Ab Initio Study of Potassium Ion Clusters of Methanol and Acetonitrile and a Systematic Comparison with Hydrated Clusters

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Ab initio calculations of the structure and binding energies of $K^+[Solv]_n$ clusters are reported for water, methanol, and acetonitrile solvents, for $n = 1-6$. It has been shown that the results obtained at the RHF/DZP//RHF/DZP level of calculation, with no basis set superposition or correlation correction, compare well, in the case of water, with other accurate treatments in the literature. A comparison of the binding energies and structures of the clusters in the three solvents is made. The enthalpies and entropies of formation of the clusters are calculated and compared with the results of experimental measurements on gas-phase clusters. An analysis of the contributions of the ion−solvent and solvent−solvent interactions to the binding energies is also presented.

Introduction

Experimental investigations have focused on the gas-phase clustering of water,[1−6] methanol,[7−9] acetonitrile,[10] and other ligands[11−13] onto the alkali metal ions, particularly sodium and potassium ions. These studies involved the determination of thermodynamic quantities such as enthalpy, entropy, and free energy changes for the successive binding of water, methanol, and acetonitrile. For other ligands, gas-phase studies were concerned with the binding enthalpy and stability of ion−ligand complexes of 1:1 mole ratio. Experimental techniques have also been used for measurement of the photoionization of the gas-phase clusters, and the ionization potentials of alkali metal atom clusters have recently been reported.[14−19] These experimental findings have encouraged theoretical studies. Consequently, many theoretical investigations[20−31] on the clustering of water with the alkali metal atoms and ions have been reported in recent years, using basis sets of various sizes at different levels of theory. Theoretical methods are applied to the gas-phase clusters to augment the data available from experiment and also to provide information on clusters that are impossible to investigate with any available experimental technique. Studies of clusters containing metal atoms and ions have been used as an approach to the analysis of solution behavior. Solvation effects can alter the kinetics and mechanism of the ion−ligand complexation in solution, and significant differences have been observed[32] between the solvent effect of protic solvents such as water and methanol and aprotic solvents such as acetonitrile on the stability of ion−ligand (macrocyclic polyether) complexes.

Ab initio calculations on clusters of acetonitrile and methanol with the potassium ion have been undertaken as a necessary preliminary to the theoretical study of the effect of microsolvation on the relative binding affinities of crown ethers for the ion in three different solvents: water, methanol, and acetonitrile. Crown ethers display the ability to bind specific metal cations selectively, and the selectivity is found to be strongly influenced by the nature of the solvent. The stabilities of the K^+/15-crown-5 complexes are found[32] to be in the order acetonitrile > methanol ≫ water. Very recently,[33] ab initio calculations on microsolvation have been carried out in order to find the origin of this variation in stability in different solvents.

In this paper, ab initio calculations on the gas-phase clustering of water, methanol, and acetonitrile with the potassium ion are presented. Results relating to the water clusters obtained in this work are first compared with the reported ab initio results in the literature. A systematic comparison is then made between the potassium ion clusters of aqueous and nonaqueous solvents in terms of various parameters. The theoretical results are also compared with experimental measurements on gas-phase clusters.

Method

The molecular structures of $K^+[Solv]_n$ ($n = 1-6$, Solv = H_2O, CH_3OH, CH_3CN) were optimized by using the quasi-Newton method with the GAMESS-UK program.[34] No molecular symmetry constraint was applied; a full optimization of all bond lengths, angles, and torsion angles was carried out. Initially, 6-31G basis sets[35] were used for carbon, oxygen, and hydrogen atoms and the double-ζ basis set of Ahlrichs[36] for the potassium ion, since no 6-31G basis set is currently available for this ion in the GAMESS-UK program. The optimized geometry for each cluster, obtained at the RHF/6-31G,DZ level, was used as the initial geometry, which was then further optimized with a larger basis set, where double-ζ and polarization functions (DZP)[36,37] were included for all atoms. To estimate the effect of the convergence threshold, a final optimization of $K^+[CH_3OH]$ was attempted with the reduced tolerance of 0.000 10 hartree/bohr at the DZP level, beginning from a structure that had been optimized using a 0.001 hartree/bohr convergence limit. After a further 185 iterations at the lower threshold, convergence had not been attained, but the energy had been lowered by only 0.33 kcal/mol. Therefore, considering the size of the cluster, the convergence threshold of 0.001 hartree/bohr was employed for all optimizations. No corrections for basis set superposition errors (BSSEs) were carried out since the BSSEs are expected to be negligible at

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TABLE 1: Total Molecular Energies (au) and Binding Energies, ΔE_B (kcal/mol),[a] of Solvated Potassium Ion

			RHF/6-31G,DZ		RHF/DZP		
n	solv	config	total energy	$-\Delta E_b$	total energy	$-\Delta E_B$	$-\Delta E_B$[b]
1	H_2O	linear	−675.023 197	22.83	−675.077 868	18.51	18.9
	CH_3OH		−714.025 681	22.63	−714.104 668	18.04	18.35[c]
	CH_3CN		−730.906 991	25.30	−730.990 031	23.15	
2	H_2O	linear	−751.041 536	43.53	−751.151 932	35.58	35.8
	CH_3OH		−829.046 046	42.84	−829.204 591	34.06	
	CH_3CN		−862.807 129	47.21	−862.974 270	43.61	
3	H_2O	trigonal	−827.055 229	61.31	−827.222 463	50.43	50.9
	CH_3OH		−944.062 965	60.88	−944.302 225	48.64	
	CH_3CN		−994.700 639	64.96	−994.951 701	59.79	
4	H_2O	SPL	−903.060 478	73.79	−903.286 833	61.42	63.2
	CH_3OH		−1059.069 062	72.14	−1059.394 408	59.80	
	CH_3CN		−1126.584 225	76.48	−1126.919 989	70.24	
4	H2O	TH	−903.064 671	76.42	−903.289 989	63.40	63.7
	CH_3OH		−1059.074 470	75.53	−1059.396 434	61.07	
	CH_3CN		−1126.586 869	78.14	−1126.923 069	72.18	
5	H_2O	SQP	−979.064 348	85.41	−979.349 937	71.61	73.8
	CH_3OH		−1174.078 692	85.61	−1174.485 036	69.98	
	CH_3CN		−1258.464 313	85.80	−1258.888 455	80.81	
5	H_2O	TBP	−979.067 116	87.15	−979.352 024	72.92	76.9
	CH_3OH		−1174.081 933	87.64	−1174.485 285	70.14	
6	CH_3CN	OCT	−1258.466 960	87.47	−1258.888 878	81.07	
	H_2O		−1055.063 708	94.20	−1055.410 201	80.02	88.1
	CH_3CN		−1390.340 550	92.71	−1390.848 706	86.22	

