as previously observed [2], but also for the radical anion of toluene, where the experimental splitting constants determined by ESR in solution [5] denote a preferential stabilization of ψ_A, in agreement with the result we obtain for a medium with $\epsilon \geqslant 3.5$.

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Solvent–Solvent Interactions in First Neighbour Models for Aqueous Electrolyte Solutions

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First neighbour models (FNM) as a useful tool for the interpretation of the structure function of liquids are widely used more recently in X-ray diffraction studies. Their basic concept is to calculate a model structure function by assuming regular polyhedra for the nearest neighbours in the liquid, varying the structural parameters while the best fit with the experimental curves is reached [1].

A lot of FNM's have been applied for aqueous electrolyte solutions, but the basic interest is connected with the description of hydration phenomena. As a consequence, the assumption for the solvent–solvent interactions to be identical with those in pure water, is commonly accepted [2]. In this version (FNM1) a difference curve after subtraction of the experimental structure function of the pure water from that of the solution will serve for the models of hydration and ion association. Significant changes in the solvent structure are shown, however, *e.g.* by the molecular dynamics study of aqueous halide solutions [3]. In a modified version, FNM2, we assign a tetrahedron to the first neighbours of the 'free' solvent molecules (not included in the hydration shells). An increasing in the first neighbour distances $\sim$2.91–2.96 Å instead of 2.84 Å

in pure water and their rms deviations make us possible to characterize the structure making and structure breaking role of the cations [4]. In a third version, FNM3, the assumption of symmetry is also dropped.

As a consequence, the coordination numbers can change, and for the alkali chloride solutions they may differ significantly from those of FNM2, determined by the symmetry of the given polyhedra (Table I). These features of the models are tested even by the pair-correlation functions derived from the FNM's.

TABLE I.

	FNM2	FNM3	
CN_{ww}	4.0	3.0	
r_{ww} (Å)	2.94	2.97	2 *M* KCl
l_{ww} (Å)	0.103	0.20	
CN_{ww}	4.0	3.5	
r_{ww} (Å)	2.94	2.99	4 *M* KCl
l_{ww} (Å)	0.109	0.20	

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A Theoretical Approach to the Evaluation of the Contribution of Many-Particle Interactions to Distribution Functions and Thermodynamics

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The time-averaged coordination number of a fluid is no less than four. It means that any interaction includes at least three particles situated at short distances from each other. There is no doubt that