Effect of Divalent Metal Ions on the Viscosity of Natural Rubber from Manihot glaziovii

J.F. RODRIGUES[*][#], F.C. OLIVEIRA[**], N.M.P.S. RICARDO[*],

AND M.C.P. LIMA[*]

The effect of divalent metal ions on the intrinsic viscosity of natural rubber (NR) from Manihot glaziovii *has been investigated. The molar mass of cis-1,4-polyisoprene from* Manihot *rubber was found to be* $\overline{M}_v$ = 1.0 × 10⁶ *and the intrinsic viscosity* [η] = 5.66 dL/g, *for toluene solution at 30 °C. Some metal ions such as* Ca^{2+} *and* Sr^{2+} *increase the NR viscosity in toluene solution (6.00 dL/g and 6.26 dL/g for 15.0 μmol of metal ion/g of rubber, respectively). Others such as* Mg^{2+}, Zn^{2+} *and* Cu^{2+}, *decrease the NR viscosity to 4.82 dL/g, 4.73 dL/g and 4.96 dL/g respectively, for the same addition of metal ion/g of rubber. A correlation between relative variation of intrinsic viscosity ([η]NR+M/[η]NR) and cation radius has been proposed. A relative variation greater than unity for large cations has been observed, while for small metals such variation was less than 1. Cations that decrease the intrinsic viscosity do not lead to alteration in the activation energy of flow (E$_a$) for the 0.5% (w/v)(E$_a$ = 7.3 kJ/mol) solution. Cations that increase [η] also cause an increase of E$_a$ to 7.8 kJ/mol and 7.6 kJ/mol for NR solutions containing* Sr^{2+} *and* Ca^{2+}, *respectively. Intramolecular crosslinks may be formed with small and large cations. No evident interaction has been detected between metal ions and synthetic cis-1-4-polyisoprene. The interaction between NR and metal ions may be due to naturally occurring non-rubber constituents, probably those containing carboxylic groups.*

Manihot glaziovii, popularly known in Brazil as manicoba, is a plant that produces natural rubber, and belongs to the *Euphorbiaceae*. According to Bennett[1] and Seifriz[2], *Hevea* NR and *Manihot* NR have the same structure, slightly different molar mass and close hydrocarbon contents (87.9–94.5 and 84.1%, respectively). Serier[3] discussed its history, biology, cultivation and economic aspects. Rodrigues *et al.*[4] determined that this rubber is constituted mainly of *cis*-1,4-polyisoprene units, and that the band of $\overline{M}_v$ is situated between 1.0 × 10⁶ and 1.5 × 10⁶ g/mol. Studies on the formation of interpenetrating polymer networks[5] and thermal degradation[6] have been carried out with *Manihot* NR. A retardation effect of thermal degradation of this rubber was observed using Fe^{3+} (Barros *et al.*)[7].

It is known that natural rubber contains various types of naturally occurring non-rubber

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* Deptº de Química Orgânica e Inorgânica, UFC, Cx. Postal 12.200, CEP 60.455-760, Fortaleza - Ceará, Brasil
** Deptº de Geociências, UECE, Limoeiro do Norte - Ceará, Brasil
# Corresponding author

substances, comprising neutral lipids, glycolipids, phospholipids, proteins, amino acids and inorganic constituents.

Eng *et al.*[8] suggested that proteins and amino acids are directly bonded to the polymer. Tanaka[9] proposed a structure of *Hevea* NR with branching points formed by complex lipid groups with association of protein involved in gel formation.

The specific effect of metal ions on the viscosity of polyelectrolyte is well known[10]. This kind of effect on neutral polymer is less common. In this work the effect of divalent cations on the viscosity of natural rubber from *Manihot glaziovii* and synthetic rubber is evaluated. The contribution of naturally occurring non-rubber materials and the correlation with Tanaka's model are discussed.

EXPERIMENTAL

Materials

The latex used was obtained from *Manihot glaziovii*, collected and spontaneously coagulated in June 1996, in the district of Pacatuba, State of Ceará, situated in northeastern Brazil. Approximately 4.0 g of this rubber was dissolved in 200 mL of CHCl$_3$ at room temperature, in darkness, under nitrogen, for one day and then filtered. The coagulation was performed with methanol (1L) and the remaining solvent was evaporated under vacuum to a constant weight. The purified rubber was stored at −10°C, in darkness.

