CORRELATION EQUATIONS of IONIC HYDRATATION in IONIC GROUPS of s-,p-,d-ELEMENTS

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A connection between thermodynamic parameters of dissolution of ions in a solution is considered. In four groups of ions with the same electronic configuration the equations of correlation between enthalpy hydratation and ionic radii of hydrated ions are received.

During dissolution of substances there is an interaction of the dissolved substances to solvent. The re ceived products during dissolution form solvates. If as solvent water is used hydrates are formed.

It is possible to present, that a connection in hydrates is carried out as a result of two connected interactions: a) an electrostatic interaction between polar molecules of substances; b) an interaction owing to occurrence of hydrogen connection. Hydrogen connection realized between two atoms also has donor-acceptor character. Depending on system under investigation an energy of a hydrogen connection is 8-40 kJ/mole.

Two uncoupled electrons and a polarity of water molecule play an important role during dissolution of substances in water. Molecules of water are represented by four poles of charges. These charges are placed on vertices of a tetrahedron: two positive and two negative. The hydrogen connection between molecules of water together with an electrostatic attraction of electric dipole moments define properties of water.

In ionic crystals connection is caused basically by electrostatic interaction of opposite charged ions. Ionic crystals being dissolved in water form electrostatic associates. Owing to dissolution of crystals at first there are a destruction of its crystal lattice and creations of ions, and then hydration of these ions takes place. At dissolution polar molecules of water can be considered as electric dipoles.

Dielectric permeability of water ε under standard conditions is high and equal to ε=78.47. Value of ε is higher only for several liquids, for example for cyanhydrogen acid. For temperature dependence of dielectric permeability of water proceeding from experimental data [1] we have received: ε=178.5-0.3 T. Here T=273-373 K. The coefficient of correlation ρ calculated by a method of least square, is equal to -0.9967.

Change of Gibbs energy of dissolution process is determined from the equation

$$\Delta G_{dis} = \Delta H_{dis} - T\Delta S_{dis} . \qquad (1)$$

where ΔH_{dis} and ΔS_{dis} are enthalpy and entropy of dissolution accordingly.

Value of ΔG_{dis} which characterizes a change connected with removal of an ion from vacuum and put in solvent, can be estimated from Born equation:

$$\Delta G_{dis} = -N_A \frac{(Z_i e)^2}{2r_i}\left(1-\frac{1}{\varepsilon}\right), \qquad (2)$$

where N_A is Avogadro number; $Z_i e$ is a charge of hydrated ion;
r_i is ionic radius; ε is dielectric permeability of solvent. In any environment $\varepsilon > 1$.

From (2) it follows, that $\Delta G_{dis} < 0$. Value of ΔG_{dis} should become more negative for ions with smaller radius and the big charge in solvents with higher dielectric permeability. Values of ΔG_{dis} received from equation (2) at 298 K are in the agreement with the experimental data.

Value of ΔH_{dis} of ionic compound can be determined as follows:

$$\Delta H_{dis} = \Delta H_{hydro} + \Delta U_{lat} . \qquad (3)$$

where ΔH_{hydro} is enthalpy of hydrated ion, ΔU_{lat} is energy of destruction of a crystal lattice of compound .Here $\Delta H_{hydro} < 0$; $\Delta U_{lat} > 0$.

Value of ΔH_{hydro} is determined by a change of heat at transition of one mole of ions from vacuum into water solution. From formula (3) a total value of ΔH_{hydro} of hydrated cations and anions in a solution can be determined. Hydration enthalpy of anions (cations) of binary compound is determined from experimental data for ΔH_{hydro} for cations (anions) of the same compound.

From (3) it follows, that for different compounds ΔH_{dis} can have various signs. Enthalpy of dissolution of ionic crystals in water at 298 K usually has a negative sign. For some crystals in water $\Delta H_{dis} > 0$, for example for $CaCl_2 \cdot 6H_2O$, NH_4Cl, NaCl, $Na_2SO_4 \cdot 10H_2O$ [2].

Value of hydrated ion depends on its charge and ionic radius. Cations are hydrated stronger, than anions of similar charge. It is caused by the fact that positive area of a water dipole is located in space less compactly, than negative area of a dipole.

Absolute values of ΔH_{hydro} of hydrated ions are increased according with increase of ions charge. In groups of ions with the same electronic configuration with increase of ion radius absolute value ΔH_{hydro} of this ion decreases.

Dependences such as $\Delta H_{hydro} = f(r, Å)$ for different groups of ions are processed by a method of least square. As the initial data we used ΔH_{hydro} /2/and ionic radii $r(Å)$ [2, 3] for the following groups of ions with the same electronic configuration:

Li^+, Na^+, K^+, Rb^+, Cs^+ (I); Be^{+2}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} (II);
Sc^{3+}, Y^{3+}, La^{3+}(III); F^-, Cl^-, Br^-, I^- (IV)

In the table the obtained equations of correlation $\Delta H_{hydro} = ar(Å) - b$ are given(where a and b are constants) for

the groups (I)-(IV) ions with the same electronic configuration. Dependences between the indicated parameters of hydrated ions received by a method of least square are characterized by high coefficients of linear correlation.

Table.

The correlation equations for number of ions with the same electronic configuration.

Number of Ions (I)-(IV)	Correlation equation $\Delta H_{hydr.}(kJ\ mole) = a\ r(\AA) - b$	Coefficient of correlation ρ
Li^+. Na^+. K^+. Rb^+. Cs^+	249 r - 723	0.9869
Be^{2+}. Mg^{2+}. Ca^{2+}. Sr^{2+}. Ba^{2+}	1247 r - 3029	0.9778
Sc^{3+}. Y^{3+}. La^{3+}	1837 r - 5606	0.9936
F^-. Cl^-. Br^-. I^-	250 r - 784	0.9921

[1] *I.T.Goronovski, J.P. Nazarenko, E.F. Necratch.* Brief chemistry directory. Kiev. Naukova Dumka, 1974, p. 767.

[2] *M.H. Karapetiants, S.I. Drakin.* General and inorganic chemistry. M.Chemistry, 1981, p.158.

[3] *Ch. Kittel.* Introduction to Solid State Physics. Trans. from En. M.Science. 1978, p.144.

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s-, p-, d- ELEMENTLƏRİ İONLARININ HİDRATLAŞMASININ KORRELYASİYA TƏNLİKLƏRİ

İonların su məhlulunda həll olması zamanı termokimyəvi parametrlər arasındakı əlaqələr araşdırılmışdır. Eyni tipli elektron konfiqurasiyasına malik olan s-, p-, d- elementləri ionları üçün korrelyasiyalar tapılmışdır. Dörd qrup ionlar üçün korrelyasiya tənlikləri alınmışdır. Hidratlaşma entalpiyası və hidratlaşan ionların radiusları arasında empirik asılılıqlar təyin edilmişdir.

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КОРРЕЛЯЦИОННЫЕ УРАВНЕНИЯ ГИДРАТАЦИИ В ПОДГРУППАХ ИОНОВ s-, p-, d- ЭЛЕМЕНТОВ

Рассмотрена связь между термодинамическими параметрами растворения ионов в растворе. В четырех подгруппах ионов s- , p- , d- элементов, с однотипной электронной конфигурацией методом наименьших квадратов получены уравнения корреляции. Установлена связь между энтальпией гидратации и ионными радиусами гидратируемых ионов.

Received: 25.01.02