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Shear-Resistant Drag Reduction Polymers Part I. Molecular Investigations of Polymer Drag Reduction and the Development of Laboratory Screening Methods

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Polyacrylic acid (PAA) is a water-soluble polymer that is well suited for studying molecular influences on polymer drag reduction behavior since its polymer chain conformation and size in water are extremely sensitive to solution conditions. Effects of PAA molecular weight and solution factors such as pH and water quality were investigated. Solution pH is the most important factor governing conformation of polyelectrolytes such as PAA; a higher pH (leading to size expansion) gives a higher drag reduction. As is known, molecular weight is an intrinsic factor in polymer drag reduction. Another critical factor for PAA drag reduction is water quality, since mineral ions present in water can induce collapse of the polymer molecules and subsequently, the drag reduction becomes null. However, in mineral-free water (obtained by either demineralization or chemical treatment), PAA drag reduction is remarkable. Laboratory testing using 5-inch diameter rotating disk flow (Continued)					
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and 1/4-inch diameter pipe-flow systems was established and the influence of such variables on PAA drag reduction was evaluated using these flow systems.

Guar gum, alleged to be a roll-off-free drag reduction polymer, was tested together with a PAA having a relatively low molecular weight ($M_w \approx 2 \times 10^6$) under mineral-free water conditions. The same shear stability profile was observed for the PAA drag reduction, except for PAA being twice as efficient in drag reduction as guar gum. This indicates that the shear stability of guar gum is not intrinsic to its structure but due to the low molecular weight ($\leq 10^6$).

Testing results of PAA drag reduction under varied conditions in the NRL pipe-flow system were in good agreement with those in the NOSC 1-inch pipe-flow system. An unusual association behavior of ultra-high molecular weight PAAs was observed in rotating disk flow.

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SHEAR-RESISTANT DRAG REDUCTION POLYMERS

Part I. Molecular Investigations of Polymer Drag Reduction and the Development of Laboratory Screening Methods

INTRODUCTION

The technical literature contains numerous references to a loss in drag reduction performance of polymers ("roll off") in high shear fields (Ref. 1, 2). The process is attributed to a rupturing of the polymer chain due to hydrodynamic loading. In recent years, a model of the process was developed that predicts cumulative stressing of the polymer backbone, and rupture around the midpoint (Ref. 3, 4). The model has been verified in detailed studies of polymer solutions after exposure to hydrodynamic shear fields. Analysis of the sheared polymer using chromatographic techniques revealed molecular fragments that were nominally 1/2, 1/4, etc., of the original chain lengths (Ref. 3, 4). Thus, roll-off can be attributed, at least in part, to the breaking up of the polymer molecule in the drag reduction process.

Thus, a working hypothesis for an attack on the roll-off problem can be formulated as follows: alleviate the shear-induced breakdown of polymer chains by designing and constructing polymer molecules that are intrinsically more resistant to the forces experienced in the shear field.

A large data base in the evaluation of polymers for drag reduction has been generated in the tests carried out over a number of years by NOSC in the Morris Dam 1-inch pipe-flow facility (Ref. 5). Commercially available materials from a wide variety of sources have been examined, leading to some general observations about relative performance of particular classes of polymeric materials. For most of the materials examined, only rather sparse information was obtainable from the manufacturers about the composition, molecular weight, purity, etc. In the case of some materials, it was also observed that the drag reduction performance changed with storage time, and that duplicate batches obtained from the vendor sometimes differed in performance.

NRL chemists had studied phenomenological aspects of drag reducing polymers in the early 1970's (for a review, see Ref 6). Shear degradation of polymers had been observed using laboratory-based equipment such as rotating disks and small

scale pipe flow, and some molecular approaches to improved shear resistance were developed (Ref. 7).

In the present work, the NRL objective was to develop polymer systems whose efficiency in the higher U regimes would meet projected performance requirements. On the basis of its earlier involvement in the synthesis of shear-resistant polymers, efforts were to focus on both increases in efficiency and improvement in roll-off characteristics. In pursuing the goals, NRL was to rigorously examine (from a chemical structure viewpoint) the information that had been collected in the NOSC pipe-flow tests; to pursue leads that had been uncovered in those tests; and to design new molecular systems using the principles established in previous NRL studies of shear-resistant polymers. Additionally, since the synthesis of new material for drag reduction testing was to be a mainstay of the effort, and only small quantities of material might be available, it would be necessary to establish reliable laboratory screening methods. Reliability would be determined by correlation of lab scale results with those from 1-inch pipe tests at Morris Dam. An important departure from previous studies was that the drag reduction performance was to be measured in sea water. As is reported here, the performance of some polymers is strongly affected by the presence of sea water salts.

This report covers studies of the shear resistance of two polymer systems, polyacrylic acid and guar gum (neither of which turned out to have the required characteristics), and the establishment of reliable laboratory screening methods.

EXPERIMENTAL

Materials - polyacrylic acid (PAA)¹ and polyacrylamide (PAM) were made by polymerization of respective monomer, namely acrylic acid (AA) and acrylamide (AM). Some are laboratory-made and others are commercial products. Their chemical structures are given in Fig.1.

Sample Preparation - A weighed amount of dry polymer (or gel form) of PAA was dissolved in a weighed amount of deionized (DI) water (or tap water) to give a 180 ppm (or a higher concentration) solution by stirring overnight. Low

¹PAA is a weak acid. When neutralized with a strong base, sodium hydroxide, for example, it forms sodium salt, namely polyacrylic acid sodium salt (PAA Na). This is a highly water-soluble polyelectrolyte and its molecules are expanded in solution due to the charge repulsion of the dissociating groups. PAA used here refers to PAA Na for convenience unless otherwise specified.

concentration samples were made by dilution of this stock solution. Stock solution is normally consumed within two days.

Flow Systems and Drag Reduction Measurement - The NRL Rotating disk flow apparatus (Fig.2) is constructed from a stainless steel disk (12.7 cm in diameter and 0.318 cm in thickness), a cylindrical plastic container (14 cm in diameter and 1.8 cm in height) and an electric transducer to monitor the torque on the disk which is rotated at 2800 rpm² ($Re \approx 1 \times 10^6$). Drag reduction (DR) was calculated from the torque changes in the presence and absence of polymer in solution.