[a] 1 au = 627.51 kcal/mol. [b] Taken from ref 30 except for methanol. The calculations of ref 30 include a counterpoise correction for BSSE and an MP2 correction for correlation effects. [c] Taken from ref 14. Energies in au of the cation and solvents are $E(K^+) = -599.001\,450$ (DZ), $-599.001\,514$ (DZP); $E(H_2O) = -75.985\,358$ (6-31G), $-76.046\,861$ (DZP); $E(CH_3OH) = -114.988\,163$ (6-31G), $-115.074\,398$ (DZP), and $E(CH_3CN) = -131.865\,225$ (6-31G), $-131.951\,633$ (DZP).

TABLE 2: Incremental Binding Energy[a] and Enthalpy[a] from Theory and Experiment for the Gas-Phase Reactions $K^+[H_2O]_{n-1} + H_2O \rightarrow K^+[H_2O]_n$

	RHF/DZP//RHF/DZP[c]	MP2/6-31+G*//RHF/6-31+G* [d]		MP2/aug-cc-pVDZ/pCVDZ[e]		exptl [f]
$n-1$, n[b]	$-\Delta E_{n-1,n}$	$-\Delta E_{n-1,n}$	$-\Delta H_{n-1,n}$	$-\Delta E_{n-1,n}$	$-\Delta H_{n-1,n}$	$-\Delta H_{n-1,n}$
0 → 1	18.5	18.9	18.3	17.9	17.3	17.9
1 → 2	17.1	16.9	15.5	15.4	14.0	16.1
2 → 3	14.9	15.1	13.7	13.6	12.3	13.2
3 → 4	13.0	12.8	11.4	10.3	9.6	11.8
4 → 5	9.5	13.2	10.9	11.4	10.2	10.7
5 → 6	7.1	11.2	10.4	12.0	10.4	10.0

[a] In kcal/mol. [b] Clusters of D_{2d}, D_3, S_4, C_2, and D_3 symmetry for the values of $n = 2$, 3, 4, 5, and 6, respectively. [c] This work. [d] Taken from ref 30. [e] Taken from ref 28. [f] Experimental values taken from ref 2.

the DZP level. The thermochemical analysis of acetonitrile clustering onto K^+ up to the value of $n = 4$ was carried out with the DZP optimized structure. The force constants and vibrational frequencies were calculated numerically using standard procedures within the GAMESS-UK program and the DZP basis set.

All the ab initio calculations were carried out on a Silicon Graphics INDY workstation in the Department of Pure and Applied Chemistry and on an SG Power Challenge Computer at the computer Centre of the University of Strathclyde. The INTERCHEM program[39] on a Silicon Graphics workstation was used to visualize all clusters.

Results and Discussion

The total binding energies, $\Delta E_B(n)$, of the $K^+[\text{Solv}]_n$ ($n = 1-6$, Solv = H_2O, CH_3OH, and CH_3CN) complexes are evaluated by

$$\Delta E_B(n) = E[K^+(\text{Solv})_n] - E[K^+] - nE[\text{Solv}] \qquad \text{(i)}$$

The values of $\Delta E_B(n)$, obtained using two basis sets of different quality at the RHF level of theory, are presented in Table 1. The binding energies determined at the RHF/(6-31G, DZ) level differ significantly from the corresponding DZP values, and this difference increases with the size of the clusters. The difference between the binding energies obtained using 6-31G,DZ and DZP basis sets is much larger for water and methanol clusters as compared with that found for acetonitrile. The 6-31G,DZ binding energies for the clusters of water and methanol with $n = 1$ are overestimated by ≅4 kcal/mol compared to the DZP values, and the difference reaches ≅17 kcal/mol when n increases to 6. This contrasts with the case of acetonitrile clustering, where the differences (≅2 kcal/mol for $n = 1$ to ≅6 kcal/mol for $n = 6$) show a much smaller increase with cluster size.

The gas-phase binding energies of $K^+[H_2O]_n$ ($n = 1-6$) obtained in this work at the RHF/DZP//RHF/DZP level are compared with the literature values in Table 2. Glendening and Feller have reported[30] the gas-phase binding energies of K^+-$[H_2O]_n$ using the 6-31G* basis set at the RHF and MP2 level of theory and applying the counterpoise correction for basis set superposition error (BSSE). While the calculations of ref 28 are at a higher level of theory, the agreement with experiment is not as good as that achieved in ref 30. Some of the results of ref 28 are also included in Table 1 for comparison, but in subsequent discussion of thermodynamic properties we have referred only to ref 30. For a comparative study of the three solvents it has been thought better to start from the level of

TABLE 3: Incremental Binding Energies[a] and Thermodynamic Values[b] for the Gas-Phase Reactions $K^+[Solv]_{n-1}$ + Solv → $K^+[Solv]_n$

	CH_3OH		CH_3CN				
	$-\Delta E_{n-1,n}$	$-\Delta H_{n-1,n}$	$-\Delta E_{n-1,n}$	$-\Delta H_{n-1,n}$		$-\Delta S_{n-1,n}$	
$n-1$, n	calc	exptl[c]	calc	calc	exptl[d]	calc	exptl[d]
0 → 1	18.04	21.9	23.15	22.83	24.4	21.29	21.5
1 → 2	16.02	18.0	20.46	19.22	20.6	24.72	24.2
2 → 3	14.58	14.5	16.18	16.09	18.2	35.76	28.3
3 → 4	12.43	12.5	12.39	15.00	13.6	54.27	27.5
4 → 5	9.07		9.52				
5 → 6			4.52				

[a] In kcal/mol. [b] Enthalpies are in kcal/mol, and entropies are in cal/(mol K). [c] Experimental values are taken from ref 7. [d] Experimental values taken from ref 10.

