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Components of Dielectric Constants of Ionic Liquids[1]

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In this study *ab initio*-based methods were used to calculate electronic polarizability and dipole moment of ions comprising ionic liquids [1]. The test set consisted of a number of anions and cations routinely used in the ionic liquid field. As expected, in the first approximation electronic polarizability volume turned out to be proportional to the ion volume, also calculated by means of *ab initio* theory. For ionic liquid ions this means that their electronic polarizabilities are at least an order of magnitude larger than those of traditional molecular solvents like water and DMSO. On this basis it may seem surprising that most of ionic liquids actually possess modest dielectric constants, falling the narrow range between 10 and 15. The lower than first expected dielectric constants of ionic liquids has been explored in this work via explicit calculations of the electronic and orientation polarization contributions to the dielectric constant using the Clausius-Mossotti equation and the Onsager theory for polar dielectric materials. We determined that the electronic polarization contribution to the dielectric constant was rather small (between 1.9 and 2.2) and comparable to that of traditional molecular solvents. These findings were explained by the interplay between two quantities, increasing electronic polarizability of ions and decreasing number of ions present in the unit volume; although electronic polarizability is usually relatively large for ionic liquid ions, due to their size there are fewer ions present per unit volume (by a factor of 10 compared to traditional molecular solvents). For ionic liquids consisting of ions with zero (*e.g.* BF_4) or negligible (*e.g.* NTf_2) dipole moments the calculated orientation polarization does not contribute enough to account for the whole of the measured values of the dielectric constants. We suggest that in ionic liquids an additional type of polarization, "ionic polarization", originating from small movements of the centre of the charge on the ions might be present. According to our estimations, this ionic polarization contribution to the dielectric constant could be rather significant (between 8 and 10 for some ionic liquids). In collaboration with Douglas R. MacFarlane, School of Chemistry, Monash University.

[1] E. I. Izgorodina, M. Forsyth and D. R. MacFarlane, Phys. Chem. Chem. Phys., 11, 2452, 2009.

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