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Average orbital electronegativity and lattice energy: the relationships for NaCl

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Abstract. In the present work, it is shown, by using NaCl as example, that there are very close relationships (in fact, a causality relationship) between lattice energy, hydration enthalpies and average orbital electronegativity, explaining the thermodynamic stability of ionic crystals. It is show that, for NaCl, the $2I$ (the ionic strength-like term) that appears in the Glasser-Jenkins equations coincides with the e average orbital electronegativity, as defined by L.M. Viting.

Keywords: Lattice energy, Glasse-Jenkins equation, average orbital electronegativity.

INTRODUCTION

Roughly speaking, ionic strength can be defined as the concentration of ionic charge in solution. This so paramount concept was introduced by G.N. Lewis in 1921 [1], in order to face the fact that solutions of weak electrolytes follow the law of mass action, but solutions of strong electrolytes do not, and that there was no adequate explanation for this discrepancy at that time. According to Coffey [2] this was considered the most pressing problem in physical chemistry at that time, until Lewis would define his concept of “ionic strength,” which would give a practical method for determining the activity of strong electrolytes.

Leslie Glasser and Donald Brooke Jenkins [3] had deduced/formulated an empirical equation with a ionic strength-like term that works very well to calculate the latticed enthalpies for ionic compounds. Recently [4] Glasser has revisited his main achievements regarding this equation and concluded that the ionic strength-like terms provide conveniently calculated coulomb sums for systems with finite collections of charges.

Glasser-Jenkins equation was, for example, employed to provide a thermochemical explanation for the stability of unusual compounds such as NaCl_3 and NaCl_7 [5].

The main goal of the present work it is to show that there is a very close relationship (in fact, a causality relationship) between Glasser-Jenkins equation and the concept of average orbital electronegativity, as defined by L.M. Viting, explaining, therefore, the thermodynamic stability of NaCl.

METHODOLOGY

The quantum chemical calculations were performed by using Spartan [6]. The SE-PM6 approach was chose, taking into account its minor computation time consuming and its reliability for calculations involving inorganic systems, as verified for PtF_6 [7].

RESULTS AND DISCUSSIONS

In terms of molar concentration, ionic strength is:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (1)$$

where c and z are the solute concentration (mol/L) and charge, respectively.

In pure water, the ionic strength of NaCl is, of course, zero. The solubility of NaCl in water at 25°C is 35.7 g/100 mL [8]. Taking the NaCl density as 2.165 g/cm³ and the water density as 1.00 g/cm³, we can calculate to a NaCl saturated aqueous solution, a concentration of 5.24 mol/L, and an ionic strength of the same value, since NaCl is a 1:1 electrolyte. Hence, $2I = 10.48$ mol/L.

In pure (solid) NaCl, taking the same density value, the “concentration” can be calculated as 37.01 mol/L and the ionic strength as 37.01 mol/L, and $2I = 74.02$ mol/L.

Summarizing, we have, to NaCl: pure water ($2I = 0$), in a 2.0 mol/L aqueous solution ($2I = 2.00$), saturated aqueous solution ($2I = 10.48$) and in the pure solid ($2I = 74.02$).

In The Glasser-Jenkins equation (a generalized version of the Kapustinskii equation) [3]:

$$U_{\text{POT}} = \frac{2AI}{\langle r \rangle} \left(1 - \frac{\rho}{\langle r \rangle} \right) \quad (2)$$

where $\langle r \rangle$ is the weighted-mean cation-anion sum and ρ is a compressibility constant (derived from Born-Mayer theory, usually chosen as 0.0345 nm). The term $A = (1/2N_A M e^2 / 4\pi\epsilon_0)$, where N_A /molecules mol⁻¹ is the Avogadro's constant and M is the Madelung constant of the rock salt -sodium chloride-type lattice = 121.4 kJ mol nm⁻¹. To NaCl, and using the Na⁺ and Cl⁻ ionic radii (coordination number six) as 0.102 nm and 0.181 nm, respectively [9] equation (2) provides a calculated U_{POT} value of 753.4 kJmol⁻¹ in very good agreement (-2.02%) with the reference value [3] of 769 kJmol⁻¹.

In equation (3) there is an ionic strength-like term:

$$\sum n_i z_i^2 = 2I \quad (3)$$

where n_i is the number of ions (not the mol/L or mol/kg concentration, as considered for solutions) with integer charge z_i ; and the summation is taken over all the types of ions, i , in the formula unit. To NaCl, $2I = 2$.

As previously shown [8] to a series of 1:1, 1:2, 1:3 and 1:4 (cation:anion) salts, the lattice and hydration

enthalpies are very closely related and a series of very simple empirical equations were obtained. To a 1:1 salt:

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

where ΔH_{hyd}^+ and ΔH_{hyd}^- are the hydration enthalpies of the respective cation and anion. To NaCl the percentage difference between calculated and reference values was of only +1.8 % [10].

