Multinuclear NMR Study of Supramolecular Restructuring in Organic Solute/H_2O/Ions Systems

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1H, 23Na, 35Cl, 79Br and 81Br NMR chemical shifts (d) and signals half widths (D1/2) have been measured in some organic solute/H2O/ions systems (tetrahydrofuran(THF)/H2O/Na^+/Cl^- and in 3-methylpyridine(3MP)/H2O/Na^+/Br^-) at different mass fractions of salt (X). Discontinuous changes in slope of d = f(X) and D1/2 = f(X) have been found in 23Na and 81Br NMR spectra of 3MP/water/NaBr solution at X = 0.1 and T = 301 K and at X = 0.07 and T = 294 K. The sensitivity of NMR parameters depends more on composition of solution for the anions (Cl^- and Br^-) than for the cations (Na^+). A very strong relaxation effect for 81Br nuclei with relaxation rates reaching 14 000 s^{-1} was observed. The results are explained in terms of hydrophobicity and ion - molecular clustering. Effect of strong relaxation was interpreted using the model proposed by Hertz and Holz (J. Phys. Chem., 1974, **78**, 1002-1013). According to this the configuration of dipoles, which are placed at the same time in the hydrophobic hydration sphere of the solute molecules and in the first hydration shell of anions, becomes more or less coherent. It causes a huge electric field gradient on the anions and thus very strong relaxation effects. No similar configuration of dipoles is formed for cations. Their relaxation behavior is rather normal. Conclusions are supported by the quantum chemical *ab initio* density functional theory calculations of tensors of magnetic screening and electric field gradients.