EMPIRICAL RULES FOR SOLUTE-SOLVENT INTERACTIONS IN FUSED SALTS AND CONCENTRATED AQUEOUS SOLUTIONS

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ABSTRACT

It was found that the same empirical rules concerning the relative standard free energies for solvation of monoatomic ions referred to a definite ion as recently found for solvation in usual solvents, also hold for that in fused salts. Using these rules, we could found the absolute values of solvation energies, the absolute acidities and basicities of fused salts, and some linear relationships also in concentrated aqueous solutions concerning the activity coefficients of ions and water. On the basis of these facts, the solute-solvent interactions in fused salts and the concentrated aqueous solutions of salts were also found to be elucidative by the electron donor-acceptor concept.

INTRODUCTION

The aim of this paper is to provide an empirical method for estimating the standard chemical free energy of solvation \( \Delta G^0_{i}(g^s) \) of a cation \( i \) (anion \( x \)) in a fused salt solvent \( s \) and to elucidate the electron donor-acceptor interaction between ions and species in fused salts or in concentrated aqueous solutions, where \( g \) means the gas phase. In different fused salts, there is a difficulty in comparing the electrode potential due to the absence of a common standard reference electrode, comparable to the hydrogen electrode in aqueous solutions. This problem had remained unsolved till recently even for usual non-aqueous solvents. Recently, we found two empirical rules concerning the standard chemical free energy of solvation of ions in aqueous and non-aqueous solvents; namely \( \Delta G^0_{i,g^s} = \beta_s (\Delta G^0_{i,g^s} / z_i) = \varepsilon_i \rho_a^s \) for an individual cation, where \( z_i, \varepsilon_i, \beta_s \) and \( \rho_a^s \), denote respectively, valence, a constant characteristic of the cation \( i \),
constants characteristic of solvent s, w means water (1). On the other hand, \( \Delta G^0_{i, g + s} = F_s \Delta G^0_{i, g + w} = \varepsilon_s (\rho^A_X - 0.8) \) were found to hold for the solvation of an individual anion. On the basis of these rules we can estimate the absolute values of chemical free energies of solvation of ions. Also we have successfully obtained the absolute standard EMF \( \Phi^0_{i, s} \) of the following electrode reaction in solvent s, if the surface potential of solvent \( \chi_s \) is known:

\[
M_i^{z_i} + z_i e^- = M_i
\]

By this method, we have determined the \( \Delta G^0_{i(x), g - s} \) and \( \Phi^0_{i(x), s} \) for more than 70 species of monoatomic ions in 15 solvents, such as organic solvents, and liquid hydrazine and ammonia. Furthermore, this method has been applied to fused salt systems with two or three components. In 10 systems, \( \Delta G^0_{i(x), g + s} \) and \( \Phi^0_{i(x), s} \) of monoatomic ions from 5 to 45 species have been determined (2).

These empirical rules have been established on the basis of the electron donor-acceptor concept. This paper is concerned with the electron donating and accepting properties, that is, the absolute basicity \( \rho^A_X \) and absolute acidities \( \varepsilon_i \) and \( \varepsilon_s \) which affect the interactions between monoatomic ions and surrounding species in fused salts and in concentrated aqueous solutions.

**BASIC CONSIDERATION**

Recently, we have found an empirical method for estimating the standard chemical free energy of solvation \( \Delta G^0_{i, g + s} \) of an ion in any solvent, by use of the relative standard free energy of solvation, \( i \Delta j(\Delta G^0_{i, g + s}/z) \) of an ion i referred to that of a definite ion j in the same solvent s and an extrathermodynamic assumption as described in the latter. The relative quantity \( i \Delta j(\Delta G^0_{i, g + s}/z) \) can be defined by the following equation;

\[
i \Delta j(\Delta G^0_{i, g + s}/z) = (\Delta G^0_{i, g + s}/z_i) - (\Delta G^0_{j, g + s}/z_j)
\]

where \( \Delta G^0_{i, g + s}/z_i \) and \( \Delta G^0_{j, g + s}/z_j \) denote the standard electrochemical free energy of solvation of ions i and j. The electrochemical one \( \Delta G^0_{i, g + s}/z_i \) may be given by the chemical part of the solvation energy \( \Delta G^0_{i, g + s}/z_i \) and the surface potential \( \chi_s \) of the solvent;

\[
\Delta G^0_{i, g + s}/z_i = (\Delta G^0_{i, g + s}/z_i) - F \chi_s
\]
The last term in eq.[3] for an ion \(i\) equals that in a similar equation for \(j\). Therefore, eq.[2] can be rewritten by the chemical ones;

\[
i \Delta j(\Delta G^o_{g+s/z}i, g+s/z) = (\Delta G^o_{j, g+s/z}) - (\Delta G^o_{j, g+s/z})
\]

