



# Grand Canonical Monte Carlo coupled multiscale simulation for electrochemical and solvent parameters of silver halide systems in water



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## ABSTRACT

Grand Canonical Monte Carlo methods in conjunction with continuum Multiscale simulation to estimate the hydration energies and surface potentials of silver halides as demonstrated elsewhere is employed by incorporating random distribution of molecules, nearest neighbor distances and hydration numbers. The extent of dehydration during each step and the corresponding variation in the hydration numbers are evaluated, assuming the validity of hard spheres. These estimates are then employed to deduce the redox potential of the reaction viz.  $2\text{AgX}_{(\text{solution})} \rightleftharpoons 2\text{Ag}_{(\text{solid})} + \text{X}_{2(\text{gas})}$ . The dependence of these values on the nature of the halides and solvation characteristics is indicated.

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## 1. Introduction

The estimation of redox potentials of  $\text{M}^{\text{n+}}/\text{M}$  and  $\text{M}/\text{MX}/\text{X}^-$  from first principles is a challenging task in view of the necessity to obtain data pertaining to (i) the electrochemical behavior of MX and (ii) its solubility in a chosen solvent. In this context, an attempt to evaluate the reduction potential of  $\text{Ag}^+\text{L}_2/\text{Ag}^0\text{L}_2$  (where  $\text{L} = \text{H}_2\text{O}$ ) and  $\text{Ag}^+/\text{Ag}$  from electrochemical parameters and thermochemical data is noteworthy. However, the evaluation of reduction potentials pertaining to couples such as  $\text{Ag}/\text{AgCl}/\text{Cl}^-$  is far more involved since silver halides are sparingly soluble and their hydration energies are not directly obtainable from conventional simulation techniques. Although the ionic hydration energies can be estimated from diverse thermodynamic approaches and various simulation strategies, it is preferable to formulate new procedures which incorporate the molecular nature of  $\text{AgX}$  as an entity.

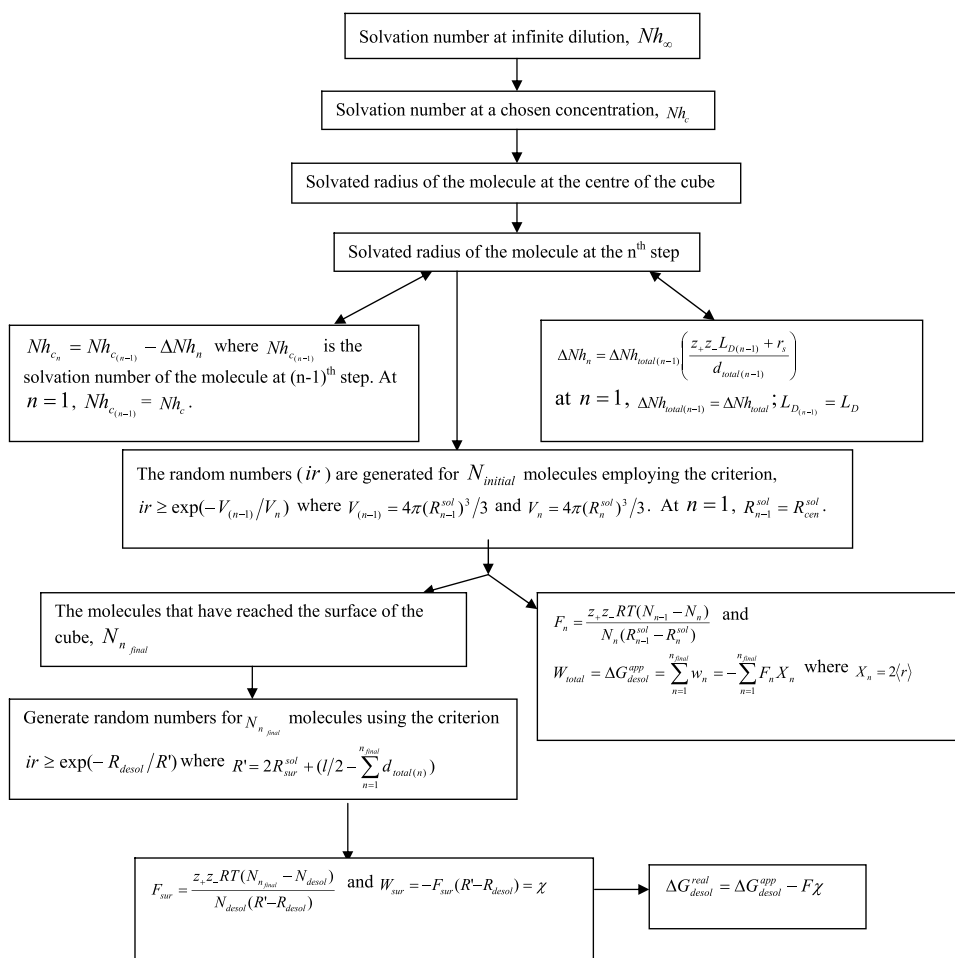
It is of interest to mention that silver halides are unique as regards their electronic structures, which endow them with unusual properties viz. complexation, precipitation, photosensitivity etc [1–16]. Hence estimation of the quantities pertaining to silver

