Anion−Water Clusters $A^-(H_2O)_{1-6}$, A = OH, F, SH, Cl, and Br. An Effective Fragment Potential Test Case

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The ability of the effective fragment potential (EFP) method, a quantum mechanical/molecular mechanical (QM/MM) approach, to describe the hydration of five simple anions (OH^-, F^-, SH^-, Cl^-, and Br^-) by one to six water molecules was investigated. The results were compared with experimental data and ab initio calculations: Hartree−Fock (HF) and second-order Møller−Plesset (MP2). With the exception of the addition of the first water molecule, the EFP method was able to reproduce both the experimental and HF differential enthalpies of hydration. None of the three levels of theory reliably reproduced the experimental total enthalpies of hydration, and the EFP and HF results were found to be in poor agreement. The charge-transfer/exchange-repulsion component of the model appears to be inadequate in describing systems exhibiting large amounts of charge transfer (e.g., the OH^- and F^- systems). Two model chemistries based upon the EFP method were also examined. While the use of HF and MP2 single-point energy calculations at EFP-optimized geometries offered little improvement over the results obtained at the EFP level, the use of effective fragment potentials to model the second hydration shell of the larger anion−water clusters proved very successful. This latter result suggests that the method may be useful in the description of much larger hydrated systems.

Introduction

Anions represent a large and important class of chemical species. In addition to their role as counterions, they also serve as reactants and intermediates. Their behavior is strongly solvent dependent; for example, the nucleophilicity of halides in nonpolar solvents ($F^- > Cl^- > Br^- > I^-$) is reversed in polar, protic solvents (i.e., $I^- > Br^- > Cl^- > F^-$).[1] A detailed understanding of anion−solvent interactions is required to explain such a dramatic solvent effect. While experimental methods (most notably mass,[2] vibrational,[3] and photoelectron[4] spectroscopies) can offer invaluable insights into solute−solvent interactions, computational approaches often yield a much more complete structural and energetic picture. It should also be noted that ab initio calculations are often essential in the interpretation of rotational, vibrational, and electronic spectra. In the modeling of solvation phenomena, computational chemists possess two major paradigms from which to choose: continuum and microsolvation approaches.

Continuum methods,[5] in which the solvent is treated in bulk as a polarizable medium, have generally been turned to first. This has been due in part to their relative simplicity and attendant low computational cost. Unfortunately, this very simplicity makes their application to anionic systems problematic. In polar, protic media (e.g., water), anions are predicted to have asymmetric solvent environments.[6] As such, a homogeneous continuum may not provide an adequate description of the solvation of anions.

In microsolvation approaches,[7] solvent molecules are included explicitly in the calculation, permitting the solvent to array itself in an asymmetric fashion about the anion. However, a significant increase in computational expense results when the solvent as well as the solute is considered explicitly. Moreover, questions regarding long-range interactions persist, especially for charged systems, and the adequate modeling of such interactions is thought to require large numbers of solvent molecules. As the number of solvent molecules increases, so does the number of degrees of freedom in the system. This leads to issues surrounding the adequate sampling of the configuration space.

It is worth mentioning that another approach to the problem of solvation combines the continuum and microsolvation methods. Here, the solute and a small number of solvent molecules are embedded in a continuum. Topol and co-workers[8] have published the results of such an investigation that is particularly relevant to the current study in that it deals with the hydration of halides.

A number of quantum mechanical/molecular mechanical (QM/MM) methods[9] have been developed in an attempt to mitigate the increase in computational cost associated with microsolvation approaches. Stevens, Gordon, and co-workers have developed a generalized potential derived from first principles known as the effective fragment potential (EFP), a complete description of which may be found in the literature.[10] In this method, the system of interest is divided into quantum mechanical and classical regions. The quantum mechanical region, also known as the “active region”, contains those elements of the system undergoing quantum events (e.g., the formation or breaking of bonds). The remainder of the system is treated classically and is referred to as the “ spectator region”. Interactions between the two regions and within the spectator region are governed by three one-electron terms in the Hamiltonian. These three terms account for electrostatic (ES), polarization (POL), and charge-transfer (CT)/exchange-repulsion (EX) interactions. Because the most expensive part of any ab initio computation involves two-electron integrals, the inclusion of one-electron terms results in little additional cost. In the current context, effective fragment potentials are used to model water molecules. With the DH(d,p)++ basis set, these potentials

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eliminate 31 basis functions per water molecule from any calculation. The EFP method has been successfully applied to a variety of chemical systems.[11]

In this paper we describe an investigation into the ability of the effective fragment potential to reproduce ab initio (Hartree−Fock) results for simple anion−water clusters $A^-(H_2O)_{1-6}$, A = OH, F, SH, Cl, and Br. The EFP results are also compared to experimental thermodynamic results.[2] This paper compliments our previous study into the efficacy of the EFP method to describe the hydration of simple cations.[12] With this study a preliminary survey of the method's ability to reproduce the thermodynamics and structures of a wide range of solvated main group systems is completed. For a current and thorough review of the experimental and theoretical aspects of the hydration of halides, consult the paper of Robertson and Johnson.[13]

Methods

The EFP for water was developed to reproduce results at the restricted Hartree−Fock (RHF) level with the double split-valence basis set of Dunning and Hay to which sets of polarization functions were added to the oxygen (six d orbitals) and hydrogen (three p orbitals) atoms, i.e., RHF/DH(d,p).[14] This underlying level of theory was, therefore, employed in the current study. It has been shown in the literature that diffuse basis functions are essential to the description of anionic systems.[15] Therefore, sets of diffuse functions were added to all heavy (sp orbitals) and hydrogen (s orbital) atoms.[16] This basis is referred to as "DH(d,p)++" and was used in all the reported calculations.

