



Chapter III

Results and Discussion

As emphasized in Chapter I the sulfonation of simple alkenes with SO_3 and SO_3 complexes can lead to different reaction mechanisms with the resulting products being a function of the type of alkenes, sulfonating reagent, solvent, and temperature.

In this case, NR contains a double bond in each repeating unit, which makes it highly reactive to sulfonation by acetyl sulfate. Unlike EPDM, where the number of double bond can be controlled, this cannot be done with NR. The work done by Makowski et al. [14] was carried out with EPDM having an amount of about 5 wt% double bonds in the ter-polymer only. The heterogeneous solutions obtained in benzene and hexane medium, mentioned in the previous chapter, were likely to be an indication of a non-homogeneous sulfonation reaction along the rubber chains as a result of the presence of a double bond in each polymer unit. Only in a CHCl_3 medium obtained a homogeneous solution but not above a concentration of 0.80 mole% of sulfonic content. Above this concentration a heterogeneous solution was also obtained.

Free sulfonic acids are not stable for a long time at elevated temperature, and for extended periods at room temperature, they tend to degrade and crosslink. Therefore, after the determination of the sulfonic content by titration with 0.01 N ethanolic KOH, neutralization with $Zn(OAc)_2$, $Pb(OAc)_2$ and $Mg(OAc)_2$ was immediately followed to form the ionic bridge which is a more stable system. It assumed that all crosslink sites are $-SO_3^- M^{2+} SO_3^-$. Mohajer and coworkers [18] showed that in order to obtain a good ionomer, the neutralization should be carried out to the equivalence point i.e. the stoichiometric neutralization point.

They studied the stress-strain behavior as a function of the type of neutralization. The partial neutralization resulted in a material displaying poor elongation and low recovery. This is expected since unionized functional groups have weak interaction and do not participate in the formation of strong multiplet junction points. Moreover the unneutralized acid groups will degrade over a period of time. On the other hand, excess neutralization did not change the Young's modulus because it did not significantly increase the number of junction points and the molecular weight between "crosslinks", M_c . The addition of excess neutralizing agent to the ionomer resulted in the absorption of the inorganic component by the polymer matrix and acted as filler, which influenced the rheological and thermomechanical properties. Usually, neutralized products

are not covalent crosslinked, however, as shown by their solubility in a mixture of hydrocarbon and alcohol that prefers to solvate ionic moieties in solution [13].

3.1 Characterization of Sulfonated NR

In order to observe the chemical and possibly the physical changes taking place during sulfonation and neutralization, modified-NR was characterized by IR, and ^1H - and ^{13}C NMR spectroscopy.

3.1.1 IR Analysis

As expected, these changes were readily observed in the IR spectrum by comparison with NR as shown in Figures 3.1-3.3.

Table 3.1. Observed functional group changes in sulfonated NR

Wavenumber (cm^{-1})	Assignment	Change
3400	✓ OH	Increase
1170	✓ S=O	Increase
1030	✓ S=O	Increase
600-700	✓ C-S	Increase

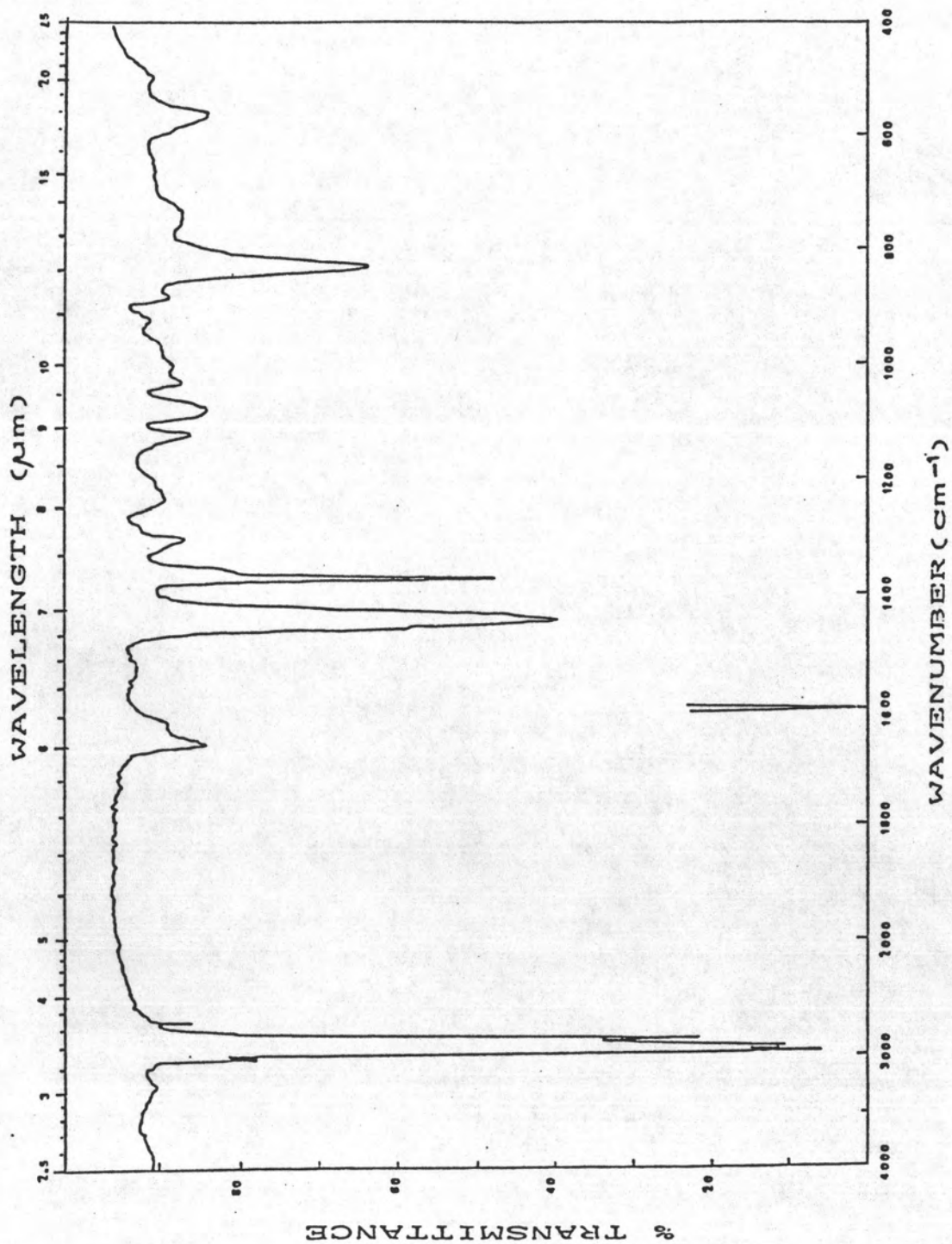


Figure 3.1. Infrared spectrum of NR (KBr pellet).

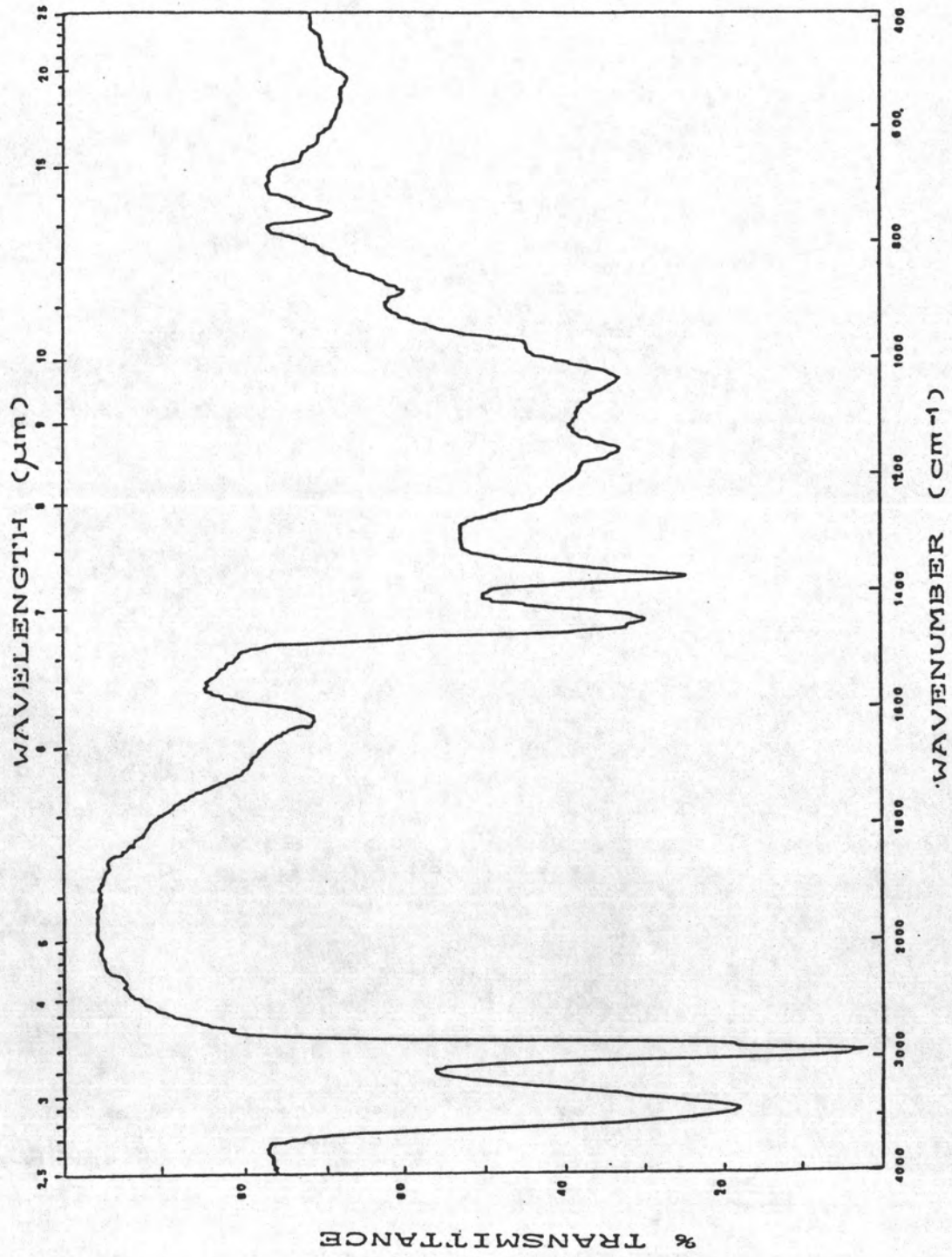


Figure 3.2. Infrared spectrum of 12.0 mmole of sulfonic acid per 100 g NR (KBr pellet).

