

Amphoteric Nature of Water is a reflection of change of molecular polarizability – A Theoretical Justification

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Abstract

From laboratory to simple as well as complex biological systems, it is water that plays the most important role as reaction medium. Even many organic reactions in laboratory, popularly done in organic solvents so far, are now being run in aqueous medium, giving rise to a new branch of Chemistry known as Green Chemistry. This has been possible due to a very 'flexible' nature of water, actually the manifestation of some physico-chemical properties at the molecular level. One such property is the molecular polarizability. The molecular polarizability depends on the molecular size of a single water molecule. The aim of present work is to focus on the amphoteric nature of water molecule in terms of polarizability, a size dependent physico-chemical property of water molecule in predominantly ionic and predominantly covalent form.

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1. Introduction

Water is amphoteric, i.e. it exhibits flexibility to act as an acid or a base in different cases. Whatever may be the explanation, it is the reorganization of electronic charge around the water molecule that enables it to act as acid or base in different cases. This reorganization or reorientation of electronic charge around the molecule results from the response of the electronic charge cloud to the external field, which is generally weak in molecular domain. This response is a very important fundamental property of water molecule, known as polarizability. So far, when talking about chemical, physical and physico-chemical processes occurring in aqueous medium, we are interested in the 'bulk' properties of water than in properties of discrete water molecules. However, bulk properties of water are the manifestation of one or more microscopic properties at the molecular level. Molecular size plays an important role behind such molecular properties.

The absolute size of a single water molecule is a matter that merits further consideration as many size dependent physico-chemical properties at molecular level are responsible for one or more bulk properties of water. We have a knowledge of experimental molecular volume of water as estimated from its density at certain temperature and pressure and number of molecules present in the specified volume. Nonetheless, that cannot exclude the effect of environment. The present attempt calculates the absolute size of water molecule theoretically by (i) considering its tetrahedral structure, and (ii) proposing an ellipsoidal model of electronic charge distribution around the water molecule exploiting the absolute radii of H and O atoms. These absolute atomic radii have been calculated earlier adopting Slater's idea [1]. We designate the theoretically calculated size of water molecule as 'environment-independent absolute size' of water molecule.

Further, relying upon volume-polarizability linear relationship, the polarizability of water molecule has been calculated as a function of molecular size in predominantly covalent as well as ionic forms and has been used to explain and correlate the amphoteric behavior with the covalent and ionic forms of water molecule. It is evident that when water molecule acts as base, its electrons are prone to be donated, i.e. it is much more

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polarizable than when it acts as an acid and ready to accept electrons. The polarizability of a single water molecule has been calculated by exploiting the evaluated 'environment-independent' absolute size of water molecule.

2. Method

The present work involves the calculation of water molecule in two different methods.

Firstly, I have modeled the electronic charge distribution forms an ellipsoid considering the 'bent' structure of water molecule. The half of major axis (a), half of minor axis (b) and the height of the ellipsoid have then been calculated using absolute radii of H and O atoms [1] Then the volume of the water-ellipsoid has been calculated exploiting the absolute radii of H and O.

From the ratio of the volume of water-ellipsoid and the sum of the volume occupied by two H atoms and one O atom a factor is obtained which has been justifiably defined as the quantitative measure of delocalization of electronic charge cloud due to the formation of water molecule (monomer) from two H and one O atoms.

In the second method, the volume of the water molecule (monomer) has been calculated by considering its tetrahedral structure that results from sp^3 hybridization of O atom. The edge length of the regular tetrahedron has been calculated from O-H bond length of 1.029 Å [2] and the regular tetrahedral bond angle of H-O-H, i.e., 109.5°.

Finally, the radius of the equivalent sphere having the same volume as that of the water-ellipsoid has been calculated and is used to evaluate the isotropic polarizability of water molecule theoretically.

2.1 Calculation of molecular size:

Slater [3,4,5] argued that there must be a connection between empirically determined atomic and ionic radii with the wavefunctions of atoms and ions. He pointed out the existence of a significant relation between the atomic and ionic radii and the distance of maximum charge density in the outermost shell of the atom or ion. To be more precise, the distance of the principal maxima of the radial charge density distribution function of the outermost electron from the nucleus of an atom or ion may be considered as its theoretical atomic radius. Relying upon Slater's definition, the absolute radii for atoms of 103 elements has been calculated theoretically [1]. In the present work, the theoretical radii of O and H from that work [1] has been exploited to calculate the volume of water-ellipsoid.

