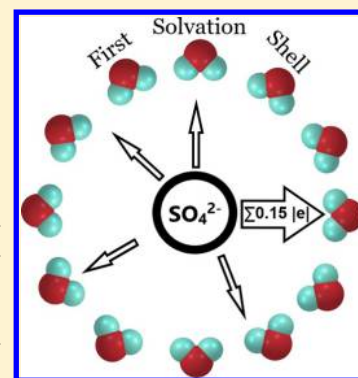


Hydrated Sulfate Clusters $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ ($n = 1-40$): Charge Distribution Through Solvation Shells and Stabilization

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Supporting Information

ABSTRACT: Investigations of inorganic anion SO_4^{2-} interactions with water are crucial for understanding the chemistry of its aqueous solutions. It is known that the isolated SO_4^{2-} dianion is unstable, and three H_2O molecules are required for its stabilization. In the current work, we report our computational study of hydrated sulfate clusters $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ ($n = 1-40$) in order to understand the nature of stabilization of this important anion by water molecules. We showed that the most significant charge transfer from dianion SO_4^{2-} to H_2O takes place at a number of H_2O molecules $n \leq 7$. The SO_4^{2-} directly donates its charge only to the first solvation shell and surprisingly, a small amount of electron density of $0.15|e|$ is enough to be transferred in order to stabilize the dianion. Upon further addition of H_2O molecules, we found that the cage effect played an essential role at $n \leq 12$, where the first solvation shell closes. During this process, SO_4^{2-} continues to lose density up to $0.25|e|$ at $n = 12$. From this point, additional water molecules do not take any significant amount of electron density from the dianion. These results can help in development of understanding how other solvent molecules could stabilize the SO_4^{2-} anion as well as other multicharged unstable anions.



INTRODUCTION

Hydrates of the sulfate dianion SO_4^{2-} play a significant role in chemistry and biochemistry where they appear as units of solutions and molten substances. This textbook compound occurs in drinking water, soils, and atmospheric aerosols.¹ While sulfate aggregates participate in earth processes such as cloud formation,² hydrated sulfate minerals were even detected on the Martian surface³ meaning sulfate ubiquity through the solar system. Moreover, sulfate dianion is also known as strong kosmotropic molecule in terms of Hofmeister series.⁴ Because of the strong intramolecular Coulomb repulsion of the two excess charges, an isolated sulfate dianion was shown to be unstable,⁵⁻⁷ whereas it is stabilized in the condensed phase by solvation in solution or counterions in solid. As for the gas phase, Blades and Kebarle⁶ observed stable hydrated sulfate clusters with four additional water molecules. Then, Wang and co-authors made a game changing discovery revealing that only three water molecules are necessary for sulfate dianion stabilization.⁷ Further study was continued in series of recent experimental and theoretical works on the structure and stability of the solvated sulfate dianion.⁸⁻²⁴

These intriguing systems deserved much attention in the scientific community and, no doubt, they bear interesting chemical and physical properties, and many of them are not studied yet. In the present work, we report our computational study of charge distribution in $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ ($n = 1-40$)

clusters. We show that the most significant charge transfer takes place at $n < 7$. Though even above this value, SO_4^{2-} still donates a certain amount of the charge to water molecules; such transfer is not so intense, and the cage effect is mostly responsible for further stabilization. It is well known that the sulfate dianion becomes stable only at $n = 3$. However, we performed calculations both for $n = 1$ and 2 in order to track how the charge distribution behaves from the quantum mechanical point of view.

COMPUTATIONAL METHODS

For $n = 1-3$ $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$, we used the Coalescence Kick procedure to obtain low lying isomers. Coalescence Kick was designed to carry out unbiased machine search of global minimum (GM) on the potential energy surface out of the large set of initial structures. Within this procedure, we used the PBE0²⁵ level of theory and the 6-31+G* basis set.²⁶ For $\text{SO}_4^{2-}(\text{H}_2\text{O})$, $\text{SO}_4^{2-}(\text{H}_2\text{O})_2$, and $\text{SO}_4^{2-}(\text{H}_2\text{O})_3$, we searched out of 5000 initial geometries, and then, we selected five lowest lying isomers within 20.0 kcal/mol from GM. In these calculations, we chose water molecules and sulfate as stable subunits and searched for structures where water molecules

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and sulfate are randomly distributed in a cube. After that, we reoptimized them at the more sophisticated PBE0/aug-cc-pVDZ²⁷ level of theory. Relative energies of the lowest isomers were calculated within the PBE0/aug-cc-pVTZ level of theory including zero-point energy correction. The resulting geometries of these three stoichiometries were not surprising: hydrogens of water molecules form double hydrogen bonds with oxygen atoms of the sulfate anion [Figure 1].

