Computational methods in solution chemistry

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<u>Abstract</u> - The rapid development of computer speed and capacities has given access to computational research methods in wide areas of solution chemistry. The main methods for such applications are quantum chemical calculations on supermolecular systems and statistical simulations of the Monte Carlo and Molecular Dynamics type. The usage of these research tools is illustrated by an investigation on the structure of one molar zinc chloride and copper chloride solutions. Starting from <u>ab-initio</u> calculations, the construction of suitable intermolecular potential functions with approximate 3-body correction terms is shown, and these functions are then used in Monte Carlo simulations for aqueous solutions of the metal chlorides. The results of these simulations are discussed with respect to experimental data, proving that the computational methods can give very detailed information on structural questions, partly exceeding the limitations of experimental approaches.

INTRODUCTION

Due to the rapid development of computer technology, virtually every field in science has been penetrated and expanded by computational methods. In solution chemistry, computer applications for evaluating spectroscopic data, the solution of equations for complicated equilibria and other computer-assisted analyses of experimental data have become routine, although in many aspects they remain subject to further research and development.

The availability of fast computers in the past decade has, however, opened solution chemistry to yet some other computational research tools, formerly restricted to limited applications and specialized theoretical chemists. These tools - mainly quantum chemical calculations and statistical simulations of the Monte Carlo and Molecular Dynamics type - are widely applicable now to larger molecular systems and to solutions of practical chemical interest. Especially for the investigation of microstructures formed in solution, these tools are nowadays sometimes even superior to experimental methods. In the following, the principle way of such computational approaches to systems in the liquid state will be briefly outlined, and the capabilities of the methods will be demonstrated by a few new examples.

QUANTUM CHEMICAL CALCULATIONS

General remarks

Calculations based on an approximate solution of the Schrödinger equation can be applied to relatively large molecular and supermolecular systems nowadays. Due to the specific nature of important interactions in solutions (Van der Waals, hydrogen bonding, ion-solvent), such

calculations have to be performed mostly at the <u>ab-initio</u> level, as semiempirical methods do usually not account sufficiently for these binding mechanisms. The development of software for such calculations (e.g. HONDO, GAUSSIAN 88) and a rich choice of suitable basis sets have made the access to this method much easier, although reasonable application needs a considerable amount of theoretical knowledge and practical experience. Another important factor broadening the applicability of <u>ab-initio</u> calculations to systems relevant for the solution chemist was the development of suitable effective core potentials including relativistic corrections for heavier atoms, giving access to calculations of compounds containing virtually all kinds of atoms in the periodic system.

The usage of quantum chemical calculations for the solution chemist extends from investigations on various aggregates and/or complex species formed in solution to the development of intermolecular potential functions describing the interaction between all species present in a condensed (liquid) system. Typical applications of the first type are calculations of solvated solutes (e.g. hydrated ion structures) or of various hypothetical species expected to be formed according to potentiometric or spectroscopic investigations of solutions.

The quantum chemical evaluation of intermolecular potential functions has become a more and more important application of such calculations, as the availability of such potential functions is a precondition for the performance of simulations, either of the Monte Carlo or Molecular Dynamics type. This application deserves some more detailed attention, especially since the quality of such functions is essential for obtaining correct structural and other data from the simulations.

Whereas for the first simulations of simple liquids (rigid spheres with weak interactions) empirical potentials of the Lennard-Jones type were sufficient, almost all systems of interest for the experimental solution chemist involve unsymmetric solvent molecules and directional solute-solvent or solvent-solvent interactions, e.g. through hydrogen bonds or - energetically most significant - ion-dipole or dipole-dipole (and higher) interactions. The correct description of such interactions demands an explicit consideration of the molecular structure and most of the forces acting between the species involved. For strong interactions, some weak contributions can be neglected, allowing the use of simple <u>ab-initio</u> calculations without consideration of correlation energy. These calculations are performed then for a large number of points of the energy surface, including all possible relative orientations of two or more interacting species. In the most usual case, only two species are included, leading to the so-called pair potential functions. Fig. 1 illustrates such a function, showing the energy as a function of the location of a zinc(II) ion in the x-y plane around a water molecule lying in the same plane.

