SOLVATION OF IONS BY DIPOLAR APROTIC SOLVENTS AND WATER. A CNDO/2 STUDY

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Solvation of Li^+, Be^{2+}, Na^+, Mg^{2+} and Al^{3+} ions has been studied in binary mixtures with dimethyl sulphoxide, dimethylformamide, acetonitrile and water, and in ternary mixtures of the organic solvents with water. The CNDO/2 quantum chemical method was used to calculate the energies of solvation, molecular structures and charge distributions for the complexes acetonitrile...ion (1 : 1, 2 : 1, 4 : 1), dimethyl sulphoxide...ion (1 : 1), dimethylformamide...ion (1 : 1), and acetonitrile (dimethyl sulphoxide, dimethylformamide)...ion...water (1 : 1 : 1).

Solvation of ions in the gas phase and in solution has recently been a subject of increased research interest. This is due to accumulated experimental evidence on solvent effects on solutes and on interactions in solution, which affect physicochemical and chemical processes occurring in solvents. Ion solvation is therefore of great importance in physical, inorganic and organic chemistry, biochemistry, and molecular biology[1,2].

Ion solvation has been dealt with by a number of investigators, both experimentally[3-6] and along theoretical lines[7-10]. The field of experimental studies of solvation phenomena is very broad. The interest is centred mainly on acquiring information about energy changes associated with solvation effects and about structural changes. The studies on the structure are aimed primarily at determining the solvation or hydration number of an ion, *i.e.*, the number of solvent molecules directly bound to the ion, staying with it during its translatory motion. Particularly useful for such studies is the NMR technique[11,12]. The energy aspects of solvation are studied by means of calorimetry[13] and mass spectrometry (reactions in crossed molecular beams)[14].

An extensive volume of theoretical work has been done on ion solvation. Most earlier studies made use of the classical electrostatic theory and later the statistical mechanics, but recently the centre of interest has shifted to the field of quantum chemistry[15].

The theoretical and experimental studies were first concerned exclusively with aqueous solutions[16], and later also with non-aqueous solvents[17]. In recent years, interest has become focused on mixed solvents[18,19].

THEORETICAL

Theoretical studies of solvation effects can be classified into two groups according to whether the continuum model or the discrete (supermolecule) model is adopted

to describe the solvent. In the continuum model, the solvent is treated as a homogeneous, isotropic, polarizable dielectric continuum surrounding an ion or a molecule. The dielectric effects of solvent are then expressed[20] in terms of the electrical multipole moments of solute and the induced reaction field in the continuum (Kirkwood[21] and Onsager[22] equations). The current trend, however, is towards using combinations of classical and quantum chemical[23,24] or statistical thermodynamic[25,26] relations.

In the discrete model, the solvent molecules are considered as particles of defined size and charge distribution, coordinatively disposed around the ion or molecule which is being solvated. The resulting structure is called the supermolecule. It should, however, be borne in mind that results obtained from calculations based on this concept apply to solvation in the gas phase. Nevertheless, the interactions of solvated ion or molecule which build up the primary solvation shell represent a significant contribution to the energy of solvation at infinite solution. This is why calculations based on the supermolecule model are of greater importance than they might appear[15], and may therefore be applied even to a study of solutions. The energy of interaction is obtained by the MO methods as the difference between the total energy of an aggregate (E_a) and the sum of the energies of all the molecules involved (E_i).

$$\Delta E = E_a - \sum_i E_i \qquad (1)$$

The total energy is usually obtained from a SCF calculation.

Choice of Systems and Calculation Methods

Interactions of Li^+, Be^{2+}, Na^+, Mg^{2+} and Al^{3+} ions with water, acetonitrile (AN), dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) have been investigated on the basis of the supermolecule model. The study was carried out for 1 : 1 cation...solvent (water, AN, DMF, DMSO) complexes; 1 : 2 and 1 : 4 cation...acetonitrile complexes; and 1 : 1 : 1 mixed water...cation...solvent (AN, DMF, DMSO) complexes. The energies and structures of the supermolecules were calculated by the standard CNDO/2 semiempirical method[27], using the CNINDO program[28] in standard parametrization. Calculations both with and without inclusion of *d*-orbitals were performed for third-row elements. Experimental geometries of solvent molecules taken from the literature[29] were kept fixed during geometrical optimization of the complexes. The supermolecule geometries are shown in Figs 1 – 10.

