

# Solution Behavior of Ionomers. III. Sulfo-EPDM-Modified Hydrocarbon Solutions

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## Synopsis

The solution viscosity of polymer thickened hydrocarbons normally decreases markedly as temperature is increased. It has been observed that metal sulfonate ionomers, such as sulfonated ethylene propylene terpolymer, or sulfo-EPDM, when dissolved in a mixed solvent behave much differently. Specifically, sulfonated ionomers, dissolved in xylene or paraffinic oils with low levels of a polar cosolvent, can provide solutions whose viscosities are either relatively constant or can actually increase with increasing temperature. This isoviscosity effect can be manifested over broad temperature ranges and is mechanistically different from the behavior of conventional polymer solutions. This unusual behavior is explained on the basis of a simple equilibrium involving solvated ion pairs and is shown to be a specific example of a general phenomenon.

## INTRODUCTION

The viscosities of simple liquids usually decrease significantly as temperature is increased. Similarly the viscosity-temperature dependence of most polymer solutions is such that the viscosity decreases monotonically with increasing temperature. There are some exceptions to this general viscosity-temperature behavior which occur in the vicinity of a phase separation for a particular polymer solution. Such solutions can manifest viscosities which increase or remain constant over restricted temperature ranges. However, these phenomena do not generally offer an approach to control of solution viscosity over broad temperature ranges. An alternate approach to modifying viscosity decay with increasing temperature is that involving a given polymer system in a "poor" solvent at low temperatures. Under these conditions an increase in temperature will permit increased solvation of the polymer chains and offset the viscosity decrease to some degree.<sup>1</sup>

This paper describes an approach to the control of polymer solution viscosity which can alter the normal decrease in viscosity with change in temperature to a marked degree. Specifically, we show that suitable sulfonated ionomers dissolved in hydrocarbon solvents with low levels of a polar cosolvent can provide solutions whose viscosity-temperature relationship is markedly different from that of conventional polymers. Such solutions can possess viscosities which actually increase or are constant over wide temperature ranges. This unusual behavior is explained on the basis of a simple equilibrium and is shown to be a specific example of a general phenomenon.<sup>2</sup>

## EXPERIMENTAL

The sulfonated polymers were prepared by procedures described in earlier publications.<sup>3-5</sup> In general, these polymers were prepared by solution sulfonation employing acetyl sulfate as the sulfonating agent. The ethylene-propylene-diene terpolymer (EPDM) was a polymer of 20 Mooney (212°F) with an approximate number average molecular weight of 25,000 containing 55% ethylene, 40% propylene, and 5% ethylidene norbornene. EPDM was sulfonated in hexane solvent at room temperature. The polymers were neutralized and recovered by solvent flashing in hot water. Reagent conversions of about 90% of sulfonate were generally obtained. The sulfonate content of the recovered polymer was determined by sulfur analysis of the salt as well as by titration of the sulfonic acid precursor. Sulfonate level in this paper is described as milliequivalents per 100 grams of polymer (or meq/100 g). The preparation and characterization of sulfonated EPDM has been described in detail in Ref. 6, Example 5.

Characterization of these sulfonated polymers in terms of molecular weights or molecular weight distributions is difficult due to the strong ionic associations prevailing even in dilute solution. The apparent molecular weights, reduced viscosities, and intrinsic viscosities are highly dependent on the solvent environment. Under conditions where the ionic associations can be virtually eliminated or minimized, the apparent molecular weights of the sulfonated adducts appear similar to those of the starting polymer.<sup>7</sup>

Solutions of polymers were prepared in stoppered volumetric flasks using magnetic stirrers for agitation. When required, mild heating in a water bath at temperatures of 60–70°C with stirring was employed to effect solution. The polymer was weighed into the volumetric flask to an accuracy of 0.001 g. Sufficient quantities of the desired cosolvent mixtures were prepared in volumetric flasks so as to provide stock solvent supplies for solution preparations.

Viscosity measurements were obtained with a Model LVT Brookfield viscometer employing a U.L. adapter for low viscosity solutions and various size spindles for higher viscosity measurements as required. Viscosities were obtained over a shear rate range of about  $10^{-1}$ – $10^2$  s<sup>-1</sup>. The effect of shear rate on solution viscosity was investigated employing a Contraves Viscometer. The solutions of this study were observed to exhibit Newtonian behavior over the shear rate range investigated; however, departures from Newtonian behavior may be observed in more viscous solutions or at higher shear rates.

The reduced viscosity, or viscosity number [defined as  $(\eta - \eta_0)/\eta_0 c$ , where  $\eta$  is the viscosity of the polymer solution,  $\eta_0$  is the viscosity of the solvent or mixed solvent, and  $c$  is the concentration of polymer (g/100 mL)]; was measured with a standard Ubbelohde viscometer.