The NRL 1/4-inch diameter pipe flow system³ (Fig.3) has a configuration that is purposely designed to resemble the NOSC pipe (1-inch in diameter) flow system so that an effective correlation can be made between material evaluation results from the two flow systems. The set up of the flow system is outlined in Fig.3. A 600 ppm polymer solution is made by gentle stirring polymer powder (or gel form) in water. The resulting clear homogeneous and viscous solution is diluted to a desired concentration such as 3 or 6 ppm. This is then transferred into the 20-liter reservoir tank, which is pressurized to 250 psi by N₂ gas. Before the actual DR test, an operational preparation is made on setting up the computer program and checking and/or adjustment of the pressure drop on the analog pressure transducer. When the pipe flow is started, flow rate is controlled by a solenoid valve in the flow meter automatically and data are collected through the analog/digital (A/D) converter and stored into the computer. DR is calculated and a DR profile of ΔB versus U^* is printed out.

RESULTS AND DISCUSSION

Polyacrylic acid (PAA) was chosen as a first candidate among shear resistant polymers for NOSC 1-inch pipe flow testing, since PAA was found to be one of the most shear stable polymers in our early work on drag reduction (Ref. 6). As a first trial, a commercial product, PAA ($M_w = 2 \times 10^6$) was tested in the 1-inch diameter pipe flow at 36 ppm using Morris

²This is the maximum r.p.m. attainable by this apparatus, which is capable of measuring a maximum drag reduction of 40%. Its shear strength is calculated by applying an equation from Dorfman, L.A., Hydrodynamic Resistance and the Heat loss of Rotating Solids. Translated from Russian by N. Kemmer, Oliver and Boyd, England (1963).

³All components are stainless steel.

dam lake water⁴. The result showed that drag reduction of this PAA was negligible as shown in Fig.4. This was suspected to result from a strong ion sequestering activity of PAA towards mineral ions in lake water, through which the polymer molecules are flocculated (total molecular collapse), leading to a drastic decrease in drag reduction since polymer drag reduction is known to have a strong dependence on the molecular dimension (Ref. 8).

Dimensional changes of polymers in solution are best manifested by polyelectrolytes represented by PAA (Ref. 7), because their molecular size in solution is sensitive to the degree of neutralization of the acid groups on PAA and the amount of salt existing in solution. Increasing neutralization promotes the dissociation of PAA leading to macromolecular chain expansion, while a massive addition of salt to PAA solution induces macromolecular size contraction. This situation is severe with mineral ions such as calcium and magnesium ions in the lake water. Drag reduction evaluation of the PAA ($M_w = 2 \times 10^6$) using the NRL rotating disk flow system illustrates (Figs.5 and 6) the importance of molecular dimensionality influenced by external conditions. A comparison is made with neutralization effects of PAA on drag reduction; when PAA as free acid is fully neutralized by the addition of alkali, the DR shows a marked enhancement (Fig.5). A drastic change occurs in DR when neutralized PAA is tested in tap water (Fig.6), which confirms NOSC testing results in Morris Dam water (Fig.4). In tap water, DR of PAA is null, however when the tap water is treated with EDTA⁵, the DR reaches almost the same level as that in DI water.

The EDTA is a more powerful sequestering agent than PAA, and preferentially tie up the mineral ions, preventing them from flocculating the PAA. Thus, the PAA molecules remain extended as they do in DI water (Fig.7). The Effect of EDTA on DR of PAA using our rotating disk in mineral-containing water was satisfactorily reproduced in our 1/4-inch pipe flow testing (Fig.8). A comparable result was obtained as well in 1-inch NOSC pipe flow testing (Fig. 9).

⁴Average mineral content was found to be Ca^{++} , 23.6 ppm and Mg^{++} , 11.7 ppm

⁵Ethylenediamine tetraacetic acid sodium salt: a powerful chelating agent.

For comparison, DR evaluation of guar gum⁶ (structure in Fig. 10) and PAA was carried out side by side in the NOSC 1-inch pipe flow facility. These results are shown in Fig. 11 a) and b). Interestingly enough, DR profiles of shear stability have a close resemblance between these two totally different polymer structures, except that DR of PAA is twice as efficient as that of guar gum. The outcome of this testing is of special importance, because there has been a common belief in guar gum as a "Roll-off-free polymer", which has prevailed in the drag reduction community. It is realized now that the shear stability of guar gum is not owing to any intrinsic property but to the relatively low molecular weight ($\leq 1 \times 10^6$). With high molecular weight, guar gum would roll off as does PAA (see ultra-high-molecular weight PAA in Fig. 8). Due to the semi-rigid structure, high molecular weight guar gum would not be an efficient drag reducer, although unlike PAA its DR is little affected by external conditions such as pH and mineral ions in solution.

A new discovery was made with ultra-high-molecular-weight PAA in a high shear rotating disk flow (but not in the pipe flow), indicating that chain degradation is not the only reason for shear instability of polymers. Under certain conditions, DR of PAA decreases sharply as if chain degradation were occurring. However, this was found to be not the case: the once-lowered drag reduction recovered instantaneously and nearly completely upon the addition of a minute amount of NaCl (Refs. 9 and 10) as shown in Fig. 12. We showed that the drastic decrease in DR is related to an interchain aggregation of PAA induced by flow (Ref. 10). As stated above, a relatively low molecular weight PAA does not show such a behavior (see Fig. 6). Even with the same high molecular weight PAA (CC2-36) under the same solution condition, DR of the polymer in pipe flow does not exhibit this behavior (see Fig. 8).

Such a difference in polymer behavior depending on the flow systems may result from the fact that the retention time of polymers in the pipe flow is so short that a conformational advancement toward aggregation is unlikely. One can raise questions immediately as to whether the same behavior of PAA is observable with other polymers. With polymers such as polyacrylamide (PAM) and polyethylene oxide (PEO), drag reduction recovery has not been observed.

⁶It is a nonionic, water-soluble polysaccharide having a molecular weight less than 1×10^6 . A disadvantage of guar gum is relatively rapid biodegradability in aqueous solution.

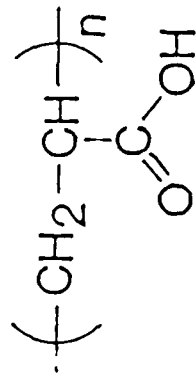
CONCLUSIONS

DR behavior of PAA is sensitive to the solution condition, particularly the presence of certain mineral ions with which the DR is completely lost. Addition of an ion sequestering agent such as EDTA to mineral-containing water, however, restores PAA DR performance to the levels observed in DI water. Guar gum, reputedly a highly roll-off resistant polymer, shows a high shear stability in rotating disk flow as well as in pipe flow. However, this stability does not result from the intrinsic property of guar gum structure but from a relatively low molecular weight ($\leq 10^6$), since a PAA having $M_w \approx 2 \times 10^6$ shows an identical profile of shear stability in pipe flow (NOSC 1-inch pipe) and yet is twice as effective as guar gum.