However, the assumption of additivity of such pair potentials in the course of a simulation is not always justified and can lead to serious errors for systems with strong interactions, as will be shown later with the example of solvated transition metal ions. The inclusion of a third or fourth species into the evaluation of the energy surface of the system complicates the calculations considerably and increases the computational effort to a large extent. Ways are sought therefore to simplify the inclusion of such 3-, 4- and n-body effects into the intermolecular potential functions. Ab initio calculations on a few supermolecular species can already indicate the importance of such effects.

Example: intermolecular potential functions for zinc(II) and copper(II) with water and chloride

From quantum chemical calculations on transition metal ion hydrates (ref. 1-3) it was to be expected that pair potentials would most probably fail in statistical simulations, due to the
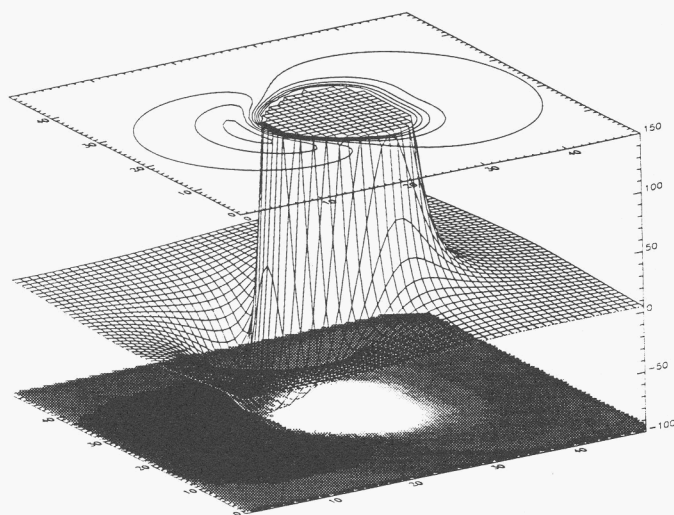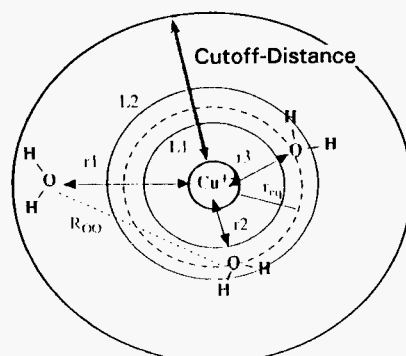
Fig. 1. Energy Surface for zinc(II) - water (zinc ion approaching water within its molecular plane). The uppermost part shows isoenergetic contours, the middle part the 3-dimensional surface and the lower part areas of stabilization (dark) and destabilization (light).

NEAREST NEIGHBOUR LIGAND CORRECTION

r1 .. Cu^{++} - O
r2, r3 .. Cu^{++} -NNL
L1 .. inner limit
L2 .. outer limit for NNL
r_{eq} .. equilibrium distance

NNL .. Nearest Neighbour Ligands

Fig. 2. Illustration of Nearest-Neighbour Ligand Correction for copper(II) - water potential and other water molecules as nearest neighbour ligands.

importance of 3-body corrections in the ion-ligand interactions. The general role of such effects in the prediction of correct solution structures has also been pointed out since long (ref. 4-7), and as a general rule one can expect them to become the more significant, the stronger the ion-ligand interaction becomes. For zinc(II) and copper(II) ions in water, Monte Carlo simulations with a conventional pair potential lead to wrong hydration numbers of 8 for both ions (ref. 8, 9). Inclusion of (at least) 3-body effects was inevitable therefore. Since the usual evaluation of a suitable function, fully taking 3-body effects into account, consists of a large number of ab-initio calculations on water-ion-water and corresponding water-water aggregates and subsequent fitting of a correction function to these energy values, it is very demanding in time as well as computational effort. Thus a new approach has been proposed and tested for the case of zinc(II) and copper(II) ions in water. This procedure, referred to as "Nearest Neighbour Ligand Correction (NNLC)" hereafter, is based on the evaluation of an intermolecular potential function between an ion already bound to one water molecule, and a second water molecule at varying locations (ref. 8, 9). A 3-body correction algorithm (the NNLC) contains the distance between the centres of both ligands as geometrical parameter, and is invoked in the simulation for all ligands residing already in the first hydration shell at or near the energetic minimum positions. A schematic representation of the correction algorithm is given in Fig. 2.