RESULTS AND DISCUSSION

The distance, r, between the cation and the electronegative atom of solvent (see Figs 1 – 10) was optimized for each complex. The results are given in Tables I to X.

For comparison, available experimental values, results of other authors, and theoretical values obtained by *ab initio* calculations are listed in Table XI.

The System Ion...acetonitrile, 1 : 1, 1 : 2 and 1 : 4 Complexes

Results obtained for these complexes are given in Tables I to IV. The optimal structures for 1 : 1 and 1 : 2 complexes were found to be linear. For 1 : 4 complexes, tetrahedral structure was preferred over square-planar geometry. The energies of solvation obtained from calculations without inclusion of d-orbitals are distinctly lower in absolute values than those calculated with d-orbitals considered (for complexes with Na^+, Mg^{2+} and Al^{3+} ions). Apart from the primary interaction between the nitrogen lone pair of acetonitrile and the orbitals of σ symmetry on the metal atoms,
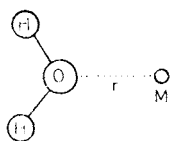

FIG. 1
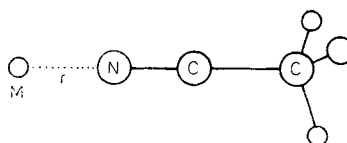
Geometry of the system ion...water

FIG. 2

Geometry of the system ion...acetonitrile
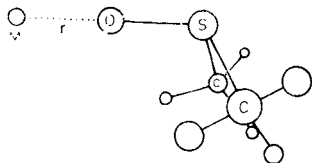
FIG. 3

Geometry of the system ion...dimethyl sulphoxide

FIG. 4

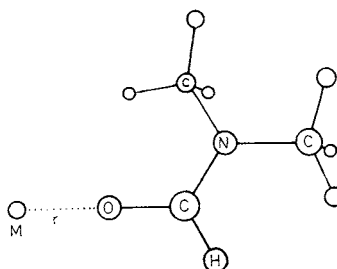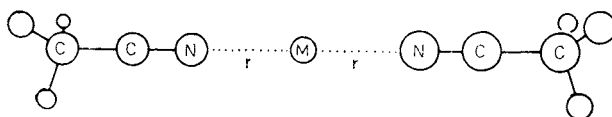Geometry of the system ion...dimethylformamide

FIG. 5

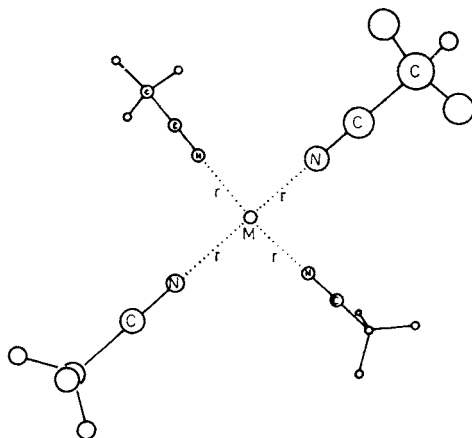Geometry of the system acetonitrile...ion...acetonitrile

Fig. 6

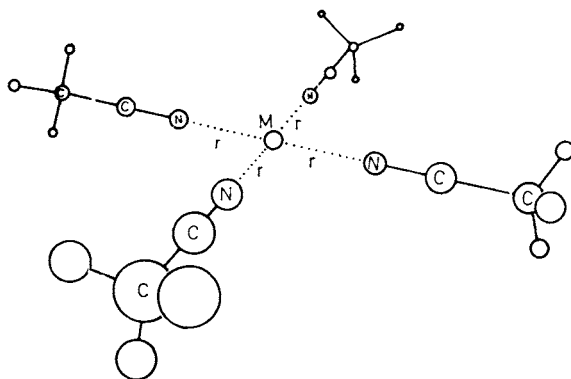Geometry of the system ion...4 acetonitrile molecules (tetrahedral)

