

Solution Studies of Metal Sulfonate Ionomers IV: Effects of Cosolvents

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Synopsis

Previous studies have shown that metal sulfonated ionomers display unusual solution behavior. Typically, ionomers, such as metal sulfonated EPDM or sulfonated polystyrene, are readily dissolved in mixed solvents, such as hydrocarbons plus alcohols. Such mixed solvents can provide unusual viscosity-temperature behavior due to the strong inter- or intramolecular interactions of the ionic groups.

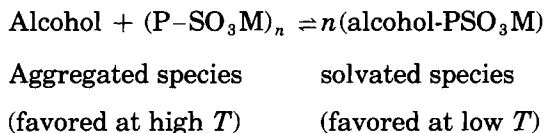
This paper is concerned with studies directed at a variety of polar cosolvents, including amines, alcohols, acids, amides, and esters, in interactions with zinc sulfonated ethylene propylene diene monomer (sulfo-EPDM). Within various classes of compounds the structural effects of such cosolvents on the solution viscosities of sulfonate ionomers have been elucidated. Generally, amines and alcohols have been found to be the most effective cosolvents. Amines appear to form a specific complex with zinc and can virtually eliminate ion pair association at extremely low levels. Within a homologous series, those compounds of shortest hydrocarbon chain length provide the most effective solvation of the ionic groups of sulfonated EPDM. The effect of structure of the amines or alcohols on solution viscosity has shown the efficiency of cosolvent interaction proceeding as normal > iso > secondary > tertiary in the alcohol series. These results are interpreted as a consequence of the cosolvent solvating the ionic groups wherein the more bulky cosolvents are least effective in solvating the metal cations.

INTRODUCTION

Physical properties, especially rheological properties of hydrocarbon polymers, can be altered significantly by introducing a small amount (1–3 mol %) of ionic groups upon their backbone chain.^{1–3} The property changes are caused by the ionic cross-links that arise from association of the ionic groups. The degree of association and the temperature range over which the association occurs can be controlled by adding appropriate polar “plasticizers.” This concept has been used to prepare polymers that possess good melt flow properties at elevated temperature, providing improved processability while still maintaining physical cross-links at lower temperatures. A thermo-plastic elastomer, such as sulfonated EPDM (ethylene-propylene-diene terpolymer) is an example of this concept in which the level of sulfonation, the choice of metal cation, and the specific plasticizer can dominate the property-flow balance.^{4,5}

To fully utilize this concept, an understanding of the interaction between the ionic groups with polar molecules is useful. The interaction of polar cosolvents and metal sulfonate ionomers have been examined in solution as one approach to gain such understanding. Some rather unusual solution phenomena have been observed during these studies. Previous publications^{6–9} have summarized the solution behavior of such systems and

rationalized them in terms of a rather simple equilibrium for such interactions:



This equilibrium suggests that, at appropriate alcohol levels, an increase in temperature would induce a greater degree of aggregation and therefore an increase in solution viscosity under certain conditions. This behavior has been observed with a number of different ionomers.

Previous dilute solution viscosity studies⁵ concentrated on a limited number of alcohols as cosolvents for sulfonated ionomers. The current study was initiated with the objective of extending cosolvent solution investigations to

1. Screen various functional group types to determine their cosolvent capabilities for zinc sulfonated EPDM: alcohols, amines, esters, amides, and acids.

2. Determine, within a homologous series (alcohols and amines), the effect of chain length on solution viscosity

3. Compare the effect of different isomers of the same cosolvent type upon solution viscosity

EXPERIMENTAL

The ionic polymers employed in these studies were sulfonated EPDM (30, 20, and 10 mE per 100 g sulfonate level, Zn neutralized), sulfonated polystyrene, (1.7 mol % SO_3Na), and carboxylated polystyrene (2 mol % carboxylate, Na salt). Unless specified, the sulfonate level on zinc sulfo-EPDM is 30 mE per 100 g. Solutions of sulfonated EPDM in the various cosolvent mixtures were prepared in stoppered Erlenmeyer flasks by agitation at room temperature. Solutions for reduced viscosity determination were prepared in volumetric flasks, polymers were weighed to an accuracy of 0.001 g, and the initial 2% concentration solution diluted with the appropriate solvent system to provide a range of polymer concentrations. Screening experiments, such as those described in Table I, were conducted at cosolvent concentrations of 1 and 5%. Subsequent measurements were typically performed at cosolvent concentrations at comparable molar concentrations.

Viscosity measurements of the sulfo-EPDM solutions were obtained with a model L.V.T. Brookfield viscometer at the three highest possible rotational speeds. Different spindles for different viscosity ranges and a UL adaptor for very dilute solutions were applied. Five readings of viscosity were usually obtained at each rotational speed, and their average taken to be the final value. In some cases the viscosities of systems that appeared to be phase separated were attempted and approximate values obtained; those values are indicated in parentheses. In all other cases homogeneous solutions were

TABLE I
Effect of Various Cosolvents on Zinc Sulfo-EPDM (30 mEq per 100 g); 3% Polymer in Xylene with Cosolvent Levels of 1 and 5%^a

Cosolvent	Solubility			
	1% (25°C)	Mol/L	5% (25°C)	Mol/L
Methyl alcohol	S	0.25	S	1.25
Ethyl alcohol	S	0.17	S	0.85
Propyl alcohol	S	0.13	S	0.67
Butyl alcohol	S	0.11	S	0.55
Pentyl alcohol	S + G	0.092	S	0.46
Hexyl alcohol	S + G	0.08	S	0.40
Heptyl alcohol	S + G	0.071	S	0.35
Octyl alcohol	S + G	0.063	S	0.32
Decyl alcohol	S + G	0.052	S	0.26
<i>n</i> -Butylamine	S	0.10	S	0.51
<i>n</i> -Pentylamine	S	0.087	S	0.44
<i>n</i> -Hexylamine*	S	0.076	S	0.38
<i>n</i> -Octylamine*	S	0.061	S	0.30
<i>n</i> -Decylamine*	S	0.05	S	0.25
Diethylamine	S	0.097	S	0.45
Dibutylamine	S	0.059	S	0.30
Dihexylamine	S	0.043	S	0.21
Dioctylamine	S	0.033	S	0.17
Tributylamine	S	0.042	S	0.21
Trihexylamine	S	0.029	S	0.15
Trioctylamine	S	0.023	S	0.11
Dimethylphthalate	G	0.061	G	0.31
Diethylphthalate	G	0.050	G	0.25
Dibutylphthalate	G	0.037	G	0.19
Dihexylphthalate	G	0.030	G	0.15
Dioctylphthalate	G	0.025	G	0.126
Didecylphthalate	G	0.020	G	0.10
Formamide	S + G	0.25	S + G	1.25
Acetamide	S + G	0.17	S + G	0.85
Proponamide	S + G	0.14	S + G	0.71
Butylamide	S + G	0.115	S + G	0.57
Stearamide	S + G	0.035	S + G	0.18
Formic acid	S + G	0.265	S + G	1.33
Acetic acid	S + G	0.175	S + G	0.87
Propionic acid	S + G	0.134	S + G	0.67
Butyric acid	S + G	0.109	S + G	0.55
Octanoic acid	S + G	0.063	S + G	0.32
Decanoic acid	S + G	0.052	S + G	0.26