Synthetic polyisoprene, 97% *cis*-1,4- with $\overline{M}_n = 8 \times 10^5$ g/mol, was purchased from Aldrich.

Metal Incorporation

To a 50 mL of purified NR (2 g/dL in CHCl$_3$), a small amount (less than 1 mL) of aqueous metal ion solution (0.01 mol/L and 0.02 mol/L) was added dropwise and the mixture was stirred for 24 h. The ions added (Mg^{2+}, Ca^{2+}, Sr^{2+}, Cu^{2+} and Zn^{2+}, as chloride salts) were prepared in order to obtain metal concentrations of 0.1, 0.5, 1.0, 3.0, 5.0, 10.0 and 15.0 µmol/g of NR. These values are in the same order of magnitude as for the natural occurrence of divalent metal ions· that have been studied[11-13]. The effect of certain metallic contamination such as Cu^{2+}, Mn^{2+} and Fe^{3+} was also investigated over this range of concentration[14]. Films were prepared by pouring the solution into teflon dishes and allowing them to spread and evaporate to dryness. Thin films (120 µm–140 µm thickness) were obtained and stored at −10°C in the absence of light.

Viscosity Measurements

Measurements were carried out on diluted toluene solution prepared by stirring samples of films for a period of 24 h, followed by filtration in a sintered-glass plate. Clear solutions were obtained. Analyses were carried out on Ubbelhode viscometer with capillary diameter of 0.5 mm, with toluene as the solvent and a flow-time of 77 s at 30°C. The temperature was maintained at 30.0°C±0.1°C in all experiments. All flow-times were obtained by averaging three readings. Rubber concentration was in a range of 0.15 g/dL and 0.40 g/dL. Five different concentrations and extrapolations based on Huggins equation were employed for the determination of intrinsic viscosities. Least square analyses were performed for all linear relationships.

The viscosity measurements for the determination of activation energy of flow were performed using a Brookfield Model DV-III, with shear rate of 200 s^{-1} The concentration of NR solution in toluene and of the metallic ions was kept constant at 0 5% (w/v) and 10 0 µmol/g of NR, respectively

The solutions were progressively heated from 10°C up to 50°C, at a pace of 0 74°C/min Measurements for the cooling period (from 50°C down to 10°C) were also performed

RESULTS AND DISCUSSION

Characterisation of *Manihot glaziovii* Rubber

The intrinsic viscosity of the sample used in this work was 5 66 dL/g, for toluene solution at 30°C Using Mark-Houwink-Sakurada equation $[\eta] = 1\ 90 \times 10^{-4} \overline{M}_v^{0\ 745}$ (Chirico)[15]. M_v was calculated as $1\ 01 \times 10^6$ g/mol

Some metal ions and nitrogen were detected in purified rubber by x-ray fluorescence and elemental analysis (*Table 1*) Results indicated that iron content in *Manihot* rubber is higher than in *Hevea* rubber Other inorganic constituents are similarly distributed Nitrogen content is higher than typical values for NR Protein content is 3 5%, calculated as %N × 6 25 (Marks *et al*)[19]

Effect of Metal Concentration on the Intrinsic Viscosity of Natural Rubber

Table 2 showed that the addition of various divalent cations on NR produced different changes in $[\eta]$ This behaviour could be due to the addition of water, solvent used to prepare the solution of the metal salts, which would promote gel formation and/or cause conformational change in rubber molecule, induced by the difference in protein or fatty acid solubilisation, despite of water evaporation prior to the determination of viscosity

Films were prepared following the same procedure of addition of metal solution, but in absence of salt Intrinsic viscosities of NR from films prepared with 50, 100 and 500 µL of water/50 mL of toluene solution were 5 67 5 65 and 5 65 dL/g, respectively These additions were correspondent to metal concentration of 0 5, 1 0 and 5 0 µmol/g of NR The results were similar to that obtained in the absence of water or aqueous solution 5 66 dL/g

These lead to the conclusion that even if gel has been formed by the addition of water, the complete removal of this solvent during film formation, together with the subsequent solubilisation in toluene of the dried NR, restore its original conformational characteristics

