The influence of the charged obstacles on thermodynamics and dynamics in electrolyte solutions

B. Hribar-Lee[a] V. Vlachy[a] and M. Jardat[b]

[a] *University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčceva 5, 1001 Ljubljana, Slovenia, E–mail: barbara.hribar@fkkt.uni-lj.si*
[b] *UPMC Univ Paris 06, UMR 7195, PECSA, F-75005 Paris, France*

To investigate the effect of the charged obstacles on the equilibrium properties of electrolyte solutions the self-diffusion and single ion activity coefficients of ions of size symmetric electrolytes were studied in the presence of charged obstacles within a 'soft' version of the primitive model of electrolyte solutions. The Brownian dynamics method was used to calculate the self-diffusion coeffcients, and the replica Ornstein-Zernike theory was used to calculate the individual activity coefficients of mobile ionic species. The results are compared with those of fully annealed systems.

In most cases the self-diffusion and activity coefficients of counterions and co-ions in the presence of charged obstacles follow the trends of the fully annealed solutions, the presence of charged obstacles modifies these trends only in a few situations. The behavior of the simplest systems is explained via the mean-field approach: co-ions are, due to the repulsive interaction, excluded from the area around obstacles. Introduction of multi-valent charges into the system changes this result when the concentration of obstacles is low: the behavior of the system is determined by a subtle balance between attractive and repulsive interactions. Our study allows us to clearly identify the effects due to obstacles, and to separate them from those arising from the composition of the solution. Thermodynamic and dynamic results are consistent in explaining the behavior of the systems studied.