^a S = soluble; G = gel; (*) solutions were somewhat cloudy but contained no gel.

achieved. Viscosity of the sulfo-polystyrene solutions for reduced viscosity calculations were determined with a no. 1 Ubbelohde viscometer.

All viscosity measurements were performed at 25°C in a temperature-controlled water bath (accurate to ± 0.05 degrees). In some cases, viscosities were obtained at 50 and 75°C in an oil bath. At least 25 min was allowed for temperature equilibrium before measurements were made.

RESULTS AND DISCUSSION

Screening of Cosolvents for Sulfo-EPDM

A summary of the effectiveness of the cosolvents is listed in Table I. Of the polar cosolvents tested, amines and alcohols appear to be the most effective cosolvents by far. Amines, insofar as they dissolve the polymer at lower concentrations, are generally more effective than alcohols. Amines also provide polymer solutions of lower viscosity, indicative of less ionic association.

Amides show some capability as cosolvents at a higher temperature (50°C) but are not effective at room temperature (25°C). This behavior could be attributed to the tendency of most amides to be crystalline and therefore less soluble in these solutions at 25°C. Several acids produce thin, partially gelled solutions at a higher temperature (50°C).

The least effective cosolvents that have been tested are esters, specifically acetates. The polymer remains as a gel even when the volume concentration of these cosolvents is raised to 5 vol % and the temperature to 50°C.

Effect of Chain Length

Alcohols

In a homologous series of alcohols at the same molar concentrations (1.25 M), the general trend shows that the viscosity of polymer solutions decreases with decreasing cosolvent chain length (see Fig. 1 and Table II). This observation suggests that the lower analogs solvate the ionic groups more effectively, as previously reported.⁷

Over the temperature range investigated (25–75°C), the viscosity of the solutions with higher alcohol concentration (1.25 M) decreases as temperature increases (Fig. 1); at lower alcohol concentration (0.25 M concentration), viscosity generally increases as temperature increases (Fig. 2). By comparing Figs. 1 and 2 it can be found that as alcohol concentration is increased, viscosity of the polymer solution decreases, as previously shown.⁹

Amines

To a first approximation amine cosolvents behave similarly to alcohols with the viscosities of solutions with *n*-amines lower for those members in the series with lower alkyl chain length (Fig. 3 and Table III). Over the temperature range investigated (25–75°C) the viscosity of these solutions decreases monotonically as temperature increases (Fig. 3). Unlike alcohols, even at quite low amine concentration, the viscosity-temperature profile is "normal"; that is, the viscosity decreases with increasing temperature.

These findings are consistent with the thesis that amines interact much more strongly with the zinc cation than do alcohols. Thus, those ionomer solutions with amines as cosolvents do not display "isoviscous" behavior at temperatures or cosolvent levels typically observed with alcohols.

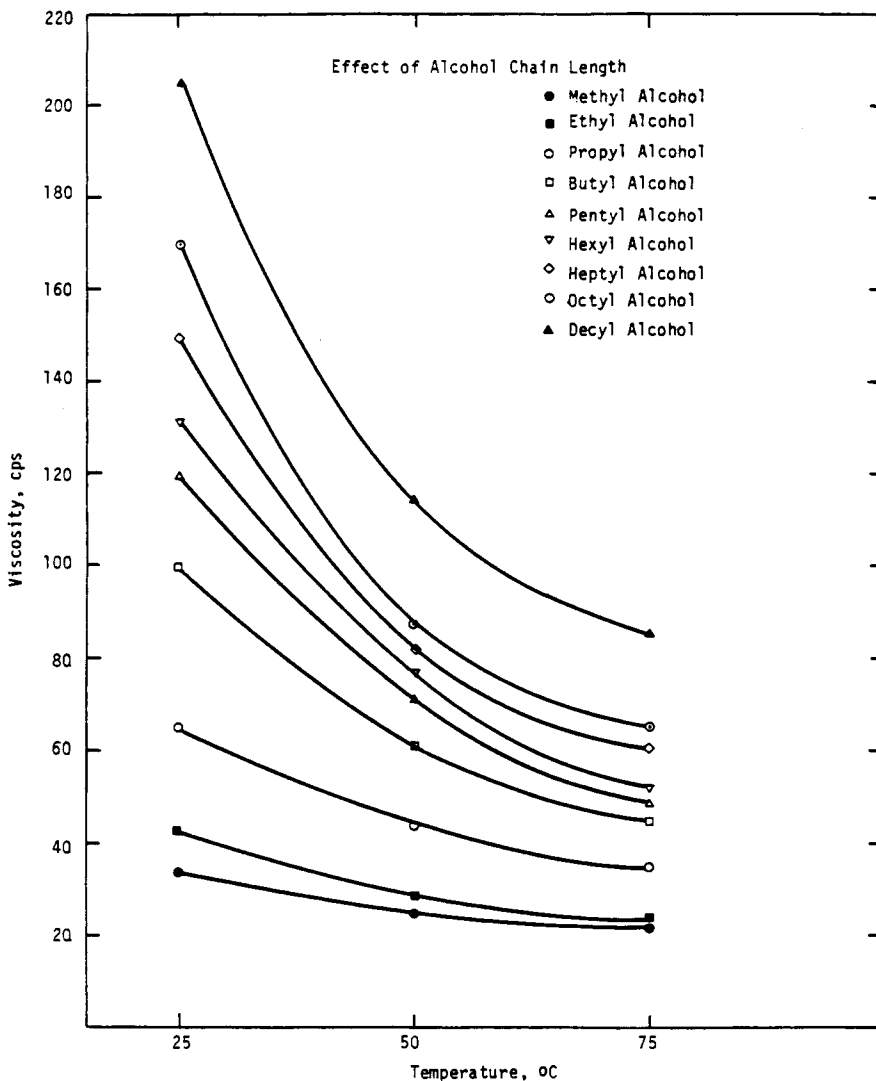


Fig. 1. Viscosity versus temperature, 3% sulfo-EPDM in 1.25 M alcohol-xylene.

