ionomers are decreased by a small amount of absorbed water, it is needed to pay a great attention to the absorbed water into samples [13]. Therefore, all the samples measured in our study were dried completely until water contents in the samples reach to a very low constant value. The aim of this study is to clarify the effect of blend ratio and kind of ions on viscoelastic properties at a melt state. In order to fulfill this purpose, we investigated linear viscoelastic properties by dynamic shear measurements.

2. Experiment

2.1. Materials

The samples we used here are poly(ethylene-co-methacrylic acid) (EMAA) ($M_w=94\,500$, $M_n=19\,200$) with a methacrylic acid content of 5.4 mol% and ionomers made of the EMAA. These ionomer samples are partially neutralized by sodium, magnesium or zinc ions. We prepared two sodium ionomers, a magnesium ionomer and a zinc ionomer. The neutralization degrees of two sodium ionomers are 38 and 54%. The neutralization degree of ionomers neutralized by magnesium and zinc are 54 and 59%, respectively. Hereafter these samples are abbreviated as EMAA-38Na, EMAA-54Na, EMAA-54Mg and EMAA-59Zn. We refer a blend sample of a EMAA with a metal cation Y(*a*) and a EMAA with a metal cation Z(*b*) as EMAA-Y(*a*)/Z(*b*), where *a* and *b* are the neutralization degrees for the ionomer EMAA-Y and EMAA-Z, respectively. All the samples were kindly provided by Mitsui-DuPont Polychemicals Co. Ltd. All of blend samples were prepared by melt blends of two of EMAA-Y's (Y = 38Na, 54Na, 54Mg and 59Zn) by using a counter-rotating twin-screw extruder (Ikegai PCM-30, $L/D=31.5$ (L/D means length/diameter)) at 200 °C. The list of samples used in this study is shown in Tables 1–3. In order to obtain reproducible data, a great attention was paid to an elimination of moisture in the samples before measurements by drying them in a vacuum oven at 80 °C for at least one week. From the study done by Nishioka et al. [13], it is considered that samples in our study were desiccated enough to eliminate the effect of moisture. The disk shape samples were prepared by a compression molding machine (Toyoseiki, Mini-Test-Press-10) under 15 MPa at 190 °C for 5 s and then rapidly cooled under 10 MPa.

3. Rheology measurement

Dynamic shear measurements were performed under a

Table 1
The samples for binary blends of EMAA-54Na and EMAA-59Zn

Sample abbreviation	Zn:Na ion ratio (mol)	EMAA-59Zn:E-MAA-54Na weight ratio (wt%)
EMAA-54Na(100)	0:100	0:100
EMAA-59Zn(9)/54Na(91)	5:95	8.8:91.2
EMAA-59Zn(23)/54Na(77)	14:86	23.4:76.6
EMAA-59Zn(31)/54Na(69)	20:80	31.4:68.6
EMAA-59Zn(48)/54Na(52)	33:67	47.8:52.2
EMAA-59Zn(65)/54Na(35)	50:50	64.7:35.3
EMAA-59Zn(79)/54Na(21)	67:33	78.6:21.4
EMAA-59Zn(88)/54Na(12)	80:20	88.0:12.0
EMAA-59Zn(97)/54Na(3)	95:5	97.2:2.8
EMAA-59Zn(100)	100:0	100:0

nitrogen atmosphere by using a rotational rheometer (Rheometrics, ARES) in the frequency range from 0.01 to 100 rad/s at 140, 160, 180 and 200 °C, which are substantially above their melting temperature. The parallel disk rheometer with a diameter of 25 mm is used for measurements of sodium ionomers, magnesium ionomers and their blend samples, and that with a diameter of 15 mm is used for other samples due to their high viscosities.

4. Results and discussion

We have examined the dynamic shear measurements for EMAA-38Na, EMAA-54Na, EMAA-54Mg, EMAA-59Zn and their blend ionomers. Firstly, in case of ionomer neutralized by a single kind of metal cation, the resultant G' and G'' curves were horizontally shifted to the curve at a reference temperature 140 °C in order to obtain a master curve. In the past studies done by Nishio et al. and Takahashi et al., it has been confirmed experimentally that the time-temperature superposition is valid from 140 to 200 °C for EMAA ionomer including only a single kind of ionic metal [14–16]. In our study, for the samples neutralized by a single kind of metal cation, the same results with previous ones were obtained. Secondly, as the same with the previous experiment for a single cation system, we performed experiments of ionomer system neutralized with binary cations. Fig. 1 reveals that master curves can be constructed