theory that, perhaps because of cancellation of errors, is in the best agreement with the experimental results for water. The binding energies obtained in this work using the DZP basis set compare well with the values of Glendening and Feller[30] for the clusters of up to 4 water molecules. It is clear that, with the DZP quality basis set, the combined effect of the basis set superposition error and correlation effect is almost negligible. The binding energy of the clusters for ($n = 1, 4$) reported by Glendening and Feller is overestimated slightly by 0.5 kcal/mol. For the clusters of 5 and 6 water molecules, the binding energy obtained in this work is overestimated by 2 and 8 kcal/mol, respectively, because of the absence of the correlation treatment. Without correlation, the binding energy for the K^+-$[H_2O]_6$ cluster is reported to be −82.1 kcal/mol, which is 2 kcal/mol larger than the value obtained using the DZP basis set. The need for a treatment that includes correlation in the ab initio study of the larger clusters is therefore confirmed by these calculations.

The total binding energy of the potassium ion clusters with all the solvents increases almost linearly with the value of n. The binding energy of the methanol clusters up to the limit of five solvent molecules is consistently less exothermic by ≅1.5−2.0 kcal/mol than the respective value for the water clusters (except for $n = 1$, where the difference is only 0.4 kcal/mol). The calculated incremental binding energies, $\Delta E_{n-1,n}$, for methanol and acetonitrile clusters are compared with the experimentally measured[7,10] successive binding enthalpies, $\Delta H_{n-1,n}$, in Table 3. The $\Delta E_{n-1,n}$ values are not directly comparable with $\Delta H_{n-1,n}$. It is apparent that the experimental gas-phase binding enthalpy for methanol clustering[7] is more exothermic than the corresponding value for gas-phase water clustering,[2] in contradiction with the results obtained in this work. Since the influence of the ion is expected to diminish for large clusters, the thermodynamic functions for each clustering step should approach the values for condensation of the clustering species as a limit. The thermodynamic values[7] for condensation of water and methanol at 300 K are respectively $\Delta H°_{cond} = -10.52$ kcal/mol, $\Delta S°_{cond} = -28.41$ cal/(mol K), $\Delta G°_{cond} = -2.05$ kcal/mol for water, and $\Delta H°_{cond} = -9.08$, $\Delta S°_{cond} = -26.98$, and $\Delta G°_{cond} = -1.04$ for methanol. Thus, water addition should tend to a more exothermic limit than methanol addition. This tendency is in accord with the calculations but not with the experimental results on small clusters. For the completely solvated ion in the pure liquids, the transfer from water to methanol for K^+ is $\Delta G_t^{W\rightarrow M} = +2.3$ kcal/mol,[40,41] $\Delta H_t^{W\rightarrow M} = -4.5$ kcal/mol,[40,42] and $\Delta S_t^{W\rightarrow M} = -22.5$ cal/mol K.[40,42]

To summarize, the experimental free energy changes for both condensation and ion solvation favor solvation by water over methanol, but the single ion heats of transfer, $\Delta H_t^{W\rightarrow M}$, point to the opposite conclusion. The results of the calculations reported in this work appear to be consistent with the former, rather than the latter view.

The binding energy of acetonitrile to the potassium ion is seen to be considerably stronger than that of water, and the difference increases with the increasing size of the cluster up to the value of $n = 3$ (Table 1). This is the reflection of the much higher dipole moment of acetonitrile ($\mu = 4.12$ D). In acetonitrile the dipole is localized on the C≡N bond with the positive charge on the relatively inaccessible carbon atom in the middle of the molecule, $CH_3-C^{\delta 1}\equiv N^{\delta 2}$ ($\delta 1 = 0.0487e$, $\delta 2 = -0.1993e$), where Mulliken charges have been used. The negative pole located on the nitrogen is very accessible and the large acetonitrile dipole moment leads to a large $\Delta E_{0\rightarrow 1}$ for K^+ and acetonitrile. As a consequence the acetonitrile value for $\Delta E_{0\rightarrow 1}$ is considerably larger than the $\Delta E_{0\rightarrow 1}$ for water. For clusters of more than 3 solvent molecules, the difference in $\Delta E_{n-1,n}$ (Tables 2 and 3) between water and acetonitrile clustering reduces sharply as n increases and the crossover in successive binding energies occurs with the addition of a fifth solvent molecule. The successive binding energy for the sixth water is more exothermic than the corresponding acetonitrile cluster value.

The calculated incremental solvation enthalpies, $\Delta H_{n-1,n}$, for the acetonitrile clusters are also shown in Table 3 and compared with experimental values.[10] The agreement between theory and experiment is reasonably good, being in the range of ±10% for $n = 1-4$. The binding energy obtained from ab initio calculations corresponds to 0 K, and thermal corrections must be included to obtain the binding enthalpy at 298 K, which is compared with the experimental value. For water clustering onto alkali and alkaline earth metal ions, the calculated[26,28,30,43] binding enthalpy, which is always smaller (less exothermic) than the corresponding binding energy, is found to be in very good agreement with the experimental results. In particular, the calculated binding enthalpy of water clustering onto K^+ is reported to be in very good agreement with the experimental binding enthalpy. The corresponding binding energy is in excellent agreement with the binding energy found in this work, as explained in the earlier section. Overall consideration of these results, comparing the results for water and acetonitrile clustering, leads to the conclusion that the experimental values of the successive binding enthalpies for acetonitrile clustering are anomalous and may have been overestimated. The calculated results in the present work do not include the effect of correlation, but the correlation correction for smaller clusters is almost negligible, as discussed in the earlier section, and would not lead to calculated binding energies more exothermic than the corresponding observed binding enthalpy. A smaller correction would not remove the anomaly discussed above.

