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# Adsorption Effects of Highly Polarizable Organic Compounds on Electrode Kinetics

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Adsorption effects of ureas and thioureas on electrode kinetics were studied by using the electrode reactions of $Zn^{2+}/Zn(Hg)$ and $Eu^{3+}/Eu^{2+}$. The standard rate constant for $Zn^{2+}/Zn(Hg)$ is controlled by the inner-layer permittivity. The effect of this permittivity has been explained in terms of the solvent reorganization energy. The effect of the adsorbates on the electrode kinetics of $Eu^{3+}/Eu^{2+}$ cannot be explained in terms of the inner-layer permittivity. These two results suggest different locations for the formation of the activated complex: Inside the adsorption layer for $Zn^{2+}$ and just outside layer for $Eu^{3+}$.

Various factors governing electrode kinetics have been reviewed with respect to the electroreduction of inorganic cations in the presence of organic adsorbates.[1,2] In general, organic adsorbates lower the electroreduction rate, but some adsorbates increase the rate; especially markedly thiourea accelerates the reduction of $In^{3+}$,[3] $H_3O$,[4] and $Zn^{2+}$ and $Bi^{3+}$.[2] No satisfactory explanation, however, has yet been given to this accelerating action of thiourea. Recently, Sykut *et al.*[5] found that the acceleration of the electroreduction of $Zn^{2+}$ and $Bi^{3+}$ requires both that the capacity of adsorbate solution should be larger than that of base electrolyte solution and that lone pair electrons should be present in the adsorbate, and they termed this cooperative action the "cap-pair" effect. This effect is speculated to be correlated intimately to a larger permittivity of the surface adsorption layer. Then, this effect was studied more precisely by using highly polarizable organic compounds: thiourea (TU), 1,1-dimethylthiourea (DMTU), tetramethylthiourea (TMTU), urea (U), 1,1-dimethylurea (DMU), and tetramethylurea (TMU). The electrode reactions of $Zn^{2+}/Zn(Hg)$ and $Eu^{3+}/Eu^{2+}$ were chosen as representative of reactions of deposition and simple charge-transfer types, respectively.

## Experimental

Most of the organic compounds used as adsorbates were of high-purity reagent grade, but they were further purified by double distillation (TMU) or double recrystallization from methanol (DMU) or distilled water (U, TU, TMTU, and DMTU). Only DMTU was synthesized by reaction of dimethylcyanamide with thiourea.[6]

Since the double-layer parameters for the adsorbates have been obtained mainly in 0.5 M NaF solution (1 M=1 mol dm$^{-3}$), the electrode reaction of $Zn^{2+}/Zn(Hg)$ was studied in 0.5 M NaF solutions containing $1.0\times10^{-3}$ M of $Zn^{2+}$ and an adsorbate at various concentrations. On the other hand, the electroreduction of $Eu^{3+}$ was carried out in 0.5 M aqueous $NaClO_4$ containing $0.93\times10^{-3}$ M of $Eu^{3+}$ and an adsorbate at different concentrations, because $Eu^{3+}$ formes a precipitate of $EuF_3$ in the aqueous NaF solution. In this case, the double-layer parameters for the adsorbates are assumed not to differ from those in 0.5 M NaF.

Polarographic measurements were carried out with a three-electrode system consisting a polarograph (Yanaco, P-8 Polarograph) equipped with a dropping mercury electrode at 25 °C, and the instantaneous current at the end of drop life was recorded. The drop time was mechanically adjusted to 3.5 s, and the flow rate of mercury was 3.03 mg s$^{-1}$. The apparent standard rate constant $k_s^{app}$ for $Zn^{2+}/Zn(Hg)$ with the standard electrode potential −1.003 V *vs.* SCE[7] was evaluated according to the analytical procedure for quasi-reversible systems.[8,9] When the concentration of thioureas (TU, DMTU, and TMTU) exceeds the level corresponding to surface coverage about 0.3, the systems yield reversible current-potential curves. For such systems, only the standard rate constant at full coverage was evaluated by the faraday impedance method.[10] On the other hand, $k_s^{app}$ for $Eu^{3+}/Eu^{2+}$ with the standard potential −0.600 V *vs.* SCE[11] was evaluated according to the equation for irreversible systems.[8]

## Results and Discussion

*Adsorption Behavior of Adsorbates.* According to adsorption behavior the adsorbates used in the present study can be classified into two groups, ureas (U,[12] DMU,[13] and TMU[14]) and thioureas (TU,[15,16] DMTU,[13] and TMTU[17]). The orientation common to the ureas at the mercury/aqueous solution interface is the positioning of the C=O bond nearly parallel to the electrode surface. The fit to the Langmuir isotherm observed for U and DMTU indicates the absence of interaction between adsorbed molecules. However, only TMU, which shows a fit to the Frumkin isotherm, exhibits a small positive interaction parameter, which means an attractive interaction between adsorbed molecules around the potentials where the reductions of $Zn^{2+}$ and $Eu^{3+}$ take place.

On the other hand, the orientation common to the thioureas is the positioning of the C=S bond fully vertical to the electrode surface. A repulsive interaction between adsorbed molecules is indicated by the positive values of the second virial coefficient for TU[16] and the negative values of the interaction parameters for DMTU and TMTU.

