

Spectroscopic Studies of the Anomalous Viscosity–Temperature Relationship of Sulfonated EPDM Ionomer Solution

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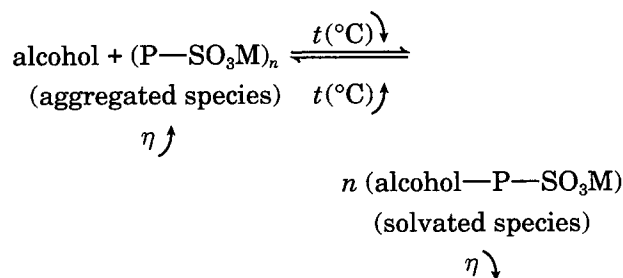
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SYNOPSIS

FTIR and ESR studies of sulfonated EPDM ionomers in xylene/alcohol show that alcohol solvation of $-\text{SO}_3\text{M}$ occurs and the extent of solvation relates to the species and concentration of the metallic ions and the molar concentration of $-\text{OH}$ from the cosolvent (alcohol) and temperature. The relationship between these factors and the viscometric behaviors of the ionomer solution were investigated. The results of these two studies are quite consistent with each other. At the molecular level the solvation of the metallic ion with the cosolvent plays a key role in the anomalous viscosity–temperature behavior of ionomer solutions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Ionomers are a class of ion-containing polymers that have ions in concentrations up to 10–15 mol % distributed in nonionic backbones. They can readily dissolve in mixed solvents containing hydrocarbon solvent and small amounts of polar cosolvents (e.g., alcohol). Such solutions display anomalous viscosity–temperature relationships different from conventional polymer solutions, for example, the viscosity increases with increasing temperature.^{1,2} These viscosity observations are interpreted by various researchers^{1,3} as arising from the preferential interaction of the cosolvent with the $-\text{SO}_3\text{M}$ groups at low temperature and can be rationalized in terms of a rather simple equilibrium as follows:



This equilibrium suggests that, at appropriate alcohol levels, an increase in temperature would induce a greater aggregation leading to an increase of solution viscosity. Many viscosity investigations^{1–3} manifested macroscopically and indirectly the existence of the above equilibrium, but surprisingly few studies demonstrated the formation of ionic aggregation microscopically and directly. Fitzgerald and Weiss⁴ studied the effects of solvents on the ionic interactions in lightly sulfonated polystyrene (SPS) ionomers, using Fourier transform infrared spectroscopy (FTIR) and electron spin resonance spectroscopy (ESR). They focused specifically toward the influence of the solvent environment on the cation–anion and cation–cation interactions but did not show the relationship between the ionic interaction and the viscometric behavior of the ionomer solutions.

The work described in the present article concerns the solvation of $-\text{SO}_3\text{M}$ by the cosolvent (alcohol) in the mixed solvent of xylene/alcohol for sulfonated ethylene propylenediene monomer (EPDM) ionomers (SEPD_M-M) using FTIR and ESR spectroscopy. The principal focus lies in the effect of solvation extent on the ionic aggregation and viscosity of solution, in order to reveal the essentials of the anomalous viscosity–temperature relationships for the ionomer solution.

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EXPERIMENTAL

The starting EPDM employed in these studies was a commercial product with an approximate number average molecular weight of 1.5×10^5 containing 55% ethylene, 40% propylene, and 5% ethylidene norbornene (by moles). SEPDM was prepared by solution sulfonation, then neutralized with metal acetates and recovered by solvent flashing in hot water. The sulfonate content of the resulting ionomers was determined by sulfur analysis of the salt. Details of preparation and characterization of SEPDM are described elsewhere.⁵

Three samples of SEPDM-Na with various sulfonate contents were prepared and generally neutralized completely with NaAc, but samples of SEPDM-Mn used for ESR measurement were neutralized partially or completely with $\text{Mn}(\text{Ac})_2$ as shown in Table I.

The absolute viscosities of the polymer solutions were obtained by a Rheotest-2 type rotary viscometer. The reduced viscosity was measured with a standard Ubbelohde viscometer.

FTIR spectra were obtained using a Nicolet 170SX spectrometer with the samples containing polymer at ca. 8 g dL^{-1} concentration. In each case, the solvent spectrum was subtracted from the solution spectrum.

ESR measurements were made with a JEOL FES-FEIXG spectrometer operating at X-band frequency with 100-kHz field modulation.