Incremental entropies $\Delta S_{n-1,n}$ ($T = 298.15$ K) obtained from a RHF calculation using the DZP basis set for the gas-phase reaction $K^+[CH_3CN]_{n-1} + CH_3CN \rightarrow K^+[CH_3CN]_n$ are shown in Table 3 along with the experimental values from Davidson and Keberle.[10] For $n = 1$ and $n = 2$ the agreement with experiment is excellent, being in the range of ±2%. For the cluster containing 3 acetonitriles, the agreement with experiment is poor, and for $n = 4$ it is significantly worse. This is because of the large number of low-frequency modes, which contribute most strongly to the entropy.[28] These low-frequency modes may also possess sizable anharmonic corrections, making it very difficult to compute accurate absolute entropies for floppy molecules in large clusters. Feller et al.[28] have obtained

TABLE 4: Binding Energy (ΔE_B), Solvent−Solvent Contribution (ΔE_S), and Solute−Solvent Contribution (ΔE_M) in kcal/mol for $[K(Solv)_n]^+$ Complexes ($n = 1-6$) Calculated at the RHF/DZP Level

n	solv	config	$-\Delta E_B$	ΔE_S	$-\Delta E_M$
1	H_2O	linear	18.51	0.05	18.56
	CH_3OH		18.04	0.56	18.60
	CH_3CN		23.15	0.00	23.15
2	H_2O	linear	35.58	0.87	36.45
	CH_3OH		34.06	2.10	36.16
	CH_3CN		43.61	1.19	44.80
3	H_2O	trigonal	50.43	3.19	53.62
	CH_3OH		48.64	3.63	52.27
	CH_3CN		59.79	4.46	64.25
4	H_2O	SPL	61.42	7.75	69.17
	CH_3OH		59.80	6.66	66.46
	CH_3CN		70.24	9.90	80.14
4	H_2O	TH	63.40	6.52	69.92
	CH_3OH		61.07	5.82	66.89
	CH_3CN		72.18	8.42	80.60
5	H_2O	SQP	71.61	12.62	84.23
	CH_3OH		69.98	10.19	80.18
	CH_3CN		80.81	15.86	96.67
5	H_2O	TBP	72.92	10.57	83.49
	CH_3OH		70.14	9.61	79.75
6	CH_3CN	OCT	81.70	16.10	97.17
	H_2O		80.02	18.40	98.42
	CH_3CN		86.22	24.58	110.80

incremental entropy changes in excess of the experimental values by 20−25% for 4 → 5 and by nearly 100% for 5 → 6 for the reactions $K^+[H_2O]_{n-1} + H_2O \rightarrow K^+[H_2O]_n$, using the 6-31+G* basis set at both the RHF and MP2 level of theory. Use of larger basis sets, such as aug-cc-pVDZ, did not improve the result at all.

Although the total stabilization energies of the water and methanol clusters are close to each other, their structures are different, and therefore, to find the origin of stability, the total binding energy of the cluster was divided into two contributions following a similar method applied by Hashimoto and Morokuma.[24,26] The solvent−solvent contribution, $\Delta E_S(n)$, and the solute−solvent contribution, $\Delta E_M(n)$, are defined by eqs ii and iii, respectively.

$$\Delta E_S(n) = E[(\mathrm{Solv})^{\#}] - nE[\mathrm{Solv}] \qquad \text{(ii)}$$

$$\Delta E_M(n) = E[K^+(\mathrm{Solv})_n] - E[K^+] - E[(\mathrm{Solv})^{\#}{}_n] \qquad \text{(iii)}$$

Here, $E[(\mathrm{Solv})^{\#}]$ is the energy of a complex of nH_2O molecules whose structure is fixed at that of the $[K^+(\mathrm{Solv})_n]$ complex and $\Delta E_S(n)$ gives the interaction energy among the solvent molecules in the complex. The $\Delta E_M(n)$ is the interaction energy between the prepared solvent cluster and the K ion, and the sum of the two components gives the total binding energy $\Delta E_B(n)$.

$$\Delta E_B(n) = \Delta E_S(n) + \Delta E_M(n) \qquad \text{(iv)}$$

The values of $\Delta E_S(n)$ and $\Delta E_M(n)$ of the complexes are accumulated in Table 4. The solute−solvent contribution, $\Delta E_M(n)$, is exothermic and is the main contributor to the total binding energy for all n examined here. The solvent−solvent contribution is always positive (repulsive) and thus destabilizes the system. Comparison of the $\Delta E_M(n)$ and $\Delta E_S(n)$ values for $K^+[H_2O]_n$ shows a trend in accord with that found in $Na^+[H_2O]_n$ for $n \leq 4$. For a given n, the value of $\Delta E_S(n)$ is smaller within the $(H_2O)_n{}^{\#}$ clusters of the potassium ion complexes than in the corresponding water clusters of the sodium ion complexes,[26] because the $H_2O\cdots OH_2$ distance in $K^+[H_2O]_n$ is larger than in $Na^+[H_2O]_n$. The stabilizing solute−solvent contribution, $\Delta E_M(n)$, is larger in the case of sodium, probably because of higher electrostatic interaction of Na^+−water in the complex. Thus, $\Delta E_M(n)$ in $Na^+[H_2O]_n$ is so large that, even after subtraction of the destabilizing factor $\Delta E_S(n)$, the resulting binding energy is still greater by 8−14 kcal/mol than that found in any of the $K^+[H_2O]_n$ complexes in the range $n = 1$ to $n = 4$. In $K^+[CH_3CN]_n$, for $n \leq 4$, the total binding energy $\Delta E_B(n)$ comes entirely from the $K^+\cdots NCCH_3$ interaction, $\Delta E_M(n)$. For $n = 5$, the $\Delta E_S(n)$ is also a major contributor to the binding energy and its importance increases as n grows. On the other hand, for $K^+[CH_3OH]_n$, the $K^+\cdots OHCH_3$ interaction $\Delta E_M(n)$ determines the binding energy for all n considered. The large difference in $\Delta E_B(n)$ between water and acetonitrile clustering for $n \leq 4$ is a result of the greater strength of the $K^+\cdots NCCH_3$ interaction as compared to $K^+\cdots OH_2$. The difference decreases as n increases because the contribution of the $CH_3CN\cdots NCCH_3$ interaction is greater than that of $H_2O\cdots OH_2$. Methanol clustering to K^+ is less exothermic compared to water clustering, as mentioned earlier, because the $K^+\cdots OHCH_3$ interaction is weaker than that of $K^+\cdots OH_2$, and this ion−solvent interaction largely dominates over the solvent−solvent interaction in determining the binding energy.

