Ion size effect on electrophoretic mobility of a colloidal particle

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One of the main assumptions of the standard electrokinetic model is that ions behave as point like entities. Many recent works modify this classic model taking into account the finite ion size, introducing steric interactions among ions by means of an excess electrochemical potential. Two main conclusions can be drawn from these studies: the corrections to the standard electrokinetic model are only significant for high surface charges and/or bulk electrolyte concentrations and, in order to fit experimental data, it is necessary to consider effective ionic radii much larger than the hydrated ionic radii appearing in the literature. While the first restriction is not important for microelectrode systems in which high surface charges are used in practice, it is an important limitation for electrokinetic phenomena in colloidal suspensions in which the surface charges are relatively low.

In a recent work [1], we compared the corrections introduced into the equilibrium standard electrokinetic model by the Bikerman and the Carnahan-Starling expressions. Our main conclusion was that high and low surface charge conditions must be examined independently. At high surface charges, both the Bikerman and the Carnahan-Starling models can provide acceptable representations of the same measured results but due to different physical processes. For low surface charge values, however, the Bikerman model nowhere approaches saturation values so that the obtained results are close to the classical Poisson-Boltzmann solution while the Carnahan-Starling equation presents important deviations even in this situation. The bottom line is that the Carnahan-Starling model appears to be able to provide an interpretation of the electrokinetic potential vs. surface charge dependence in the case of colloidal particles suspended in aqueous electrolyte solutions.

In the present work we calculate the out of equilibrium behaviour of a colloidal suspension using both the Bikerman and the Carnahan-Starling equations for the steric interactions. The obtained results agree and extend our previous equilibrium study: in all cases the steric interactions improve upon the standard model predictions so that the surface potential, and electrophoretic mobility are larger (in modulus) [2]. Moreover, unlike the Bikerman equation, the Carnahan-Starling expression leads to corrections that are substantial even for electrolyte solution concentration and surface charge density values typically encountered in colloidal suspensions.

Acknowledgements The financial supports of Ministerio de Economía y Competitividad (project FIS2013-47666-C3-2-R), Junta de Andalucía (project PE-2012 FQM-694), and University of Jaén and Caja Rural de Jaén (Project UJA2015/06/23.v) are gratefully acknowledged.

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