RESULTS AND DISCUSSION

Viscometric Behavior of Ionomer Solution

Plots of η_{sp}/C versus C for SEPDM-Na and SEPDM-Mn in xylene/alcohol solution are quite different from that of the base EPDM as shown in Figure 1; there is a marked increase of η_{sp}/C for the ionomers. At high polymer concentrations, a pronounced intermolecular association occurs leading to the enhancement of viscosity substantially above that of EPDM. It can be seen by the comparison of curve 2 and curve 3 that the ionic aggregation ability is $\text{Mn} > \text{Na}$. At low polymer concentration intramolecular associations result in a significantly lower

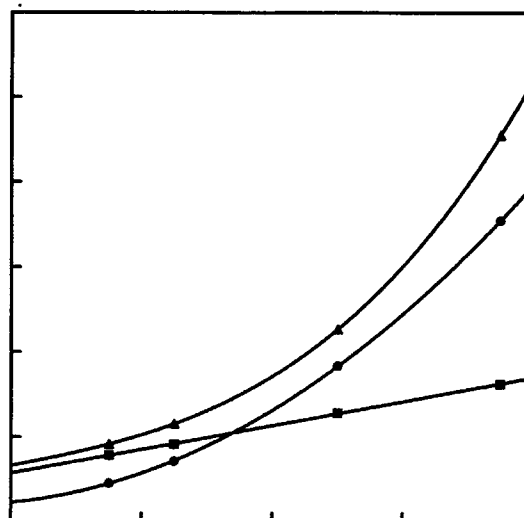


Figure 1 Plots of η_{sp}/C vs. C for (1) EPDM; (2) -Na-2, and (3) -Mn-2 at 25°C . Solvent: xylene/*n*-hexanol ($v/v = 95/5$).

hydrodynamic volume for SEPDM-Na leading to the decrease of viscosity below that of EPDM. For SEPDM-Mn, η_{sp}/C is higher than that of EPDM for the whole concentration range, which indicates that some intermolecular interactions may still exist at low concentrations.

For the metallic ions of the same valence, the smaller the radius of the solvated ion, the stronger its interaction with $-\text{SO}_3\text{M}$ will be.⁶ However, for the metallic ions of different valence, the effect of valence cannot be ignored as for the case of Mn^{2+} in comparison with Na^+ in this investigation. Although there are no data for the hexanol-solvated radii of Mn^{2+} and Na^+ yet, it can be inferred⁷ that the former is larger by the use of their hydrated radii (Mn^{2+} 0.6 nm and Na^+ 0.4 nm)⁸ for reference. Then, if judged by the ionic size only, it may be concluded that the ionic aggregation of Mn^{2+} should be lower. But this is not the case as shown in Figure 1. This indicates that the +2 valence of Mn^{2+} plays an important role in determining the stronger interaction of Mn^{2+} with $-\text{SO}_3^-$.

Figure 2 compares the reduced viscosity-temperature behaviors of EPDM and SEPDM-M in mixed solvent xylene/*n*-hexanol ($v/v = 95/5$). η_{sp}/C of EPDM shows a monotonic decrease as temperature

Table I Degree of Sulfonation and Neutralization of EPDM

Sample	-Na-1	-Na-2	-Na-3	-Mn-1	-Mn-2
Sulfonate content (mol)	0.36	0.47	0.67	0.47	0.47
Degree of neutralization (%)	100	100	100	40	100

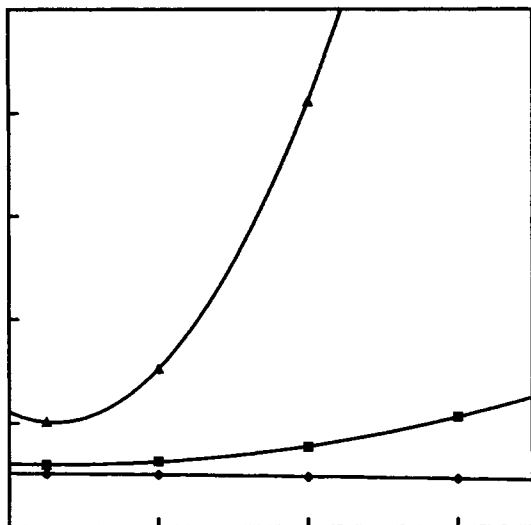


Figure 2 Plots of η_{sp}/C vs. temperature for (1) EPDM, (2) -Na-2, and (3) -Mn-2. Solvent: xylene/*n*-hexanol ($v/v = 95/5$); concentration: 1.0 g dL⁻¹.

increases as expected, but the effect of temperature on SEPDM-M is clearly anomalous. This is usually interpreted⁹ as a consequence of polymer association resulting from the desolvation of metallic ions in ionomer solution as temperature is increased. Although the solvation ability of Mn²⁺ is stronger than Na⁺ due to its higher valence and smaller crystalline radius (Mn²⁺ 0.080 nm, Na⁺ 0.095 nm),⁸ the extent of viscosity increase with increasing temperature is SEPDM-Mn > SEPDM-Na (see Fig. 2), reflecting that the +2 charge of Mn²⁺ plays a more important role than the dehydration effect for the ionic aggregation.