All structures were fully optimized at the RHF/DH(d,p)++ level; the criteria for structural convergence were a maximum gradient of less than 0.012 kcal/(mol Å) and an RMS gradient of less than 0.004 kcal/(mol Å). To verify that all optimized structures corresponded to minima, their Hessian matrices were also computed at the RHF/DH(d,p)++ level. These matrices were calculated analytically for clusters with ab initio water molecules and numerically with double differencing for clusters with EFP water molecules. The Hessian matrices also permitted zero-point energies (ZPEs) to be computed. All ZPEs were scaled by an empirical factor of 0.9135 to compensate for the known overestimation of vibrational frequencies at the RHF level with double-ζ-quality basis sets.[17] Enthalpies were not corrected from 0 to 298 K as this was found to have only a minor impact on the results.[18] A similar conclusion was reached in our earlier work on alkali-metal/alkaline-earth-metal cation−water clusters.[12]

To assess the influence of dynamic electron correlation upon our results, second-order Møller−Plesset[19] (MP2/DH(d,p)++) single-point energy calculations were carried out at the HF-optimized geometries. The frozen core (fc) approximation was employed. This level of theory has been previously shown to accurately reproduce experimental proton affinities.[20] (Proton affinities for the five anions of interest were calculated at this level (Table 1S in the Supporting Information). A mean error of −1.5 kcal/mol and standard deviation of 2.2 kcal/mol were determined.[21])

To simplify the discussion of the following results, the following nomenclature has been used to refer to the various levels of theory: HF ≡ RHF/DH(d,p)++; MP2 ≡ MP2(fc)/DH(d,p)++//RHF/DH(d,p)++; EFP ≡ EFP/DH(d,p)++. For the HF and MP2 calculations, all atoms were treated ab initio, while, in the EFP case, only the anion was treated ab initio. All calculations were performed with the GAMESS program,[22] which is freely available from Iowa State University at www.msg.ameslab.gov.

TABLE 1: Anion Structures Used in Total and Differential Enthalpy Calculations[a]

n	EFP	HF	MP2
		$OH^-(H_2O)_n$	
1	(1)	(1)	(1)
2	(1,1)	(1,1)	(1,1)
3	(3)	(3)	(3)
4	(4)	(4)	(4)
5	(4) + [1]	(2,2) + [1]	(3) + [2]
6	(5) + [1]	(4) + [2]	(4) + [2]
		$F^-(H_2O)_n$	
1	(1)	(1)	(1)
2	(1,1)	(1,1)	(1,1)
3	(3)	(3)	(3)
4	(3,1)	(2,2)	(3,1)
5	(4,1)	(2,2) + [1]	(2,2) + [1]
6	(5) + [1]	(5) + [1]	(4) + [2]
		$SH^-(H_2O)_n$	
1	(1)	(1)	(1)
2	(2)	(1,1)	(2)
3	(3)	(2,1)	(2) + [1]
4	(4)	(4)	(4)
5	(4) + [1]	(2,2) + [1]	(2,2) + [1]
6	(5) + [1]	(4) + [2]	(4) + [2]
		$Cl^-(H_2O)_n$	
1	(1)	(1)	(1)
2	(2)	(1,1)	(2)
3	(3)	(3)	(3)
4	(4)	(4)	(4)
5	(4) + [1]	(2,2) + [1]	(3) + [2]
6	(5) + [1]	(5) + [1]	(4) + [2]
		$Br^-(H_2O)_n$	
1	(1)	(1)	(1)
2	(2)	(2)	(2)
3	(3)	(3)	(3)
4	(4)	(4)	(4)
5	(2,2) + [1]	(2,2) + [1]	(3) + [2]
6	(5) + [1]	(5) + [1]	(5) + [1]

[a] Nomenclature: parentheses, number of water molecules in the first hydration shell; brackets, number of water molecules in the second hydration shell; (*n*,*m*)/[*n*,*m*], *n* and *m* water molecules in the first and second groups, respectively. See Figure 1 for graphic illustrations and the text for details.

Results and Discussion

The initial geometries that were chosen for optimization were based upon previous results found in the literature.[6] In every case, several low-energy structures, computed at the highest level of theory, were selected. No attempt was made to locate all minima for a given cluster size; this was especially true for the $A^-(H_2O)_{5,6}$ clusters. It should be noted, however, that within a class of configurations (e.g., surface or internally solvated) for a cluster of a given size, the range of energies is typically small. To cite but one example from the literature, Masamura[6o] located two $OH^-(H_2O)_5$ clusters with (4) + [1] configurations (vide infra) at the MP2/aug-cc-pVDZ level. The range of energies for these species was only 0.7 kcal/mol. As such the failure to find a global minimum should not significantly alter the conclusions reached in the current study.

A simple nomenclature has been adopted for the description of anion−water clusters (Table 1). Structures have been labeled on the basis of the number of water molecules in their respective hydration shells: parentheses are used to denote the number of water molecules in the first shell, while brackets have been used to signify the numbers of water molecules in the second shell. When water molecules are arrayed into a number of different groups within a given shell, the number of water molecules in each group has been specified. For example, three low-energy

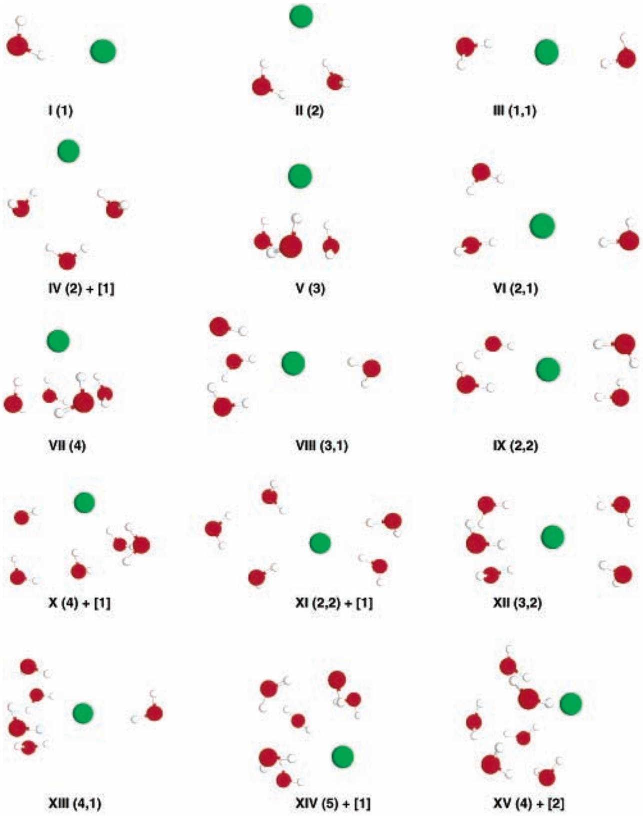

Figure 1. Schematic illustrations of anion structures used in the current study. See Table 1 for a description of the nomenclature.

structures were found for the $A^-(H_2O)_3$ clusters (see Figure 1). Structures **V** and **VI** both have three water molecules in their first shells. While these three water molecules form a single group in structure **V**, two groups (one with two water molecules and another with one) are present in structure **VI**. Therefore, structure **V** is referred to as “(3)” and structure **VI** as “(2,1)”. In the case of structure **IV** with two water molecules in the first shell and one in the second, it is referred to as “(2) + [1]”. No attempt has been made to name specific interactions (e.g., donor−acceptor relations in hydrogen bonds). This level of detail can only serve to obscure the conclusions drawn in the present study.