Amines of Varying Steric Structure

The influence of different steric structures of butyl, hexyl, and octyl amines on solution viscosity are given in Figs. 4, 5, and 6 and Tables III and IV, respectively. These figures show that, at higher amine concentration, amines with simpler steric structures decrease the viscosity of the polymer solution more effectively. Surprisingly, the opposite behavior is seen at lower amine concentrations (< 0.1 mol/L).

The viscosities of polymer solutions with trialkylamines as cosolvents show minima over the concentration spectrum between 0.025 and 0.05 molar concentration. This amine level is close to that of the sulfonate level present and suggests a 1:1 amine-metal sulfonate interaction. The diamines are

TABLE II
Influence of Various Alcohols on Sulfo-EPDM Solution Viscosities at Different
Temperatures (3% Sulfo-EPDM in Xylene)

Alcohol	Mol/L	Solution viscosity (cP)		
		25°C	50°C	75°C
Methanol	0.25	—	—	—
	1.25	34	25	22
Ethanol	0.25	213	336	607
	1.25	42	29	24
Propanol	0.25	336	557	979
	1.25	65	44	35
Butanol	0.25	576	945	1365
	1.25	99	61	45
Pentanol	0.25	840	1060	1505
	1.25	119	71	48
Hexanol	0.25	1130	1230	1633
	1.25	131	77	52
Heptanol	0.25	1153	1230	1634
	1.25	150	82	60
Octanol	0.25	1182	1110	1631
	1.25	169	87	65
Decanol	0.25	1525	1247	1856
	1.25	204	114	85

relatively less sensitive in their concentration effect on the viscosity of polymer solutions than the primary amines.

The behavior of trialkylamines at low concentrations can be rationalized as a consequence of a stronger association of the tertiary amines with the zinc cation, thereby reducing ion pair association and solution viscosity. The effect of tertiary amines at higher concentrations is evident with tributyl-, trihexyl-, and trioctylamines and shows a significant viscosity increase with cosolvent concentration.

This behavior is unexpected and not easily explained. We suggest that several amine groups can interact with each metal sulfonate group and thereby increase polymer hydrodynamic volume with a consequent viscosity increase. Similar behavior is not observed with any other cosolvents in our studies; additional studies are in progress to understand this behavior.

The effect of temperature on solution viscosity of zinc sulfo-EPDM with primary, secondary, and tertiary amines is shown in Figs. 3, 7, and 8. In the case of tertiary amines at low concentrations (0.042 *M*), solution viscosity is relatively insensitive to temperature. These results suggest tertiary amines as cosolvents may induce isoviscous behavior with temperature in such solutions, but only at extremely low cosolvent levels.

Effects of Various Structural Isomers on Cosolvent Efficiency

The structure of cosolvent molecules is a major factor determining the degree of interaction between ionic group and cosolvent. These structural effects have been studied with different isomers of butyl alcohols and amines. The results from four butyl alcohols and four butyl amines (normal butyl, isobutyl, secondary butyl, and tertiary butyl; Fig. 9, Table V) show

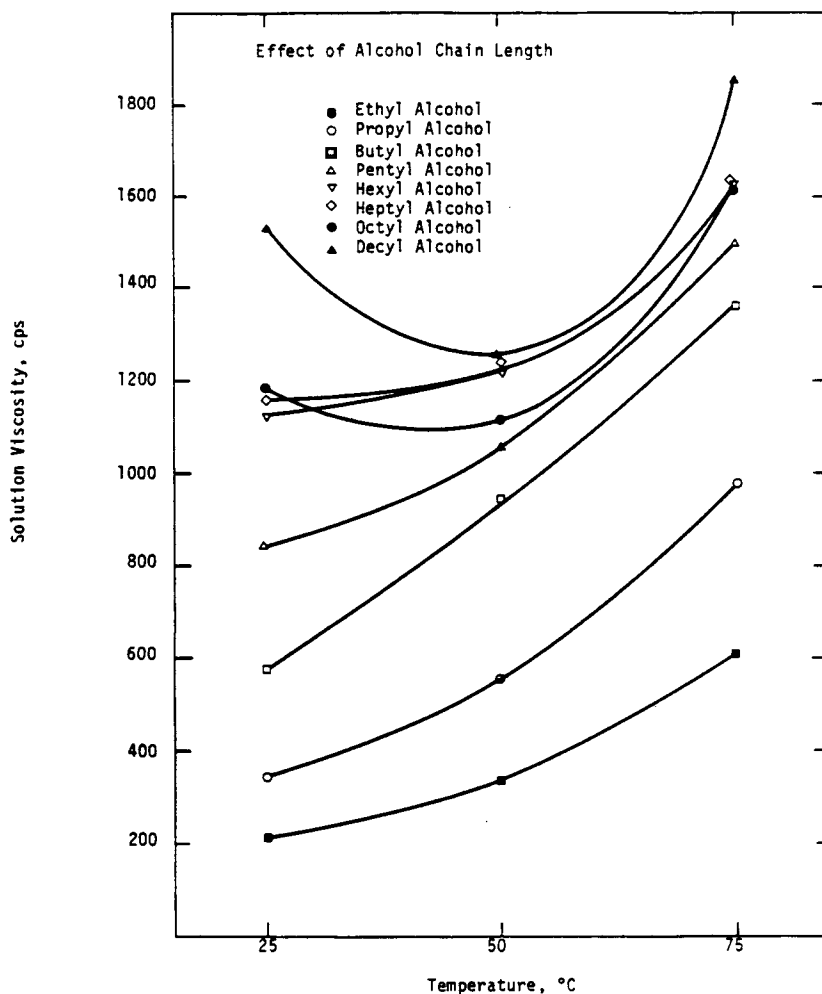


Fig. 2. Viscosity versus temperature, 3% sulfo-EPDM in 0.25 *M* alcohol-xylene.