FTIR Analysis

The local structure of the SO₃⁻ anion is tetrahedral and has C_{3v} symmetry. When the electrostatic field associated with the metallic cation polarizes the anion, the symmetry of SO₃⁻ changes to C_s symmetry. Fitzgerald and Weiss found that the polarization causes the SO₃⁻ asymmetric stretch to split into a doublet that absorbs at around 1200 cm⁻¹ ($\tilde{\nu}_{asym}$) while the symmetric stretching vibration of the SO₃⁻ ion absorbs at around 1040 cm⁻¹ ($\tilde{\nu}_{sym}$). But the polarization effect of cation on anion, or the stretching vibration of the SO₃⁻ anion, would decrease when the bonding between the cation and anion is weakened by the solvent or by the cation solvation. Consequently, the extent of $\tilde{\nu}_{asym}$ and $\tilde{\nu}_{sym}$ decrease can be considered as a measure for the solvation strength of the metallic ions.

The results of FTIR investigation for SEPDM-Na-2 and SEPDM-Mn-2 are listed in Table II. For the case of no solvent, $\tilde{\nu}_{-Mn} > \tilde{\nu}_{-Na}$ indicates the polarizing effect of Mn²⁺ is higher than Na⁺. In the presence of mixed solvent $\tilde{\nu}$ decreases and $\Delta\tilde{\nu}$ for -Mn is larger than for -Na, indicating that the solvation of Mn²⁺ is stronger, which is in harmony with the results shown in Figure 2. However, the $\tilde{\nu}$ of the solvated -Mn ionomer in mixed solvents is higher than those of -Na ionomer; this implies that the polarizing effect of the solvated Mn²⁺ is superior to Na⁺, which is more feasible for ionic aggregation. This supports the interpretation given above for the viscosity results shown in Figure 1.

ESR Analysis

Effect of Metallic Ion Content

ESR analysis is a useful tool to probe the interaction between paramagnetic cations. For instance, the nuclear spin quantum number of Mn²⁺ equals $\frac{5}{2}$ and the isolated Mn²⁺ ions exhibit six hyperfine lines in the ESR spectrum. When the Mn²⁺ ions aggregate together, the hyperfine structure may no longer be well resolved and the spectrum broadens or becomes a single broad line, depending on the extent of ion aggregation.⁴

Figure 3 is the ESR spectra for SEPDM-Mn in xylene/*n*-hexanol ($v/v = 80/20$) at 25°C. Curve (a) for SEPDM-Mn-1 shows the clear hyperfine structure, indicating that the Mn²⁺ ions do not interact with each other. Curve (b) for SEPDM-Mn-2 shows some poorly resolved hyperfine structure, indicating that the associated Mn²⁺ ions (or ionic aggregation) dominate the spectrum. This is attributed to the higher concentration of Mn²⁺ in SEPDM-Mn-2 (100% neutralization) and the lesser extent of solvation for each Mn²⁺ ion. This is also the case for the increase of viscosity of the ionomer solution with increasing degree of sulfonation as shown in Figure 4. It is noteworthy that η rises much faster with sulfonation at high temperature than at

Table II Effect of Solvent on Stretching Vibrations of Sulfonate Anion in EPDM Ionomers

Solvent	$\tilde{\nu}_{asym}$ (cm ⁻¹)		$\tilde{\nu}_{sym}$ (cm ⁻¹)	
	-Na	-Mn	-Na	-Mn
No solvent	1185	1201	1034	1052
Xylene/ <i>n</i> -hexanol ($v/v = 90/10$)	1170	1171	1024	1040
$\Delta\tilde{\nu}$	15	30	10	12