Structures. Comparisons are made between the EFP and HF structures. These comparisons are important in their own right as the EFP method was designed to reproduce results at the Hartree−Fock level of theory. A statistical summary of these comparisons is given in Table 2. (More detailed structural information may be found in Tables 2S−7S in the Supporting Information.) What experimental structural data are available come mainly from vibrational spectroscopy.[3] These results are most conclusive for the smaller clusters ($n < 3$) and ambiguous for the larger systems.

Two types of hydrogen bonding have been selected for comparison: that between the anion and the water molecules of the first hydration shell ($A^-\cdots H$) and that between the water molecules of the first and second shells ($O\cdots H$). The EFP structures evince $A^-\cdots H$ hydrogen bonds that are consistently longer than those predicted at the HF level of theory (mean 0.04 Å). This mean difference decreases with increasing cluster size: $n = 1$, mean 0.10 Å; $n = 6$, mean 0.02. Given the weak nature of these interactions, such agreement should be considered good. The fact that the standard deviation is somewhat large (standard deviation 0.10 Å) shows that the EFP method does not reproduce all of the HF structures equally well. While there does not appear to be one anion that performs consistently poorly, the OH^- and F^- systems possess some of the larger differences, especially for the smaller clusters.

TABLE 2: Statistical Comparison of EFP and HF Structures ($\Delta = r_{EFP} - r_{HF}$)[a]

structure	r	mean	std dev	N
	$A^-(H_2O)$			
(1)	$A^-\cdots H$	0.10	0.14	5
	$O\cdots H$			
	$A^-(H_2O)_2$			
(2)	$A^-\cdots H$	−0.01	0.08	6
	$O\cdots H$			
(1,1)	$A^-\cdots H$	0.06	0.13	4
	$O\cdots H$			
	$A^-(H_2O)_3$			
(2) + [1]	$A^-\cdots H$	0.08	0.10	5
	$O\cdots H$	−0.04	0.01	5
(3)	$A^-\cdots H$	0.07	0.11	5
	$O\cdots H$			
(2,1)	$A^-\cdots H$	0.01	0.12	9
	$O\cdots H$			
	$A^-(H_2O)_4$			
(4)	$A\text{–}\cdots H$	0.04	0.11	5
	$O\cdots H$			
(3,1)	$A^-\cdots H$	0.05	0.10	4
	$O\cdots H$			
(2,2)	$A^-\cdots H$	0.01	0.11	8
	$O\cdots H$			
	$A^-(H_2O)_5$			
(2,2) + [1]	$A^-\cdots H$	0.04	0.11	8
	$O\cdots H$	−0.02	0.02	4
(3) + [2]	$A^-\cdots H$	0.05	0.09	5
	$O\cdots H$	−0.04	0.01	5
	$A^-(H_2O)_6$			
(5) + [1]	$A^-\cdots H$	0.02	0.09	15
	$O\cdots H$	−0.05	0.01	5
(4) + [2]	$A^-\cdots H$	0.02	0.09	10
	$O\cdots H$	−0.05	0.01	10
	$A^-(H_2O)_{1-6}$			
	$A^-\cdots H$	0.04	0.10	89
	$O\cdots H$	−0.04	0.02	29
	total	0.02	0.10	118

[a] $A^-\cdots H$ = hydrogen bond between the anion and water molecules; $O\cdots H$ = hydrogen bond between water molecules. Distances are given in angstroms. See the text for details.

The above situation is reversed for the $O\cdots H$ hydrogen bonds. Here, the bond lengths predicted at the EFP level are on average 0.04 Å shorter than those found for the HF structures. The standard deviation of 0.02 Å is one-fifth that found for the $A^-\cdots H$ hydrogen bonds. This agreement is more than satisfactory.

The complete data set leads to a mean difference of only 0.02 Å, but it also possesses a somewhat larger standard deviation of 0.10 Å. One is led to conclude that the EFP method is capable of reproducing the second hydration shell of the HF structures, while it is less effective in describing the first shell. Finally, it is worth noting that the EFP method failed to locate only one cluster found at the HF level: (2,2) + [1], Cl^-. On the other hand, the HF level failed to find eight minima recognized by the EFP method: (2), OH^- and F^-; (2,1), Br^-; (3,1), Br^-; (2,2) + [1], OH^-, SH^-, and Cl^-; (3) + [2], F^-. The fact that the EFP model found eight structures not found at the HF level further indicates that the model has difficulties describing some of the anion−water interactions. This result should not be too surprising, however, given that the model was developed to model more weakly interacting systems, i.e., hydrogen bonds to neutral species.[10]

TABLE 3: Differential Enthalpies of Hydration ($\Delta\Delta_rH°$) of Anions at 0 K (kcal/mol)[a]

