



## Factors affecting the solubility of ionic compounds



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### ARTICLE INFO

#### Article history:

Received 29 April 2015

Received in revised form 5 July 2015

Accepted 5 July 2015

Available online 22 July 2015

#### Keywords:

Anions

Cations

Solubility rules

Ionic compounds

### ABSTRACT

In order to provide a more robust understanding for the general solubility rules provided in most chemistry introductions, the charge densities for common ionic cations and anions are computed via quantum chemical methods. It is shown that low charge densities on either the cation or, especially, the anion promote solubility. The lowest anion charge densities produced correspond to chlorate, perchlorate, and acetate which are known always to be soluble for the analyzed cations. Silver has the lowest charge density of the cations examined, but is rarely soluble, only with these three singly-charged polyatomic anions and the related nitrate anion. The silver chloride bond is 8 kcal/mol stronger than silver chlorate and 12 kcal/mol stronger than silver nitrate. Sodium chloride is 6 kcal/mol weaker than silver chlorate with potassium chlorate 8 kcal/mol weaker. Hence, silver monomer salts are shown here to produce high bond energies to atomic anions showcasing why charge density alone cannot explain aqueous solubility, even though it is a good marker in a general sense.

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### 1. Introduction

The solubility of ionic compounds is one of their most basic physical properties. It is understood theoretically that ionic crystals in a saturated solution are in equilibrium with the hydrated ions [1]. This equilibrium is pushed toward increased solubility by decreases in lattice energy and by decreases in the energy of hydration of the ions. The competition of the two factors leads to complexities in predicting the solubility of an ionic compound. Empirical tables predicting the solubility of ionic compounds have been developed and are regularly published in introductory-level collegiate chemistry textbooks [2]. However, explaining the solubility of any given individual compound has proven very difficult [3].

Instruction of chemistry concepts to entry-level students is sometimes a mix of half-truths and gross approximations built as such in order to get students thinking in the proper manner but without overwhelming them with details. For instance, quantum chemists will say that the delineations between covalent, ionic, hydrogen, etc. bonding are really just a continuum of electron probabilities, and even this is a poor definition [4,5]. However, these classifications are taught to students, and errors creep into their consciousness as to how molecules behave. Recently, Devarajan and coworkers [6] raised question as to whether deeper descriptions of chemical bonding need to be put into the

traditional pedagogy of chemical bonds and bonding. Their conclusions appear to suggest that more complete concepts need to be used for instruction, especially for hydrogen–halide bonds, so that more competent students are created. As a result, the specter of pedagogical depth is raised in many of the basic tenants of chemical instruction.

Aqueous ionic solubility is another such example, and is actually intimately tied to the idea of the chemical bond [3]. There exist several explanations within general chemistry texts or online discussion boards as to why certain ionic compounds are soluble in water and why others are not in contradiction to the general solubility rules. Work by Osuna and coworkers [7] indicates that stepwise explicit microsolvation leads to favorable charge separations for the constituent atoms in alkali-halide diatomics. As a result, the standard ions are favored for bond cleavage in water, whereas the neutral atoms are favored as dissociated products in the gas phase.

However, there lacks a systematic analysis of more fundamental properties such as the molecular volume and the intimately related charge density property even though such phenomena are known to permeate the underlying chemical physics of solvation [1,3,4]. In order to develop simple theoretical explanations for ionic solubility, this work produces the volumes for a number of typical ions from quantum chemical computations. From this, the charge densities of these ions are determined and compared to the solubilities of several ionic compounds. Additionally, bond energies are computed for several exceptions to these trends in order to provide a more complete picture.

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## 2. Computational details

Gaussian09 [8] can compute molecular and molar volumes as part of its standard release and is the computational program utilized herein for this purpose. B3LYP [9,10] geometry optimizations (for polyatomic systems) and single-point energy computations (for atoms) are computed with the typical 6-31G\* basis set [11] where available (*p*-block atoms and *d*-block atoms above period six) as well as the DZP basis set [12–14] for all systems. The cations and anions chosen are fairly common ones discussed in most general chemistry texts.

The computed molar volume is divided by Avogadro's number to arrive at the ionic volume. Dividing this number by the Coulomb-converted charge for a given ion produces the charge density in C/cm<sup>3</sup>. Besides the charge density, the bond energy is also explored as a consideration in the solvation of these ions. The bond energy is simply determined from the energy sum of the dissociated ionic products minus that of the actual molecular monomeric compound. The bond energy is then used to obtain information about the bonding nature and covalent character of these bonds. Several ionic compounds are used as examples with the bond energies used to explain some of the exceptions in the standard ionic solubility tables and the general trends of charge density.

## 3. Results and discussion

Table 1 lists the B3LYP/6-31G\* and B3LYP/DZP molar volume, ionic (molecular or atomic) volume, and charge density. Anionic species are given in the top of Table 1 with the cations in the bottom. Those cations without data entries in the 6-31G\* half do not have available and comparable basis set constructions available for use. The magnesium B3LYP/DZP computations failed to converge after several attempts. Even though the DZP basis set has been well-used and has largely fallen out of vogue of late, its simplicity makes it available for use across the periodic table especially for density functional computations of period six atoms.

