Lattice Energies from Hydration Enthalpies: Some acid-base and Structural Considerations

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Abstract—In the present work, using reference values for the hydration enthalpies for a series of mono, di, tri and tetra cations, as well as reference values for the lattice energies of a series of none, di, tri and tetrahalides, it is shown that reliable lattice energies for such halides can be calculated by \( U_{POT} = (\Delta H_{hyd}^+ + \Delta H_{hyd}^-) \), by \( U_{POT} = (\Delta H_{hyd}^+ + 2\Delta H_{hyd}) \), by \( U_{POT} = (\Delta H_{hyd}^+ + 3\Delta H_{hyd}) \) or by \( U_{POT} = (\Delta H_{hyd}^+ + 4\Delta H_{hyd}) \) for mono, di, tri and tetrahalides, respectively. Linearized improved versions of such simple equations, parametrized in order to take into account factors such as dilution and entropic contributions, were also obtained. Lattice energies for a series of halides and other salts are calculated by using the obtained empirical equations, providing results in very good agreement with literature reference values. Furthermore, a series of empirical equations were derived, relating several acid-base parameters with lattice energy. It is shown that the cation and anion volumes (obtained by X-ray data), are very closely related with the cation and anion absolute hardness, that is, are very closely related with the frontier (HOMO and LUMO) orbitals energies.

Keywords—Lattice energies, hydration enthalpies, empirical equations.

I. INTRODUCTION

Lattice energy is a prominent parameter in chemistry, since it could be related with a series of properties of a given compound, such as solubility, melting point, etc. (Dasent, 1982). Furthermore, hydration enthalpy is one of the fundamental quantities for the thermodynamics of aqueous systems.

Most recently, we have been developed an empirical equation to calculate the lattice energies for metal monohalides from average orbital electronegativities (de Farias, 2017). In the present work, are derives empirical equation that allows the calculation of lattice energies for +1, +2, +3 and +4 salts (specially halides) based only on hydration enthalpies.

II. METHODOLOGY, RESULTS AND DISCUSSION

The up to date hydration enthalpies for group 1 monocations and group 17 monoanions (Housecroft, 2017) as well as the lattice energies \( U_{POT} \) to the respective halides (Glasser, 2000; Mu, 2000) are summarized in Table 1. As can be verified, the sum of cations and anion hydrations enthalpies are in very good agreement with the lattice energies for the respective metal halides. Taking into account the uncertainties that there are in both, \( U_{POT} \) and \( \Delta H_{hyd} \) values, such agreement is really quite good. Hence, the following equation can be derived:

\[ U_{POT} = (\Delta H_{hyd}^+ + \Delta H_{hyd}^-) \]  

where \( \Delta H_{hyd}^+ \) and \( \Delta H_{hyd}^- \) are the hydration enthalpies of the respective cation and anion.

Table 1: Hydration enthalpies (kJmol⁻¹) for group 1 monocations and group 17 monoanions, and lattice energies (kJmol⁻¹) for group 1 halides.

| Cation/Anion | \( \Delta H_{hyd}^+ \) | \( \Delta H_{hyd}^- \) | \( U_{POT} \) (Ref.) | \% Δ |
|--------------|----------------|----------------|-------------------|---|
| Li⁺          | 578.1          | 57.3           | 635.4             | +1.2 |
| Na⁺          | 463.3          | 54.3           | 517.6             | +7.7 |
| K⁺           | 380.3          | 75.9           | 456.2             | +10.0 |
| Rb⁺          | 355.2          | 91.6           | 446.8             | +13.0 |
| Cs⁺          | 330.6          | 124.1          | 454.7             | +1.9 |
| F⁻           | 463.7          | 45.9           | 509.6             | +1.8 |
| Cl⁻          | 319.5          | 91.6           | 411.1             | +2.7 |
| Br⁻          | 288.7          | 75.9           | 364.6             | +4.1 |
| I⁻           | 246.8          | 57.3           | 304.1             | +4.6 |

| Salt | \( \Delta H_{hyd} \) | \( U_{POT} \) (Ref.) | \% Δ |
|------|----------------|-------------------|---|
| LiF  | 1042           | 1030              | +1.2 |
| LiCl | 898            | 834               | +7.7 |
| LiBr | 867            | 788               | +10.0 |
| LiF  | 825            | 730               | +13.0 |
| NaF  | 927            | 910               | +1.9 |
| NaCl | 783            | 769               | +1.8 |
| NaBr | 752            | 732               | +2.7 |
| NaI  | 710            | 682               | +4.1 |
| KF   | 844            | 808               | +4.6 |
| KCl  | 700            | 701               | -0.1 |
When lattice energy is plotted as a function of the sum of the respective cation and anion hydration enthalpies, the curve shown in Figure 1 (r = 0.9687) is obtained, from which the following empirical equation is derived:

\[ U_{POT} = 0.820 (\Delta H_{\text{hyd}}^+ + \Delta H_{\text{hyd}}^-) + 118.236 \]  

