Available online at www.sciencedirect.com

SCIENCE DIRECT®

Chemical Physics 310 (2005) 59–66

Chemical Physics

www.elsevier.com/locate/chemphys

Dehydration energies of alkaline earth metal halides – a novel simulation methodology

V. Sudha, S. Harinipriya, M.V. Sangaranarayanan *

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Received 6 August 2004; accepted 6 October 2004
Available online 11 November 2004

Abstract

The apparent dehydration energies and surface potentials of diverse alkaline earth halides are computed employing a novel simulation methodology incorporating hydration numbers, ion pairing effects and random distribution of molecules. The progressive variation of the hydration numbers and hydrated radii are estimated. The significance of the formalism in rationalizing the trend in the variation of the solubility, lattice energy, etc. is indicated.

Keywords: Alkaline earth metal halides; Simulation; Surface potential; Dehydration energies; Hydration numbers; Random distribution

1. Introduction

The behaviour of electrolytes in aqueous solutions is of interest in several contexts such as (i) double layer capacitance in metal/solution [1] and liquid/liquid interfaces [2], (ii) charge transfer processes [3], (iii) the stability of DNA and RNA quadruplex structures by salt solutions [4,5], (iv) bioavailability in drug design [6] and (v) analysis of phase equilibria in chemical engineering [7], etc. All solutes get hydrated by water and the hydration number is defined as the number of water molecules associated with a chosen solute and the concept of hydration number has immense utility in the mechanism of ion transport across biological cell membranes [8,9] and channels [10,11] wherein the size of the hydrated species in comparison to that of the pore or the channel plays a crucial role and in interpreting the ability of the hydrated species to interact with organic functional groups in the channels [12,13]. Also, hydration number of the electrolytes is a central factor in the folding/unfolding of proteins [14], DNA intercalation reactions and the specificity of protein – DNA interactions [15]. Further, in the formation of aerosols of different salt content [16–19], the solubility of natural gas in deep brines [20] and in the leaching of minerals [21], the concept of hydration is of importance. In view of the extensive role of hydration phenomena as stated above, the estimation of energetics associated with hydration has been a central focus in the field of solution chemistry.

Several computational methods such as Widom particle insertion methods [22], umbrella sampling [23], biased simulation procedure [24], extended ensemble method [25], etc. have been employed in estimating the hydration energies of ionic species. Despite the availability of intensive computational tools within the frame work of Monte Carlo [26] or molecular dynamics [27] simulations, the hydration energies of univalent [28,29] cations and anions and organic compounds [30] of low molecular weight can alone be accomplished till now. Hence, in order to evaluate the hydration energies of diverse systems, a simple and robust approach that can

---

[*] Corresponding author. Tel.: +91 44 22578269; fax: +91 44 22570545.
E-mail address: mvs@chem.iitm.ac.in (M.V. Sangaranarayanan).

0301-0104/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2004.10.030

handle high concentrations without much computational difficulty is required.

In this paper, we propose a methodology for the estimation of dehydration energies of alkaline earth metal halides by calculating the extent of dehydration of an entirely hydrated molecule. The ionic pair is considered as an entity and the molecular radii is written as a sum of the cationic and anionic radii based on the hard sphere model [31,32].

2. Methodology

While the essential features of the simulation methodology have been discussed earlier [32], a few salient aspects are provided below for clarity. The appropriate number of electrolyte (metal halide) and solvent (water) molecules are chosen pertaining to a cubic simulation box of length l having the boundary conditions along x and y axes. The hydrated molecules, present at the central region of the simulation box, were allowed to move to the surface of the cube by shedding their hydration sheath in successive steps and then to vacuum as dehydrated entities in a single step. Thus the estimation of apparent and real dehydration energies as well as the surface potentials pertaining to vacuum/solution interface can be achieved by evaluating the number of molecules that arrive at the surface of the cube and those that reach vacuum.

The parameters Nh_∞, Nh_c and Nh_{c_n} denote respectively, the hydration numbers at infinite dilution, chosen concentration and nth step. ΔNh_n denotes the change in the hydration number at the nth step. The radius of the hydrated molecule at the center of the simulation box, at the nth step, at the surface of the cube and that of the dehydrated species are represented as $R^\mathrm{hyd}_\mathrm{cen}$, R^hyd_n, $R^\mathrm{hyd}_\mathrm{sur}$ and R_desol, respectively. The parameters N_initial, N_{n_final} and N_desol denote respectively, the number of electrolyte molecules chosen, the number of molecules arriving at the surface of the cube and those reaching vacuum. The actual and expected mean displacement of the molecules at the nth step are denoted as X^real_n and x^exp_n, respectively. The mean nearest neighbor distance is $\langle r\rangle$ while the discretised Debye length is represented [32] as $L_{\mathrm{D}(n-1)}$.

