tion, are shown. The experimental value is calculated with $\tau_c = 10^{-12}$ s. N is the number of water molecules, and the averages are calculated from 200 000 configurations.

The origin of the field gradient at the nuclear site has been discussed by several authors. Hertz [2] means that the dominating contribution to the field gradient comes from the water dipoles in the first hydration shell. Deverell [3], on the other hand, ascribes the distortion of the ionic electron cloud, when colliding with a water molecule, the largest contribution.

By a detailed analysis of the configurations generated in the Monte Carlo procedure, we hope to bring some more light on the problem. So far the results indicate that the water molecules closest to the ion are far from tetrahedrally arranged, thus giving a non-zero contribution to the field gradient at the nuclear site. They also seem to be quite mobile. These findings are in qualitative agreement with suggestions made by Friedman [4].

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A.M.O. Study of Solvent Effects in Substituted Benzene Radical Anions

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In this paper we report the results of a theoretical investigation dealing with the effect of the solvent upon the relative stability of the symmetric (ψ_S) and antisymmetric (ψ_A) electronic configurations of substituted benzene radical anions. The problem has been investigated using a modified SCF-MO INDO procedure, which includes the solvation effects in the way suggested by Constanciel and Tapia [1].

The computations have been carried out for a series of monosubstituted benzene radical anions $(C_6H_5\text{–}X)^{\overline{\cdot}}$, with X = OH, CN, CH_3 and the energy differences $\Delta E = E_S - E_A$ between the energies of the symmetric (E_S) and antisymmetric (E_A) configurations computed for various values of the dielectric constant ϵ are listed in Table I, including also the gas phase situation ($\epsilon = 1$).

The substituents listed above have been chosen because they represent situations where the conjugative interactions are significantly different. We have already shown [2], in fact, that the conjugative effect is the dominant factor that determines the preferential stabilization of one of the two configurations ψ_S and ψ_A, that in the absence of the perturbation due to the substituent are degenerate.

In all cases where the substituent has just the π-type lone pair (X = OH) or a filled–unfilled π-system characterized by a high energy HOMO and a low energy LUMO (X = CN), there is a largely dominant conjugative interaction that dictates the preferential stabilization. In these cases the solvent plays only a minor role, as shown by the results listed in Table I, since the solvent has not the effect to alter the dominant character of an interaction that is largely dominant in the gas phase.

TABLE I. Energy Differences $\Delta E = E_S - E_A$ (kcal/mole) for Various Monosubstituted Benzene Radical Anions at Various Values of the Dielectric Constant ϵ.

Substituent	$\epsilon = 1.0$	$\epsilon = 5.0$	$\epsilon = 20$	$\epsilon = 80$
OH	7.99	12.27	14.12	14.43
CN	−13.86	−13.99	−14.54	−14.97
CH_3	−4.75	1.47	2.94	3.81

However, when there is not a largely dominant interaction as in the case of X = CH_3, where the HOMO is at low energy and the LUMO at high energy, the effect of the solvent can become critical. In this case, our computations show that ψ_A, that is less stable than ψ_S in gas phase, becomes more stable when the medium has a dielectric constant greater than ~3.5 and the trend becomes more pronounced with the increase of the dielectric constant.

Radical anions are known for all the compounds we have examined, except phenol which may be compared with anisole [3]. The experimental results agree well with our computational results, not only for the radical anions of phenol and benzonitrile [4], 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 ~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