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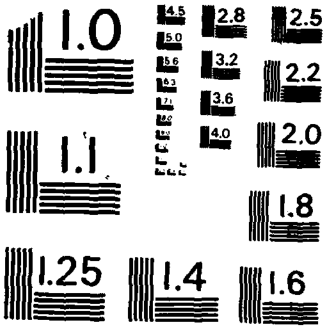

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SOLUTION PROPERTIES OF AMPHOLYTIC IONOMERS IN ORGANIC SOLVENTS

FINAL REPORT

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U. S. ARMY RESEARCH OFFICE

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

ion-pair comonomer, 2-methacryloyloxyethyltrimethylammonium-2-methacryloyloxyethanesulfonate, ionomer, self-emulsion polymerization.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The ion-pair comonomer, 2-methacryloyloxyethyltrimethylammonium-2-methacryloyloxyethanesulfonate (METMA·MES) was copolymerized in dimethyl formamide medium using a free radical initiator (AIBN) with the following methacrylate monomers: methyl, iso-butyl, t-butyl, n-butyl, t-butylaminoethyl, n-hexyl and n-lauryl methacrylates. The ion content of the copolymer was kept below 10 mole percent. This combination of ionic and non-ionic monomer units in a polymer yields ionomeric materials. Except for methyl methacrylate ionomers, all the other

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ionomer dissolved in the solvent of ~~our~~ interest: a 2:1 molar ratio mixture of 2-methyl-cyclohexanol and isopropylamine (Liquid A). The Brookfield viscosity measured with 5 w/v % solution of these ionomers showed that all the ionomers behaved as Newtonian fluid, with the exception of n-lauryl methacrylate ionomers. Even though the Brookfield viscosity was nearly three times larger if the ionomer yield was kept below 50%, the solution did not have non-Newtonian properties. The molecular weights of these ionomers were found to be of the order of 2 - 3 x 10^5. To increase the molecular weight of the ionomers, two emulsion polymerization techniques, viz., self-emulsion and regular emulsion, were used. In the self-emulsion technique the ionic monomer itself acts as the emulsifier. Ionomers synthesized by the self-emulsion technique did not dissolve in Liquid A. When an external emulsifier, Triton X-405, was used, high molecular weight ionomers (10^6) were obtained, and a 1 w/v % solution of these ionomers showed non-Newtonian behavior.

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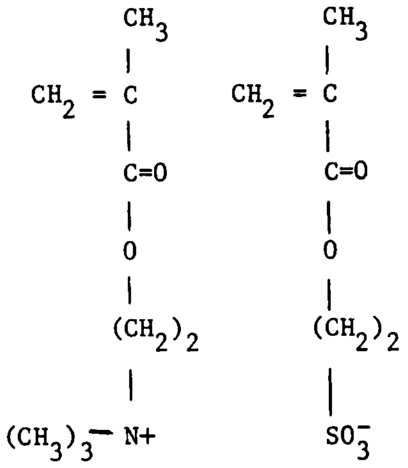
SOLUTION PROPERTIES OF AMPHOLYTIC IONOMERS IN ORGANIC SOLVENTS

Objectives:

The objective of this project was to synthesize high molecular weight ampholytic acrylate ionomers and study their solution behavior in a mixed solvent: 2-methylcyclohexanol/isopropyl amine (2:1 molar ratio).

Experimental:

The ion-pair comonomer, 2-methacryloyloxyethyltrimethylammonium-2-methacryloyloxyethanesulfonate (Fig. 1) was synthesized according to a previously reported procedure (1). This ampholytic monomer was copolymerized with various methacrylate monomers. The content of the ampholytic monomer in the copolymers was kept below 10 mol % and the resulting materials are considered to be ampholytic ionomers.



$CH_2=C(CH_3)-C(=O)-O-(CH_2)_2-N^+(CH_3)_3 \qquad CH_2=C(CH_3)-C(=O)-O-(CH_2)_2-SO_3^-$

Fig. 1. Structure of ampholytic monomer

The solubilities of the ampholytic ionomers were tested in various organic solvents (Table 1). Molecular weights of the ionomers were measured using GPC and Laser Light Scattering instruments. Dilute solution viscosity was measured in a standard Ubbelohde type viscometer. The concentrated solutions rheology of the ionomers in Liquid A (a 2:1 molar ratio mixture of 2-methylcyclohexanol and isopropyl amine) was tested using a Brookfield viscometer and a Rheometrics Mechanical Spectrometer.

