

A Quantum Chemical Study on the Ion Influence on Linear Water Polymer

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Quantum chemical model calculations have been performed using an STO-3G basis set for linear water polymers under the influence of electrostatically approximated cations and anions. It is found that the influence of the cations on the ligand chains can be described properly as a purely electrostatic interaction from the third water molecule on. The mutual influencing of cation and anion in ion pairs separated by more than one solvent molecule seems to be also a merely electrostatic one. An estimation of the range of these electrostatic forces is given.

Recently, one of the present authors (S.F.) has shown experimentally that any simple ion or molecule in aqueous solution requires a certain volume of solution for the maintenance of the free motion and named the latter "molecular space."¹⁾ This raised several questions concerning the nature and the extent of the ion-solvent interactions being responsible for this phenomenon.

Due to technical and computational limitations, usual quantum chemical calculations concerning the interactions of ions with solvent molecules can take into account only a few solvent molecules and represent, therefore, a rather poor approximation to the reality of solutions. Several attempts have been made, therefore, to take into account the conditions of the solution by means of perturbation terms or electrostatic approximations.²⁻⁴⁾ Large computations of some examples of solvated ions⁵⁾ and a study on the interaction of a cation with an anion through 2—3 water molecules⁶⁾ allow a limited comparison of the results obtained by the approximations with those of full *ab initio* calculations.

Recent calculations of hydrated ions by the MESQUAC-MO-method^{4,7)} allowed to obtain ion-solvent interaction energies up to the third shell and proved to form a good basis for the discussion of the structural influence of the ion on the surrounding water layers and hence for the phenomenon of the "molecular space."

In the work presented here, we have carried out model calculations on the nature of ion/solvent interactions as a function of the distance between the ion and the water molecules. A molecular model consisting of cation and/or anion bonded to a linear water chain was used for this purpose. It was to be expected that this model would indicate something about the relevant contributions to the binding of solvent molecules even at larger distances and hence form a useful basis for the construction of larger theoretical models for hydrated ions.

Experimental

General Remarks. The idea to reduce the computational problem by means of a partial electrostatic treatment is based on general considerations on importance and range of the contributions to the chemical bond. For ions with

ns^2np^6 valence electron configuration, the description as electrostatic point charges seems to be reasonable within certain limitations, as it has been shown already in an analogous example.³⁾ The interaction between two solute entities, either ions or molecules, which are separated over a larger distance, may be interpreted in terms of the typical "quantum effect" of interference,⁷⁾ which is proportional to the overlap integral and hence decreasing exponentially with the distance r , whereas the electrostatic terms, decreasing with r^{-1} , will be effective even at a larger distance and hence can be a dominant factor of interaction over such distances. One of the main scopes of this work was to find out at what distance electrostatic effects will dominate the quantum effects. If one attempts to describe a model for the interaction of an ion with a "chain" of water molecules applying an electrostatic approximation for the central ion, the description of the ion interaction with the first water molecule will be somewhat less satisfactory. For the ion-binding to the first water molecule, however, accurate MO-HF-SCF calculations have been performed,⁸⁾ and including the consideration of the experimental gas phase interaction energies, the results of our simplified model calculation can be controlled easily.

Performance of the Calculations. The cations were taken into account by means of the point charges of +1 and +2 for alkali and alkaline earth metal ions, respectively, sited at the *ab initio* SCF energy optimized distances from the oxygen of the water molecule (C_{2v} symmetry). The procedures taken here are same as that shown in a previous paper⁹⁾ for the case of ion-amide interactions. The corresponding values are given in Table 1.

The water molecule(s), linked to a chain of increasing length ($n=1,2,\dots,8$) were considered by a nonempirical all-electron (*ab initio*) LCAO-MO-SCF treatment using an STO-3G basis set.⁹⁾ In order to evaluate the effect of the ion species, the energy of the chain was calculated with and without the "perturbation" by the point charges representing the ions. Subtracting both energy values the ion solvent interaction energy is obtained. Dividing this value by the number of water molecules building up the chain, one obtains the stabilization energy per water molecule,

TABLE 1. THE DISTANCE BETWEEN THE POINT CHARGE OF THE METAL ION AND THE COORDINATIVE CENTER OF THE WATER MOLECULE

Bond	Distance/Å	Bond	Distance/Å
Li-O	1.85	Mg-O	1.85
Na-O	2.10	Ca-O	2.10
K-O	2.63	Ba-O	2.46
Cs-O	2.80	I-H	1.87
Be-O	1.46		

