THE JOURNAL OF
PHYSICAL CHEMISTRY B
LETTERS

Published on Web 10/04/2006

Estimating the Hydration Enthalpies of Neutral Alkali Metal Atoms

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*Received: August 8, 2006; In Final Form: September 14, 2006*

Using existing data on the ionization energies of alkali metal atoms in small clusters of water, a thermodynamic cycle is proposed from which the hydration enthalpies of the neutral metal atoms can be estimated. Where comparisons are possible, the results are in reasonable agreement with those obtained using both experimental and ab initio methods. Application of the thermodynamic cycle to neutral alkali metal atoms solvated in ammonia yields solvation enthalpies that are significantly lower than those obtained for water.

Introduction

There are numerous compilations providing data on the hydration enthalpies of metal cations, and for singly charged ions such values are known with reasonable accuracy for metals spanning the periodic table.[1,2] Less well known are the corresponding values for neutral metal atoms. However, it is possible to identify instances where knowledge of neutral atom hydration enthalpies may be of significance. One example is the chemistry of the upper atmosphere (the D-region), where sporadic layers of neutral sodium atoms are known to form in the mesosphere as a consequence of meteor ablation.[3] Also taking place in the D-region are chemical processes that ultimately lead to the appearance of water clusters.[4] Any attempt to understand the interaction between the water clusters and neutral sodium atoms from the sporadic layers could benefit from data on the hydration enthalpy of the metal.

A route to estimating these data comes from several recent experiments on neutral metal/water clusters.[5−7] These experiments have shown that, irrespective of the metal, the measured ionization energies of $M(H_2O)_n$ complexes, where M is an alkali metal, converge to a constant value once n is > 8. This value is 3.12 eV and can be equated with the vertical detachment energy of an electron solvated in a water cluster, which for a cluster of infinite size is estimated to be 3.2 eV.[8,9] The interpretation of the ionization data being that the metal atom undergoes spontaneous ionization when associated with the water molecules and what is removed is a surface-bound electron. Calculated ionization energies for small $M(H_2O)_n$ clusters support the trend seen in the experimental results.[10−15] The observation of a limiting value for the ionization energy the metal/water complexes offers the opportunity to propose a thermodynamic cycle, which links the gas-phase results with data on the ionization energies of the free metal atoms and the bulk hydration enthalpies of the metal cations.[16,17] The proposed cycle is shown in Scheme 1, where the unknown quantity is the hydration enthalpy of the neutral metal atom. IE(M) is the ionization energy of a metal in the gas phase, ΔH_{hyd} is the hydration enthalpy of the metal cation, PET(e^-) is the photo-electric threshold for a solvated electron in bulk water, and

SCHEME 1
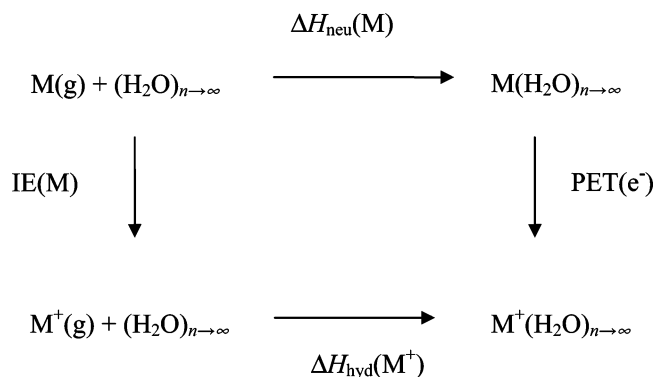
ΔH_{neu} is the hydration enthalpy of the neutral metal atom. n is assumed to be very large. Although the gas-phase experiments appear to converge to the VDE (vertical detachment energy) value for an anionic water cluster,[8,9] the PET result has been chosen because it takes account of the reorganization energy gained when the water structure reverts to its neutral configuration. For the step $M^+(g) + (H_2O)_{n→∞}$ to be fully representative of M^+ solvation, the water structure needs to be characteristic of the energy minimum for bulk liquid. The most significant message from the gas-phase experiments is that the ionization energy drops to a constant value, irrespective of the metal. Support for the use of the PET value comes from recent work by Vondrak et al.[18] who have recorded electron photoemission signals from sodium atoms deposited on ice and determined a threshold energy of 2.3 ± 0.2 eV. The interpretation is that sodium on the surface is ionized and a solvated electron is photodetached.[18]