that normal alcohols or amines give the lowest viscosity, followed by iso and secondary isomers. The tertiary butyl isomers give ionomer solutions of the highest viscosity. These data indicate that those cosolvents with least steric hindrance are more effective in interacting with the zinc cation. On a molar basis, amines are much more effective in reducing the viscosity of the polymer solution compared with the corresponding alcohols. An exception appears to be tertiary butylamine. Viscosities of solutions prepared with this cosolvent were consistently higher than that obtained with the corresponding tertiary butyl alcohol. Solvation of the zinc cation is apparently reduced markedly in the case of *t*-butyl amine cosolvent.

Analogous experiments with zinc sulfo-EPDM of lower sulfonate level (10 mE per 100 g) and three different cyclic amines as cosolvents are shown in Fig. 10 and compared with methanol. Sulfo-EPDM of this sulfonate level is soluble in xylene with a viscosity of about 6000 cP at 2% polymer under these conditions. It is apparent that, as the amine concentration approaches

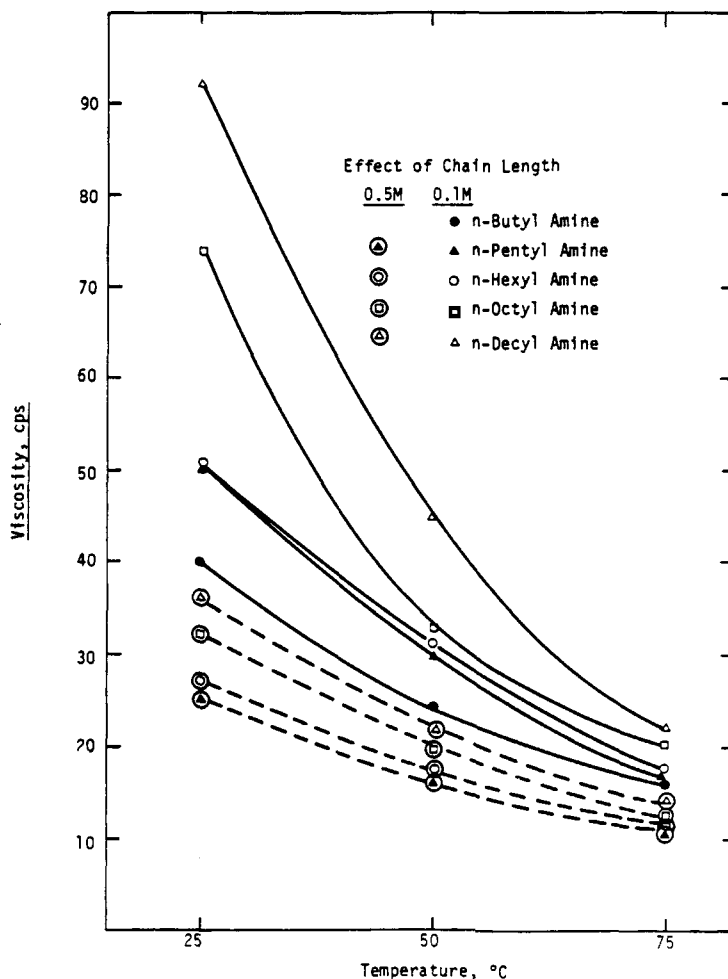


Fig. 3. Viscosity versus temperature, 3% sulfo-EPDM in 0.1 M *n*-amine-xylene and 0.5 M *n*-amine-xylene.

TABLE III
Influence of Various Amines on Sulfo-EPDM Solution Viscosities at Different Temperatures (3% Sulfo-EPDM in Xylene)

	Amine (Mol/L)	Viscosity (cP)			Amine (Mol/L)	Viscosity (cP)		
		25°C	50°C	75°C		25°C	50°C	75°C
<i>n</i> -Butyl	0.10	40	24	16	0.50	41	23	12
<i>n</i> -Pentyl	0.10	50	30	17	0.50	25	16	11
<i>n</i> -Hexyl	0.10	50	31	17	0.50	27	17	11
<i>n</i> -Octyl	0.10	74	32	20	0.50	32	20	12
<i>n</i> -Decyl	0.10	82	45	22	0.50	36	22	14
Diethyl	0.10	31	19	14	0.50	24	16	12
Dibutyl	0.10	53	25	20	0.50	28	20	17
Dihexyl	0.10	74	57	27	0.50	38	28	22
Diocetyl	0.10	97	76	31	0.50	51	38	28
Tributyl	0.042	42	35	26	0.20	59	28	20
Trihexyl	0.042	38	27	24	0.20	58	34	20
Triocetyl	0.042	41	30	26	0.20	66	35	23

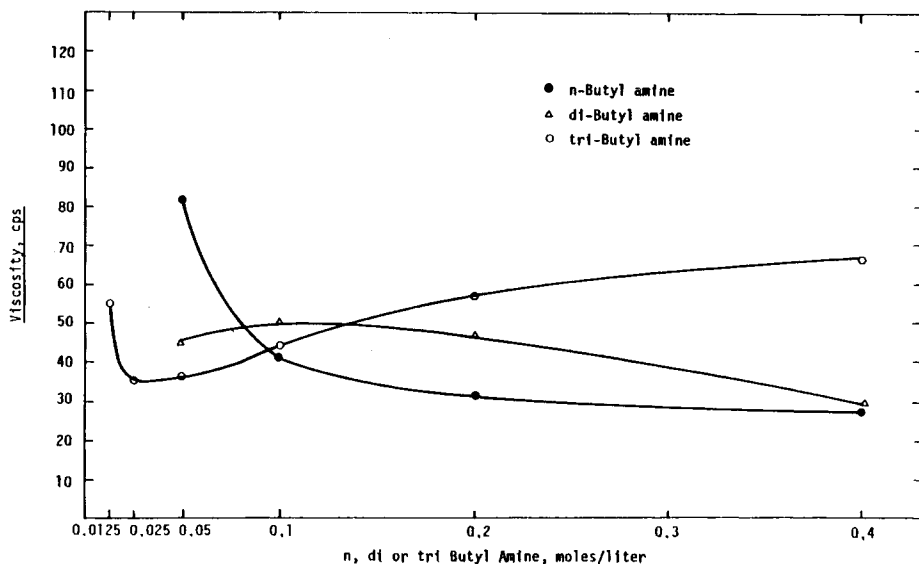


Fig. 4. Viscosity versus amine concentration, 3% Sulfo-EPDM in *n*, di-, or triamine-xylene.