The potential functions for ion-water interactions fitted to the calculated energy points contain a pair potential part (parameters a_1 to a_4) and the NNL correction (parameters a_5 and a_6):

$$E = \Sigma\ q_i q_j / r + a_1 / r^3 + a_2 / r^4 + a_3\ exp(-a_4\ r) + (4.0 - r)\ a_5\ exp(-a_6\ R_{OO})$$

With these potential functions, Monte Carlo simulations for zinc(II) and copper(II) ions at infinite dilution lead to correct hydration numbers for the first hydration shell, and to hydration energies and structural data close to the values from experiment (ref. 10).

In order to compare simulation results to more experimental data, simulations had to be performed for "real" solutions, i.e. solutions with a known concentration of salts of these ions. In both cases, the chlorides were chosen for this purpose.

In these solutions, numerous pair interactions have to be considered, and for some of them, suitable intermolecular functions already existed:

(1) water - water: MCY potential (ref. 11)

(2) water - chloride: KPC potential (ref. 12)

(3) water - copper(II): NNL corrected potential (ref. 8)

(4) water - zinc(II):   NNL corrected potential (ref. 9)

for the other potentials, functions had to be constructed:

(5) copper(II) - copper(II)   (6) zinc(II) - zinc(II)

(7) copper(II) - chloride   (8) zinc(II) - chloride

Potentials (5) and (6) were constructed on the basis of ab-initio calculations with the same DZV-ECP basis sets as used in (ref. 8) and (ref. 9), respectively, fitting the SCF energy data to the functional forms:

$$E = q_i q_j/r + a_1 \exp(-a_2 r) \qquad \text{(copper)}$$
$$E = q_i q_j/r + a_1/r^6 + a_2/r^{12} \qquad \text{(zinc)}$$

The parameters resulting for copper - copper and zinc - zinc interactions are:

	copper	zinc
a_1:	14381.0	3531.2
a_2:	2.88840	669607.3

For the (strongly attractive) ion - chloride potentials it was evident that the same approximate 3-body corrections should be employed as for the ion-water potentials. For the zinc(II) - chloride potential, the nearest neighbour ligand correction could be performed in exactly the same manner as for the zinc(II) - water potential, calculating the energy surface for a chloride ion in the field of a zinc ion carrying already one hydration water molecule. The Cl - O distance then becomes the relevant geometrical parameter for the NNL correction term. The energy data were then fitted to a function of the type:

$$E = \Sigma q_i q_j + a_1 \exp(-a_2 r) + NNLC$$
$$NNLC = (4.0 - r)^2 a_3 \exp(-a_4 R_{Cl-O})$$

where 4.0 is the cut-off limit, up to which the correction algorithm is invoked during the fitting procedure and later, during the simulation.

In the case of copper(II) - chloride, an additional problem had to be solved: even when a copper(II) ion already carries one solvent ligand, at larger copper - chloride distances electron transfer occurs from copper to chloride, resulting in copper(I) and a chlorine atom. The open-shell UHF formalism used for these calculations does not forbid such a transfer, and hence such calculations could not be used for the construction of a suitable copper(II) - chloride energy surface. However, when a second water ligand is fixed at the copper(II) ion, it remains copper(II) throughout all possible interactions with a chloride ion, and also chloride retains its anionic nature. Therefore, the potential function was constructed on the basis of ab-initio calculations of a chloride ion in the field of a copper ion carrying two water molecules at equilibrium distance, with a fixed O - Cu - O angle of 90 degrees. The fitting procedure was performed with the same function as for zinc(II) - chloride, taking always the shorter Cl - O distance as parameter for the NNL correction term.