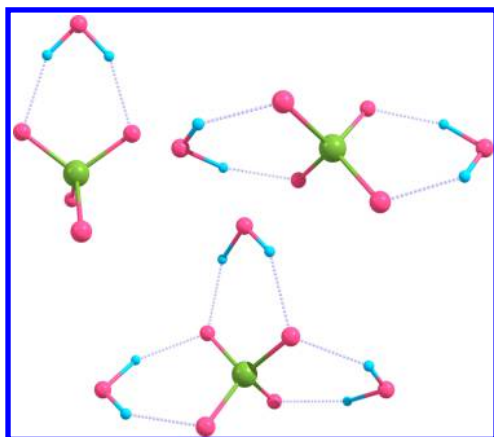


Figure 1. $\text{SO}_4^{2-}(\text{H}_2\text{O})$, $\text{SO}_4^{2-}(\text{H}_2\text{O})_2$, and $\text{SO}_4^{2-}(\text{H}_2\text{O})_3$ structures. Hereinafter, S atoms are green, O atoms are red, and H atoms are blue. Dotted lines indicate H bonds.

Geometries of clusters with $n = 4-7$ were taken from the work of Boldyrev and Wang²⁸ and co-workers and then reoptimized within the PBE0/aug-cc-pVDZ level of theory. We took geometries of clusters with larger $n = 8-40$ from the comprehensive investigation of Johnston and co-workers.²⁹ The overall methodology of obtaining these clusters is described in detail in their work. We also reoptimized these structures at the PBE0/aug-cc-pVDZ level of theory, and no significant changes were observed. After that, we performed NBO analysis³⁰⁻³² within the PBE0/aug-cc-pVTZ method. This procedure allows us to extract plenty of information from structures including unit charges which are issues of interest in the present work. By means of AdNDP analysis,^{33,34} which is an extension of NBO, we examined the pathway of charge distribution through solvation shells. Additionally, we constructed a classical physics model of SO_4^{2-} stabilization with the cage effect. We replaced every atom of the water molecule with point charges (positive on hydrogens and negative on oxygens). The values of charges were taken by the way they would perform the same dipole moment as a solitary water molecule. Then, vertical detachment energies of such systems were calculated. All calculations mentioned were performed using the Gaussian09 package.³⁵

RESULTS AND DISCUSSION

In Figure 2, we present the dependence of the amount of the negative charge located on the sulfate dianion on the number of water molecules in the cluster. We can see that the most intense charge transfer from sulfate to water molecules takes place at $n \leq 7$ and even above this number, the charge still decreases until $n = 10$ but in a less degree. Intuitively, we expected a hyperbolic further character of this curve, assuming that SO_4^{2-} will donate less and less charge to additional water molecules. However, the results were much more surprising

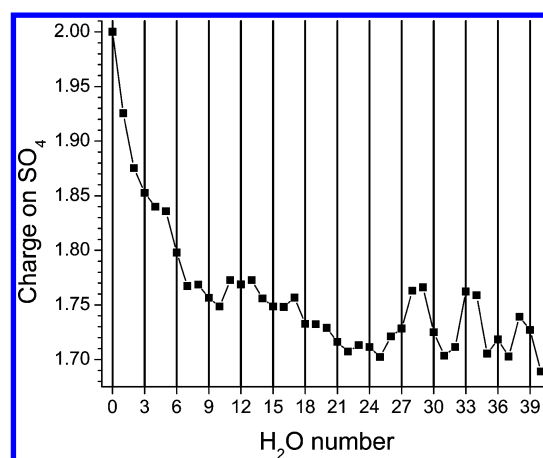


Figure 2. Dependence of the sulfate charge on the water molecule number.

than we initially guessed. Clusters with $n = 11, 12,$ and 13 form a plateau which is higher than neighboring charge values for $n = 10$ and $n = 14$. After this pretty flat region, we can observe charge decreasing in range $n = 14-22$.

The same curve pattern can be found in Figure 3, where we present data on the mean hydrogen bond length between water molecules and sulfate. At $n \geq 8$, these two graphs explicitly correlate with each other.

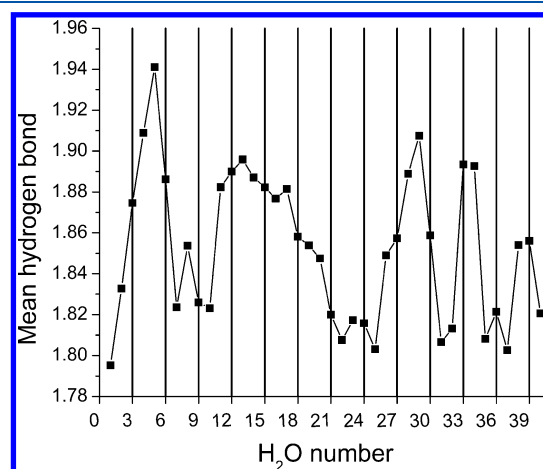


Figure 3. Mean hydrogen bond length between water molecules and the sulfate ion, $r_{\text{O}^{\text{H}_2\text{O}}^{\text{SO}_4}^{\text{MS}}}$, for the putative global minimum structures of $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ clusters as a function of the number of water molecules, n .