[4]

As seen from the thermodynamical cycle shown in Fig.1, the standard electrochemical free energy of solvation \(\Delta G^o_{i, g+s}\) of an ion \(i\) can be expressed in terms of the standard electrochemical free energy of formation of an ion \(i\) \(M_iZ_i\) and the electrons \(Z_i e^-\), \(\Delta G^o_{i}\), and the absolute standard electromotive force, \(\Phi^o_{i, s}\) of the ion/pure substance electrode in solvent \(s\);

\[
\Delta G^o_{i, g+s} = \Delta G^o_{i} - Z_i F \Phi^o_{i, s}
\]

[5]

where \(\Phi^o_{i, s}\) is given by the difference in the standard electrochemical potentials \(\Phi^o_{e, g}\) and \(\Phi^o_{e, m}\) of the electron \(e^-\) in the gas phase and in the electrode \(m\);

\[
F \Phi^o_{i, s} = \Phi^o_{e, g} - \Phi^o_{e, m}.
\]

[6]

The value of \(\Delta G^o_{i}\) is also given by the standard free energies of atomization \(A_i\) of \(M_i\) and the ionization \(I_i\) of \(M_i, g\) in the gas phase;

\[
\Delta G^o_{i} = A_i + I_i
\]

[7]

Using the eqs.[2] and [5] for ions \(i\) and \(j\), we obtain;

\[
i \Delta j(\Delta G^o_{g+s/z}i, g+s/z) = (\Delta G^o_{j, g+s/z}) - (\Delta G^o_{j, g+s/z}) - F \Phi^o_{i, j, s}
\]

[8]

where \(\Delta G^o_{i}\) denotes the standard free energy of formation of an ion \(j\) \(M_jZ_j\) and electrons \(Z_j e^-\) in the gas phase from its pure substance \(M_j\), and \(F \Phi^o_{i, j, s}\) and its numerical value can be known as the standard potential of the electrode reaction expressed by eq.[1] of \(i\) species referred to that of a similar reaction of \(j\) species in the same solvent. In this way \(i \Delta j(\Delta G^o_{g+s/z})\) can be expressed in terms of the well-defined measurable thermodynamic quantities \(\Delta G^o_{i}\), \(\Delta G^o_{j}\) and \(F \Phi^o_{i, j, s}\).

Using the values in thermodynamic tables in the literature, we could obtained the quantities \(i \Delta j(\Delta G^o_{g+s/z})\) for many species of monoatomic ions in 15 solvents, as described above. We have found three linear relationships between the relative quantities \(i \Delta j(\Delta G^o_{g+s/z})\) and the ionization energy of cations divided by \(Z_i, I_i/Z_i\). Monoatomic cations are divided into three groups \(\{a, b \) and \(c\}\) and the cations in each group are classified by the electronic configura-
tion. In these relationships, the absolute value $\Delta G^0_{ij}g^{-s}/z$ could be obtained on the extrathermodynamic assumption that the electronic configuration of the ideal ion is a rare gas type, its ionization energy $I_i$ equals zero and such an ion has no chemical interaction with any solvent. In this way, we could know the absolute value of $\Delta G^0_{ij}g^{-s}/z_i$ for all ions available here and it could be expressed as the function of $I_i/z_i$. In this way, we have found two empirical rules named the first(I) and second(II) ones, and further have found to be applicable to the bond energy of gaseous di- and tri-atomic metal halides $D'MX_n$, if we consider the bond strength of the molecule as defined by the energy required to separate the constituent atoms into the cation $M^n^+$ and the anion $X^-$. These empirical rules and the related correlations are summarized in Table I.

Table I. Summary of Empirical Rules and Related Correlations for Solvation of Ions and Bond of $MX_n$.

| Solvation (cation $i$) | Bond of $MX_n$ | Solvation (anion $x$) |
|-----------------------|----------------|-----------------------|
| Rule I                |                |                       |
| $\Delta G^0_{i,g^{-s}}=\beta_s\Delta G^0_{i,g+\omega}$ | $D'MX_n = \beta_x D'MCl$ | $\Delta G^0_{x,g^{-s}}=\beta_s\Delta G^0_{x,g+\omega}$ |
| Rule II               |                |                       |
| $\Delta G^0_{i,g^{-s}/z_i}=\varepsilon_i\rho_s^a$ | $D'MX_n/n=\varepsilon_i\rho_x^a$ | $\Delta G^0_{x,g^{-s}}=\varepsilon_s(\rho_x^a-0.08)$ |
| $\beta_s=\rho_s^a/\rho_w=\rho_b/\rho_w=\rho_c/\rho_w$ | $\beta_x=\rho_x/\rho_C$ | $\beta_s=\varepsilon_s/\varepsilon_w$ |
| $\rho_s^a=0.099(DN+8.83),eV$ | $\varepsilon_s=0.30(AN+211.2)$ |

