# ION SOLVATION BY DIPOLAR APROTIC SOLVENTS.
## AN *ab initio* STUDY

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The paper deals with the solvation of $Li^+$, $Be^{2+}$, $Na^+$, $Mg^{2+}$, and $Al^{3+}$ ions in dimethyl-sulphoxide, dimethylformamide, acetonitrile, and water. The *ab initio* quantum chemical method was used to calculate the solvation energies, molecular structures, and charge distributions for the complexes water...ion, acetonitrile...ion, dimethyl sulphoxide...ion, and dimethylformamide ...ion. The interaction energies were corrected for the superposition error. Complete geometry optimization was performed for the complex water...ion. Some generalizations are made on the basis of the results obtained.

The solvation of ions accompanies most physicochemical and chemical processes in solutions. In some cases, it also occurs in gas phase reactions. Lately, increasingly greater importance has been attached to this phenomenon, and experimental (see, for example, refs[1−4]) as well as theoretical[5−10] studies have been made. Both the approaches are directed primarily at determining the structural and energy changes accompanying the process.

At present, there is an extensive volume of theoretical papers concerned with the subject. The centre of interest has shifted to the fields of quantum chemistry[9], statistical mechanics, and molecular dynamics[10].

## THEORETICAL

The studies dealing with solvation effects of molecules and ions can generally be divided into two groups according to whether the continuum or the discrete model is used to describe the solvent. A combined continuum and discrete model has also been considered.

In the present study we use the discrete model, in which the solvent molecule interacting with the solvated ion or molecule is pictured as a discrete particle of defined size and charge distribution. This interaction leads to the formation of the so called supermolecule, whose structure and energy relations can be studied by means of quantum chemical calculations. It should be noted that results of this type of calculation relate to the solvation in the gas phase, but they may also be used to estimate the solvation energies for very dilute solutions.

In the discrete model, the interaction energy is defined as the difference between the total energy, $E_a$, of the aggregate and the sum of the energies, $E_i$, of the solvating molecule and the

solvated ion:

$$\Delta E = E_{\mathrm{a}} - \sum_i E_i .$$ (1)

The energies of the subsystems and supersystems can be obtained by the Hartree–Fock SCF *ab initio* method.

The interaction energy should be corrected for the superposition error of the basis set (BSSE) used in the calculation[11]. The energy $E_i$ for each subsysem can then be calculated using the. basis set of the supersystem (with the nuclear charges on the other subsystem taken as zero), Let $E_1$ denote the energy of the ion with a supplementary basis set at the position of the solvent and let $E_2$ represent the energy of the solvent in a basis set extended to include the functions centred at the ion position. The corrected energy, $\Delta E_{\mathrm{c}}$, is obtained as

$$\Delta E_{\mathrm{c}} = E_{\mathrm{a}} - (E_1 + E_2) .$$ (2)

The BSSE energy contribution is given by

$$\Delta E_{\mathrm{BSSE}} = \Delta E - \Delta E_{\mathrm{c}} .$$ (3)

The present paper is a continuation of our previous theoretical study of ion solvation by means of the CNDO method[12].

### Choice of the System and the Method

Using the supermolecule model, we studied theoretically the interactions of $Li^+$, $Be^{2+}$, $Na^+$, $Mg^{2+}$, and $Al^{3+}$ ions with models of the following solvents: water (*I*), acetonitrile (AN) (*II*), dimethyl sulphoxide (DMSO) (*III*), and dimethylformamide (DMF) (*IV*). In all cases, 1 : 1 cation...solvent complexes were investigated. Solvation energies and supermolecule structures were calculated by the *ab initio* method with the minimal STO-3G basis set, using the GAUSSIAN 70 (ref.[13]) and HONDO (ref.[14]) programs. The geometries of the solvent molecules as indicated by X-ray data[15] were held fixed during optimization of the ion-solvent distances.

### RESULTS AND DISCUSSION

The distance, $r$, between the cation and the electronegative atom of the solvent was optimized for each complex. The results are given in Tables I to V. For comparison, available experimental data and results of other workers are listed in Table VI. The optimized geometries of the supermolecules are as follows.

