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Polyelectrolyte solutions in solvents of extremely high dielectric constant THOMAS SEERY, University of Connecticut, SERGEY FILLIPOV, JIRI PANEK, PETER CERNOCH, PETR STEPANEK, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic — The physics of polyelectrolyte solutions are of great importance in understanding various processes in nature but they pose a challenge due to their complex behavior. For strong electrolytes discussed here the fraction of the condensed counterions depends on the charge density of polyion, i.e., 1-1/zλ where z is the valence of the counterions, and λ is the reduced coupling constant defined by .$\lambda = l_B/a$Here a is the distance between ions on the polyion and l_B is the Bjerrum length $l_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon kT}$ where e is the elementary charge, ε the dielectric constant of the solvent, k the Boltzmann constant and T absolute temperature. The Bjerrum length is the distance between charged species (counterions, co-ions or charged monomers) when the electrostatic energy between them is equal to the thermal energy kT. We exploit the strong temperature dependence of dielectric constant of N-methylformamide to vary the Bjerrum length in a solution of polyelectrolytes (sodium polystyrene sulfonate) and to thus investigate the dynamic properties of salt-free solutions over a broad temperature range, from +54 to –58^{o}C. Fast and slow diffusion processes are observed. The ratio of diffusion coefficients, D_s/D_f , increases and the ratio of amplitudes A_s/A_f decreases, both by a factor of about two in this temperature range corresponding to the expected temperature variation of the Bjerrum length.

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