For an electrolyte $M^{z_+}_{\upsilon_+}N^{z_-}_{\upsilon_-}$ in water, Nh_∞ is given by [33]

$$Nh_\infty = \frac{(v_+z_+r_+^3 + v_-z_-r_-^3)}{r_\mathrm{s}^3}, \tag{1}$$

where r_s denotes the radius of the water molecules while Nh_c is represented as

$$Nh_\mathrm{c} = Nh_\infty(1 - d_\mathrm{s}/\langle r\rangle). \tag{2}$$

The bare crystallographic radii of the ionic species are denoted as r_+ and r_- while d_s is the diameter of water molecules. The ratio $r_\mathrm{s}Nh_\mathrm{c}/(Nh_\infty - Nh_\mathrm{c})$ denotes the enhancement in the radius of the hydrated electrolyte whereby

$$R^\mathrm{hyd}_\mathrm{cen} = R_\mathrm{desol} + [r_\mathrm{s}Nh_\mathrm{c}/(Nh_\infty - Nh_\mathrm{c})]. \tag{3}$$

A convenient expression to estimate $\langle r\rangle$ based on the hard sphere model is as follows [34]

$$\langle r\rangle = (3/4\pi c)^{1/3}\exp(\eta)[\Gamma(4/3) - b], \tag{4}$$

where

$$b = \sum_{n=0}^{\infty}\frac{(-1)^n\eta^{(n+4/3)}}{n!(n+4/3)}, \tag{5}$$

and the dimensionless density η is given as $\eta = 4\pi c d^3_\mathrm{desol}/3$; c is the concentration of the electrolyte expressed in molecules/Å^3 (using the appropriate molarity and Avogadro number) and $\Gamma(4/3)$ denotes the Gamma function [35].

The extent of variation of hydration numbers is a crucial parameter introduced in our analysis and is postulated as

$$\Delta Nh_n = \Delta Nh_{\mathrm{total}(n-1)}\left(\frac{L_{\mathrm{D}(n-1)} + r_\mathrm{s}}{d_{\mathrm{total}(n-1)}}\right), \tag{6}$$

where $L_{\mathrm{D}(n-1)}$ is the "Debye length" at $(n-1)$th step, n varies from 1 to n_final and $d_{\mathrm{total}(n-1)}$ is the remaining distance the hydrated molecules have to travel to reach the surface of the cube at the $(n-1)$th step. In the present context, a modified "discrete" Debye length is defined as

$$L_{\mathrm{D}(n-1)} = \left(\frac{z_+z_-\varepsilon\varepsilon_0 k_\mathrm{B}T}{(z_+^2 + z_-^2)N_\mathrm{B}e^2}\right)^{1/2}, \tag{7}$$

and $N_\mathrm{B} = N_\mathrm{initial} + N_\mathrm{sol}$ while k_B is the Boltzmann constant, ε and ε_0 denote the dielectric constant of the solvent and the permittivity in free space. (The number of solvent molecules is denoted by N_sol.) Note that N_initial varies with each step movement and hence the subscript for the Debye length.

The random numbers (ir) are generated for N_initial molecules subject to the condition $ir \geqslant \exp(-V_n/V_{(n-1)})$ where $V_{(n-1)} = 4\pi(R^\mathrm{hyd}_{n-1})^3/3$ and $V_n = 4\pi(R^\mathrm{hyd}_n)^3/3$. The simulation yields the number of molecules arriving at the second step which is the new value of N_initial and the procedure is carried out till

$$\sum_{n=1}^{n_\mathrm{final}} x^\mathrm{exp}_n = d_\mathrm{total} \tag{8}$$

and

$$R^\mathrm{hyd}_\mathrm{sur} - R_\mathrm{desol} \simeq 1\ \text{Å}, \tag{9}$$

where $d_\mathrm{total} = l/2$ denotes the total distance the hydrated molecules cover *en route* their movement from the center of the cubic box to its surface. The thermodynamic force associated with each dehydration step is given by [36]

$$F_n = \frac{z_+z_-RT(N_{n-1} - N_n)}{N_n(R^\mathrm{hyd}_{n-1} - R^\mathrm{hyd}_n)}, \tag{10}$$