(2)

Such phenomena (\( U_{POT} = \Delta H_{\text{hyd}}^+ + \Delta H_{\text{hyd}}^- \)) can be explained if we take into account that in the solid state (where cations are surrounded by anions and anions by cations, e.g. in a 6:6 environment, as in NaCl), or in solution (where both, cations and anions are surrounded by the solvent molecules), both, cations and anions are “looking for” (thermodynamic) stability.

In these systems, stability means to interact with positive of negative species in order to equalize their electronic chemical potentials (Parr, 1978), and such stability is achieved by exothermic interactions, with the total amount of energy required by the cation (or by the anion) been the same, no matter if the interactions occurs with other anions (or cations) in the solid state or, as in a aqueous solutions, with the negative (or positive) poles of the solvent molecules.

The same procedures were repeated to group 2 halides, and the respective data are summarized in Table 2. The experimental hydration enthalpies for group 2 dications are those provided by (Smith, 1977). The agreement between reference and lattice energies calculated by using the equation:

\[ U_{POT} = (\Delta H_{\text{hyd}}^+ + 2\Delta H_{\text{hyd}}^-) \]

are very good, as verified in Table 2 data, and Figure 2.

| Cation | \(-\Delta H_{\text{hyd}}^0\) | \(\Delta H_{\text{hyd}}^{2+}\) | \(U_{POT}\) (Ref) | \(\Delta\%) |
|--------|----------------|----------------|-----------------|-------|
| Be\(^{2+}\) | 2494 | | | |
| Mg\(^{2+}\) | 1921 | | | |
| Ca\(^{2+}\) | 1577 | | | |
| Sr\(^{2+}\) | 1443 | | | |
| Ba\(^{2+}\) | 1305 | | | |
| F\(^-\) | 463.7 | | | |
| Cl\(^-\) | 319.5 | | | |
| Br\(^-\) | 288.7 | | | |
| I\(^-\) | 246.8 | | | |
| BeF\(_2\) | 3421 | 3526 | -3.0 |
| BeCl\(_2\) | 3133 | 3033 | +3.3 |
| BeBr\(_2\) | 3069 | 2914 | +5.3 |
| BeI\(_2\) | 2988 | 2813 | +6.2 |
| MgF\(_2\) | 2848 | 2978 | -4.4 |
| MgCl\(_2\) | 2560 | 2540 | +0.8 |
| MgBr\(_2\) | 2498 | 2451 | +1.9 |
| MgI\(_2\) | 2415 | 2340 | +3.2 |
| CaF\(_2\) | 2504 | 2651 | -5.5 |
| CaCl\(_2\) | 2216 | 2271 | -2.4 |
| CaBr\(_2\) | 2154 | 2134 | +0.9 |
| CaI\(_2\) | 2071 | 2087 | -0.8 |
| SrF\(_2\) | 2370 | 2513 | -5.7 |
| SrCl\(_2\) | 2082 | 2170 | -4.1 |
| SrBr\(_2\) | 2020 | 2040 | -1.0 |
| SrI\(_2\) | 1937 | 1976 | -2.0 |
| BaF\(_2\) | 2232 | 2373 | -6.2 |
| BaCl\(_2\) | 1944 | 2069 | -6.0 |
| BaBr\(_2\) | 1882 | 1995 | -5.7 |
| BaI\(_2\) | 1799 | 1890 | -4.8 |

Table 2: Hydration enthalpies (kJmol\(^{-1}\)) for group 2 dications and group 17 monoanions, and lattice energies (kJmol\(^{-1}\)) for group 2 halides.