At the same time, at $n \leq 7$, the charge monotonously goes from the sulfate molecule without any peaks, and a pretty large slope in Figure 2 does not correlate with the graph in Figure 3. This leads us to the conclusion that the stabilization of the sulfate dianion by charge transfer is the most pronounced at $n \leq 7$ because this molecule donates its charge so willingly in these clusters. Though the charge still transfers from the sulfate to water at some regions on Figure 2 for higher n , it obviously correlates with the mean hydrogen bond length and is a side effect of the orientation. Based on the NBO analysis, and the well-known fact that three water molecules are necessary for SO_4^{2-} stabilization, it can be concluded that about 0.15|e| should migrate from the dianion in order to make it stable. After complete reoptimization at the PBE0-D3³⁶ and B3LYP-

D3³⁷ levels of theory, we can see that this value is independent of the functional used. Inclusion of empiric Grimme's dispersion correction also did not affect charge distribution. Although local density may depend on the partitioning mechanism, we believe that the time-tested NBO localization scheme is the most suitable for this study. However, the exact value of $0.15|e|$ should be comprehended in a more qualitative way, pointing out that even slight charge transfer makes the SO_4^{2-} dianion stable. In sum, one may consider this result the following way: delocalization of about $0.15|e|$ within the NBO scheme is needed in order to make the SO_4^{2-} dianion stable.

Therefore, the so-called cage effect is mostly responsible for further stabilization of bigger clusters and greater n values. In Figure 4, we present our classical physics approximation of

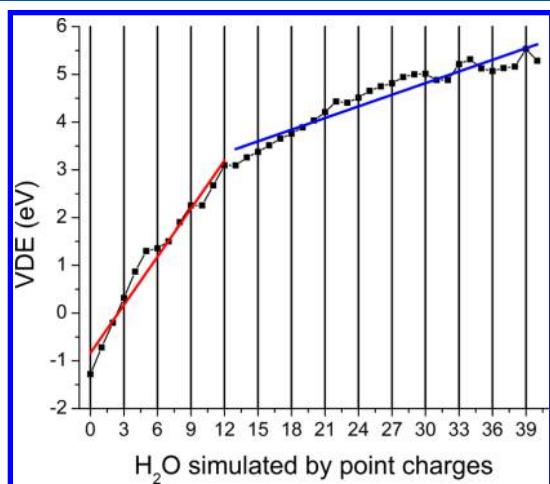


Figure 4. VDE of system SO_4^{2-} with point charges in respect to the number of modeled water molecules. Red line: linear fitting of $n = 0-12$ region. Blue line: linear fitting of $n = 13-40$ region.

sulfate stabilization by the presence of point charges which mimic the solitary water dipole moment. The charge transfer does not occur in such systems.

We consider the stability in terms of vertical detachment energies (VDEs). As it is depicted in Figure 4, the cage effect has the most significant influence on the system at $n \leq 12$, where the first solvation shell is closed. Red and blue lines are linear fitting curves for $n = 0-12$ and $n = 13-40$, respectively. Obviously, there is a noticeable difference in slopes which indicates a decrease in further stabilization rate. Results of calculations including Grimme's dispersion corrections³⁶ at the PBE0-D3 and B3LYP-D3³⁷ levels of theory are identical with ones obtained within the PBE0 functional (see the Supporting Information).

One more important result was obtained using AdNDP analysis. We examined electron density transfer through the first, second, and third solvation shells in terms of occupation numbers (ONs) using a direct search procedure implemented in the AdNDP program. A comprehensive manual for this procedure can be found in the work of Boldyrev and co-workers.³⁸ We defined the first solvation shell as water molecules which are directly bonded to the SO_4^{2-} dianion. The second solvation shell is a set of water molecules which are connected by hydrogen bonds to H_2O molecules from the first solvation shell and are not directly attracted by the sulfate dianion. The third one is defined by water molecules attracted neither by the sulfate dianion nor by the first solvation shell

but by water molecules from the second shell. We treated the amount of the donated charge in terms of ON of multicentered bonds in comparison with ON of one-centered lone pair of oxygen. Let us discuss our observations for the $\text{SO}_4^{2-}(\text{H}_2\text{O})_{18}$ cluster as an example. As for the first shell, three water molecules are attributed to each oxygen atom of sulfate. As for the second shell, we defined a water molecule attributed to certain oxygen of sulfate if at least two out of three atoms in H_2O are closer to this sulfate oxygen than to the rest of sulfate oxygen atoms. Solvation shells attributed to a selected oxygen atom and the whole cluster are depicted in Figure 5. Detailed calculations are placed in the Supporting Information.

