

# diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

## Ionic Aggregation in Metallocene Olefin Polymerization Catalysts: A PFG NMR Study

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### I. Introduction

Metallocenes are organometallic compounds of the group IV metals where at least one of the metal ligands is a cyclopentadienyl which when activated with an appropriate co-catalyst, have remarkably high olefin polymerization activities. The activated catalyst is comprised of an anion-cation pair and the strength of the ionic interaction is one of the parameters that control the catalyst activity as well as other catalytic properties such as the stereochemistry of the olefin coordination.

A variety of different solvents can be used when the polymerization is performed in the liquid phase. These solvents can have a wide range of ionic strengths, with a resulting impact on the equilibrium constant for the ion pair dissociation and the possibility of ionic aggregation. We investigate these possibilities using  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{11}\text{B}$  PFG NMR studies of the activated catalyst and on ammonium borate salts which are model compounds of the catalyst. The equivalent radius of a diffusing sphere was calculated from the measured self-diffusion coefficients using the Stokes-Einstein relation.

### II. Results

For both the model system and catalyst system, only ions associated as ion pairs or higher order ionic aggregates are observed depending on the concentration and dielectric constant of the solvent. These larger aggregates are comprised of a discrete number of ion pairs with a single aggregation number. We calculate the aggregation number from the energy minimized structures of ion-pair multiplets using molecular mechanics simulations. The aggregation of ions in solvents with low dielectric constant is consistent with the expected physical chemistry of electrolytes in solution as initially described in the classic work of Bjerrum.

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