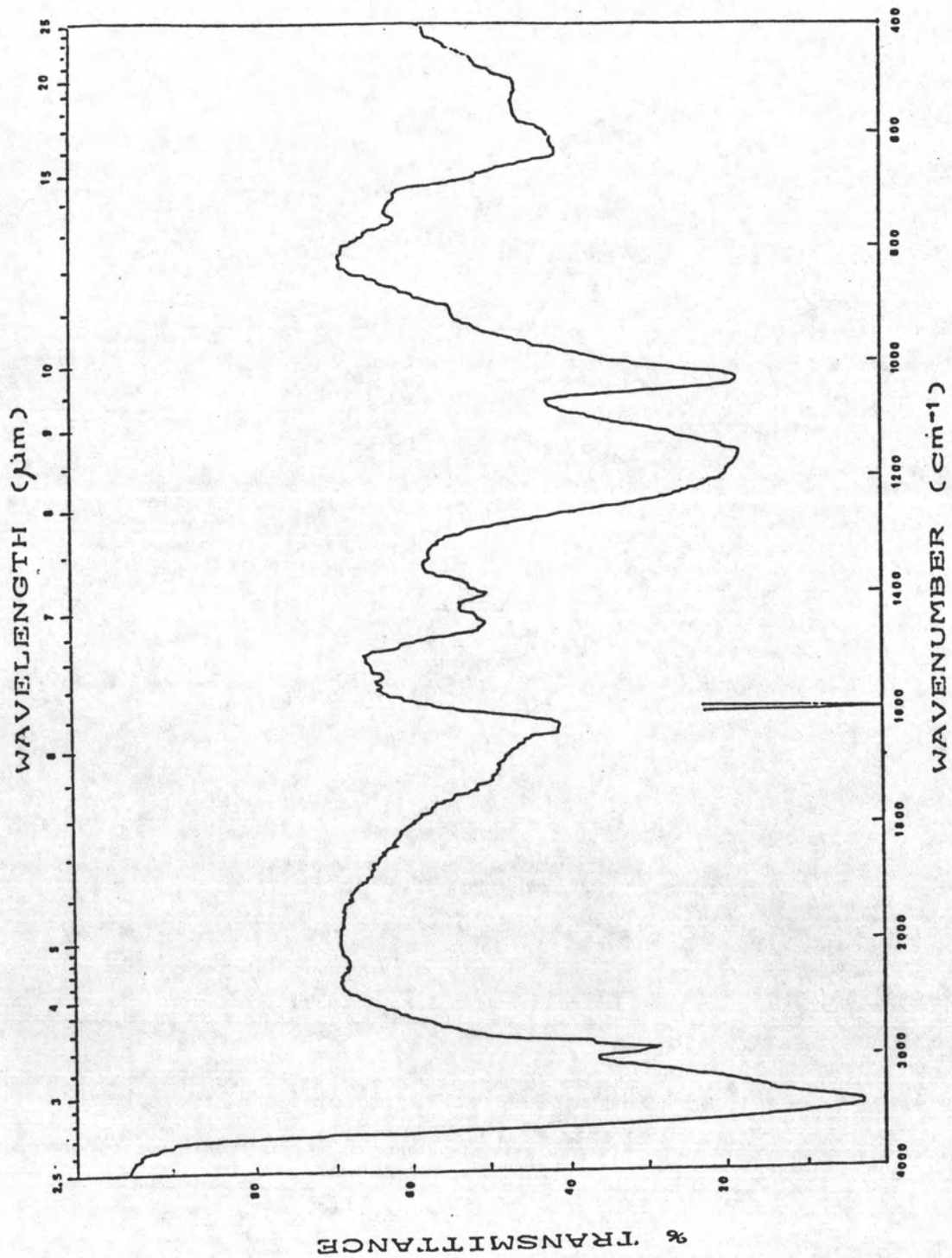


Figure 3.3. Infrared spectrum of 33.3 mmole of sulfonic acid per 100 g NR (KBr pellet).

Figure 3.1 shows the starting NR, similar to the cis-1,4-polyisoprene of Aldrich reference spectra [26], and Figures 3.2-3.3 represent the sulfonated rubber at a low and high sulfonate content of 12.0 and 33.3 mmole of sulfonic acid per 100 g NR. The new IR absorption bands characteristic of the modified-NR are given in Table 3.1.

At 3400 cm^{-1} absorption of the OH stretching vibration of the $-\text{SO}_2-\text{OH}$ group occurs. Two other stretching bands appeared at 1030 and 1170 cm^{-1} representing the symmetric and asymmetric vibration of S=O, respectively. And at $600-700\text{ cm}^{-1}$ the weak absorption band of the C-S is observed. These four major peaks confirm that sulfonation along the polymer chain took place. Also, at a higher sulfonic group content usually intra- and/or intermolecular hydrogen bonding interaction occur, and affect the shape of the absorption bands. This is evidenced by a broadening of the OH and S=O stretching bands in Figure 3.2 and 3.3, illustrating an increase in hydrogen bonding as the $-\text{SO}_3\text{H}$ concentrations increased.

3.1.2 ^1H NMR Spectra

The ^1H NMR spectra of NR and sulfonated NR are shown in Figures 3.4-3.5, and the chemical shift values of the different types of proton are given in Table 3.2. The sulfonic proton could not be detected as acidic protons are known to be very labile regarding low sulfonation and thus very difficult to detect by NMR analysis. The fast proton

exchange between the sulfonic proton and the deuterated chloroform is faster than the rate of detection. As indicated in the IR section, the presence of the sulfonic group is apparent in the IR spectrum but could not be confirmed by ^1H NMR analysis. The presence of sulfur, however, was detected qualitatively by X-ray fluorescence.

Table 3.2. Observed ^1H NMR chemical shifts of NR and sulfonated NR.

Carbon Assignment	Chemical shift of NR (ppm)	Type of proton	Chemical shift of Sul. NR (ppm)	Type of proton * could not be identified
1	2.05	$-\text{CH}_2-\text{C}(\text{CH}_3)=$	2.02	$-\text{CH}_2-\text{C}(\text{CH}_3)=$
2	5.11	$=\text{CH}$	5.11	$=\text{CH}$
3	2.01	$-\text{CH}_2-\text{CH}=\text{}$	2.02	$-\text{CH}_2-\text{CH}=\text{}$
4	1.66	$-\text{CH}_3$	1.67	$-\text{CH}_3$
5	-	-	2.61	*
6	-	-	2.68	*
7	-	-	2.75	*
8	-	-	4.72	*

Four additional proton resonance peaks are observed after sulfonation. The peak at 4.72 ppm is indicative of a $\text{CH}_2=$ proton; and the three other peaks at 2.61, 2.68 and

JEOL FX-90Q
 SAMPLE NR
 SOLVENT CDCl₃
 ORIGIN _____
 NUCLEUS _____
 IRMODE H-10M2
 PD _____
 FREQU _____
 ORSET _____
 EXREF _____
 TEMPERATURE ΔT
 SCANS _____
 DATE 12/5/87
 OPERATOR HLT
 REMARKS _____

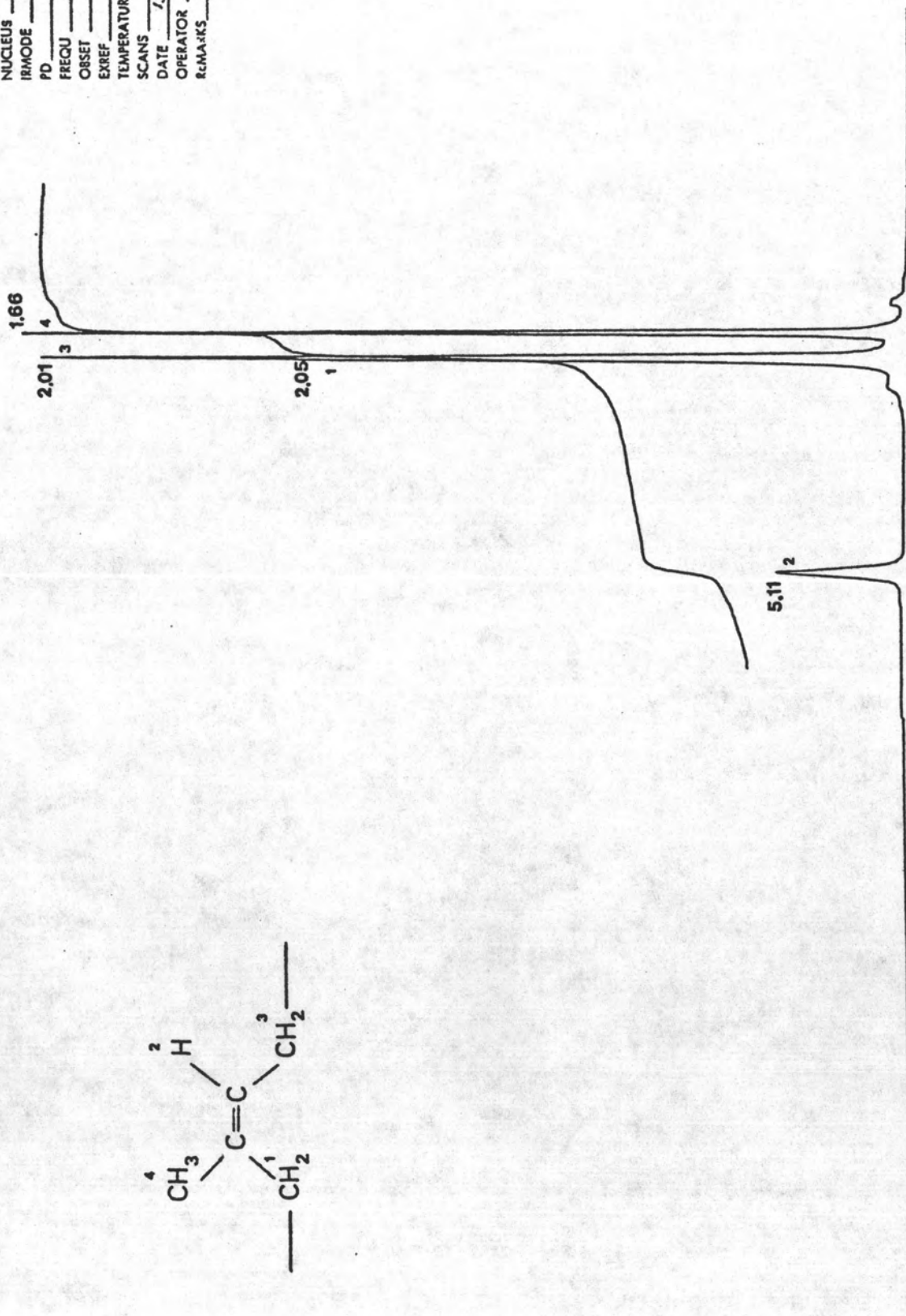


Figure 3.4. ¹H NMR spectrum of NR in CDCl₃.

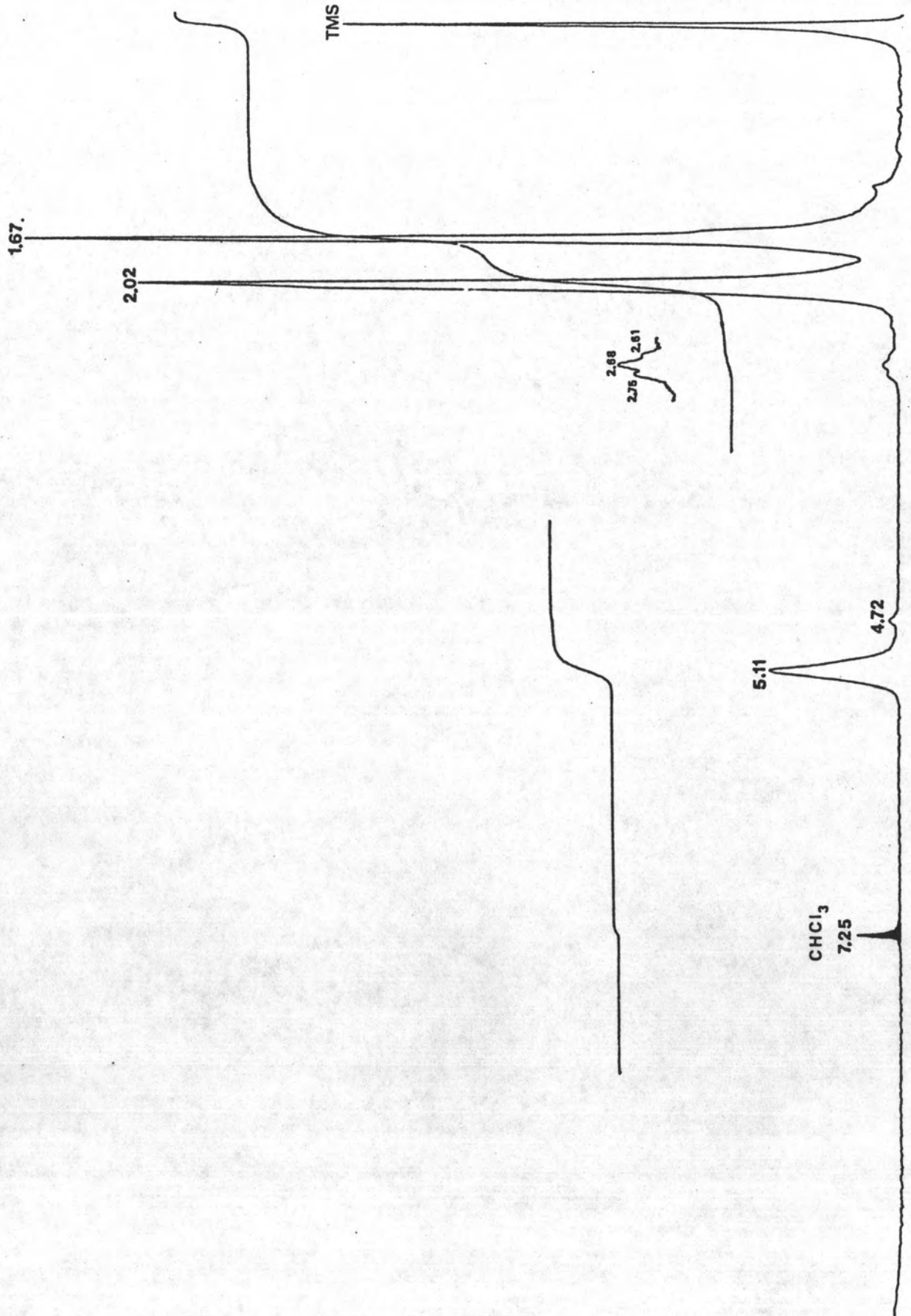


Figure 3.5. ^1H NMR spectrum of sulfonated NR in CDCl_3 .