As the mass of any molecule is high, compared to their sizes, all molecules are considered to be spherical. However, in the present work, I attempt to portray the structure of molecule in more details as the primary interest lies in the size of a discrete water molecule. To this end, I have included the bent structure (consequence of sp^3 hybridization of O atom) and eventually the electronic distribution around the molecule has been considered to be ellipsoidal in shape.

The volume of an ellipsoid is given by the formula

$V = \frac{4}{3}\pi a b c$, where, a = the half of the major axis, b = the half of the minor axis and c = the half of the height.

Considering the free rotation of water molecule about C_2 axis, I have modeled the water-ellipsoid having $a = b \neq c$, in which 'a', and 'c' are approximated as follows:

Due to normal modes of vibration of O-H bonds, the O atom bounces up and down so that there is an equilibrium between two ellipsoids having same 'a' and 'b' but different c. In two extreme cases, $c = r_O$ (for ellipsoid I, Figure 1.) and $c = 2r_O$ (for ellipsoid II, Figure 2.)

In the first ellipsoid,
 $a = b = 2r_H = 1.0584 \text{ \AA}$

and $c = r_O = 0.4652 \text{ \AA}$

and in the second ellipsoid,

$a = b = 2r_H = 1.0584 \text{ \AA}$

and $c = 2r_O = 0.9304 \text{ \AA}$

where r_O and r_H are the absolute radii of Oxygen and Hydrogen atoms respectively. As in both of the above the cases $c < a$, both the ellipsoids are 'oblate spheroids'.

I propose that the actual ellipsoid should be the 'resonance' of these two, and so I calculated the volume of both the oblate spheroids and then took the average of two.

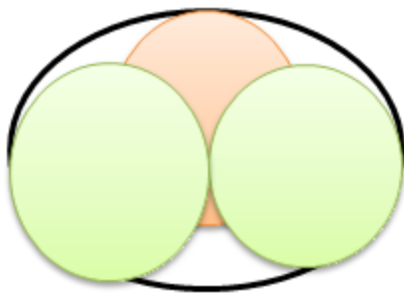


Figure 1. Ellipsoid I

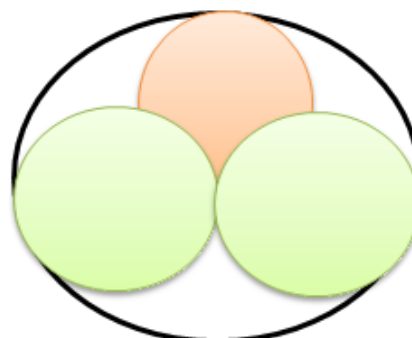


Fig.2. Ellipsoid II

The volume of the water-ellipsoid was calculated as:

For the first ellipsoid,

$$(V_{\text{ellipsoid}})_I = \frac{4}{3}\pi a b c = \frac{4}{3}\pi a^2 c = 2.18375 \text{ \AA}^3$$

For the second ellipsoid,

$$(V_{\text{ellipsoid}})_{II} = \frac{4}{3}\pi a b c = \frac{4}{3}\pi a^2 c = 4.3675 \text{ \AA}^3$$

$$\text{So, } V_{\text{ellipsoid}} = \frac{1}{2}[(V_{\text{ellipsoid}})_I + (V_{\text{ellipsoid}})_{II}] = 3.275625 \text{ \AA}^3$$

The sum of volume occupied by two H and one O atoms, which has been calculated using the absolute radii [1] is 1.6640 \AA^3

It is seen that the volume of water ellipsoid is greater than the sum of volume occupied by two H and one O atoms in space. This is because of the linear combination of atomic orbitals of two H atoms and one O atoms gives rise to the molecular orbitals that occupy much larger volume in space due to the delocalization of electronic charge around the water molecule and we find that the volume of ellipsoid is 1.9685 times greater than the sum of the volumes of two H and one O atoms. This factor is the quantitative index of electronic charge delocalization and also represents the inhomogeneity of the electronic charge cloud around the molecule.

I define this factor as the proportionality constant in polarizability-size relationship as this gives the quantitative idea of extent of increase in delocalization of electronic charge around the water molecule due to the formation of molecular orbital (wavefunction) from atomic orbitals (wavefunctions).