Fig. 1: Lattice energies for group 1 halides, as function of the sum of the hydration enthalpies to the respective cations and anions.
When lattice energy is plotted as a function of the sum of the respective cation and (plus 2) anion hydration enthalpies, the curve shown in Figure 2 (r = 0.9775) is obtained, from which the following empirical equation is derived:

$$ U_{\text{POT}} = 0.909 (\Delta H_{\text{hyd}}^{2+} + 2\Delta H_{\text{hyd}}^{-}) + 248.573 \quad (4) $$

The same procedures were repeated to group some halides, and the respective data are summarized in Table 3. The experimental hydration enthalpies for trications are those provided by (Smith, 1977). In Tables 1-3, the $U_{\text{POT}}$ values taken as references are those previously reported (Glasser, 2000; Mu, 2000).

The agreement between reference and lattice enthalpies calculated by using the equation:

$$ U_{\text{POT}} = (\Delta H_{\text{hyd}}^{3+} + 3\Delta H_{\text{hyd}}^{-}) $$

(5)

is very good, as verified in Table 3 data.

| Cation | $\Delta H_{\text{hyd}}^{0}$ | $\Delta H_{\text{hyd}}^{3+}$ | $U_{\text{POT (Ref)}}$ | $\Delta \%$ |
|--------|----------------|----------------|----------------------|-----------|
| Fe$^{3+}$ | 4430 | | | |
| Al$^{3+}$ | 4665 | | | |
| Ti$^{3+}$ | 4154 | | | |
| Ti$^{4+}$ | 4105 | | | |
| Cr$^{3+}$ | 4560 | | | |
| Ga$^{3+}$ | 4700 | | | |
| F$^{-}$ | 463.7 | | | |
| Cl$^{-}$ | 319.5 | | | |
| Br$^{-}$ | 288.7 | | | |

Table 3: Hydration enthalpies (kJ mol$^{-1}$) for some trications and group 17 monoanions, and the lattice energies (kJ mol$^{-1}$) for the respective halides

Fig. 2: Lattice energies for group 2 halides, as function of the sum of the hydration enthalpies to the respective cations and (x 2) the hydration enthalpies to the anions.

When lattice energy is plotted as a function of the sum of the respective cation and (plus 3) anion hydration enthalpies, the curve shown in Figure 3 (r = 0.9515) is obtained, from which the following empirical equation is derived:

$$ U_{\text{POT}} = 1.012 (\Delta H_{\text{hyd}}^{3+} + 3\Delta H_{\text{hyd}}^{-}) - 30.211 \quad (6) $$

Fig. 3: Lattice energies for trication halides, as function of the sum of the hydration enthalpies to the respective cations and (x 3) the hydration enthalpies to the anions.

When lattice energy is plotted as a function of the sum of the respective cation and (plus 4) anion hydration enthalpies, the curve shown in Figure 3 (r = 0.9515) is obtained, from which the following empirical equation is derived:

$$ U_{\text{POT}} = 1.012 (\Delta H_{\text{hyd}}^{4+} + 4\Delta H_{\text{hyd}}^{-}) - 30.211 \quad (6) $$

The same procedures were repeated to some +4 cations halides, and the respective data are summarized in Table 4. The experimental hydration enthalpies for tetracations are those provided by (Smith, 1977).

The agreement between reference and lattice enthalpies calculated by using the equation:
\[ U_{\text{POT}} = (\Delta H_{\text{hyd}}^{+} + 4\Delta H_{\text{hyd}}^{-}) \]  
(7)

is very good, as verified in Table 4 data.

Table 4: Hydration enthalpies (kJmol\(^{-1}\)) for Zr\(^{4+}\) and Sn\(^{4+}\) and group 17 monoanions, and the lattice energies (kJmol\(^{-1}\)) for the respective halides.

|       | \(-\Delta H_{\text{hyd}}^{a}\) | \(\Delta H_{\text{hyd}}^{4+}\) | \(U_{\text{POT}}\) (Ref) | \(\Delta\%\) |
|-------|-------------------------------|-----------------|-----------------|---------|
| Zr\(^{4+}\) | 6953                          |                 |                 |         |
| Sn\(^{4+}\) | 7591                          |                 |                 |         |
| F\(^-\)    | 463.7                         |                 |                 |         |
| Cl\(^-\)   | 319.5                         |                 |                 |         |
| Br\(^-\)   | 288.7                         |                 |                 |         |
| I\(^-\)    | 246.8                         |                 |                 |         |
| ZrF\(_4\)  | 8808                          | 8971            |                 | -1.8    |
| ZrCl\(_4\) | 8231                          | 8144            |                 | +1.1    |
| ZrBr\(_4\) | 8108                          | 7984            |                 | +1.6    |
| ZrI\(_4\)  | 7940                          | 7801            |                 | -1.8    |
| SnCl\(_4\) | 8869                          | 8930            |                 | -0.7    |
| SnBr\(_4\) | 8746                          | 8852            |                 | -1.2    |

Fig. 4. Lattice energies for tetracation halides, as function of the sum of the hydration enthalpies to the respective cations and (x 4) the hydration enthalpies to the anions.