2.75 ppm are most likely to come from the methine proton at the carbon-3. A similar chemical shift was observed during epoxidation of NR [27] but only one peak was present. The presence of three peaks in our case, cannot presently be explained.

3.1.3 ^{13}C NMR Spectra

The ^{13}C NMR experimental data are listed in Table 3.3 and the respective spectra are shown in Figures 3.6 and 3.7. The modes of analysis were a completely ^1H decoupled C-13 NMR spectrum (COM) and a partially ^1H decoupled C-13 NMR spectrum (OFR).

Table 3.3. Observed ^{13}C NMR chemical shifts of NR and sulfonated NR.

Carbon Assignment	Chemical shift of NR (ppm)	Type of ^{13}C	Chemical shift of Sul. NR (ppm)	Type of ^{13}C * could not be identified
1	32.3	$-\underline{\text{C}}\text{H}_2-\text{C}(\text{CH}_3)=$	32.2	$-\underline{\text{C}}\text{H}_2-\text{C}(\text{CH}_3)$
2	135.2	$\text{CH}_3-\underline{\text{C}}=$	135.2	$\text{CH}_3-\underline{\text{C}}=$
3	125.1	$=\underline{\text{C}}-\text{H}$	125.0	$=\underline{\text{C}}-\text{H}$
4	26.5	$-\underline{\text{C}}\text{H}_2-\text{CH}=\text{}$	26.4	$-\underline{\text{C}}\text{H}_2-\text{CH}=\text{}$
5	23.4	$-\underline{\text{C}}\text{H}_3$	23.4	$-\underline{\text{C}}\text{H}_3$
6	-	-	15.9	*
7	-	-	39.6	*
8	-	-	40.0	*
9	-	-	124.1	*
10	-	-	123.4	*

In Figure 3.7 (COM mode), there are two methyl carbon resonances at 23.4 and 15.9 ppm. The peak at 15.9 ppm indicates that a new methyl carbon was formed during sulfonation but cannot be identify at this stage of the investigation. Regarding the peaks at 39.6 and 40.0 ppm they are indicative of a substituted carbon by the sulfonic group. Due to the electron withdrawing effect of $-\text{SO}_3\text{H}$ on carbon-3, a tertiary carbon atom, a down field chemical shift is expected. The presence of two peaks at about the

same resonance could be a result of a rearrangement effect or a different configuration occurring during sulfonation. The two additional peaks at 123.4 and 124.1 ppm suggest a sulfonic substitution at carbon-3 but in this case being a quaternary carbon atom [28] suggesting that a second product is present. The closeness of the two peaks may again be a result of rearrangement or configuration effect.

On the basis of the IR and NMR data, we expect the sulfonated products shown in Figure 3.8 to be either E or F or combination of the two. Also, according to the work done on the sulfonation of unsaturated compounds [23], the experiment conditions used in our case, lead to two products: (a) The acetyl sulfate as the sulfonating agent attacked the double bond at the carbon-3 by substitution of the hydrogen by the SO_3H group for one product, and (b) causing a shift in the double bond between carbon-2 and 5, by elimination of a hydrogen of the methyl group, resulting in a second sulfonated product. Figure 3.9 shows the reaction scheme yielding the two sulfonated NR.

JEOL FX-90Q

SAMPLE NR
SOLVENT CDCl₃
ORIGIN _____
NUCLEUS C-13
IRMODE C-13
PD _____
FREQU _____
OBSSET _____
EXREF _____
TEMPERATURE RT
SCANS _____
DATE 12/5/87
OPERATOR LS
REMARKS _____

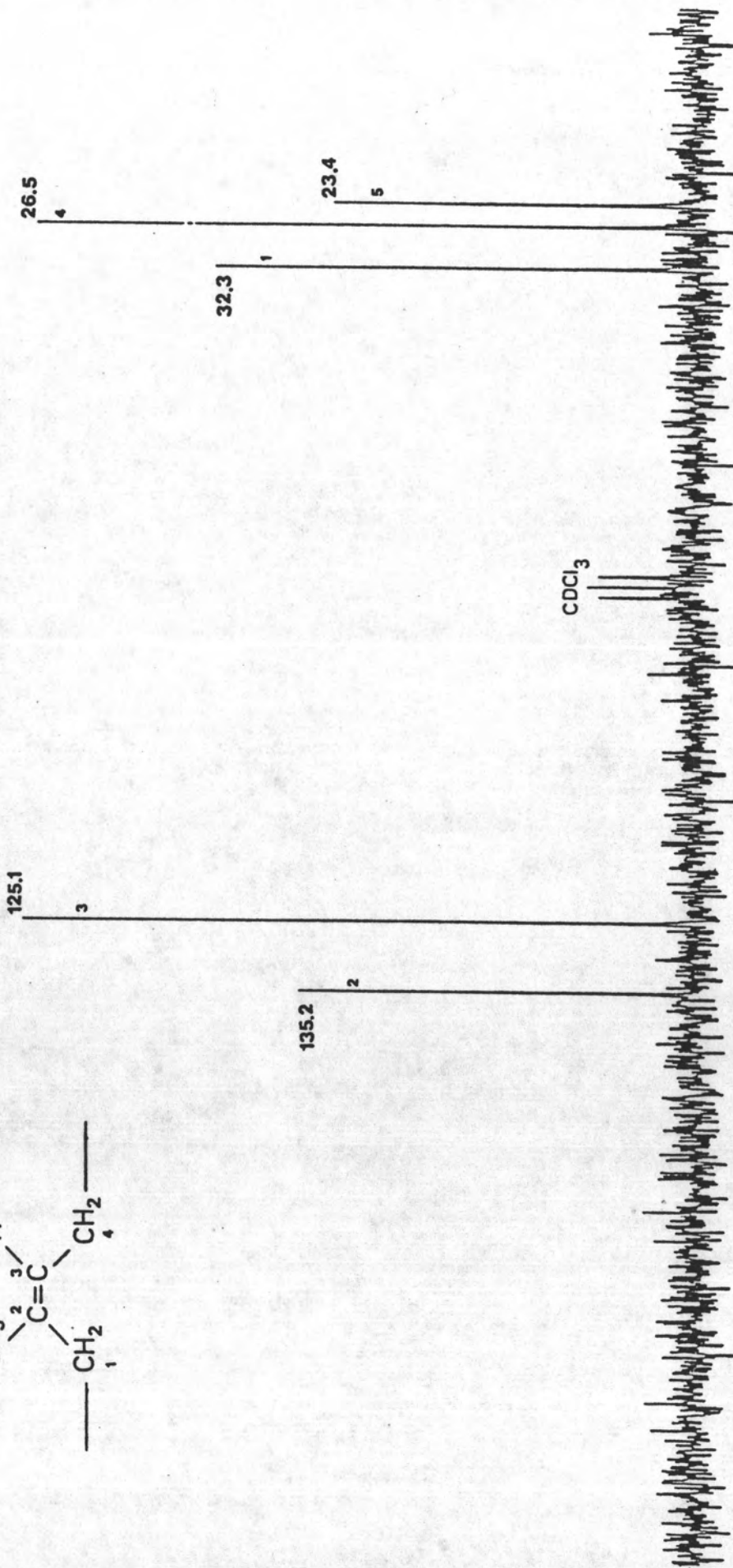
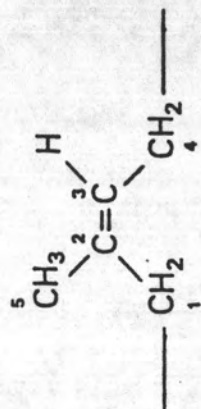


Figure 3.6. ¹³C NMR spectrum of NR in CDCl₃.

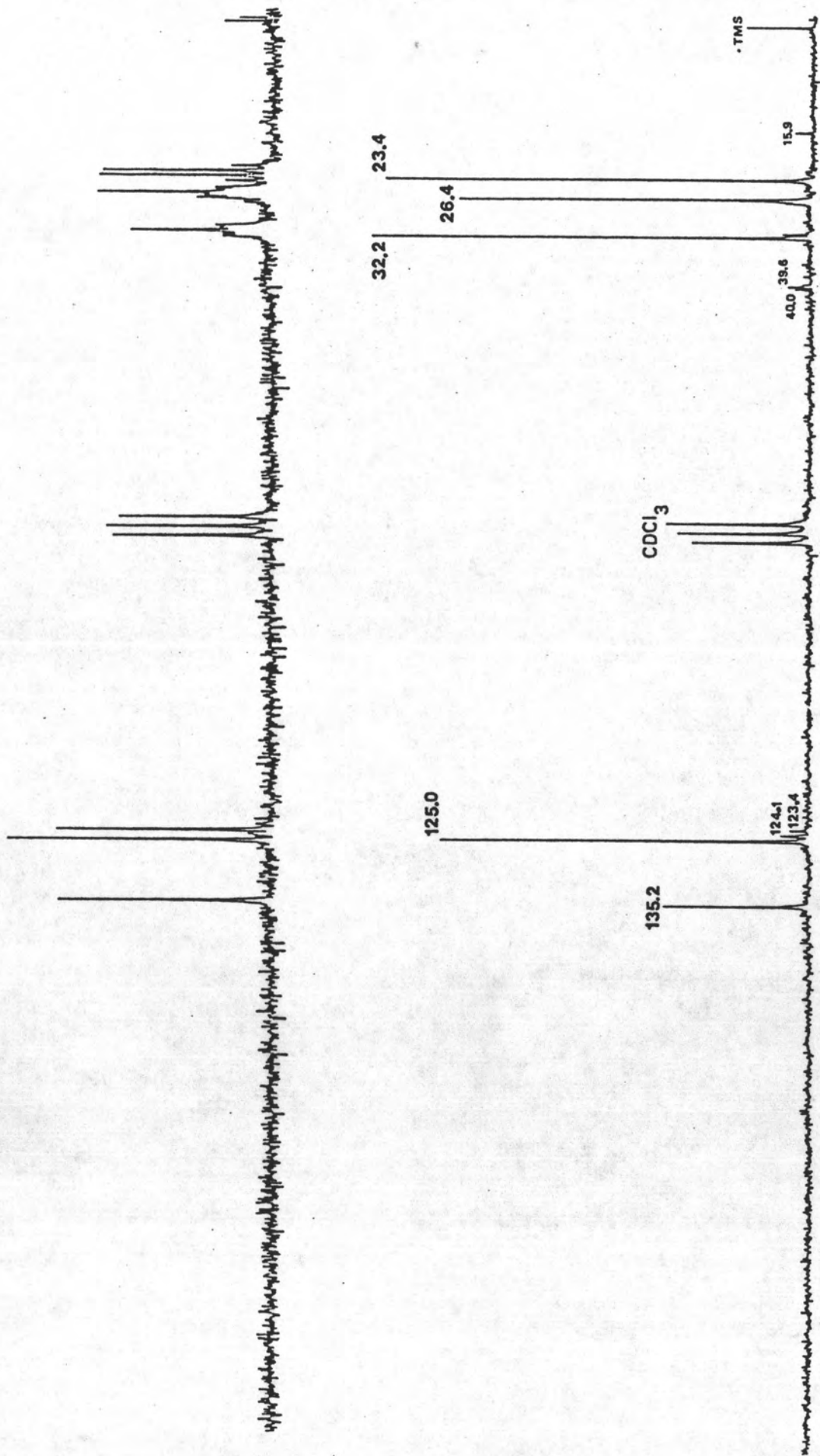


Figure 3.7. ^{13}C NMR spectrum of sulfonated NR in CDCl_3 .

The above spectrum represents the OFR mode and the COM mode is represented below.