The proposed cycle can be represented by the equation

$$\Delta H_{neu}(M) = IE(M) + \Delta H_{hyd}(M^+) - PET(e^-) \quad (1)$$

The rationale behind eq 1 is that, on forming a dilute solution, the metal atom undergoes the transformation $M → M^+ + e^-(aq)$, where $e^-(aq)$ represents a solvated electron that has entered the conduction band of bulk water. PET(e^-) then equates with the photoelectron threshold for the bulk solvent ($n = ∞$).[19,20]

10.1021/jp065106g CCC: $33.50   © 2006 American Chemical Society

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J. Phys. Chem. B, Vol. 110, No. 42, 2006 **20743**

TABLE 1: Solvation Enthalpies in kJ mol^{-1} Calculated from Eq 1 for Alkali Metal Atoms

	Water		
atom	IE(M)[#]	$\Delta H_{hyd}(M^+)^a$	$\Delta H_{neu}(M)^b$
Li	520	−514	−226
Na	495	−406	−143
K	419	−322	−135
Rb	403	−297	−126
Cs	376	−276	−132
	Ammonia		
atom	IE(M)^c	$\Delta H_{solv}(M^+)^a$	$\Delta H_{neu}(M)^d$
Li	520	−559	−174
Na	495	−441	−81
K	419	−353	−69
Rb	403	−319	−51
Cs	376	−294	−53

^{a} Taken from ref 17. ^{b} Using PET(e$^-$) as 232 kJ mol^{-1}. ^{c} Taken from: http://www.webelements.com. ^{d} Using PET(e$^-$) as 135 kJ mol^{-1}.

Figure 2. Solvation enthalpies for neutral alkali metal atoms in ammonia calculated from eq 1. Also shown is a result derived from a recent theoretical study.
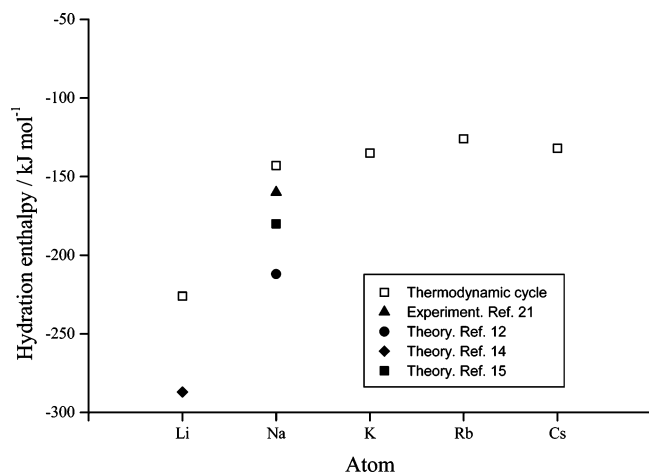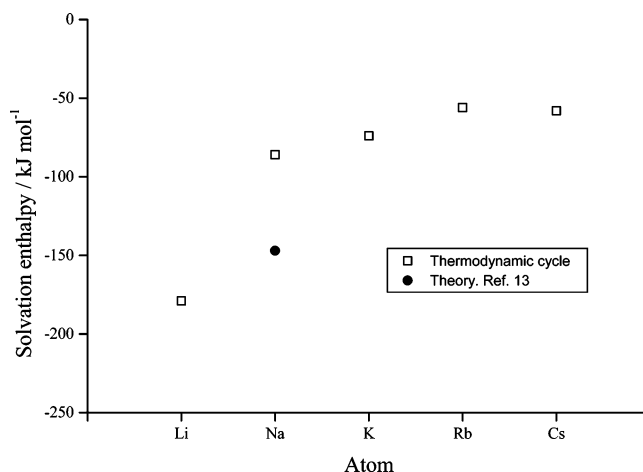

Figure 1. Hydration enthalpies for neutral alkali metal atoms calculated from eq 1. Also shown are binding energies derived from recent experimental and theoretical studies.

