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Volume Changes Accompanying the Stepwise Complex Formation in Aqueous Solutions. Cu(II)-bpy Complexes

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Densities of aqueous solutions containing copper nitrate and bpy (bpy = 2,2'-bipyridine) were measured to evaluate the partial molar volumes of $[Cu(bpy)]^{2+}$, $[Cu(bpy)_2]^{2+}$, and $[Cu(bpy)_3]^{2+}$. Volume increments by coordination of bpy were determined for each step and were analyzed.

The volume change ΔV associated with complex formation in solutions plays an important role in combining the dynamic information on reaction mechanism with the static one on interactions between complex ions and solvent molecules. Complex formation is generally a multi-step reaction. If various kinds of complex ions exist simultaneously, it is hard to evaluate the volume increase corresponding to each stepwise reaction. We have tried to see quantitatively the ΔV of stepwise complex formation when some complex species are predominating at certain ligand concentration in aqueous solutions. Analysis of stability data1) tells us that complex formation between ion Cu^{2+} and ligand 2,2'-bipyridine (bpy) (**1**), Cu^{2+} + bpy → $[Cu(bpy)]^{2+}$ (**2**), $[Cu(bpy)]^{2+}$ + bpy → $[Cu(bpy)_2]^{2+}$ (**3**), and $[Cu(bpy)_2]^{2+}$ → $[Cu(bpy)_3]^{2+}$ (**4**), is especially suitable to investigate as a first step of our work, for as will be shown below, distribution curves for the Cu(II)-bpy complex ions **2**, **3**, and **4** are well separated.

Commercial products of $Cu(NO_3)_2 \cdot 3H_2O$ (**5**) and **1** were used without further purification. Aqueous solution of **5** at 0.01 M was prepared and its exact concentration was determined by the EDTA titration as 0.01033 M. At this concentration the hydrolysis of the ion Cu^{2+} is negligible.2,3) This solution of **5** was used as solvent for **1** and densities of solutions were measured at 25 ℃ at various concentrations of **1** using high-precision density meter Anton Paar 60/602. Temperature control was better than 0.01 ℃.

Numerically similar stability constants are available for the formation of **2** - **4** in aqueous solutions of 0.05 M $KNO_3$4) and 0.1 M KCl.5) But, our final results are independent of some differences in stability constants.4,5) Distribution of the complexes **2** - **4** shown in Fig. 1. was obtained assuming that formation constants remain the same in water as in 0.05 M KNO_3 or 0.1 M KCl. The numbers ① - ⑫ indicate the systems investigated. As is seen from Fig. 1 the complex formation between Cu^{2+} and **1** is characterized by the facts that the peaks corresponding to the complexes **2** - **4** are distinctly separated and that the formation of **2** and **3** is nearly linear with respect to concentration of **1** in the related regions.

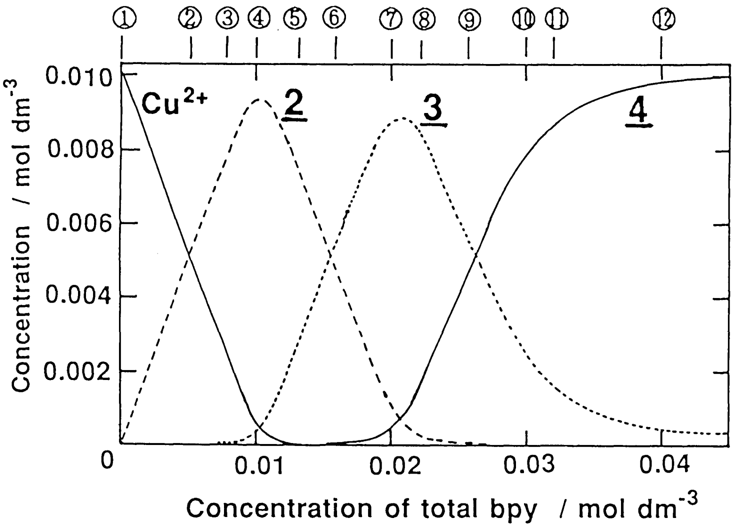

Fig. 1. Distribution of Cu(II)-bpy Complexes in H_2O at 25 ℃.

At each system ① - ⑫ we calculated the molar mass for the hypothetical solute $[Cu(bpy)_1](NO_3)_2$ (**6**) as the average of molar mass of all ionic species present in solutions. For the solute **6** the apparent molar volumes V_ϕ were calculated using the conventional relation expressed below:

$$V_\phi = \frac{1000}{c\, d_1}(d_1 - d) + \frac{M_2}{d_1} \qquad (1)$$

where c is the concentration [mol dm^{-3}], M_2, the molar mass [g], d the density [g cm^{-3}], and subscript 1 refers to solvent. In the systems ⑧ - ⑫ the amount of free **1** becomes gradually appreciable and in the system ⑫ the concentration of free **1** is a little less than 0.01 M. Therefore, we corrected the solvent densities d_1 by interpolating the density data of aqueous solutions of **1** reported earlier.6) The partial molar volumes at infinite dilution V_2° were estimated by subtracting from V_ϕ the contribution due to ion-ion interaction given by the Debye-Hückel theory. The differences between partial and apparent quantities are always 1.0 cm^3 mol^{-1}, for the concentration of the hypothetical solute **6** remains unchanged in any system. The accuracy of V_2° value is ca. ± 0.5 cm^3 mol^{-1} or a little less.