Water or oil temperature controlled baths were used for viscosity measurements from 25°C to as high as 150°C. Viscosities at 0°C were obtained in a water-ice bath. About 15 min of temperature equilibration was allowed prior to viscosity measurement. Repeated measurements were made until reproducibility was obtained. Brookfield viscosities were determined for at least three spindle rotational speeds for every solution measured.

Thermal mechanical analyses (TMA) were determined on compression molded samples (at 175°C for sulfo-EPDM) having a thickness of 0.015 in. The TMA

measurements were conducted on a DuPont Thermal Analyzer, Model 900, with a loading of 10 g, at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Properties of Sulfo-EPDM

The synthesis and properties of sulfonated ionomers have been the subjects of several recent publications.<sup>3-5</sup> It is appropriate to highlight a few aspects of such materials very briefly here. The sulfonation/neutralization of EPDM (terpolymers of ethylene/propylene/diene monomer) to rather low levels is readily affected under conditions previously described. At levels of metal sulfonate content above 5–10 meq/100 g polymer, a marked change in physical properties of this elastomer are observed. At ambient temperatures tensile properties are improved, and melt viscosity at elevated temperatures is increased. At sulfonate levels of 30 meq/100 g (or about 1 wt % sulfur) the resulting polymer appears to have the properties of a covalently crosslinked elastomer.<sup>8</sup>

Figure 1 compares the softening behavior (via thermal mechanical analysis) of sulfonated EPDM with that of the unsulfonated precursor. The sulfonated polymer possesses a broad, rubbery plateau which exists to temperatures some 100–150°C higher than for EPDM. This plateau is evidence of strong ionic association<sup>2,3</sup> and is attributed to Coulombic association of the ion pair groups pendant to the hydrocarbon polymer.<sup>2,4</sup>

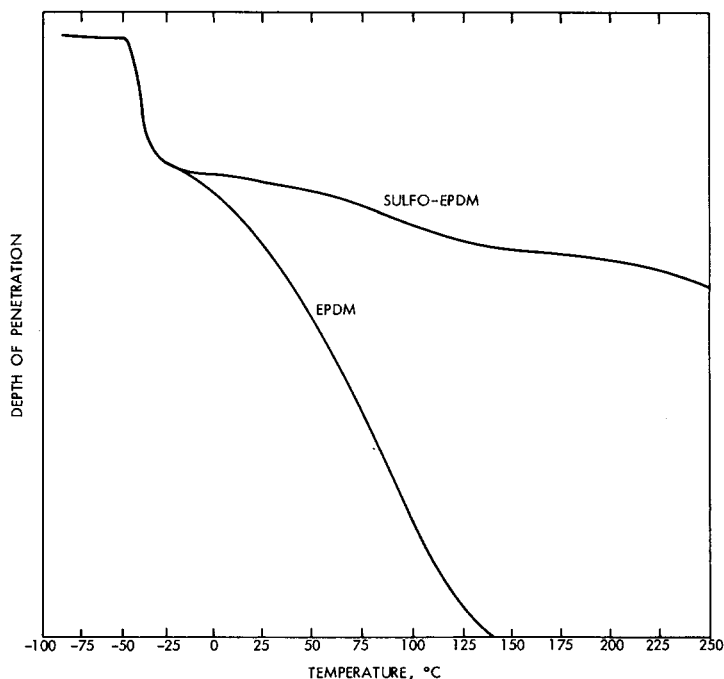


Fig. 1. Thermomechanical analysis of 30 meq sulfo-EPDM, zinc salt, and EPDM. Penetration mode, 10 g wt, 10°C/min heating rate.

TABLE I  
 Viscosity of Zinc Sulfo-EPDM in Xylene or Xylene-Hexanol as Function of Sulfonate Content  
 (2 g POLYMER/100 mL)

Sulfonate level (meq/100 g)	Viscosity in xylene (cP)	Viscosity in mixed solvents 98% xylene/2% hexanol (cP)
0	5.0	4.5
5	8.5	5.7
10	20,000	9
20	Gel	55
30	Gel	—

One of the consequences of this association of metal sulfonate groups is that these ionic associations can be quite temperature-resistant and do not show a sharp transition as temperature is increased. In this respect sulfonated ionomers are unlike other polymers whose properties are controlled by crystalline melting points or glass transitions. In these latter cases the cooperative nature of the transitions causes them to be relatively sharp. Clearly this is not the case with the sulfonated ionomers.<sup>3</sup>

### Solution Behavior in Xylene Based Solvents

The solution behavior of these ionomers also reveals the presence of strong ionic associations, and can be rather unique when contrasted to that of unfunc-