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Poly(acrylic acid) (PAA)



Poly(acrylamide) (PAM)

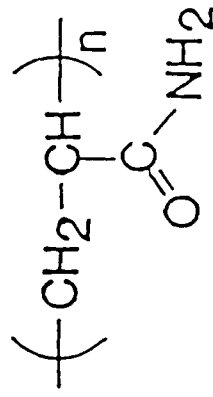


Fig. 1

Rotating Disk Apparatus

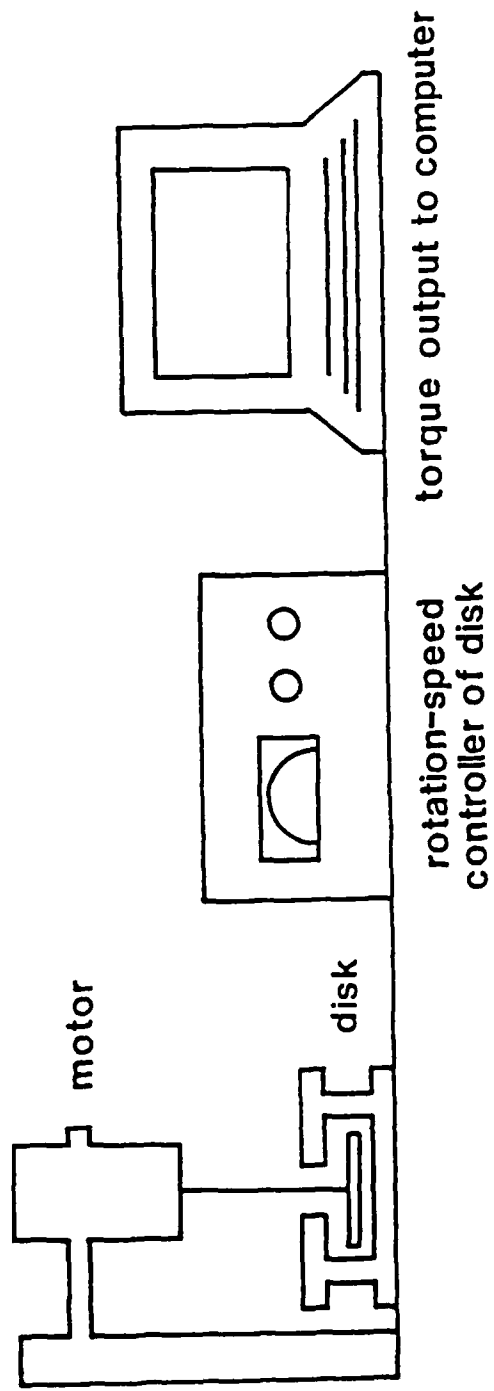
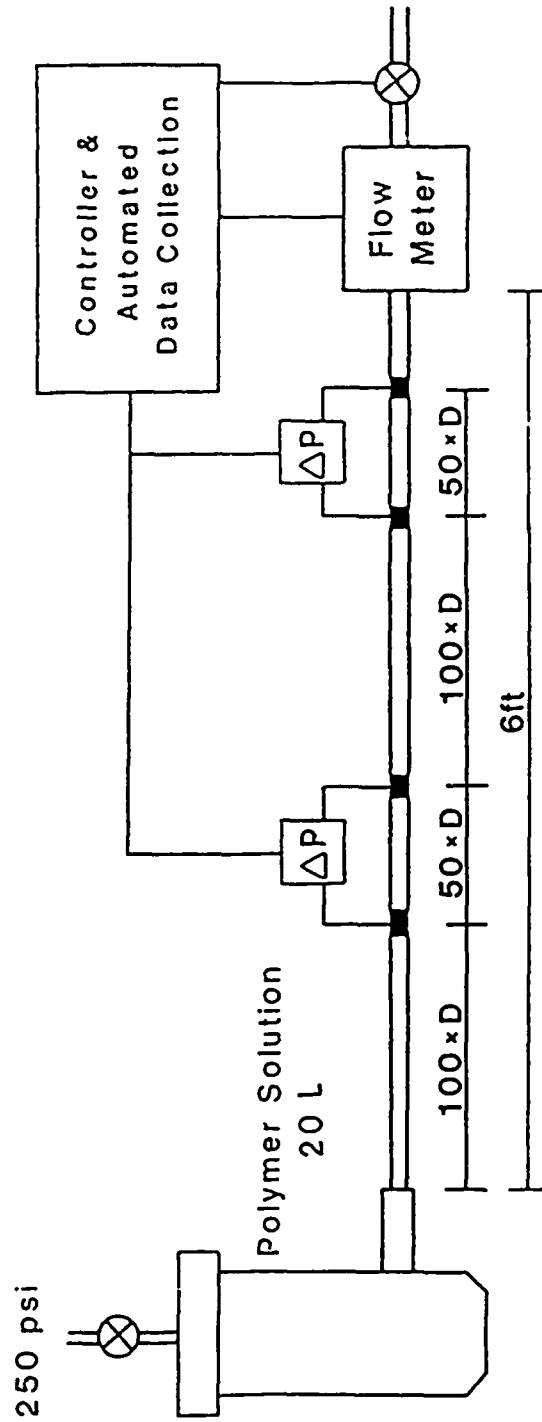


Fig. 2

NRL PIPE FLOW SYSTEM



D (pipe diameter) = 1/4 inch

Fig. 3

NOSC Test

PAA(Mw $\approx 2 \times 10^6$)

