

Translational and rotational dynamics of methanol molecules in NiCl₂-methanol solutions: MD simulations vs. quasi-elastic neutron scattering

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The high-resolution quasi-elastic neutron scattering (QENS) technique has been applied to study the translational and rotational diffusion of methanol molecules in pure methanol (MeOH) at different temperatures and various NiCl₂ concentrations. Molecular dynamics (MD) simulations have been carried out in the NVT ensemble to explore the particle dynamics and microscopic structures of the experimentally investigated systems.

The translational diffusion coefficients derived from the QENS measurements of pure MeOH at the different temperatures agree well with the values reported in literature. Our results clearly indicate that the translational diffusion coefficient of methanol decreases (*i*) with decrease in temperature, and (*ii*) with increase in the concentration of NiCl₂ in MeOH, whereas the rotational diffusion coefficient is not so affected by variation of temperature or electrolyte concentration. The present MD simulations confirm the above experimental findings.

The MD results show that mainly the solvent molecules present in the bulk govern the dynamic behaviour of MeOH molecules in its electrolyte solutions. The translational diffusion coefficients of the Ni²⁺, of MeOH molecules in the first solvation shell of Ni²⁺, and also of its counter-ion, the Cl⁻, are very close to each other and follow similar trends with change in concentration of the electrolyte.

Analysis of molecule dynamics in terms of diffusion coefficients and auto-correlation functions of angular and centre-of-mass velocities, and unit vectors of dipole moment show that a cation of small size and high charge, such as Ni²⁺, forms dynamically well-defined solvation shell. Also, with decrease in the ion-molecule distance, the mobility of solvent molecules decreases significantly for such ions of high charge density.