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Project 06-3811 Final Report - Arthur C. Watterson

Abstract

This investigation was concerned with the preparation of several types of ampholytic polymers and ionomers for studies in drag reduction, hydrophobic interactions and nuclear magnetic resonance phenomena. The polyampholytes studied have included polymers and polyacrylamide ionomers of 3-methacrylamidotrimethylammonium 2- acrylamido-2-methyklpropane sulfonate (MPTMA/AMPS) and 2-methacryloyloxyethyl-N,N-dimethyl-N-dodecylammonium 2-methacryloyloxyethanesulfonate(MEDMA/MES). Hydrophobic interactions were incorporated by addition of small amounts n-Butyl Acrylate to the acrylamide ionomers. In general, the acrylamide ionomers showed good drag reducing capabilities, good salt tolerance and shear stability in both pipe flow and rotating disk drag reduction measurements. Addition of the hydrophobic interactions increased drag reduction capacity in sea water as compared NaCl solution or deionized water.

Shear thickening or antithixotropic behavior was observed for poly MEDMA/MES. An unusual oscillating shear behavior was also observed for the acrylamide ionomer.

NMR studies on the ionomers gave information on the relative amounts and strengths of the intra- vs. interchain ionic interactions as well as information on the motion of the carbons in gels.

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FINAL REPORT

AQUEOUS SOLUTION PROPERTIES OF AMPHOLYTIC IONOMERS

N00014-83-K-0674

1989

1. RESEARCH RESULTS

During the past few years, our research group has become interested in the synthesis and solution properties of various ampholytic polymers. These polyampholytes have been derived from sulfobetaines, in which the positive and negative charges are on one pendant group (1-3), or from the homopolymerization of an ion-pair comonomer, in which the positive and negative charges either alternate or exist in a random, pendant configuration (4-12). As reported previously, the ion-pair comonomers are a vinylic cation/vinylic anion salt, wherein no nonpolymerizable low molecular weight ions are present.

The objectives of the present investigation were: to study the effects of variations in the structure and ion-pair content of ampholytic polymers on the solution properties of these materials. In particular, we will focus on the effects on drag reduction, hydrophobic interactions and nuclear magnetic resonance (NMR) phenomena.

DRAG REDUCTION STUDIES

Ampholytic ionomers were prepared from the ion-pair comonomer 3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulfonate, MPTMA•AMPS and acrylamide. Ionomers of two different ion contents, 1.5 and 6.2 mole percent were prepared and their drag reducing capacity compared with polyacrylamide, PAm, hydrolyzed polyacrylomide, HPAm, (32% carboxyl) and Dow-Pusher 700 (Hydrolyzed Polyacrylamide containing 30 mole % carboxyl). In pipe flow measurements, the 6.2% ionomer showed higher drag reduction at all concentrations in the 25-100 ppm range when compared to the PAm, HPAm and Dow-Pusher samples. In addition, the ionomer retained greater drag reduction capability in 1.0M and 3.0M NaCl solutions. The ionomer also retained a greater percentage of its drag reducing capability after multiple passes in the pipe flow experiments and in rotating disk experiments, indicating a better shear resistance than PAm. The low-ion content ionomer in fact retained nearly 100% of its drag reducing capability in the rotating disk experiment in pure water, 1.0M and 3.0M salt solutions.

In summary, the ampholytic acrylamide ionomers showed better drag reduction and salt tolerance, and less shear degradation than polyacrylamide and its hydrolyzed products. A paper on these studies has been published. (Current Topics in Polymer Science Ref.)

To investigate the addition of hydrophobic interactions on drag reduction, three samples were prepared and studied.

The compositions of the samples are listed as follows:

1A-1-71: Am + MPTMA•AMPS (1.49%);

S-43: Am + n-Butyl Acrylate (3%);

S-48: Am + MPTMA•AMPS (1.5% = n-Butyl Acrylate (1%).

The drag reducing phenomenon can be shown by several methods, such as, Friction Factor (f) vs. Reynolds Number (Re), % Drag Reduction (%DR) vs. Re, and Pressure Drop vs. Solution Velocity. For the data in Table I, Drag Function (ΔB) vs. Shear Function (U^*) is used, where ΔB and U^* are:

$$\Delta B = 8^{1/2}\ (1/F - 2\log(ReF) + 0.91),\ F = f^{1/2}.$$

$$U^* = (f_p \langle V \rangle^2/8)^{1/2} = (\Delta PD/4L)^{1/2},$$

fp: friction factor of polymer solution.

$$f_p = (\Delta P/\eta)(D/L)(2/\langle V \rangle^2).$$

$\langle V \rangle$: average velocity of solution passing through pipe.