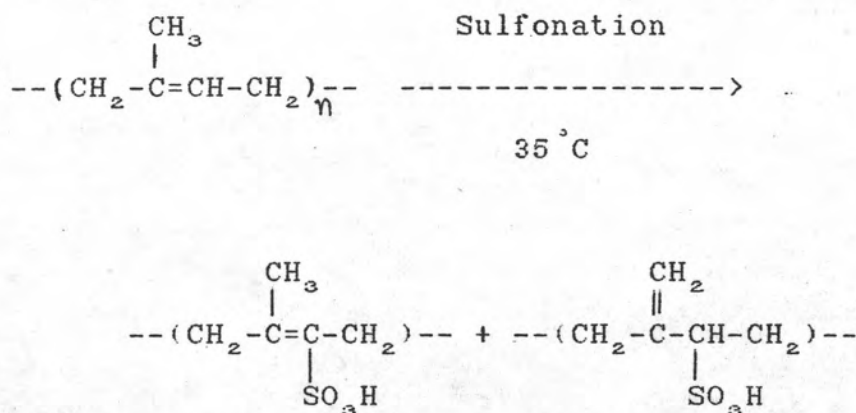


Figure 3.8. Reaction scheme yielding two types of sulfonated NR.

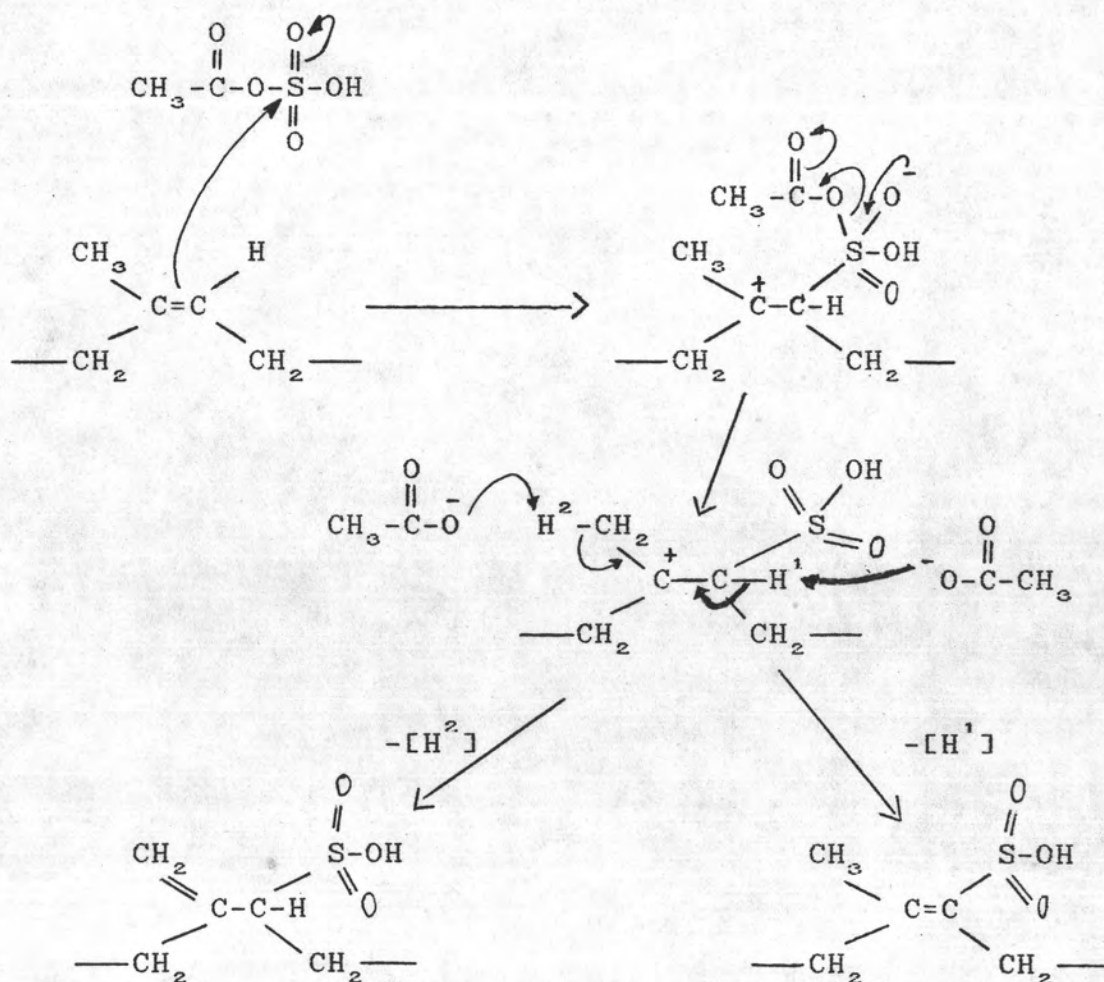


Figure 3.9. Mechanism of sulfonation with acetyl sulfate.

3.2 Effect of Sulfonation on Viscosity-Average Molecular Weight (\bar{M}_v)

An important polymer characterization analysis to perform is the one on the MW of the modified NR. The MW stability during the sulfonation is necessary in our attempt to synthesis NR-ionomers. Changes in the MW during the reaction would obviously affect the properties of the resulting product. In the past many of the problems associated with chemical modification of NR were directly concerned with keeping the MW changes under control [29]. One of the problems encountered is degradation and the other is cyclization. The \bar{M}_v data are given in Table 3.4 indicate a substantial decrease from 3.9×10^5 to 2.1×10^5 .

Table 3.4. Effect of sulfonation on molecular weight

Mole %	Yield %	\bar{M}_v
0.00	—	3.9×10^5
0.18	93.3	2.9×10^5
0.24	92.1	2.6×10^5
0.30	89.6	2.2×10^5
0.38	86.8	2.1×10^5
0.62	88.0	2.1×10^5
0.82	79.2	2.1×10^5

Mole % = (mole of sulfonic acid/1 g of NR) x 68.12 x 100
 68.12 = MW of cis-1,4-polyisoprene repeating unit.

Yield % = $\frac{(\text{weight of sulfonated NR}) \times 100}{(\text{weight of NR})}$

Indeed, the first point that concerned was the propensity of NR to cyclize under acid conditions. Cyclization as well as degradation could cause a considerable drop in solution viscosity. The extent of such reaction depends on the experimental conditions. Cyclization is known to occur at elevated temperature around 100-150°C, and by using a strong mineral acid such as H₂SO₄. This, however, is not our case since the sulfonation was carried out at 35°C and with acetyl sulfate. A free sulfuric acid is usually responsible for cyclization of NR, but since in this study prepared acetyl sulfate with an excess of acetic anhydride, the free sulfuric acid could not be present in the reaction mixture. Cyclization then was not likely to occur under these reaction conditions.

Other side reactions most likely to occur, however, are degradation and crosslinking. The high drop in \bar{M}_v as indicated in Table 3.4 is an indication that chain scission may have occurred rather than crosslinking. Indeed, the NR has a high possibility to bond scission to form allyl radical as represented in Chapter I.

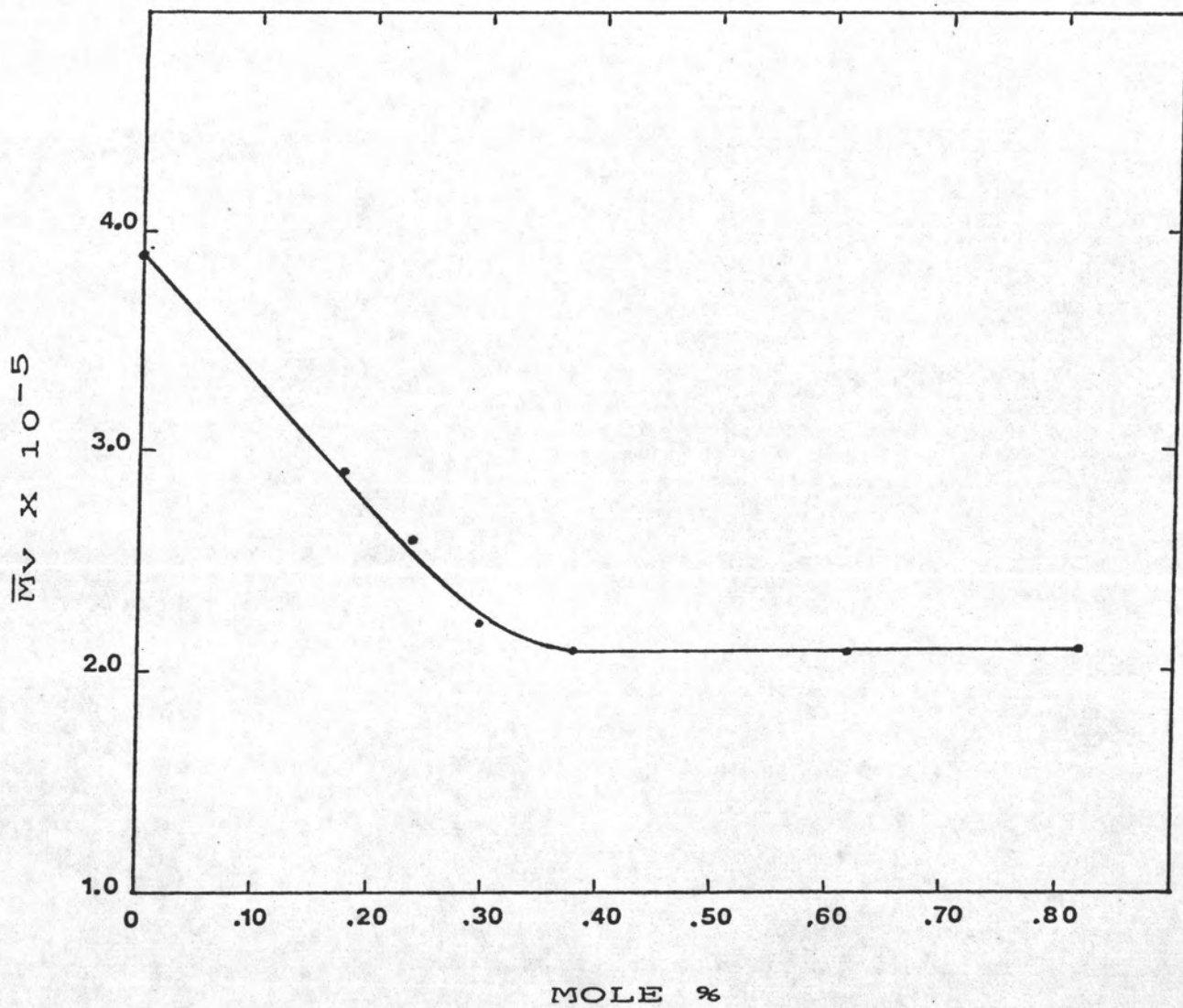


Figure 3.10. Effect of sulfonation on \bar{M}_n .

Figure 3.10 illustrates the \bar{M}_v data, and shows that between 0 and 0.30 mole % of sulfonic acid content the degradation rate is constant. A plateau, however, was reached after 0.30 mole %. This may indicate that at this concentration, a fortuitous balance between a viscosity increase due to sulfonation, and degradation as a result of bond scission, is reached. Indeed, it would be expected that the viscosity of the sulfonated NR would increase. Lundberg and Makowski in their investigation of the sulfonation of polystyrene found an increase in viscosity [30]. In this case, however, the \bar{M}_v of sulfonated NR decreased to a minimum of 2.1×10^5 , which it may refer to as the limiting (critical) molecular weight i.e. the size of the longest molecule which can move without further degradation [31]. Another plausible explanation for the leveling off of the MW as the number of $-\text{SO}_3\text{H}$ groups along the rubber chain was increasing as a result of increasing the acetyl sulfate concentration in the reaction medium, is the formation of hydrogen bonding between the sulfonic groups of a neighboring polymer chain. Indeed, the formation of hydrogen bonding below a concentration of 0.30 mole% of sulfonic acid is possibly too low to have an effect on the MW.

The indication that degradation occurred during sulfonation, is thus clear. The drop in MW was most likely to come from degradation via chain scission, and which may be oxidative in nature since the reaction was not carried out under inert atmosphere. Also, due to the composition

of dry NR which includes constituents such as proteins, carbohydrates, lipids, and inorganic materials, and represent about 6% of the rubber composition, it is not known whether these constituents through a synergistic effect with the reactants used during the sulfonation, induced degradation. Purposely we did not purified the masticated NR in order to see how our reaction conditions will affect the resulting products. Whether degradation occurred via a homolytic or heteterolytic, or both, the chain scission mechanism is not known since the reaction was carried out in polar solvent.