The resulting final parameters for both functions were:

	copper	zinc		copper	zinc
a_1:	39028.4	60995.2	a_3:	1465.26	5526.58
a_2:	3.16840	3.40713	a_4:	1.87799	2.50965

Having available now all 8 potential functions needed, simulations for the one molar zinc chloride and one molar copper chloride solutions could be carried out.

All ab-initio calculations were performed at the DEC 3100 workstations of our institutions, using the HONDO VII program.

MONTE CARLO SIMULATIONS

For the simulations, the densities of the one molar solutions were measured. From this density, the elementary box length for a simulation system representing such solutions at a given temperature, consisting of 222 water molecules, 4 metal ions and 8 chloride ions, were evaluated to be 19.035 and 18.947 Å for copper chloride and zinc chloride solutions at 20 / 25 °C, respectively. In the Monte Carlo simulations, starting from random configurations, the Metropolis sampling algorithm (ref. 13) and periodic boundary conditions were employed. A spherical cut-off for exponential terms of half of the box length was introduced, and Ewald corrections were performed for all long-range interactions.

Copper chloride solution

The process of equilibration took 3 million configurations, after which sampling was performed for another 2.3 million configurations. During these, the average number of nearest neighbours to be considered in the NNL correction was found to be 1.53, associated with a correction energy of 69.0 kJ/mol for water molecules in the first hydration shell. Chloride ligands rarely came close enough to the metal ion, resulting in a correction energy below 0.4 kJ/mol. In Fig. 3 the most important radial density distribution functions and their integrations are shown:
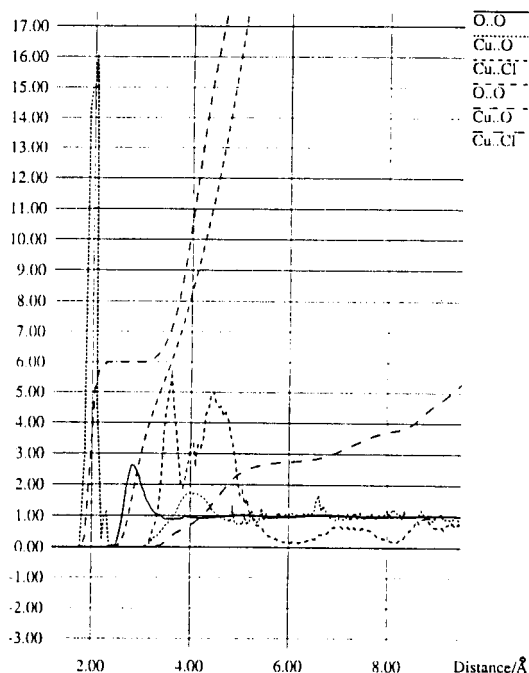
RDF-value/Integration

Fig. 3. Radial distribution functions and their integrations for 1 M copper chloride solutions
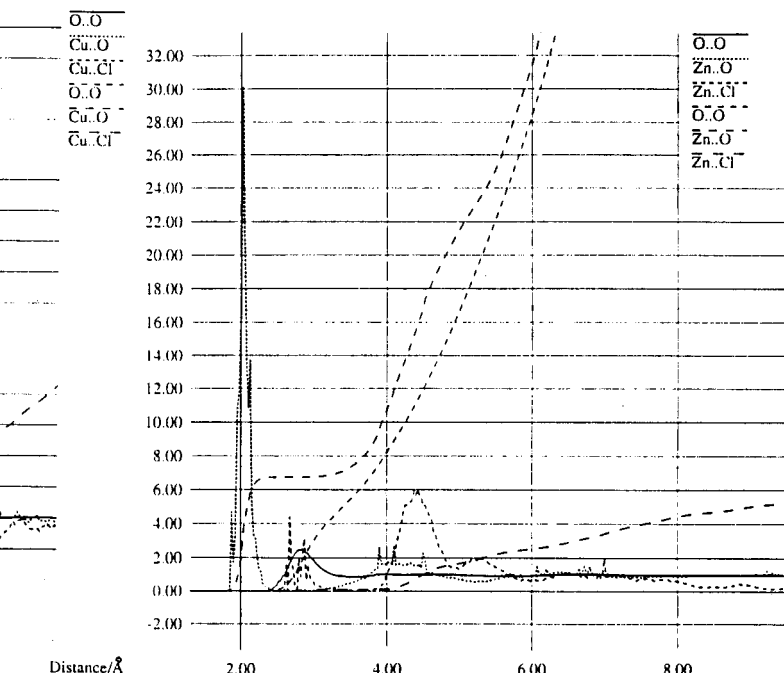
Fig. 4. Radial distribution functions and their integration for 1 M zinc chloride solutions