In Table I, the parameters $\rho_s^a$ or $\varepsilon_s$ and $\rho_x^a$ or $\varepsilon_x$ mean the absolute basicity or acidity of a solvent and that of an anion or a cation. $\rho_s^a$ and $\varepsilon_s$ were found to be regarded as the absolute values of Gutmann's and Mayer's electron donor and acceptor numbers, DN and AN (3), respectively. It is obvious from Table I that the solvations is due to the electron donor-acceptor interaction.
RESULTS

Applying the donor-acceptor concept to fused salt systems on the basis of the following equation at \( T^0 K \) where the temperature effect was taken into account, instead of eq.[8], we have found the same two empirical rules in 10 fused salt systems with two or three components as obtained in the non-aqueous solvents;

\[ i \Delta j(\Delta G_{i\rightarrow j}^0/g_{i\rightarrow j}/z_i(T) = (\Delta G_{i\rightarrow j}^0/z_i(T) - (\Delta G_{j\rightarrow i}^0/z_j(T) - FE_{i\rightarrow j}^0/s(T) [9] \]

The relative quantities for various ions were estimated by use of the quantities of \( \Delta G_{i\rightarrow j}^0(T) \) and \( E_{i\rightarrow j}^0(T) \) mainly quoted the data in (4) and (5). The empirical rule I was found to hold for fused salt systems as exemplified in Fig.2. The value of \( -\Delta G_{i\rightarrow j}^0/g_{i\rightarrow j}/z_i(T) \) in fused salt was given by the intersection of this line with the vertical one in Fig.2 on the basis of the empirical rule I and eq.[4]. The empirical rule II was also found to hold for fused salt systems as shown in Fig.3. In this way, \( \Delta G_{i\rightarrow j}^0/g_{i\rightarrow j}/z_i(T) \), \( \beta_s \) and \( \rho_s \) for 10 systems were determined which are summarized in Table II with the standard deviation \( \pm \delta \) from the rule I.

| Fused Salt       | Temp. \( ^0 K \) | \( \Delta G_{i\rightarrow j}^0/g_{i\rightarrow j}/z_i(T) \) | \( \Phi_{i\rightarrow j}^0/s(T) \) | \( \beta_s \) | \( \rho_s \) | \( \pm \delta \) |
|------------------|------------------|---------------------------------|-------------------|--------|--------|----------|
| LiCl-KCl         | 723              | 5.50                            | 4.43              | 0.970  | 0.919  | 0.23     |
| MgCl2-NaCl-KCl   | 748              | 5.11                            | 4.69              | 0.937  | 0.887  | 0.23     |
| AlCl3-NaCl-KCl   | 423              | 5.53                            | 4.62              | 0.957  | 0.906  | 0.30     |
| LiNO3-KNO3       | 450              | 4.86                            | 5.30              | 0.997  | 0.944  | 0.11     |
| NaNO3-KNO3       | 523              | 5.18                            | 4.95              | 0.968  | 0.917  | 0.13     |
| Li2SO4-K2SO4     | 898              | 5.45                            | 3.50              | 1.035  | 0.980  | 0.30     |
| NaSCN-KSCN       | 435              | 4.80                            | 5.14              | 0.911  | 0.863  | 0.33     |
| CH3COOLi-CH3COOK | 495              | 11.28                           | 3.23              | 1.013  | 0.950  | 0.05     |
| Li2C03-Na2C03    | 973              | 4.51                            | 4.12              | 0.923  | 0.874  | 0.03     |
| Li2SO3-KP03      | 823              | 4.82                            | 4.29              | 0.972  | 0.920  | 0.02     |

It is surprizing that \( \beta_s \) is quite close to unity in any fused salt available. The absolute standard EMFs \( \Phi_{i\rightarrow j}^0/s(T) \) are also summarized in Table II. The value of \( \Phi_{i\rightarrow j}^0/s(T) \) were determined by use of \( \Delta G_{i\rightarrow j}^0/g_{i\rightarrow j}/z_i(T) \) on the basis of eq.[3] and the assumption of \( \chi_s = 0 \), due to a random distribution for the surface dipoles of fused salts at higher temperatures as compared with the aqueous solution (2). This assumption
seems to be permissible, because an experimental result has shown that the surface potential at mercury-aqueous solution interface decreases with an increase of temperature and vanished at 85°C (6).