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TABLE 2. STABILIZATION ENERGIES PER WATER MOLECULE FOR CHAIN LENGTHS OF 1—8 AND EXPERIMENTAL (10) AND FULL *ab initio* RESULTS (8) FOR THE MONOHYDRATES ($n-1$), ALL VALUES IN kcal/mol

n	Li	Na	K	Cs	Be	Mg	Ca	Ba	I
1	34.1	26.4	16.6	14.8	122.3	74.2	56.7	40.6	5.8
exp.	34.0	24.0	17.9	—	—	—	—	—	—
SCF(9)	36.0	23.9	16.6	—	—	80.0	53.0	—	—
2	22.2	17.7	11.6	10.5	74.8	47.7	37.5	27.9	5.0
3	16.2	13.1	8.9	8.1	53.1	34.7	27.7	21.0	3.6
4	12.6	10.2	7.0	6.4	40.8	26.8	21.5	16.4	2.8
5	10.4	8.5	5.9	5.4	33.3	22.1	17.9	13.7	2.7
6	8.8	7.2	5.0	4.6	28.1	18.7	15.1	11.7	2.5
7	7.7	6.3	4.4	4.1	24.3	16.3	13.2	10.2	2.1
8	6.7	5.5	3.9	3.6	21.4	14.3	11.6	9.9	2.0

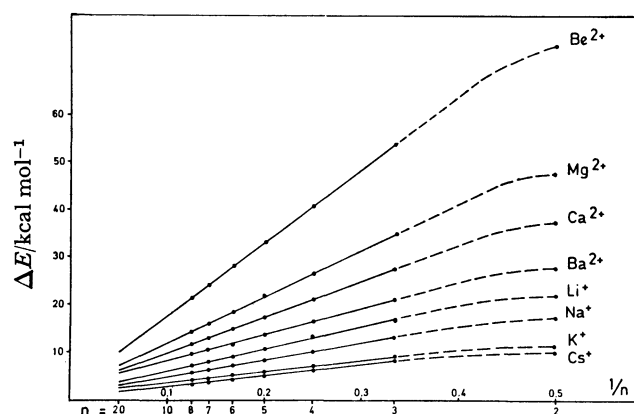


Fig. 1. Stabilization energy per water molecule for varying chain lengths and ions versus the inverse number of water molecules in the polymer.

which will be the basis for further discussion.

The geometry of the chain was based on the following values: O—H=0.96 Å, O/H/O=104.5°, O...H—O=2.75 Å. Furthermore, we have performed some calculations on ion pair interactions, *i.e.*, the interaction between the cation and the anion separated from each other by solvent molecules. For this purpose, iodide ion was taken as the counter anion which was linked to the other end of the water chain.

All calculations have been performed using a modified GAUSSIAN 70 program at the FACOM 230-60/75 computer of the Institute of Physical and Chemical Research at Wako City.

Results and Discussion

Applicability of the Method. The use of the electrostatic approximation for the ions is somewhat problematic due to the neglect of some binding effects and the charge transfer. In the case of the main group metal ions, however, these effects could be shown to be of rather minor magnitude.^{4,7)} The energies calculated within our model approach here prove this once more being in quite satisfactory agreement with the binding energies obtained by either full *ab initio* calculations or gas phase experiments (*cf.* Table 2). We can expect, therefore, that the electrostatic approach for the ions is justified and would not influence the reliability of the results to

a serious extent.

Binding of Single Ions to the Water Chain. In Table 2 the binding energies per water molecule in a chain containing 1 to 8 molecules are listed. As can be seen from Fig. 1, they decrease linearly with $1/n$ from the third water molecule on, which actually means a decrease following the law of Coulomb interactions decreasing with $1/r$. We can conclude, therefore, that for a correct description of the ion-solvent interaction concerning the first and second water molecules, we need the formalism of quantum theory allowing to reflect redistribution of electron density within the solvent molecules upon ion influence. For the more far located water molecules (*i.e.* the third and all further molecules), a purely electrostatic interaction of ion and solvent molecules seems to exist. It will be sufficient, therefore, to use an electrostatic approximation for these solvent molecules when discussing their interaction with the ion. This gives a further proof for the applicability of the MESQUAC-MO method to such systems.^{4,7)} This statement is expected to hold even for ions not having the noble gas electron configuration, as the stronger quantum effects appearing in the ion-solvent binding of such ions should be restricted mainly to the interaction with the first solvation layer. The absolute value for the interaction energy calculated for the iodide ion with water is also in good agreement with the corresponding *ab initio* value and the widely discussed effect of this low binding energy on the phenomenon of "negative" hydration.¹¹⁾ For Cs⁺, however, which also shows negative hydration, this phenomenon cannot be predicted from the present calculation. The reasons for the latter fact are to be seen mainly in the uncertainty of the ion-ligand distance chosen according to the ionic radii only, and in an artificial stabilization for larger cations due to the merely electrostatic description. For iodide ion, this failure could be avoided partially using the distances obtained in previous full *ab initio* calculations.

