Shear Rheology and Salt Effect on Polyelectrolyte Solutions

Banani Mishra, Mithra K., Sidhartha S. Jena
Department of Physics and Astronomy, National Institute of Technology Rourkela, 769008, India
banani1mishra@gmail.com

ABSTRACT SUMMARY

The rheological characteristics of poly(acrylic) acid solution at different polymer and salt concentrations were studied. The shear thinning behavior for all the samples were verified and zero shear rate viscosities were obtained using Cross model equation. The non-Newtonian behavior and the strong influence of different intermolecular interactions on polymer dynamics and configuration are explained.

INTRODUCTION

Polyelectrolytes have great impact in our daily life as many biological polymers or macromolecules such as DNA, proteins are polyelectrolytes and they are charged by nature. The extensive applications of polyelectrolytes are observed in biomedical and pharmaceutical industry as well as in the coating industry. These are used as dental adhesives, restorations, controlled release devices etc. The high adsorption quality makes them useful in water treatment and coating industry where they are regarded as flocculants and thickeners. So considering the thickener behavior, it has shown a great deal with rheology. The polyelectrolytes show shear thinning especially at low shear rates because of its large size in solutions for which these are treated as industrial additives for different high-shear applications.

EXPERIMENTAL METHODS

Poly(acrylic) acid of molecular weight a was dissolved in Tris buffer of and in sodium chloride salt (NaCl) solutions of different concentration. Proper dilution took place to observe both salt and polymer concentration effect on shear viscosity as a function of shear rate by using rheometer of parallel plate geometry. The zero shear rate viscosities were calculated using Cross model which is explained as follows:

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + (K\gamma')^m} + \eta_\infty$$

Where; $\eta_0$is the zero shear rate viscosity, $\eta_\infty$is the infinite shear rate viscosity, $K$is the characteristic time of the solution and $m$is the rate index.

RESULTS AND DISCUSSION

The decrease in apparent viscosity with rise in shear rate is observed for all polymer concentration. At low shear rate, the polymer attains the Newtonian behavior and after a certain critical shear rate, the viscosity decreases monotonically which implies that the shear thinning increases with increase in shear rate approaching non-Newtonian behavior.

CONCLUSION

Polyelectrolyte solution rheology is complex in nature because of its sensitiveness towards the presence of ions in the solution. The dynamic response and rheological properties show significant variation with and without salt thereby providing interesting phenomenological behaviors.

REFERENCES

1. Boris C., Colby H. *Macromolecules* 1998, 31, 5746-5755.
2. Wyatt B., Liberatore W. *J. Appl. Polym. Sci.* 2009, 114, 4076-4084.

ACKNOWLEDGEMENTS

BM, MK and SJ acknowledge DST INSPIRE fellowship for financial assistance.

1st Controlled Release Asia Meeting, 24-25 September Singapore

Shear Rheology and Salt Effect on Polyelectrolyte Solutions

Banani Mishra, Mithra K. and Sidhartha S. Jena

Department of Physics and Astronomy, National Institute of Technology, Rourkela-769008, Odisha, India

Email id- banani1mishra@gmail.com

Motivation

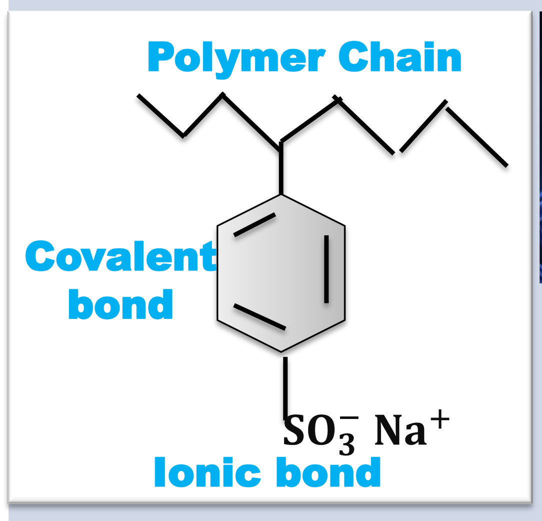
A fundamental understanding of polyelectrolyte solution rheology is captious in the current scientific field. Because we encounter charged polymer systems in daily life in the forms of biology, drug delivery and industrial applications. For non-polyelectrolytes, the dramatic changes in viscosity due to increase of polymer concentration can be related to the onset of entanglement and the rheology becomes controlled by reptation processes. But in case of polyelectrolyte systems, the polymer-polymer interaction can lead to significant effects on the rheological characteristics of the material. Here the electrostatic forces are dominant over the normal intermolecular interactions which is why this is unique from other flexible polymers. Addition of inert electrolyte e.g. NaCl results in strong electrostatic screening thereby showing conformational transition of the polymer which leads to significant shear-dependent behavior of the viscosity of the polyelectrolyte solutions.

Introduction

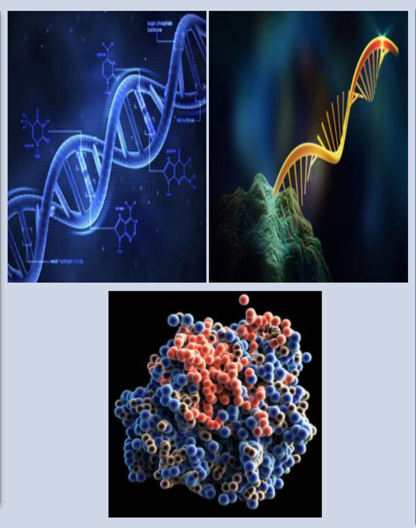
Polymer solutions or suspensions are responsible for joint lubrication in the human body, provide stability to inks and paints, making food products rich and creamy. In all these applications, the rheological characteristics of the polymer solutions have great influence in defining product performance and functionality.