ΔP: pressure drop across test section.

D: pipe diameter.

L: test section length.

η: viscosity.

f: friction factor of solvent.

The function ΔB can describe the fluid structure more closely than the % drag reduction, and its value is proportional to the value of % drag reduction. The function $\log U^*$ is used to describe the wall shear stress of fluid passing through the pipe. Of course, the higher $\log U^*$ values indicates the higher Reynolds Numbers. The results of the drag reduction studies are shown in

Table I.

Table I
DRAG REDUCTION RESULTS

	S-43	S-48	1A-1-71
Shear Stability in Water (Compared with PAm	markedly improved	markedly improved	markedly improved
$\Delta B_{max.}$ in Water	12.0(3ppm)	6.0(3ppm)	9.0(6ppm)
$\Delta B_{max.}$ in Seawater			
3ppm	9.5	9.5	---
6ppm	12.0	14.5	7.5
12ppm	16.0	16.5	11.0
$\Delta B_{max.}$ in Water/ $\Delta B_{max.}$ in Seawater	1/0.79(3ppm)	1/1.58(3ppm)	1/0.83(6ppm)
logU* at $\Delta B_{max.}$ Seawater			
3ppm	-0.25	-0.15	---
6ppm	-0.1	-0.1	1.39
12ppm	0.0	0.1	1.35

It can be seen from Table I that S-43 reveals excellent drag reducing effect in deionized water. This result may be due to the hydrophobic properties of n-BA. However, the ratio of $\Delta B_{max.} \cdot water / \Delta B_{max} \cdot seawater$ of S-43 is lower than that of 1A-1-71. This may indicate that the salts, especially $CaCl_2$ and $MgCl_2$, can break down the agglomerated hydrophobic structure of S-43 in its seawater solution more easily than that of 1A-1-71 in seawater solution.

It is most interesting that S-48, the terpolymer of Am/MPTMA•AMPS/n-BA, reveals better drag reducing effect in seawater than in deionized water. We have not observed any other samples exhibiting this unusual phenomenon.

Sample 1A-1-71 shows better drag reducing effects in NaCl solution compared to deionized water. By contrast, its $CaCl_2$ (or $MgCl_2$) solutions and seawater solution are much poorer than the deionized water solution.

At 6ppm level in seawater, not only S-48 but also S-43 shows very good drag reducing effect, and is even better than the copolymer of acrylamide and acrylic acid studied in the Naval Research Laboratories.

It is also quite interesting that samples, S-43 and S-48, show $\Delta B_{max.}$ at lower logU*, that is, the optimum drag reduction appears at lower Reynolds Numbers (or lower shear stresses). This indicates that the polymer solutions provide optimum drag reduction in relatively shear stable condition.

HYDROPHOBIC INTERACTIONS

An hydrophobic ampholytic polymer and ionomer were prepared from 2-methacryloyloxyethyl-N,N-dimethyl-N-dodecylammonium 2-meth-acryloyl-oxyethanesulfonate, MEDMA/MES. Emulsions of poly(MEDMA/MES) may be precipitated with the addition of small amounts of salt, but resolubilizes the polymer with additional salt. Shear thickening behavior (antithixotropy) with a time dependence was observed for solutions of poly(MEDMA/MES) in DMF. Ionomers of MEDMA/MES with acrylamide showed unusual fluctuating shear dependency in DMF solutions. Clearly the mix of ionic and hydrophobic interactions affect the solution properties of these materials. Two papers were published on these materials (Polym. Prepr. 30 (1), 336 (1989)) and Polym. Prepr. 30 (1), 333 (1989))

NMR STUDIES

Utilizing the unusual observation of ^{14}N-^{13}C coupling in ^{13}C enriched samples of MPTMA•AMPS/acrylamide ionomers, insight into the ionic interactions was obtained. Qualitatively intra-chain interactions were favored with low charge density ionomers and interchain interactions begin to predominate at higher charge densities. (A paper was published based on these studies. (Polym. Prepr. 29 (1), 164 (1988)). Information on the gelation of MEDMA/MES was obtained from the ^{13}C relaxation times of the gel solutions. Considerable restriction of motion was observed near the ionic sites. A paper was published on these studies. (Polym. Prepr. 30 (1), 432 (1989)).

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