The Cu..O RDF displays a very distinct peak for the first hydration shell of the ion, centred around 2.0 Å with a very small satellite, probably representing water molecules in intermediate structures during exchange processes. Integration over the peak leads to the hydration number of exactly 6.0. A second shell is recognized at 4.0 Å, which - integrated up to 5 Å - contains another 12 water molecules. Distance and number of water molecules indicate that each water in the first sphere is hydrogen bonded to 2 molecules of the second sphere.

The Cu..Cl RDF clearly proves that no species is formed, where chloride binds directly to the copper ion ($CuCl^+$.n H_2O). The double peak between 3.1 and 6.0 Å however shows that a variety of solvent-separated ions is formed. Integration up to the first local minimum at 3.85 Å shows that the first peak with a maximum at 3.6 Å contains 0.5 chloride ions, i.e. every second copper ion in solution is linked to a chloride ion via one water molecule. For higher concentrated copper chloride solutions, direct copper ion - chloride binding results as well (ref. 14). Such results seem of particular interest for a more detailed interpretation of electrochemical results and simulations of titrations, where species distributions were evaluated (ref. 15, 16), since by these experimental methods one can hardly distinguish between "contact" and "solvent-separated" ion pairs.

Some more details can be obtained from the simulation's results by performance of a coordination number distribution analysis. In the case of the one molar copper chloride solution, an exclusive number of 6 is obtained, assuming a sphere with radius 2.5 Å for the first hydration layer. This is quite different in the case of zinc ion, as will be shown in the next chapter.

The water-water (O..O) RDF in the system is not much different from that of the pure solvent indicating no larger perturbation of the solvent's general structure.

The Cl..O RDF (not shown in the figure) has its first maximum at the distance expected for Cl...H-O hydrogen bonding, unambiguous allocation of a minimum after a first shell is not possible; integration up to 4 Å leads to 9.6 water molecules. The diffuse structure of the anion's hydration sphere shows that the position of the chloride ions and of the water molecules surrounding them is clearly governed by the cations present in solution.

Zinc chloride solution

It took over 4 million configurations, until the average energy started fluctuating around a stationary value, indicating thermal equilibrium. During the sampling process it became clear that there exist several energetically almost identical configurations for the first shell of ligands around zinc ion. Exchange processes occur only after a large number of configurations so that sampling was performed over 5 million configurations to obtain a good picture of the average structure distribution.

The average number of nearest neighbours considered in the NNL correction was 3.12 and thus differs considerably from the case of copper chloride. For zinc chloride, not only water - water, but also chloride - water corrections are significant, the corresponding energies being 28.0 and 10.0 kJ/mole, respectively. As in the case of zinc(II) and copper(II) ion at infinite dilution, considerable differences were observed in the structures formed around the cations also in one molar chloride solution. The RDFs in Fig. 4 illustrate some of these features.