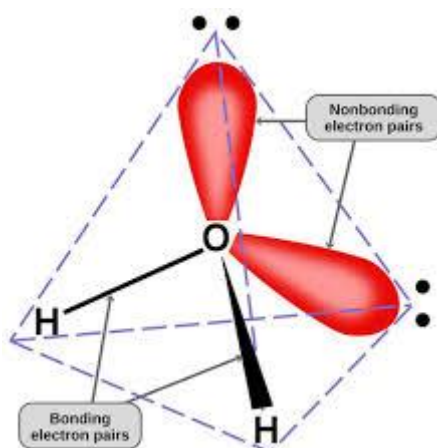


Figure 3. Tetrahedral Water Molecule (Image courtesy: Google, URL1)

Next, I calculate the volume of water-tetrahedron. The O-H bond-length is taken from the work of Ghosh *etal*[2] as 1.029 \AA and the bond angle is taken as 109.5° , which is the normal bond angle in a regular tetrahedron.

The edge length of the regular tetrahedron is given by:

$$l = 2[\text{O-H bond length} \times \cos(90^\circ - 0.5 \text{ of H-O-H bond angle})]$$

$$= 2[1.029 \times \cos(90^\circ - 0.5 \text{ of } 109.5^\circ)]$$

$$= 1.6806 \text{ \AA}$$

The volume of the tetrahedron

$$V_{\text{Tetrahedron}} = l^3 / (6\sqrt{2}) = 0.559538 \text{ \AA}^3$$

This is the volume of the water-tetrahedron that is formed due to the sp^3 hybridization of O atom that leads to the formation of four sp^3 hybrid orbital in space, the angle between each two being 109.5° . As there are two lone pairs of electrons present in the molecule, the structure of the water molecule becomes ‘bent’ having H-O-H angle reduced to 104.5° due to larger lone pair-lone pair repulsion. Though the actual equivalent H-O-H angle is 104.5° , the justification of taking the bond angle as 109.5° in calculation is that, the sp^3 hybridization of O atom gives rise to four sp^3 hybrid orbitals that are oriented in space as a regular tetrahedron. I have easily calculated the edge-length from which the volume of the regular tetrahedron has been calculated. Though there is a shrinkage in H-O-H bond angle due to larger lone pair-lone pair repulsion, there is a proportional increase in other three angles leaving the volume of the tetrahedron same as that of the regular tetrahedron. As in the ellipsoid model, the actual ‘bent’ structure has been taken into consideration, I also find the factor by which the ellipsoid’s volume is greater than that of the tetrahedron and this becomes as 5.85416. The volume of the tetrahedron is 0.33626 times less than the sum of the volumes of one O and two H atoms and this decrease in volume is expected as tetrahedral structure is much more rigid and it represents the volume ‘within’ excluding the delocalization of electronic charge cloud.

2.2 Calculation for molecular polarizability of water from its absolute size:

Polarizability is one of the important size dependent physico-chemical property of atoms, ions and molecules. When an electric field is applied to an atom, ion or molecule, the electronic charge is modified and the symmetry of atomic, ionic or molecular charge distribution is distorted. Thus, atoms and non-polar molecules respond to the electric field by acquiring induced dipole moment. The polarizability is the constant of proportionality between the induced dipole moment and the strength of the applied electric field. If the applied field is very strong, the induced dipole also depends on the higher powers of the strength of the applied electric field. Then the coefficients of higher powers of the field strength are known as hyper-polarizability; but if the strength of the external electric field is small, the higher powers can be safely neglected and for small field, the response is totally linear.

By polarizability, Pearson [6,7] meant the ease of deforming the valence electron cloud of any chemical specie – atom, ion or molecule, by an external electric field much weaker than that would be needed to ionize the system. Brinck *et al*[8] have shown that for nonpolar molecules, polarizabilities are directly proportional to their volumes. From quantum mechanical point of view, polarizability can be treated as the perturbation of charge cloud due to small uniform electric field. If a system is in a central force field, like atoms or ions, it must have spherical symmetry. If the symmetry is disturbed by the application of a small external electric field, the system is perturbed. Moreover, Feynman [9] stated that there might be some special cases in which the polarizability is the same in all directions, known as isotropic polarizability. For non-polar molecules, the Clausius-Mossotti equation [10] indicates that the polarizability is directly related to the volume of the molecules. Even the linearity of linear volume polarizability relation has been assessed quantum mechanically [8]. Moreover, it has also been suggested that there must be some quantitative correspondence between the atomic radii and the cube root of polarizability of atoms [11].