halides should per force include implicitly or otherwise, their structural characteristics. In our earlier work [17–20], we have proposed a new simulation methodology incorporating random distribution of molecules, concentration-dependent hydration numbers, mean displacements etc under hard sphere approximation. The essential feature of the proposed strategy consisted in postulating an entirely hydrated molecular species at the initial step and estimating the step-wise dehydration energies en route their arrival at vacuum. In contrast to conventional simulation techniques, the new approach invoked the volume ratios as the criterion during the random number generation protocol. The validity of the formalism was demonstrated for computing hydration energies of halides of alkali and alkaline earth metals, lanthanides and actinides [12,17–20]. As indicated earlier, analysis pertaining to silver halides is far more involved. In order to circumvent this aspect, the analysis of redox potentials of silver halide systems is first converted into the estimation of their dehydration energies with the help of a suitable thermochemical cycle and subsequently, the requisite electronic structures of  $\text{AgX}$  are included via the corresponding lattice energies.

The objectives of the present work are to (i) estimate the dehydration energies of  $\text{AgX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) using Monte Carlo simulation method; (ii) evaluate the 'redox potentials' of  $\text{Ag}/\text{AgX}$  systems incorporating the electronic structure of  $\text{AgX}$ ; (iii) compute the sol-

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**Scheme 1.** The steps and the parameters involved in the simulation methodology [12].

ubility product of silver halides and (iv) in future to extend the analysis to non-aqueous solvents.

## 2. Hydration behavior of silver halides

Silver halide is an important molecule for electrode surfaces. The silver metal ions are genuine charge carriers giving a certain electrolytic conductivity [21,22]. Hence the investigation of the hydration behavior and solubility of silver halides is an important task.

### 2.1. Simulation methodology for dehydration energy of AgX

In our simulation methodology [12,17–20], the hydrated silver halide molecules at the center of the cubic box, shed their hydration sheaths progressively while arriving at the surface of the cube and there from escape to vacuum as dehydrated entities. Thus the simulation is employed for obtaining the number of molecules that (i) arrive at the surface of the cube and (ii) subsequently reach vacuum, via random numbers generation employing volume ratio as the criterion. These values are then employed in the definition of the thermodynamic force so as to deduce the real and apparent dehydration energies, as shown below. The essential input parameters of the present analysis are (i) the molecular radii of silver halides ( $R_{\text{desol}}$ ), considered as a sum of cationic ( $r_+$ ) and anionic ( $r_-$ ) radii and (ii) the radius of water molecules ( $r_s$ ). Using these two parameters, an explicit expression for the hydration number

of the molecules at infinite dilution is formulated. Subsequently, the hydration number at a chosen concentration is written, incorporating the random distribution of species. As it is customary, the saturated solution of silver halide molecules is considered here, the rationale behind this assumption being that (i) the expression for the redox potential of AgX/Ag as derived from the thermochemical cycle (cf. Scheme 1) does not include the concentration terms explicitly, (ii) despite the saturation level of AgX, the number of AgX molecules are lower than that of water molecules and hence the halide molecules will always be surrounded by water molecules and needs excess energy to escape to vacuum.

The expressions for hydration number, hydrated radius, boundary conditions and acceptance criteria involved in the simulation depends on Temperature, Volume and change in concentration of hydrated AgX in each step movement. Thus, the simulation was carried out in the (T,V,c) ensemble and the silver chloride molecules assumed as hard spheres were placed in a cubic box of length  $l \text{ \AA}$  (Scheme 1). The number of water molecules is fixed as 18000 while the number of electrolyte molecules is chosen in accordance with the box size and concentration. Although several models exist in the literature for water molecules, for simplicity water molecules are assumed as hard spheres in the current methodology [12,15]. The boundary conditions (i)  $d_{\text{total}(n)} = d_{\text{total}(n-1)} - x_n$  and (ii)  $R_n^{\text{hyd}} = R_{\text{sur}}^{\text{hyd}} \approx R_{\text{desol}} + 1$  ( $n$  varies from 1 to  $n_{\text{final}}$ ), were employed and the cube was confined along  $z$ -axis. The distance traveled by the AgX molecules will be half the length of the cube ( $d_{\text{total}(n-1)} = l/2$ ) at  $n = 1$  and  $x_n$  denotes the displacement of the molecule at  $n^{\text{th}}$  step [12].

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