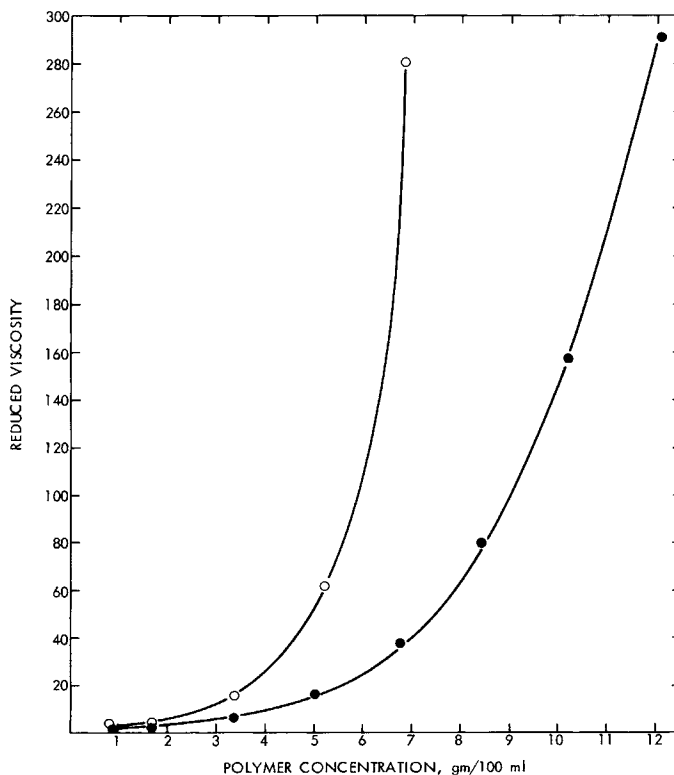


Fig. 2. Reduced viscosity vs. concentration of (○) 5 meq sulfo-EPDM, zinc salt, and (●) EPDM in xylene.

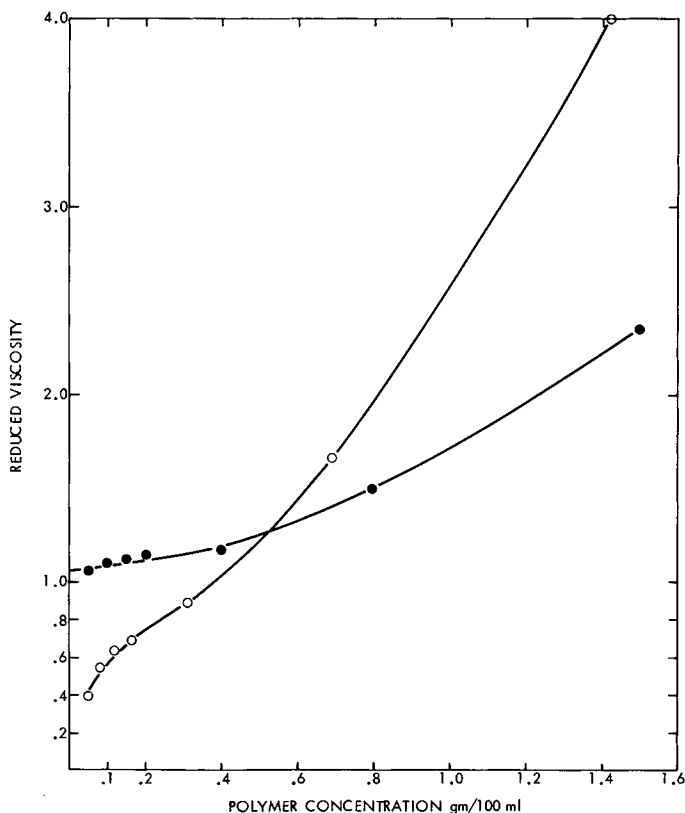


Fig. 3. Reduced viscosity vs. concentration of (O) 30 meq sulfo-EPDM, zinc salt, and (●) EPDM in 95 xylene/5 methanol.

tionalized polymers. Noncrystalline EPDM is readily soluble in a variety of hydrocarbon solvents such as xylene. Sulfonated EPDM, however, is markedly different from EPDM in solubility behavior. Some evidence of the behavior of zinc sulfo-EPDM at varying sulfonate levels is seen in Table I.

At low sulfonate levels of 5–15 meq/100 g the polymers are soluble in xylene, but are extremely effective in increasing the viscosity of the resulting solutions. For example, the reduced viscosity–concentration behavior of zinc sulfo-EPDM of 5-meq sulfonate level is compared with that of unmodified EPDM in Figure 2. At polymer concentrations above several percent there is a marked increase for the reduced viscosity of the sulfo EPDM as contrasted to that of the base EPDM. This behavior is even more marked with increasing sulfonate level, or with more strongly associating cations.