the zinc sulfonate concentration, ionic association is nearly eliminated. (The precursor EPDM has a viscosity of about 5 cP at 2% concentration in xylene.) In this respect, 2,2'-dipyridyl is nearly 1000× more effective than methanol in disrupting ion pair association. It is also evident that substantial reductions in viscosity occur at amine contents less than stoichiometric levels based on sulfonate content. Presumably, this is a consequence of the marked influence of a few ionic associations dominating solution viscosity so that a slightly reduction in associating groups dramatically reduces solution viscosity.

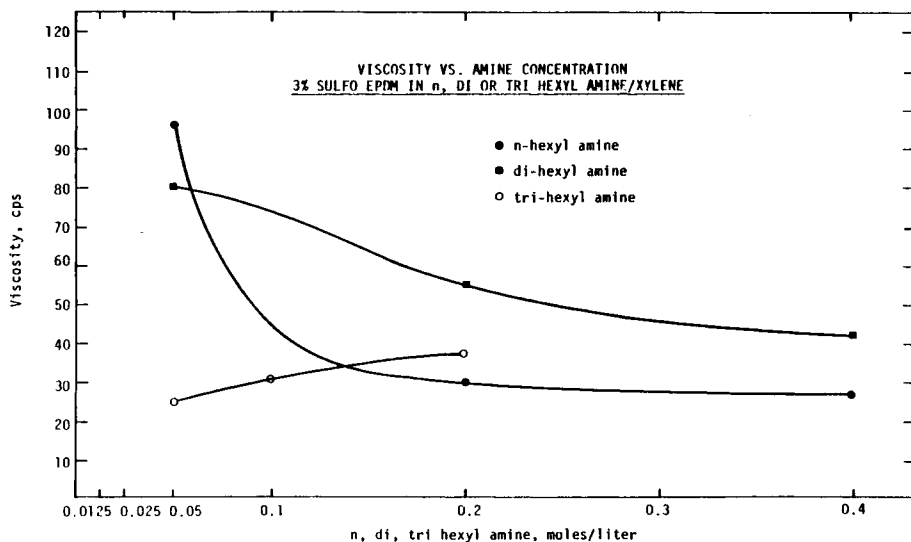


Fig. 5. Viscosity versus amine concentration, 3% Sulfo-EPDM in *n*, di, or tri-hexyl amine-xylene.

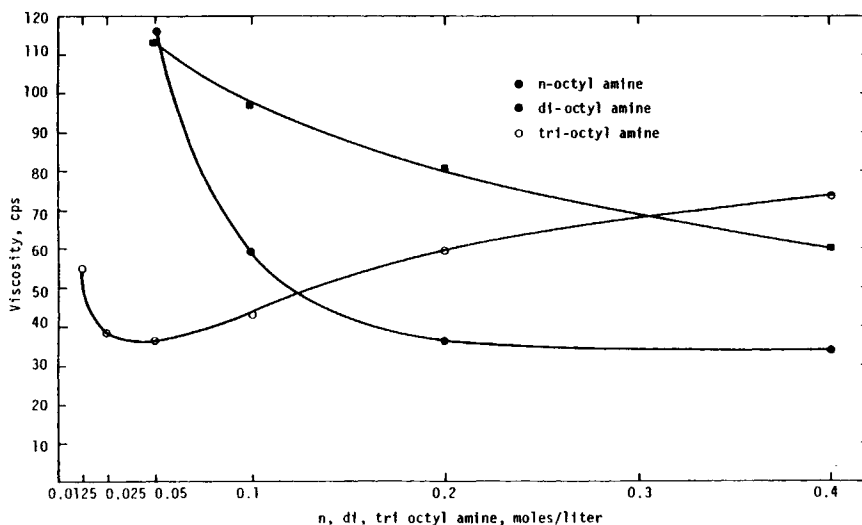


Fig. 6. Viscosity versus amine concentration, 3% Sulfo-EPDM in *n*, di, or trioctyl amine-xylene.

Comparing SPS and CPS with Amines as Cosolvents

Sodium Sulfonated Polystyrene (SPS)

Reduced viscosity measurement at different SPS concentrations were made. The curves for *n*-butyl, *n*-octyl, and diethylamine (Fig. 11) (5 vol %) are all relatively close, indicating the degree of interaction between ionic groups of SPS and mono- and diamines are approximately the same. Under these conditions the interactions of amines with the sodium cations are about the same as those observed with alcohols.⁹ The interaction of amines with the zinc cation are much more pronounced than with sodium.

TABLE IV
Influence of Primary, Secondary, and Tertiary Amines on Sulfo-EPDM Viscosities, (3% Sulfo-EPDM, Zn Salt in Xylene, Viscosities in Centipoise at 25°C)

Amine (mol/L)	0.0125	0.025	0.05	0.1	0.2	0.4
<i>n</i> -Butyl	—	—	81	41	32	27
<i>n</i> -Pentyl	—	—	94	47	30	24
<i>n</i> -Hexyl	—	—	96	45	30	27
<i>n</i> -Octyl	—	—	116	59	36	33
<i>n</i> -Decyl	—	—	210	89	52	36
Diethyl	—	—	53	51	35	24
Dibutyl	—	—	45	50	46	29
Dihexyl	—	—	80	74	55	42
Diocetyl	—	—	113	97	81	60
Tributyl	55	36	36	44	57	66
Trihexyl	—	—	24	31	38	—
Triocetyl	55	38	37	43	59	73