Effect of Metal Ions on the Viscosity of Synthetic *cis*-1,4-polyisoprene

In order to verify the contribution of hydrocarbon on the interaction of NR with metal ions, intrinsic viscosity was determined with synthetic rubber in the presence of a cation which increases $[\eta](Ca^{2+})$ and a cation that decreases $[\eta](Cu^{2+})$(*Table 3*)

No evident trend on intrinsic viscosity *versus* calcium concentration was observed The mean value of 3 46 ± 0 03 dL/g was comparable with $[\eta]$ of NR in the absence of metal (3 42 dL/g) This kind of deviation (1% and 2%) is in the range of accuracy of $[\eta]$ determination[20] No trend was also verified in

TABLE 1. COMPARISON BETWEEN RUBBER CONSTITUENTS FROM
MANIHOT GLAZIOVII AND *HEVEA BRASILIENSIS*

Element	Manihot (%)	μmol/g NR	Hevea (%)			Refs
Al	0 153	5 7	NA			–
K	0 003	0.8	NA			–
Ca	0.041	10.2	0 0025	–	0 075[a]	13
Fe	0.003	0 5	0 00013	–	0 0013[a]	16
Cu	0.002	0.3	0.0005	–	0.002[a]	12
Zn	0.005	0.8	0 0065	–	0.025[a]	11
N	0 56	400	0.32	–	0 40	17,18

NA Data not available

[a]Obtained from metal content in latex taking into account that rubber represents approximately 40% of this latex.

TABLE 2 EFFECT OF METAL IONS CONCENTRATION ON THE INTRINSIC
VISCOSITY OF NATURAL RUBBER FROM *MANIHOT GLAZIOVII*

[M^{n+}] μmol/g of rubber	[η](dL/g)				
	Ca^{2+}	Sr^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}
0	5.66	5 66	5 66	5 66	5.66
0 5	5 84	5 77	–	5.54	5 62
1 0	5.88	5 86	5 50	5.42	–
3 0	5.89	5.94	5 21	5.33	5 42
5.0	5.94	–	5.18	5.05	5.33
8.0	5.91	6 16	4.94	–	5 18
10 0	–	6 18	4 81	4 83	5 02
15 0	6 00	6 26	4 82	4 73	4 96

TABLE 3 EFFECT OF METAL CONCENTRATION ON THE INTRINSIC
VISCOSITY OF SYNTHETIC RUBBER

$[M^{n+}]$	$[\eta]$(dL/g)	
μmol/g of rubber	Ca^{2+}	Cu^{2+}
0	3 42	3 42
0 1	3 48	3 40
0 5	3 46	3 41
1 0	3 44	3 51
5 0	3 50	3 35
10 0	3 44	3 00

copper concentration up to 5 0 μmol/g of NR (mean value of 3 42 ± 0 06 dL/g) As no interaction between Ca^{2+} and Cu^{2+} *versus* polyisoprene has been detected, the one between NR and metal ions may be processed or induced through other natural components contained in the rubber

The addition of 10 0 μmol of copper/g of NR decreases the intrinsic value in 0 42 dL/g This could be due to the effect of this metal ion on the rubber degradation The film containing Cu^{2+} utilised for the determination of [η] was stored for four days The same film stored for a month gave intrinsic value of 0 87 dL/g This concentration of copper was sufficient to degrade the polymer The extension of degradation was dependent on stored time and on metal concentration Gan and Ting[17] observed that treating latex with Cu^{2+}, [η] of the resulting rubber was reduced significantly (from 6 10 dL/g to 0 66 dL/g) In their experimental procedure the polymer was made in contact with approximately 1 0 mmol of Cu^{2+}/g of NR for four days In fact, the overall result observed by the authors could be due to the effect of Cu^{2+} on NR degradation plus the

effect of this metal ion on the intrinsic viscosity of rubber

Presumed Model of Interaction

The presence of a small-molecule cosolute with the polymer in solution can lead to a variety of effects involving diverse types of interactions between the two components and the solvent There is generally a modification in the size and/or shape of the polymer molecules, as well as changes in the interaction between them, reflected in variation in the Huggins viscosity slope parameter[10], k_H

Molyneux[10] divides cosolute effects into two main types specific effects and generic effects Specific effects occur at relatively low cosolute concentrations (i e , less than about 100 millimolar) and are frequently sensitive to small changes in the structure of the cosolute molecule and in the polymer chain unit These effects are taken as result from binding of the cosolute molecule by the polymer chain (i e , a form of an association or complex between them) Generic effects occur only at relatively high cosolute concentration and show low sensitivity due to the detailed nature of the cosolute molecule and the polymer chain unit

The extremely low concentration of metal ions (cosolute) and sensitivity in viscosity changes in relation to small changes of these species, in addition to the tendency to stabilisation with increasing metal content, lead to the conclusion that divalent metal ions interact with natural rubber into 'specific effect'.