Combining equations 2 and 4, we have:

$$(\Delta H_{\text{hyd}}^+ + \Delta H_{\text{hyd}}^-) = \frac{2AI}{\langle r \rangle} \left(1 - \frac{\rho}{\langle r \rangle} \right) \quad (5)$$

Taking the previously presented values to A , ρ and r :

$$2I = (\Delta H_{\text{hyd}}^+ + \Delta H_{\text{hyd}}^-) / 376.68 \quad (6)$$

To Na⁺ and Cl⁻ the hydration enthalpies are, respectively [11] 463.3 kJmol⁻¹ and 319.5 kJmol⁻¹. Hence, $2I = 2.08$. Proving the relationship/agreement between Equations (2) and (6), or, in other words, the relationship between solid state and diluted aqueous solution data.

As previously shown [12] the lattice energies for inorganic monohalides can be consistently calculated by using the cation radius and the halide average orbital electronegativity.

The average orbital electronegativity of molecules, as introduced by Viting [13] can be calculated by

$$\dot{X} = \sum n_i \chi_i / \sum n_i \quad (7)$$

where χ_i is the electronegativity of the i th atom and n_i is the number of this sort in the formula unit. To NaCl, $\dot{X} = 2.05$ [10]. The first point to be noted here is the coincidence (?) to NaCl, between the \dot{X} and $2I$ values.

Using the empirical equation [10]:

$$U_{\text{POT}} = (-2.739 r^+ + 650.676) \dot{X} + (3.796 r^+ - 370.851) \quad (8)$$

where r^+ = cation radius (in pm) and \dot{X} is the average orbital electronegativity for the considered monohalide, a calculated value of U_{POT} to NaCl in very good agreement with the reference value (+1.2%) was obtained [10].

Of course, combining Equations (2) and (8) a relationship between \dot{X} and $2I$ can be established,

$$(-2.739 r^+ + 650.676) \dot{X} + (3.796 r^+ - 370.851) = \frac{2AI}{\langle r \rangle} \left(1 - \frac{\rho}{\langle r \rangle} \right) \quad (9)$$

Making the proper substitutions, we found: $\dot{X}/2I = 0,97 \approx 1$. So, the fact that to NaCl $2I = \dot{X}$ is not a coincidence. Hence, It is show that, for NaCl, the $2I$ (the ionic strength-like term) that appears in the Glasser-Jenkins equations coincides with the e average orbital electronegativity, as defined by L.M. Viting [11].

By using a Semi-Empirical approach, gas phase NaCl was modeled as a linear molecule (Figure 1), with E_{homo} and E_{lumo} being calculated as -9.47 and 0.03 eV, respectively. Taking into account that by Koopmans' theorem $E_{\text{homo}} \approx E_i$ (first ionization energy) and $E_{\text{lumo}} \approx E_{\text{ea}}$ (electron affinity), we can, by using the equation (to convert Mulliken into Pauling electronegativity values):

$$X = 0.187 (E_i + E_{\text{ea}}) + 0,17 \quad (10)$$

calculate an (Pauling) electronegativity value of 1.997 to gas phase NaCl, in total agreement with the previous considerations to $2I$ values and its physicochemical meaning.

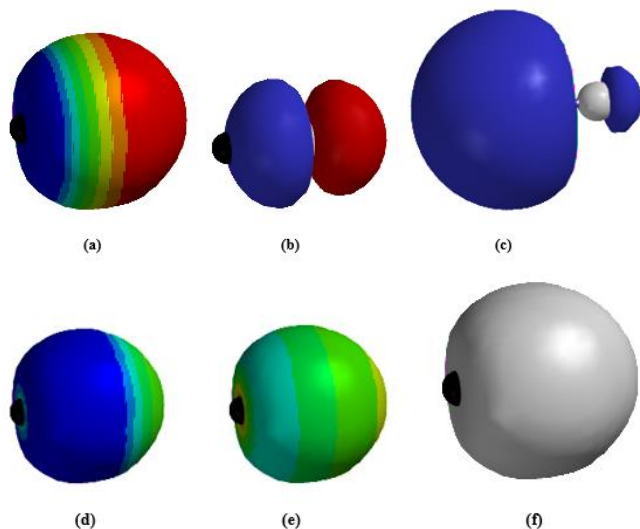


Figure 1. SE-PM6 calculated surfaces: electrostatic potential map (a) homo orbital (b), lumo orbital (c), local ionization potential map (d), lumo map (e) and electron density (f) to gas phase linear NaCl.

The fact that to NaCl, $2I = 2$ in Glasse-Jenkins equation, in L.M. Vitting average orbital electronegativity definition and in a 2.0 mol/L aqueous solution, shows that gas phase, solution phase and solid state phase thermochemistry of NaCl are closely related by the same physicochemical principles.

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