Fig. 7

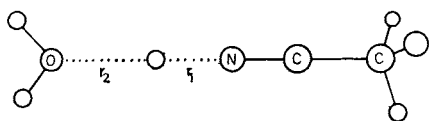Geometry of the system ion...4 acetonitrile molecules (square-planar)

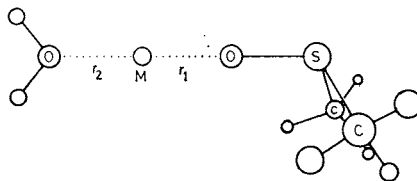Fig. 8

Geometry of the system water...ion...aceto-
nitrile

Fig. 9

Geometry of the system water...ion...di-
methyl sulphoxide

inclusion of d-orbitals brings in another interaction between π-orbitals of acetonitrile and the corresponding d-orbitals of the metal atom. This interaction shifts the charge from the occupied orbital of acetonitrile to the metal atom, thus in the same direction

TABLE I

The system acetonitrile...ion

Ion	d-orb.	M	N	M—N	Δq	ΔE [kJ/mol]	r [nm]
Li$^+$	—	0·6779	−0·1170	0·5607	0·3221	−385·34	0·21
Be^{2+}	—	1·1764	−0·1530	1·1572	0·8236	−1 377·84	0·16
Na$^+$	—	0·9192	−0·1992	0·1453	0·0808	−82·80	0·32
Mg^{2+}	—	1·7586	−0·2608	0·4073	0·2414	−269·40	0·26
Al^{3+}	—	2·3469	−0·2454	0·8871	0·6531	−834·63	0·22
Na$^+$	−|	0·7611	−0·1490	0·3636	0·2389	−317·52	0·26
Mg^{2+}	−|	1·5836	−0·2150	0·6367	0·4164	−614·41	0·23
Al^{3+}	−|	2·2397	−0·2487	1·0818	0·7603	−1 299·51	0·20

Legend to Tables I to X

Calculated values of charges, energies and equilibrium distances

Ion	kind of ion
M	charge on ion
N(O)	charge on nitrogen (oxygen) atom
O$_{(1)}$	oxygen atom of dimethyl sulphoxide or dimethylformamide
O$_{(2)}$	oxygen atom of water
M—N(O)	Wiberg index of the bond M—N(O)
Δq	charge transferred from solvating system to ion (in units of negative charge)
d-orb.	d-orbitals included ($+$) or disregarded ($-$) in calculation
ΔE	energy of solvation in kJ mol^{-1}
r	equilibrium distance between solvated ion and solvating system in nm
r_1	equilibrium distance between ion and dimethylformamide or dimethyl sulphoxide
r_2	equilibrium distance between ion and water

FIG. 10

Geometry of the system water...ion...di-
methylformamide
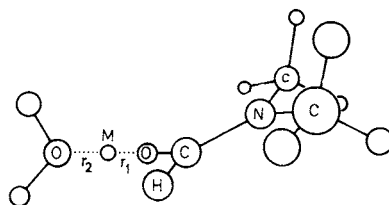
as does the primary interaction between the nitrogen lone pair of acetonitrile and the metal atom orbitals. As a consequence, shorter equilibrium distances are obtained from calculations allowing for the d-orbitals.

The maximum difference between the equilibrium distances for the whole range of complexes studied is 0·02 nm, indicating that the distance between the solvated ion and the solvent is not significantly affected by the size of the solvation shell. For both types of calculation, the equilibrium distance decreases with increasing atomic number of ion in a row, *i.e.*, with increasing charge on ion. The energy of solvation, on the other hand, is proportional to the atomic number of ion and hence to its charge. Of course, the absolute values of the energy of solvation vary in proportion to the number of acetonitrile molecules involved in the solvation of an ion.