3.3 Effect of Sulfonation on Degree of Water Absorption

Makowski et al. [14] deduced that the presence of strongly ionic groups in an amorphous polymer will promote water absorption. They stated that the degree of absorption depends on the characteristic of the metal used for neutralization and the percent sulfonic content. Also, Bagrodia et al. [17] proposed that the electronic configuration of the metal cation used for neutralization, which in turn governs its ionic/covalent character of the cation, is a very important parameter in determining many of the differences properties. There are various factors which indirectly support the more covalent character of Zn^{2+} relative to Ca^{2+} , K^+ , and Ba^{2+} . Specifically, zinc compounds have lower decomposition energies than the corresponding calcium and potassium compounds. For example, the decomposition energy of

potassium, calcium and zinc sulfate is 164, 95 and 66 Kcal/g mol, respectively. Zinc compounds also have lower melting points than corresponding calcium or potassium compounds. For example, zinc sulfate melts at 600°C while the melting point of potassium sulfate and calcium sulfate is 1069°C and 1450°C , respectively. The higher melting points are more typical of ionic crystals, whereas those of covalent crystals are generally lower. Thus, we believe that the covalent character of the cation, which in turn is governed by its electronic configuration, is a very important parameter in influencing the properties of ionomers.

With the introduction of the $3d^{10}$ level electrons in the zinc atom, which poorly shield the nucleus, zinc is more polarizable and hence zinc compounds are more covalent. For example, Hg^{2+} and Ca^{2+} have the same charge and nearly the same ionic radii, but the Hg compounds are more covalent than the corresponding calcium compounds. The electronic configuration of Ca is $[\text{Ar}] 4s^2$ devoided of "d" shell electrons while for mercury, it is $[\text{Xe}] 4f^{14}, 5d^{10}, 6s^2$. In our case, regarding the electronic configuration of Mg, It is $[\text{Ne}] 3s^2$ devoided of "d" shell electrons while for lead, it is $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^2$. Thus, the electronic configuration appears to be a very important parameter affecting the behavior of metal-neutralized products.

Another plausible concept these authors have used to explain the ionic/covalent character is the polarizability of an atom as a criterion for defining "hard" and "soft" acids and bases. Pearson [32, 33] defined a soft base as one in which the valence electrons are easily distorted, polarized, or removed. A hard base has the opposite properties i.e., it holds on to its valence electrons much more tightly. Likewise, a hard acid is defined as one of small size, high positive charge and with no valence electrons that are easily distorted or removed. Strictly speaking, it is the acceptor atom of the acid which has these properties. In conclusion, a soft acid is one in which the acceptor atom is of large size, small or zero positive charge, or has several valence electrons which are easily distorted.

Table 3.5 gives the water absorption data of the Mg^{2+} , Zn^{2+} , and Pb^{2+} cations used in the neutralization of sulfonated NR, and their immersion time. Figures 3.11-3.15 illustrate their respective % water absorption as a function of time.

Figure 3.11 indicates that at a concentration of 0.18 mole% $-SO_3H$ groups, and neutralized with Mg^{2+} , the material absorbs more water than when neutralized with Zn^{2+} and Pb^{2+} . A plateau was reached for the three products after 280 hours of immersion. Figure 3.12 at a concentration of 0.30 mole% $-SO_3H$ groups, a high water absorption is observed as a result of a higher metal ion

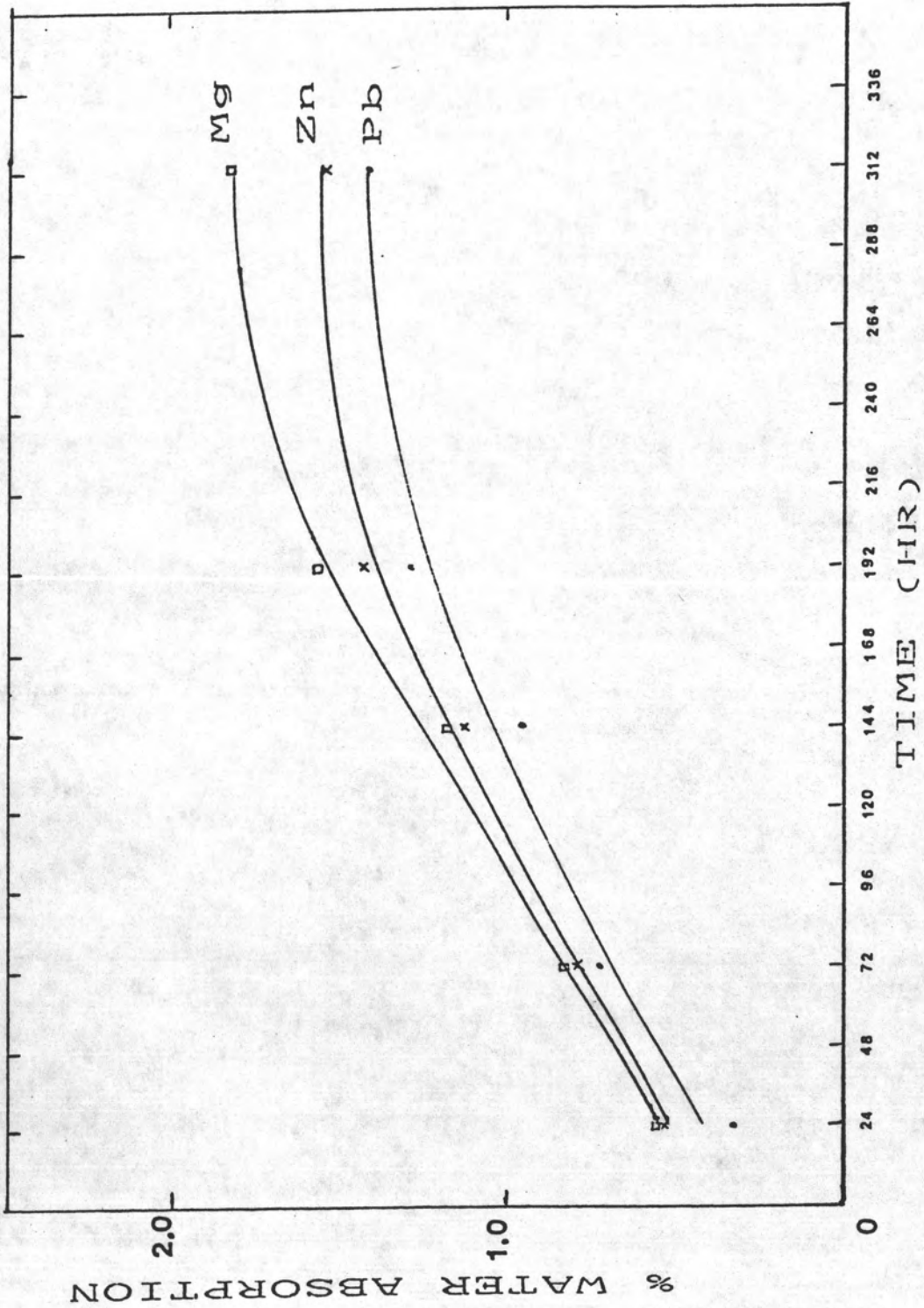


Figure 3.11. Percentage of distilled water absorbed as a function of immersion time at 35°C by a 0.18 mole% sulfonated NR sample.

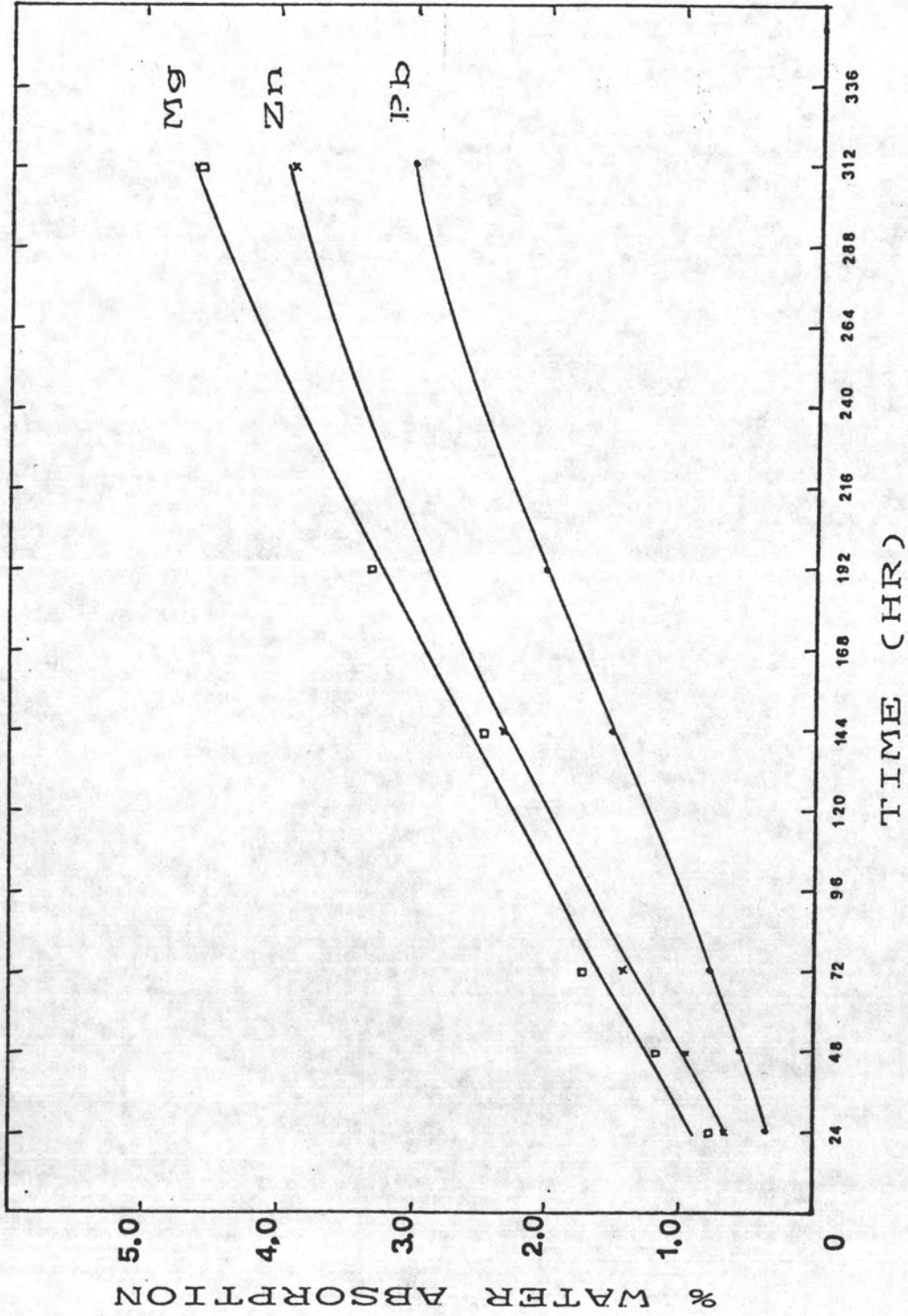


Figure 3.12. Percentage of distilled water absorbed as a function of immersion time at 35°C by a 0.30 mole% sulfonated NR sample.