At higher sulfonate levels these polymers become highly swollen, but do not dissolve in hydrocarbons. The viscosification at low sulfonate levels and the insolubility at higher sulfonate levels has been demonstrated<sup>2</sup> to arise from ionic association. The addition of modest levels of polar cosolvents such as alcohols, amines, and acids can markedly reduce or eliminate the ionic association as shown in Table I. Previous studies<sup>2,6,9</sup> have shown that the nature of the cosolvent, its concentration, etc., are very important in controlling the degree of association and therefore the resulting solution viscosity.

To a first approximation the interaction of cosolvent and ionic groups has been

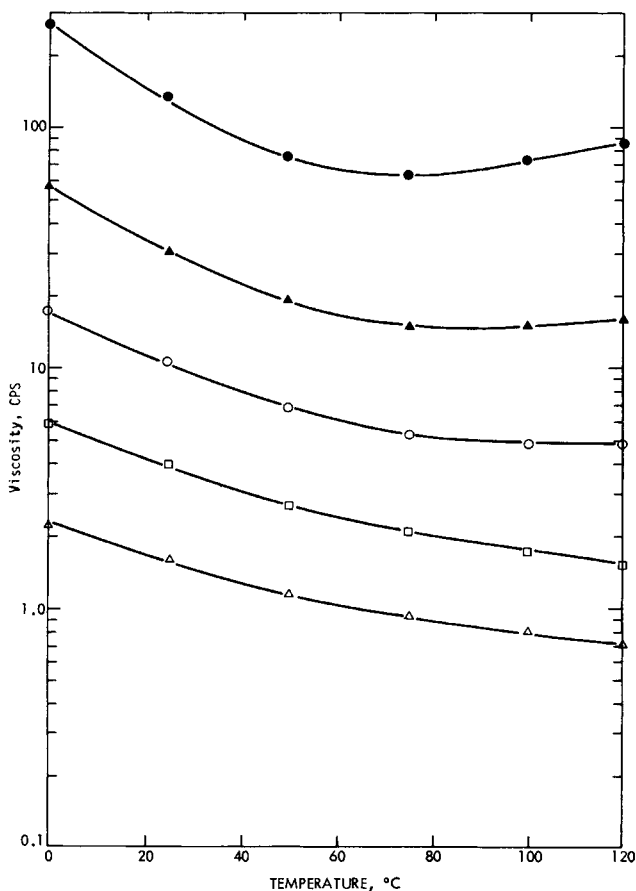
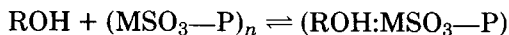


Fig. 4. Viscosity-temperature relaxation slips for 20 meq sulfo-EPDM, zinc salt in 90 xylene/10 hexanol at concentrations of ( $\Delta$ ) 0.5%, ( $\square$ ) 1%, ( $\circ$ ) 1.5%, ( $\blacktriangle$ ) 2%, and ( $\bullet$ ) 3%.

interpreted<sup>2,6</sup> in light of an equilibrium as follows:



alcohol + aggregated sulfonate groups	solvated sulfonate groups
(favored at high $T$ )	(favored at low $T$ )

It is emphasized that this equilibrium describes only the interaction of sulfonated groups and the polar cosolvent. As such, the contributions of polymer backbone and the rest of the solvent is ignored. Nevertheless, this equilibrium can successfully describe the solution behavior of sulfonated ionomers in those solvents or solvent mixtures where the metal sulfonate groups exist as ion pairs. This treatment does not apply under conditions where the sulfonate groups are sufficiently ionized that polyelectrolyte behavior obtains. Polyelectrolyte behavior for sulfonate ionomers typically has been observed<sup>10</sup> only in those solvents of relatively high polarity (dielectric constant  $> 15$ ) and therefore that behavior will not concern us in this paper.

The reduced viscosity of Sulfo EPDM is compared with that of EPDM in a mixed solvent system in Figure 3. Under these conditions, ionic associations