TABLE 1

Solubility of isobutyl methacrylate ionomer (5 mol % ion content) in different organic solvents.

Solvent	Solubility	Solvent	Solubility
Liquid A	+	Dimethyl sulfoxide	-
Benzyl alcohol	+	Diethanolamine	-
Butanone	+	Carbon disulfide	-
3-Pentanone	+	Triethylphosphate	-
2,4-Pentadione	+	N-Methylpyrrolidone	-
Cyclohexanone	+	Acetonitrile	-
Chloroacetone	+	Diethanolamine	-
Chloroethanol	+	Tetrahydrofuran	*
Acetaldehyde	+	Trichlorethylene	*
2-Methoxyethylamine	+	Toluene	*
N,N-Dimethylformamide	+	Chloroform	*
N,N-Dimethlacetamide	+	Cyclohexanol	*
Nitrobenzene	+	2,3-Butanediol	-

N.B. +, soluble; -, insoluble; *, swells but not soluble

RESULTS AND DISCUSSION

Solution Polymerization:

The synthesis of ionomers was first carried out in the following organic solvents: Liquid A, benzyl alcolhol, isopropyl alcohol, dimethyl sulfoxide, N-N-dimethylformamide and benzene. Only the ionomers synthesized in DMF contained the ionic monomer equivalent to the feed and showed higher viscosity in Liquid A due to the ionic association. Therefore, DMF was used as the standard solvent for all the acrylate ionomers synthesized. The dilute solution viscosity measurements showed that the Huggin's relation held for the ionomers only when there was salt present in the solvent (Fig. 2). The Brookfield viscosity of the concentrated solutions (5 wt/vol %) in Liquid A increased with increasing ion content (Fig. 3). However, these ionomers, except for n-lauryl ionomer, showed no shear rate dependency (Fig. 4). Since our aim was to convert Liquid A to a viscoelastic fluid, we decided to increase the molecular weight of the ionomers. The molecular weight of the ionomers synthesized by this technique ranged from 200,000 to 300,000 g/mol.

Self-Emulsion Polymerization:

When an ampholytic ion-pair comonomer and an acrylate monomer were mixed in water medium, an emulsion formed and that emulsion was found to be good enough to carry out polymerization (2). Following the same idea of self-emulsion polymerization, we have also synthesized the ionomers. None of the ionomers, however, synthesized by this technique dissolved in any organic solvent. Therefore, no further work was done with these ionomers.

Emulsion Polymerization:

The ion-pair comonomer was copolymerized with acrylate monomers in an emulsion produced by Triton X-405. The molecular weight of the ionomers synthesized by this technique were very high, 9 x 10^6 g/mol. The Brookfield viscosity decreased with an increase of shear rate for all the acrylate ionomers synthesized. The steady-shear and dynamic properties of the solutions of the ionomers in Liquid A were tested in a Rheometrics Mechanical Spectrometer (RMS 7200). The zero shear viscosity followed the order, $\eta \propto c^4$, starting from the 1% ionomer solution. This indicates that the entanglement is present even in a 1% solution. The recovery compliance was found to be proportional to the second power of concentration, which is commonly observed for narrow molecular weight distribution polymers.

CONCLUSION

The result of this research was that ampholytic polymers could be made that were soluble in organic solvents containing added electrolyte (see previous reports) as well as being able to display viscoelastic properties in a designated solvent.