The sharp first peak in the Zn..O RDF, located at 2.05 Å, contains a very significant shoulder peak at 2.15 Å. Integration to different limits of the peak leads to the following values: 2.10 Å / 5.0, 2.15 Å / 6.0, 2.5 Å / 6.75. Similar to the case of infinite dilution, 6 seems to be the preferred but not "ideal" hydration number for the first shell. The result is a "compromise", where some first-shell hydration waters are always in a non-ideal position not far from the equilibrium distance, thus forming the shoulder peak in the RDF. Another interesting difference are the small first peaks in the Zn..Cl RDF below 3 A. Coordination number distribution analysis shows, that 5 % of the zinc ions have a chloride ion directly bound to them - also a nonneglible influence on the first shell's structure. For water molecules in this first shell, the coordination numbers are distributed as following:

up to 2.10 Å (local minimum): 3 water molecules: 4.8 % 4 water molecules: 22.7 %, 5: 39.7 %, 6 water molecules: 32.1 %, 7 water molecules: 0.5 % ; up to 2.50 Å (separation between the first and the second shell): 6 water molecules: 25.1 %, 7 water molecules: 74.9 %, quite a different picture compared to copper.

The solvent-separated ion pairs are clearly represented by the large peak at 4.5 Å of the Zn..Cl RDF, which corresponds to the second large peak in the Cu..Cl RDF of Fig. 1. Analysing the number of chloride ions contained in this peak up to 4.5 Å, the following coordination number distribution results: 0: 38.5 %, 1: 48.6 %, 2: 12.8 %. These data can be compared to an experimental evaluation of species distribution in approximately one molar aqueous zinc chloride solution (ref. 16), where it was found that 48 % of zinc ions should be just hydrated ions, 21 % were assigned to the species $ZnCl^+$, 5 % to $ZnCl_2$, 10 % to $ZnCl_3^-$ and 15 % to $ZnCl_4^{2-}$. Our value for a chloride coordination number of zero (only water as ligands) is not much different from that. To explain the differences observed for the chloride containing species, we probably have to consider also another peak in the Zn..Cl RDF, which appears at a distance of 5.4 Å from the ion. If coordination numbers are evaluated to that limit, coordination numbers up to 4 contribute significantly, although their percentual representation clearly follows the order 1 > 2 > 3 > 4. Due to the strong ion-ion interactions extending also over such a distance, apparently various solvent-separated ion pairs (and higher associates) containing the anion in the second solvation sphere, are jointly observed as one species by the electrochemical methods, and the models used in simulating the system may therefore lead to uncertainties in the species assignment and hence also in their evaluated distributions.

As in the previous case, the O..O RDF does not exhibit significant deviations from the pure solvent.

All Monte Carlo simulations were also performed at the DEC 3100 workstations of our institutions, using the program MC90 (ref. 17).

CONCLUSIONS

The examples presented here can demonstrate that quantum chemical calculations and statistical simulations are a very powerful tool to deal with structural questions of species formed in electrolyte solutions. Besides the methodical feasibilities, the performance of all computational work on low-price workstations within very reasonable computing times shows that such investigations have become independent of access to large central host computers and thus very economical, also compared to experimental equipment needed for evaluation of the structural data available through such computations. The further increase of computational power of personal workstations and the constant decrease of the price for this equipment indicate prosperous future possibilities.

Despite of these encouraging developments, there still exist several limitations for the application of computational methods in solution chemistry. Although they are not so much of principal nature, they provide still many challenging tasks for future research. First, there is the "bottleneck" of constructing all necessary intermolecular potential functions for simulating realistic many-component liquid systems. Besides the considerable computational effort even for pair potentials, more and more sophisticated functions are needed, when 3- and 4-body effects become significant (as shown in our examples) or if one intends to evaluate macroscopic quantities (e.g. dielectric constants, specific heat) or spectroscopic data (e.g. vibrational spectra) for a pure liquid or solution. Second, also the simulations themselves become more complicated and computer-time intensive with increasing number of species and/or particles to be included in the elementary box (e.g. for dilute solutions). Despite rapidly increasing computer capacities and speed, continuous program development will therefore remain still for a long time an important (and time consuming) task of the computational chemist working in the field of solution chemistry.

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