n	exptl	EFP	error	HF	error	MP2	error
$OH^-(H_2O)_{n-1} + H_2O \rightarrow OH^-(H_2O)_n$[b]							
1	−26.5 ± 1.0	−18.2	8.3	−22.9	3.6	−26.2	0.3
2	−17.6 ± 1.0	−17.0	0.6	−19.1	−1.5	−21.8	−4.2
3	−16.2 ± 1.0	−16.0	0.2	−15.6	0.6	−17.7	−1.5
4	−12.0 ± 1.0	−13.8	−1.8	−12.0	0.0	−15.2	−3.2
5	−11.5 ± 1.0	−10.4	1.1	−9.9	1.6	−13.0	−1.5
6	−11.2 ± 1.0	−11.1	0.1	−9.1	2.1	−14.0	2.8
$\Delta_rH°$(calcd) − $\Delta_rH°$(exptl)		mean	1.4 (0.0)	mean	1.1	mean	−1.2
		std dev	3.5 (1.1)	std dev	1.8	std dev	2.5
$\Delta_rH°$(EFP) − $\Delta_rH°$(HF)		mean	2.7 (0.1)				
		std dev	2.6 (1.6)				
$F^-(H_2O)_{n-1} + H_2O \rightarrow F^-(H_2O)_n$[c,d]							
1	−23.3 ± 2.0	−17.7	5.6	−23.5	−0.2	−26.4	−3.1
2	−19.2 ± 0.5	−15.9	3.3	−18.5	0.7	−20.2	−1.0
3	−15.3 ± 0.4	−14.4	0.9	−14.8	0.5	−16.6	−1.3
4	−13.9 ± 0.4	−13.0	0.9	−11.9	2.0	−14.5	−0.6
5	−12.3 ± 0.4	−10.8	1.5	−10.3	2.0	−12.9	−0.6
6	−10.9 ± 0.4	−10.9	0.0	−8.4	2.5	−12.4	−1.5
$\Delta_rH°$(calcd) − $\Delta_rH°$(exptl)		mean	2.0 (1.3)	mean	1.2	mean	−1.4
		std dev	2.1 (1.2)	std dev	1.1	std dev	0.9
$\Delta_rH°$(EFP) − $\Delta_rH°$(HF)		mean	3.3 (0.1)				
		std dev	3.0 (1.9)				
$SH^-(H_2O)_{n-1} + H_2O \rightarrow SH^-(H_2O)_n$[e]							
1	−14.2 ± 0.2	−10.8	3.4	−10.6	3.6	−13.6	0.6
2	−12.6 ± 0.3	−10.5	2.1	−10.1	2.5	−13.2	−0.6
3	−11.7 ± 0.5	−10.0	1.7	−9.1	2.6	−12.4	−0.7
4	NA	−10.8	NA	−9.2	NA	−12.7	NA
5	NA	−8.2	NA	−8.4	NA	−12.3	NA
6	NA	−10.5	NA	−8.3	NA	−12.7	NA
$\Delta_rH°$(calcd) − $\Delta_rH°$(exptl)		mean	2.4 (1.9)	mean	2.9	mean	−0.2
		std dev	0.9 (0.3)	std dev	0.6	std dev	0.7
$\Delta_rH°$(EFP) − $\Delta_rH°$(HF)		mean	−2.4 (−2.6)				
		std dev	0.9 (0.9)				
$Cl^-(H_2O)_{n-1} + H_2O \rightarrow Cl^-(H_2O)_n$[d]							
1	−14.7 ± 0.6	−11.0	3.7	−11.2	3.5	−13.6	1.1
2	−13.0 ± 0.4	−10.6	2.4	−10.3	2.7	−13.2	−0.2
3	−11.8 ± 0.3	−11.1	0.7	−9.8	2.0	−13.6	−1.8
4	−10.6 ± 0.3	−9.9	0.7	−9.1	1.5	−12.1	−1.5
5	−9.5 ± 0.3	−8.0	1.5	−7.5	2.0	−9.9	−0.4
6	−8.8 ± 0.4	−10.6	−1.8	−9.1	−0.3	−13.8	−5.0
$\Delta_rH°$(calcd) − $\Delta_rH°$(exptl)		mean	1.2 (0.7)	mean	1.9	mean	−1.3
		std dev	1.9 (1.6)	std dev	1.3	std dev	2.1
$\Delta_rH°$(EFP) − $\Delta_rH°$(HF)		mean	−1.3 (−1.8)				
		std dev	0.6 (0.5)				
$Br^-(H_2O)_{n-1} + H_2O \rightarrow Br^-(H_2O)_n$[d]							
1	−11.7 ± 0.4	−9.5	2.2	−11.1	0.6	−13.3	−1.6
2	−11.6 ± 0.3	−9.4	2.2	−10.5	1.1	−13.4	−1.8
3	−11.4 ± 0.4	−10.4	1.0	−10.9	0.5	−14.5	−3.1
4	−11.0 ± 0.2	−9.4	1.6	−9.8	1.2	−13.0	−2.0
5	−10.8 ± 0.3	−7.2	3.6	−7.1	3.7	−9.7	1.1
6	−10.3 ± 0.5	−10.5	−0.2	−10.3	0.0	−14.7	−4.4
$\Delta_rH°$(calcd) − $\Delta_rH°$(exptl)		mean	1.7 (1.6)	mean	1.2	mean	−2.0
		std dev	1.3 (1.4)	std dev	1.3	std dev	1.8
$\Delta_rH°$(EFP) − $\Delta_rH°$(HF)		mean	1.4 (0.9)				
		std dev	0.7 (0.5)				
Totals							
$\Delta_rH°$(calcd) − $\Delta_rH°$(exptl)		mean	1.7 (1.0)	mean	1.5	mean	−1.3
		std dev	2.1 (1.3)	std dev	1.4	std dev	1.8
$\Delta_rH°$(EFP) − $\Delta_rH°$(HF)		mean	0.0 (−0.5)				
		std dev	1.9 (1.2)				

[a] Parenthetical values omit $n = 1$ values. See the text for details. [b] Experimental values are from ref 2c. [c] Experimental values are from ref 2d. [d] Experimental values are from ref 2e. [e] Experimental values are from refs 2f and 2g.

Energetics. Differential (eq 1) and total (eq 2) enthalpies of hydration of the five anions by one to six water molecules were calculated at 0 K. These values along with those from experiment are given in Tables 3 and 4. It should be noted that the