Table 1 summarizes results where eq 1 has been applied to the alkali metal atoms lithium through to cesium. The values calculated for $\Delta H_{neu}(M)$ have also been plotted in Figure 1. Limited comparison is possible with experimental[21] and theoretical data[12,15] on the hydration energies of both sodium and lithium with small numbers of water molecules, and these results are also presented in Figure 1. The calculated results represent summations over individual energy differences that have been either calculated or measured by experiment for the process $M(H_2O)_{n-1} + H_2O \rightarrow M(H_2O)_n$ for $n \leq 5$ or 6. In one respect, the calculated results are probably lower limits to the true hydration enthalpy; however, the results are also binding energies rather than enthalpies, and so no account is taken of the effects of zero point energy or the thermal population of vibrational modes. For sodium there is agreement between values derived from eq 1 and the experimental data of Schulz et al.,[21] and also at least one set of the calculated results; however, the latter appear to be very sensitive to the theoretical method used (see below for more general comments on the differences seen in Figure 1). There is some similarity between the trend shown by the results plotted in Figure 1 and values for the standard reduction potentials of the alkali metals.[22] This correlation is not too unexpected given that the latter are proportional to the energetics of electron gain by cations of the metals concerned. However, the fact that the results are almost constant for sodium through to cesium also deserves some

comment. One possible explanation is a size effect; neutral lithium being the smallest of the atoms may be able to penetrate the water surface without breaking any hydrogen bonds. In contrast, the larger atoms (sodium−cesium) could reside on the surface prior to ionization, which would match the interpretation of data on the interaction of neutral sodium with ice.[18] Similarly, comparisons between calculated data on lithium and sodium with small water clusters[12,13] show that lithium prefers to occupy an interior site, whereas sodium prefers to reside on the surface. This picture of atom solvation could be viewed as the neutral equivalent of either "structure-making" or "structure-breaking", as discussed for different-sized cations in aqueous solution.[17]

The cycle has also been applied to alkali metal atoms dissolved in liquid ammonia. The appropriate data are summarized in Table 1, and the calculated solvation enthalpies for the neutral metal atoms are plotted in Figure 2. The PET value taken for bulk ammonia is 135 kJ mol^{-1}.[23] The overall trend in the data set is very similar to that found for the metals taken up by water; however, the values for ammonia are all lower by approximately 75 kJ mol^{-1}. The availability of supporting theoretical results is more limited and there is some discrepancy between the solvation energy for sodium determined from the data given by Hashimoto and Morokuma[13] and the result obtained from the thermodynamic cycle. Interestingly, the calculations by Hashimoto and Morokuma[13] show sodium to be more stable with small numbers of ammonia molecules when associated with an interior site, and this structural difference is responsible for Na(NH$_3$)$_4$ being slightly more stable than (surface-bound) Na(H$_2$O)$_4$. However, the circumstances change as the clusters become larger and hydrogen bonding and many-body interactions begin to make an important contribution to the solvation energy.[13] The results shown in Figure 2 would suggest that these latter interactions become even more significant when behavior in the bulk solvents is compared.

The idea developed in this paper applies primarily to metals that, on contact with a solvent, dissociate to form a cation and a solvated electron. The alkali metals readily fall into this category, with the result that solvation enthalpies can be estimated for atoms of the neutral metal. An examination of all the results shown in Figures 1 and 2 shows that the data derived from eq 1 are all consistently higher than any of the results taken from both experiments and calculations on small clusters. There are two possible reasons for this disagreement: first, the results obtained from eq 1 are based on data related to bulk measurements; in contrast the experimental and calculated

results are derived from data on clusters. It is quite possible, therefore, that metal atoms in the latter are not sufficiently solvated as to be fully ionized, which from the experiments of Fuke and co-workers[6,7] appears to require at least 10 water molecules, and many more in the case of ammonia. A second possible source of the differences seen in Figures 1 and 2 is use of the PET energy rather than the vertical detachment energy (VDE). The latter is larger, which in eq 1 would make the ΔH_{neu}-(M) values more negative, and therefore closer in magnitude to the results derived from experiment and theory. However, for reasons discussed above, use of the VDE would not be a correct representation of the events portrayed by the proposed thermodynamic cycle.

There is some evidence that neutral magnesium and calcium in clusters of water molecules form Mg^+ and $Ca^+ + e^-(aq)$,[24] in which case eq 1 could be used to estimate the hydration enthalpy of neutral Mg and Ca. However, that may not be possible because of the absence of data on the hydration enthalpies of Mg^+ and Ca^+. Interestingly, comparable experiments on the ionization energies of $Mg(NH_3)_n$ clusters show no evidence of convergence to the PET value for liquid ammonia.[25] If a metal, such as magnesium, were to transfer two electrons into a solvent to give M^{2+}, then the appropriate form of eq 1 would be: $\Delta H_{neu}(M) = IE(M) + IE(M^+) + \Delta H_{hyd}(M^{2+}) - 2\,PET(e^-)$.

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