A Theoretical Study on Negative Solvation by Means of Quantum Chemical Calculations on the I(H₂O)⁻-Complex

Bernd M. Rode

Institut für Anorganische und Analytische Chemie der Universität Innsbruck,
Innrain 52a, A-6020 Innsbruck, Austria

By means of an "ab initio" all electron treatment of the I⁻/H₂O complex in various geometrical arrangements, it has been attempted to derive some arguments for the general discussion about the phenomenon of negative solvation, based on the background of quantum chemistry. The most stable conformation of the complex is indicated to have C_{2v} symmetry. Rotating of this conformation by 180° leads to an arrangement whose destabilization energy has about the same value as the complex formation energy, which, on the other hand, is only slightly higher than the hydrogen bond energy between two water molecules. These results contradict the formation of an almost rigid first hydration sphere and allow, further, the interpretation of the negative solvation by means of a "cooperative effect" between ion-solvent complex and other solvent molecules, in full agreement with the work of Engel and Hertz.

1. General Remarks on the Phenomenon of Negative Solvation

The solutions of certain salts show an increased fluidity compared to the pure solvent. This "structure breaking" effect (or "negative solvation") has been observed especially in aqueous solutions (e. g. of Cs-salts or iodides), where it was called negative hydration by Samoilov first [1]. In general, this means that the motions of the solvent molecules are faster in such solutions than in the pure solvent.

In the literature there exists a lot of work concerning this phenomenon (see [2, 3] and Ref. therein). The use of NMR relaxation studies [3] allowed a more sophisticated investigation of the structure breaking effect in water as well as in nonaqueous solvents.

Two theoretical models have been proposed for the description of this special behaviour of some ions in their solutions. The first one, by Frank and coworkers [4, 5], assumes the structure breaking effect to be localized further out from the ion, the latter being surrounded by a rather rigid and tightly bonded solvent layer. The second one, by Gurney [2] and Samoilow [1] provides the effect of structure breaking to be extended up to the surface of the ion. The physical analysis of the negative solvation phenomenon given in the fundamental work of Engel and Hertz [3], in connection with their experimental results, has supplied striking arguments for the second model, which has been extended also to some more detail by these authors. These arguments will be discussed later in connection with our results.

Further, we will try to analyze whether the interpretation given to the NMR relaxation results according to this model, can be brought into agreement with the results of the quantum chemical treatment of a typical solvate complex with structure breaking abilities. For these calculations, we chose the ion I⁻, which represents a quite suitable example of negative hydration.

2. The Choice of the Models and the Method of Calculation

2.1. The Geometrical Arrangements for the Solvate Complex

The 1:1 complex I(H₂O)⁻ has been considered as model compound in three basic configurations. The first one (Fig. 1 A) represents the conformation which is known to be the most stable one for analogous complexes of small anions e. g. F⁻. The other configurations (B and C) result from the first one
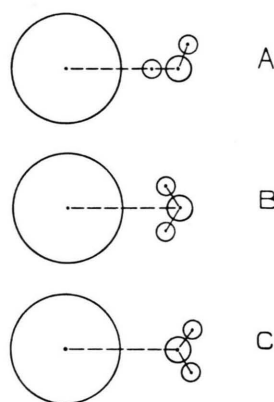

Fig. 1.

by rotating the water molecule around the oxygen atom. This geometrical operation gives a simple model for the "tumbling" of the water molecule due to thermal motions in the solution.

The I . . . O distance was fixed at the value of 4.50 Å according to the specific properties of the iodine basis set [6], the H_2O molecule was taken in its experimental geometry [7]. The experimental I . . . O distance was found to be approximately 3.5 Å in concentrated solutions of LiJ [8] and NH₄J [9] in water. This discrepancy will be discussed later. For a comparison of the hydrogen bond strengths between I⁻ and water and between two water molecules, respectively, we performed also calculations of the I(H₂O)⁻ complex in configuration A (Fig. 1) and of the water dimer, with energy optimized J − O and O − O distances.