TABLE 4: Total Enthalpies of Hydration ($\Delta_r H°$) of Anions at 0 K (kcal/mol)[a]

n	exptl	EFP	error	HF	error	MP2	error
$OH^- + nH_2O \rightarrow OH^-(H_2O)_n$[b]							
1	−26.5 ± 1.0	−18.2	8.3 (8.3)	−22.9	3.6 (3.6)	−26.2	0.3 (0.3)
2	−44.1 ± 1.4	−35.2	8.9 (4.4)	−42.0	2.1 (1.0)	−48.0	−3.9 (−2.0)
3	−60.3 ± 1.7	−51.2	9.1 (3.0)	−57.6	2.7 (0.9)	−65.7	−5.4 (−1.8)
4	−72.3 ± 2.0	−65.0	7.3 (1.8)	−69.6	2.7 (0.7)	−80.9	−8.6 (−2.2)
5	−83.8 ± 2.2	−75.4	8.4 (1.7)	−79.5	4.3 (0.9)	−93.9	−10.1 (−2.0)
6	−95.0 ± 2.4	−86.5	8.5 (1.4)	−88.6	6.4 (1.1)	−107.9	−12.9 (−2.2)
$\Delta_r H°$(calcd) − $\Delta_r H°$(exptl)		mean	8.4	mean	3.6	mean	−6.8
		std dev	0.6	std dev	1.6	std dev	4.7
$\Delta_r H°$(EFP) − $\Delta_r H°$(HF)		mean	4.8				
		std dev	1.7				
$F^- + nH_2O \rightarrow F^-(H_2O)_n$[c,d]							
1	−23.3 ± 2.0	−17.7	5.6 (5.6)	−23.5	−0.2 (−0.2)	−26.4	−3.1 (−3.1)
2	−42.5 ± 2.1	−33.6	8.9 (4.4)	−42.0	0.5 (0.2)	−46.6	−4.1 (−2.0)
3	−57.8 ± 2.1	−48.0	9.8 (3.3)	−56.8	1.0 (0.3)	−63.2	−5.4 (−1.8)
4	−71.7 ± 2.1	−61.0	10.7 (2.7)	−68.7	3.0 (0.8)	−77.7	−6.0 (−1.5)
5	−84.0 ± 2.2	−71.8	12.2 (2.4)	−79.0	5.0 (1.0)	−90.6	−6.6 (−1.3)
6	−94.9 ± 2.2	−82.7	12.2 (2.0)	−87.4	7.5 (1.2)	−103.0	−8.1 (−1.4)
$\Delta_r H°$(calcd) − $\Delta_r H°$(exptl)		mean	9.9	mean	2.8	mean	−5.6
		std dev	2.5	std dev	3.0	std dev	1.8
$\Delta_r H°$(EFP) − $\Delta_r H°$(HF)		mean	7.1				
		std. dev.	1.6				
$SH^- + nH_2O \rightarrow SH^-(H_2O)_n$[e]							
1	−14.2 ± 0.2	−10.8	3.4 (3.4)	−10.6	3.6 (3.6)	−13.6	0.6 (0.6)
2	−26.8 ± 0.4	−21.3	5.5 (2.8)	−20.7	6.1 (3.0)	−26.8	0.0 (0.0)
3	−38.5 ± 0.6	−31.3	7.2 (2.4)	−29.8	8.7 (2.9)	−39.2	−0.7 (−0.2)
4	NA	−42.1	NA	−39.0	NA	−51.9	NA
5	NA	−50.3	NA	−47.4	NA	−64.2	NA
6	NA	−60.8	NA	−55.7	NA	−76.9	NA
$\Delta_r H°$(calcd) − $\Delta_r H°$(exptl)		mean	5.4	mean	6.1	mean	0.0
		std dev	1.9	std dev	2.6	std dev	0.7
$\Delta_r H°$(EFP) − $\Delta_r H°$(HF)		mean	−2.2				
		std dev	1.8				
$Cl^- + nH_2O \rightarrow Cl^-(H_2O)_n$[d]							
1	−14.7 ± 0.6	−11.0	3.7 (3.7)	−11.2	3.5 (3.5)	−13.6	1.1 (1.1)
2	−27.7 ± 0.7	−21.6	6.1 (3.0)	−21.5	6.2 (3.1)	−26.8	0.9 (0.4)
3	−39.5 ± 0.8	−32.7	6.8 (2.3)	−31.3	8.2 (2.7)	−40.4	−0.9 (−0.3)
4	−50.1 ± 0.8	−42.6	7.5 (1.9)	−40.4	9.7 (2.4)	−52.5	−2.4 (−0.6)
5	−59.6 ± 0.9	−50.6	9.0 (1.8)	−47.9	11.7 (2.3)	−62.4	−2.8 (−0.6)
6	−68.4 ± 1.0	−61.2	7.2 (1.2)	−57.0	11.4 (1.9)	−76.2	−7.8 (−1.3)
$\Delta_r H°$(calcd) − $\Delta_r H°$(exptl)		mean	6.7	mean	8.4	mean	−2.0
		std dev	1.8	std dev	3.2	std dev	3.3
$\Delta_r H°$(EFP) − $\Delta_r H°$(HF)		mean	−1.7				
		std dev	1.7				
$Br^- + nH_2O \rightarrow Br^-(H_2O)_n$[d]							
1	−11.7 ± 0.4	−9.5	2.2 (2.2)	−11.1	0.6 (0.6)	−13.3	−1.6 (−1.6)
2	−23.3 ± 0.5	−18.9	4.4 (2.2)	−21.6	1.7 (0.8)	−26.7	−3.4 (−1.7)
3	−34.7 ± 0.6	−29.3	5.4 (1.8)	−32.5	2.2 (0.7)	−41.2	−6.5 (−2.2)
4	−45.7 ± 0.7	−38.7	7.0 (1.8)	−42.3	3.4 (0.8)	−54.2	−8.5 (−2.1)
5	−56.5 ± 0.7	−45.9	10.6 (2.1)	−49.4	7.1 (1.4)	−63.9	−7.4 (−1.5)
6	−66.8 ± 0.9	−56.4	10.4 (1.7)	−59.7	7.1 (1.2)	−78.6	−11.8 (−2.0)
$\Delta_r H°$(calcd) − $\Delta_r H°$(exptl)		mean	6.7	mean	3.7	mean	−6.5
		std dev	3.4	std dev	2.8	std dev	3.6
$\Delta_r H°$(EFP) − $\Delta_r H°$(HF)		mean	3.0				
		std dev	0.7				
Totals							
$\Delta_r H°$(calcd) − $\Delta_r H°$(exptl)		mean	7.6	mean	4.8	mean	−4.6
		std dev	2.6	std dev	3.3	std dev	4.0
$\Delta_r H°$(EFP) − $\Delta_r H°$(HF)		mean	2.2				
		std dev	4.0				

[a] Parenthetical values are errors per H_2O molecule. See the text for details. [b] Experimental values are from ref 2c. [c] Experimental values are from ref 2d. [d] Experimental values are from ref 2e. [e] Experimental values are from refs 2f and 2g.