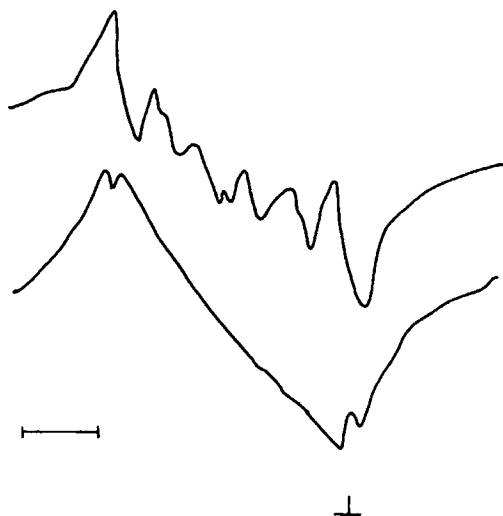


Figure 3 ESR spectra of SEPDM-Mn in xylene/*n*-hexanol ($v/v = 80/20$) at 25°C: (a) -Mn-1 and (b) -Mn-2.

low temperature. In the case of low sulfonation, $\eta_{70^\circ} < \eta_{50^\circ} < \eta_{25^\circ}$ conforms to the usual viscosity behavior of solution. But in the case of sulfonation > 0.65 , $\eta_{70^\circ} \gg \eta_{50^\circ} > \eta_{25^\circ}$ indicates the ionic aggregation is strengthened as a consequence of the weakening of ionic solvation at high temperature.

Effect of Cosolvent

The effect of the content of cosolvent on the ESR spectrum of SEPDM-Mn is shown in Figure 5. For a solution containing hexanol (20 vol %) the hyperfine structure is well resolved, but the spectrum is broadened as hexanol content decreases and finally only a single broad line appears for solution

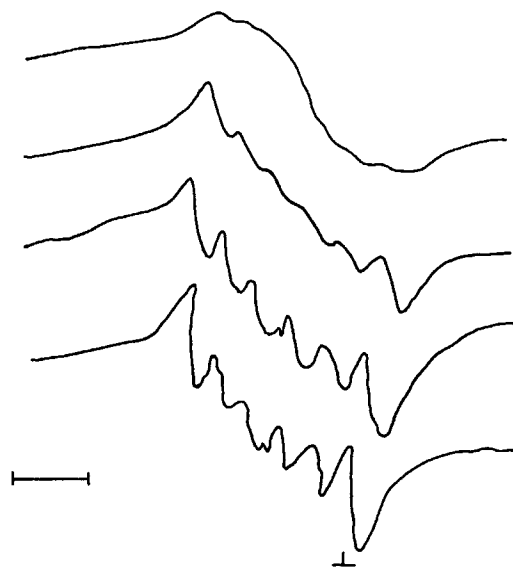


Figure 5 ESR spectra of SEPDM-Mn-1 in xylene/*n*-hexanol (v/v) at 25°C.

containing no cosolvent. This is obviously caused by the hexanol solvation of Mn^{2+} in favor of the isolation of ions. The viscosity-alcohol content plots (Fig. 6) show the same result, that is, η decreases with increasing alcohol content.

Figure 7 compares the solution spectra of SEPDM-Mn in xylene/alcohol with various alcohols as cosolvent. The volume concentrations of alcohols are all equal to 5 vol %. The six hyperfine lines become more poorly resolved from ethanol to nonanol as a result of the weaker solvation of Mn^{2+} with the lower molar concentration of —OH from higher alcohols. The viscometric behavior of

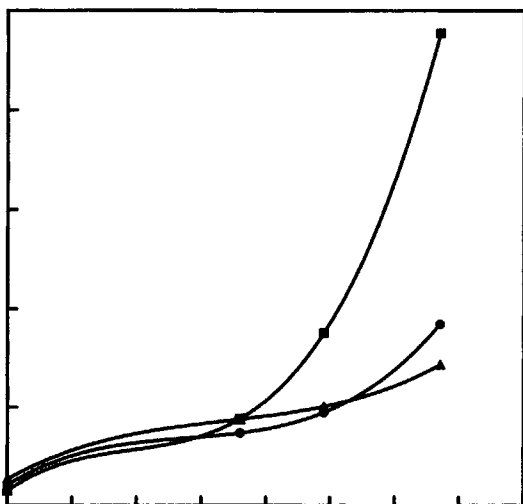


Figure 4 Plots of η vs. degree of sulfonation for SEPDM-Na at concn 2 g dL⁻¹. Solvent: xylene/*n*-hexanol ($v/v = 95/5$).

