

Debye Process in Ibuprofen Glass-Forming Liquid: Insights from Molecular Dynamics Simulation

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By means of molecular dynamics simulations, dynamical properties of racemic ibuprofen glass-forming liquid are investigated at different temperatures from 360 to 500 K. The origin of the peculiar low amplitude Debye-type relaxation observed experimentally by dielectric relaxation spectroscopy is addressed (Bras, A. R.; Noronha, J. P.; Antunes, A. M. M.; Cardoso, M. M.; Schönhals, A.; Affouard, F.; Dionisio, M.; Correia, N. T. *J. Phys. Chem. B* **2008**, *112*, 11087). Single and total dipolar autocorrelation functions are calculated. It is found that the behavior of the total dipole correlation is dominated at short and long times by the single function. It mainly originates from the antiparallel dipoles correlations in agreement with a value of the Kirkwood correlation factor slightly smaller than unity. The simulation suggests that the long time Debye-type decay of the dipole–dipole correlation is dominated by the internal cis–trans conversion of the O=C–O–H group coupled to the change of the intermolecular linear/cyclic HB structures. The overall rotation of the molecules is about 1–2 decades faster than the cis to trans transformation, so all the O=C–O–H group environments are equal on average. The effective rotational potential energy barriers of the O=C–O–H groups due to the surroundings are thus averaged and dipolar relaxation follows a simple Debye law. It is found that cyclic dimers inhibit the cis to trans conversion unlike the linear dimers and trimers which favor this conversion and stabilize the trans isomer. It is well in line with the very low amplitude of the dielectric strength associated with the Debye relaxation observed experimentally and its increase when the liquid is maintained isothermally above the melting temperature since this amplitude mainly relates to the low fraction of ibuprofen molecules in the trans conformation. A comparison is made with the Debye-type relaxation found in microstructured monohydroxy alcohols.

I. Introduction

In the framework of the glass transition phenomena, there has been recently revived interest for hydrogen-bonded (HB) liquids composed of molecules of low molecular weight such as alcohols, polyols, or sugars. An important issue is to characterize the complex mechanisms underlying the different relaxation dielectric processes and to precisely identify the dielectric contribution truly resulting from the structural relaxation.^{1–8} From dielectric relaxation spectroscopy (DRS) investigations, most of the molecular glass-formers show multiple non-single exponential (non-Debye) relaxation processes.⁸ In most cases, the lowest frequency and dominant process (i.e., the slowest one) is identified to the so-called α -relaxation associated to the cooperative molecular motions and the dynamic glass transition. Some other higher frequency secondary processes corresponding to localized motions are also usually observed, such as the so-called β -Johari–Goldstein and γ -processes.^{8,9}

For unclear reasons, it is known for decades that some monohydroxy alcohols or amides hydrogen bonded (HB) glass-forming systems in which the –OH or the –NH group is

sterically accessible behave differently. At the lowest frequencies, they exhibit a surprising very intense peak corresponding to a purely exponential or Debye-type decay.^{10–17} This peak (noted process I in the following) is always accompanied by a few decades smaller amplitude and a few decades higher frequency mainly non-exponential relaxation (process II). At higher frequencies, another relaxation is also frequently detected and often attributed to the Johari–Goldstein process β_J - α ⁹ (process III). The problem of the origin of the Debye-type relaxation and the way it contributes to the liquid structural relaxation or its viscosity continues to be a matter of debate and has motivated many experiments and models, but a complete understanding is still lacking.

In fact, some models have been postulated but none of them can be considered as fully accepted since they cannot completely describe all the features observed for the liquids exhibiting Debye-type relaxation. It was originally proposed that Debye-type dielectric relaxations mainly originate from the rates of breaking and reforming of hydrogen bonds linked to the rotation of the permanent dipole moment of the hydroxyl group.^{14,18,19} As postulated by Johari and Dannhauser,¹⁵ the lower frequency Debye process should be at the origin of the true structural relaxation since it contributes to about 90% of the total dielectric relaxation strength. It would result from simultaneous and

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