Any changes in conformation caused by binding of the cosolute will be reflected in the corresponding changes in intrinsic viscosity. Those systems that increase the value of [η] give rise to a more expanded conformation. A decrease in [η] indicates a more compact conformation.

The reduction in intrinsic viscosity (*Table 2*) caused by the presence of Zn^{2+}, Mg^{2+} and Cu^{2+} may be ascribed to a reversible crosslinking of segment at the end of the natural rubber molecule by the bonded cosolute ions *i.e.*, its simultaneous attachment to two otherwise distantly linked parts of the same segment (intrachain crosslinking). The corresponding increase in the Huggins slope parameter (*Table 4*) may be ascribed to the (transient) intermolecular crosslinking effect of the bonded cosolute ions.

On the other hand, the increase in [η] was observed in the presence of Ca^{2+} and Sr^{2+}. This increase in [η] is accompanied by a small decrease in the Huggins parameter (*Table 4*), which is insignificant considering the existing error of 5% for the k_H determination[20]. In this case, it is evident only in the formation of a more expanded conformation.

In order to clarify the influence of metallic ions on the interaction between the NR molecules in solution, the determination of viscosity in different temperatures was

performed, as well as calculation of activation energy of flow. The rubber viscosity decreases when the temperature increases, both in absence and in presence of divalent metallic ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Cu^{2+} and Zn^{2-}).

This may be attributed to: (a) the energy required to overcome the potential energy barrier (activation energy of flow) upon transition from one equilibrium to the next; (b) degradation of polymer; or (c) conformational (ordered-disorder) transition. No degradation occurs, during the period of experiment, since the temperature dependence at viscosity for a 0.5% solution was the same on heating as during cooling. An ordered NR conformation at 10°C does not exist and so an ordered-disorder conformational transition, like helix-coil, is not possible. The decrease in viscosity when the temperature is increased is due to the existence of activation energy of flow.

An Arrhenius-Frenkel-Eyring equation [η = Bexp(E_a/RT)][21] was applied to the η-T data. A simple linear dependence of ln η *vs* T^{-1} was observed for all solutions, as confirmation of no ordered-disorder transition. *Figure 1* displays some curves that represent the behaviour of NR, both in presence and in absence of some metals studied in this work. Curves for other metallic ions have shown similar aspects. From the slope of the straight lines, the activation energy of flow (E_a) was calculated (*Table 5*).

It is well known that the value of E_a is affected by factors that determine the flexibility and the intermolecular interaction, primarily by the microstructure of the chain and content of polar groups. The lowest activation energy of flow is exhibited by compounds with high chain flexibility and a weak intermolecular

TABLE 4 HUGGINS SLOPE PARAMETER OF NR TOLUENE SOLUTION IN
THE PRESENCE OF DIVALENT METALLIC IONS

Metal concentration (μmol/g of NR)	k_H				
	Ca^{2+}	Sr^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}
0	1 18	1 18	1 18	1 18	1 18
5 0	1 09	1 15	1 17	1 08	1 26
10 0	0 94	1 07	1 94	1 39	1 46
15 0	0 84	1 01	2 06	1 62	2 15

[η] in dL/g

TABLE 5 ACTIVATION ENERGY OF FLOW FOR NR

	E_a (kJ/mol) Divalent metallic ions[**]				
NR[*]	Ca^{2+}	Sr^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}
7 3	7 6	7 8	7 3	7 3	7 3