The polarizability of a conducting sphere of radius r is given by

$$\alpha = r^3$$

For an atom, ion or molecule, due to inhomogeneity of electron cloud, under the influence of perturbing electric field, the actual formula of polarizability is

$$\alpha = Kr^3$$

where K is the proportionality constant and represents the inhomogeneity of electron cloud, r is the absolute radius of the atom, ion or molecule (considering it to be spherical). There have been many proposals for the value of ‘ K ’ [12, 13] for atoms. Relying upon the above ideas and extending the idea of Clausius and Mossotti [10] I have calculated the polarizability of water molecule. The linearity of volume-polarizability of atoms, ions and molecule is an established fact. I have calculated the radius of the equivalent sphere having the same volume of the water-ellipsoid. This radius is 0.921178 \AA . The proportionality constant ‘ K ’ has been calculated as 1.9685. So, following the above equation ($\alpha = Kr^3$), the polarizability of a discrete water molecule has been calculated as 1.5387 \AA^3 .

When water molecule is predominantly ionic, there is no electronic charge cloud around the two H^+ ions. I propose that the total polarizability in this ionic form is due to the O^{2-} ion. The polarizability of O^{2-} ion has already been reported as 0.74782 \AA^3 [14] and this is the polarizability of water in ionic form. So, polarizability of water molecule decreases with decrease in covalent character and increase in ionic character.

3. Results and Analysis

The calculated volume of water tetrahedron, water ellipsoid and molecular polarizability are tabulated below.

Table 1. The calculated molecular volume of water-tetrahedron, water-ellipsoid, radius of the equivalent sphere of volume $V_{\text{ellipsoid}}$, inhomogeneity constant and molecular polarizability of water

$V_{\text{tetrahedron}}$	0.559538 Å ³
$V_{\text{ellipsoid}}$	3.275625 Å ³
Radius of the equivalent sphere of volume $V_{\text{ellipsoid}}$	0.921178 Å
K	1.9685
Total volume of two H and one O atoms	1.6640 Å ³
α	1.5387 Å ³

From Table 1, it is clear that the volume of the ellipsoid is greater than the sum of volume occupied by two H and one O atoms separately, which in turn is greater than the volume of the tetrahedral water molecule. It can be very rightly explained on the basis of greater electronic charge delocalization around water molecule as a result of formation of molecular orbitals from linear combination of atomic orbitals. This delocalization has been taken into consideration in 'water-ellipsoid' model. Moreover, in this model, the molecular rotation about C_{2v} axis and normal modes of stretching vibrations of O-H have also been taken into consideration during the calculation of axes of the 'oblate spheroid' structure of water molecule.

In case of water tetrahedron, the molecular shape is much more symmetric and rigid and hence, very localized. Since the tetrahedral structure predominantly represents the fixed bond length and bond angle, the delocalization of the electronic charge has not been considered and the volume becomes less than that occupied by two H and one O atoms.

In order to show the strength of the present method, I have also compared the molecular polarizability values calculated with other available data in Table 2.

Table 2. Comparison of molecular polarizability (α) of water

Nir et al. (1973) [15]	1.456 Å ³
Murphy and Raleigh (1977) [16]	1.47 Å ³
Brinck et al (1993) [8]	1.45 Å ³
Ge and Lu (2017) [17]	1.59 Å ³
	1.61 Å ³
	1.47 ± 0.003 Å ³ (exptl.)
α (present work)	1.5387 Å ³

The comparison shows that the calculated value of the present work is in good agreement with others.

4. Conclusion

The amphoteric nature of water is well known. It is one of the many unique properties of water molecule that makes it the most capable solvent, a common ligand as well as an effective reaction medium. In the present work I have emphasized the polarizability of water molecule as the single most important factor that plays the most important role in characterizing water as 'acid' or a 'base' and also on the 'environment-independent absolute' size of a single water molecule on which the molecular polarizability solely depends. When water acts as a base its electrons are susceptible to be donated, i.e., in terms of polarizability, then the

water molecule is more polarizable. While as an acid, it is ready to accept electrons and will be less polarizable. In this calculation, I have shown that polarizability decreases with increase in ionic character of water molecule. I believe it can be concluded that acidic nature of water increases with increase in ionic character and basic nature increases with increase in covalent character i.e., when water acts as an acid its ionic nature is prevalent and when it acts as a base, its covalent nature is prevalent.

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