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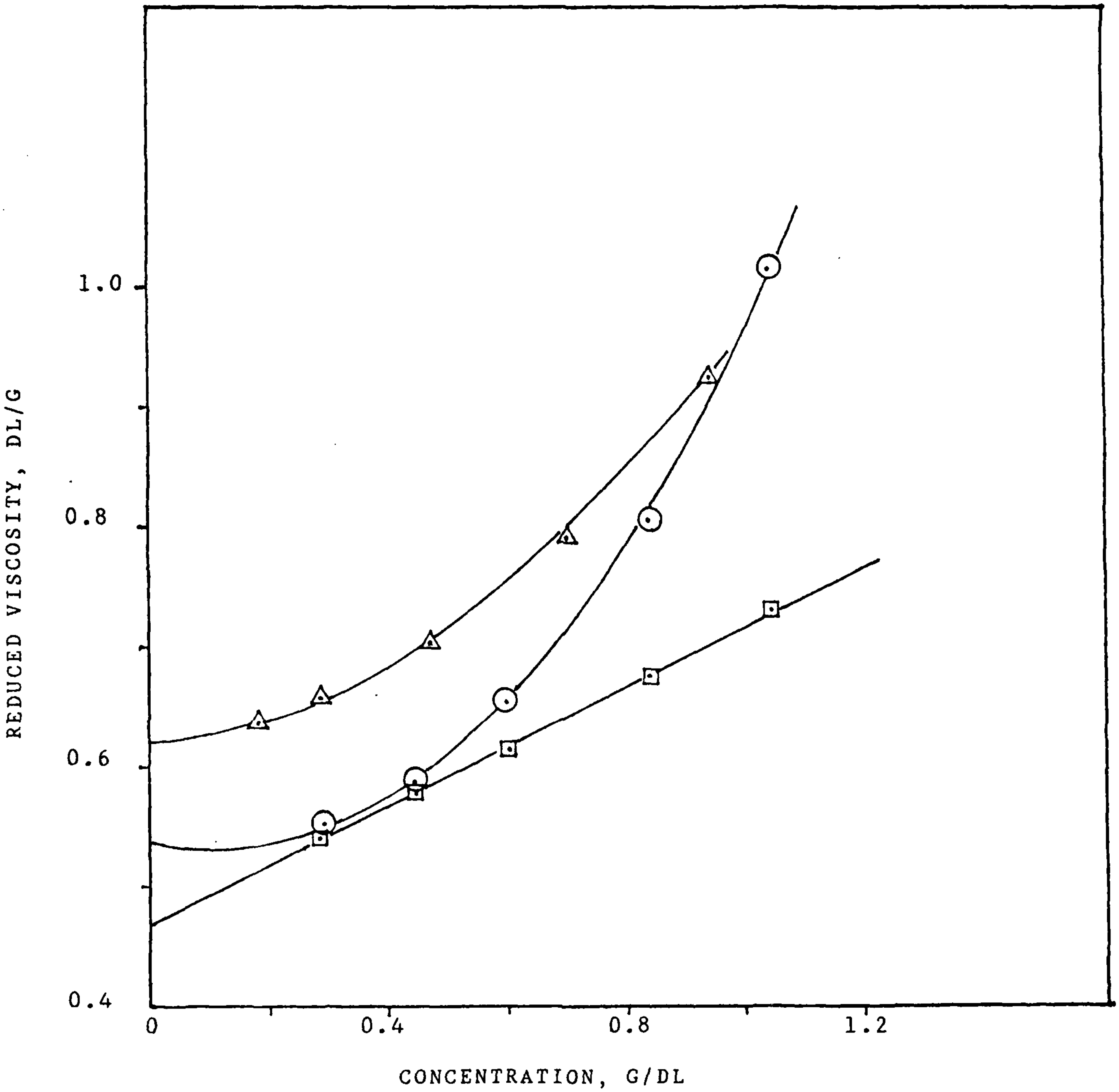

FIG. 2. DILUTE SOLUTION BEHAVIOR OF BUTYL METHACRYLATE IONOMERS (4.74 mole%) IN DIFFERENT SOLVENETS; ISOBUTYL IONOMER IN BUTANONE ⊙ , IN 0.1M LiBr/BUTANONE ⊡ ; N-BUTYL IONOMER IN BENZYL ALCOHOL △ .