36 ppm, Lake water

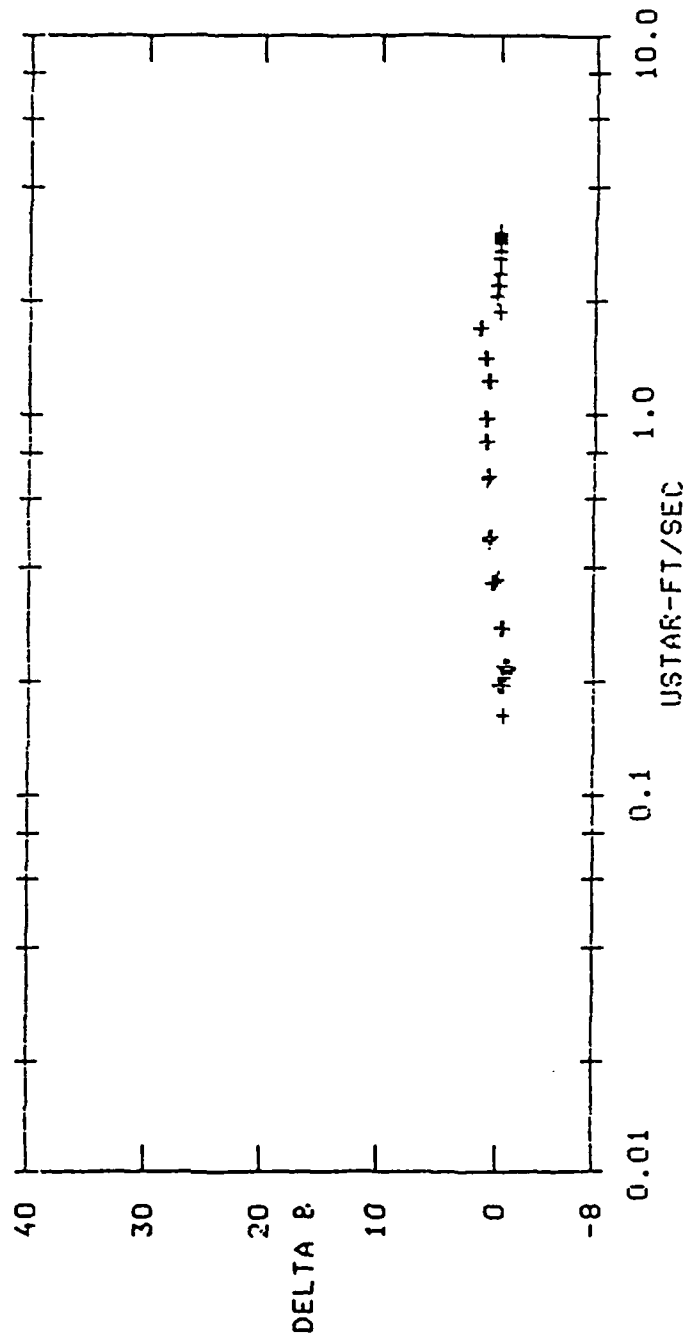


Fig. 4

NRL Test

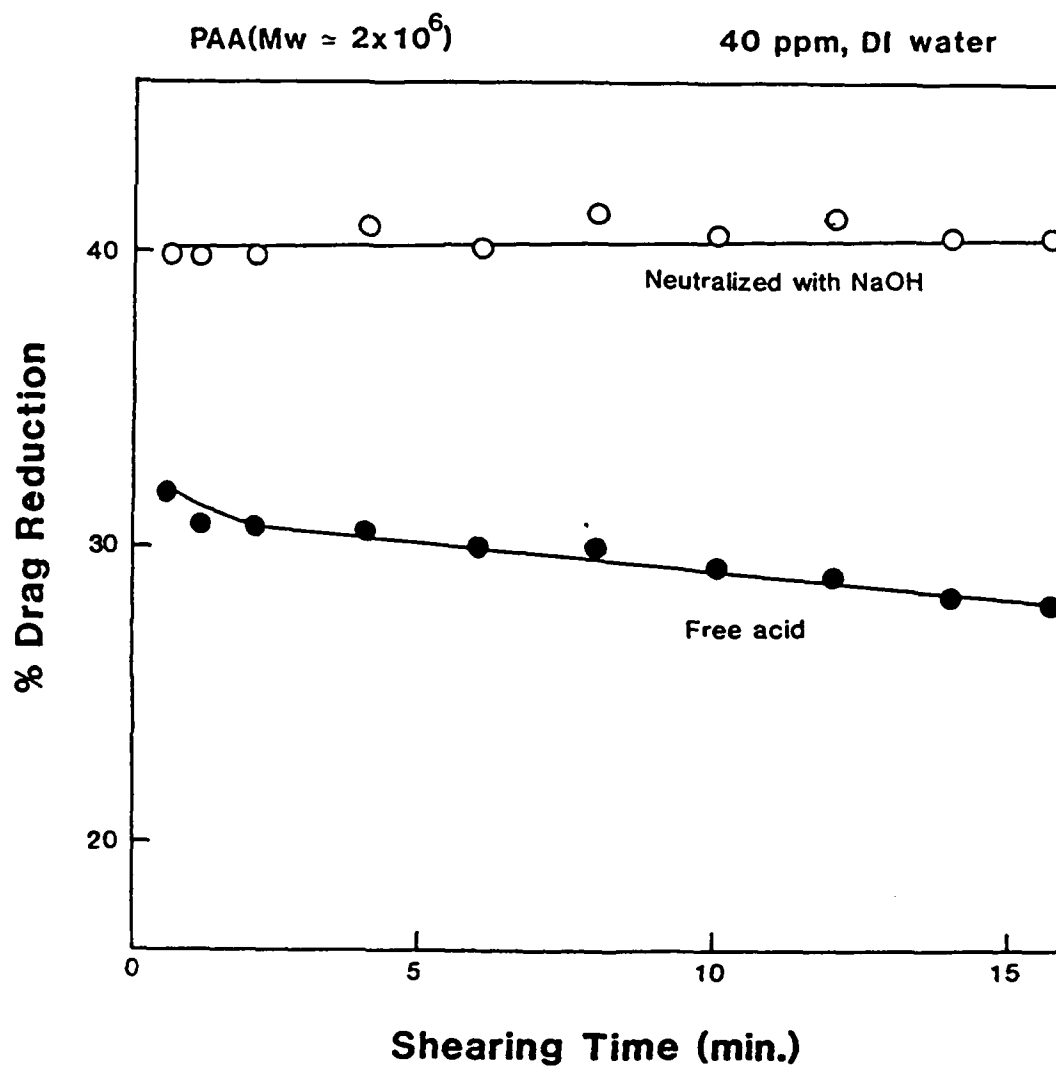


Fig. 5

NRL Test

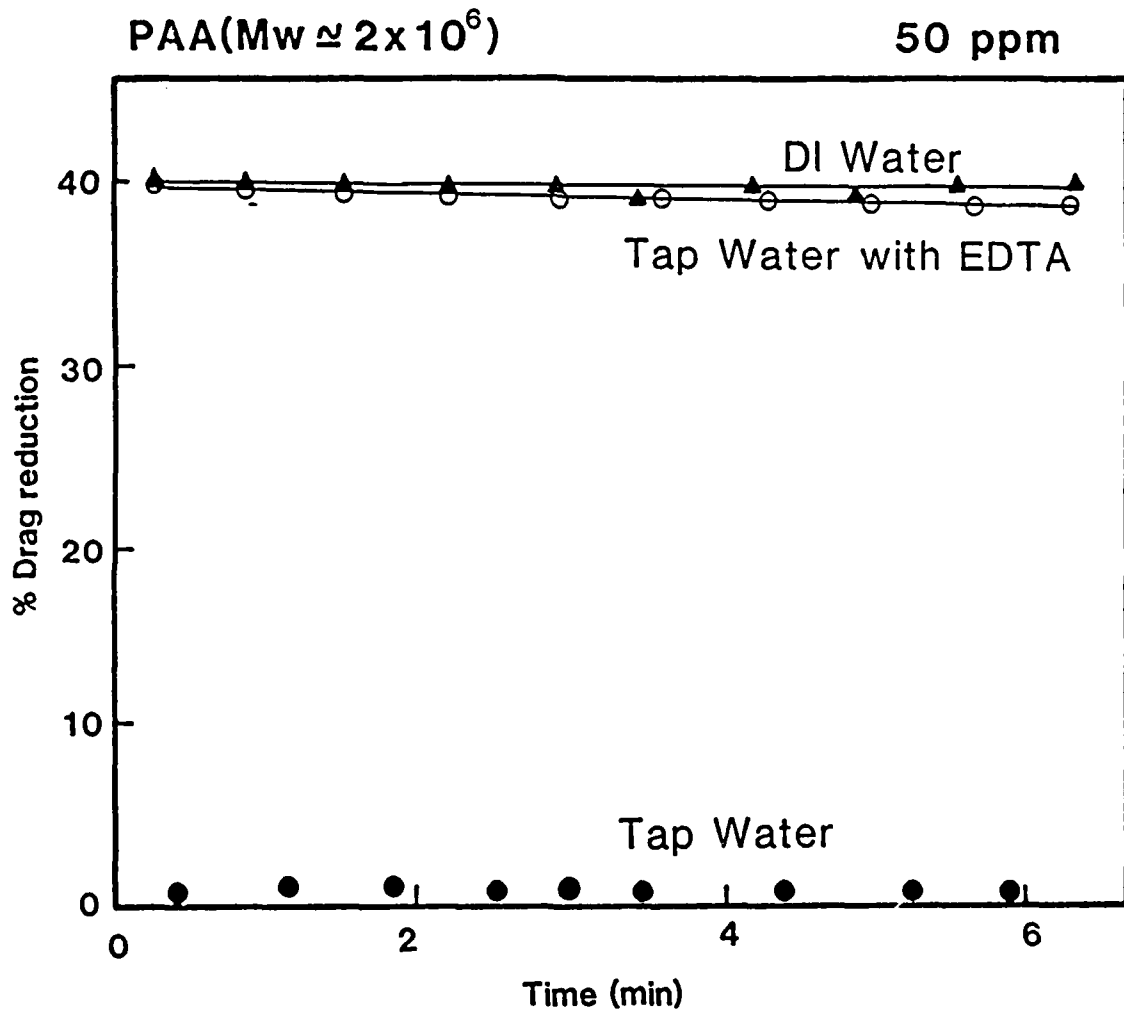


