Fluorination-Dependent Structural Changes in Butanols from MD Simulations and X-ray Scattering

Jure Kovač [a], Andrej Jamnik [a], Istvan Szilágyi [b], Matija Tomšič [a]*

[a] Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia.
[b] MTA-SZTE Momentum Biocolloids Research Group, Department of Physical Chemistry and Materials Science, Interdisciplinary Research Center, 1 Rerrich Béla tér, H-6720 Szeged, Hungary

Matija.Tomsic@fkkt.uni-lj.si

Fluorinated alcohols are attractive model systems for probing how fluorination, a key structural motif of environmentally persistent per- and polyfluoroalkyl substances (PFAS), reshapes intermolecular organization and dynamics in the liquid state. Here, we examine a series of fluorinated butanols to determine how the degree and pattern of fluorination influence their liquid structure and dynamics. Molecular dynamics (MD) simulations were performed using the OPLS-AA force field, while small- and wide-angle X-ray scattering (SWAXS) experiments were carried out for the investigated compounds. Theoretical scattering intensities were calculated from the simulation results using the complemented system approach for direct comparison with the experimental data [1-3]. As shown in Fig. 1, the resulting calculated SWAXS intensities are in good agreement with the experimental data, supporting the validity of the employed molecular models. Increasing fluorination leads to a shift of the main scattering peak towards lower q values, indicating an increase in characteristic correlation lengths associated with the polyfluoroalkyl segments. Partial scattering contributions show that this feature arises primarily from correlations between fluorinated hydrophobic moieties. Radial and spatial distribution functions reveal that fluorination affects the hydrogen bond network, particularly when substitution occurs near the hydroxyl group. Intramolecular conformational analysis indicates reduced molecular flexibility with increasing fluorination. The dynamic properties obtained from MD simulations reflect the combined influence of hydrogen bond strength and conformational preferences. Overall, the results reveal that fluorination reshapes liquid butanol structure and dynamics, primarily through changes in hydrophobic correlations, hydrogen-bond organization, and conformational constraints, providing insight into structure–property relationships relevant to PFAS-related systems.

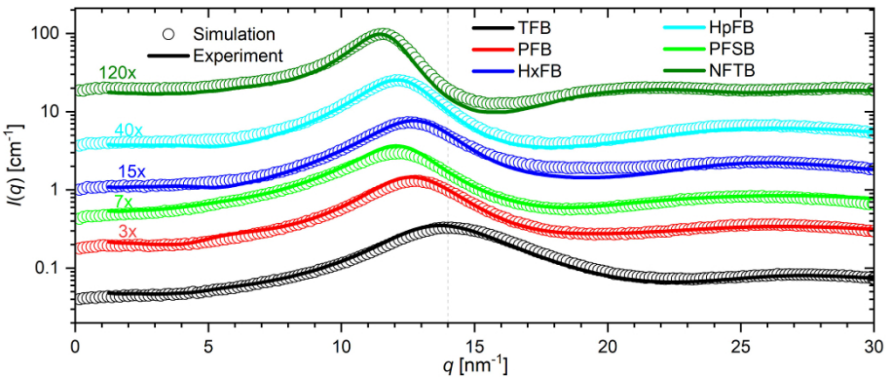

Fig.1. Experimental and calculated SWAXS curves for studied fluorinated butanols.

References:

[1] A. Lajovic, M. Tomšič, A. Jamnik, The complemented system approach: A novel method for calculating the x-ray scattering from computer simulations. J. Chem. Phys., 2010, 1 33, 174123.
[2] J. Cerar, A. Jamnik, I. Pethes, L. Temleitner, L. Pusztai, M. Tomšič, Structural, rheological and dynamic aspects of hydrogen-bonding molecular liquids: Aqueous solutions of hydrotropic tert-butyl alcohol. J. Colloid Interface Sci., 2020, 560, 730–742.
[3] J. Cerar, A. Jamnik, I. Szilágyi, M. Tomšič, Solvation of nonionic poly(ethylene oxide) surfactant Brij 35 in organic and aqueous-organic solvents. J. Colloid Interface Sci., 2021, 594, 150–159.

Acknowledgements:

We acknowledge the support from the Slovenian Research Agency (research core funding no. P1-0201 and project no. N1-0483 “Ionic Liquids and Nanoclays in Aqueous PFAS Removal”) and from the Hungarian National Research, Development and Innovation Office (project no. SNN152145).