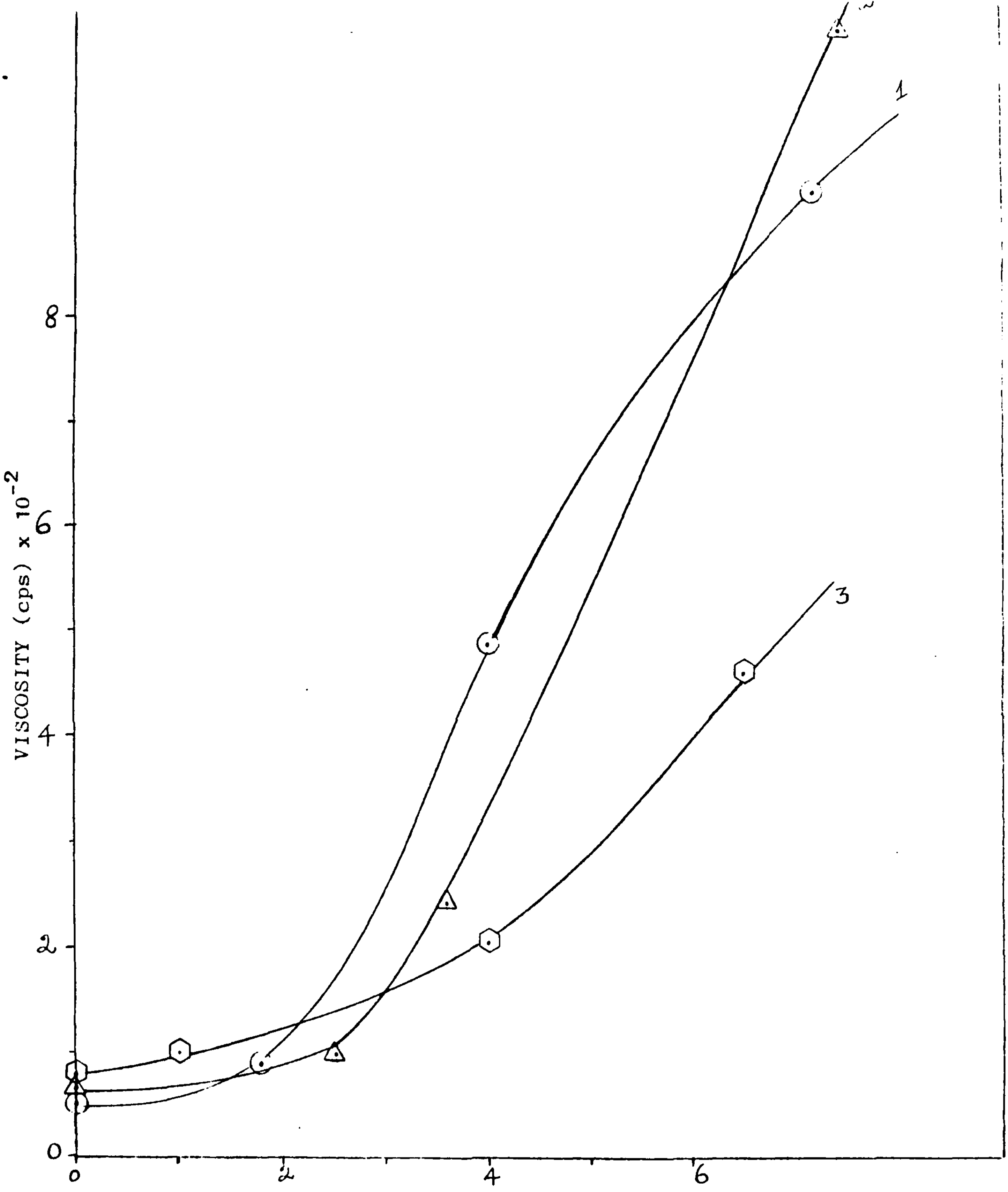

Figure 3: Effect of ionic monomer content on the viscosity of 5 % (wt./vol.) solutions of different ionomers: 1. n-butyl methacrylate ionomer, 2. n-hexyl methacrylate ionomer and 3. n-lauryl methacrylate ionomer. Solvent: Liquid A, Temperature: 30 °C, Shear Rate: 38.4 sec^{-1}.