In Figure 1, the net (Mulliken) charge on the potassium ion in $K^+[\mathrm{Solv}]_n$, calculated at the RHF/DZP level, is plotted as a function of the solvation number. It is clear that a significant amount of charge is transferred to the central potassium ion. An examination of the charge on the potassium ion in $K^+[\mathrm{Solv}]_n$ clusters shows that the fractional electronic charge transferred to the cation, which is 0.0209 after the addition of the first water, increases on addition of further water molecules ($n = 2-6$) through the values 0.0427, 0.0626, 0.0845, 0.1021, and 0.1300. Similar charge transfer (CT) effects were reported[26] for the hydrated sodium ion complexes. For methanol clustering the charge transfer from the first solvent molecule is the same as that for water, but transfer of electrons from the ligating oxygen of methanol increases slowly and reaches a value of only 0.0894 electrons for $n = 5$, 12% lower than in $K^+[H_2O]_5$. It therefore appears that the M−O bond gains more covalent character in water clustering than in methanol clustering as n increases from 1 to 5. In the case of acetonitrile clustering, the CT to the metal ion after addition of the first solvent molecule is 0.0303 electrons, 45% higher than for water and methanol. As n increases from 2 to 6, the corresponding fractions are 0.0653, 0.0838, 0.115, 0.1484, and 0.2050. Thus the K−N bond develops a much greater covalent character in comparison with the K−O bond in $K^+[H_2O]_n$ for any given n value.

The bond length between the potassium ion and the oxygen/nitrogen atom of solvent in $K^+[\mathrm{Solv}]_n$ has been compared in Figure 2. For water- and methanol-solvated potassium ion, the $K^+\cdots O$ bond length increases monotonically as n increases. For all values of n, the $K^+\cdots O$ distance in $K^+[CH_3OH]_n$ is slightly larger than that of $K^+[H_2O]_n$. This ion−oxygen distance and the charge transfer described in the earlier section are consistent with the relative binding energy of the water and methanol complexes. The $K^+\cdots N$ distance in $K^+[CH_3CN]_n$ is much larger than that of $K^+\cdots O$ in $K^+[CH_3OH]_n$ and $K^+[H_2O]_n$, for all values of n except $n = 6$. It is interesting to note that the $K^+\cdots N$ distance increases up to $n = 4$ and then decreases rapidly. Thus smaller $K^+\cdots N$ distance for $n = 5$ and 6 compared to $n = 4$ makes the solvent−solvent interaction larger. This larger destabilizing factor contributes to the rapid falloff of the successive binding energies.

The vertical ionization potentials (IPs) of the potassium complexes with the water, methanol, and acetonitrile molecules

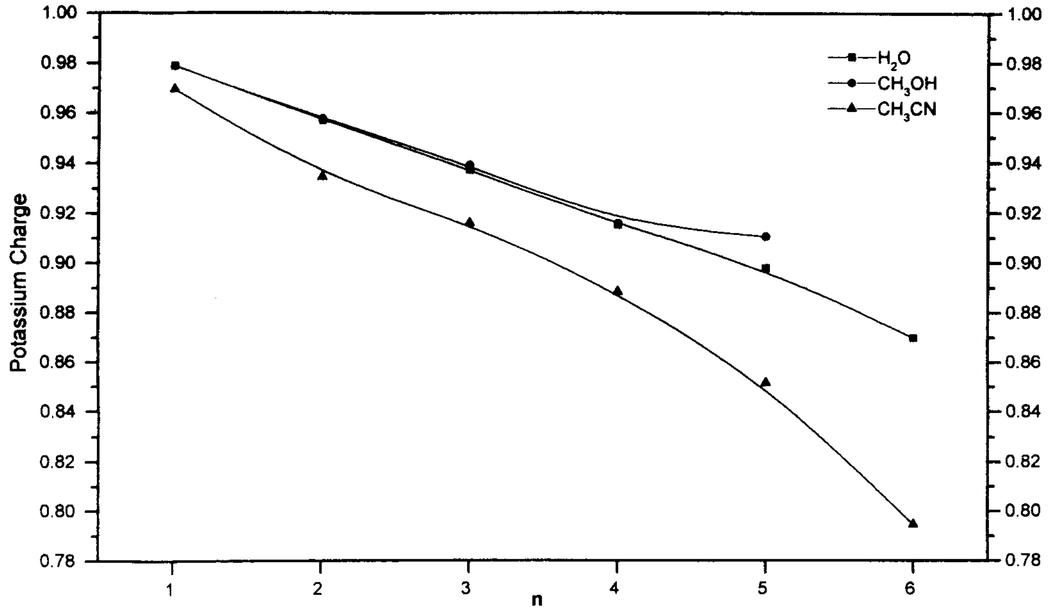

Figure 1. Plot of Mulliken charge on the potassium cation vs *n* in the $K^+[Solv]_n$ clusters (Solv = H_2O, CH_3CN, $n = 1-6$; Solv = CH_3OH, $n = 1-5$).

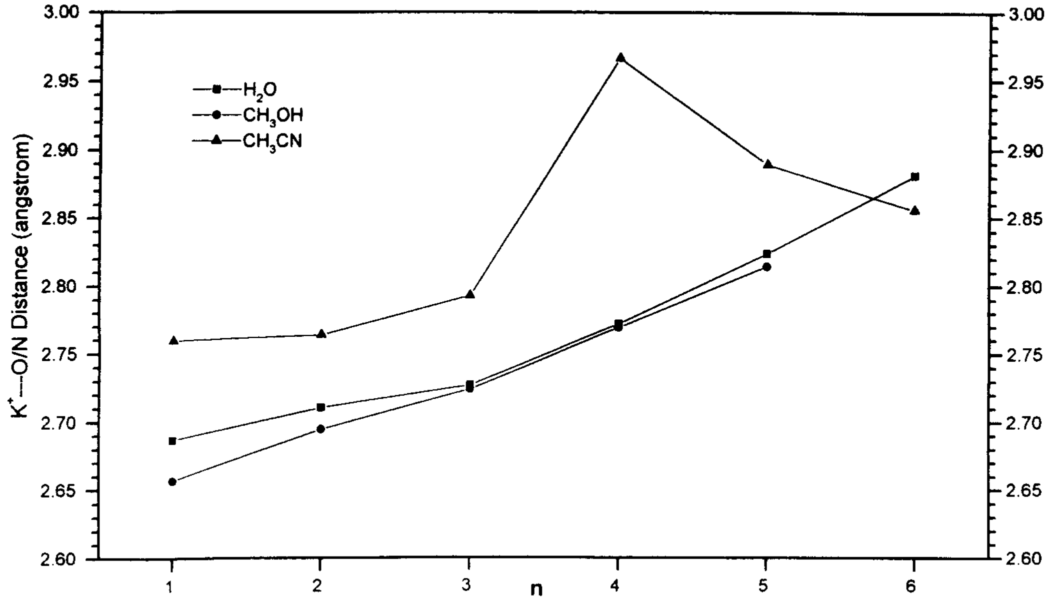

Figure 2. Variation of K^+---O bond length with coordination number.