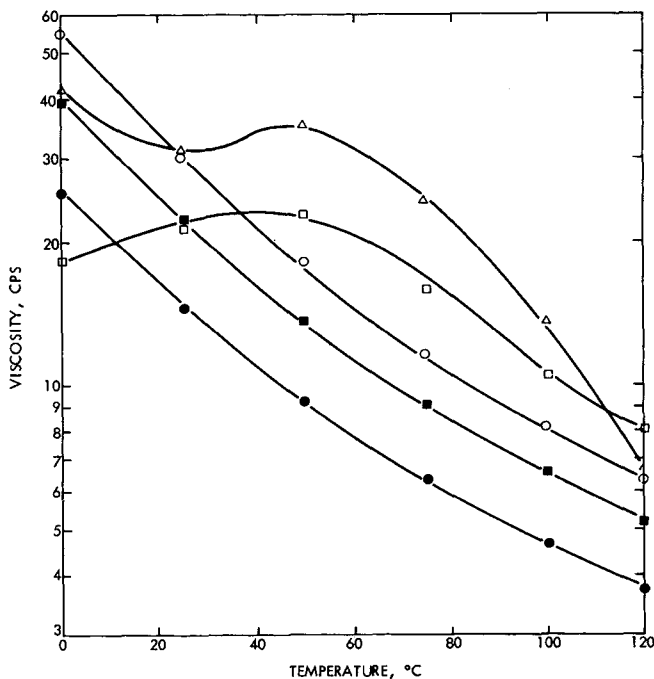


Fig. 5. Viscosity-temperature relationships of 20 meq sulfo-EPDM, zinc salt at 1% concentration in ( $\Delta$ ) 0.55% hexanol/xylene and ( $\square$ ) 0.75% hexanol/xylene and EPDM at concentrations of ( $\circ$ ) 4.5%, ( $\blacksquare$ ) 4%, and ( $\bullet$ ) 3.5% in 0.6% hexanol/xylene.

are reduced, but not completely eliminated. Consequently, at high polymer concentrations, pronounced intermolecular association occurs thereby increasing the reduced viscosity substantially above that of EPDM. At lower concentrations the reduced viscosity of sulfo-EPDM is less than that of EPDM, indicating intramolecular association. These intramolecular associations result in a sig-

TABLE II  
Viscosity of Sulfo-EPDM-Oil Solutions at Various Polymer Levels as Function of Hexanol Concentrations at 25°C<sup>a</sup>

	Viscosity (cP)
<i>(Polymer concn of 1.0 g/100 mL) alcohol concn</i>	
0%	Gel
0.5%	250
1%	225
2%	135
4%	115
oil	35
oil + EPDM	93
<i>(Polymer concn of 1.5 g/100 mL) alcohol concn</i>	
0%	Gel
0.75%	1300
1.5%	580
3	230
6	215

<sup>a</sup> Zinc Sulfonate level = 20 meq/100 g.

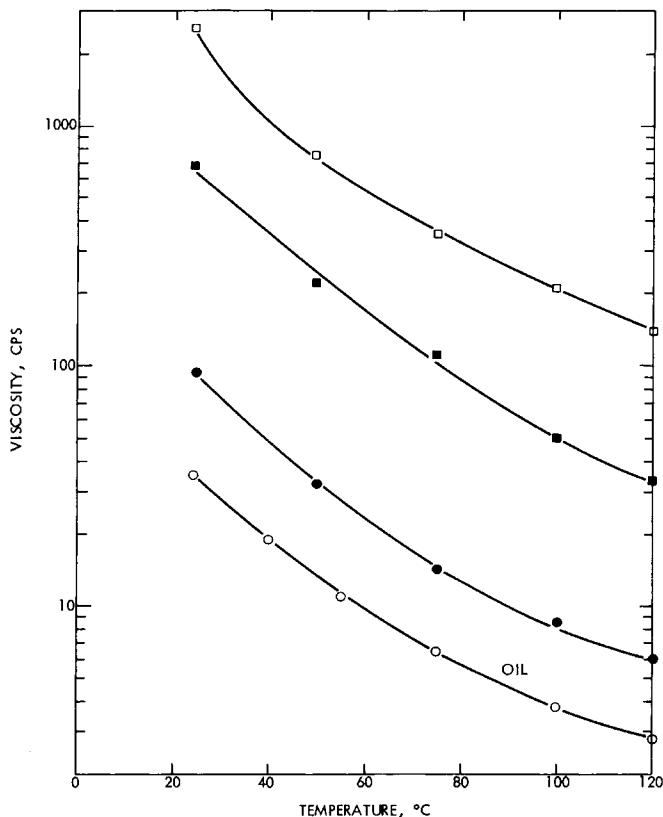


Fig. 6. Viscosity-temperature relationships for (□) 30 meq sulfo-EPDM, zinc salt in 90 oil/10 hexanol, (■) 3%, (●) 1% concentration of EPDM in oil, and (○) oil.

nificantly lower hydrodynamic volume for sulfo-EPDM as compared with EPDM. Obviously, the type and level of cosolvent employed will govern the degree of association in these systems. At higher cosolvent levels with strongly solvating cosolvents associations can be minimized.<sup>2</sup>

To a first approximation, the intersection of the two curves in Figure 3 can be regarded as specifying the concentration  $C^*$ , where the polymer coils start to overlap. Alternatively,  $C^*$  can also be regarded as the point at which a balance has been achieved between intra- and intermolecular associations, thus masking the effect of ion association. The value of  $C^*$  observed here may or may not be the same as that observed for the unsulfonated EPDM. It is important to note that the observations relating to the solution behavior of the ionomers described in this paper are based on polymer concentrations above  $C^*$ . Consequently, the intermolecular interactions are those which predominate in controlling viscosity in this discussion.