TABLE II

The system acetonitrile...ion...acetonitrile

Ion	d-orb.	M	N	M—N	Δq	ΔE [kJ/mol]	r [nm]
Li^+	—	0·3713	−0·1037	0·4891	0·6287	−863·42	0·21
Be^{2+}	—	0·5786	−0·0633	0·9944	1·4214	−2 748·70	0·16
Na^+	—	0·8446	−0·1962	0·1393	0·1554	−162·46	0·32
Mg^{2+}	—	1·5510	−0·2462	0·3814	0·4490	−504·63	0·26
Al^{3+}	—	1·8674	−0·2216	0·8109	1·1326	−1 506·36	0·22
Na^+	+	0·5303	−0·1327	0·3567	0·4697	−616·34	0·26
Mg^{2+}	—	1·2629	−0·1915	0·5727	0·7371	−1 152·67	0·24
Al^{3+}	—	1·6293	−0·1997	0·9854	1·3707	−2 372·41	0·20

TABLE III

The system 4 acetonitrile molecules...ion (square-planar)

Ion	d-orb.	M	N	M—N	Δq	ΔE [kJ/mol]	r [nm]
Li^+	—	0·0478	−0·0912	0·3696	0·9522	−1 462·83	0·22
Be^{2+}	—	0·2754	−0·0829	0·6190	1·7246	−3 971·88	0·17
Na^+	—	0·7128	−0·1822	0·1280	0·2872	−291·96	0·32
Mg^{2+}	—	1·3375	−0·2336	0·2822	0·6625	−863·16	0·27
Al^{3+}	—	1·6000	−0·2498	0·5167	1·4000	−2 281·84	0·23
Na^+	+	0·1084	−0·1032	0·3387	0·8916	−1 166·59	0·26
Mg^{2+}	+	0·6065	−0·1349	0·5371	1·3935	−2 078·88	0·23
Al^{3+}	+	0·9630	−0·1573	0·7588	2·0370	−3 933·27	0·21

The charge transfer from a solvent molecule to cation is highest for 1 : 4 complexes, both tetrahedral and square-planar. It reaches an extreme value for the system $Li^+\ldots4\ (CH_3CN)$ (tetrahedral), where the solvated ion is assigned a weakly negative charge. For the 1 : 2 and 1 : 1 complexes, the transferred charge is proportionately smaller. In the case of Be^{2+}, for example, the charge transfer for 1 : 4, 1 : 2 and 1 : 1 complexes is, respectively, 1·83, 1·42 and 0·83 units of negative charge. Inclusion of d-orbitals in the calculation leads to an increase in charge transfer which is highest for 1 : 4 complexes (from 0·3, 0·7 and 1·52 to 0·91, 1·45 and 2·14 for Na^+, Mg^{2+} and Al^{3+}, respectively). Charge delocalization between the solvated ion and the solvating system is higher for d-orbital complexes which, consequently, are more stable energetically (see the values of the energy of solvation, and the interaction

TABLE IV

The system 4 acetonitrile molecules...ion (tetrahedral)

Ion	d-orb.	M	N	M—N	Δq	ΔE [kJ/mol]	r [nm]
Li^+	—	0·0167	−0·0799	0·4044	1·0167	−1 540·03	0·22
Be^{2+}	—	0·1708	−0·0604	0·6774	1·8292	−4 275·94	0·18
Na^+	—	0·7054	−0·1832	0·1327	0·2946	−298·79	0·32
Mg^{2+}	—	1·3050	−0·2278	0·3014	0·6950	−887·92	0·27
Al^{3+}	—	1·4930	−0·2301	0·5724	1·5070	−2 376·46	0·23
Na^+	+	0·0868	−0·1028	0·3472	0·9132	−1 183·31	0·26
Mg^{2+}	+	0·5498	−0·1263	0·5589	1·4502	−2 126·89	0·23
Al^{3+}	+	0·8593	−0·1435	0·7939	2·1407	−4 044·94	0·21

