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Theoretical Estimation of the Solubilities of Lanthanoid Iodates in Dimethyl Sulfoxide-Water Mixtures

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Synopsis. By using a Modified Born equation, the solubilities of sparingly soluble lanthanoid iodates in dimethyl sulfoxide-water mixtures have been successfully estimated.

Recently Miyamoto et al.[1] have reported the solubilities of lanthanoid iodates in dimethyl sulfoxide (DMSO)-water mixtures. They have qualitatively accounted for these values of solubilities, using the theory of Davis, Ricci, and Sauter[2] for solubility. In their theory, the famous Born equation[3] is applied to the calculation of the interaction energy of an ion with a solvent. Recently, Abe[4] has modified the Born equation by considering a distance-dependent relative permittivity of a solvent. The modified equation better reproduces the observed solvation free energies of ions than does the Born equation. Moreover, Ehrenson[5] has shown that the solvent parameter in Abe's equation is the best in the inverse exponential radial dielectric function family of the modified Born equations for the correlation of the free energies of solvation. In this paper, therefore, an attempt has been made to account quantitatively for the solubilities of lanthanoid iodates by using Abe's equation instead of the Born equation in the theory of Davis, Ricci, and Sauter.

Theoretical Treatment

Let us consider that a sparingly soluble salt, $A_{\nu+}B_{\nu-}$, dissolves in a given solvent i at a concentration of c_i (molarity) and that the salt is completely dissociated into spherical ions:

$$A_{\nu+}B_{\nu-} \longrightarrow \nu_+ A^{(z_+)+} + \nu_- B^{(z_-)-} \tag{1}$$

Following the theoretical treatment of Davis et al.[2] one obtains the following final equation by replacing the Born equation with Abe's equation:[4]

$$\ln\left(\frac{c_2}{c_1}\right) = \frac{e^2}{2kT} \times \frac{z_+z_-}{z_+ + z_-} \times \left(\frac{z_+}{r_+} + \frac{z_-}{r_-}\right) \times \{\eta_1'(\varepsilon_{r,1}) - \eta_2'(\varepsilon_{r,2})\} - A \times (z_+z_-) \times \left\{\frac{I_1^{1/2}}{(T\varepsilon_{r,1})^{3/2}} - \frac{I_2^{1/2}}{(T\varepsilon_{r,2})^{3/2}}\right\}, \tag{2}$$

where e the charge of the proton; k, the Boltzmann constant; T, the temperature (K); r_+ and r_-, the radii of the cation and the anion respectively; $\varepsilon_{r,i}$, the relative permittivity of the solvent i, and A=4.2013×10^6 mol$^{-1/2}$ dm$^{1/2}$ K$^{3/2}$. Here,

$$\eta_i'(\varepsilon_{r,1}) = \frac{1}{\ln \varepsilon_{r,i}} - \frac{1}{\varepsilon_{r,i} \ln \varepsilon_{r,i}}, \tag{3}$$

and

$$I_i = \frac{1}{2} \times (\nu_+ z_+^2 + \nu_- z_-^2) c_i . \tag{4}$$

The second term on the right-hand side of Eq. 2 is the logarithmic mean activity coefficients, that have been calculated by the limiting Debye-Hückel equation on the assumption that the activity coefficients corresponding to the molarity and mole fraction are approximately the same for sufficiently dilute solutions of the salt.[6] When the Born equation is used instead of Abe's, one obtains an equation corresponding to Eq. 2 in which $\{\eta_1'(\varepsilon_{r,1}) - \eta_2'(\varepsilon_{r,2})\}$ is replaced with $(1/\varepsilon_{r,1} - 1/\varepsilon_{r,2})$.

In applying Eq. 2, as the solvent 1 we must choose a standard solvent whose c_1 value is already known. It is, however, impossible to evaluate explicitly the c_2 value by using the $\varepsilon_{r,2}$ value, because the c_2 value is contained not only in ln (c_2/c_1) but also in the ionic strength of I_2, according to Eq. 4. The c_2 value was, therefore, numerically obtained as follows. The pure solvent of water for which the solubility of the lanthanoid iodate is the highest was chosen as the standard solvent. The solubility, therefore, decreases in the DMSO-water mixture with an increase in the component of DMSO. Accordingly, by gradually decreasing the c_2 value, independent calculations of the values of both the right- and left-hand sides of Eq. 2 could be repeated by means of a computer until a close agreement (within 10^{-4}) between the values of the two sides was obtained. Thus, the c_2 value was evaluated.