*Water...Ion Complexes.* The calculated results for these complexes are given in Table I. By comparing these values with experimental or *ab initio* data obtained from larger basis sets (Table VI), it is evident that the STO-3G calculation considerably overestimates the solvation energy. The situation improves by introduction of the BSSE correction. A very good agreement with both experimental and theoretical data is obtained for the sodium cation. In the case of magnesium and lithium cations, the agreement may be considered as reasonable. Somewhat poorer agreement is found for beryllium and aluminium cations. The equilibrium distances agree very well, except for $Na^+$ and $Mg^{2+}$ ions, where the deviation exceeds 0·01 nm. The

equilibrium distances decrease, whereas the solvation energies increase, with increasing atomic number of ions within a row of the periodic system. The net charge on the electronegative oxygen atom of water participating directly in the solvation interaction remains constant within 0·1 of the charge unit for all the systems studied.
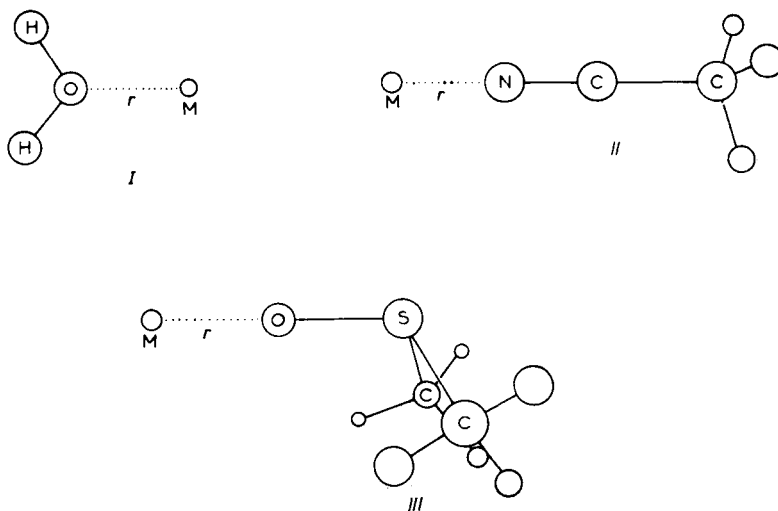




The charge transfer from the solvating water molecule to the ion is proportional to the atomic number of the ion or its valency. The relative strength of the solvation interaction as measured by the magnitude of the cation-oxygen overlap population is again directly proportional to the atomic number of the ion (or its valency) within a row. This is a consequence of the solvation interaction strength being determined primarily by the strength of the electrostatic interaction between the cation charge and the dipole moment of water.
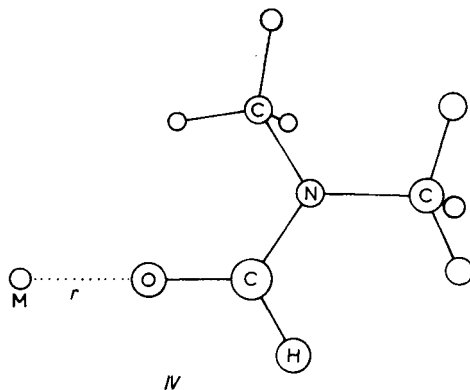
Complete optimization of the system $M^{n+}...H_2O$ resulted in virtually no change in the structure of the water molecule. Small alterations in the intramolecular geometry had a negligible effect on the interaction energies or the ion...water equilibrium distances. The values for the completely optimized systems are given in Table V. In view of these findings, we did not vary the structure of the subsystems in further studies and neglected the effect of the intramolecular geometry alterations on the intermolecular structure and the interaction energy.

*Acetonitrile...Ion Complexes.* The calculated characteristics of the optimized complexes are given in Table II. The correction to the solvation energy for the superposition error is again significant; in the case of the sodium complex, for example, its application gives nearly the experimental value $(-129.7 \text{ kJ mol}^{-1})$. Our results for $Li^+$ and $Na^+$ are also in good agreement with *ab initio* data obtained by using the extended 4-31G basis set[16]. It is of interest to note that the interaction with the third-row cations involves not only the interaction between the lone electron pair on the nitrogen and the $s$ and $p$ orbitals of the metal, but also an interaction between the $\pi$ orbitals of acetonitrile and the corresponding $d$ orbitals of the metal

TABLE I

The system water...ion

| Ion | $M$ | $O$ | $M$–$O$ | $\Delta q$ | $r$ | $\Delta E$ | $\Delta E_c$ |
|---|---|---|---|---|---|---|---|
| $Li^+$ | 0·7282 | −0·3382 | 0·1890 | 0·2718 | 0·17 | −334·0 | −199·8 |
| $Be^{2+}$ | 1·4508 | −0·3401 | 0·3074 | 0·5492 | 0·15 | −862·5 | −729·2 |
| $Na^+$ | 0·8805 | −0·4083 | 0·0790 | 0·1195 | 0·20 | −181·9 | −104·4 |
| $Mg^{2+}$ | 1·7016 | −0·4304 | 0·1739 | 0·2984 | 0·18 | −496·4 | −390·0 |
| $Al^{3+}$ | 2·4267 | −0·3973 | 0·2616 | 0·5733 | 0·17 | −1 010·2 | −892·6 |