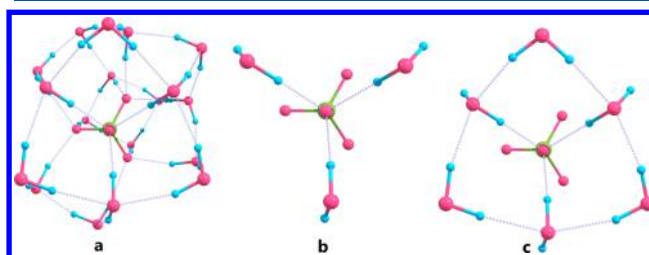


Figure 5. (a) $\text{SO}_4^{2-}(\text{H}_2\text{O})_{18}$ cluster; (b) first solvation shell attributed to one oxygen atom; (c) first and the second solvation shell attributed to one oxygen atom.

Because solvation shells are explicitly determined now, we can examine the evolution of electron density distribution through them. In Table 1 we present ONs for two valence lone

Table 1. ON of Multicentered Bonds

	ONs	
	1st lone pair	2nd lone pair
oxygen atom	1.872	1.865
oxygen atom + attributed first solvation shell (Figure 5b)	1.897	1.894
oxygen atom + attributed first solvation shell + attributed second solvation shell (Figure 5c)	1.897	1.894
oxygen atom + attributed second solvation shell	1.872	1.865

pairs of one selected sulfate oxygen under different calculation conditions:

- (1) Lone pairs of oxygen without taking into account any water molecules;
- (2) Lone pairs of oxygen with contribution from water molecules of the first solvation shell attributed to this oxygen (which also can be interpreted as the multicenter bond);
- (3) Both the first- and the second-attributed solvation shells are taken into account;
- (4) Lone pairs of oxygen plus the second solvation shell.

Based on data presented in Table 1, we can conclude that only the first solvation shell significantly contributes into the ONs. Therefore, the direct $\text{SO}_4^{2-} \rightarrow \text{H}_2\text{O}$ charge transfer occurs only between the dianion and the first solvation shell. In other words, once the first solvation shell is closed, the residual charge distribution on higher order shells, which is much less in its intensity, takes place as first-to-second and second-to-third solvation shell transitions but not as direct dianion-to-second or dianion-to-third shell transitions. Taking into account this result, and also the fact that the most intense

charge transfer takes place at $n \leq 7$ and the cage effect plays an important role at $n \leq 12$, many important investigation modeling behavior or stability of sulfate in aqueous solutions might be substantially accelerated according to our results.

CONCLUSIONS

The SO_4^{2-} dianion and its water clusters attract a considerable interest of researchers. In the present work, we studied the charge distribution and its effect on stabilization of local water clusters formed by sulfate dianion SO_4^{2-} . We showed that the most significant charge transfer takes place in clusters $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ with $n \leq 7$ where the unstable SO_4^{2-} dianion intensively donates its charge to water molecules in order to weaken the Coulomb repulsion of its two extra electrons. Though this compound continues to donate its charge to water in clusters with $n \geq 7$, this transition is not so intense, and the pattern of the charge curve explicitly correlates with the dependence of the mean hydrogen bond length on the number of water molecules at $n \geq 7$. According to NBO analysis, the donation of about 0.15|e| to water molecules is enough to make the dianion stable. However, one should bear in mind that atomic charges are not rigorously determined and may depend on the partition scheme. Therefore, this value can be used as a guide for assessing how many other solvent molecules are necessary for SO_4^{2-} stabilization.

Additionally, we performed calculations of sulfate dianion stability to vertical detachment of the electron. Using the classical physics model in which charge transfer does not occur and water molecules are simulated by point charges, we showed that the cage effect plays an important role in stabilization at $n \leq 12$ and is not significant at larger n . AdNDP analysis revealed that the sulfate dianion donates its charge directly and intensively only to the first solvation shell. The further charge distribution (which is not so essential) occurs via shell-shell interactions. We believe that these results could be used as a receipt for biochemical, environmental, and even outer space studies and significantly accelerate them.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b01744.

Details of the AdNDP analysis, VDEs calculated with Grimme's dispersion correction and Cartesian coordinates of all calculated structures (PDF)

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Notes

The authors declare no competing financial interest.

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