When lattice energy is plotted as a function of the sum of the hydration enthalpies, the curve shown in Figure 4 (r = 0.9969) is obtained, from which the following empirical equation is derived:

\[ U_{\text{POT}} = 1.303 (\Delta H_{\text{hyd}}^{4+} + 4\Delta H_{\text{hyd}}^{-}) - 2566.765 \]  
(8)

Of course, Eq. (2), (4), (6) and (8) are improved versions of Eq. (1), (3), (5) and (7), and are parametrized in order to take into account factors such as dilution and entropic contributions (Persson, 2010; Hünenerber, 2011).

In order to verify the reliability and general application of Eq.(1), (3) and (5), they were employed to calculate the lattice energies for a series of halides. Despite the fact that the equations were obtained based on data for halides, they were also applied to salts with another kind of anions. The employed auxiliary data and the obtained results are summarized in Table 5. Of course, is possible to apply the values calculated by Eq.(1), (3) and (5) in Eq. (2), (4) and (6) and obtain a new set of calculated values.

Table 5: Calculated lattice energies (kJmol\(^{-1}\)) for a series of salts, employing Eq. (1), (3) or (5). The reference hydration enthalpies and lattice energies are in kJmol\(^{-1}\).

|       | \(-\Delta H_{\text{hyd}}^{a}\) | \(U_{\text{POT}}\) | \(U_{\text{POT}}\) (Ref) | \(\Delta\%\) |
|-------|-------------------------------|-------------------|-------------------|---------|
| Cu\(^+\)     | 593                           |                  |                  |         |
| Ag\(^+\)   | 473                           |                  |                  |         |
| Au\(^+\)   | 615                           |                  |                  |         |
| TI\(^+\)   | 326                           |                  |                  |         |
| F\(^-\)    | 463.7                         |                  |                  |         |
| Cl\(^-\)   | 319.5                         |                  |                  |         |
| Br\(^-\)   | 288.7                         |                  |                  |         |
| I\(^-\)    | 246.8                         |                  |                  |         |
| CuF       | 1057                          | 1088             |                  | -2.8    |
| CuCl      | 913                           | 996              |                  | -8.3    |
| CuBr      | 882                           | 978              |                  | -9.8    |
| CuI       | 840                           | 966              |                  | -13.0   |
| AgF       | 937                           | 974              |                  | -3.8    |
| AgCl      | 793                           | 918              |                  | -13.6   |
| AgBr      | 762                           | 905              |                  | -15.8   |
| AgI       | 720                           | 892              |                  | -19.3   |
| AuCl      | 935                           | 1066             |                  | -12.3   |
| AuBr      | 904                           | 1059             |                  | -14.6   |
| AuI       | 862                           | 1070             |                  | -19.4   |
| TIF       | 790                           | 920              |                  | -14.1   |
| TICl      | 646                           | 822              |                  | -21.4   |
| TIBr      | 615                           | 798              |                  | -22.9   |
| TII       | 573                           | 762              |                  | -24.8   |

Cu\(^{2+}\)  2100
Mn\(^{2+}\)  1841
Zn\(^{2+}\)  2046
Cd\(^{2+}\)  1807
Ni$^{2+}$ 2105  
Co$^{2+}$ 1996  
Sn$^{2+}$ 1556  
Be$^{2+}$ 2494  
Mg$^{2+}$ 1921  
Ca$^{2+}$ 1577  
Sr$^{2+}$ 1443  
Ba$^{2+}$ 1305  

BeS 3989 3770 +5.8  
MgS 3416 3238 +5.5  
CaS 3072 2966 +3.6  
SrS 2938 2779 +5.7  
BaS 2800 2643 +5.9  
CuS 3595 3694 -2.5  
MnS 3336 3795 -12.0  
NiS 3600 3415 +5.4  
ZnS 3541 3674 -3.8  
SnS 3051 3201 -4.7  
CdS 3302 3460 -4.6  
CoS 3491 3653 -4.4  
CuF$_2$ 3027 3102 -2.4  
CuCl$_2$ 2739 2824 -3.0  
CuBr$_2$ 2677 2774 -3.5  
CuI$_2$ 2594 2694 -3.7  