Polyelectrolyte

Polyelectrolytes are a class of macromolecules consisting of ionizable groups. These groups can be dissociated in polar solvents. Many biological polymers are polyelectrolytes.



Schematic representation of polyelectrolyte



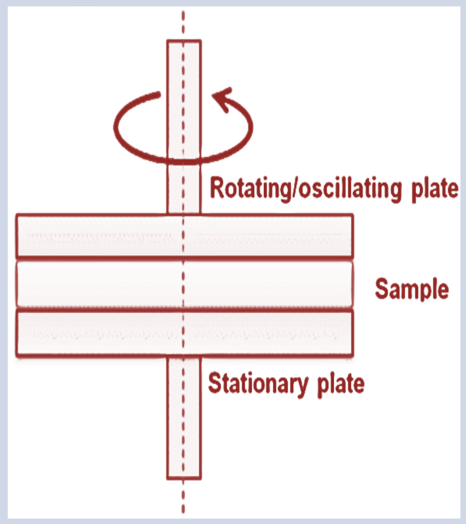
Natural PELs

Poly(acrylic) acid (PAA)

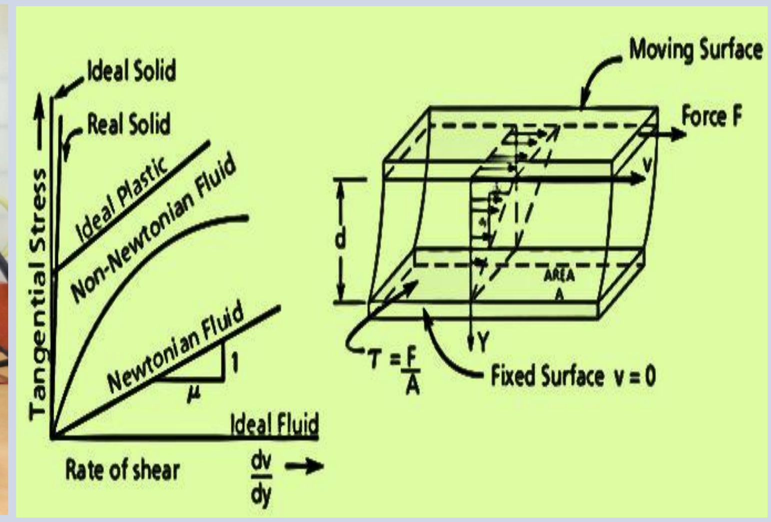
Different types of synthetic polyelectrolytes are also available apart from natural ones. Some examples are; sodium polystyrene sulfonate (NaPSS), polyacrylic acid (PAA), polymethacrylic acid (PMAA), polyvinyl pyridine (P2VP) etc. Among these, Polyacrylic (acid) is a water-soluble polyelectrolyte system containing good adsorption property, widely used as fluid thickener, and as a dispersing , emulsifying agent in pharmaceuticals and cosmetics, paper industry and aeronautics applications.

Rheology

Rheology is the study of material deformation and flow behavior linking different polymer characteristics. Among verities of flow, steady shear flow is easy to generate and has the central importance in the field of rheology.



Parallel Plate Rheometer



Shear Rheology

From shear rheology, the important material(liquid) property viscosity (η) can be determined from the measured shear stress (τ) and applied shear rate ($\dot{\gamma}$), given in equation (1):

$$\eta(\dot{\gamma}) = \tau(\dot{\gamma})/\dot{\gamma} \quad \text{.........(1)}$$

The equation (1) is analogous to Newton's law for simple liquids except that the mentioned viscosity (apparent viscosity) is a function of shear rate and not a constant parameter.

Most widely encountered time-independent non-Newtonian fluid behavior is Shear–Thinning which is characterized by apparent viscosity. Cross presented the following empirical equation to calculate zero shear viscosity widely known as Cross Model equation:

$$\frac{\eta-\eta_\infty}{\eta_0-\eta_\infty} = \frac{1}{1+m(\dot{\gamma})^n} \quad \text{............(2)}$$

Result & Discussion

- The non-Newtonian behavior is verified from the flow curves which shows the shear thinning behavior of the polyelectrolyte.
- With rise in PAA conc. from 0.1wt% to 1wt%, the zero shear viscosity (η_0) obtained from Cross Model increases by a factor of 1000.
- The observed increase in viscosity with polymer conc. is due to the crowding/obstruction of polymer chain whereas the reason of decreasing nature of viscosity with rise in salt concentration is due to the enhancement of screening effect.

Conclusion

The complex nature of polyelectrolyte solution rheology is owing to the fact that its sensitiveness towards the presence of ions in solution. This shows interesting phenomenological behavior in case of dynamic response and rheological characteristics.

Acknowledgement & References

BM, MK and SJ acknowledges DST INSPIRE for financial assistance.

- Boris C., Colby H. Macromolecules 1998, 31, 5746-5755.
- Wyatt B., Liberatore W. J. Appl. Polym. Sci. 2009, 114, 4076-4084.
- Wang Y., Pethrik R., Hudson N., Schaschke C. Ind. Eng. Chem. Res. 2012, 51, 16196-16208.