TABLE V

The system water...ion

Ion	d-orb.	M	O	M—O	Δq	ΔE [kJ/mol]	r [nm]
Li^+	—	0·8463	−0·2829	0·2764	0·1537	−187·58	0·24
Be^{2+}	—	1·4905	−0·2474	0·8340	0·5095	−882·15	0·17
Na^+	—	0·9811	−0·3141	0·0367	0·0189	−22·65	0·38
Mg^{2+}	—	1·9161	−0·3528	0·1591	0·0839	−89·97	0·29
Al^{3+}	—	2·6748	−0·3419	0·5458	0·3252	−344·88	0·24
Na^+	+	0·8859	−0·2848	0·2037	0·1141	−134·21	0·29
Mg^{2+}	+	1·7836	−0·3113	0·3863	0·2164	−293·11	0·25
Al^{3+}	+	2·5547	−0·3138	0·7524	0·4453	−679·69	0·21

diagram in Fig. 11). Comparison of tetrahedral and square-planar complexes shows greater values of charge transfer, and hence of charge delocalization, for the tetrahedral arrangement. These effects confer greater stability to the tetrahedral complexes. Examination of the charge population on the nitrogen atom of acetonitrile molecule reveals a much more uniform charge distribution for the complexes studied than for the solvated ion. Inclusion of d-orbitals has a noticeable effect only with 1 : 2 and 1 : 4 complexes, where higher delocalization of charge occurs through its transfer to the solvated ion, resulting in a reduction of the charge on the nitrogen atom. However, these changes are, on the average, an order of magnitude smaller than those associated with charge transfer from the solvating molecule to the ion.

TABLE VI

The system dimethyl sulphoxide...ion

Ion	d-orb.	M	O	M—O	Δq	ΔE [kJ/mol]	r [nm]
Li^+	—	0·7282	−0·4058	0·4577	0·2718	−339·39	0·22
Be^{2+}	—	1·1515	−0·3567	1·3563	0·8485	−1 507·32	0·16
Na^+	—	0·9556	−0·4633	0·0754	0·0444	−68·71	0·34
Mg^{2+}	—	1·8001	−0·5139	0·3092	0·1999	−255·76	0·27
Al^{3+}	—	—	—	—	—	—	—
Li^+	+	0·7366	−0·3146	0·4242	0·2634	−320·88	0·22
Be^{2+}	+	1·2147	−0·2715	1·2118	0·7853	−1 413·63	0·16
Na^+	+	0·7799	−0·3095	0·3343	0·2201	−266·13	0·26
Mg^{2+}	+	1·6003	−0·3595	0·6521	0·3997	−566·79	0·23
Al^{3+}	+	2·1959	−0·3429	1·1951	0·8041	−1 340·44	0·20

TABLE VII

The system dimethylformamide...ion

Ion	d-orb.	M	O	M—O	Δq	ΔE [kJ/mol]	r [nm]
Li^+	—	0·7670	−0·3436	0·3666	0·2330	−332·37	0·23
Be^{2+}	—	1·2329	−0·2604	1·1960	0·7671	−1 388·62	0·16
Na^+	—	0·9540	−0·3760	0·0741	0·0460	−58·76	0·34
Mg^{2+}	—	1·8293	−0·4432	0·2821	0·1707	−225·89	0·27
Al^{3+}	—	—	—	—	—	—	—
Na^+	+	0·8026	−0·3389	0·2971	0·1914	−264·50	0·27
Mg^{2+}	+	1·6118	−0·3740	0·6287	0·3882	−550·50	0·23
Al^{3+}	+	—	—	—	—	—	—

