ESTIMATE OF ELECTROSTATIC SOLVATION FREE ENERGY OF ELECTRON IN VARIOUS POLAR SOLVENTS BY USING MODIFIED BORN EQUATION

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The modified Born equation was tentatively applied to estimate the electrostatic free energies of solvation of the electron in various polar solvents. The related data of halide ions and a datum of the hydration free energy of the electron obtained by radiation chemical studies were used for the numerical calculations.

The modified Born equation[1] has been applied to predict a decrease of the free energy of solvation with decreasing size of the ions or increasing polarity of the solvent. Recently, Strehlow,[2] Senda and Takahashi,[3] and Tanaka and Ogata[4] extensively discussed on its application especially in relation to the standardization of the electrode potentials among non-aqueous solvents and the donor numbers of various solvents.

On the other hand, the hydration free energy of the electron was estimated by Baxendale[5] and Jortner and Noyes[6] from thermodynamic data of radiation chemical reactions. Some theoretical calculations of the hydration energy of the electron have also been carried out on the basis of a square-well model[7] and semi-continuum model.[8] The use of the modified Born equation seems to be promising for the extensive estimation of the solvation free energy of the electron in various solvents. A tentative treatment presented in this paper implies an unreal quantity of an ionic radius of a solvated electron, which may correspond to the charge distribution of a solvated electron. However, the estimated values of the electrostatic solvation free energies of the electron in various polar solvents seem to be useful, because the data available at this stage are only of an aqueous solution.

The details of the calculation are as follows: The modified Born equation for the solvation free energy of anion is expressed in terms of the charge interaction in a dielectric medium and the effective increment of the ionic radius due to solvation as given by

$$-\Delta G_- = \frac{N(ze)^2}{2} \left(1 - \frac{1}{\varepsilon}\right) \left(\frac{1}{r^- + R^-}\right) \tag{1}$$

where ΔG_- is the electrostatic free energy change of the anion by solvation, z the ionic valency, ε the dielectric constant of the medium, r^- the crystallographic radius of the anion and R^- the effective increment of the radius in solution, which

accounts for the dielectric saturation, the ion-solvent interaction *etc.* Other symbols are of their usual significances.

When we compare the solvation free energies of anions A^- and B^- in a given medium, the following expression is derived from Eq. (1),

$$-d\Delta G_- = -\Delta G_A - (-\Delta G_B) = \frac{Ne^2}{2} (1 - \frac{1}{\varepsilon}) (\frac{1}{r_A^- + R^-} - \frac{1}{r_B^- + R^-}) \qquad (2)$$

where R^- is assumed to be equal for A^- and B^- in the same solvent.

By using Eqs. (1) and (2) approximate estimates of the solvation free energies of the electron in various solvents were carried out as follows,

(1) The value of R^- in each solvent was estimated by substituting the known values of $-\Delta G_-$[9-14] and r^-[15] of halide ions, and ε into Eq. (1).

(2) By introducing $R^- = 0.25 \overset{\circ}{A}$, $-\Delta G_e = 1.71$ eV[6] and $\varepsilon = 78$ for the case of water into Eq. (2), the crystallographic radius of the hydrated electron, r_e^-, was calculated to be $3.9 \overset{\circ}{A}$. This quantity is a hypothetical one, but may have a meaning corresponding to the cavity radius of the hydrated electron as will be discussed later.

(3) By using the value of $r_e^- = 3.9 \overset{\circ}{A}$ and the datum of R^- for each solvent, the solvation free energy of the electron was calculated from Eq. (1).

The results obtained are summarized in Table 1. The value of $R^- = 0.25 \overset{\circ}{A}$

Table 1. Values of effective increment of radius, R^-, and solvation free energy of electron, ΔG_e, in various polar solvents.

Solvent	BuOH	NH$_3$	EtOH	MeOH	AN
ε	17.7	23.0	24.5	32.6	38
R^-, $\overset{\circ}{A}$	0.58	1.08	0.51	0.55	1.0
				(0.37)*	(0.61)*
$-\Delta G_e$, eV	1.51	1.38	1.56	1.56	1.42
				(1.62)**	(1.54)**

Solvent	DMSO	HCOOH	PC	H$_2$O	HCONH$_2$
ε	48.9	57.0	64.4	78.5	84
R^-, $\overset{\circ}{A}$	0.45	0.13	0.79	0.25	0.25
		(0.38)*		(0.25)*	
$-\Delta G_e$, eV	1.61	1.75	1.51	1.71	1.70
		(1.64)**			

* Values were obtained by Strehlow.[2]

** Values were calculated by using Strehlow's data on R^-.

for water is identical with the value obtained by Strehlow,[2] but the values cal-
culated for MeOH, AN and HCOOH are somewhat different from those given by Strehlow.

Jortner and Noyes[6] estimated the radius of the charge distribution for the
hydrated electron using a semi-empirical equation, and found the radius of 2.98 Å.
On the other hand, Blandamer et $al.$[7] discussed the correlation between the cavity
radius and the lattice parameter from the point of view of the square-well model,
and determined the radius of 2.10 Å.

Moreover, according to the theoreti-
cal studies by Fueki and his co-work-
ers[8] the cavity radius at the confi-
gurational minimum was estimated to
be 1.93 Å for a tetrahedral structure
and 2.46 Å for an octahedral struc-
ture of the hydrated electron.   It
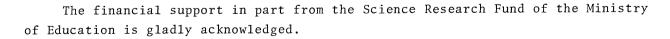is noticed that these data vary wide-
ly.

The correlation of $-\Delta G_-$ of hal-
ide ions to the reciprocal of the
ion-to-H_2O distances determined by
the X-ray diffraction method[16-18]
gives a straight line as shown in
Fig. 1.   Assuming that the same re-
lationship holds for the hydrated e-
lectron, the cavity radius is deter-
mined to be 2.93 Å from the value of
$-\Delta G_e = 1.71$ eV by taking into account
of the radius of water molecule as
great as 1.38 Å.

In view of these data mentioned
above, it seems that the calculated
value of 3.9 Å from the modified Born
equation is a little over-estimated.

Fig. 1. Estimate of $r_{e^- - H_2O}$ by plotting
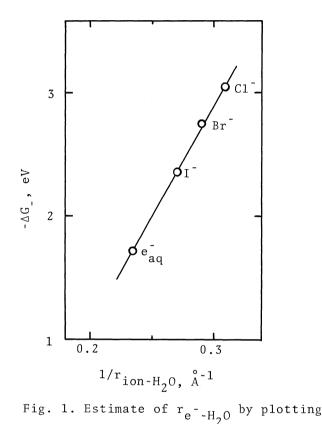$-\Delta G_-$ against $1/r_{ion - H_2O}$ for halide ions.

It is found that a trend of val-
ues, ΔG_e, calculated for solvents with hydroxyl groups is the same with that of ex-
perimental values obtained by means of photo-electron emission method.

A comparison of these calculated values of ΔG_e with those determined experimen-
tally will be reported elsewhere.

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