Fig. 6

Crosslinking of carboxylic acid groups
by metal ions in tap water

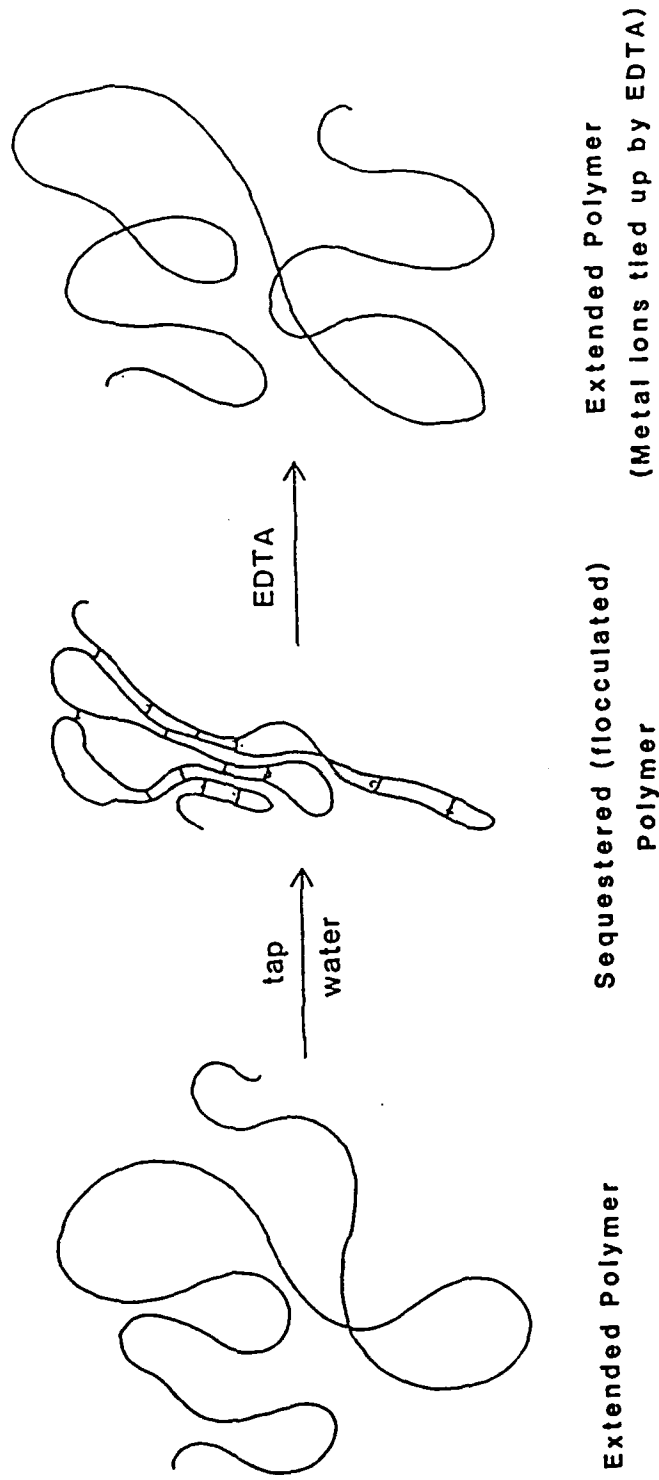


Fig. 7

NRL Test

CC2-36, PAA(Mw = 8×10^6)