MnF$_2$ 2768 2803 -1.2  
MnCl$_2$ 2480 2551 -2.8  
MnBr$_2$ 2418 2482 -2.6  
MnI$_2$ 2335 2388 -2.2  

Mn$^{3+}$ 4544  
La$^{3+}$ 3296  
Ce$^{3+}$ 3337  

MnF$_3$ 5935 6012 -1.3  
MnCl$_3$ 5503 5556 -1.0  
LaCl$_3$ 4255 4242 +0.3  
LaBr$_3$ 4162 4280 -2.8  
LaI$_3$ 4036 3986 +1.3  
CeCl$_3$ 4296 4348 -1.2  
CeBr$_3$ 4203 4418 -4.9  
CeI$_3$ 4077 4061 +0.4  

In Table 5, the experimental hydration enthalpies for cations are those provided by (Smith, 1977). Except for F$^-$, Cl$^-$, Br and I$^-$, for which were used the values provided by Housecroft (Housecroft, 2017), the hydration enthalpies for anions are those provided by (Smith, 1977).

As can be verified from Table 5 data, Eq. (1) works very well for CuF and AgF. However, as the anion hardness decreases, the agreement between calculated and reference values turns bad. This is a surprisingly result, since Cu$^+$ and Ag$^+$ are soft acids, and F$^-$ is hard base. For example, when applying average orbital electronegativities to calculated lattice energies (de Farias, 2017), it was verified (in agreement with HSAB theory) that the worst results were obtained, exactly, to CuF and AgF.

On the other hand, for all copper (II) halides, Eq. (3) provides very good results. Hydrated Cu(I), d$^{10}$, [Cu(H$_2$O)$_6$]$^+$ exhibits a tetrahedral geometry, whereas hydrated Cu(II), d$^9$, [Cu(H$_2$O)$_6$]$^{2+}$ has an octahedral structure, with Jahn-Teller distortion (Persson, 2010). The same structures (tetrahedral and octahedral) are those exhibited by Cu(I) and Cu(II) halides (Villars, 2014). Hence, for Cu(I) halides, the crystal field stabilization energy (CFSE) is zero, whereas for Cu(II) compounds, there is a net CFSE to be computed (Pfennig, 2015).

So, it is possible to suppose that Eq.(1) works better for compounds for which a zero or minor CFSE is computed (a natural conclusion, since it was obtained by using experimental data for group I halides).

The spectrochemical series for the halides is F$^->$Cl$^->$Br$^->$I$^-$ (Pfennig, 2015), and all halides anions are weaker field ligands than water. Since, considering only the halides, F$^-$ is the ligand with the strongest field, this is the explanation why to exchange four water molecules by four F$^-$ ions in the coordination sphere of Cu(I) leads to a very good lattice energy calculated by using Eq. (1), whereas the results turns progressively bad for Cl$^-$, Br$^-$ and I$^-$.

It is also necessary to consider that, despite the fact that Li$^+$ is a hard acid and that Cu$^+$ is a soft acid, four coordinated Li$^+$ (Mähler, 2012) and four coordinated Cu$^+$ (Shannon, 1976) have the same radius: 60 pm. Hence, like in Kapustinskii equation (Kapustinskii, 1956), eq.(1) is closely related with the cation radius.

Furthermore, the number of water molecules in the coordination sphere increases form Li$^+$ to Cs$^+$ (Persson, 2010; Mähler, 2012), and then, whereas Li$^+$ is also four coordinated (like Cu$^+$), Na$^+$ and K$^+$, for example, have six and eight water molecules in their coordination sphere (Persson, 2010; Mähler, 2012). Then, the entropic contribution is more prominent for Cu$^+$ than to Cu$^{2+}$ halides, if the lattice energies are calculated by using hydration enthalpy data.

Based on the results obtained to Ag$^+$ halides (Table 5) can be concluded that Eq.(1) provides underestimated lattice energy values for compounds with a high degree of covalence, and that such disagreement (between calculated and reference values) increases as the degree of covalence increases. Since Ag$^+$ is a soft acid, the degree of covalence increases from F$^-$, Cl$^-$ (hard bases) to Br (borderline base) and I$^-$ (soft base).
For Au(I) halides the obtained results are really not good. However, it is necessary to remember that for gold, \((Z = 79)\), relativistic contributions matters (Leszczynski, 2010), and that gold is the element with the (proportionally) higher relativistic contraction/effects. The relativistic and non-relativistic equations can be related by using \(\gamma = 1/[1-(v^2/c^2)]\), where \(v\) is the velocity of the considered body (in our case, an electron). The velocity of the 1s electron is \(\approx Z/137\), where \(Z\) is the atomic number. Hence, \(\gamma = 1/[1-((Z/137)^2/c^2)]^{1/2}\). For gold \((Z = 79)\), and so \(\gamma = 1.224\).