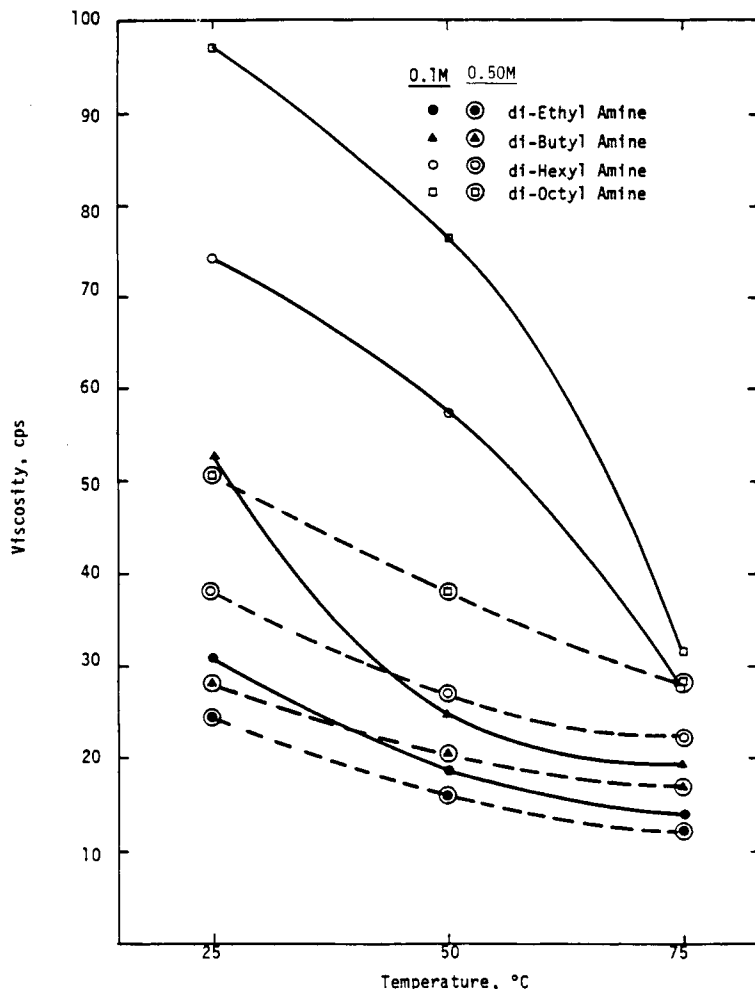


Fig. 7. Viscosity versus temperature, 3% sulfo-EPDM in 0.1 and 0.50 M diamine in xylene.

Sodium Carboxylated Polystyrene (CPS)

Carboxylated polystyrene does not dissolve in *n*-amine-xylene solution. It is concluded that amine molecules do not interact with the sodium carboxylated group to the same degree that they do with the sulfonated polymer. This behavior is consistent with previous studies.⁷

Interpretations

To a first approximation the alcohols examined as cosolvents in this study interact with sulfonated polymers in accord with the simple equilibrium previously proposed. This "solvation" is presumed to arise from a rather weak ion dipole interaction between the metal cation and the alcohol, thereby weakening the ion pair interactions prevailing in the absence of cosolvents. This hypothesis explains the available information relating to alcohol cosolvents, but additional information is required to describe the solvated species. Current studies suggest that the alcohol-cation interaction is suf-

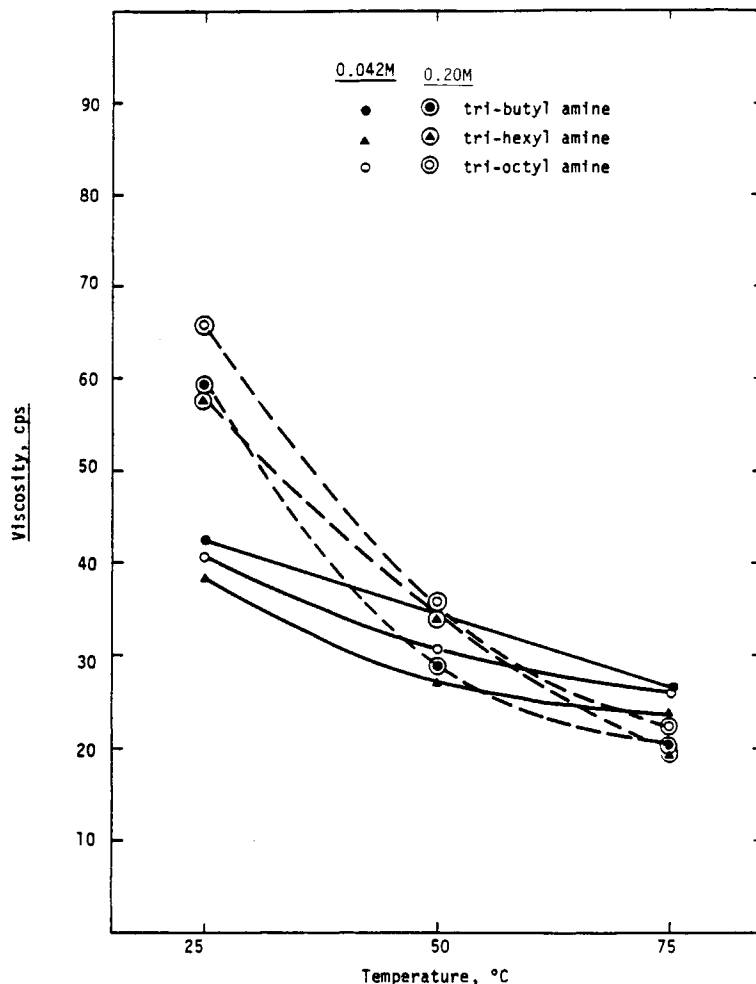


Fig. 8. Viscosity versus temperature, 3% sulfo-EPDM in 0.042 and 0.20 *M* triamine-xylene.

ficiently weak that nearly 1000 mol of alcohol are required per cation to solvate 50% of the cation species. Additional studies are in progress.

In the case of the amine cosolvents, it is apparent that the interactions of amines and zinc sulfo-EPDM are different from those of alcohols or other cosolvents. Clearly, the ability of amines to coordinate with the zinc cation to form a strong complex provides a rationale for these viscosity observations. Similar complexes are not observed with such cations as sodium and magnesium, but appear with zinc and transition metal cations. The practical implications of these findings in polymer-polymer interactions will be discussed in future publications.