#### Effect of Temperature on Viscosity of Solution of Sulfo-EPDM in Mixed Solvents

One of the interesting consequences of the equilibrium postulated above is that increasing the temperature of a sulfonated ionomer in mixed solvents can



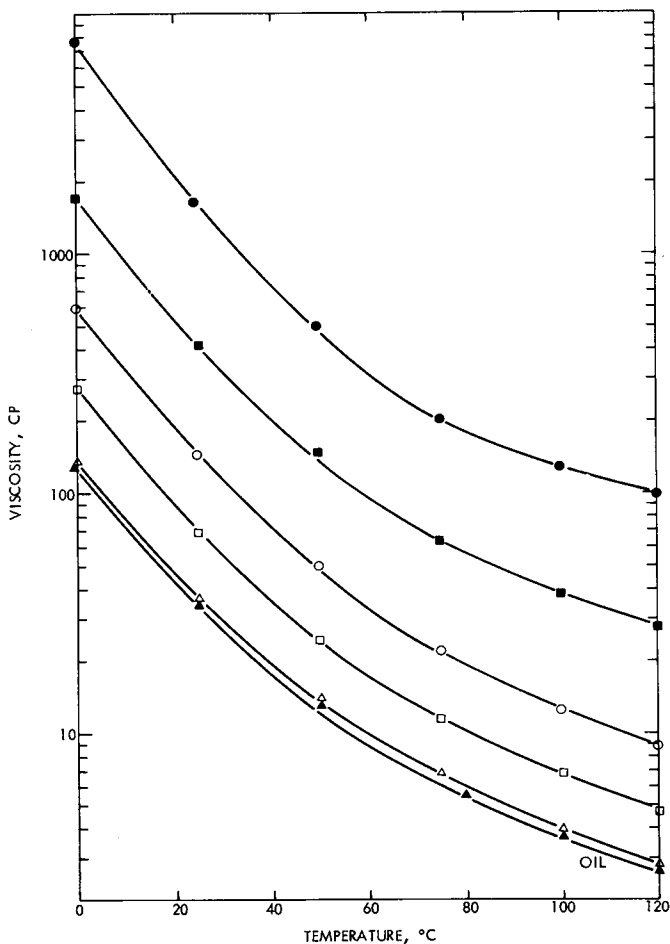


Fig. 7. Viscosity-temperature relationships of 20 meq sulfo-EPDM, zinc salt at concentrations of (●) 3%, (■) 2%, (○) 1.5%, (□) 1%, and (△) 0.5% in 90 oil/10 hexanol vs. (▲) oil.

result in unusual viscosity changes. Some evidence of this behavior is shown in Figure 4. At low polymer concentrations in a xylene/hexanol (90/10) mixture, the viscosity diminishes with increasing temperature. At higher polymer concentrations  $> 1.5\%$  the viscosity is relatively constant or increased over the temperature ranges of 60–120°C.<sup>10</sup> This viscosity-temperature behavior has been observed with other ionomers and interpreted as a consequence of increased apparent molecular weight of the associating polymer as temperature is increased.<sup>2,3</sup> This phenomenon is observed at polymer concentrations  $> 1\%$  where intermolecular associations are most pronounced.

Lower amounts of alcohol cosolvent induce a significant change in the viscosity-temperature profile for sulfo-EPDM. Figure 5 compares the viscosity-temperature behavior of EPDM and sulfo-EPDM in mixed solvents at low alcohol contents. The viscosity behavior of EPDM is not significantly affected by the presence of minor amounts of cosolvent. Relatively large amounts of EPDM are required to achieve viscosities in the range of 20–30 cP at 25°C. Furthermore, the solutions show a monotonic decrease as temperature is increased, as expected.

