ION SOLVATION IN MIXED SOLVENTS. AN *ab initio* STUDY

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The paper is concerned with the solvation of Li^+, Be^{2+}, Na^+, Mg^{2+}, and Al^{3+} ions in the mixed solvents acetonitrile...water, dimethyl sulphoxide...water, and dimethylformamide... water. The complexes acetonitrile...ion...acetonitrile are also studied. The *ab initio* quantum chemical method with the minimal STO-3G basis set was used to calculate the equilibrium distances, solvation energies, three-particle energy contributions, charge distributions, and overlap populations for the above systems. Optimum structures of the 1 : 1 : 1 complexes were determined on the basis of the results obtained.

As a continuation of our earlier studies[1,2], we have investigated ion solvation in mixed solvents using the Hartree–Fock SCF *ab initio* method.

Mixed solvents are encountered not only in everyday chemical practice, but are of key practical importance in many other areas[3,4]. They have therefore become lately a subject of both experimental and theoretical interest.

THEORETICAL

The fundamental features of our theoretical approach have been presented in our previous work[2]. Suffice it to say at this place that we investigated ion solvation in mixed solvents on the basis of the discrete supermolecule model using the SCF method with the STO-3G basis set. Compared to pairwise interactions studied previously[2], the treatment of three-system interactions must involve an extra stabilization given by the three-particle contribution $\Delta E^{(3)}$ defined by

$$\Delta E(S_1...M^{n+}...S_2) = \Delta E^{(2)}(S_1...M^{n+}) + \Delta E^{(2)}(S_2...M^{n+}) +$$
$$+ \Delta E^{(2)}(S_1...S_2) + \Delta E^{(3)}(S_1...M^{n+}...S_2), \tag{1}$$

where $\Delta E(S_1...M^{n+}...S_2)$ is the overall solvation energy, $\Delta E^{(2)}(S_1...M^{n+})$ and $\Delta E^{(2)}(S_2...M^{n+})$ are the two-particle solvation energy contributions arising from the solvent...ion interactions, $\Delta E^{(2)}(S_1...S_2)$ is the two-particle energy contribution from the solvent...solvent interaction, and $\Delta E^{(3)}(S_1...M^{n+}...S_2)$ is the contribution from the interacting mixed complex. The magnitude of the term $\Delta E^{(3)}$ can be taken as a measure of the extra stabilization (or destabilization) of a ternary complex as compared to a system involving only the pairwise interactions $\Delta E^{(2)}$.

RESULTS AND DISCUSSION

In this work, we studied the following 1 : 1 : 1 mixed complexes: acetonitrile...ion...acetonitrile (I) (this is not a mixed complex in the above sense, but was included because of its analogy to the other complexes studied), acetonitrile...ion...water (II), dimethylformamide...ion...water (III), and dimethyl sulphoxide...ion...water (IV). Optimization was performed for the distances (r_1, r_2) between the cation and the electronegative atoms of both solvents entering into direct solvation interaction with the ion. The resulting structures of the complexes were as follows.
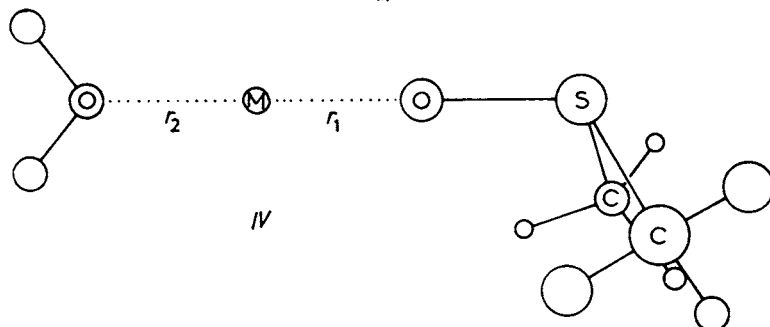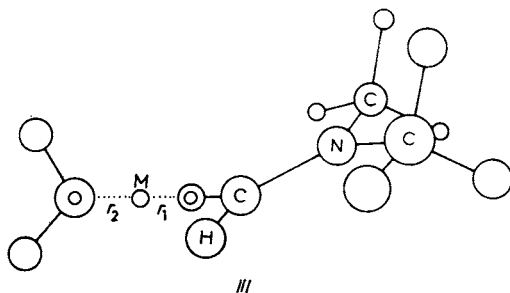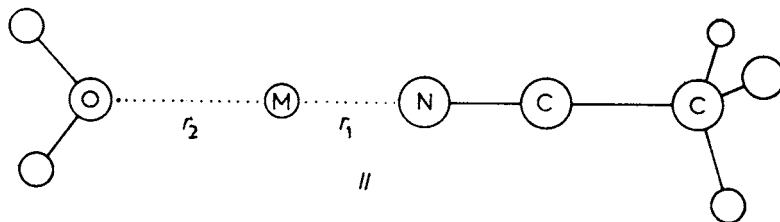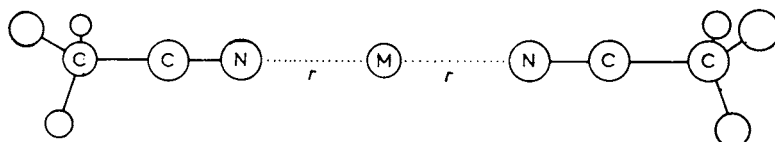
The initial geometries of the molecules were taken from an X-ray analysis[5]. The computation was performed using GAUSSIAN 70 (ref.[6]) and HONDO (ref.[7]) *ab initio* programs. The results are given in Tables I to IV. No corrections for the superposition error were made, but their estimates can be obtained (see Conclusion) by comparison with the 1 : 1 complexes[2].