have been calculated. The vertical ionization energies are calculated to be 3.44, 3.40, and 3.10 eV for $K[H_2O]$, $K[CH_3OH]$, and $K[CH_3CN]$ complexes, respectively, using the DZP basis set at the UHF level. The corresponding experimental ionization energy is 3.92[44] and 3.74[14] eV for $K[H_2O]$ and $K[CH_3OH]$ complexes, respectively. No experimental ionization energy for $K[CH_3CN]$ has been reported so far. The agreement between theory and experiment is reasonably good, and the underestimation of the theoretical ionization energies is expected.[14] If one considers the difference between the theoretical and experimental IP of the potassium atom, 0.30 eV,[15] to offset the theoretical vertical IP of $K[H_2O]$ and $K[CH_3OH]$, one would find that the deviation is 0.18 and 0.08 eV, respectively. Earlier studies[14,15] of IP for the alkali metal complexes of simple Lewis base molecules predicted lower values than those found experimentally. Inclusion of a correlation treatment at the MP2 level did not improve the result much. For the $K[H_2O]$ complex, the IP is calculated to be 3.50 eV at the MP2 level, which is only 0.06 eV larger than the values obtained at the HF level. However, the IP of $K[CH_3OH]$ obtained in this work is in excellent agreement with the reported ab initio value[14] at both the HF and MP2 level. The difference in IP between potassium complexes of water and methanol is only 0.04 eV, indicating that the methyl group does not change the electronic structure of the potassium atom. The larger difference in IP by 0.25 eV between $K[H_2O]$ and $K[CH_3CN]$ complexes indicates that the high dipole $^-N{\equiv}C^+$ of acetonitrile exerts a strong influence in changing the electronic environment of the potassium atom upon complexation. The calculated[26] vertical IP of $Na[H_2O]$ by the ΔMP2 method at the HF/6-31+G(d) level is 0.65 eV larger than the corresponding $K[H_2O]$ values obtained at the MP2/DZP level.

Geometry

The equilibrium geometries of the $K^+[CH_3OH]_n$ and $K^+[CH_3CN]_n$ clusters are shown diagrammatically in Figures 3 and 4.

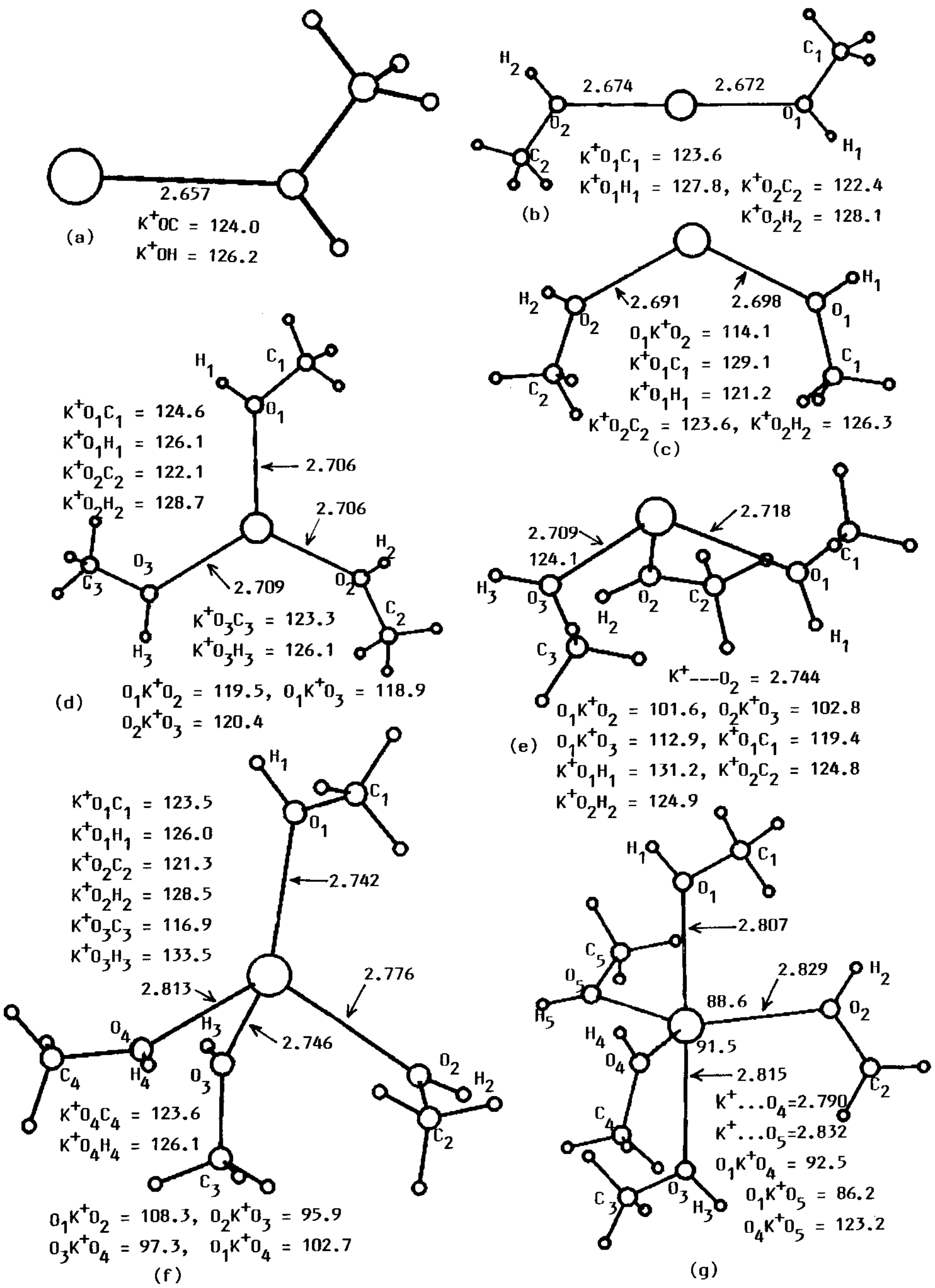

Figure 3. Optimized geometries of $K^+[CH_3OH]_n$, $n = 1-5$, clusters at the RHF/DZP level.