TABLE VIII
The system acetonitrile...ion...water

Ion	d-orb.	M	N	M—N	O	M—O	Δq	ΔE [kJ/mol]	r_1 [nm]	r_2 [nm]
Li^+	−	0.5579	−0.1270	0.4675	−0.2653	0.2629	0.4421	−608.30	0.22	0.24
Be^{2+}	−	0.7851	−0.0930	1.0442	−0.1996	0.7561	1.2149	−2 236.19	0.16	0.17
Na^+	−	0.9025	−0.1978	0.1428	−0.3066	0.0349	0.0975	−102.89	0.32	0.38
Mg^{2+}	−	1.6982	−0.2566	0.3960	−0.3442	0.1287	0.3018	−345.93	0.26	0.30
Al^{3+}	−	2.1121	−0.2328	0.8534	−0.3330	0.4608	0.8879	−1 106.41	0.22	0.24
Na^+	+	0.6519	−0.1435	0.3594	−0.2717	0.1995	0.3481	−440.93	0.26	0.29
Mg^{2+}	+	1.3860	−0.1987	0.6225	−0.2938	0.3682	0.6140	−876.34	0.23	0.25
Al^{3+}	+	1.8945	−0.2194	1.0403	−0.2918	0.6422	1.1055	−1 868.14	0.20	0.22

TABLE IX
The system dimethyl sulphoxide..ion...water

Ion	d-orb.	M	$O_{(1)}$	$M-O_{(1)}$	$O_{(2)}$	$M-O_{(2)}$	Δq	ΔE [kJ/mol]	r_1 [nm]	r_2 [nm]
Li^+	—	0·5945	−0·3980	0·4421	−0·2661	0·2545	0·4055	−496·71	0·22	0·24
Be^{2+}	—	0·9129	−0·3307	1·2637	−0·2185	0·6617	1·0871	−2 040·26	0·16	0·18
Na^+	—	0·9387	−0·4623	0·0740	−0·4623	0·0345	0·0613	−88·68	0·34	0·38
Mg^{2+}	—	1·7456	−0·5120	0·2955	−0·3455	0·1240	0·2544	−330·63	0·27	0·30
Al^{3+}	—	—	—	—	—	—	—	—	—	—
Li^+	—+	0·6012	−0·3048	0·4101	−0·2667	0·2569	0·3988	−480·58	0·22	0·24
Be^{2+}	—+	0·8478	−0·2476	1·1352	−0·2201	0·6756	1·1522	−2 100·61	0·16	0·18
Na^+	—+	0·6836	−0·3037	0·3295	−0·2757	0·1786	0·3164	−388·62	0·26	0·30
Mg^{2+}	—+	1·4117	−0·3524	0·6313	−0·2955	0·3588	0·5883	−822·59	0·23	0·25
Al^{3+}	—+	1·8817	−0·3251	1·1511	−0·2951	0·6209	1·1183	−1 888·00	0·20	0·22

TABLE X
The system dimethylformamide...ion...water

Ion	d-orb.	M	$O_{(1)}$	$M-O_{(1)}$	$O_{(2)}$	$M-O_{(2)}$	Δq	ΔE [kJ/mol]	r_1 [nm]	r_2 [nm]
Li^+	—	0·6913	−0·3514	0·2613	−0·2709	0·2606	0·3087	−445·84	0·26	0·24
Be^{2+}	—	0·8664	−0·2422	1·1188	−0·2215	0·6773	1·1336	−2 079·77	0·16	0·18
Na^+	—	0·9368	−0·3747	0·0727	−0·3071	0·0348	0·0632	−79·08	0·34	0·38
Mg^{2+}	—	1·7786	−0·4407	0·2718	−0·3463	0·1094	0·2214	−297·29	0·27	0·31
Al^{3+}	—	—	—	—	—	—	—	—	—	—
Na^+	+	0·6894	−0·3347	0·2693	−0·2652	0·2334	0·3106	−381·64	0·27	0·30
Mg^{2+}	+	1·5489	−0·3710	0·6165	−0·3257	0·1332	0·4511	−681·78	0·23	0·33
Al^{3+}	+	—	—	—	—	—	—	—	—	—

Tables I to IV also give values of the Wiberg index[30] for the solvated ion...aceto-nitrile nitrogen interaction. Inclusion of d-orbitals increases the bond strength as measured by the magnitude of the Wiberg index. For 1 : 4 complexes the Wiberg index shows a preference for tetrahedral over square-planar arrangement irrespective of whether or not d-orbitals are considered.