experimental values were obtained at 298 K.

$$A^-(H_2O)_{n-1} + H_2O \rightarrow A^-(H_2O)_n \quad (n = 1-6;\ A = OH, F, SH, Cl, Br) \quad (1)$$

$$A^- + nH_2O \rightarrow A^-(H_2O)_n \quad (n = 1-6;\ A = OH, F, SH, Cl, Br) \quad (2)$$

For the differential enthalpies of hydration ($\Delta\Delta_r H°$), Table 3 shows that the HF level of theory reproduces the experimental values quite well although they are slightly underbound (total mean error and standard deviation of 1.5 and 1.4 kcal/mol, respectively). The MP2 level offers results (total mean error and standard deviation of −1.3 and 1.8 kcal/mol) comparable to those found at the HF level but which are somewhat

TABLE 5: Differential ($\Delta\Delta_rH°$) and Total ($\Delta_rH°$) Enthalpies of Hydration of OH^- Anion (kcal/mol)[a]

$OH^-(H_2O)_{n-1} + H_2O \rightarrow OH^-(H_2O)_n$			$OH^- + nH_2O \rightarrow OH^-(H_2O)_n$		
n	ΔHF	ΔMP2	n	ΔHF	ΔMP2
1	3.3	5.2	1	3.3	5.2
2	1.1	2.2	2	4.4	7.4
3	1.0	0.6	3	5.4	8.0
4	−0.4	0.0	4	5.0	8.0
5	0.8	0.5	5	5.8	8.5
6	0.2	2.3	6	6.0	10.8
mean	1.0	1.8	mean	5.0	8.0
std dev	1.3	1.9	std dev	1.0	1.8

[a] Single-point energies based upon EFP-optimized geometries. ΔHF = HF//EFP − HF//HF; ΔMP2 = MP2//EFP − MP2//HF. See the text for details.

overbound. Comparing the EFP and HF differential enthalpies reveals that, while agreement is poor for the addition of one water molecule to the OH^- and F^- anions, overall agreement is quite good. This ability of the EFP level to reproduce HF results means that it is also capable of reproducing experimental differential enthalpies. These results imply that the EFP method offers a reliable and inexpensive way of calculating differential enthalpies of hydration for anions with two or more water molecules.

A cursory examination of the HF and MP2 total enthalpies of hydration ($\Delta_rH°$) found in Table 4 reveals that neither of these levels of theory reliably reproduces the experimental data. All but one of the HF enthalpies are underbound, and all but five of the MP2 enthalpies are overbound. The error per water molecule appears to approach some asymptotic value within each cluster series for the two levels of theory, and while this asymptotic value is rather modest, the cumulative effect results in an arithmetic increase in the total error within each series. As will be shown below, this cumulative error cannot be simply attributed to basis set superposition error (BSSE).

As mentioned in the Methods, the current implementation of the EFP method is designed to reproduce results at the RHF/DH(d,p) level of theory. A direct comparison of the EFP and HF total enthalpies clearly shows that the former does not reliably reproduce the latter for the present set of anions. While the mean differences and standard deviations for the SH^-, Cl^-, and Br^- clusters are small, those found for the OH^- and F^- clusters are quite large. Even for the SH^- and Cl^- clusters, the differences increase monotonically with the number of water molecules. Given that the HF level of theory is unable to accurately reproduce experiment, even for cases where there is good agreement between the EFP and HF results, the EFP method is not useful in reproducing experimental total enthalpies of hydration. Note that the largest error with respect to experiment is for the addition of the first water molecule. In fact, if the EFP total enthalpies are recalculated on the basis of the monohydrated cluster

$$A^-(H_2O) + nH_2O \rightarrow A^-(H_2O)_{n+1}\ (n = 1-5) \qquad (3)$$

the total errors with respect to experiment drop precipitously, usually by 50% or more.

On the basis of the above structural results, a model chemistry predicated on EFP-optimized geometries suggests itself. Table 5 lists differential and total enthalpies of hydration for the $OH^-(H_2O)_{1-6}$ clusters, where the enthalpies are derived from single-point calculations at the HF or MP2 levels of theory at EFP-optimized geometries. Comparison of the model and all ab initio results for the differential enthalpies shows good agreement. Here, the mean difference between the RHF/DH(d,p)++//EFP/DH(d,p)++ and RHF/DH(d,p)++//RHF/DH(d,p)++ levels is only 1.0 kcal/mol (standard deviation 1.3 kcal/mol), while the mean difference between the MP2/DH(d,p)++//EFP/DH(d,p)++ and MP2/DH(d,p)++//RHF/DH(d,p)++ levels is 1.8 kcal/mol (standard deviation 1.9 kcal/mol). Clearly, the HF//EFP model results in slightly improved agreement with the HF//HF level; the added cost of the model appears, however, not to be worth the modest improvement especially for $n > 1$ water.

TABLE 6: Differential ($\Delta\Delta_rH°$) and Total ($\Delta_rH°$) Enthalpies of Hydration of $A^-(H_2O)_{5,6}$ Clusters (kcal/mol)[a]

	$A^-(H_2O)_4 + H_2O \rightarrow A^-(H_2O)_5$[b]		$A^-(H_2O)_5 + H_2O \rightarrow A^-(H_2O)_6$		$A^- + 6H_2O \rightarrow A^-(H_2O)_6$	
A^-	ΔHF	ΔMP2	ΔHF	ΔMP2	ΔHF	ΔMP2
OH^-	0.0	4.0	−1.0	4.2	−1.0	8.2
F^-	0.0	3.3	−0.4	1.2	−0.4	4.5
SH^-	−0.8	4.7	−0.9	3.2	−1.7	7.9
Cl^-	−0.4	2.9	−0.5	1.7	−0.9	4.6
Br^-	−0.2	3.8	−0.8	0.7	−1.0	−4.5
mean	−0.3	3.7	−0.7	2.2	−1.0	4.1
std dev	0.3	0.7	0.3	1.5	0.5	5.1

[a] First hydration shell ($n = 4$), ab initio; second hydration shell ($m = 1, 2$), EFP. ΔHF = HF+EFP − HF; ΔMP2 = MP2+EFP − MP2. See the text for details. [b] The Δ values for the differential and total enthalpies are the same for the five water clusters.