Methanol-Solvated Potassium Ion: $K^+[CH_3OH]_n$ (n = 1−5). The C−O and C−H bond lengths of the isolated methanol molecule obtained in this work are 1.403 and 0.943 Å, respectively, at the RHF/DZP level, and both are 0.02 Å shorter than the experimental value.[45] The C−O bond length is significantly affected by the coordination with K^+, and the C−O−H angle is also changed slightly upon coordination (Figure 3). The C−O bond length increases by 0.023 to 1.426 Å in $K^+[CH_3OH]$ and then decreases to 1.417 Å as n increases to 5. The C−O−H angle increases by 1° upon complexation and then approaches the isolated molecule value as n increases. In all methanol-solvated clusters, the potassium ion is coordinated with oxygen in such a way that the angle K− O−H (where H is the −OH group hydrogen) has a value of 128° ± 4°.

Two isomers of $K^+[CH_3OH]_2$ have been optimized. The structure **b** in Figure 3 is the "interior structure",[26] having a linear arrangement of O−K−O, and structure **c** is the "surface structure",[26] where K^+ is situated on the surface with an O−K−O angle of 114°. The interior structure is only 0.55 kcal/mol more stable and has the shorter K−O bond length by 0.021 Å compared with the surface structure. Of the two optimized isomers of $K^+[CH_3OH]_3$, the surface structure **e** (Figure 3) is only 0.36 kcal/mol less stable than the interior structure **d**, where the K−O bond is shorter by 0.016 Å. Similar phenomena have been reported[26] for the hydrated clusters of neutral sodium. In the interior structure, **d**, all three methanol molecules are arranged symmetrically around the central K^+. To assess the effect of the unsymmetrical arrangement of methanol solvent, one of the methanol molecules was rotated around the K−O bond, keeping all other geometrical parameters fixed. The barrier to rotation resulting from the interference of the two methyl groups was found to be only 0.33 kcal/mol. Therefore, in the interior structure of $K^+[CH_3OH]_2$, it is unlikely that changes between the cis and trans conformations of the methyl group will yield any appreciable perturbation on the total energy of the cluster. For the clusters of n = 4 and 5, all the isomers

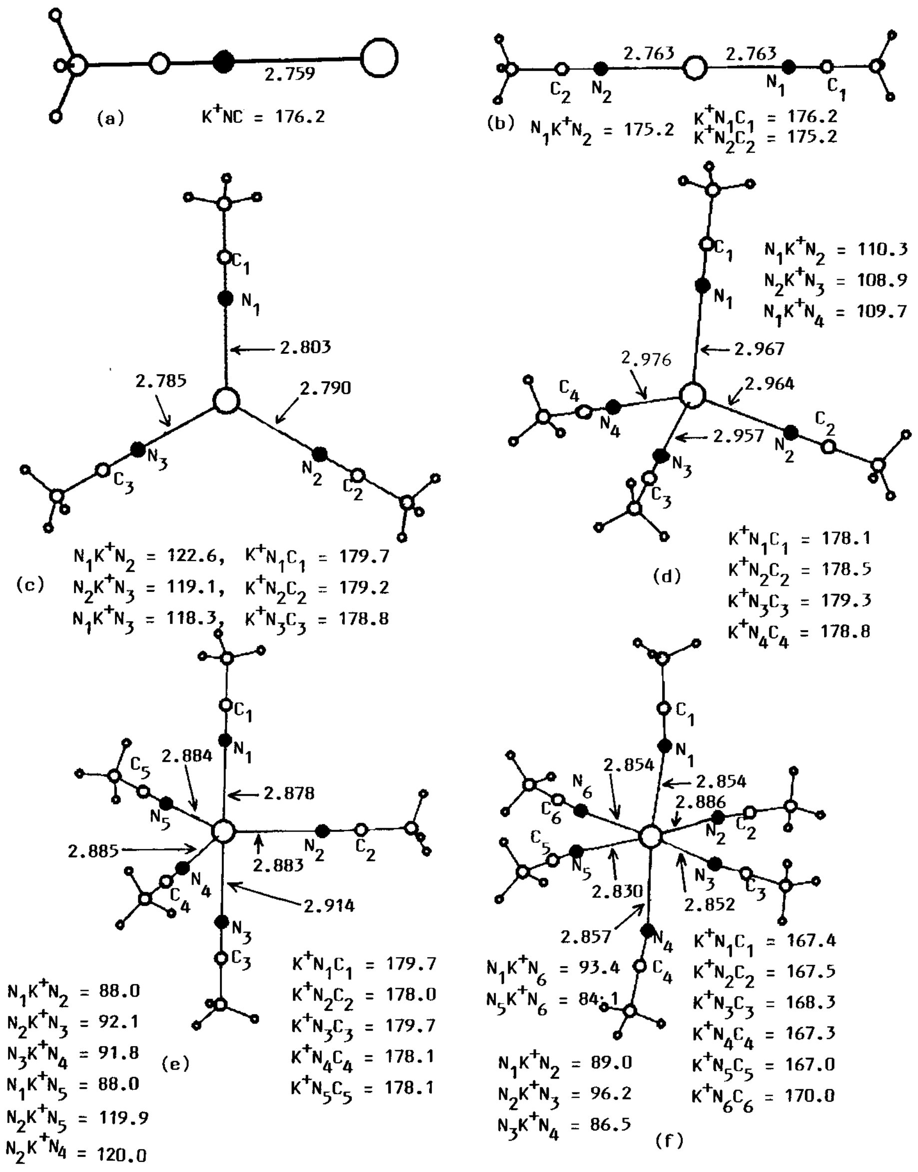

Figure 4. Optimized geometries of K$^+$[CH$_3$CN]$_n$, $n = 1-6$, clusters at the RHF/DZP level.

optimized are of the interior structure. Of the two isomers of K$^+$[CH$_3$OH]$_4$, the tetrahedral structure (Figure 3f) is more stable than the square planer by 1.27 kcal/mol because of the smaller solvent−solvent interaction in the tetrahedral structure. However, for the $n = 5$ cluster, the energy difference between trigonal bipyramid (Figure 3g) and square pyramid is negligible at only 0.16 kcal/mol.