Table 2
The samples for binary blends of EMAA-54Mg and EMAA-59Zn

Sample abbreviation	Zn:Mg ion ratio (mol)	EMAA-59Zn:E-MAA-54Mg weight ratio (wt%)
EMAA-54Mg(100)	0:100	0:100
EMAA-59Zn(19)/54Mg(81)	20:80	18.6:81.4
EMAA-59Zn(31)/54Mg(69)	33:67	31.4:68.6
EMAA-59Zn(48)/54Mg(52)	50:50	47.8:52.2
EMAA-59Zn(65)/54Mg(35)	67:33	64.7:35.3
EMAA-59Zn(79)/54Mg(21)	80:20	78.5:21.5
EMAA-59Zn(95)/54Mg(5)	95:5	94.6:5.4
EMAA-59Zn(100)	100:0	100:0

Table 3
The samples for binary blends of EMAA-38Na and EMAA-54Mg

Sample abbreviation	Zn:Mg ion ratio (mol)	EMAA-59Zn:EMAA-54Mg weight ratio (wt%)
EMAA38Na(100)	0:100	0:100
EMAA-54Mg(26)/38Na(74)	20:80	26.0:74.0
EMAA-54Mg(41)/38Na(59)	33:67	41.3:58.7
EMAA-54Mg(59)/38Na(41)	50:50	58.7:41.3
EMAA-54Mg(74)/38Na(26)	67:33	73.8:26.2
EMAA-54Mg(85)/38Na(15)	80:20	84.9:15.1
EMAA-54Mg(100)	100:0	100:0

for blend samples, of (a) EMAA-59Zn(48)/54Na(52), (b) EMAA-59Zn(31)/Mg54(69) and (c) EMAA-54Mg(41)/38Na(59). Results of all blend samples neutralized with different kind of metals and with different ratio of metal cations are shown in Fig. 1. In the consequence of oscillatory shear experiments, the time–temperature superposition principle are applicable for all ethylene ionomers neutralized with not only a single metal cation but also binary metal cations in this study.

It has been found that, within the frequency range measured in this study, the time–material superposition rule [15,16] is applicable to all series of the blends. Namely, the master curve for each samples can be superposed on that of

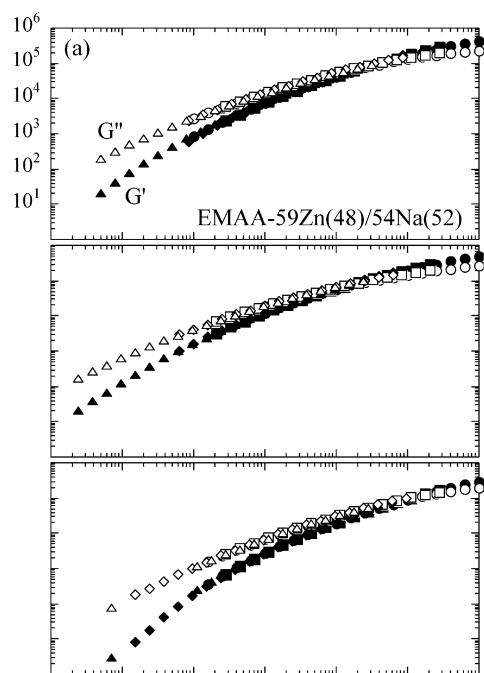


Fig. 1. Master curves of G' (closed symbols) and G'' (open symbols) for EMAA-59Zn(48)/54Na(52) (a), EMAA-59Zn(31)/54Mg(69) (b) and EMAA-54Mg(41)/38Na(59) measured at various temperatures: (●,○) 140 °C, (■,□) 160 °C, (◆,◇) 180 °C, (▲,△) 200 °C. The reference temperature is 140 °C.

EMAA by horizontal shifts as follows

$$G', G''(\omega, \text{EMAA}) = G', G''(\omega a_T, \text{EMAA} - X) \quad (1)$$

$$G', G''(\omega, \text{EMAA}) = G', G''(\omega a_T, \text{EMAA} - Y(a)/\text{EMAA} - Z(b)) \quad (2)$$

where a_T is a time–material shift factor obtained by using EMAA at 140 °C as a reference. EMAA-X means EMAA, EMAA-38Na, EMAA-54Na, EMAA-54Mg and EMAA-59Zn, and EMAA-Y/EMAA-Z means binary mixtures of ionomers with different ionic metals. The arguments a and $b(=100-a)$ are values of weight percent for the ionomers EMAA-Y(a) and EMAA-Z(b), respectively. We call the resultant master curve obtained by the time–material superposition rule ‘Super Master curve’.