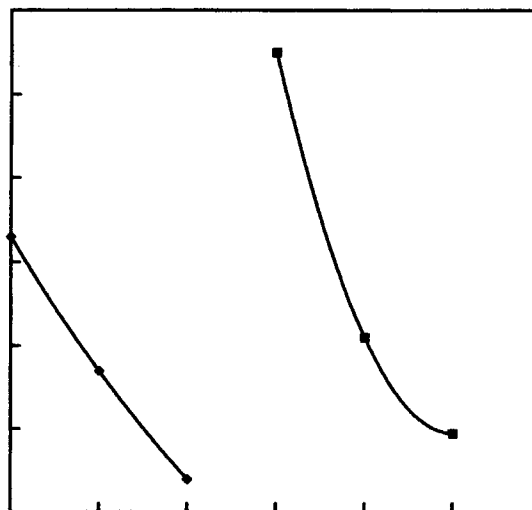


Figure 6 Plots of η vs. alcohol (vol %) for SEPDM-Na-1 in xylene/*n*-hexanol at 25°C. Concn (g dL⁻¹): (1) 1.0 and (2) 2.0.

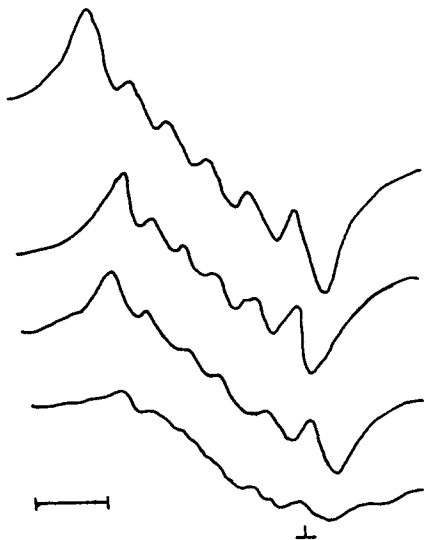


Figure 7 ESR spectra of SEPDM-Mn-1 in xylene/alcohol ($v/v = 95/5$) at 25°C .

SEPDM-Na solutions exhibits the same trend as shown in Figure 8, that is, η of the solutions containing 5 vol % alcohol are $C_6 < C_9 < C_{12}$ (cf. curves 1, 2, 4). But in the case of equal molar concentration of alcohol ($=0.4 \text{ mol L}^{-1}$), η of the solutions are nearly equal (cf. curves 3–5). In consequence, it can be concluded that in the ionomer solutions with xylene/alcohol as solvent, the quantity of $-\text{OH}$ from alcohol plays a key role in determining the solvation of metallic ions and the size of the alcohol molecules has nothing to do with the solvation. Similar results are reflected also in the ESR spectrum. The ESR study of sulfonated butyl rubber ionomer in xylene/alcohol solution was performed recently in our laboratory and it was found that well-resolved hyperfine structure appeared for all solutions containing $0.4 \text{ mol} \cdot \text{L}^{-1}$ of various alcohols. The details will be presented in the next article.

Effect of Temperature

Figure 9 shows the ESR spectra of SEPDM-Mn in xylene/*n*-hexanol ($v/v = 95/5$) at various temperatures. The hyperfine structure becomes obscure gradually from 20 to 80°C , indicating that the rise of temperature promotes the desolvation of the metallic ions in favor of their aggregation. Thus, the ESR results support the explanations given above for the anomalous viscosity-temperature relationship of the ionomer solutions (Figs. 2, 4).

It is not difficult to infer that over some temperature region where the desolvation of metallic ion is not so sensitive to temperature, the anomalous viscosity-temperature relationship should no longer exist as shown by curve 1 in Figure 8. At $t > 70^{\circ}\text{C}$

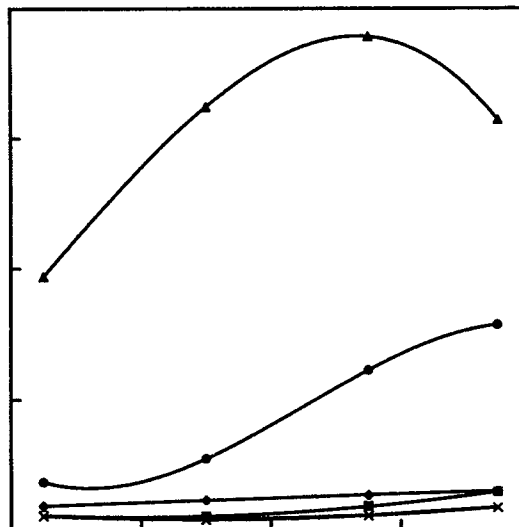


Figure 8 Plots of η vs. temperature for SEPDM-Na-2 in xylene/alcohol at concn 2 g dL^{-1} . Alcohol content (5 vol %): (1) $n\text{-C}_{12}$, (2) $n\text{-C}_9$, and (4) $n\text{-C}_6$ ($\sim 0.4 \text{ mol L}^{-1}$). Alcohol content (0.4 mol L^{-1}): (3) $n\text{-C}_{12}$ and (5) $n\text{-C}_9$.