[*]E_a of NR toluene solution (0 5% w/v) in absence of metallic ions

[**]10 0 μmol/g of NR

interaction It can be observed in *Table 5* that the value of 7 3 kJ/mol obtained for NR in the absence of metal is kept unchanged when each of the following cations is added Mg^{2+}, Zn^{2+} and Cu^{2+} This is an indication that the intermolecular interaction of NR molecules dissolved in toluene to 0 5% (w/v) is not affected by the presence of these ions These are the ions that cause the decrease in the intrinsic viscosity The formation of intramolecular crosslink seems to be dominant even· at this concentration The crosslink formation between points from the same chain probably makes the metallic ions inaccessible for binding to points from different chains At higher concentrations it is possible that interchain crosslink happens, as suggested by the Huggins constant

The E_a values for NR in the presence of Ca^{2+} and Sr^{2+}, 7 6 kJ/mol and 7 8 kJ/mol, respectively, are significantly superior to the NR in the absence of metal (7 3 kJ/mol) These ions are those that induce the increase in the intrinsic viscosity In this case, an increase in the intermolecular interaction is observed, which may be caused by the formation of intermolecular crosslinks
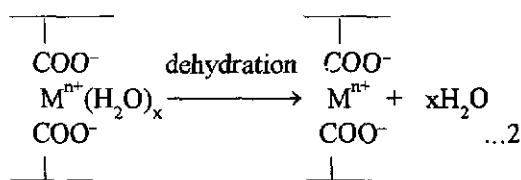
Considering that the divalent metallic ions do not lead to alteration in the intrinsic viscosity of synthetic rubber, the interaction between these ions and the NR may be processed through other natural components but the hydrocarbon.

As the majority of metallic ions used in this work interact predominantly with ligand groups containing negatively charged oxygen, it is assumed that the interaction is done by carboxylate groups.

In fact, the interaction between metallic ions and carboxylate was suggested by Gan and Ting[17] as well as by Burfield[22]. The effect of metal ions on storage hardening was attributed by Gan and Ting[17] to interaction with carboxylate ions from fatty acid or/and protein, as represented below:

$$M^{n+} + nRCOO^- \rightarrow (RCOO^-)_n M^{n+} \quad ...1$$
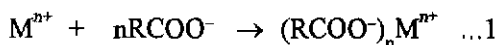
Burfield[22] suggested that the carboxylic groups in rubber could react with metal ions to form ionic crosslinks, as follows:

$$
\begin{array}{ccc}
| & & | \\
COO^- & \text{dehydration} & COO^- \\
M^{n+}(H_2O)_x & \longrightarrow & M^{n+} + xH_2O \\
COO^- & & COO^- \quad ...2 \\
| & & |
\end{array}
$$

The effect of metal ions on the intrinsic viscosity and activation energy of flow of NR could be promoted by interaction with abnormal groups of natural rubber, probably anions from fatty acid and protein.

Infrared spectra were obtained for NR in the presence and absence of metallic ions, as an attempt to detect any alteration in the characteristic band for the hydrocarbon or for the carboxylates originated from their non-rubber components (protein, amino acids and fatty acids). No alteration has been detected. Gan and Ting[17] also did not observe any change in the infrared spectra for purified and unpurified latex, both in the presence and in the absence of metallic ions, even considering that the interaction should be occurring through the carboxylate. Certainly, it will be necessary for a more detailed study due to the fact that the COO⁻ bands appear at a very low intensity, the reason being the quantity of non-rubber constituents in relation to the polyisoprene.

Tentative Correlation with Ionic Radius

Effect of ionic radius on the interaction metal – polyelectrolyte in aqueous solutions is well known. Morawetz[23] established that the order of binding increases as the cation radius decreases for a complex of inner sphere. There are inner sphere and outer sphere complexes. If the binding is directly between ionic sites of polymer and metal cation, a inner sphere complex is formed. In outer sphere complexes the hydration shell of metal cation remains during the binding. In organic solvents, Bekturganova[24] showed that the association ability of cations with polymer also increases with decreasing ion radius, in similar way of inner sphere in aqueous solution.

