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Note

A RELATIONSHIP BETWEEN HYDRATION ENTHALPIES AND IONIZATION ENERGIES OF METAL IONS

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The general relationship between the charge density of cations and their hydration enthalpies is well known. Those cations of smaller size and higher charge have higher heats of hydration. The solvation forces can be considered as ion–dipole forces so that a relationship results having the form

$$\Delta H_{\mathrm{h}}(\mathrm{kcal\ mole^{-1}}) = -166Z^2/r_{\mathrm{eff}} \qquad (1)$$

where Z is the charge on the ion and r_{eff} is its effective radius (Å) [1]. In eqn. (1) r_{eff} is usually taken as the ionic radius plus a constant (about 0.85 Å) which is about the apparent radius of the oxygen atom in water [2]. While this approach has certainly been widely cited as a correlation between hydration enthalpy and ionic size and charge, it is possible to establish other relationships that are useful when the ionic radius is unknown (for such species as Mg^+, Al^{2+}, etc.). Since the characteristics of size and charge are related to ionization energy, it is suggested that hydration enthalpy may be related to that property. The purpose of this report is to describe a relationship between the total ionization energy and the enthalpy of hydration of a large number of metal cations.

METHODS AND DATA

The data used to establish the relationship between the total ionization energies and the hydration enthalpies are shown in Table 1. Total ionization energies were computed from the values given by Huheey [3] and the hydration enthalpies are those given by Dobbs [4]. Linear regression was used to determine the constants in the equation

$$\Delta H_{\mathrm{h}}(\mathrm{kcal\ mole^{-1}}) = M(\mathrm{IE}) + B \qquad (2)$$

where (IE) is the total ionization energy necessary to produce the ion. Using

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TABLE 1

Ionization energies and hydration enthalpies

Ion	Total IE (kcal mole^{-1})	ΔH(kcal mole^{-1})		%Error
		Actual	Calcd.	
Li^+	124.4	120.1	99.7	16.98
Na^+	118.5	98	94.9	3.21
K^+	100.1	78.6	79.7	1.43
Rb^+	96.32	75	76.6	2.16
Cs^+	89.79	63	71.3	13.10
H^+	313.6	257.3	255.2	0.80
Ag^+	174.7	108	141.1	30.60
Cu^+	178.2	108.3	143.9	32.90
Tl^+	140.8	76.6	113.2	47.76
Mg^{2+}	523.0	451	427.4	5.24
Ca^{2+}	414.7	375	338.3	9.78
Sr^{2+}	385.7	338	314.5	6.95
Ba^{2+}	350.9	312	285.9	8.37
Cr^{2+}	513.6	450	419.6	6.75
Fe^{2+}	554.6	448	453.3	1.19
Mn^{2+}	532.1	436	434.9	0.26
Co^{2+}	574.6	460	469.8	2.13
Ni^{2+}	595.1	486	486.6	0.13
Zn^{2+}	630.9	480	516.1	7.52
Cu^{2+}	646.1	493	528.6	7.21
Cd^{2+}	597.3	426	488.4	14.66
Al^{3+}	1228.3	1087	1007.2	7.35
Cr^{3+}	1227.5	990	1006.5	1.67
Fe^{3+}	1261.4	1125	1034.4	8.06
Ga^{3+}	1319.5	1049	1082.1	3.16
In^{3+}	1215.1	968	996.3	2.92
La^{3+}	825.9	797	676.4	15.14
Tl^{3+}	1299.8	966	1065.9	10.35
V^{3+}	1169.2	860	958.6	11.46
Y^{3+}	902.7	824	739.5	10.26

the linear relationship, the hydration enthalpy was calculated for each ion and these values were compared with the experimental values which were taken as correct. The percent error was then calculated for each ion. In order to determine if differences between the percent relative error for groups were significant, a t-test was performed with the formula being used

$$t = \frac{\left(\bar{X}_i - \bar{X}_j\right)}{\sqrt{\left(\frac{(N_i - 1)S_i^2 + (N_j - 1)S_j^2}{N_i + N_j - 2}\right)\left(\frac{N_i + N_j}{N_i N_j}\right)}} \qquad (3)$$

where $\bar{X}_i$ and $\bar{X}_j$ are the mean relative errors for the two groups being compared, S_i^2 and S_j^2 are the variances of the mean relative errors of the groups, and N_i and N_j are the populations of the two groups [5]. This formula represents the t-test for conditions where the variances for the two groups are approximately equal.