Acetonitrile...Ion...Acetonitrile Complexes. The results for these symmetrical complexes are given in Table I. Apparently, neglecting the BSSE correction for this large system leads to a considerable overestimation of the solvation energy (when compared, for example, with Li^+ and Na^+ complexes calculated using the extended 4-31G basis set[8]). This may be stated even in the absence of suitable experimental data for comparison. The solvation energy increases with increasing atomic number of ions within a row. The equilibrium distances of both the solvating molecules of acetonitrile from the solvated ion in the resulting structure are identical for all complexes studied, as can be expected on the basis of the symmetry of the system. The distances decrease with increasing atomic number of ions within a row of the periodic system. The three-particle energies are generally positive and increase with increasing atomic number within a row. Their values are approximately 10% of the total interaction energy. Thus application of the additivity rule to the calculation of the interaction energy would give rise to relatively large errors. The most stable complexes are those with Al^{3+} and Be^{2+} ions. The charge distributions over the solvated cations indicate that the positive charge increases with increasing atomic number within a row. The charge on the electronegative nitrogen atom of each solvating molecule of acetonitrile also increases with the atomic number within a row. The same tendency is observed for the ion-nitrogen overlap populations. The charge transfer from the solvating molecules to the ion is directly proportional to the valency of the ion, the largest values again being found for the systems involving Al^{3+} and Be^{2+}.

Water...Ion...Acetonitrile Comlexes. The results for these complexes are given in Table II. Again, there is a tendency for the solvation energy to increase with increasing atomic number of ions within a row. The equilibrium distances, however, are influenced by the heterogeneity of the solvating molecules. They tend to decrease in both cases (*i.e.*, for both water and acetonitrile) with increasing atomic number within a row, but a difference of 0·01 nm is found in several cases. The three-particle energies increase with increasing atomic number of ions within a row, but on the average are lower than those for the preceding complex. The charge transfer from the solvating molecules to the ion also increases with the atomic number within a row. The charges on the electronegative atoms of the solvating molecules directly interacting with the ion (*i.e.*, the nitrogen atom of acetonitrile and the oxygen atom of water) markedly differ for solvated ions of low atomic numbers, becoming roughly equal for high atomic numbers. In both cases, there is again a tendency for the charges

on the electronegative atoms to increase with increasing atomic number, although for water molecule this effect is very subtle. The overlap populations for the interaction between the cation and the nitrogen atom of acetonitrile are greater than those for the interaction between the cation and the oxygen atom of water. In both cases, the overlap becomes larger as the atomic number of ions within a row increases.