2.2. The Calculation Method

For all calculations, the HF − LCGO − MO − SCF method was used employing an uncontracted 9s/6p/2d GLO basis set [6] for iodine and a 3s/1p GLO basis set for H_2O [1], which both have been used successfully in previous calculations on iodine compounds [11, 12]. In the basis set for the heavy atom, two additional s functions are being formed by the d functions, which are represented by six groups each, leading thereby to an effective basis size of 11/6/2. The details of the basis set and its exponents have been described already elsewhere [6].

The use of a small basis for the water molecule was necessary, in order to obtain an equivalent quality of description with regard to that of the heavy atom, but will surely reduce the significance of the results to a semiquantitative, if not even qualitative level.

The calculations have been performed in part at the UNIVAC 1108 computer of the University of Karlsruhe and in part at the CDC 3300 computer of the University of Innsbruck. Details of the program are given in Reference [13].

3. Results of the Calculations

3.1. Rotation of the Water Molecule in the Field of the Iodine Anion

For a fixed I . . . O distance (4.50 Å), the configuration 6 (Fig. 2) is predicted to be the most stable one, followed by A. This is in contrast to certain experimental results [8, 9, 10, 14]. The data re-

Table 1. Total energies and stabilization energies.

Species	Total energy (a.e.u.)	Stab. energy (kcal/mole)
I⁻	−6380.2929	—
H₂O	− 67.0875	—
I(H₂O)⁻(A) [a]	−6447.3917	−6.8
I(H₂O)⁻(B) [a]	−6447.3960	−9.8
I(H₂O)⁻(C) [a]	−6447.3701	+6.5
I(H₂O)⁻(A) [b]	−6447.3845	−2.6
I(H₂O)⁻(A) [c]	−6447.3920	−7.3
(H₂O)₂ [b]	− 134.1794	−2.8
(H₂O)₂ [c]	− 134.1849	−6.2

[a] Fixed I . . . O distance (see text), [b] exptl. geometry, [c] energy optimized.

ported in Ref. [8] regard a 6 M solution of LiI and the Li⁺ may also contribute to stabilize configuration A. In a very recent paper Langer and Hertz [10] have investigated a 6 M KI solution. Again they find preferential population of configuration A, however the distribution of configurations is spread over a wide range. Recent molecular dynamic studies by Heinzinger and Vogel [14] of 2.2 M solutions of LiI led also to the conclusion, that the water molecules in the first hydration sphere show an orientation towards the I⁻ ion according to configuration A. On the other hand, these studies also show, that cation-water, anion-water and water-water interactions are related to each other, possibly influencing thereby the equilibrium geometry of the I⁻-water complex.

The concentration maintained in all of these investigations (2.2 − 6 M) does not allow, however, a direct comparison with the calculations, since the conditions of such solutions are already quite different from those of dilute ones and almost not comparable with our model of the isolated I(H₂O)⁻ complex. The small energy difference between configurations A and B can easily be covered by solution effects. For the energy optimization (Chapter 3.2) of the I . . . O distance, however, we chose the "experimental" arrangement, i. e. configuration (A), since within the limitations of our basis set, the small difference between configurations (A) and (B) does not allow a doubtless decision for one of them. The total energies and the complex formation (i. e. solvation) energies derived from these are listed in Table 1. From these values, we can find that a rotation of the water molecule in the field of the anion can lead to a destabilized configuration with an energy increase in relation to the separated

ion and H_2O molecule of almost the same amount as the solvation energy in the "proper" (energy minimum) arrangement. The calculated complex formation energy seems to be rather realistic, since the energy for the displacement of one water molecule from the complex $I^-(H_2O)_n$ has been estimated to be around 6 kcal/mole, from considerations based on experimental data [3]. Further, the realization of configurations where the water molecule is "repelled" from the ion, has been postulated to occur under the conditions of thermal motions, too, and plays an important part in the discussion of the negative hydration [3]. In the discussion of these results we will try to show that the similarity of the energy values for stabilization and repulsion, respectively, supports the strongly the arguments of Engel and Hertz concerning the mechanism of negative hydration.