Some evidence comparing zinc and magnesium sulfo-EPDM in xylene with methanol and trioctylamine cosolvents is shown in Table VI. Although the viscosities of all four solutions are comparable at polymer concentrations of 1% or less, there is a marked difference at higher polymer concentrations,

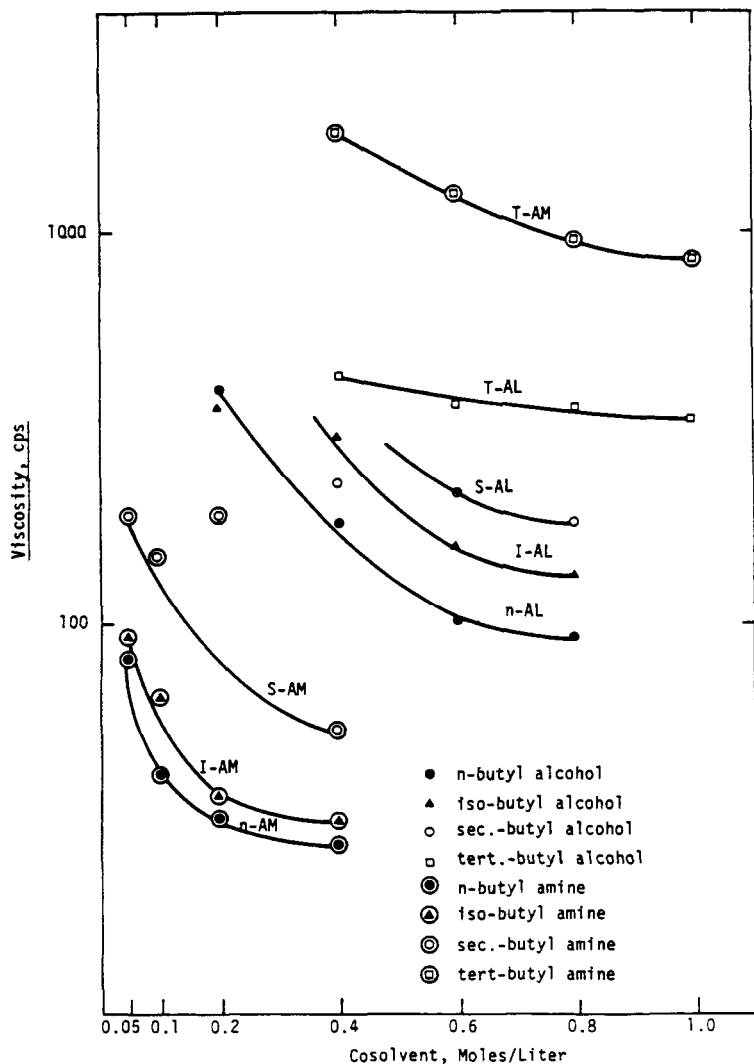


Fig. 9. Viscosity versus cosolvent concentration, 3% sulfo-EPDM in xylene.

TABLE V
Cosolvent Efficiency and Viscosity of Normal, Iso, Secondary, and Tertiary Butyl Alcohols and Amines (3% Conc. Sulf. EPDM Zn Salt in Xylene)

Cosolvent (mol/L)	0.05	0.1	0.2	0.4	0.6	0.8	1.0
<i>n</i> -Butyl alcohol	Gel	Gel	(400)	181	102	92.4	—
Iso-butyl alcohol	Gel	Gel	(360)	(300)	158	138	—
sec-Butyl alcohol	Gel	Gel	Gel	(230)	217	192.5	—
tert-Butyl alcohol	Gel	Gel	Gel	434	369	360	334
<i>n</i> -Butylamine	81.2	40.9	31.9	27.4	—	—	—
Iso-butylamine	92.3	64.8	36.3	31.0	—	—	—
sec-Butylamine	(190)	(150)	(190)	53.5	—	—	—
tert-Butylamine	—	—	—	1854	1294	970	872

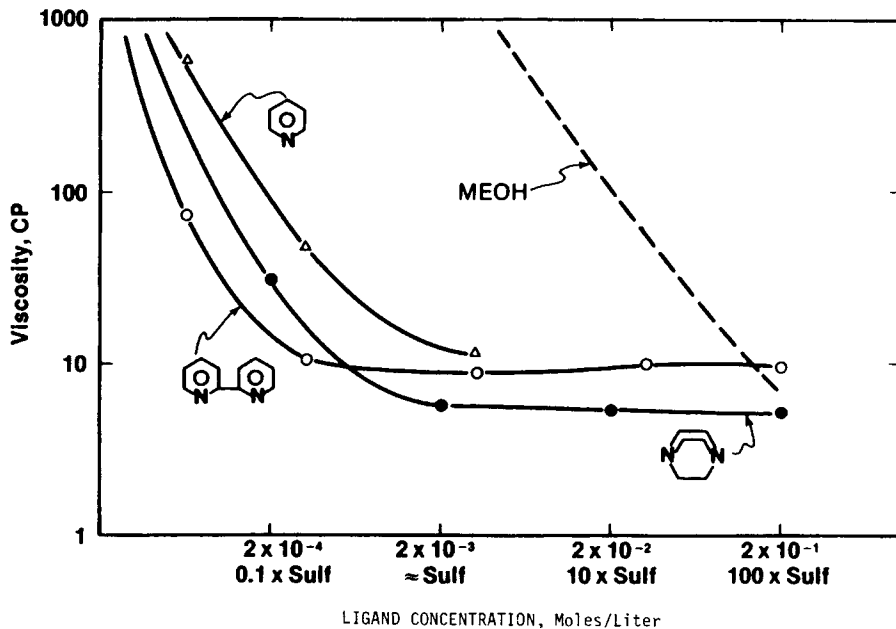


Fig. 10. Effect of various ligands on solution viscosity (2% concentration sulfo-EPDM (10 mEq, Zn) in xylene).

especially at 4% polymer. The Mg sulfo-EPDM/trioctylamine system displays very high viscosities, demonstrating a very weak amine-magnesium interaction as suggested above. In the case of the methanol as cosolvent for both polymer samples, the viscosities at 4% polymer are similar to that expected for the unfunctionalized EPDM (about 40 cP). Therefore, little ion pair association is present. The trioctylamine cosolvent virtually eliminates ion pair association for the zinc salt, even though the amine cosolvent is present at a molar level of about 1/10 that of the alcohol cosolvent. These results suggest that, with those metal cations, which normally will not form coordinate complexes, alcohols and amines will behave similarly with relatively weak solvation tendencies. In the case of zinc and transition metal, a strong interaction occurs with amines and a relatively weak one with alcohols.