The applicability of the time–material superposition indicates that the relaxation spectrums of all the blends have the same distribution shape as that of EMAA, but have different time scales. This means that a new structure is not formed after blending.

In Figs. 2–4, Super-Master curves of G' and G'' obtained from master curves of the blend ionomers were made by using the master curve of EMAA at 140 °C as the reference curve. Figs. 2–4 show a superposition of moduli of all blend samples, i.e. EMAA-59Zn/54Na, EMAA-59Zn/54Mg and EMAA-54Mg/38Na on those of EMAA by using horizontal shifts, respectively. For all samples, the master curves of G' and G'' agree well with that of EMAA at high frequency region. At a low frequency region, however, the master curves of the storage moduli G' 's of all blend samples a little bit deviate from that of EMAA, although the master curves of the loss moduli G'' 's for all blend samples are very close to that of EMAA. As a candidate to explain this small deviation, it is considered that chemical reactions of each ‘COOH’ in polymer chains were occurred in blend ionomers.

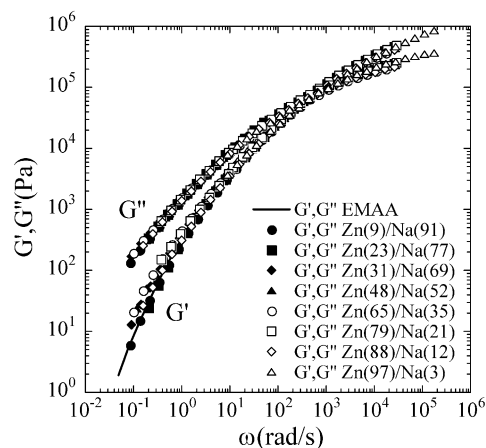


Fig. 2. Super-Master curves of G' and G'' obtained from the master curve of EMAA and blend samples of EMAA-54Na and EMAA-59Zn. The reference curve is EMAA at 140 °C.

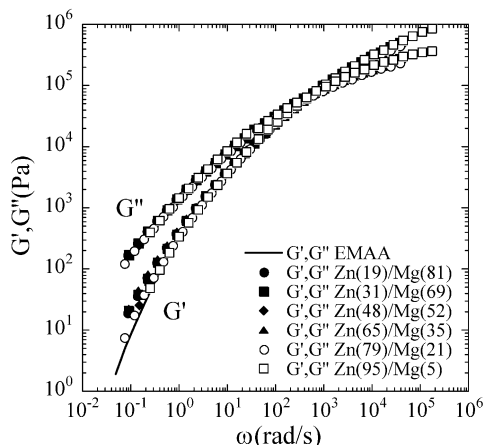


Fig. 3. Super-Master curves of G' and G'' obtained from the master curve of EMAA and blend samples of EMAA-54Mg and EMAA-59Zn. The reference curve is EMAA at 140 °C.

Since the data that are used for the Super Master curve at the low frequency region are measured at a high temperature (200 °C), acid anhydrides can be formed easily at such a high temperature. As a result, cross-linking reactions were occurred between polymer chains by forming acid anhydrides, which yields the small deviation of the storage modulus from the Super Master curve of G' in the low frequency region.

However, the details of this phenomenon is still not clear and more detailed analysis are needed.

Zero shear viscosities η_0 of blend samples can be calculated by following equation;

$$\eta_0(\text{blend}) = \eta_0(\text{EMAA})a_T \quad (3)$$

where $\eta_0(\text{blend})$ and $\eta_0(\text{EMAA})$ mean zero shear viscosities of blend ionomers and EMAA, respectively. The coefficient a_T means the shift factor to superpose the observed data of moduli on the Super-Master curve. Although there were deviations in G' from the Super Master curve at the low

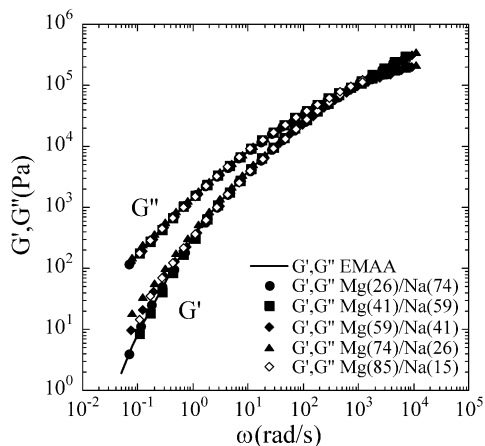


Fig. 4. Super-Master curves of G' and G'' obtained from the master curve of EMAA and blend samples of EMAA-38Na and EMAA-54Mg. The reference curve is EMAA at 140 °C.