3.2. Comparison of the Hydrogen Bond Energies in $I(H_2O)^-$ and $(H_2O)_2$

The hydrogen bond energies in the solvate complex and in the water dimer have been calculated optimizing the $I \ldots O$ and $O \ldots O$ distances with respect to total energy, in order to get some information about the reliability of the basis set.

From experimental data, the $I \ldots O$ distance is expected to be approximately 3.50 Å, the $O \ldots O$ distance has been determined to 2.76 Å. For these experimental geometries we obtain hydrogen bond energies of 2.6 kcal/mole in the $I(H_2O)^-$ complex and 2.8 kcal/mole in the water dimer (exptl.: 5.0 kcal/mole [15]). Geometry optimization leads to an $O \ldots O$ distance of 3.15 Å for the water dimer at its energy minimum, connected with a stabilization energy of 6.2 kcal/per mole for the hydrogen bond. For the $I \ldots O$ distance, minimization of the energy leads to a value of 4.2 Å and 7.3 kcal/mole hydrogen bond energy. The apparently too high $O \ldots O$ and $I \ldots O$ distances are supposed to result from the use of the small, unsophisticated basis sets, which especially for H_2O, do not contain enough "flexible" functions. This specific property has been taken into acount previously by fixing the $I \ldots O$ distance at a higher value. As a further consequence of our basis set, we have to expect an artificial improvement of the H_2O basis by the iodine basis functions with small exponents. This artificial basis improvement should lead also to an elevated hydrogen bond stabilization energy (we estimate about $+5$ to $+15\%$),

which must be taken into account in the interpretation of the calculations. Thus, from the results of these calculations and those discussed previously, we can conclude, that the energy gain upon hydration of I^- will be equal to or only slightly larger than the energy needed for breaking one hydrogen bond between two water molecules. This holds as well for the experimental distances (2.6 and 2.8 kcal/mole) as for the optimized distances, which, however, lead to better energy values (7.3 and 6.2 kcal/mole).

4. Discussion of the Results with Respect to the Phenomenon of Negative Solvation

4.1. The $I(H_2O)_n^-$-Complex

From the results obtained for the 1:1 complex of the I^- anion with H_2O and the general knowledge about solvated ions in the liquid phase we can derive some further conclusions. Due to the rapid exchange of solvent molecules in the first solvation layer (in this case still facilitated by the small solvation energy), several arrangements of the $I(H_2O)_n^-$-complex will be realized with one or more water molecules in a "desorientated" position to the ion [3]. Our calculations have shown that this desorientation is accompanied by a remarkable destabilization, raising thereby the mean energy of the solvate complex. The calculated value for this "repulsion energy", which is relatively high compared to the solvation energy in the case of I^-, supports strongly the result of Engel and Hertz, that the average situation around this ion corresponds to a higher energetic state than the situation of a neutral solvated particle, which would not lead to any "repelling" positions for the solvent molecules. A further analysis of the energetic situation of the I^- ion in water solution cannot be given without taking into account also the binding forces between the solvent molecules themselves. This will be done in the following section.

4.2. The Influence of Complex Formation on the Structure of the Solvent

The comparison of the hydrogen bond energies for $I(H_2O)^-$ and $(H_2O)_2$, as well as the comparison with the solvation energy in the most stable conformation of the complex have shown all of these quantities to have rather similar values. If we subtract the energy used for breaking the hydrogen

bonds of water molecules involved in the solvation process to other water molecules, from the energy being gained by complex formation with I^-, we obtain a rather small or even zero net gain of energy. The similarity of the interaction energies for both the H_2O/H_2O and I^-/H_2O systems means that there does not exist — in contrast to the assumption of Frank and coworkers [4, 5] — any energetic foundation for the formation of a rigid solvation layer around the ion. Thus, the thermal motions in the solution can lead only to complex arrangements with destabilizing properties. Since the number of possible arrangements with a more or less destabilizing effect is rather high compared to the few conformations showing no destabilization or even stabilization (which, however, can also be only rather small), such destabilizing arrangements should always be present, due to entropic reasons, to a remarkable extent.