12 ppm (pH = 7.9)

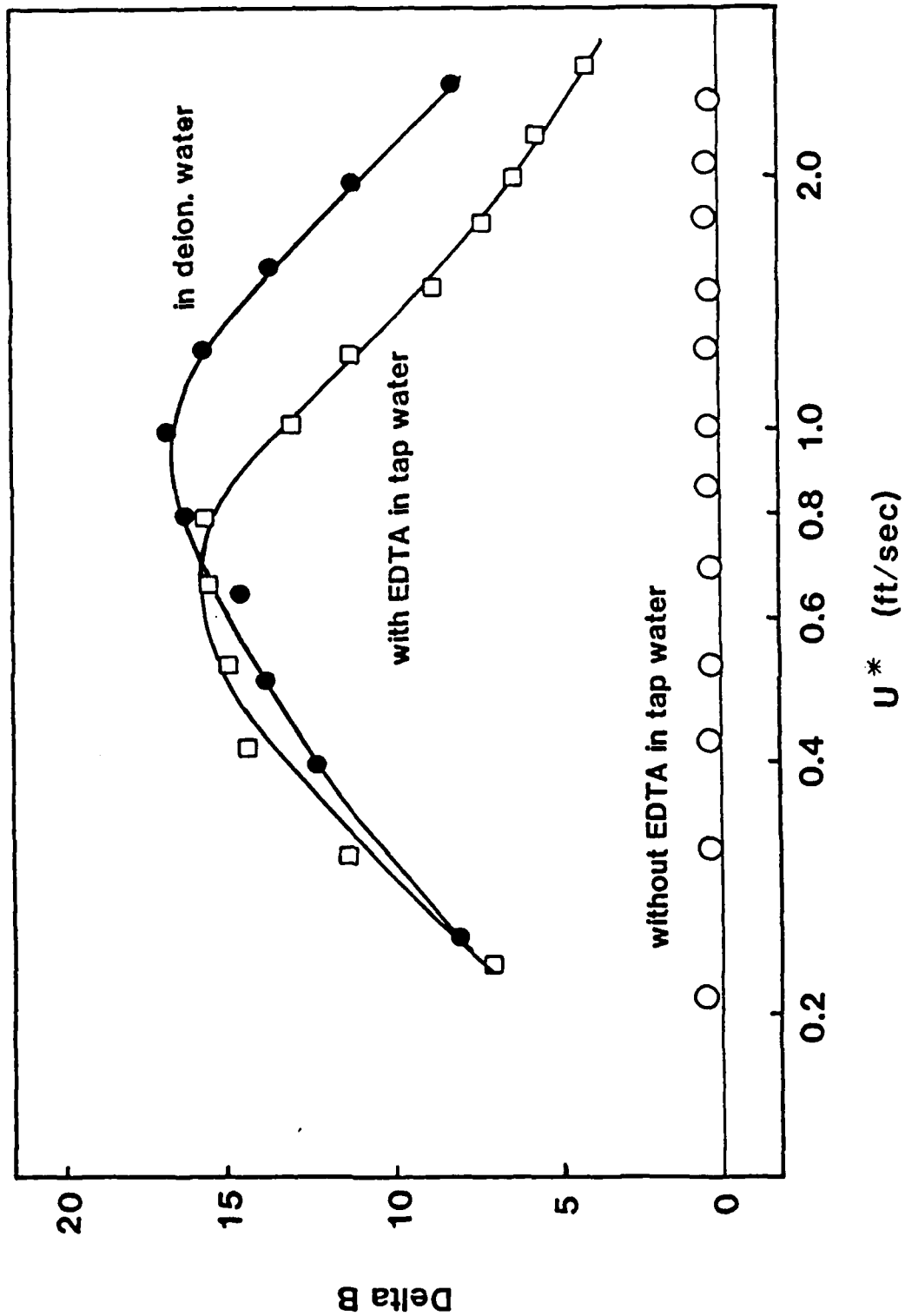


Fig. 8

NOSC TEST

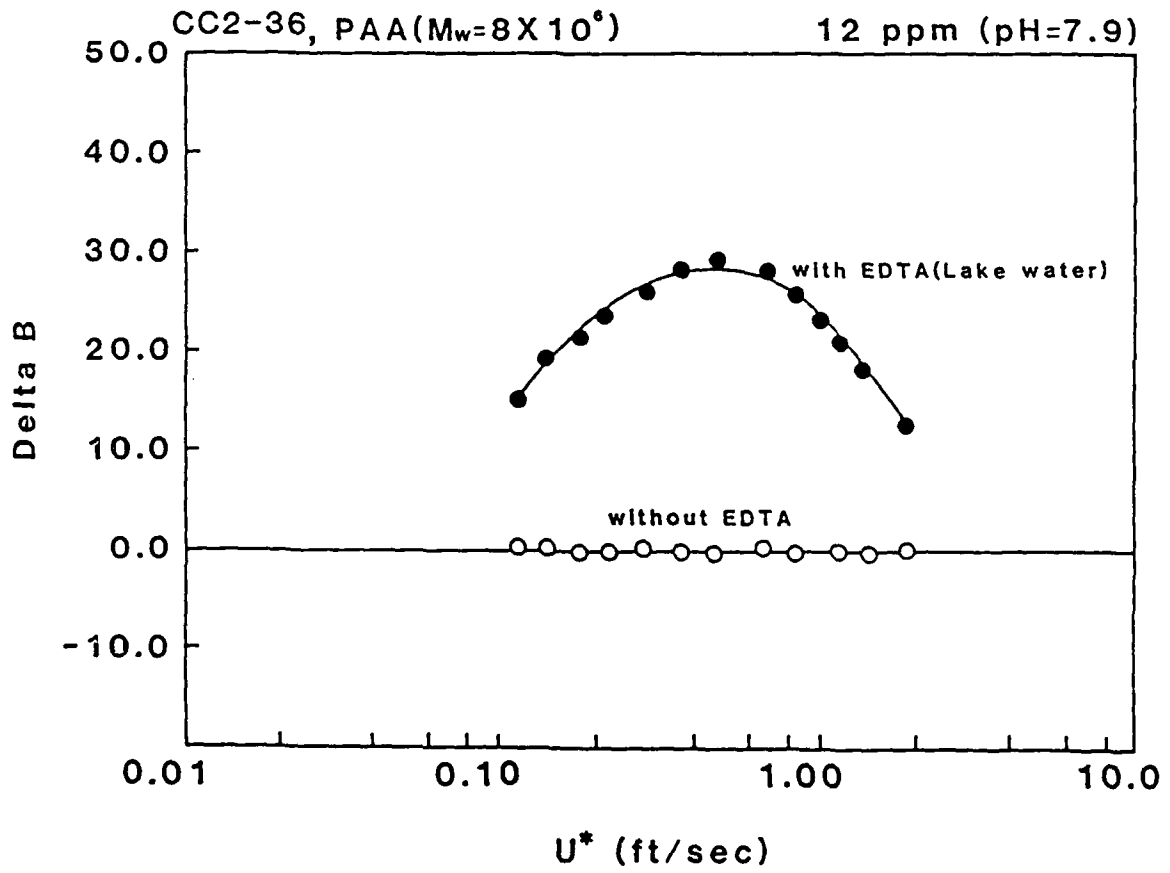


Fig. 9

Guar Gum