TABLE II

The system acetonitrile...ion

| Ion | $M$ | $N$ | $M$–$N$ | $\Delta q$ | $r$ | $\Delta E$ | $\Delta E_c$ |
|---|---|---|---|---|---|---|---|
| $Li^+$ | 0·6895 | −0·2121 | 0·2223 | 0·3105 | 0·18 | −297·6 | −225·2 |
| $Be^{2+}$ | 1·3586 | −0·3000 | 0·3904 | 0·6414 | 0·15 | −911·7 | −857·8 |
| $Na^-$ | 0·9012 | −0·2970 | 0·0623 | 0·0988 | 0·21 | −164·5 | −133·6 |
| $Mg^{2+}$ | 1·7105 | −0·3666 | 0·1712 | 0·2895 | 0·19 | −533·0 | −488·8 |
| $Al^{3+}$ | 2·3220 | 0·4219 | 0·3376 | 0·6780 | 0·17 | −1 231·0 | −1 180·8 |

atom. This has been discussed in greater detail in our previous paper[12]. The equilibrium distances follow the same trend as found for the water...ion complexes (in most cases they also show the same absolute magnitudes). Very good agreement between the calculated and experimental equilibrium distances was found for the sodium cation (0·210 and 0·212 nm). The negative charge on the nitrogen atom of

TABLE III

The system dimethyl sulphoxide...ion

| Ion | $M$ | $O$ | $M\text{-}O$ | $\Delta q$ | $r$ | $\Delta E$ | $\Delta E_c$ |
|-----|-----|-----|-----|-----|-----|-----|-----|
| $Li^+$ | 0·4541 | −0·4164 | 0·2990 | 0·5459 | 0·15 | −583·4 | −352·0 |
| $Be^{2+}$ | 1·1082 | −0·4163 | 0·4449 | 0·8918 | 0·13 | −1 483·2 | −1 300·8 |
| $Na^+$ | 0·8486 | −0·6057 | 0·0918 | 0·1514 | 0·19 | −261·5 | −182·0 |
| $Mg^{2+}$ | 1·5652 | −0·6199 | 0·2241 | 0·4348 | 0·17 | −806·4 | −691·8 |
| $Al^{3+}$ | 1·8838 | −0·4341 | 0·2153 | 1·1162 | 0·16 | −1 767·2 | −1 636·6 |

TABLE IV

The system dimethylformamide...ion

| Ion | $M$ | $O$ | $M\text{-}O$ | $\Delta q$ | $r$ | $\Delta E$ | $\Delta E_c$ |
|-----|-----|-----|-----|-----|-----|-----|-----|
| $Li^+$ | 0·5724 | −0·2790 | 0·2547 | 0·4276 | 0·16 | −434·8 | −282·1 |
| $Be^{2+}$ | 1·1792 | −0·3057 | 0·4296 | 0·8208 | 0·13 | −1 251·4 | −1 117·3 |
| $Na^+$ | 0·8815 | −0·3782 | 0·0754 | 0·1185 | 0·20 | −199·4 | −141·5 |
| $Mg^{2+}$ | 1·6225 | −0·4553 | 0·2085 | 0·3775 | 0·17 | −658·6 | −566·9 |
| $Al^{3+}$ | 2·2000 | −0·3992 | 0·3379 | 0·8000 | 0·16 | −1 520·1 | −1 419·0 |

LEGEND TO TABLES I TO IV

Calculated values of charges, energies, and equilibrium distances

| | |
|-----|-----|
| $M$ | net charge on the ion |
| $N(O)$ | net charge on nitrogen (oxygen) atom |
| $M\text{-}N(O)$ | ion–nitrogen (oxygen) overlap population |
| $\Delta q$ | charge transferred to the ion from the solvating system |
| $r$ | solvated ion – solvating system equilibrium distance (nm) |
| $\Delta E$ | solvation energy (kJ mol$^{-1}$) |
| $\Delta E_c$ | BSSE corrected solvation energy |

TABLE V

Geometry parameters and charge distribution characteristics for completely optimized ion...water complexes[a]. For comparison, values obtained by incomplete optimization with the geometry of the water molecule unchanged and the ion–oxygen distance optimized are given in parentheses

| System | $\alpha$ | $r_{O-H}$ | $E$ | $r_{M-O}$ | $M$ | $O$ |
|--------|----------|-----------|-----|-----------|-----|-----|
| $H_2O$ | 100·02 | 0·9894 | −74·965901 | | | |
| $Li^+...OH_2$ | 103·99 | 0·9767 | −82·226809 (−82·222995) | 0·1697 (0·1700) | 0·7275 (0·7282) | −0·3277 (−0·3382) |
| $Be^{2+}...OH_2$ | 107·85 | 0·9964 | −88·732647 (−88·728610) | 0·1467 (0·1500) | 1·4386 (1·4508) | −0·3271 (−0·3401) |
| $Na^+...OH_2$ | 103·80 | 0·9801 | −234·816672 (−234·814219) | 0·1994 (0·2000) | 0·8827 (0·8805) | 0·3867 (−0·4083) |
| $Mg^{2+}...OH_2$ | 106·16 | 0·9828 | −271·663286 (−271·661310) | 0·1806 (0·1800) | 1·7022 (1·7016) | −0·4155 (−0·4304) |
| $Al^{3+}...OH_2$ | 107·42 | 1·0100 | −312·607769 (−312·601612) | 0·1707 (0·1700) | 2·5067 (2·4267) | −0·3713 (−0·3973) |