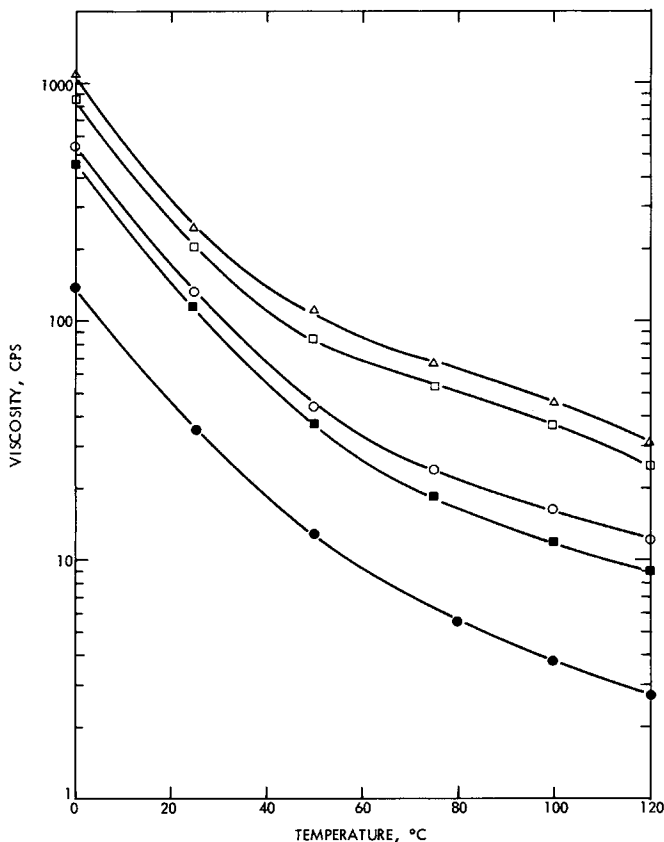


Fig. 8. Viscosity-temperature relationships for 20 meq sulfo-EPDM, zinc salt at 1% wt concentration in ( $\Delta$ ) 0.5% hexanol/oil, ( $\square$ ) 1% hexanol/oil, ( $\circ$ ) 2% hexanol/oil, and ( $\blacksquare$ ) 4% hexanol oil vs. ( $\bullet$ ) oil.

The sulfo-EPDM-based solutions achieve equivalent viscosity levels at relatively low polymer levels ( $\sim$ 1%). The effect of temperature on the sulfonated EPDM solution is clearly anomalous, showing a maximum near 50°C. It is clear from these studies that at low cosolvent levels marked deviations from conventional polymer behavior are observed, especially in the viscosity-temperature relationships observed for semidilute polymer solutions.

### Solution Behavior in Oil-Based Systems

EPDM without residual crystallinity is readily soluble in paraffinic oils. Sulfonated EPDM dissolves readily in oils at sulfonate levels of  $\sim$ 10 meq/100 g, but the use of a polar cosolvent is required to dissolve sulfo-EPDM of higher sulfonate levels. With appropriate levels of cosolvent, homogeneous solutions are obtained which appear Newtonian with polymers containing up to 30 meq of sulfonate content. Selected cations (calcium, barium, etc.), however, associate sufficiently strongly that homogeneous solutions are difficult, if not impossible to prepare. Lower sulfonate contents and/or cosolvent addition are required to achieve true solutions.

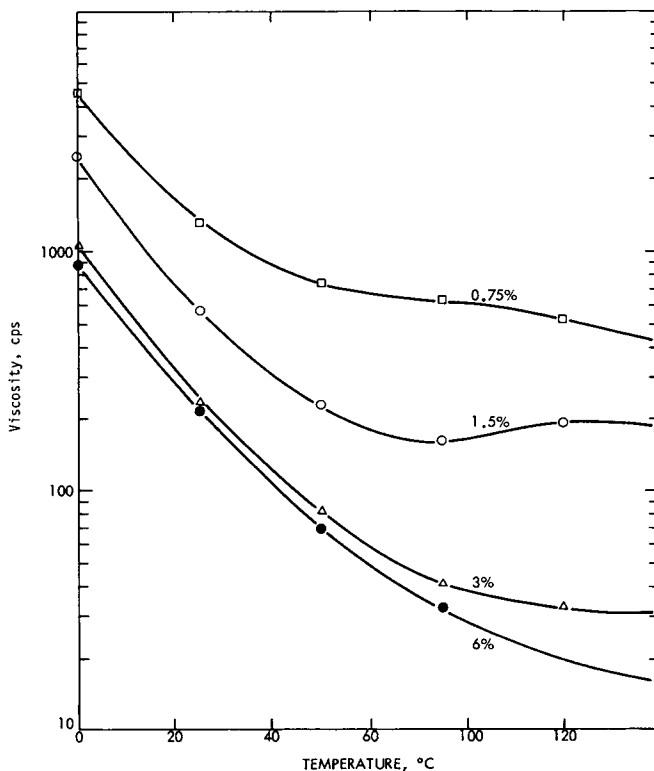


Fig. 9. Viscosity-temperature relationships for 20 meq sulfo-EPDM, zinc salt at 1.5 wt % concentration in ( $\square$ ) 0.75% hexanol/oil, ( $\circ$ ) 1.5% hexanol/oil, ( $\Delta$ ) 3% hexanol/oil, and ( $\bullet$ ) 6% hexanol/oil.

The effect of alcohol concentration on the viscosity of Sulfo EPDM at 25°C is shown in Table II. At polymer concentrations of 1% the alcohol reduces the viscosity of the sulfo-EPDM solution to a modest degree. At higher alcohol contents the viscosity approaches that of the unfunctionalized EPDM in oil. At 1.5% polymer concentration the effect of alcohol is more pronounced. In the absence of alcohol a homogeneous gel is obtained in both cases.

