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The non-dominance of counterions in the spherical electrical double layer: an integral equation and simulational study ENRIQUE GONZÁLEZ-TOVAR, IVÁN GUERRERO-GARCíA, MARTíN CHÁVEZ-PÁEZ, Instituto de Física, Universidad Autónoma de San Luis Potosí, México. — The ionic cloud around a charged colloid (or electrode) immersed in an electrolyte is known as the electrical double layer (EDL). An important amount of theoretical and simulational work in this topic has been done in the frame of the restricted primitive model (RPM) of an electrolyte, in which the ionic size correlations are taken into account considering equal-sized ions. Ionic size asymmetry, on the other hand, has been explored to much less extent. One possible explanation to this can be found in the common belief that counterions dominate the EDL, i.e., that away from the zero-charge point the properties of the EDL are essentially equal for size-symmetric and size-asymmetric electrolytes if the counterions are the same in both cases. Recent developments, however, clearly show that size asymmetry can induce dramatic effects on the structure and properties of EDLs. In the present work we report Monte Carlo simulations and theroretical results that exhibit that the counterions not always rule the properties of the EDL, e.g. the ionic size asymmetry enhances the phenomenon of charge reversal (i.e., the overcompensation of the bare charge of the macroion) and the screening due to the electrolyte. Additionally, we find that the predictions of the HNC/HNC and HNC/MSA integral equations are in good agreement with simulations in a wide range of conditions.

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