[a] $\alpha$ H—O—H angle in degrees; $r_{O-H}$ O–H distance in nm; $E$ energy of the system in a.u.; $r_{M-O}$ ion–oxygen equilibrium distance; $M$ net charge on the ion; $O$ net charge on oxygen atom

TABLE VI

Some experimental and theoretical values for the systems studied. $\Delta E$, solvation energy in kJ . . mol$^{-1}$; $r$, ion...oxygen (nitrogen) distance in nm

| Type of value | Ion | Water...ion | | Acetonitrile...ion | | Reference |
|---------------|-----|------|---|------|---|-----------|
| | | $\Delta E$ | $r$ | $\Delta E$ | $r$ | |
| Experiment | $Li^+$ | −142·26 | 0·185 | | | 7 |
| | $Na^+$ | −100·42 | 0·220 | −129·70 | 0·212 | 7, 2 |
| SCF/STO-3G calculation | $Li^+$ | −143·93 | 0·189 | | | 17 |
| | $Be^{2+}$ | −585·76 | 0·150 | | | 7 |
| | $Na^+$ | −100·00 | 0·225 | | | 18 |
| | $Mg^{2+}$ | −334·72 | 0·195 | | | 7 |
| | $Al^{3+}$ | −753·12 | 0·175 | | | 7 |
| SCF/4-31G calculation | $Li^+$ | | | −200·00 | 0·188 | 16 |
| | $Na^+$ | | | −149·79 | 0·225 | 16 |

acetonitrile increases continuously with increasing atomic number of ions within a row. The cation-nitrogen overlap population and the charge transferred from the acetonitrile molecule to the solvated cation exhibit the same tendency to increase with increasing atomic number of ions within a row.

*Dimethyl Sulphoxide...Ion Complexes.* The results obtained by optimization of these complexes are given in Table III. The average correction for the superposition error is over $100 \text{ kJ mol}^{-1}$. The equilibrium distances decrease with increasing atomic number within a row. Compared with those for the previous two types of complex, they are lower in absolute value by an average of $0·02 - 0·03 \text{ nm}$. Hence, the absolute values of the positive charges are lower compared to those for the previous complexes. The negative charge on the electronegative oxygen atom of the solvating DMSO molecule shows an interesting behaviour differing from that for the complexes with water and acetonitrile. It is virtually identical for the interactions with $Li^+$ and $Be^{2+}$ and also for $Na^+$ and $Mg^{2+}$. The overlap population for the interaction between the cation and the oxygen atom of dimethyl sulphoxide increases with increasing atomic number within a row, with the exception of the aluminium cation for which an unexpected decrease is observed.

*Dimethylformamide...Ion Complexes.* The calculated results for these complexes are given in Table IV. The BSSE corrections are mostly lower than $100 \text{ kJ mol}^{-1}$. The equilibrium distances are comparable to those for the DMSO...ion complexes. The charge transferred from the solvating DMF molecule to the ion follows the same trend as found for the above complexes. In contrast to the previous complexes, there is not definite increase in the net charge on the oxygen atom of DMF within the second row. The charge on the oxygen atom in the $Al^{3+}$...DMF complex is smaller than that for the $Mg^{2+}$..DMF complex, the same anomaly as found for the DMSO...ion complexes. The cation-oxygen overlap population shows the same behaviour as observed for the water and acetonitrile complexes (without an anomaly for the aluminium cation).

## CONCLUSION

The *ab initio* nonempirical quantum chemical method was used for STO-3G optimization of 1 : 1 cation...solvent complexes with water, acetonitrile, dimethyl sulphoxide, or dimethylformamide as the solvent. The calculated results include the optimum equilibrium ion-solvent bond distances, the solvation energies, the superposition errors, the charge distributions, and the charge transfer from the solvating molecule to the solvated ions. As the atomic number of the solvated cation increases within a row of the periodic system, the charge on the cation and the overlap population for the interaction of the solvated cation with the electronegative atom of the solvating molecule increase, whereas the equilibrium distance between the solvated

cation and the solvating molecule decreases. The negative charge on the electronegative atom of the solvating molecule follows no definite trend. The charge density on the solvated cation is proportional to the size of the solvating molecule, following the order $H_2O > AN > DMF > DMSO$.

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