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An Interpretation of the "Molecular Space" on the Basis of Quantum Chemical Calculations of Hydrated Ions

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Quantum chemical calculation has been made for the sizes of the hydration shells of the metal ions as well as for the binding energies of water molecules in the hydration shells. The results of the both calculations give the basis of the size of the molecular space.[1)] Although the experimental value of the molecular space, $(20\pm 5A)^3$, does not exactly agree with the calculated value, we assume that the quantum chemically obtained hydration sphere refers to the molecular space.

Several experimental results concerning aqueous solutions of salts have indicated that there exists a well defined minimal volume of solvent which is needed by each ion to maintain "regular" behavior in a thermodynamic as well as in a kinetic sense.[1,2)] ESR investigations of aqueous solutions in gels allowed to determine this volume to be $(20\pm 5A)^3$ for copper and some other simple organic molecules.[1)] Hence this apparently essential volume was named "molecular space."[1)] Within this context it is of particular interest that the concentration of salt in the sea water as well as the salt concentration in "biosolutions" as human blood serum is adjusted to an amount, which still corresponds to the maintenance of this "molecular space" for the ions.

Previous quantum chemical calculations on ions linked to linear water polymers have shown that the upper limit of ion solvent interaction corresponds to the size of the experimentally determined molecular space for a series of monovalent and divalent ions.[3)] These calculations could give, however, only an estimation of upper limit of interaction range and, due to methodical simplification, not yet reflect well the situation of a fully solvated ion in solution.

Using the common *ab-initio* MO-SCF calculation method, the treatment of such large systems (an ion surrounded by several hydration layers) will lead to dimensions of the calculation, which cannot be managed so far. On the other hand, semiempirical methods are also not suitable for the correct description of such systems[4,5)] and also lead to rather ambiguous results due to the neglect of most 2-electron integrals and introduction of numerous empirical parameters. The recently developed MESQUAC (Mixed Electrostatic Quantum Chemical) MO-SCF method allows a treatment of quite large complex systems at a reasonable computational effort.[6,7)] The results obtained for some hydrated ions[6)] are in very satisfactory agreement with experimental values and with results obtained by *ab initio* calculations near HF-limit. It was to be expected, therefore, that this method should be the most useful way for calculating ions with several hydration layers and to obtain therby a theoretical explanation for the experimental facts concerning molecular space.

Experimental

MESQUAC Concept. The details of the method have been published already elsewhere,[6)] so that at this point a very brief survey will be given. The principle of the method is a separation of the total system into an "essential" part (usually the ion +1 or several ligands) and a second part ("outer part"), including the other ligands or even some bulk solvent. The "essential part" is calculated within the framework of the all-electron *ab initio* MO-SCF method, the "outer part" introduced as electrostatic perturbation term to the Hamiltonian, constructed according to the molecular geometry of the ligands in this outer part. The electrostatic fractional charges used in building up this perturbation terms are those being obtained from previous *ab initio* calculations on smaller ion-ligand-systems, performing a MULLIKEN population analysis.[6)]

The method could be shown recently to work also satisfactorily in the case of transition metal ions,[8)] and even for these systems computing times are still quite short. For this reason, we have chosen the monovalent ions of Li(I), Na(I) and K(I), and the divalent ions of Mg(II), Ca(II), Mn(II) and Zn(II) for this work. Mn(II) and Zn(II) seemed to be a useful supplement to the main group metal ions, since they also possess a "symmetrical" electron configuration (d^5 and d^{10}, respectively), one being a typical open shell (high spin) system, the other one a closed shell system, but containing d electrons.

Performance of the Calculations. The Gaussian basis sets being used for ions and ligands have been given already in the references.[5,6,8)] The geometries of the first hydration shells have been chosen according to experimental results of X-ray investigations of aqueous salt solutions[9,10)] or to optimized MO-SCF geometries.[12,13)] The geometries of the further solvation layers were constructed assuming hydrogen bonding of each water molecule to two water molecules in the next higher shell (0···0 distance 2.70 Å), in a 90° twisted configuration. For most of the ions both tetrahedral and octahedral coordinations have been considered. Some data obtained for Ti(III) aquacomplexes[8)] are included for comparison of the results of this work with those of a tervalent ion.