frequency region, we could have a good agreement of the calculated shear viscosities with those obtained by experiments using the shift factor a_T determined in the high frequency region. As seen from Figs. 2–4, this is simply because the contribution of G' to η_0 is much smaller than that of G'' . Fig. 5(a)–(c) shows zero shear viscosities calculated from Eq. (3) for each blend samples. In the blend (a) EMAA-59Zn/54Na and (b) EMAA-59Zn/54Mg, first, the viscosities are almost constant until the content of EMAA-59Zn reaches to about 65 wt%. Secondly, in the region where the content of EMAA-59Zn is more than about 65 wt%, the viscosity increases. On the other hand, in case of (c) EMAA-54Mg/38Na blend systems, the tendency of zero shear viscosities were completely different from the other two cases. As seen from Fig. 5(c), the result shows that η_0 increases linearly with the content of EMAA-54Mg. In order to explain such different behaviors depending on the kind of metal cations, we focus on the role of metal cation in the blend samples. This behaviors of η_0 can be explained by acid-cation exchange mechanism proposed by Vanhoorne and Register [17]. They studied the effect of the protons of acid groups on the melt rheology of partially neutralized EMAA ionomer. By removing the protons by etherification of the acid group, they have found that the role of the protons in sodium ionomers is different from that in zinc ionomers [17]. In case of sodium ionomers, a sodium ion is not only paired with a single COO^- but also connects with two COOH acid groups by coordinate bonds. Due to this effect, COOH acid groups tend to exist around sodium ions, and therefore the sodium ion and a proton can be exchanged between COO^- -Na and COOH . This ‘acid-cation exchange’ mechanism [17] allows a polymer segment to easily diffuse from one ion aggregate to others, and lowers the friction for the segmental motion as shown in Fig. 6. Whereas, in case of zinc ionomers, a zinc ion is coordinated with two COO^- groups due to ionic bonds, and no COOH group exists around zinc ions. Thus, in zinc ionomers the acid-cation exchange does not take place, and the zinc ionomer has much higher viscosity (and a longer relaxation time) than that of the sodium ionomers at an equivalent neutralization. In case of an ionomer including sodium metals, the acid-cation exchange mechanism is effective because COOH groups exist in ionic aggregates, and therefore the viscosity becomes low. In cases of (a) and (b), it has been reported that sodium and magnesium ions can coexist with zinc ions in the same aggregate [11,18]. If the fraction of EMAA-59Zn is about 65 wt% or lower in (a) EMAA-59Zn/54Na system and in (b) EMAA-59Zn/54Mg blend system, there might exist enough amount of COOH groups in ionic aggregates, and the acid-cation exchange can be taken place frequently enough to keep their viscosities almost constant. The results of FT-IR spectra measured by Tachino et al. [11, 18] support that these two kind of metal cations can coexist in the same ionic aggregate. The blend of the zinc and sodium ionomer, and the blend of the zinc and magnesium ionomer show each new peak of carboxylate asymmetric