Solvent Separated Ion Pairs. The stabilization energies per water molecule in chains separating cations and anion are listed in Table 3. As can be shown from Fig. 2, the mutual interaction of the ions through the water chain seems to follow the $1/n$ (*i.e.*, the $1/r$) Coulomb law for any case where more than one solvent

TABLE 3. STABILIZATION ENERGIES PER WATER MOLECULE FOR SOLVENT SEPARATED ION PAIRS OF ALKALI IODIDES, FOR CHAIN LENGTHS 1—8 (in kcal/mol)

<i>n</i>	Li(water)I	Na(water)I	K(water)I	Cs(water)I
1	101.2	91.1	76.7	73.8
2	48.5	43.3	35.9	34.5
3	32.5	29.0	24.0	23.1
4	22.9	20.3	16.8	16.1
5	18.1	16.1	13.3	12.7
6	14.6	13.0	10.7	10.3
7	12.5	11.1	9.1	8.5
8	10.7	9.5	7.8	7.5

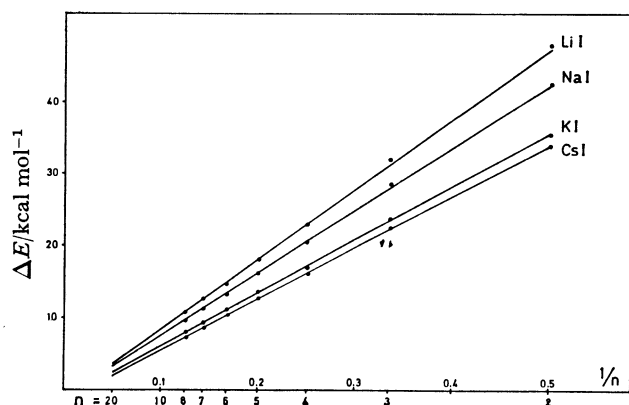


Fig. 2. Stabilization energy per water molecule for varying chain length and ion pairs versus the inverse number of water molecules in the polymer.

molecule is present. We can expect therefore also for larger solvent separated ion pairs that an electrostatic description of the cation/anion interaction will be quite satisfactory and sufficient.

The Range of Interactions. The level of 7.1 kcal/mol, being the hydrogen bond energy within the STO-3G *ab initio* framework, actually represents the "critical level" down to which ion-solvent binding energy might have some influence on the solvent structure. The linear chain model, however, is insufficient for the description of the solution reality, since it is an idealized structure, not taking into account effects of 3-dimensional solvates, thermal motions and entropic contributions, which all will lead to a faster decrease of structural influence of the ions. It is, however, useful for a rough estimation of a theoretical upper limit of the range of interaction under "optimal" conditions, *i.e.*, in a well ordered solvent matrix. For such a case, we have to expect, according to the values of Tables 2 and 3, rather far reaching effects of binding. This seems to be in agreement with some recent discus-

sions within the framework of an extended donor-acceptor theory.¹²⁾

Besides representing an estimation of the possible upper limit of interaction ranges, these data might get some practical importance in systems, where a peculiar ordering of the solvent molecules can take place, as for example in quick frozen solutions or in gel matrices.

Summarizing thus the results of our model calculations, we can assume that the application of mixed electrostatic-quantum chemical calculation procedures, taking into account far reaching binding effects by purely electrostatic terms, seem to be justified. The same can be expected for the theoretical investigation of solvent separated ion pairs containing more than one water molecule as a dielectric between the ions. The range of these electrostatic effects will depend very strongly on the degree of ordering of these solvent molecules and hence be influenced strongly by thermal and entropy effects. Finally, a construction of theoretical models describing well ordered solvent matrices will have to consider rather large unities in order to describe all interactions possible in such a system.

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