derived under assumption that the pair correlation function is constant. It is shown that the accumulation of ions close to the walls is solely due to the repulsions between the ions and it is argued that ion binding in polyelectrolyte system can be understood as caused by the incapability of the bulk solution to sustain a substantial net charge over moderately large distances.

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Successive Approximations in the Quantum-Chemical and Statistical-Mechanical Study of Aqueous Solutions, particularly with Biomolecule Solutes

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The present paper reports Monte Carlo simulation results calculated at room temperature for a variety of aqueous systems, whose interaction potentials had been obtained by fitting quantum-mechanical *ab-initio* calculations, at CI (water–water potential [1]) or SCF-LCAO-MO level [2–4]. Unless otherwise stated, our systems were clusters consisting of one solute molecule and 200–250 water molecules, *in vacuo*; the pairwise additivity approximation was also used.

1) We simulated the two systems glycine–water (neutral molecule and zwitterion) [5]; their solvation structure was elucidated by means of orientational correlation functions (OCF's) and radial distribution functions (RDF's) [5]. The picture obtained by these means was found to be in broad, qualitative agreement with the information one can gain from (orientationally-optimized solute–water) isopotential contour maps.

2) We simulated the systems serine–water (neutral molecule and two conformers of the zwitterion) [6] and calculated RDF's and OCF's, hydrogen- and oxygen-atom probability density (PD) maps, and also investigated the spacial dependence of the average water–water and solute–water interaction energies. We also calculated PD maps for glycine zwitterion, and all the corresponding isopotential contour maps. Some water molecules are strongly hydrogen-bonded to hydrophilic groups (not to the alcoholic one) and, beyond them, there exists a rather rich and complex hydrogen-bonded network, resulting by a subtle balance between solvent–solvent and solvent–solute interactions, which is rather sensitive to conformational effects.

3) We also simulated a system consisting of an Na^+ cation, glycine zwitterion and water. Thermodynamic and structural results showed the Na^+ to be localized in the same plane as the $-COO^-$ group and close to it; no water molecules were found in the neighbourhood of the $COO^- \cdots Na^+$ pair, whereas the solvation of the amino group was not dramatically altered [7,8].

4) One could argue that a cluster *in vacuo* is not a very good approximation to a dilute solution; on the other hand, usage of periodic boundary conditions would probably require an even larger number of solvent molecules, and possibly an Ewald–Kornfeld summation for electrostatic potentials. As an alternative approach, we decided to consider our cluster as contained in a spherical cavity [9] surrounded by a homogeneous and isotropic dielectric continuum, with the same dielectric constant as the pure solvent. The potential energy of the cluster due to the 'dielectric reaction' was evaluated according to classical electrostatics; calculations on two serine zwitterion conformers showed a moderate increase (about 5%) in the solvation energy [10].

5) In order to test the validity of the pairwise additivity approximation, quantum-mechanical calculations were carried out on the $Li^+(H_2O)_2$ system, and two non-pairwise-additive three-body potential functions were extracted from the total interaction energies [11]. One of them appeared to be a short-range repulsive correction; the other one could be interpreted classically, as due to water bond polarization. Both terms were suitably generalized to a system $Li^+ (H_2O)_n$, and Monte Carlo simulation was carried out on clusters with $n \leqslant 6$, both with and without the many-body correction [11]. Comparison with available measured [12] and simulation [13] results showed a significantly improved agreement with experiment.

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Theoretical and Computational Studies of Biomacromolecule–Water Interactions

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Although it is conventional wisdom that water plays a very significant role in the structure, stability, dynamics and interactions of many biochemical systems, the operation of such solvent effects at the molecular level is very poorly understood. Any adequate theoretical or computational approach to *e.g.* the statics and dynamics of protein–solvent interactions at this microscopic level necessarily requires knowledge of the various interatomic potential functions. That such chosen functions should be realistic is underlined by the very marginal stability of native protein structures, their free energies being generally only around 10–20 kcal mol^{-1} lower than their denatured conformations; this represents the energy of only 2–4 hydrogen bonds.

Within this context, our recent work has been directed at (*a*) the effects of changes in water structure itself, and in solvent organisation around ions and macromolecules, as the model potentials are varied, and (*b*) the establishment of reliable potential functions, largely through quantum mechanical calculations. Particular stress is placed on a thorough testing of these potentials at relatively well-defined macromolecule–solvent interfaces, such as are found in protein crystals whose structures have been refined to *very* high (1.5 Å or better) resolution. Computer simulation and model-building studies of several suitable systems (*e.g.* insulin, pancreatic trypsin inhibitor, coenzyme B_{12}) will be described, and the current problems and possible solutions discussed. The particular importance of the cooperative nature of the hydrogen bond is emphasised, especially as it may seriously affect solvent–ion and solvent–macromolecule interactions.

An Experimentalist Point of View on Quantitative Elaboration of Theoretical Models

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In a number of problems of solute–solute–solvent interaction, information on the geometrical structure of solvent in the near neighbourhood of solute is now available. This was obtained from a variety of experiments as well as from numerical calculations. The present trend in computer simulation as well as in experimental techniques seems to appropriately be towards an extension of this information to include thermal disorder.

Despite these efforts, other aspects of solute–solute–solvent interaction do not seem likely to find exhaustive answers through a study of the geometrical configurations of solvent molecules around the solute.

More detailed calculations of inter- and intramolecular dynamical behaviour would not only add appreciably to our knowledge and description of the behaviour of water in the phase-space. It would also provide ampler grounds for comparison between theoretical expectations and experimental findings, now available in this area. In turn, this could hopefully provide a better insight on the possible role of solvent motional modes on solute–solute–solvent interaction.

Molecular Dynamics Simulations of Aqueous Electrolyte Solutions

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In the molecular dynamics simulations the classical equations of motion are solved numerically for a