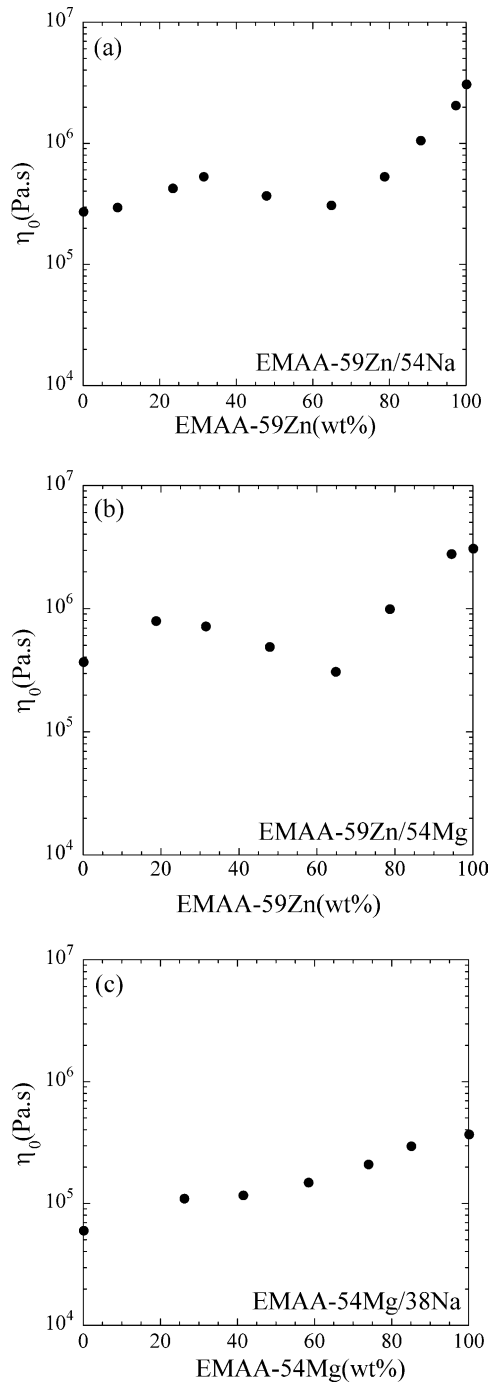


Fig. 5. Zero shear viscosity and time–material shift factor (EMAA at 140 °C as the reference) as a function of composition in the blend of (a) EMAA-54Na and EMAA-59Zn, (b) EMAA-54Mg and EMAA-59Zn and (c) EMAA-38Na and EMAA-54Mg.

$\nu(\text{COO}^-)$ in FT-IR spectra measurement, which indicates the formation of each new structure. It is considered that the new peak is caused by a conjugated binary metal salt of the sodium–zinc mixed ionomer [11]. This means that sodium and zinc ions exist within the same ionic aggregate. In the similar way in sodium–zinc mixed ionomer, magnesium and zinc ions also coexist within the same ionic aggregate. From

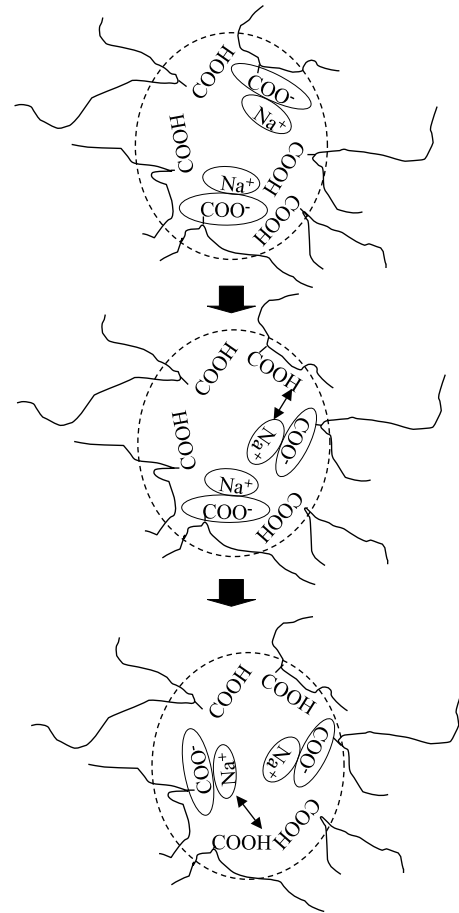


Fig. 6. Schematic drawing of 'acid-cation exchange' mechanism.

these results of these FT-IR experiments, it is expected that the acid-cation exchange can take place frequently. As seen from Fig. 5(a) and (b) in the region where the content of zinc ionomer is less than 65 wt%, the viscosity is almost constant. In the region where the content of zinc ionomer is greater than 65 wt%, the viscosity increases with increasing of contents of zinc ionomers, because the amount of zinc is larger than that of sodium or magnesium. In case of (c), the behavior of viscosity is different from (a) and (b), the viscosity increases linearly with the content of magnesium ionomer. Since each metals in the system (c) occurs the acid-cation exchange, so the viscosity is simply given by the sum of the contribution from each component of blends. Therefore, it is considered that the viscosity is increased linearly with increasing the content of magnesium ionomer.

5. Conclusion

The present study on the rheological characterization of ethylene ionomer neutralized with binary metal cations under a molten state provided the following new findings.

- (1) Dynamic shear properties of ethylene ionomers neutralized with binary metal cations were investigated. The time–temperature superposition principle was applicable to blend ionomers from 140 to 200 °C. These master curves of blend samples were able to be superposed well on a single Super Master curve by horizontal shifts. At the low frequency region around 10^{-1} rad/s, the storage modulus G' gave small deviations from the Super Master curve which is determined by the fitting in the high frequency region. It is considered that this deviation is caused by occurring acid anhydride. The viscosity η_0 obtained from experiments was consistent with η_0 calculated by Eq. (3) using a_T which is determined by the fitting in the high frequency region.
- (2) The values of zero shear viscosities are different depending on the kind of metal cations. The difference is coming from whether the acid cation exchange occurs or not. The acid cation exchange mechanism did not take place in a transition metal, but occurred in an alkaline and alkaline earth metal. When the transition metal and the alkaline (or alkaline earth) metal exist within the same ionic aggregate, the acid-cation exchange can take place frequently.

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