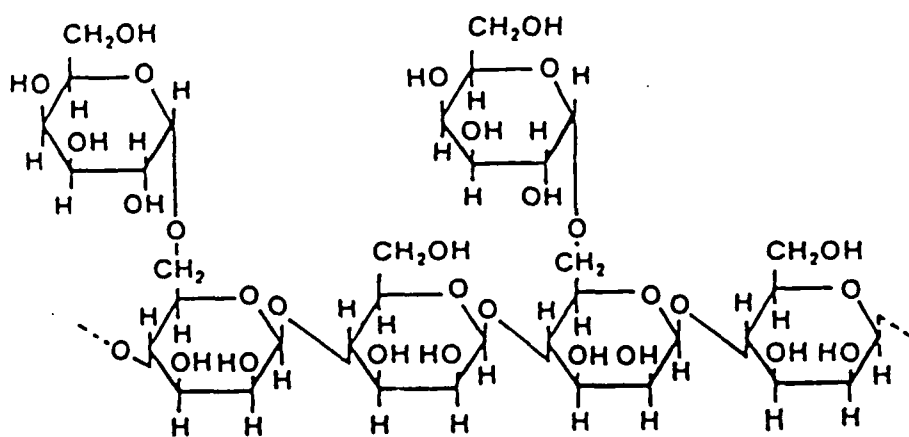


Fig. 10

NOSC Test

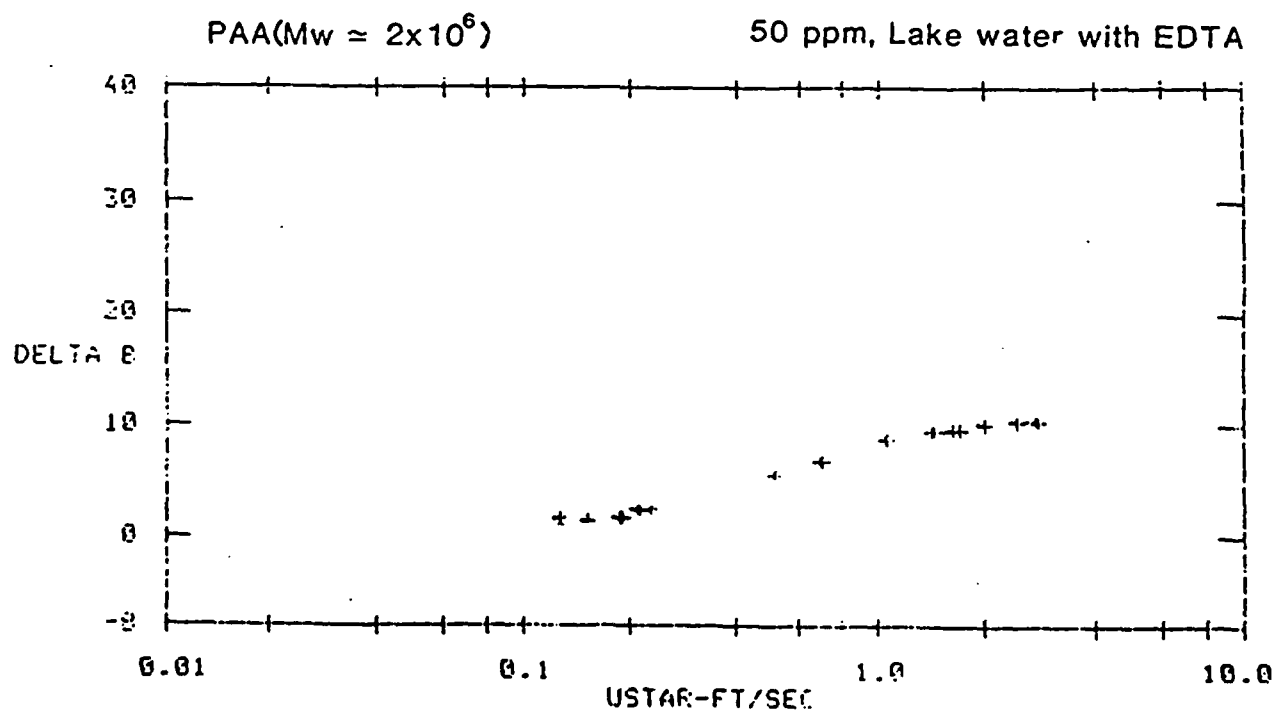
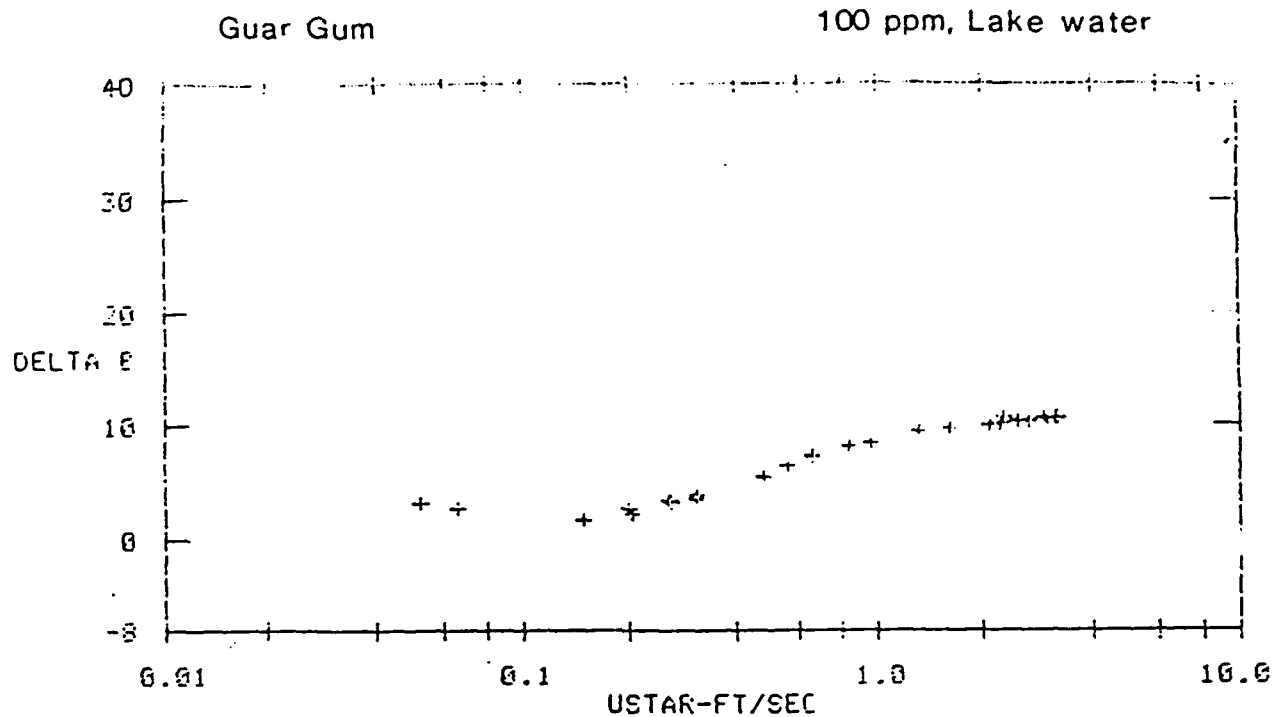


