## Thermodynamic Modeling of Polyelectrolyte Solutions with the eNRTL Model

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Polyelectrolytes are polymers that have charged functional groups along the backbone chains. The charged functional groups are electrostatically attached with counterions that carry opposite charges. The counterions are able to dissociate in solutions so that the charged polymers attractive to counterions and repulsive to co-ions form. Such behavior makes polyelectrolytes applicable in processes of separation, purification, biomedical, and energy storage systems [1-3]. A thermodynamic description of phase equilibrium of the mobile ions including both counterions and co-ions in polyelectrolyte solutions draws great interest of research. Early works used Gibbs energy models [4-7]. There had been no limiting law for polyelectrolyte solutions like Debye-Hückel theory for simple electrolytes until Manning put forward his counterion condensation theory in 1969 [8]. He defined the dimensionless linear charge density of polyelectrolytes as the Manning parameter and stated that counterions would condense on the charged functional groups of polyelectrolytes when charge density was larger than a certain critical value. Using Manning's model as the limiting law, Danner used the NRTL model to calculate excess Gibbs free energy, activity, and osmotic coefficients [9-10]. Sadowski combined Manning's limiting law and Perturbed-Chain Statistical Association Fluid Theory to describe vapor-liquid and swelling equilibrium [11]. Recently, Kamcev tried to apply the counterion condensation theory to predict activity coefficients of mobile ions in cross-linked ion exchange membranes in equilibrium with simple electrolyte solutions [12]. This work calculates the total excess Gibbs free energy of polyelectrolyte systems from three contributions. Manning's limiting law is used to capture the "point-toline" electrostatic interaction between mobile ions and charged functional group, as well as counterion condensation. The Pitzer-Debye-Hückel formulation is applied to account for the "point-to-point" electrostatic interactions between each charged particles in the solution. And the eNRTL theory is used to deal with the local short-range interactions between all molecular and ionic species. [13] In addition to the binary NRTL interaction parameters, the dimensionless charge density of polyelectrolytes is required to describe the polymer chains, which can be determined either by physical structure of the polymer or regression of experimental data. The eNRTL model is capable of systematically correlating and extrapolating thermodynamic properties of all components in polyelectrolyte solutions. With a limited number of parameters, this model calculates phase equilibrium of mobile ions in polyelectrolytes including ion exchange membranes, osmotic coefficients, and Gibbs free energy of the solution in better agreement with experimental data, compared to using Manning's limiting law alone.

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