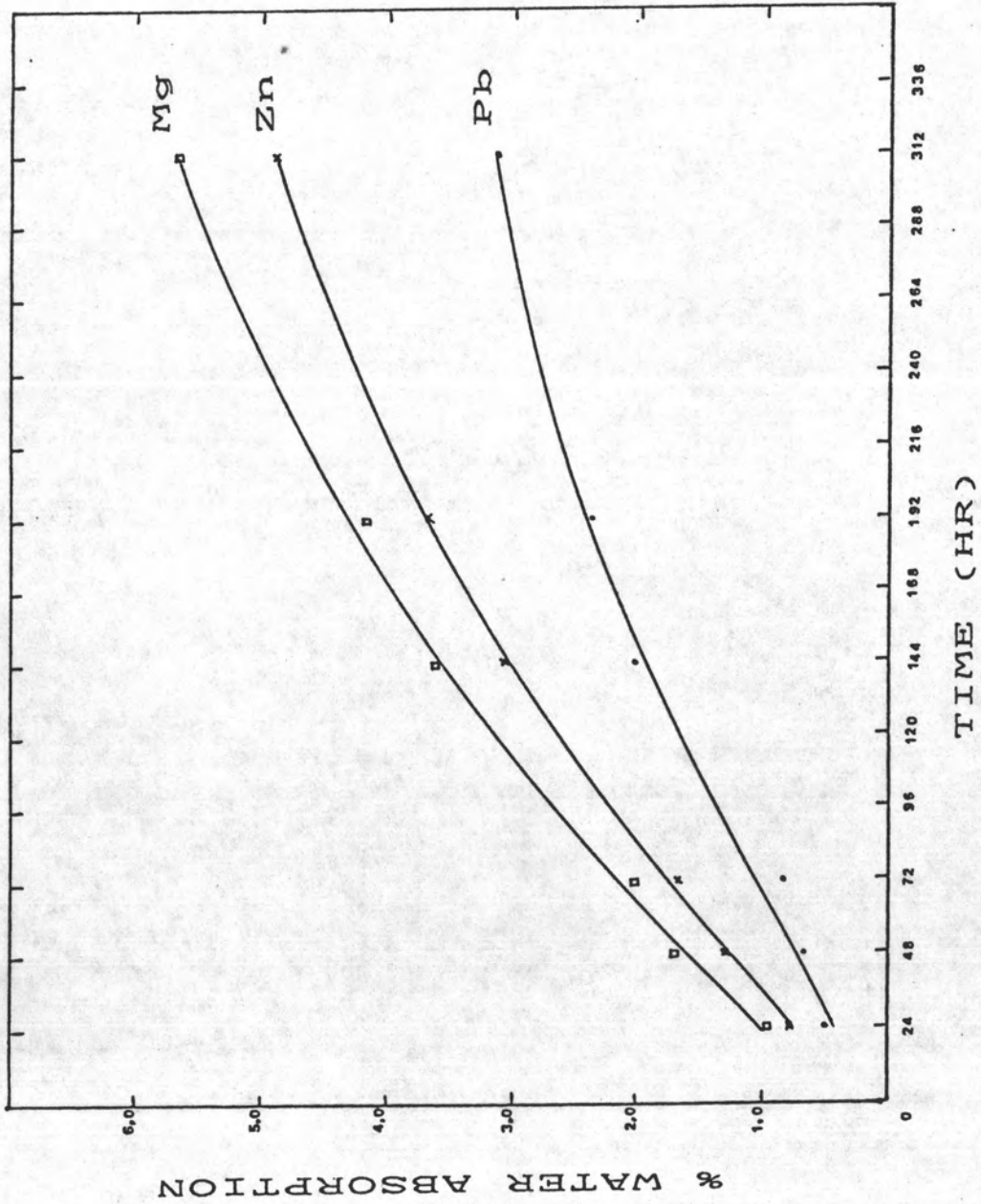


Figure 3.13. Percentage of distilled water absorbed as a function of immersion time at 35°C by a 0.38 mole% sulfonated NR sample.

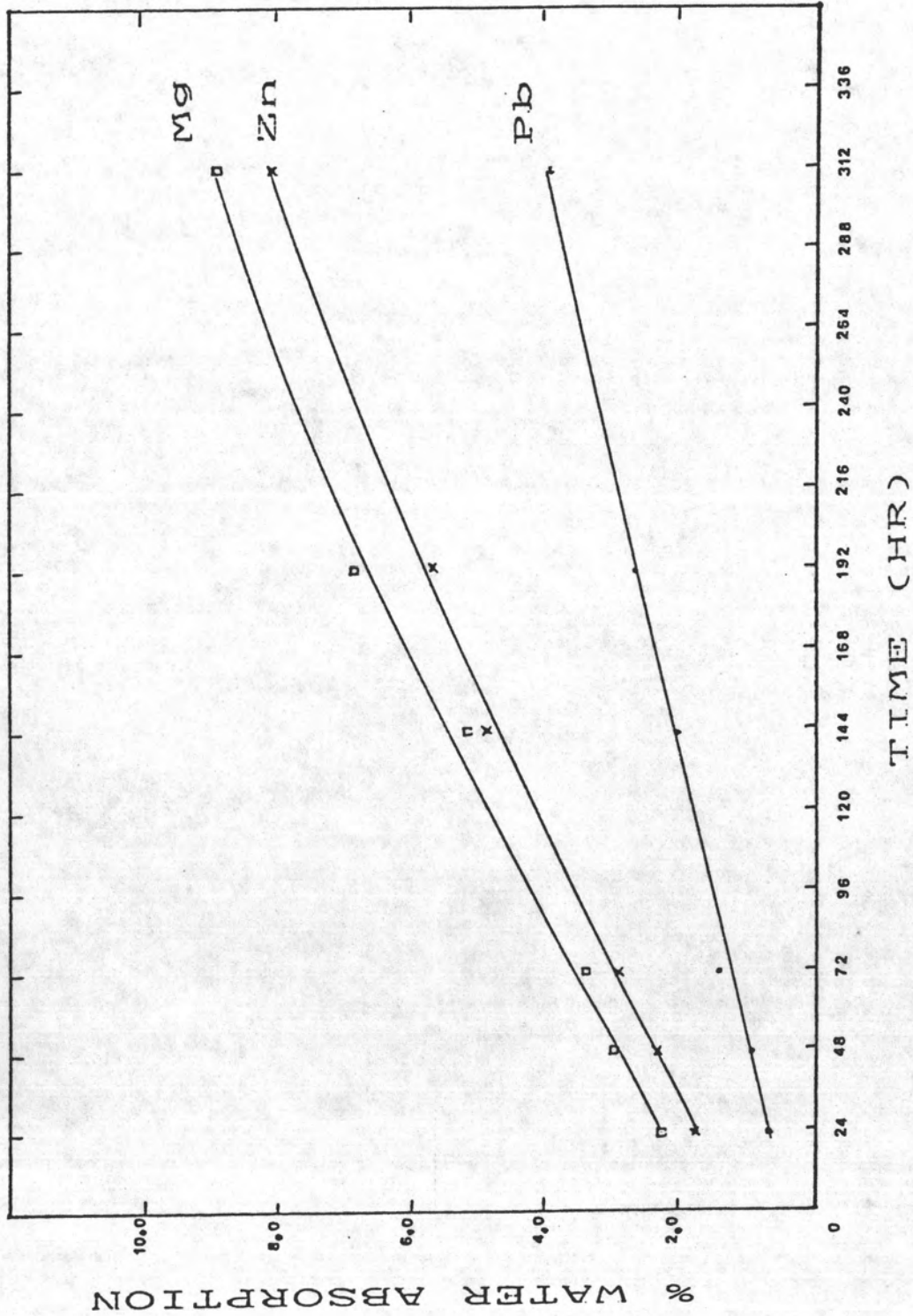


Figure 3.14. Percentage of distilled water absorbed as a function of immersion time at 35°C by a 0.62 mole% sulfonated NR sample.

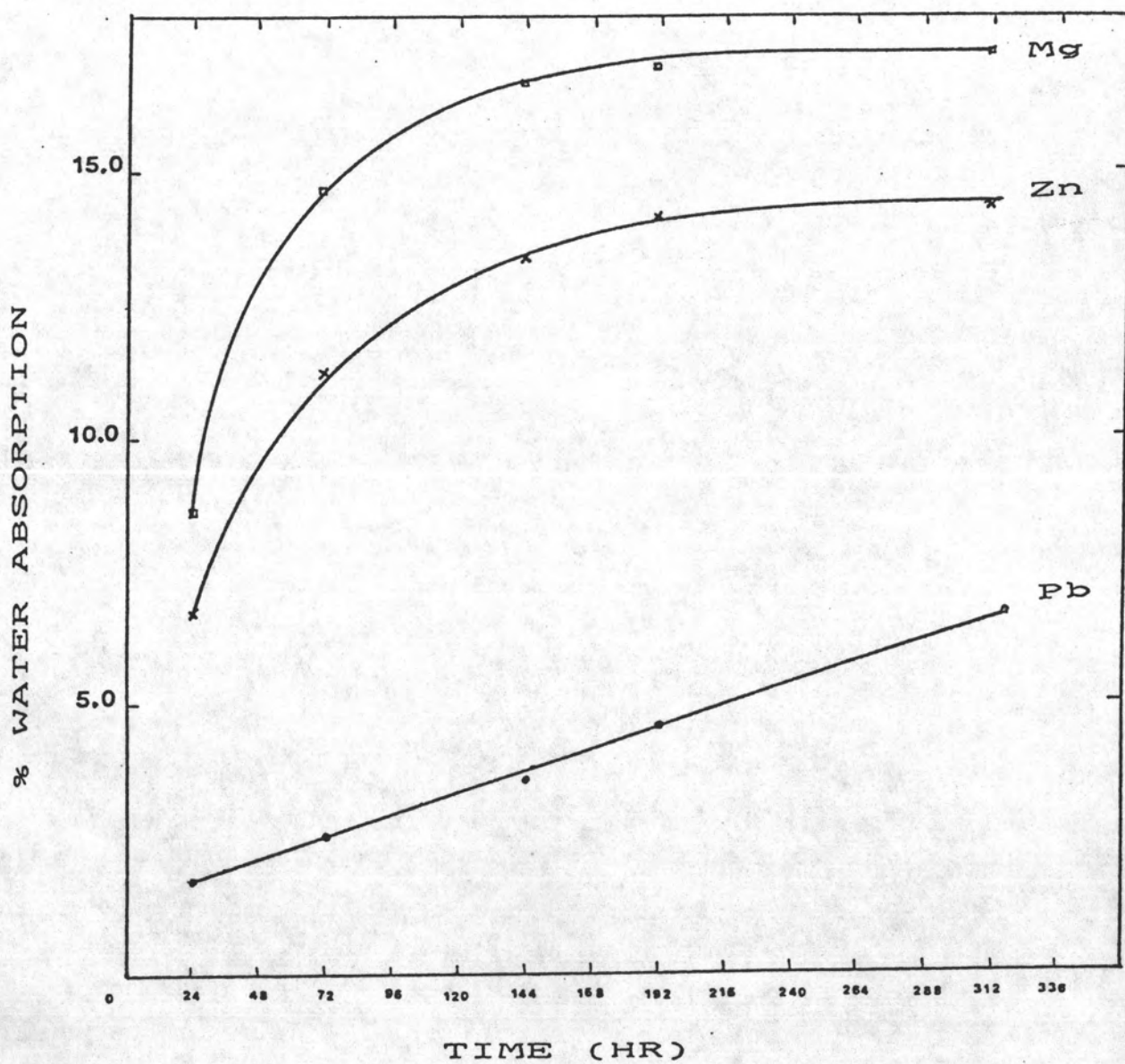


Figure 3.15. Percentage of distilled water absorbed as a function of immersion time at 35°C by a 0.82 mole% sulfonated NR sample.

concentration. Figures 3.13 and 3.14 show that as the sulfonic concentration increase, the Mg^{2+} and Zn^{2+} neutralized NR continue to have a higher water absorption rate, while the rate is much slower for the Zn compound. Finally, in Figures 3.15, at the higher sulfonic content, the Mg^{2+} and Zn^{2+} reach a water saturation point illustrated by a plateau. For the Pb^{2+} neutralized material, on the other hand, water absorption still increases linearly with time, and as shown previously with lower $-SO_3H$ contents, the water absorption is much less.

In order to see the increase in water absorption as a function of sulfonic content for each metal ion, we plotted Figures 3.16-3.18. They show that the Mg^{2+} neutralized NR gave a higher % water absorption than those of Zn^{2+} and Pb^{2+} neutralized materials. In the case of Mg^{2+} and Zn^{2+} a plateau was reached with the highest sulfonic content of 0.82 mole%. On the other hand, a linear increase for Pb^{2+} at the same concentration was observed instead, indicating a more covalent character with the Pb^{2+} cation. It indicates that the weaker the ionic character, the slower is the water absorption rate. Figure 3.18 illustrates that below the concentration of 0.82 mole% all other sulfonic contents showed a linear relationship with immersion time, except at the lowest concentration when a leveling off is observed. Overall, the findings on the three different neutralized sulfonated NR shows that Mg^{2+} has the most ionic character followed by Zn^{2+} and then Pb^{2+} . This is in agreement with ionic/covalent concept described above.

Also, according to the concept of hard and soft acids mentioned above and applied to Zn^{2+} , Mg^{2+} and Pb^{2+} , Bagrodia suggests that Zn^{2+} is on the borderline between a hard and soft acids, while Mg^{2+} is a hard acid and Pb^{2+} is also a borderline acid. Since the sulfonic group is a hard base, it associates more strongly with Mg^{2+} than with the more covalent Zn^{2+} and Pb^{2+} cations. The order of ionizability between the three cations, is therefore $\text{Mg} > \text{Zn} > \text{Pb}$. This also is in agreement with their respective water absorption data given in Table 3.5.

