Experimental and Theoretical Studies of Polymer/Solvent Viscosity Mixtures

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ABSTRACT: Viscosity of the binary mixtures of polymers/solvent: (polystyrene/toluene), (polymethylmethacrylate/acetone), (polystyrene/benzene), (polystyrene/cyclohexane), and (polymethylmethacrylate/chloroform) were measured at different temperatures by a Haake viscometer. The samples of polymer/solvents mixtures used in the viscometry measurements were in low concentration of poly-

mer (maximum concentration 0.25 g/cm³). The measured viscosities were used to evaluate the parameters of the modified Eyring's viscosity equation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1724–1729, 2004

Key words: viscosity; polymer/solvent mixtures; Eyring's equation; polystyrene; polymethylmethacrylate

INTRODUCTION

In calculations related to design and operation of plant process units, viscosity is an important transport property. Also the temperature dependency of the viscosity is a main characteristic determining the quality of the fluids and fluid mixtures. For fluid mixtures the compositions' viscosity dependency is an essential feature.

There are different routes for calculating viscosity of fluids and fluid mixtures.^{1–3} Although equations of state have widely been used for calculating thermodynamic properties, viscosity calculations are essentially based on either the corresponding state principles or Eyring's theory.^{4–6}

Some of the methods of viscosity calculations are based on a group contribution of components in the mixture. However, the models are usually limited to a certain temperature region.^{7–9}

Use of the proper mixture model is also another determining factor in calculating the viscosity of fluid mixtures. Cao et al.^{10,11} developed a viscosity–thermodynamic model, which correlated both viscosity and liquid equilibrium data by the UNIQUAC model.

Lee et al.¹² estimated the excess activation free energy of flow in Eyring theory with the aid of an equation of state. Martins et al.¹³ developed a model based on Eyring's theory and the UNIQUAC equation for calculation of the viscosity of multicomponent liquid systems. Multicomponent liquid systems appear frequently in chemical processing and the mixture viscosity has attracted much attention,^{14–19} particularly with the aim of developing models for its estimation to be implemented in computer simulation programs.

EYRING VISCOSITY MODEL

The Eyring viscosity model, derived from reaction rate theory,⁷ provides a valuable route for calculating the viscosity of pure components. The model can be derived by considering the following basic equation, which holds for a Newtonian fluid:

$$f = -\eta \frac{\Delta \nu}{l_1} \tag{1}$$

where *f* is the shear force per unit area, Δv is the difference of two molecular layer velocities, l_1 is a distance between two molecular layers, and η is the dynamic viscosity of the fluid. The difference between two molecular layer velocities can be expressed as

$$-\Delta\nu = l_2(k_f - k_b) \tag{2}$$

where k_f and k_b are, respectively, the frequency (s⁻¹) or velocity constants for forward and backward movement of the molecule and l_2 is the distance between two molecular layers in a direction perpendicular to the direction of l_1 . It is worth noting that the distances between the molecular layers in these arbitrary perpendicular directions are represented as l_1 , l_2 , and l_3 . Assuming that

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