Fig. 11

NRL Test

CC2-36

18 ppm(pH= 8.0)

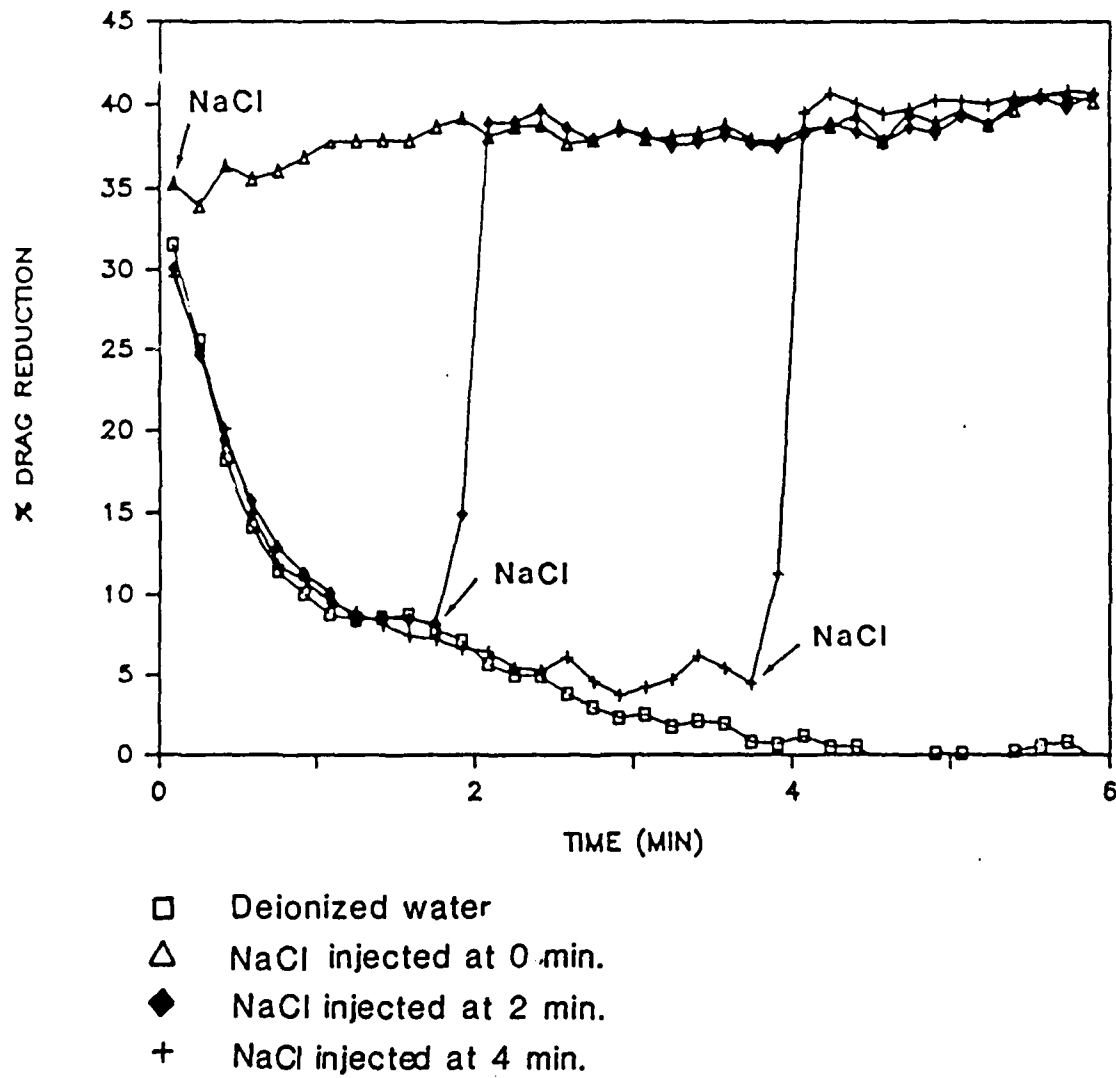


Fig. 12