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Theoretical Estimation of the Entropies of Solvation of Univalent Ions

Takehiro Abe
College of General Education, Tohoku University, Kawauchi, Aoba-ku, Sendai 980

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Synopsis. A simple theoretical expression for the entropies of solvation of univalent ions has been derived by using a modified Born equation and has been successfully applied to several ions in water and to the typical ions Rb^+ and Cl^- in various solvents.

Abraham and Liszi[1,2] have succeeded in calculating the entropies of solvation of univalent ions in nonaqueous solvents, using a one-layer solvation model in which an ion is surrounded by a local solvent layer, immersed in the bulk solvent. They obtained excellent agreement between the calculated and observed entropy changes. However, their model contains parameters such as the thickness of the local solvent layer and the variation of the dielectric constant with temperature. An attempt has been made, therefore, to present a simple expression which contains no adjustable parameters and roughly reproduces experimental ionic solvation entropies. Recently, Abe[3] presented the following equation for the free energy of solvation of an ion of charge Ze (where Z is the formal charge and e the charge of a proton) embedded in a continuous dielectric medium of solvent:

$$\Delta G^\circ_{\text{Abe}} = \frac{e^2LZ^2}{2a} \times \left(\frac{1}{\ln \varepsilon_r} - \frac{1}{\varepsilon_r \ln \varepsilon_r} - 1 \right), \tag{1}$$

where ΔG° is the increase of the standard molar Gibbs function, L the Avogadro constant, ε_r the bulk relative permittivity of the solvent, and a the radius of a spherical cavity in whose center the ion is placed. Equation 1 was derived by considering a distance-dependent relative permittivity of the solvent on the assumption that only the electrostatic free energy is predominant in the case of monoatomic and small ions. The equation reproduced experimental free energies of ions better than the Born equation[4] did.[3] Ehrenson[5] showed that the solvent parameter $\{1/\ln \varepsilon_r - 1/(\varepsilon_r \ln \varepsilon_r) - 1\}$ in Eq. 1 was the best in the inverse exponential radial dielectric function family of the modified Born equations for the correlation of the free energies of solvation. Moreover, Abe[6] showed that Eq. 1 can be successfully applied to the estimation of the solubilities of sparingly soluble lanthanoid iodates in dimethyl sulfoxide (DMSO)–water. Accordingly, in this paper, Eq. 1 has been applied in order to obtain a simple expression for the solvation entropies of ions. The results of calculations have been compared to those calculated by using the Born equation.

Theoretical Calculations and Discussion

On the assumptions that only the electrostatic contribution is dominant and that a does not depend on the temperature T(K), one can easily derive the following increase of standard molar entropy from Eq. 1 according to $\Delta S^\circ = -(\partial \Delta G^\circ / \partial T)_p$ (where the suffix p denotes constant pressure):

$$\Delta S^\circ_{\text{Abe}} = \frac{e^2LZ^2}{2a} \times \frac{(\varepsilon_r - \ln \varepsilon_r - 1)}{\varepsilon_r^2 (\ln \varepsilon_r)^2} \times \frac{d\varepsilon_r}{dT}, \tag{2}$$

where $e^2L/2 = 69.5$ nm kJ mol^{-1} ($=16.6$ nm kcal mol^{-1}, where 1 cal=4.184 J). On the other hand, ΔS° is easily given similarly from the Born equation by

$$\Delta S^\circ_{\text{Born}} = \frac{e^2LZ^2}{2a} \times \frac{1}{\varepsilon_r^2} \times \frac{d\varepsilon_r}{dT}. \tag{3}$$

Equations 2 and 3 do not contain adjustable parameters and are much simpler than the equation given by Abraham and Liszi.[1] In the present study, Eqs. 2 and 3 were applied to 10 univalent ions in water and to the typical ions Rb^+ and Cl^- in various solvents. The results of calculations were compared with experimental values[1] ($\Delta S^\circ_{\text{obsd}}$) for the 12 ions, as shown in Figs. 1, 2, and 3. In applying Eqs. 2 and 3, all the values for a, ε_r, and $d\varepsilon_r/dT$ were taken from Ref. 7 except for the ε_r value of ammonia, for which 16.9[8] (25 °C) was adopted.

All the figures show that Eq. 2 reproduces the $\Delta S^\circ_{\text{obsd}}$ values much better than does Eq. 3 and that Eq. 3 overestimates the ΔS° values as a whole. The experimental values for ΔS° have also been tabulated by Criss

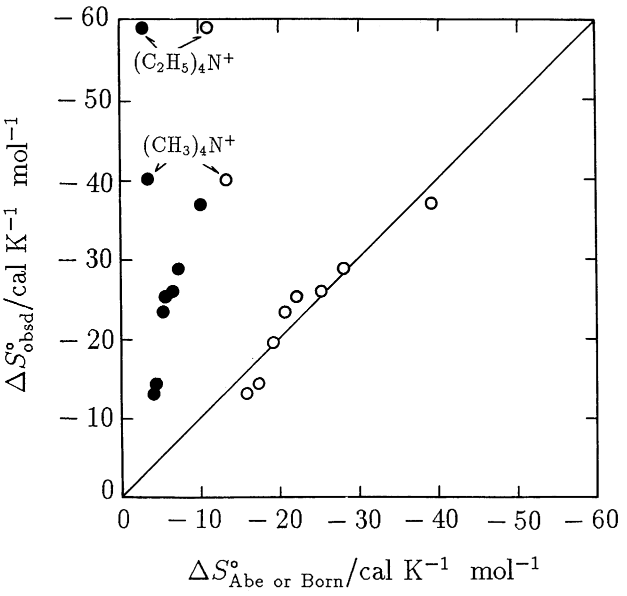

Fig. 1. Plots of observed entropies of solvation of 10 univalent ions (Na^+, K^+, Rb^+, Cs^+, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, Cl^-, Br^-, I^-, and ClO_4^-) in water (298 K) vs. $\Delta S^\circ_{\text{Abe}}$ (○) and $\Delta S^\circ_{\text{Born}}$ (●).