1 : 1 Complexes

Of this type of complex, we studied water...ion, acetonitrile...ion, dimethyl sulpho-xide...ion, and dimethylformamide...ion. The results are listed in Tables V to VII.

For the system water...ion, the energies of solvation for third-row ions calculated without inclusion of d-orbitals are too low, whereas inclusion of d-orbitals results in good agreement with experimental and other theoretical values (see Table XI). The equilibrium distances for lithium ion are comparable with those obtained by *ab initio* calculation (see Table XI). For the other ions, the values are too high, particularly when calculated without considering the d-orbitals. Inclusion of d-orbitals once again enhances the charge transfer from the solvating water molecule to the ion, for the same reasons as discussed in the section on ion...acetonitrile interactions, resulting in a corresponding reduction of charge on the oxygen atom of water, and hence an increase of the Wiberg index.

The system acetonitrile...ion has been discussed above. It may only be added at this point that, within the series of 1 : 1 complexes, it shows an analogy to the system water...ion. Because of the difference in the nature of the oxygen and nitro-
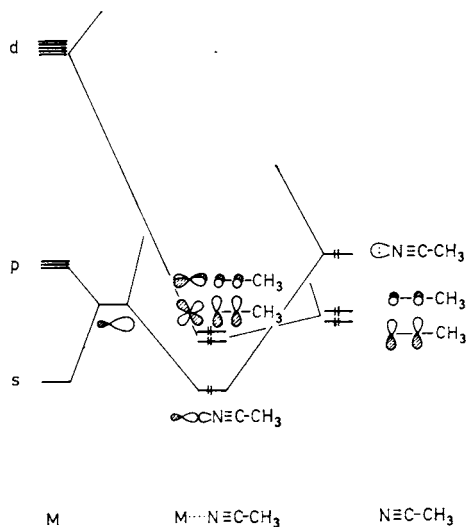
FIG. 11

Scheme of orbital interaction between aceto-nitrile and metal ion. The σ-type interaction between the lone pair and the corresponding sp hybrid represents the strongest stabilization of the complex, accompanied by the most extensive charge transfer to the metal atom. The π-type interaction is possible in calcula-tions including d-orbitals and leads to addi-tional complex stabilization and charge transfer

gen lone pairs, the system acetonitrile...ion involves higher charge transfer to the solvated ion. Equilibrium distances, energies of solvation and Wiberg indices are more realistic when calculated with allowance for d-orbitals.

The complex dimethyl sulphoxide...ion is larger than the preceding two, and calculations with inclusion of d-orbitals here involve not only the solvated ion but also the solvent molecule. This is reflected in the energies of solvation for the complexes with Li^+ and Be^{+2}. The effect of including the d-orbitals on the sulphur atom of DMSO in the calculation is to lower the stabilization energies of solvation for both ions by several tens of kJ/mol. The d-orbitals on the sulphur atom withdraw part of the electron density from the oxygen atom, thereby reducing the bonding ability of dimethyl sulphoxide. The equilibrium distances in the two complexes are not affected by these d-orbitals. Higher values of both the charge transfer to the ion and the Wiberg index obtained for these interactions also give support to results obtained from calculations disregarding d-orbitals on the sulphur atom. Inclusion of d-orbitals on the atoms of solvated ions of the third row leads to increased energies of solvation and shorter equilibrium distances. For the system Al^{3+}...DMSO no convergence was achieved in the SCF procedure when d-orbitals were disregarded.