With respect to the total enthalpies, the mean difference between the RHF/DH(d,p)++//EFP/DH(d,p)++ and RHF/DH(d,p)++//RHF/DH(d,p)++ results is 5.0 kcal/mol (standard deviation 1.0 kcal/mol). The agreement between the MP2/DH(d,p)++//EFP/DH(d,p)++ and MP2/DH(d,p)++//RHF/DH(d,p)++ levels is equally poor (mean difference 8.0, standard deviation 1.8 kcal/mol). These comparisons clearly demonstrate that the model chemistry (i.e., HF and MP2 single points at EFP geometries) does not reproduce the target levels of theory for total enthalpies. (See ref 23 for a comparison of the model with experiment.)

A further question that naturally arises is whether the EFP method is capable of describing the second hydration shell. Table 6 lists the differential and total enthalpies of hydration for the $OH^-(H_2O)_{5,6}$ clusters in which the first shell ($n = 4$) is treated ab initio while the second shell ($m = 1, 2$) is modeled via effective fragment potentials. With the present basis set, DH(d,p)++, each substitution saves 31 basis functions. Given the inconsistency of the HF level in reproducing experimental results (i.e., reproduction of experimental total enthalpies is poor), the most meaningful comparisons, to measure the success of the model, are between the results of the mixed EFP/ab initio calculations and those performed all ab initio. The mean difference between the two sets of calculations at the HF level is a mere −0.6 kcal/mol (standard deviation 0.5 kcal/mol), indicating excellent agreement between the mixed and all ab initio approaches. The agreement is not as good between the mixed and complete calculations at the MP2 level (mean difference 3.9, standard deviation 3.5 kcal/mol). On the basis of these somewhat limited findings, the use of effective fragment potentials to model second, third, etc. hydration shells appears to be a viable cost-saving approach to reproducing all ab initio results very closely. (See ref 24 for a comparison of the model with experiment.)

In an attempt to ascertain the source of error associated with the EFP results with respect to those obtained at the HF level of theory, reduced variational space (RVS) energy decomposi-

TABLE 7: RVS Energy Decomposition Performed at the RHF/DH(d,p)++ Level of Theory for the $OH^-(H_2O)_{1-6}$ and $Br^-(H_2O)_{1-6}$ Clusters[a]

n	ES/EX	POL	CT	BSSE	total	$\Delta_rH°$	error	$\Delta_rH°$(CP)	error
				$OH^-(H_2O)_n$					
1	−7.1	−11.1	−8.7	−0.6 (−0.6)	−27.5	−22.9	3.6	−22.3	4.2
2	−19.4	−17.8	−12.0	−1.2 (−0.6)	−50.4	−42.0	2.1	−40.8	3.3
3	−33.3	−20.6	−12.8	−1.8 (−0.6)	−68.5	−57.6	2.7	−55.8	4.5
4	−49.7	−20.0	−11.2	−2.7 (−0.7)	−83.6	−69.6	2.7	−66.9	5.4
5	−55.1	−24.0	−13.9	−3.2 (−0.6)	−96.2	−79.5	4.3	−76.3	7.5
6	−64.6	−25.1	−15.2	−4.2 (−0.7)	−109.1	−88.6	6.4	−84.4	10.6
						mean	3.6	mean	5.9
						std dev	1.6	std dev	2.7
				$Br^-(H_2O)_n$					
1	−7.9	−1.6	−1.8	−1.2 (−1.2)	−12.5	−11.1	0.6	−9.9	1.8
2	−15.9	−3.2	−3.8	−2.5 (−1.3)	−25.4	−21.6	1.7	−19.1	4.2
3	−24.6	−4.9	−5.5	−4.1 (−1.4)	−39.1	−32.5	2.2	−28.4	6.3
4	−32.8	−6.5	−6.6	−5.5 (−1.4)	−51.4	−42.3	3.4	−36.8	8.9
5	−38.7	−7.4	−7.6	−6.3 (−1.3)	−60.0	−49.4	7.1	−43.1	13.4
6	−46.1	−9.8	−9.7	−8.3 (−1.4)	−73.9	−59.7	7.1	−51.4	15.4
						mean	3.7	mean	8.3
						std dev	2.8	std dev	5.3

[a] Total = electrostatic/exchange (ES/EX) + polarization (POL) + charge transfer (CT). BSSE = basis set superposition error. CP = counterpoise-corrected. Parenthetical values correspond to the energy per H_2O molecule. All energies in kilocalories per mole. See the text for details.

tions[25] were performed at the HF level of theory for the $OH^-(H_2O)_{1-6}$ and $Br^-(H_2O)_{1-6}$ clusters. Along with an estimate of the basis set superposition error (BSSE), electrostatic/exchange (ES/EX), polarization (POL), and charge-transfer (CT) components of the total interaction energy are listed in Table 7. The charge-transfer component makes a significant contribution to the total interaction in the OH^- systems; this is especially true for the smaller clusters. As the charge-transfer component of the effective fragment potential for the water molecule was derived from a series of calculations on the water dimer, where it makes a minor contribution to the total interaction energy, it is not surprising that the current implementation is incapable of describing systems exhibiting a large amount of charge transfer. Further support for this conclusion is obtained from an examination of the differential charge-transfer values, i.e., $\Delta CT = CT(n + 1) - CT(n)$, for $OH^-(H_2O)_{1-6}$. For the first water the charge-transfer difference is large, and for the second water it is much smaller but remains significant ($\Delta CT(1,0) = -8.7$ kcal/mol, $\Delta CT(2,1) = -3.3$ kcal/mol). For the subsequent addition of water molecules, the charge-transfer differences amount to no more than a couple of kilocalories per mole. This appears to lead to poor agreement between the EFP and HF differential enthalpies of hydration for the one water case and very good agreement for two to six waters (see Table 3). For the Br^- clusters, the agreement of the EFP and HF results is consistently good for one to six waters. Charge transfer in the Br^- case makes a much smaller contribution to the overall interaction ($n = 1$, CT $= -1.8$ kcal/mol), and the charge-transfer differences are small for the whole range of waters. In our previous work on alkali-metal/alkaline-earth-metal cation−water systems,[12] the charge-transfer component of the effective fragment potentials was also found to be suspect for the $Mg^{2+}(H_2O)_{1-6}$ and $Ca^{2+}(H_2O)_{1-6}$ clusters. Alternative schemes for the description of charge transfer are currently being investigated in our laboratory and others.