For this argumentation, the environment of the complex, i. e. the bulk solvent plays an essential part. First, it provides a competetive interaction with the first layer ligand molecules, which is almost equivalent to that of the ion and forms, therefore, an environment of an energetic level very similar to that of the complex. Second, it enables ligand exchange processes and facilitates thereby the realization of destabilizing ligand positions in the first solvation layer, which then facilitate the motions of the ligand molecules. Since the complex itself and the bulk solvent are both necessary for the appearance of the negative solvation phenomenon, we can regard the latter as a "cooperative" effect of suitable ion complexes with the solvent.

These conclusions are supported also by experimental results [3], namely by the disappearance of structure breaking abilities upon addition of organic molecules, which lead to an isolation of the $I(H_2O)_n^-$ complex from bulk solvent molecules. We can compare this observation — made by NMR relaxation measurements — once more with the energy data of the calculations. For these measurements, a structure breaking effect means a decrease of the average reorientation time of the solvent molecules in the solution, compared to the pure solvent. The energy barrier for rotational or translational movement of a water molecule is estimated to be 4 kcal/mole [3] in the pure solvent. The rotational barrier for H_2O in the isolated I/H_2O^- complex was calculated to be about 15 kcal/mole. Thus, the observed effective decrease of the reorientation time below the value of pure water can be understood only taking into account the interaction of the complex with further ligand molecules, i. e. with the bulk water surrounding the complex, as it has been discussed above.

Summarizing the results of this discussion, we can state that our rather simplified quantum chemical treatment of one example of an ion solvent complex with structure breaking properties can be brought into full agreement with the analysis of the negative solvation effect given by Engel and Hertz and their experimental data [3]. It seems to be a further proof also for the validity of the model assumptions by Gurney [2] and Samoilov [1] and against those of Frank and coworkers [4, 5].

[1] O. Ya. Samoilov, Discuss. Faraday Soc. **24**, 141 [1957].

[2] R. W. Gurney, Ionic Processes in Solution, McGraw Hill, New York 1953.

[3] G. Engel and H. G. Hertz, Ber. Bunsenges. Physikal. Chem. **73**, 808 [1969].

[4] H. S. Frank and W. Y. Wen, Discuss. Faraday Soc. **24**, 133 [1957].

[5] H. S. Frank and M. W. Evans, J. Chem. Phys. **13**, 507 [1945].

[6] B. M. Rode, Chem. Phys. Letters **27**, 264 [1974].

[7] D. W. Posener and M. W. P. Strandberg, Phys. Rev. **95**, 374 [1954].

[8] A. Geiger and H. G. Hertz, J. Solution Chem. in press.

[9] A. H. Narten, M. D. Danford, and H. A. Levy, X-Ray Diffraction Data in Liquid Water in the Temperature Range 4—200 °C, ORNL-3997 [1966].

[10] H. Langer and H. G. Hertz, to be published.

[11] B. M. Rode, Mh. Chemie **105**, 807 [1974].

[12] B. M. Rode, J. Chem. Soc. Faraday II **1975**, 481.

[13] R. Ahlrichs, Theoret. Chim. Acta Berlin **33**, 157 [1974].

[14] K. Heinzinger and P. C. Vogel, Z. Naturforsch. **31 a**, 463 [1976].

[15] G. C. Pimentel and A. L. McClellan, The Hydrogen Bond, W. H. Freeman & Co., London 1960.