#### Effect of Temperature on Sulfo-EPDM-Oil Systems

The effect of temperature on the viscosity of EPDM in oil and the base oil is shown in Figure 6 at EPDM levels of 1% and 3%. The viscosity of the solutions decreases monotonically with temperature. For comparison sulfo-EPDM in a mixed solvent (10% hexanol-90% oil) is shown at the 3% level. The viscosity of the ionomer is substantially higher than for EPDM even with 10% alcohol present. Similar data are shown in Figure 7 for a range of sulfo-EPDM concentrations in the same mixed solvent system. To a first approximation the viscosities of these solutions all decrease comparably over the temperature range 0-120°C. The effect of temperature on viscosity, therefore, is quite similar to that observed for EPDM solutions.

At lower alcohol concentrations, however, the situation is different. At

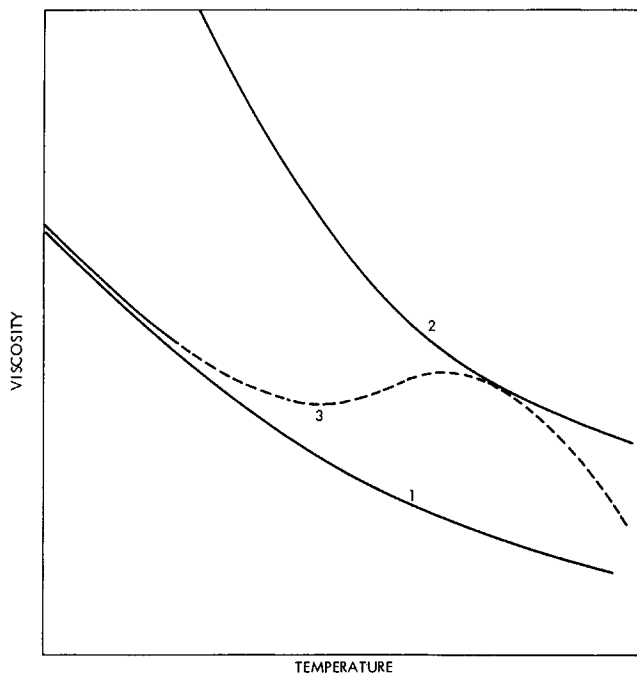


Fig. 10. Hypothetical examples of viscosity-temperature relations.

sulfo-EPDM levels of 1%, the viscosity-temperature profiles are shown in Figure 8 at several alcohol levels and compared with that of the base oil. At lower alcohol contents the viscosities at higher temperatures are substantially higher than would have been expected from comparison with the unsulfonated polymers. In effect, the entire viscosity-temperature relationship has been shifted upwards disproportionately at the higher temperature end.

The same sulfonated polymer is examined at higher polymer levels (1.5%) at several different hexanol levels in Figure 9. At the lower alcohol levels the viscosity-temperature behavior is different from that of EPDM in oil or for sulfo-EPDM at higher alcohol levels. The unusual phenomenon of viscosity being constant or increasing with temperature is consistent with observations in other hydrocarbon solvents and consistent with the equilibrium postulated. By appropriate adjustment of cosolvent levels, polymer levels, and sulfonate content, it is feasible to hold the viscosity of these systems virtually constant over a broad temperature range (25–120°C).<sup>6</sup> Alternatively, it is possible to create modified oils whose viscosities actually increase with increasing temperature. In this respect it appears that this approach of controlling hydrocarbon diluent viscosity is unique.

### Generalization of These Observations

Because this approach to viscosity control appears different from conventional polymer thickening approaches, it is useful to provide a generalized interpretation of such systems. Figure 10 provides a hypothetical viscosity-temperature scheme which describes several distinct regions. Curve 1 in Figure 10 represents

a case where a nonassociating, polymer-thickened fluid displays the normal decrease in viscosity with an increase in temperature. Curve 2 represents the decrease in viscosity with an associated species as might be experienced with a sulfonated ionomer without a polar cosolvent present. Curve 3 (dashed line) represents an associating polymer with a cosolvent present where the equilibrium postulated earlier is operative. Under these conditions at lower temperatures the behavior of the solvated species approaches the unassociating polymer. However, as temperature increases, a higher molecular weight or associated species will be formed over a specific temperature range. At sufficiently high temperatures, however, even the associating groups will ultimately diminish in degree of association and viscosity will decrease. All the observations obtained with sulfo-EPDM in mixed solvents are consistent with this rationale.

### CONCLUSIONS

The solution behavior of sulfo-EPDM in hydrocarbon solvents containing low levels of polar cosolvents appears markedly different from that of conventional hydrocarbon polymers. The viscosities of these solutions can be held relatively constant or can actually increase with increasing temperature. This unusual viscosity-temperature behavior can be explained on the basis of a simple equilibrium involving solvated ion pairs and appears to be a specific example of a general phenomenon.<sup>2</sup>

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