Based on the results achieved thus far with the amines of this study, we can suggest the following.

1. Normal amines employed as "cosolvents" appear much more effective as cosolvents when combined with zinc sulfo-EPDM, approaching a 1:1 stoichiometric relationship between zinc and amine.

2. The amine-zinc sulfonate "complex" is much stronger and persists to a higher temperature than is the case for alcohols. From a practical viewpoint amines, even at very low levels, can have pronounced effects on the bulk and solution behavior of zinc sulfonate ionomers, a phenomenon that has not been clearly delineated in the published literature.

3. Steric features of the amines play an extremely important role in the strength of the zinc sulfonate-amine complex. For example, tertiary butylamine is substantially less effective than *n*-butylamine in solvating the zinc sulfo-EPDM, as judged by solution viscosity.

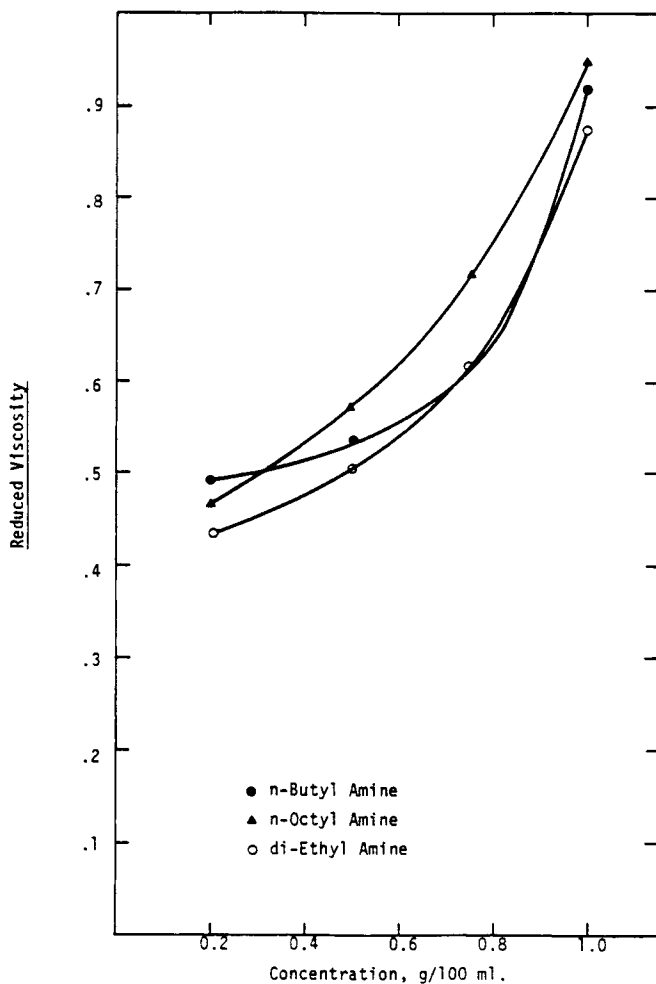


Fig. 11. Reduced viscosity versus concentration, 1.7 mol % sulfopolystyrene Na salt in xylene 5% amine cosolvent.

TABLE VI
Viscosity (Centipoise) of Metal-Sulfo-EPDM (20 mEq) Solutions Comparing Magnesium and Zinc Cations with Methanol and Trioctyl Amine as Cosolvents (5 Vol %)

Polymer concentration (g per 100 ml)	Zinc sulfo-EPDM		Magnesium sulfo-EPDM	
	5% Methanol, 95% xylene	5% Trioctylamine, 95% xylene	5% Methanol, 95% xylene	5% Trioctylamine, 95% xylene
0.125	0.79	0.88	0.81	0.90
0.25	0.88	1.01	0.93	1.04
0.5	1.15	1.4	1.24	1.45
1	2.1	2.7	2.13	3.09
2	7.4	8.9	6.5	18.1
4	49.6	46.6	47.9	795.0

4. Limited studies with sodium sulfonate polystyrene and amine cosolvents suggest much weaker interactions occur with such systems. Under these conditions amines more closely parallel the behavior of alcohols, as would be expected. Similar results are observed with magnesium sulfo-EPDM.

CONCLUSIONS

Of the various functional group types screened, amines and alcohols were found to be effective cosolvents for zinc sulfo-EPDM, with amines exhibiting a very strong interaction. This behavior is consistent with a coordination complex being formed between zinc and amine. All other cosolvents display a much weaker interaction with zinc sulfo-EPDM such that homogenous solutions are not obtained.

For both amines and alcohols, within a homologous series, analogs of shorter hydrocarbon chain length solvate the ionic groups of the sulfo-EPDM more effectively and produce solutions of low viscosity.

The effect on solution viscosity of varying the steric structure of amines is dependent upon the concentration of amine introduced. At high levels (0.2–0.4 mol/L), simpler steric structure produces lower viscosity; at low levels (about 0.05 mol/L) the opposite trend prevails. An explanation for this reversal is not yet available.

The effect of structural isomerism for both alcohols and amines in their degree of interaction with the ionic groups in decreasing cosolvent efficiency is normal > iso > secondary > tertiary (alcohol). Tertiary butylamine appears to be anomalous, producing the highest viscosity solution in a given series.

Amines were found to be effective as cosolvents (similar to alcohols) for sulfonated polystyrene (Na salt) but ineffective in their interaction with a carboxylated polystyrene sodium salt. Little difference was noted on reduced viscosity versus cosolvent concentration in comparing n-butyl, n-octyl, and di-ethyl amines with solutions of sodium sulfopolystyrene. Their behavior is quite similar to that of alcohols with this class of cations.

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