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Influence of Nanoscale Confinement on the Molecular Mobility of Ibuprofen

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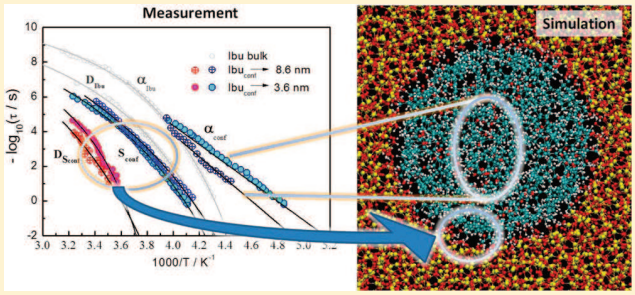
ABSTRACT: The molecular mobility of ibuprofen confined to a mesoporous silica host (MCM-41) of 3.6 nm pore diameter is investigated by dielectric relaxation spectroscopy. It is confirmed that crystallization is suppressed; therefore, depending on the temperature, the guest exists in the glassy and supercooled state inside of the pores. A detailed relaxation map is provided where multiple processes are dynamically characterized, comprised of three processes that are also found for the bulk and two additional ones. The bulk-like processes include two secondary processes, a simple thermally activated one, a γ process and a Johari−Goldstein β_{JG} process, and the one associated with the dynamic glass transition of molecules located in the pore center (α process). In confinement, all of these processes display deviations in its dynamical behavior relative to the bulk, the most dramatic one undergone by the α process, which exhibits Arrhenius-like temperature dependence upon approaching the glass transition instead of Vogel/Fulcher/Tammann/Hesse (VFTH) scaling as obeyed by the bulk. The two additional relaxations are associated with the dynamical behavior of hydrogen-bonded ibuprofen molecules lying in an interfacial layer near the pore wall, an S process for which the mobility is strongly reduced relative to the α process and a Debye-like D process for which the dynamics is closely correlated to the dynamics of the interfacial process, both exhibiting VFTH temperature dependencies. The comparison with the behavior of the same guest in the analogous host, SBA-15, with a higher pore diameter (8.6 nm) leads to the conclusion that the bulk-like mobility associated with the dynamic glass transition undergoes finite size effects being accelerated upon a decrease of the pore size with a concomitant reduction of the glass transition temperature relative to the bulk, 22 and 32 K, respectively, for the 8.6 and 3.6 nm pore diameters. The continuous decrease in the separation between the α- and β_{JG}-trace with pore size decrease allows one to conclude that confined ibuprofen is a suitable guest molecule to test the Coupling Model that predicts a transformation of the α process into a β_{JG}-mode under conditions of an extreme nanoconfinement. The overall behavior inside of pores is consistent with the existence of two distinct dynamical domains, originated by ibuprofen molecules in the core of the pore cavity and adjacent to the pore wall, from which a clear picture is given by molecular dynamics simulation.



INTRODUCTION

Nanoconfinement emerged in the past few years as a strategy to manipulate/prevent crystallization[1−3] of guest molecules and stabilize unstable metastable forms in polymorphic pharmaceuticals because their dissolution and bioavailability are usually improved.[4,5] In particular, when crystallization is avoided, it was found that the glass transition temperature (T_g) of the incorporated glass former can be affected when the restricted geometries have dimensions in the nanometer scale.[6−8] The thus-obtained state can have an enhanced mobility compared with that of the bulk where the acceleration in the dynamics is rationalized as an effect of the interference of the pore dimension with the characteristic length for the dynamic glass transition. This can result in a deviation from the typical curvature of the relaxation time of the dynamic glass transition in the activation plot (Vogel/Fulcher/Tammann/Hesse law; VFTH law) to Arrhenius dependence.[8] However, for rather low pore sizes, the guest molecules can undergo specific interactions with the pore wall, as has been shown for systems forming hydrogen bonds between the guest molecules and the inner pore surface. In this case, the molecular mobility can slow down, and the T_g value is increased.[8,9] Therefore, in general, the dynamics of molecules confined to nanoporous hosts is controlled by a counterbalance between confinement and surface effects.[8] This was shown recently by some of us by means of dielectric relaxation spectroscopy (DRS) for

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