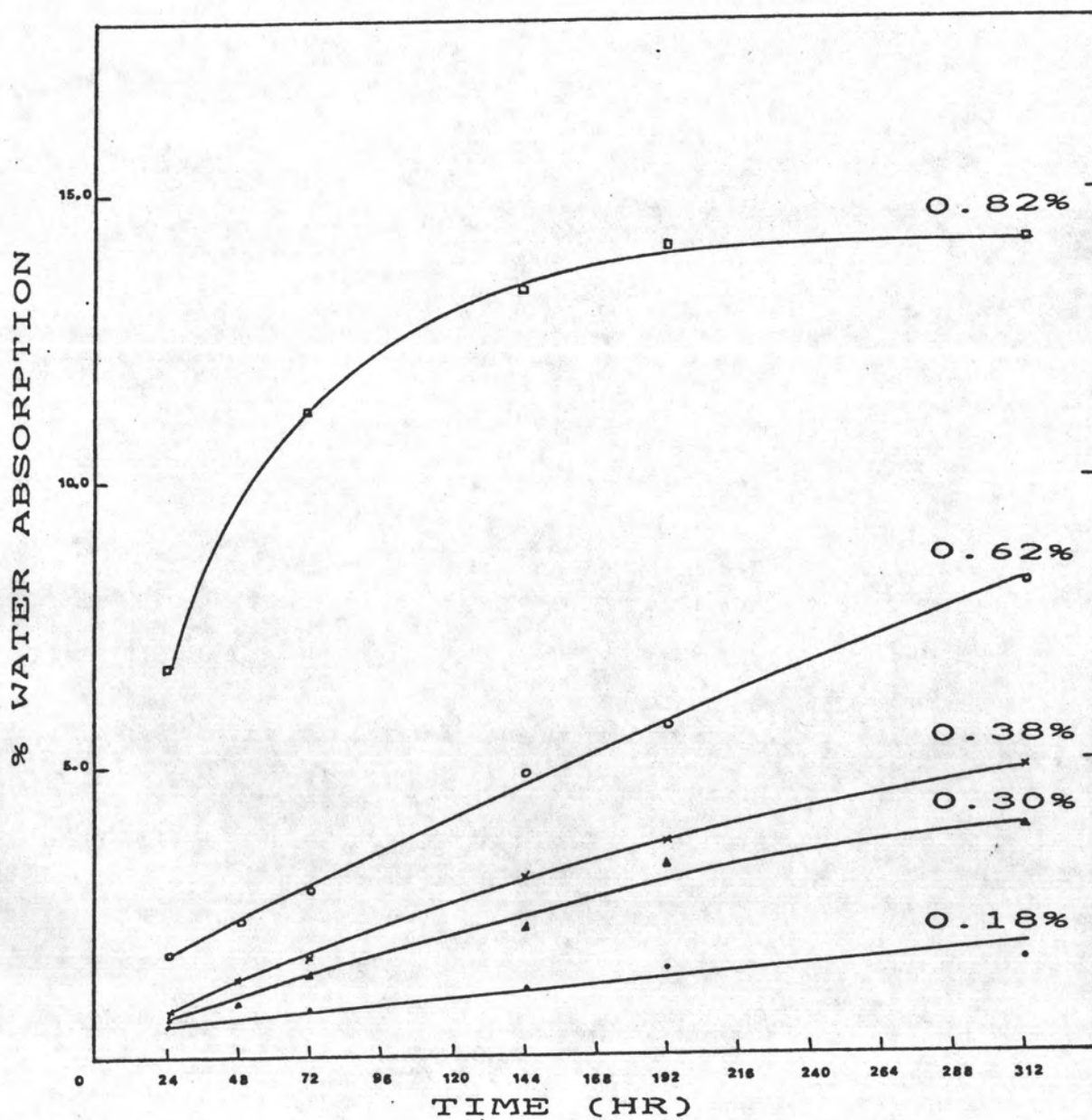


Figure 3.16. Percentage of distilled water absorbed as a function of immersion time at 35°C of sulfonated NR neutralized with zinc acetate.

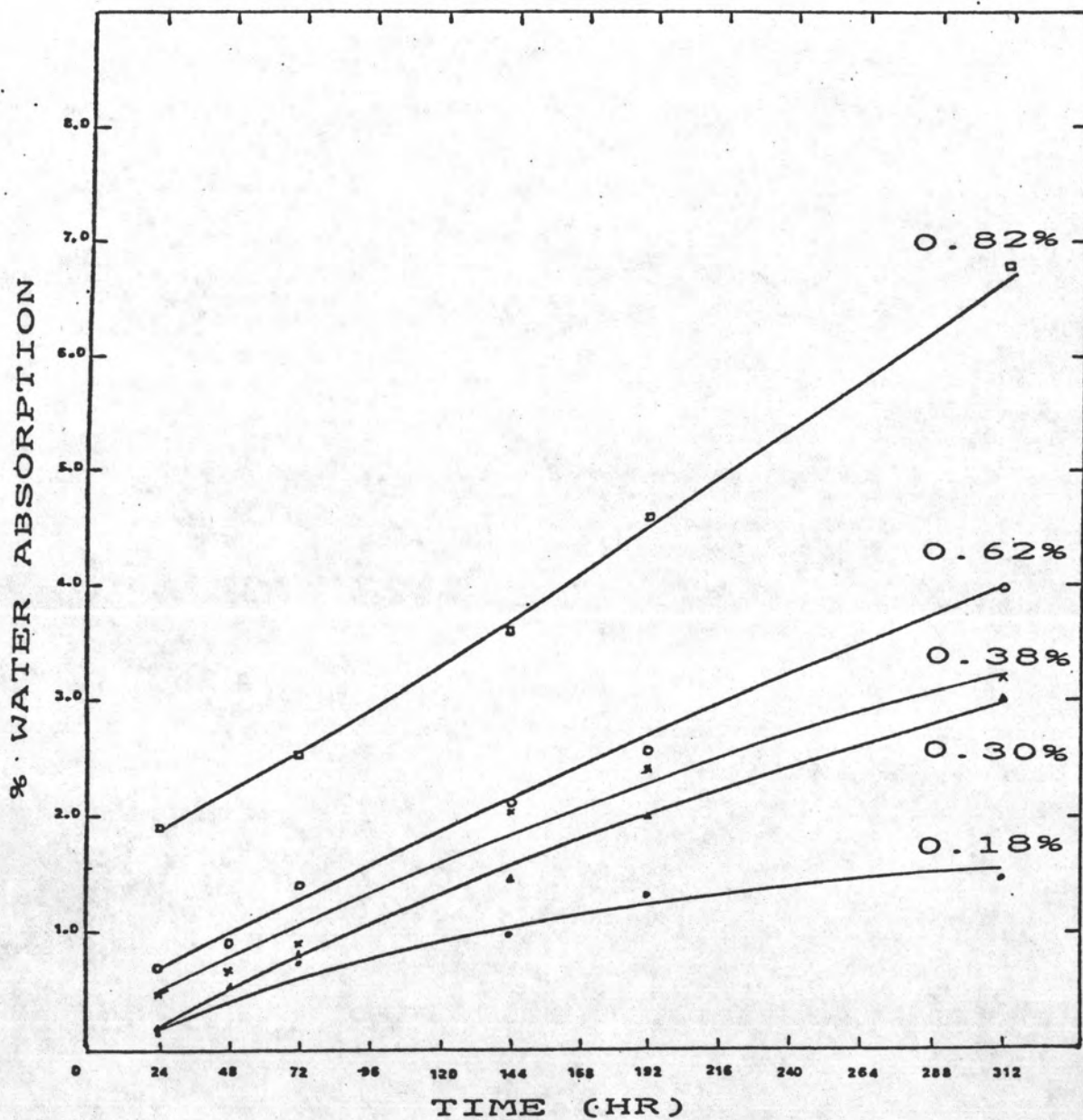


Figure 3.17. Percentage of distilled water absorbed as a function of immersion time at 35°C of sulfonated NR neutralized with lead acetate.

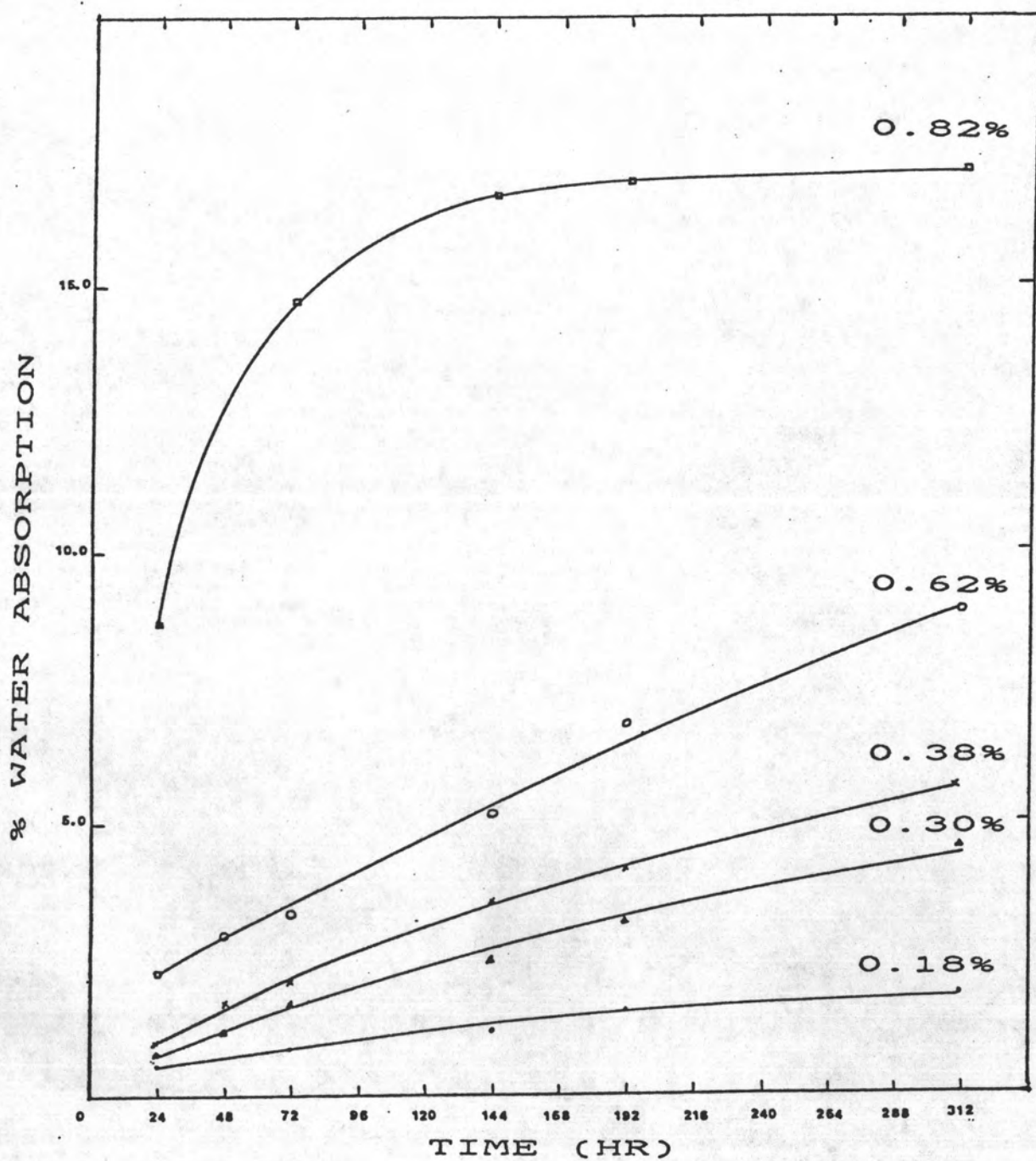


Figure 3.18. Percentage of distilled water absorbed as a function of immersion time at 35°C of sulfonated NR neutralized with magnesium acetate.