Leibler *et al*.[25] present a variation of the intrinsic viscosity as a function of solution parameters (ionic strength, complex ion concentration and the molecular weight of chains). The variation of the viscosity is defined by the authors as relative change, which in the present system is $[\eta]_{NR+M}/[\eta]_{NR}$. *Figure 2* shows that viscosity increases monotonically when Ca^{2+} and Sr^{2+} are added. In the presence
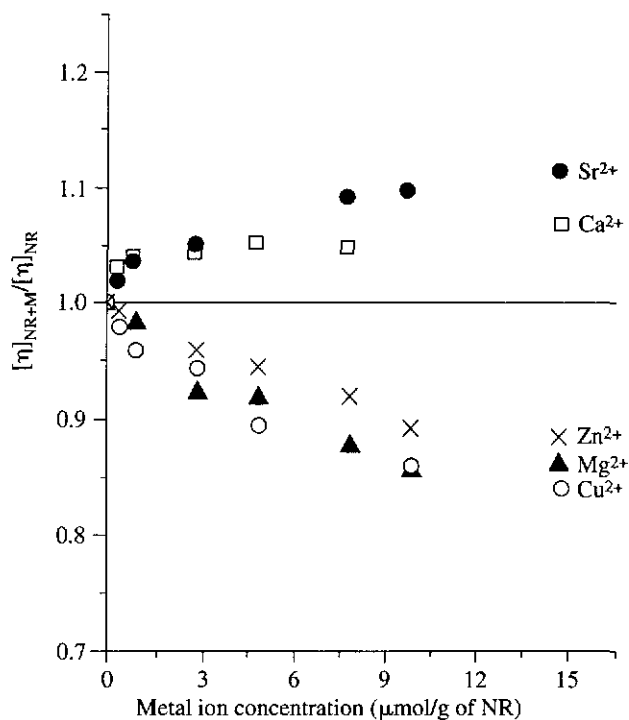
Figure 1. Specific relative variation of intrinsic viscosity ($[\eta]_{NR+M}/[\eta]_{NR}$) of natural rubber toluene solution as a function of metal cations concentration. NR from Manihot glaziovii, temperature = 30°C
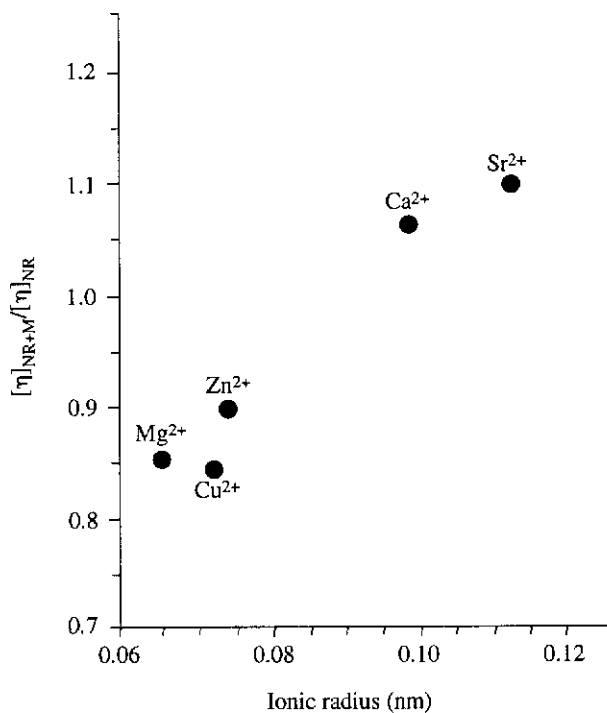

Figure 2. Correlation between relative variation of intrinsic viscosity $([\eta]_{NR+M}/[\eta]_{NR})$ and ionic radius of added metal at a concentration of 10.0 µmol/g of NR.

of Zn^{2+}, Mg^{2+} and Cu^{2+}, the viscosity decreases monotonically

Ionic radii of divalent cation of magnesium, calcium and strontium are, 0 065 nm, 0 099 nm and 0 113 nm, respectively Copper (II) and zinc (II) have ionic radii of 0 072 nm and 0 074 nm. respectively[26] A correlation of relative variation of intrinsic viscosity with ionic radius could be possible, since large metal ions displayed $[\eta]_{NR+M}/[\eta]_{NR}$ higher than 1 0 and small cations less than 1 0