Finally, basis set superposition error is of minor importance for the current systems, averaging only −0.6 kcal/mol per water molecule in the OH^- clusters. As such, BSSE does not contribute in a major way to the errors seen for the total enthalpies of hydration at the HF level. A slightly larger BSSE was found for the Br^- clusters (mean −1.3 kcal/mol per water molecule). The inclusion of a counterpoise-type correction actually leads to a larger mean error and standard deviation. More importantly, the error associated with basis set incompleteness cannot account for the error with respect to the experimental total enthalpies.

Conclusions

Both the HF and MP2 levels of theory accurately reproduce the experimental differential enthalpies of hydration for the anions studied. For two to six water molecules, the EFP method duplicated the HF values closely, and consequently, the EFP method also proved successful in reproducing the experimental data. The EFP method appears to be a cheap and reliable alternative to all ab initio calculations of differential enthalpies of hydration for simple anions by small numbers of water molecules. It is clear, however, on the basis of the results of this study, that the EFP method should not be used to model the anion−single water systems $OH^-(H_2O)$ and $F^-(H_2O)$.

Experimental total enthalpies of hydration are notoriously difficult to reproduce via computational methods. Neither the HF nor MP2 levels of theory proved capable of reliably reproducing the experimental data. Furthermore, the EFP method was found to be unable to consistently duplicate the HF values, especially for the OH^- and F^- systems. Even when the agreement between the EFP and HF results is good, the EFP method should not be used to determine total enthalpies of hydration for anionic systems as the HF level itself does not consistently reproduce experiment.

As the EFP and HF geometries were found to be in fairly close agreement with each other, a model chemistry based upon HF and MP2 single-point energies at EFP geometries was proposed. As might have been expected, this approach reproduced the all ab initio differential enthalpies extremely well. The approach did, however, fail to reproduce the all ab initio total enthalpies of hydration. Due to the limited improvement in the results, such a model chemistry does not appear to be warranted.

A second model chemistry was also examined in which the first hydration shell was treated ab initio and the second one with effective fragment potentials. This model chemistry resulted in excellent agreement with the all ab initio results for both the differential and total enthalpies of hydration. This model chemistry does, therefore, seem to be a reliable and inexpensive way of reproducing all ab initio calculations for small anion−water clusters.

Reduced variational space analyses of the HF wavefunctions for these anion−water systems suggests that the worst agreement between the EFP and HF calculations occurs when large amounts of charge transfer are present. This appears to explain why the EFP is unable to accurately reproduce HF results for $OH^-(H_2O)$ and $F^-(H_2O)$. It is also consistent with our previous results for alkali-metal/alkaline-earth-metal cation−water systems. Finally, basis set superposition error does not appear to be a factor in the failure of the HF level of theory to reproduce experimental enthalpies of hydration for some of the anion−water systems. This result is in contrast with our earlier findings for the aforementioned cation−water systems.

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Supporting Information Available: Tables 1S, proton affinities; 2S, $A^-(H_2O)$ structural data; 3S, $A^-(H_2O)_2$ structural data; 4S, $A^-(H_2O)_3$ structural data; 5S, $A^-(H_2O)_4$ structural data; 6S, A^- $(H_2O)_5$ structural data; 7S, $A^-(H_2O)_6$ structural data; 8S, differential enthalpies at 298.15 K; and 9S, total enthalpies at 298.15 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Upon correction of the differential enthalpies to 298 K (see Table S8 in the Supporting Information), slight reductions in the mean error with respect to experiment were seen at the EFP (1.7 (0 K) vs 1.0 (298 K) kcal/mol) and HF (1.5 (0 K) vs 0.9 (298 K) kcal/mol) levels of theory, while a modest increase was found at the MP2 level (−1.3 (0 K) vs −2.2 (298 K) kcal/mol). The standard deviations were essentially unchanged upon temperature correction for all three levels. Similar results were found when the total enthalpies were corrected to 298 K (see Table 9S in the Supporting Information); the mean error with respect to experiment dropped at the EFP (2.2 (0 K) vs 2.0 (298 K) kcal/mol) and HF (4.8 (0 K) vs 2.6 (298 K) kcal/mol) levels of theory, while this mean error increased at the MP2 level (−4.6 (0 K) vs −6.8 (298 K) kcal/mol). Again, the standard deviations were little changed. Furthermore, comparing the EFP and HF results at the two temperatures reveals little mean difference between the two (2.2 (0 K) vs 2.2 (298 K) kcal/mol). The standard deviations are identical (4.0 kcal/mol).

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(23) A comparison of the model results with the experimental differential enthalpies of hydration shows that the HF//EFP single-point calculations lead to larger errors than those obtained with EFP//EFP. The MP2//EFP single points lead to a slight improvement in both the mean error and standard deviation. With respect to the experimental total enthalpies, the HF//EFP single-point calculations offer no improvement over the EFP//EFP results; in fact, the mean error (8.6 kcal/mol) and standard deviation (2.2 kcal/mol) actually increase. The MP2//EFP single-point calculations lead to a dramatic improvement (mean error and standard deviation of only 1.2 and 3.1 kcal/mol, respectively). Solely on the basis of comparison with experiment, these results are superior to those obtained at the MP2/DH(d,p)++//RHF/DH(d,p)++ level (mean −6.8 kcal/mol, standard deviation 4.7 kcal/mol). However, this is fortuitous, and any optimism about these results must be tempered by the fact that, with increasing numbers of water molecules, the enthalpies appear to be trending toward overbinding ($n = 1$, error 5.5 kcal/mol; $n = 6$, error −2.1 kcal/mol). Such a model chemistry must, therefore, be exercised with caution for larger ($n \geq 7$)

clusters. Given the added expense associated with these calculations together with the inconsistent results, single-point energies (even correlated ones) at the EFP geometries do not appear to be warranted for these small anion−water clusters.

(24) At the HF level, the total enthalpies are found to have even a slightly lower error with respect to experiment (7.6 vs 7.1 kcal/mol); at the MP2 level, the total enthalpies are much better (−8.4 vs −4.0 kcal/mol). Differences for the differential enthalpies are much smaller, with the mixed approaches leading to results very similar to those predicted all ab initio.

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