Thermodynamic Modeling of the Rheological Behavior of PEG3000, PEG6000 and PEG10000 Aqueous Solutions

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In this work a model for calculating dynamic viscosity of non-newtonian PEG solutions previously developed by the authors is applied to aqueous solutions of PEG with different molecular weights (nominal molecular weights 3000 g/mol, 6000 g/mol and 10000 g/mol) at 298.15 K and at several values of shear stresses. The model is based on Eyring absolute rate theory, and in the solution theory of McMillan-Mayer. An equation of state (e.g. Soave-Redlich-Kwong equation) is used for calculating the solution osmotic pressure, and the excess molar McMillan-Mayer free energy. An expression for the viscosity of a polymer solution can be written as an explicit function of the shear stress. The proposed model contains a term that describes the viscosity of a dilute polymer solution, combined with a second term that describes the deviation from newtonian behavior, and with a third term that represents the deviation from the thermodynamic ideality.

The proposed model presents five adjustable parameters, one related to the "ad hoc" expression represents the ideal solution, the two parameters of the equation of state are related to the deviation from the thermodynamic ideality, and the last two parameters are related to the deviation from newtonian behavior.

We have measured experimental rheological data for several polymer concentrations for the three PEG molecular weights, at different shear stresses, 298.15 K and 0.1 MPa. We have used a rheometer Haake RheoStress1, with the titanium coaxial cone-cylinder rotor Z34 (DIN53019/ISO 3219). The shear stress was scanned from 0.1 Pa up to the maximum supported by the system and the equipment, equivalent to a maximum torque of 0.1 N·m.

The previously proposed model has been used for correlating the viscosity values in function of the applied shear stress and polymer solution concentration. It has been found that the agreement between the calculated values and experimental ones are within the experimental error. The dependence of the model parameters with the molecular weight of the polymer has also been studied.