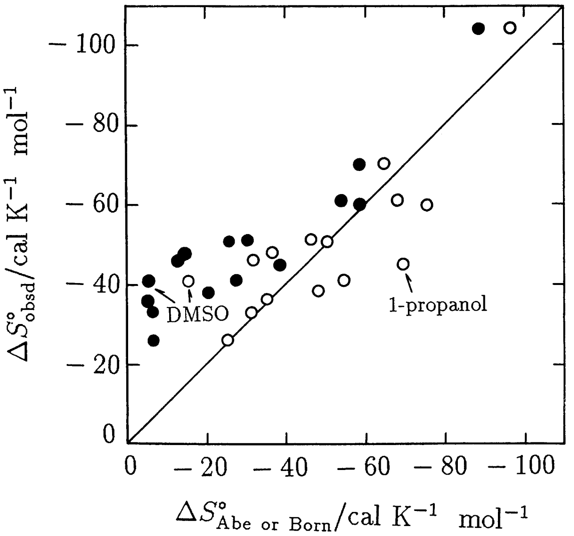

Fig. 2. Plots of observed entropies of solvation of Rb^+ in various solvents (298 K) vs. $\Delta S^\circ_{\text{Abe}}$ (○) and $\Delta S^\circ_{\text{Born}}$ (●).

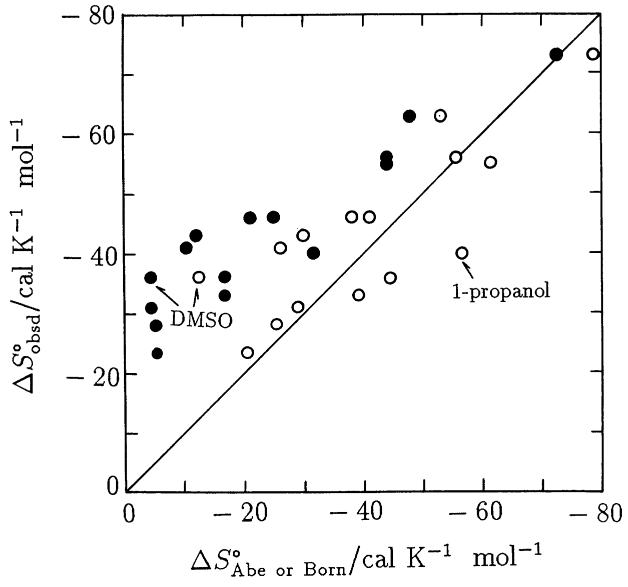

Fig. 3. Plots of observed entropies of solvation of Cl^- in various solvents (298 K) vs. $\Delta S^\circ_{\text{Abe}}$ (○) and $\Delta S^\circ_{\text{Born}}$ (●).

and Salomon.[9] Comparison of the values reported by Abraham and Liszi[1] and by Criss and Salomon led to the suggestion that errors in experimintal entropies of solvation are at least several calories K^{-1} mol^{-1}. It was, therefore, not surprising that there was only poor agreemont between the calculated and observed values. Abraham and Liszi[1,2] have combined the calculated electrostatic-entropy value with a nonelectrostatic contribution as the total entropy of solvation. According to them, the nonelectrostatic entropy values are quite small for solvents other than water. As shown in Figs. 1—3, however, Eq. 2, which was derived by considering only the electrostatic-entropic contribution, gave roughly the corresponding experimental values except for the cations $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ (Fig. 1). From this result, the nonelectrostatic-entropic contribution may be neglected in the case of atomic and small molecular ions. In the case of the large ions $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$, the nonelectrostatic-entropic contribution may not be ignored, since the methyl and ethyl groups obviously interact nonelectrostatically with the water molecules. In Figs. 2 and 3, the plots for the DMSO solvent deviated quite a bit from the lines. Cations are strongly solvated in DMSO, whose molecule has a negative charge localized on an oxygen atom.[10] For this reason, the value of $|\Delta S^\circ_{\text{obsd}}|$ for Rb^+ in DMSO is probably larger than that of $|\Delta S^\circ_{\text{Abe}}|$ which is due only to the electrostatic-entropic contribuiton. On the other hand, anions are poorly solvated in DMSO.[10] However, this fact cannot account for the large deviation of the plot for Cl^- in DMSO from the line. The deviation suggests a special interaction between Cl^- and DMSO. This special interaction seems to be the interaction between Cl^- and a hydrogen atom of the DMSO molecule, because methylsulfinylmethanide is simply genetated from DMSO[11] and DMSO is a very weak acid.[12] For hydrogen-bonded solvents, Abraham and Liszi[1] found substantial differences between the calculated and observed ΔS° values. In Figs. 2 and 3, however, only the Eq. 2 plot of 1-propanol deviated greatly from the lines. Thus, Eq. 2 may be applied to the approximate estimation of the entropies of solvation of small univalent ions.

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