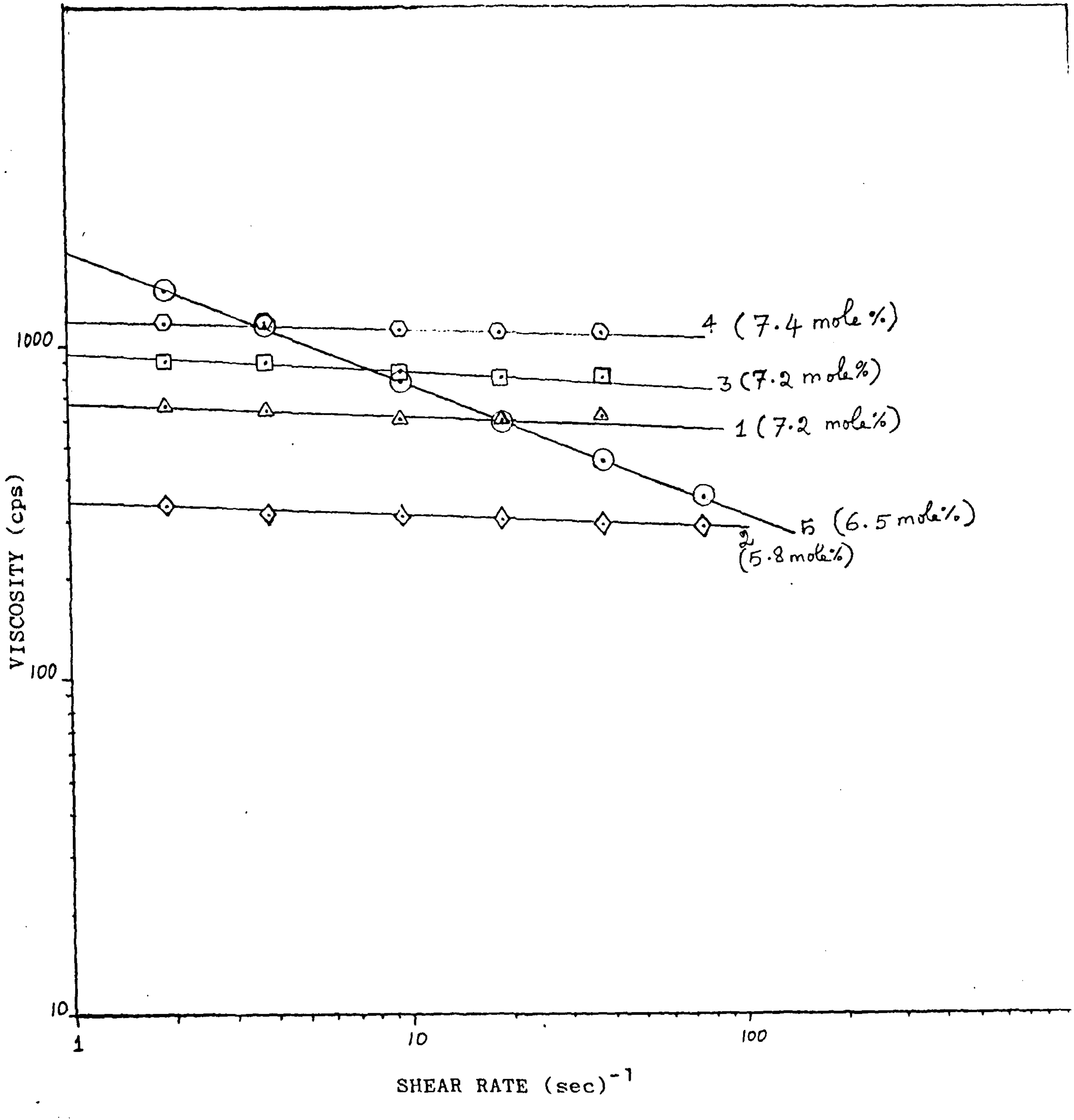

Figure 4: Shear rate dependence of 5 % (wt./vol.) solutions in Liquid A of different ionomers: 1. isobutyl methacrylate ionomer, 2. t-butyl methacrylate ionomer, 3. n-butyl methacrylate ionomer, 4. n-hexyl methacrylate ionomer and 5. n-lauryl methacrylate ionomer. Temperature: 30 °C.

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