By definition of the molar quantity the following relation holds:

$$V_2^\circ(<[Cu(bpy)_1](NO_3)_2>) = \sum_{n=0}^{3} a_n V_2^\circ([Cu(bpy)_n](NO_3)_2) \qquad (2)$$

and
$$\sum_{n=0}^{3} a_n = 1 \qquad (3)$$

where <A> means the average of species A and a_n is the mole fraction of

$[Cu(bpy)_n](NO_3)_2$. As is seen in Fig. 1, at maximum only three species coexist in solutions. For the system ① we have $V_2^o(Cu(NO_3)_2)$ in water. We applied the above equations to evaluate V_2^o of the complexes **2** - **4** in nitrate form. From the data on the systems ② - ⑤ we calculated the value $V_2^o([Cu(bpy)](NO_3)_2)$, using the appropriate $V_2^o([Cu(bpy)_2(NO_3)_2)$ value estimated from the relation $V_2^o([Cu(bpy)_i](NO_3)_2) = f(i)$. The values V_2^o $([Cu(bpy)](NO_3)_2)$ obtained from the systems ② - ⑤ are 172.5_7, 173.2_6, 174.2_0, and 173.4_5 cm^3 mol^{-1}, respectively. This excellent agreement supports the present evaluation procedure of V_2^o for the chemical species of reaction intermediates. For the systems ⑥ - ⑧ the $V_2^o([Cu(bpy)_2](NO_3)_2)$ values were evaluated using the $V_2^o([Cu(bpy)](NO_3)_2)$ value just determined and the $V_2^o([Cu(bpy)_3](NO_3)_2)$ value estimated in the same way as for $V_2^o($ $[Cu(bpy)_2](NO_3)_2)$. Finally, from the data on the systems ⑨ - ⑫ the $V_2^o([Cu(bpy)_3(NO_3)_2)$ values were determined. The estimated and determined values of $V_2^o([Cu(bpy)_3(NO_3)_2)$ agreed within experimental accuracy.

Values of $V_2^o([Cu(bpy)_n](NO_3)_2)$ for n = 0 to 3 determined in this work are summarized in Table 1. No literature value is available for V_2^o $(Cu(NO_3)_2)$. However, we can estimate it from the most recent $V_2^o(CuCl_2)$ value$^{7)}$ and those of KCl and KNO_3. The value estimated is 32.31 cm^3 mol^{-1}, which agrees satisfactorily with the value given in Table 1. For trisbpy complex, we$^{6)}$ reported the $V_2^o([Cu(bpy)_3]Cl_2)$, from which the $V_2^o([Cu(bpy)_3](NO_3)_2)$ is estimated as 438.2± 5 cm^3 mol^{-1}, a value slightly smaller than the one in Table 1. One possible reason for the difference in the value of $V_2^o([Cu(bpy)_3](NO_3)_2)$ is that previously$^{6)}$ $V_2^o([Cu(bpy)_3]Cl_2)$ was determined in solutions prepared by dissolving only $[Cu(bpy)_3]Cl_2$ into water and dissociation of ligand **1** from $[Cu(bpy)_3]Cl_2$ was disregarded. The value of this work seems to be more accurate than our previous value.$^{6)}$

Table 1. Partial molar volumes of $[Cu(bpy)_n](NO_3)_2$ at 25 ℃ $^{a)}$

	$Cu(NO_3)_2$	$[Cu(bpy)](NO_3)_2$	$[Cu(bpy)_2](NO_3)_2$	$[Cu(bpy)_3](NO_3)_2$
$V_2^o/cm^3\ mol^{-1}$	32.07	173.5	312.8	446.4
$\triangle V_2^o/cm^3\ mol^{-1}$		141.4	139.3	133.6

a) $V_2^o(bpy) = 133.7^{6)}$ cm^3 mol^{-1}.

The volume changes $\triangle V_2^o$ due to coordination of ligand **1** are not additive but they decrease gradually with increasing number n of **1**. Although the decreases in $\triangle V_2^o$ for the succcessive processes are far smaller than $V_2^o(bpy)$, the observed decreases are well beyond the experimental errors of our V_2^o determination. They may reflect the change of solute-solvent interactions and the structural change of complex ions. In solid phase the distorted-octahedral,[8)] square-pyramidal,[9)] and distorted-octahedral forms[10)] are reported for $[Cu(NO_3)(H_2O)_3(bpy)]NO_3$, $[Cu(NO_3)(bpy)_2]NO_3\cdot H_2O$ and $[Cu(bpy)_3](ClO_4)_2$, respectively. Table 1, however, shows that no significant structural change occurs for formation of the complex ions **2** - **4** in solutions. We prefer to interpret the gradual decrease in $\triangle V_2^o$ with number n of **1** in the following way: In the first step coordination of **1** two water molecules strongly compressed are released from the electrostriction layer of the ion Cu^{2+} with the result of volume increase. Such volume effects become smaller with further coordination of **1** and in the third step coordination of **1** the value $\triangle V_2^o$ becomes equal to that of free **1** in aqueous solution.

Speaking very roughly, the following relation holds:

$$V_2^o([Cu(bpy)_n](NO_3)_2) = V_2^o(Cu(NO_3)_2) + B*n \qquad (4)$$

where B = 139 for the present case. This relation may be useful in evaluating approximate V_2^o values for the complexes formed by a stepwise coordination of the same ligand.

Determination of $\triangle V_2^o$ has been reported for such systems as the case between crown ether and alkali metal ions.[11)] However, this work has opened a new aspect of the V_2^o determination of the reaction intermediates.

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