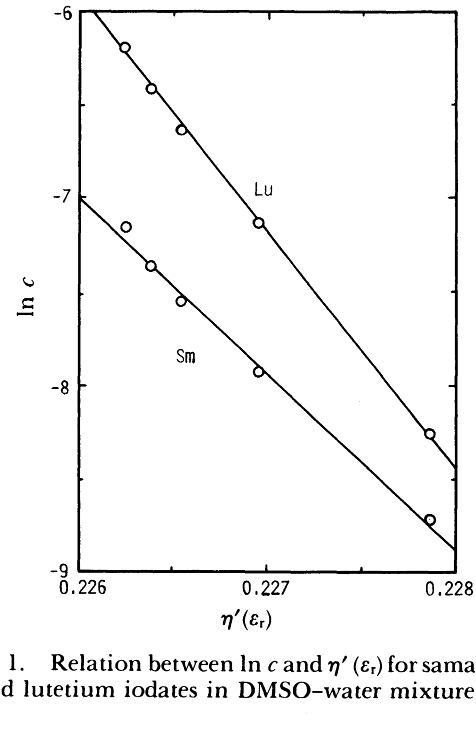

Fig. 1. Relation between ln c and $\eta'(\varepsilon_r)$ for samarium and lutetium iodates in DMSO-water mixtures.

Table 1. Solubilities of Representative Lanthanoid Iodates in DMSO-Water Mixtures at 25 °C

DMSO mass %	c_{obsd}[a)] 10^{-3}mol dm^{-3}	c_{calcd} 10^{-3}mol dm^{-3}
$Ce(IO_3)_3$		
0	1.963	—
5.03	1.495	1.558
10.03	1.261	1.397
20.09	0.905	1.037
40.03	0.428	0.537
$Gd(IO_3)_3$		
0	0.893	—
5.03	0.747	0.732
10.03	0.614	0.650
20.09	0.422	0.470
40.03	0.185	0.230
$Lu(IO_3)_3$		
0	2.036	—
5.03	1.629	1.581
10.03	1.304	1.389
20.09	0.794	0.976
40.03	0.258	0.448

a) Data from Ref. 1.

Results and Discussion

In applying Eq. 2 to the data of solubilities for the lanthanoid iodates in DMSO-water mixtures,[1)] the crystal radii of the trivalent rare earth ions[7)] were used as the r_+ values. The reported radius of 0.182 nm[8)] for IO_3^- was used as the r_- value. The ε_r values used for the DMSO-water mixtures were those indicated in a previous paper.[1)] Miyamoto et al. have shown examples of the relation between ln c and $1/\varepsilon_r$ for samarium and lutetium iodates.[1)] The corresponding relation between ln c and $\eta'(\varepsilon_r)$ is shown in Fig. 1. The figure shows that the values of ln c are linearly proportional to the values of $\eta'(\varepsilon_r)$. This means that the first term in Eq. 2 contributes dominantly to the value of ln (c_2/c_1) in the present case. The observed and calculated solubilities (c_2) for the three representative lanthanoid iodates are shown in Table 1. Table 1 shows that the solubilities calculated by the use of Eq. 2 agree, to a gross approximation, with the corresponding observed values. When the Born equation was used, similar calculations gave solubilities too much higher for the mixtures of high-DMSO components.

Binary solvent mixtures, such as the DMSO-water mixture, are accompanied by the problem of selective solvation.[9)] The observed solubilities of the lanthanoid iodates may be influenced to some extent by the selective solvation. However, the finding that Eq. 2 gives grossly approximate values of the observed solubilities means that the effects of the selective solvation are small in the present case. This is supported by the following facts. The selective solvation of ions in binary solvent mixtures depends on the standard increase of molar Gibbs function (ΔG°) for the solvation of the ions in the two pure solvents.[9b)] Up to 10 mol% of DMSO, $d\Delta G_t^\circ/dx_{\mathrm{DMSO}}$ is nearly zero for some ions in the mixtures of DMSO and water,[9c)] where $\Delta G_t{}^\circ$ is the ΔG° value of the transfer of an ion from water to the mixture and x_{DMSO}, the mole fraction of DMSO.

Thus, by using Eq. 2, one may calculate the approximate solubilities for a sparingly soluble salt in binary mixtures, as long as there is no strong selective solvation.

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