In order to reveal the effect of the components of fused salts on the absolute basicities $\rho_a^s$ obtained thus, we determined the values of $\rho_a^s$ or $\epsilon_s$ of single component fused salts by use of the standard potentials $E_{ij,s}^0$ of the following electrode reactions [10 and 11]:

\[
\begin{align*}
Tl^{2+} + 2e^- &= Ti, \\
2Cl^- &= Cl_2 + 2e^-,
\end{align*}
\]

in various molten alkali metals and alkaline earths chlorides at 1300°K. Fig. 4 showed the linear dependence of the absolute basicity $\rho^a_s$ of fused salt upon the absolute acidity $\epsilon_{M^{n+}}$ of the component cation of fused salt. The value of $\rho^a_s$ became smaller in the greater value of $\epsilon_{M^{n+}}$ of the component cation of fused salt. On the other hand, it was shown in Fig. 5 that the absolute acidity $\epsilon_s$ of fused salt also became smaller in the greater value of the absolute acidity $\epsilon_{M^{n+}}$ of the component cation of fused salt. Consequently, the interaction between solute ion and fused salt became less in the greater value of the absolute acidity $\epsilon_{M^{n+}}$ of the component cation of fused salt, in any case that the solute is a cation or an anion. At the point of view of the micro structure of such a system, it seems that the interactions are very complicated. But, it was found that the thermodynamical consideration on the basis of the electron donor-acceptor concept may be a useful method to obtain the knowledge concerning even multiple interactions among ions and molecules as shown above.

It was found that the solute-solvent interactions in concentrated aqueous solution are also related to the electron donor-acceptor nature. The Sechenov factor $K_Y = \delta \log \gamma^*_w / \delta m$ and the activity coefficient $\gamma^*_w$ of water quoted from (8) and (9) showed linear relations with the absolute acidity $\epsilon_{M^{n+}}$ of the component cation of various solute salts, as shown in Figs. 6 and 7, respectively.

SUMMARY

The standard chemical free energy of solvation of a cation in fused salt is given by the product of the absolute acidity of the cation and the absolute basicity of fused salt.
The empirically obtained linear relationships between the absolute basicity (and acidity) of single component fused salt and the absolute acidity of the component cation of fused salt are useful to estimate the absolute basicity (and acidity) of any kind of single component fused salt and furthermore the standard free energy of the solvation of ion, whose experimental data of $E_{ij}^{°}$ are absent in the literature.

It was found that the solute-solvent multiple interactions in concentrated aqueous solution affecting the activity coefficients of ions and water, are due to the electron donor-acceptor interaction.

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\[ M_{i,g} \rightarrow z_i e^{-} + M_{i,g}^{z_i} \]

\[ A_i \rightarrow z_i F_{i,s}^{0} \]

\[ \Delta G_{i,g}^{0} \rightarrow z_i e^{-} + M_{i,s}^{z_i} \]

Figure 1. The Thermodynamic Cycle for the Formation of a Gaseous Ion from Its Pure Element.

Figure 2. Relation (mol% 59:41) at 723 K and \( \Delta G_{i,g}^{0} \) at 298 K, Ag⁺ being Taken as j.
Figure 3. Relation between $\Delta G^0_{i,s(T)} / z_i$ for the same system as exemplified in Figure 2 and $I_i / z_i$.

Figure 4. Relation between $\rho^0$ at 1300°K and $E_{M^n+}$ at 0°K of the component cation of fused salt.
Figure 5. Relation between $\varepsilon_s$ at 1300°K and $\varepsilon_{M^{n+}}$ at 0°K of the Component Cation of Fused Salt.

Figure 6. Relation between the Sechenov Factor $K_Y$ of $M_1Cl_n$ and $\varepsilon_{M^{n+}}$ of the Cation, in Concentrated Aqueous Solution.
Figure 7. Relation between Activity Coefficient $\gamma_w$ of Water and $\epsilon_{M^{n+}}$ of the Cation, in Aqueous Solutions of $M_1(NO_3)_n$ (°) or $\epsilon_{M^{n+}}$ Estimated as the Mean Value of the Component Cations on the Basis of the Component Ratio in Mixed Solutions of Two (○), Three (△) or Four (□) Species of $M_1(NO_3)_n$, at the Total Mole Fraction = 0.1, T = 60°C.