Table 3.5. Effect of sulfonate content of the metal neutralized products on water absorption.
(Temperature of immersion = 35 °C)

Sample	Time of immersion (hr)						
	mole%	24	48	72	144	192	312
Zn	0.18	0.53	—	0.79	1.12	1.42	1.53
	0.30	0.60	0.90	1.39	2.29	3.28	3.88
	0.38	0.78	1.30	1.66	3.06	3.66	4.88
	0.62	1.75	2.30	2.84	4.86	5.68	8.16
	0.82	6.71	—	11.20	13.30	14.08	14.14
Mg	0.18	0.55	—	0.82	1.18	1.55	1.81
	0.30	0.74	1.12	1.68	2.43	3.18	4.58
	0.38	0.96	1.70	2.02	3.62	4.16	5.66
	0.62	2.27	2.91	3.36	5.18	6.82	8.92
	0.82	8.68	—	14.65	16.60	16.83	17.04
Pb	0.18	0.32	—	0.72	0.95	1.28	1.40
	0.30	0.34	0.54	0.75	1.45	1.99	2.99
	0.38	0.48	0.66	0.82	2.02	2.36	3.14
	0.62	0.70	0.90	1.40	2.09	2.53	3.92
	0.82	1.88	—	2.51	3.59	4.57	6.73

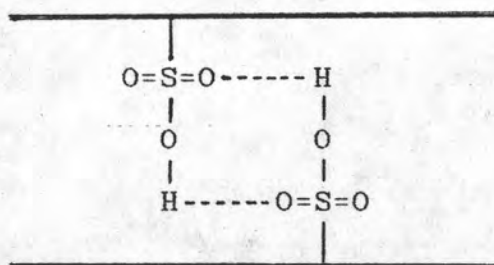
3.4 Effect of Sulfonation on Plasticity

As mentioned in the experimental chapter, in addition to the water absorption property of the neutralized sulfonated NR, the Wallace plasticity number is also important to determine in order to see the effect of the different metal ions on the plasticity or deformation property of the resulting polymers. Table 3.6 gives these data, and Figures 3.19 and 3.20 illustrate the Wallace number as a function of the mole% sulfonic acid content in NR, and as a function of the mole% of the metal neutralized NR

Table 3.6. Wallace plasticity number data

Mold % sulfonate content	Wallace number			
	Sul.NR	Zn	Mg	Pb
0.18	—	4.0	5.8	3.0
0.20	15.0	8.2	11.0	7.8
0.24	—	11.8	16.8	10.5
0.30	13.0	—	—	10.2
0.32	27.5	11.2	22.0	—
0.46	33.0	13.2	22.8	12.0
0.62	34.2	15.5	23.8	12.5
0.82	36.0	16.8	25.0	13.0

As explained in chapter II, the Wallace plasticity number of a material is defined as the ease of deformation of this material under a 100N load at 100°C. The higher the number, the harder the deformation. The effects of the sulfonic content in NR upon the plasticity are shown in Figure 3.19. The curve indicates a decrease in the Wallace number up to a 0.30 mole% of sulfonic acid content, and increases sharply to slowly level off after a 0.50 mole% content of $-SO_3H$. These data run parallel with those of \bar{M}_v until 0.30 mole% but then a rapid increase in the Wallace number occurred suggesting formation of strong hydrogen bonding between the sulfonic groups of neighboring polymer chains as illustrated below:



In Figure 3.20, on the other hand, a decrease in the Wallace number is not observed. Instead, a sharp increase in the hardness of the material occurred as a result of the presence of divalent metal ions. The plasticity number, however, begins to level off slowly after 0.30 mole%. The same trend is observed for all three metal neutralized materials. The sulfonated NR neutralized with $Mg(OAc)_2$, however, shows the highest hardness followed by Zn and Pb. This same order was

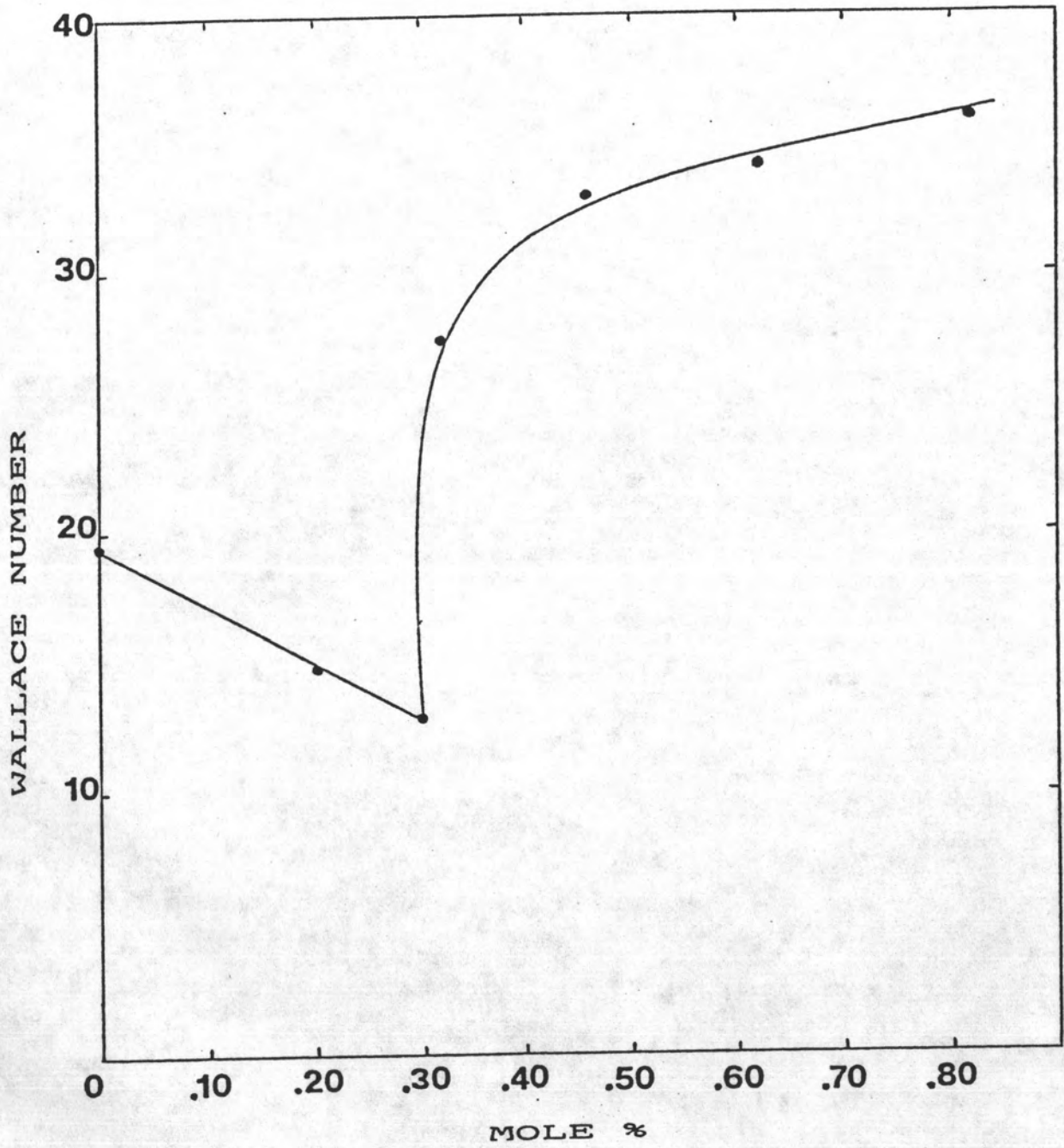


Figure 3.19. The Wallace number of sulfonated NR.

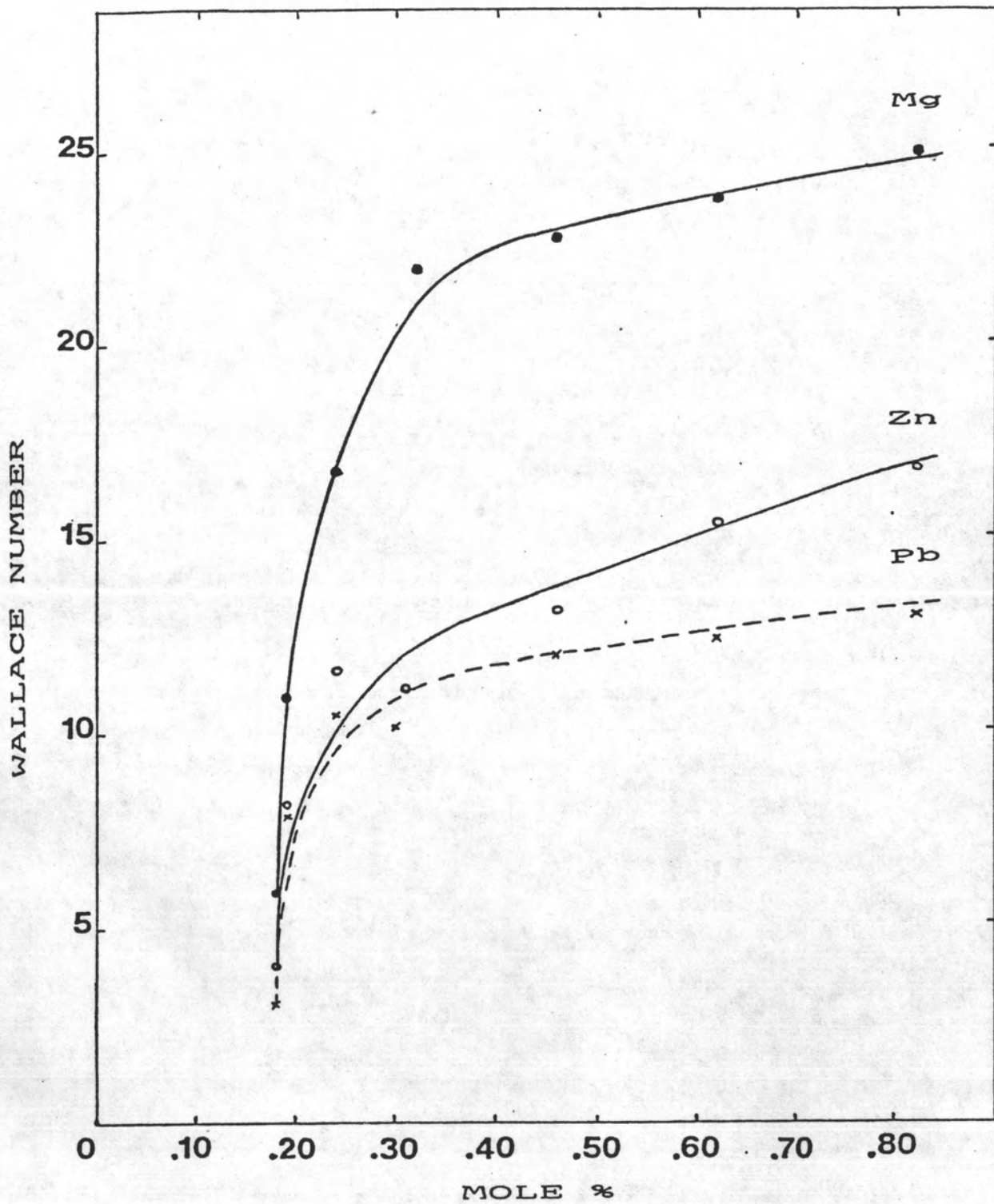


Figure 3.20. The Wallace number of metal neutralized NR.

already observed during the water absorption experiment, suggesting that Mg^{2+} is more ionic than Zn^{2+} , which is more ionic than Pb^{2+} . This would result in a stronger Mg^{2+} ionic bridge between polymer chains, than in the case of Zn^{2+} and Pb^{2+} which show a more covalent character.

These results also describes the effect of the counterion. The differences between ionic and covalent metal type, as mentioned earlier, is clearly manifested at a higher sulfonic content and at a high testing temperature. It is important to remember that metal ions give only a pseudo-crosslinked material. At low temperature it behaves as a thermoset and at high temperature as a thermoplastic. With increasing temperature the coulombic forces between ion pairs decrease and it is expected that the ionic groups may migrate between junction points by a dissociation-association mechanism referred to as ion-hopping [13].

The kinetics of ion-hopping has a dramatic influence on the macroscopic stiffness of the polymer, as evidenced by an increase in plasticity with an ionic content increase. At the same concentration of $-SO_3H$, magnesium neutralized NR has a higher plasticity number than the ones with zinc and lead ions. This is indicative of a greater and more stable ionic network. In summary, the plasticity increased with increasing sulfonation and is as well a function of the ionic/covalent character of the cation.

Comparison of the Wallace number between the neutralized and non-neutralized sulfonated NR shows that the former has a lower plasticity than the latter with polymeric acid. This is expected because the added metal lowers the intermolecular forces between aggregated sulfonic groups of neighboring chains as the acidic proton is replaced by the metal. Furthermore, the metal is embeded between polymer chains and thus acts as plasticizer by increasing the free volume in the rubber matrix, consequently making deformation easier.