By the use of lines drawn as best fit curves in *Figure 2*, $[\eta]_{NR+M}/[\eta]_{NR}$ values to 10 0 μmol of each M^{2+}/g of NR could be determined, within an accuracy of ± 0 01 In *Figure 3*, these relative variations of intrinsic viscosity are plotted against ionic radius A quite close correlation for Mg^{2+}, Ca^{2+}, Sr^{2+} and Zn^{2+} was verified The first three cations belong to the same group and preferentially bind to ligands by the same kind of electrostatic interaction Zinc (II). with d^{10} electronic configuration, is close in interaction to alkaline earth cations For this reason it displays a reasonable agreement with alkaline earth metals curve

However, a reasonable agreement was not displayed by Cu^{2+} The $[\eta]_{NR+M}/[\eta]_{NR}$ is 0 04 points below the expected value Firstly, copper (II) has a d^9 configuration It is a typical transition metal, with other influences on interaction in addition to electrostatics Secondly, the degradation of rubber, catalysed by this metal ion, could have caused the decrease in intrinsic viscosity In fact, $[\eta]$ is displaced by 0 20 dL/g, a still lower variation than the one observed in the experiment with synthetic polyisoprene in the presence of 10 0 μmol of Cu^{2+}/g of rubber (0 42 dL/g) In

this case the decrease is only due to degradation of rubber. as a result from the contact time between synthetic rubber and copper ion (4 days) The period of contact between natural rubber and Cu^{2+} was the same

CONCLUSION

Divalent metal ions interact with natural rubber in solution producing intrinsic viscosity variation which depends on the type and concentration of metal The interaction is not carried out through hydrocarbon. as it was not observed when synthetic polyisoprene was used Naturally occurring non-rubber materials could be responsible by interaction As the metallic ions utilised in this work strongly and predominantly react with ligant groups containing negatively charged oxygen, one can suggest that the interaction is done by carboxylates from fatty acid and/or from protein

A correlation with cation radius has been established Large cations displayed positive charge and small metals negative one A reasonable agreement of $[\eta]_{NR+M}/[\eta]_{NR}$ *versus* ionic radius has been verified to alkaline earth metals such as Mg^{2+}, Ca^{2+}, Sr^{2+} and Zn^{2+} The behaviour with Cu^{2+} was slightly different, probably due to the additional effect of this metal not only on the viscosity of the NR but also on its degradation, which has been observed for concentrations of 10 0 μmol/g of rubber or higher

The activation energy of flow, together with the variation of the intrinsic viscosity suggest that, for the concentrations studied, the small cations may be forming intrachain crosslinks and the large ones, interchain crosslinks
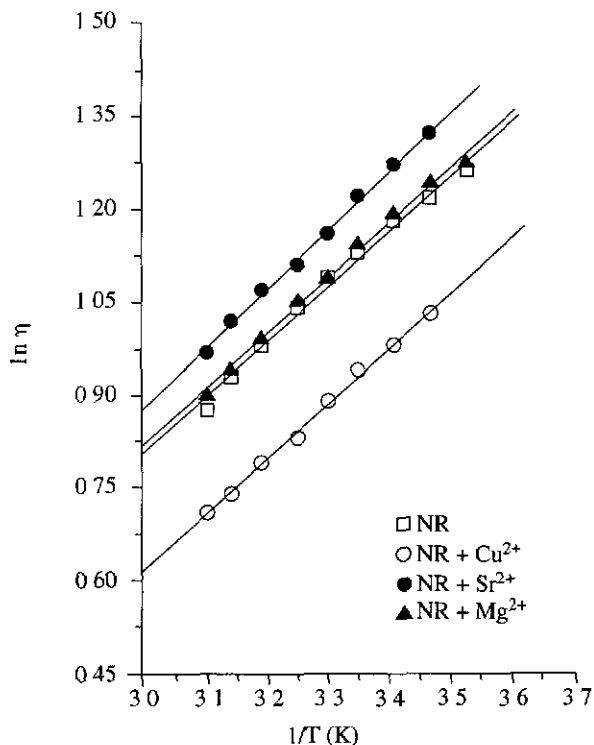
Figure 3 Ln η versus T $^{-1}$ on the absolute viscosity of NR toluene solution (0 5% w/v), in the absence and presence of 10 0 μmol/g divalent metallic ions/g of rubber

The complex lipids groups and protein according to Tanaka's model must be strongly bonded to rubber in order to make possible their association with metal ion and the concomitant reflection on the viscosity and on the activation energy of flow for the entire macromolecule

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