most metallic ions are already desolvated and the ionic interactions weakened also, then η decreases with increasing temperature just like the normal solvent viscosity behavior.

Figure 10 is another plot of η versus temperature for SEPDM-Na-2 in xylene/*n*-hexanol ($v/v = 95/5$) at various concentrations. All curves have valley shapes. In the temperature range lower than the minimum point, η decreases as temperature increases because the desolvation of the metallic ions is not sensitive to such low temperatures and the viscosity of the solvent dominates the $\eta - t$ behavior of the solution. It can be seen from Figure 10 that the temperature corresponding to the minimum point is lower for the solutions containing more me-

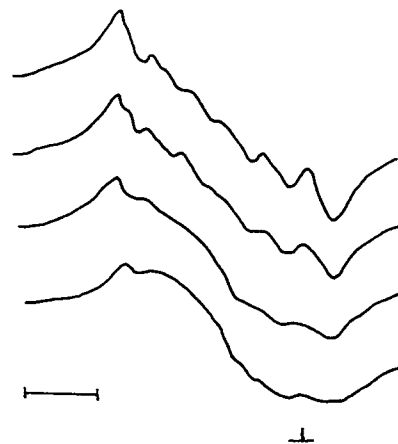


Figure 9 ESR spectra of SEPDM-Mn-1 in xylene/*n*-hexanol ($v/v = 95/5$).

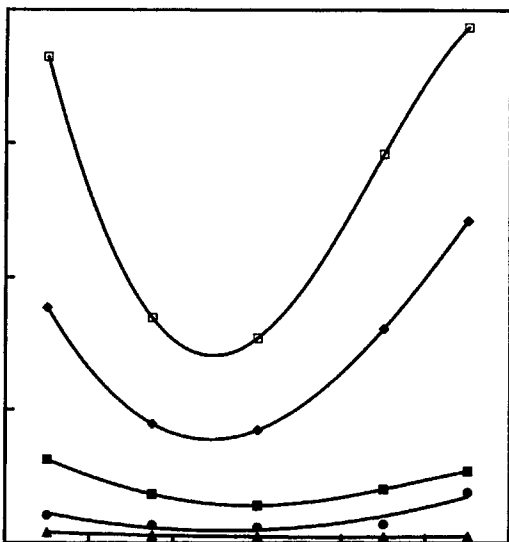


Figure 10 Plots of η vs. temperature for SEPDM-Na-2 in xylene/*n*-hexanol ($v/v = 95/5$) at various concns (g dL^{-1}): (1) 1.0, (2) 1.5, (3) 2.0, (4) 2.5, and (5) 3.0.

tallic ions. This indicates that the occurrence of ionic aggregation at lower temperature is due to the lesser extent of solvation of ions and also due to more interactions between ions at higher concentration. All these results are in agreement with those shown in Figures 3 and 4.

CONCLUSION

The FTIR and ESR studies of SEPDM-Na and SEPDM-Mn ionomers in xylene/alcohol show that alcohol solvation of $-\text{SO}_3\text{M}$ exists and the extent of that solvation relates to the following factors.

1. Species of metallic ion: Mn^{2+} shows the stronger interaction with SO_3^- than Na^+ due to its +2 valence.
2. Concentration of metallic ion: High concentration of metallic ions is favorable for ionic

aggregation, not only due to more chances for ionic interaction, but also due to the lesser extent of solvation.

3. Concentration of $-\text{OH}$ from alcohol: Molar concentration of $-\text{OH}$ is the main effect in determining the ionic solvation, and the size of the alcohol molecule has nothing to do with the solvation.
4. Temperature: Increasing temperature promotes the desolvation of the metallic ions in favor of ionic aggregation.

The viscometric studies of the ionomer solutions show that the results are consistent with the spectroscopic studies. They reveal at the molecular level that the solvation of metallic ions with cosolvent plays a key role in the anomalous viscosity-temperature relationship of the ionomer solutions.

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