Acetonitrile-Solvated Potassium Ion: K$^+$[CH$_3$CN]$_n$ (n = 1−6). The optimized structures of the acetonitrile-solvated potassium ion are given in Figure 4. As is apparent from the figure, the species have a variation in the K$^+$---N bond length, already described in the earlier section. The K$^+$---N bond length increases by 0.1 Å on going from $n = 1$ to $n = 6$ and is larger than the Ag$^+$---N bond length in the Ag$^+$[CH$_3$CN]$_n$ complex[46] for all values of n. The bond lengths of N−C, C−H, and C−C in the isolated CH$_3$CN molecule are 1.138, 1.081, and 1.475 Å, respectively. The N−C and C−H bond lengths are 0.019 and 0.023 Å smaller and the C−C bond length is 0.017 Å larger than the experimental value.[47] However, the N−C bond length obtained in this work agrees well with the reported value.[46] The C−C−H and H−C−H angles are 109.5° ± 0.5° and agree well with the experimental tetrahedral value. The bond lengths of N−C, C−H, and C−C in the solvated species are not affected by the coordination number.

In the optimized structures (Figure 4a,b) of both K$^+$[CH$_3$CN] and K$^+$[CH$_3$CN]$_2$, the N−K−N angle is distorted by 4−5° from the linear arrangement and the K−N−C angle is also found to be slightly bent by 4°. Both the structures were confirmed to be true minima, as all vibrational frequencies were real. In K$^+$[CH$_3$CN]$_3$, the K−N−C angle is almost linear, and the N−K−N angles of 120° ± 2° confirm the geometry of the structure to be in the trigonal arrangement (Figure 4c). Two isomers of K$^+$[CH$_3$CN]$_4$ have been optimized starting from different initial conformations. The tetrahedral structure (Figure 4d) is more stable than the square planar by ≅2 kcal/mol because of the solvent−solvent interaction, a destabilizing component which is larger in the square planar by 1.5 kcal/mol than in the tetrahedral structure. Moreover, the ion solute interaction in the tetrahedral complex is more exothermic by 0.5 kcal/mol than that in the square planar complex. All the N−K−N angles are in the range 109.5° ± 0.5°, confirming the structure to be in the perfect tetrahedral arrangement. Two isomers of the 5-coordinated complex have been optimized using a method similar to that employed for the 4-coordinated case. The trigonal bipyramid structure (Figure 4e) is only 0.9 kcal/mol more stable than the square pyramid structure, and this stabilization comes from the larger ion−solute interaction in the former. The N_{ax}−K−N_{ax} angle is 179.6° and the N_{eq}−K−N_{eq} angle is 119.9° ± 0.1° in the trigonal bipyramid structure. For $K^+[CH_3CN]_6$, the only structure optimized is octahedral (Figure 4f), the N_{ax}−K−N_{eq} angles are 90.0° ± 3.5°, the N_{ax}−K−N_{ax} angles are 172.6°, and the N_{eq}−K−N_{eq} angles are 172.6° and 175.3°. All CH_3CN solvent molecules are coordinated with K^+, having the K−N−C angle distorted from the linear arrangment by 12−13°.

Conclusions

The results of Table 2 for the binding energies of gas-phase $K^+[H_2O]_n$ clusters show that the RHF/DZP//RHF/DZP calculations reported here are in good agreement with the MP2/6-31+G*//RHF/6-31+G* calculations of Glendening and Feller and with the experimental results for n values up to 4 and possibly 5. Only for the case $n = 6$ is it clear that the MP2 electron correlation correction makes an appreciable contribution.

The agreement shows that it is not necessary to make basis set superposition corrections when using a basis of DZP quality.

For all solvents the increase in binding energy with n is nearly linear. For the smaller clusters, up to $n = 3$, the relative strength of the binding is in the order

$$\text{acetonitrile} > \text{water} > \text{methanol}$$

The incremental $\Delta H_{\text{Binding}+}$ values for water are slightly larger than for methanol clusters, in agreement with the fact that the enthalpy of vaporization of water is greater than that of methanol. The gas-phase experimental results for methanol are, however, anomalous in this respect. The high exothermic binding energy in the smaller acetonitrile clusters is attributable to the large, accessible, negative charge on the N atom, which can interact strongly with the ion. Larger $K^+[H_2O]_n$ are, however, more strongly bound than their acetonitrile counterparts. It has been reported that solvation shells in acetonitrile solutions with K^+ are predominantly formed with $n = 3$ or $n = 4$. The clustering effect per ion should, therefore, be expected to be stronger than in the protic solvents. The absence of larger clusters can be undestood in terms of the analysis of the binding energy into ion−solvent and solvent−solvent contributions. In the acetonitrile clusters the latter term is destabilizing and increases in relative importance with the size of the cluster.

The calculated ($T = 0$ K) binding energies have been converted to thermodynamic quantities, using the computed normal mode frequencies. While the ΔH values so obtained are reasonable and generally in good agreement with other calculations and experiment where results are available, the more sensitive ΔS values become inaccurate for large clusters. This problem has also been encountered by other workers and is clearly attributable to the poor representation of low-frequency modes in the calculations.

Calculated values of the vertical ionization potentials of the complexes are about 0.3 eV lower than the reported experimental values for the water and methanol complexes, the difference being attributable to the error in the K^+ ionization potential, which is found in all ab initio calculations at this level. The similarity of the values in the three solvents indicates that the electronic structure of the K^+ ion is not appreciably altered by the formation of the complexes.

The geometry of the clusters is shown in the figures. The trend followed by the ion−ligand bond length as a function of n is regular except in the case of the acetonitrile clusters with $n = 4$.

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