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PARAMAGNETIC NMR- AND ESR-PROBING - CONVENIENT TOOLS FOR INVESTIGATING STATE AND INTERACTIONS OF POLYELECTROLYTES IN SOLUTIONS

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NMR-paramagnetic probing is a unique method for investigation of organized media, which makes possible controlling complexation and association processes, monitoring substrate-receptor interactions, development of new contrast agents for magnetic resonance imaging on the basis of stable metal complexes with high values of the relaxivity ($R_{1,2}$).

The complexation of paramagnetic metal ions is usually accompanied by the decrease of relaxivity. However, in solutions of Gd^{3+} , Mn^{2+} and some other ions, an unexpected significant increase in the rate of relaxation was revealed in presence of anionic or nonionic surfactants. From the NMR theory the proton relaxation rate in solutions of the named ions is known to be controlled by the rotational correlation time τ_r . Therefore the relaxivity rise in solutions of anionic surfactants is a result of more slow rotation of the probe ions bound to the negatively charged surface of micelles.

The state of the solutions of the series of polymers (sodium polystyrene sulfonate, polyethyleneimine and poly-N-vinylpyrrolidone) and certain mixtures thereof was studied by NMR relaxation using manganese(II) and gadolinium(III) ions as paramagnetic probes. In solutions of an anionic polymer the growth of the NMR-relaxation efficiency ($R_{1,2}$) is observed, as well as the decrease of $R_{1,2}$ - in the case of cationic polymer. For polymer blends the nonmonotonic changes of $R_{1,2}$ are identified depending on the solution composition. For both Mn^{2+} and Gd^{3+} ions the changes in ESR spectra of their polyelectrolyte solutions were found. In case of sodium polystyrene sulfonate the ESR spectra parameters are distinct from the aqua ion's ones, as well as for polyethyleneimine solution at $pH > 7$ the ESR spectra lines broadens greatly (up to disappearance). All these effects were explained by the distinction of ion probes binding mode to polyelectrolytes of different nature. Comparison of the T_1 - and T_2 -relaxivity data for Mn(II) ions binding with micelles and polystyrene sulfonate reveals that latter substitutes one additional water molecule from the inner sphere of the metal ion. Addition of NaCl to solutions based on polystyrene sulfonate, or mixtures thereof with other polymers leads to recovery of $R_{1,2}$ values, inherent to probe's aqua ions due to the release of the latter from resin-bound state into the water.

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