Multiplying the lattice energy values calculated using Eq. (1), by \(\gamma\), “corrected” lattice energy values are calculated for gold, and are shown between parenthesis in Table 5. It is worth noting that, considering the relativistic corrected values, the agreement between calculated and reference values increases from Cl to I, in agreement with the fact the Au\(^+\) is a soft acid and Cl\(^-\) is a hard base, Br\(^-\) a borderline base and I\(^-\) a soft base.

A relativistic correction is also necessary for thallium halides. For Th, \(Z = 81\), and \(\gamma = 1.240\).

As can be verified from Table 5 data, despite the fact that it was derived from group 1 halides data, Eq. (1) works well for group 2 sulfides, as well as for other +2 cations sulfides (CuS, MnS, etc.). Hence, can be concluded that Eq.(1) works for any 1:1 compounds, despite the cation or anion charge/nature.

Housecroft (Housecroft, 2017), based on hydration enthalpy data for group 1 cations and group 17 anions, have derived the following equations:

\[
\Delta_{\text{hyd}} H^o = -(48.2 V^{-1/3}_m + 154.6)
\]

(9)

\[
\Delta_{\text{hyd}} H^o = -(214.71V^{-1/3}_m + 271.96)
\]

(10)

Eq. (9) is valid for +1 cations and Eq. (10) is valid for -1 anions. In such equations, \(V_m\) is the cation or anion volume, a paramount parameter in volume based thermodynamics, VBT (Glasser, 2011).

Hence, Eq.(1) can be rewritten as:

\[
U_{\text{per}} = \left[ -(48.2 V^{-1/3}_m + 154.6) - (214.71V^{-1/3}_m + 271.96) \right]
\]

(11)

In Eq.(11), (+) and (-) superscripts were included to differentiate between cation and anion volumes.

Furthermore, it was shown that there is a very close relationship between hydration enthalpies and absolute hardness for cations and anions. For group 1 cations (Kaya, de Farias, 2018),

\[
\Delta_{\text{hyd}} H^o = -(9.645\eta^+ + 245.930)
\]

(12)

where \(\eta^+\) = cation absolute hardness (eV).

For group 17 anions:

\[
\Delta_{\text{hyd}} H^o = -(64.601\eta^- + 12.321)
\]

(13)

Hence, Eq.(1) can be rewritten as:

\[
U_{\text{per}} = \left[ -(9.645\eta^+ + 245.930) - (64.601\eta^- + 12.321) \right]
\]

(14)

Taking Eq. (11) and (14), and multiplying both sides by -1, we have:

\[
[(48.2 V^{-1/3}_m + 154.6) + (214.71V^{-1/3}_m + 271.96)] = \left[ (9.645\eta^+ + 245.930) +(64.601\eta^- + 12.321) \right];
\]

\[
48.2 V^{-1/3}_m + 214.71V^{-1/3}_m + 426.6 = 9.645 \eta^+ + 64.601 \eta^- + 258.3;
\]

\[
48.2 V^{-1/3}_m + 214.71V^{-1/3}_m + 168.6 = 9.645 \eta^+ + 64.601 \eta^- ;
\]

\[
48.2 (V^{-1/3}_m + 4.5 V^{-1/3}_m + 3.5) = 9.645 \eta^+ + 6.7 \eta^- ;
\]

\[
[(V^{-1/3}_m + 4.5 V^{-1/3}_m + 3.5)/( \eta^+ + 6.7 \eta^-)] = 1/5
\]

Equ. (15) shows that the cation and anion volumes (obtained by X-ray data), are very closely related with the cation and anion absolute hardness, that is, are very closely relates with the frontier (homo and lumo) orbitals energies.

It is noteworthy that have been shown that (Tissander, 1998) absolute hydration enthalpy values can be calculated from a set of cluster-ion solvation data, without the use of extra thermodynamic assumptions. Hence, could be concluded that the empirical equations obtained in the present work (Eq. 15, for example), can also be related with the previously derived hydration enthalpy equations, based on cluster-pair-based approximation.

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