RESULTS AND DISCUSSION

The relationship established between the hydration enthalpy and the total ionization energy for all 30 metal ions of + 1, + 2, and + 3 charge is

$$\Delta H_h \text{ (kcal mole}^{-1}) = 0.82205 \text{ (IE)} - 2.5599 \tag{4}$$

with a correlation coefficient of 0.9896 and a standard error of measurement of 51.063. The data shown in Table 1 indicate that the errors are largest for Ag^+, Cu^+, and Tl^+. Removing these three cases from the group results in the relationship

$$\Delta H_h \text{ (kcal mole}^{-1}) = 0.81057 \text{ (IE)} + 8.8288 \tag{5}$$

with a correlation coefficient of 0.9886 and a standard error of measurement of 52.271. It is thus readily apparent that removal of Ag^+, Cu^+, and Tl^+ from the group does not significantly alter the resulting relationship.

Using eqn. (4) the mean percent error (assuming the reported values to be correct) in ΔH_h for 30 cations is 9.65%. With Ag^+, Cu^+, and Tl^+ removed from the group, the mean percent error is 6.61% with a standard deviation of 4.99. It is likely that eqn. (4) yields hydration enthalpies that are as accurate as the experimental values on which the equation is based. Ionization energies are usually known much more accurately. Since the hydration enthalpies predicted by eqns. (1) and (4) are about the same, it follows that r_{eff} can be calculated by combining the two equations. Thus, the effective ionic radius can be estimated.

The relationship between ΔH_h and total IE is shown as a scatter plot in Fig. 1. In view of the fact that the + 1, + 2, and + 3 ions form three rather separate groups, it is natural to question whether there may be a significant difference between the mean relative errors for the groups. In order to make the t-test comparison, the Tl^+, Cu^+, and Ag^+ data were not included. When mean relative errors for each of the individual groups are compared with the overall mean relative error, there is no statistically significant difference in how the overall relationship [eqn. (4)] applies to each group at the 95% confidence level. For example, while the mean relative error for the entire group is 6.61%, those of the individual groups are 6.28% (+ 1), 5.58% (+ 2), and 7.82% (+ 3). If the Tl^+, Cu^+, and Ag^+ data are included, the + 1 group has a mean relative error of 16.55% Thus, the model fits all the groups equally well.

Equation (1) can be used to calculate ΔH_h values for ions of known radii.

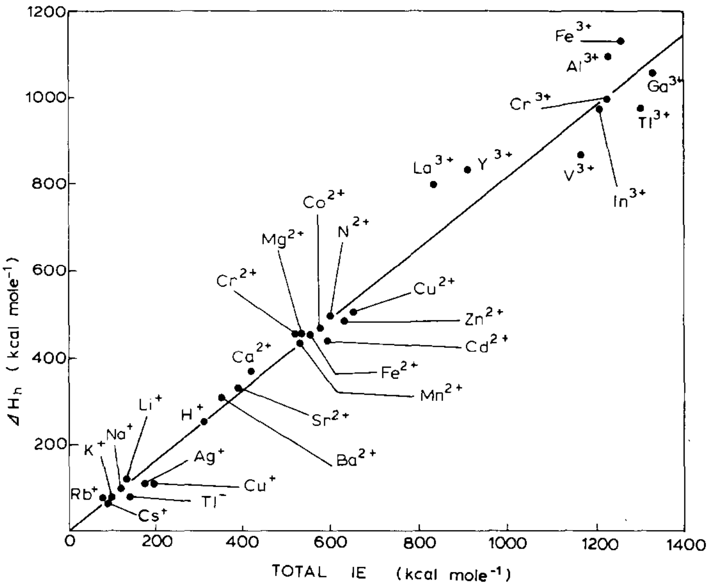

Fig. 1. Relationship between hydration enthalpy and total ionization energy.

However, for many ions the radii are not accurately known and in some cases several values for radii are published. Furthermore, radii are certainly not available for ions like Mg^+, Fe^+, or Al^{2+}. Ionization energies are known for such species. It is readily apparent that eqn. (4) provides a means to accurately estimate the hydration enthalpies for metal ions. In view of the fact that ionization energies are widely avaliable for ions having sequential charges,the relationship may provide a practical means of calculating the hydration enthalpies of ions of unknown radii.

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