Dimethylformamide...Ion...Water Complexes. The results for these complexes are given in Table III. Distinct differences are found between the equilibrium distances of the two solvating molecules. There is again a tendency for these values to decrease with increasing atomic number of the ions, with the exception of the ion...DMF distances for Al^{3+} and Mg^{2+}, which are identical. The three-particle energies are higher than those for the previous complex and are rather comparable to those for the acetonitrile...ion...acetonitrile complexes. The net charges on the cations are smaller than those for the previous two complexes. The charge distributions over the electronegative atoms of dimethylformamide and water entering into the solvation interaction increase within a row with increasing atomic number for uni- and bivalent

TABLE I

The system acetonitrile...ion...acetonitrile

Ion	M	N	M–N	N	M–N	Δq	ΔE	$\Delta E^{(3)}$	r_1	r_2
Li^+	0·4274	−0·1953	0·2092	−0·1953	0·2092	0·5726	−549·1	36·0	0·18	0·18
Be^{2+}	0·9232	−0·2844	0·3502	−0·2844	0·3502	1·0768	−1 617·6	188·0	0·15	0·15
Na^+	0·8374	−0·2833	0·0531	−0·2833	0·0531	0·1626	−307·2	15·6	0·22	0·22
Mg^{2+}	1·4978	−0·3579	0·1557	−0·3579	0·1557	0·5022	−969·3	89·0	0·20	0·20
Al^{3+}	1·9181	−0·4306	0·3028	−0·4306	0·3028	1·0819	−2 197·2	253·2	0·17	0·17

TABLE II

The system water...ion...acetonitrile

Ion	M	N	O	M–N	M–O	Δq	ΔE	$\Delta E^{(3)}$	r_1	r_2
Li^+	0·4575	−0·1981	−0·3329	0·2097	0·1855	0·5425	−603·0	26·8	0·18	0·17
Be^{2+}	0·9642	−0·2903	−0·3440	0·3589	0·2889	1·0358	−1 625·0	142·7	0·15	0·15
Na^+	0·7989	−0·2866	−0·3981	0·0574	0·0733	0·2011	−329·4	18·1	0·21	0·20
Mg^{2+}	1·4689	−0·3727	−0·4297	0·1682	0·1607	0·5311	−968·3	60·5	0·19	0·18
Al^{3+}	1·9523	−0·4314	−0·4244	0·3151	0·2453	1·0477	−2 062·1	176·6	0·17	0·17

TABLE III

The system dimethylformamide...ion...water

Ion	M	$O_{(1)}$	$O_{(2)}$	$M-O_{(1)}$	$M-O_{(2)}$	Δq	ΔE	$\Delta E^{(3)}$	r_1	r_2
Li^+	0·3647	−0·2718	−0·3308	0·2418	0·1799	0·6353	−723·2	44·3	0·16	0·17
Be^{2+}	0·8825	−0·3253	−0·3436	0·4042	0·2741	1·1675	−1 900·7	207·2	0·13	0·15
Na^{2+}	0·7806	−0·3684	−0·3976	0·0710	0·0728	0·2194	−362·6	20·5	0·20	0·20
Mg^{2+}	1·4089	−0·4525	−0·4281	0·1946	0·1571	0·5911	−1 076·2	78·5	0·17	0·18
Al^{3+}	1·8616	−0·4322	−0·4238	0·3222	0·2391	1·1384	−2 314·9	214·0	0·17	0·16

TABLE IV

The system dimethyl sulphoxide...ion...water

Ion	M	$O_{(1)}$	$O_{(2)}$	$M-O_{(1)}$	$M-O_{(2)}$	Δq	ΔE	$\Delta E^{(3)}$	r_1	r_2
Li^+	0·2568	−0·4161	−0·3270	0·2881	0·1761	0·7432	−856·0	56·2	0·15	0·17
Be^{2+}	—	—	—	—	—	—	—	—	—	—
Na^+	0·7530	−0·5987	−0·3952	0·0864	0·0713	0·2470	−417·7	25·0	0·19	0·20
Mg^{2+}	1·3721	−0·6251	−0·4215	0·2117	0·1458	0·6279	−1 209·2	91·3	0·17	0·19
Al^{3+}	1·7954	−0·5587	−0·4249	0·3283	0·2357	1·2046	−2 532·8	240·1	0·16	0·17