TABLE XI

Some experimental and theoretical values for the systems studied

Type of value	Ion	Water...ion		Acetonitrile...ion		Reference
		ΔE [kJ/mol]	r [nm]	ΔE [kJ/mol]	r [nm]	
Experiment	Li^+	$-142 \cdot 26$	$0 \cdot 185$			9
	Be^{2+}					
	Na^+	$-100 \cdot 42$	$0 \cdot 220$	$-129 \cdot 70$	$0 \cdot 212$	9, 4
	Mg^{2+}					
	Al^{3+}					
CNDO/2	Li^+	$-188 \cdot 28$	$0 \cdot 236$			31
calculation	Be^{2+}	$-910 \cdot 44$	$0 \cdot 170$			32
	Na^+	$-137 \cdot 65$	$0 \cdot 292$			32
	Mg^{2+}					
	Al^{3+}					
Ab initio	Li^+	$-143 \cdot 93$	$0 \cdot 189$			33
calculation	Be^{2+}	$-585 \cdot 76$	$0 \cdot 150$			9
	Na^+	$-100 \cdot 00$	$0 \cdot 225$			34
	Mg^{2+}	$-334 \cdot 72$	$0 \cdot 195$			9
	Al^{3+}	$-753 \cdot 12$	$0 \cdot 175$			9

The system dimethylformamide...ion resembles closely the system DMSO...ion in most of the characteristics studied. The DMF molecule does not, however, contain a third-row atom and therefore. the problems encountered with DMSO do not arise. The energies of solvation are close to those found for the system DMSO...ion, as are equilibrium distances and charge distributions. Comparison of results for Na^+ and Mg^{2+} calculated with and without inclusion of d-orbitals shows that the former alternative is to be preferred. For Al^{3+} ions, no convergence was obtained in calculations either with or without inclusion of d-orbitals.

1 : 1 : 1 *Complexes*

Three mixed complexes of the type solvent...ion...water have been studied: acetonitrile...ion...water, dimethyl sulphoxide...ion...water and dimethylformamide... ...ion...water. A striking feature of these systems is an increase in charge transfer from the solvating molecule to the ion over that found for the previous complexes. The transfer occurs from the oxygen atom of water and from the electronegative atoms of the solvents (O, N). The calculated values are listed in Tables VIII to X. As a result of higher charge delocalization in the systems, there is also, on average, a slight decrease in the values of the Wiberg index.

The optimization was based on the starting point of a fixed solvating molecule...ion distance previously calculated, the only parameter optimized being the distance between the ion and the oxygen atom of water. An exception was made with the systems of Li^+ ion with acetonitrile and dimethylformamide, where the ion...solvating molecule distance was also optimized because of discrepancy in results obtained on the basis of parameters taken from the literature. In optimization for the system dimethylformamide...ion...water, an anomaly was found in the cases of Na^+ and Mg^{2+} ions: the equilibrium distance ion...water calculated with inclusion of d-orbitals was 0·30 nm for Na^+ and 0·33 nm for Mg^{2+}. This is in variance with the general trend of the equilibrium distance from the solvating molecule decreasing as the charge on the cation is increased. The values of the charge transfer followed this trend, but a change was found for the Wiberg indices for the ion...water interaction.

Even though there are no data for other complexes of this type with which to compare our results, we may conclude, by analogy with previous calculations for the isolated systems, that in the framework of the CNDO/2 method inclusion of d-orbitals is again to be preferred. The optimal structures of all the 1 : 1 : 1 complexes studied were found to be linear (see Figs 8 to 10).

CONCLUSIONS

The CNDO/2 method was used to optimize the following complexes: ion...acetonitrile, 1 : 1, 1 : 2, and 1 : 4 (tetrahedral and square-planar); ion....water, ion...di-

methyl sulphoxide, and ion...dimethylformamide, 1 : 1; and acetonitrile...ion...water, dimethyl sulphoxide..ion...water, and dimethylformamide...ion...water, 1 : 1 : 1. For each system we have established the optimal equilibrium geometry and calculated the energy of solvation, charge distribution on atoms, charge transfer from the solvating molecule to the solvated ion, and the Wiberg index. The calculations for all the systems were carried out both with and without inclusion of d-orbitals of third-row elements. It has been found that more realistic results are obtained when d-orbitals of the solvated ions are considered while those of third-row elements incorporated in the solvating molecule are disregarded. The present treatment was performed as a preliminary study to a similar type of calculation based on a non-empirical *ab initio* method, which will be the subject of a paper to follow.

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