The calculations were performed in part at the HITAC 8700/8800 computer of the University of Tokyo, in part at the CDC Cyber 174 computer of the Vienna TU computer center.

Results and Discussion

In Table 1, the binding energies per water molecule, calculated for the first, second and third hydration shells of the ions, are listed. For the discussion of

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TABLE 1. CALCULATED BINDING ENERGIES PER WATER MOLECULE OF THE FIRST (E-I), SECOND (E-II), AND THIRD (E-III) HYDRATION SHELLS, FOR TETRAHEDRAL (Td) AND OCTAHEDRAL (Oh) COORDINATIONS, IN kcal/mol

Ion	Coordination	E-I	E-II	E-III
Li(I)	Td	25.7	9.8	1.5
	Oh	22.1	9.4	1.6
Na(I)	Td	17.3	7.6	1.5
	Oh	15.4	7.6	1.5
K(I)	Td	14.7	7.2	1.5
	Oh	14.2	6.4	1.3
Mg(II)	Td	59.4	21.6	3.3
	Oh	50.5	20.9	3.2
Ca(II)	Td	47.1	19.9	3.0
	Oh	46.9	18.3	3.0
Mn(II)	Oh	73.8	22.1	5.4
Zn(II)	Oh	71.0	22.4	5.5
Ti(III)	Oh	100.0	34.5	8.8

TABLE 2. CALCULATED VOLUMES FOR THE HYDRATED IONS INCLUDING HYDRATION LAYERS, n BEING THE NUMBER OF HYDRATION SHELLS
Values are given in $(\text{hartree})^3$.

Ion	V_1	V_2	V_3	V_4	V_5
Li(I)	457	2668	9209	24300	46870
Na(I)	681	3352	10730	27160	51271
K(I)	1051	4361	12860	31000	57160
Mg(II)	475	2668	9209	24300	46870
Ca(II)	754	3561	11182	27900	52540
Mn(II)	612	4151	10292	26340	50020
Zn(II)	537	2922	9775	25390	48550

these energy values, the hydrogen bond energy between the solvent molecules themselves (6.8 kcal/mol with the basis set used) represents a crucial limit, since stabilization and structural influence of the ion by full or partial formation of a hydration shell is not to be expected, if the energy gain by solvation does not exceed this value to some extent. The larger the difference between binding energy in the hydration layer and hydrogen bond level is, the more stable and rigid the hydration shell will be.

According to our results (Table 1), almost all ions show such a stabilization up to the second hydration shell, I(I) and Ti(III) ion being the lower and upper limit, showing possibly a somewhat different behavior (no influence on second shell for K(I), partial formation of a third shell for Ti(III)).

These results are in good agreement with some preliminary calculations one on the hydrated divalent ions Fe(II), Co(II), Ni(II), and Cu(II), which also let expect a quite strong influence on the second shell, and the other on the binding energies for the third shell below hydrogen bond level.[14]

Experimental X-ray investigations of aqueous salt solutions[9–11,15] also support our results, showing a significant structural influence of the ions up to a radius of about 5 Å around the ion, which corresponds to the distance including two hydration layers. X-Ray data have been evaluated, however, usually only for the first shell, for which the peaks are more strong and easier to analyze. The existence of the second shell (and sometimes even of a third shell) has been pointed out, however, by some of the authors.[11,15]

Discussing now the results of our calculations in connection with the concept of molecular space, another consideration will be useful and necessary, namely that of the volume occupied by an ion surrounded by 1,2,3, or more solvation layers. In Table 2, these volumes are given, as they result from the geometries being used in the MESQUAC MO calculations.

From the values for the necessary volume being assigned to an ion including 1, 2, or more solvation layers we can see that the volume corresponding to an ion with two layers —which are expected according to the calculations for most of the ions— is always smaller than $6800\ \text{hartree}^3$, corresponding to a sphere of 10 Å diameter. The volume needed after addition of a third shell will exceed, however, in all cases this value. It can be concluded, therefore, that the space being "structured" by the ions in aqueous solution corresponds to a sphere of about 10 Å in diameter.

Summarizing the results of the calculations presented here, we believe that they seem to give a reasonable theoretical foundation for the experimentally observed size of the molecular space. They are expected also to be a useful basis for further investigations of aqueous and nonaqueous electrolyte solutions by means of the calculation method being employed.

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