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
$O_{(1)}$	oxygen atom of dimethyl sulphoxide or dimethylformamide
$O_{(2)}$	oxygen atom of water
$M-N(O, O_{(1)}, O_{(2)})$	overlap population for the interaction between the ion and the electronegative atom of the solvating molecule
Δq	charge transferred to the ion from the solvating system
ΔE	solvation energy (kJ mol^{-1})
$\Delta E^{(3)}$	three-particle energy contribution (kJ mol^{-1})
r_1	equilibrium distance between ion and dimethylformamide, dimethyl sulphoxide or acetonitrile (nm)
r_2	equilibrium distance between ion and water (or ion and acetonitrile in Table I) (nm)

ions, but a slight decrease is observed for the aluminium cation. The overlap popula-
tions for the interaction between the cation and the oxygen atom of dimethylform-
amide are greater than those for the interaction between the cation and the oxygen
atom of water.

Dimethyl Sulphoxide...Ion...Water Complexes. The results for these complexes
are given in Table IV. No results are given for the beryllium complex because the
SCF calculation failed to converge in this case. The equilibrium distances between
the ion and the solvating molecule markedly differ for dimethyl sulphoxide and
water, the former being a minimum of 0·01 nm lower than the latter. For the third
row, there is again a tendency for the distance to decrease with increasing atomic
number of the ions. The three-particle energies are higher than those found for any
other type of complex investigated here. The charges on the solvated ions are lowest
for the present complex, indicating the highest charge transfer from the solvating
molecules to the ion. Clearly, this complex can be considered the most stable one of
all those studied in this work. The charge distributions over the electronegative
atoms of dimethyl sulphoxide and water directly solvating the cations show a slight

TABLE V

Comparison of calculated solvation energies with values corrected for BSSE on the basis of pair-
wise interaction calculations[a]

Ion	System			
	WaterionDMF	WaterionDMSO	WaterionAN	ANionAN
Li^+	-723	-856	-603	-549
	-436	-492	-397	-404
Be^{2+}	$-1\,901$	—	$-1\,625$	$-1\,618$
	$-1\,634$	—	$-1\,461$	$-1\,510$
Na^+	-363	-418	-329	-307
	-227	-261	-220	-245
Mg^{2+}	$-1\,076$	$-1\,209$	-968	-969
	-877	-989	-817	-881
Al^{3+}	$-2\,314$	$-2\,533$	$-2\,062$	$-2\,197$
	-877	-989	-817	-881
Al^{3+}	$-2\,314$	$-2\,533$	$-2\,062$	$-2\,197$
	$-2\,094$	$-2\,288$	$-1\,894$	$-2\,097$

[a] All values are given in kJ mol^{-1}. Upper value — uncorrected solvation energy; lower value —
BSSE corrected solvation energy.

increase with the atomic number within the third row, with the exception of the aluminium cation and dimethyl sulphoxide, where a decrease is found. The overlap populations for the interaction between the oxygen atom of the solvating molecule and the solvated ion are greater for the dipolar aprotic solvent, *i.e.*, DMSO, than for water molecules.

CONCLUSION

The mixed complexes acetonitrile...ion...water, dimethyl sulphoxide...ion...water, and dimethylformamide...ion...water, and the complex acetonitrile...ion...aceto-nitrile have been studied using the Hartree–Fock SCF *ab initio* method. Calculated results have been presented for the solvation energies, three-particle energy contributions, equilibrium distances in optimum molecular geometries, charge distributions over the atoms, charge tranfer from the solvating molecules to the ions, and overlap populations. It has been found that the solvation and three-particle energies, the charge transfer, the charge on the solvated ion, and the overlap populations for the interaction between the electronegative atoms of the solvating molecules and the solvated ion increase, while the equilibrium distances decrease, with increasing atomic number of ions within a row of the periodic system (with the exception of the di-methylformamide...ion...water complex). No definite conclusions can be made regarding the charge distributions over the electronegative atom of the solvating molecule directly interacting with the ion, because the values show many irregularities.

The calculated interaction energies are subject to the error of superposition, which is particularly great for the STO-3G calculation[9]. The interaction energies corrected for BSSE on the basis of pairwise interaction calculations[2] are given in Table V. These values are believed to be much closer to the exact interaction energies than the uncorrected values.

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