The two basis sets are largely consistent for the same systems as one would expect for two double-zeta basis sets. The DZP basis is larger; zinc, for instance, has 43 DZP basis functions while the 6-31G\* basis set contains 36. As a result, the total electronic energies differ:  $-1778.3023143 E_h$  and  $-1778.1070143 E_h$ , respectively. Interestingly for this example, the ionic volumes are identical at  $3.406 \times 10^{-24} \text{ cm}^3$  giving identical charge densities for this +2 atom of  $94,094 \text{ C/cm}^3$ . The additional functions in the DZP basis apparently do not add any further inclusion of the electron cloud and, hence, volume in this case. This is true for many of the cations since most are atomic and strongly valence making them well-defined by their localized electron clouds. Sodium, calcium, and aluminum are strong exceptions to this where the DZP basis set produces significantly smaller volumes (by a factor of 2 even ranging up to 4). As a result, only comparisons within basis sets should be and will be made. DZP is used for the quantitative comparisons made in the rest of this work since it is available for all included atoms.

### 3.1. Charge density

Weak water shells are associated with low charge density. Tight water shells are associated with high charge density. Therefore, low charge density typically is an indication of solubility whereas high charge density (and the resulting tight water shells) are believed to correlate to a lack of solubility. In large part, comparison of Tables 1 and 2 bears this out. The three lowest charge densities reported in Table 1 are perchlorate ( $1809 \text{ C/cm}^3$ ), acetate

( $1832 \text{ C/cm}^3$ ), and chlorate ( $1986 \text{ C/cm}^3$ ). Table 2 shows that each of these anions are soluble in water no matter the cation with which it is associated. Interestingly, nitrate salts are also all soluble in water even though its charge density is significantly greater at  $6963 \text{ C/cm}^3$ .

On the opposite end of the spectrum for the anions, fluoride, oxide, sulfite, carbonate, and phosphate are all insoluble except for a few cases that are consistent across this set. The first two anions from these (fluoride and oxide) have the highest charge densities for any of the anions examined at  $8148 \text{ C/cm}^3$  and  $11,277 \text{ C/cm}^3$ , respectively. However, the last three have charge densities of less than  $4100 \text{ C/cm}^3$ . The cations that allow for solvation in these anions are lithium, sodium, potassium, ammonium, rubidium, and cesium, all group I elements save for ammonium. The charge densities calculated for these counter ions are all among the lowest for this class at less than  $9000 \text{ C/cm}^3$  save for sodium. However, the alkali metals decrease in charge density going down the periodic table as a result of the same charge being distributed over progressively larger volumes. The charge densities of the cations are all significantly greater as a set than the charge densities of the anions partly since the anions are molecular and the cations are mostly atomic. The notable exception is sodium with a significantly high charge density at  $29,437 \text{ C/cm}^3$ .

Zinc has the highest charge density at over  $94,000 \text{ C/cm}^3$  with aluminum closely behind at  $91,160 \text{ C/cm}^3$ , and zinc and aluminum are soluble with the same counter anions. Counter to the argument that high charge density leads to insoluble compounds, zinc and aluminum are soluble with those anions with the lowest charge density anions of chloride, bromide, iodide, chlorate, acetate, perchlorate, and sulfate. Each of the anions have charge densities of less than  $3400 \text{ C/cm}^3$ . Carbonate is not soluble with zinc or aluminum, but its charge density is just above this threshold at  $3873 \text{ C/cm}^3$ . Interestingly, nitrate forms a soluble salt with all of the cations even though its charge density is  $6963 \text{ C/cm}^3$ .

Chloride, bromide, and iodide are also soluble with most counter anions except with silver (I), mercury I, and lead II. The anions fall in the mid-range of computed charge densities, but the cations are toward the lower end of the scale for their grouping of charge densities with silver having the lowest charge density of  $3783 \text{ C/cm}^3$  in the class. This is less than the largest alkali metal, cesium ( $4439 \text{ C/cm}^3$ ), as well as even the lone molecular cation ammonium ( $5130 \text{ C/cm}^3$ ).

As a result, the overall trend holds. The lower the charge density, the more likely a compound is to be soluble in water. A more precise statement follows from the presented results is that if either the cation or, especially, the anion portion has an extremely low charge density, the salt will be soluble in water most of the time. The notable exception for the anions is nitrate. It has a medium charge density but its nature simply makes it soluble regardless of the counter ion. While this is an exception, it makes its own rule. Silver, on the other hand, does not follow this trend with its low charge density and reluctance to solvate. Sodium has a middle charge density at  $29,437 \text{ C/cm}^3$ , but its salts are always soluble. These exceptions and break downs in the theory that charge density is directly tied to aqueous solubility show that such a model is good but incomplete. More must be taking place.

### 3.2. Covalent bonding character

Silver has the lowest charge density of any cation. It should produce soluble products. Yet, only nitrate and the dominant low charge density chlorate, acetate, and perchlorate polyatomic anions from our set can bring about solvation with silver. Chloride has a medium charge density for the anions at  $5428 \text{ C/cm}^3$ . Silver chloride is insoluble. As any chef or cook can testify, sodium chloride is highly soluble even though sodium's

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