*Effects of Adsorbates on Electrode Kinetics of $Zn^{2+}/Zn(Hg)$.* Figure 1 shows the variation of the apparent standard rate constant $k_s^{app}$ due to adsorption of the ureas and thioureas. Only with TMU, a remarkable lowering in the reduction rate was

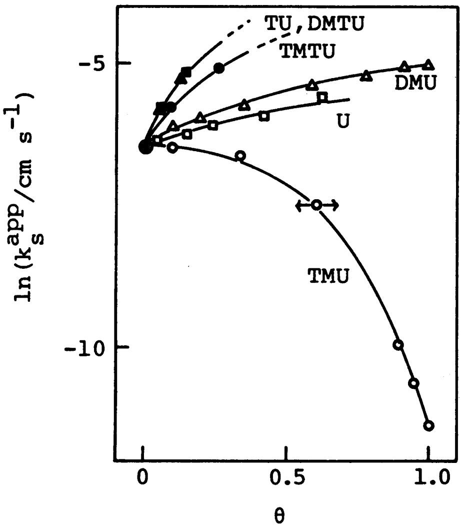

Fig. 1. Variation of ln $k_s^{app}$ for $Zn^{2+}/Zn(Hg)$ with suraface coverage at various adsorbates. Adsorbates: TU (thiourea, ■), DMTU (1,1-dimethylthiourea, ▲), TMTU (tetramethylthiourea, ●), U (urea, □), DMU (1,1-dimethylurea, △), and TMU (tetramethylurea, ○). Arrows representing a speculated coverage for TMU are due to a mixed adsorption consisting of similar two orientations differed in the occupied srera.[17]

observed, but U and DMU accelerated the reaction slightly with an increase in the coverage. The thioureas showed a strong accelerating action even at lower coverages. Since the rate constants at higher coverages could not be evaluated owing to a change into a reversible system, the standard rate constant at the full coverage was estimated by the faraday impedance method[10] only with TMTU and DMTU. The results are summarized in Table 1 together with various double-layer parameters at the full coverage, the values of which are estimated at each apparent half-wave potential $E_{1/2}$, because the rate constants were evaluated around this potential and the plot of these rate constants against potential was then extrapolated to the standard electrode potential to obtain $k_s^{app}$.

The results relating to the potential drop across the diffuse double layer $\Delta_S^2\phi$ suggest that the reduction rate is not controlled by the Frumkin effect.[18] The effect of adsorbate's dipole charges located at the solution side upon the surface concentration of reacting ion, which is to be considered for the reduction of $Eu^{3+}$ in the subsequent section, is not operative either for the reduction of $Zn^{2+}$. The electrode process of $Zn^{2+}/Zn(Hg)$ seems to proceed in the adsorption layer. However, it is found that the $\phi_1$ potential ($\Delta_1^M\phi$) in the adsorption layer[19] cannot explain the large change in ln $k_s^{app}$ with adsorbates, in analogy with the $\phi_2$ potential ($\Delta_2^M\phi$) at the Helmholtz plane. One of interfacial properties susceptible to a large change with adsorbates is the permittivity of the adsorption layer or the inner-layer permittivity $\varepsilon_1$, as can be seen from Table 1. Then, the effect of this permittivity on the rate constant was examined more precisely. For a thin adsorption layer with lower permittivity than that in the solution bulk, Afanas'ev and Damaskin[20] treated the above effect as the work involved in transferring a reacting ion from the solution bulk into the structured surface layer. But, we have treated this effect simply as the work for the activation of $Zn^{2+}$ in the adsorption layer.

When the interaction between reactant and electrode is negligibly weak and the activation free energy is mainly controlled by the solvent reorganization energy, the Marcus theory[21,22] predicts the following simplified relation for the standard rate constant:

$$\ln k_s^{app} = \text{const} - \lambda_o/4kT, \quad (1)$$

where $\lambda_o$ is a quantity relating to the solvent reorganization energy and represented by

$$\lambda_o = (ne)^2(1/2a - 1/4R)(1/\varepsilon_o - 1/\varepsilon_s), \quad (2)$$

where $ne$ is the charge transferred, $a$ the radius of the reacting ion, $R$ the distance between the center of reacting ion and the electrode surface, and $\varepsilon_o$ and $\varepsilon_s$ are the optical and static permittivities of medium, respectively. If $a$ and $R$ can be assumed to be constant for the same reaction, one may obtain the following equation related to the permittivity of the medium:

$$\ln k_s^{app} = \text{const} - (1/4kT)(ne)^2(1/2a - 1/4R)(1/\varepsilon_o - 1/\varepsilon_s). \quad (3)$$

TABLE 1. KINETIC DATA FOR $Zn^{2+}/Zn(Hg)$ AND DOUBLE-LAYER PARAMETERS AT SATURATION WITH VARIOUS ADSORBATES[a)]

| Adsorbate | $C^f_{org}$ | $E_{1/2}$ | $\alpha^{app}$ | $k_s^{app}\times10^3$ [b)] | $\Delta_S^2\phi$ | $K_1^i$ | $d_1$ | $\varepsilon_1\times10^{11}$ | $P_1\times10^{30}$ |
|---|---|---|---|---|---|---|---|---|---|
| | M | V *vs.* SCE | | cm s$^{-1}$ | mV | μF cm$^{-2}$ | nm | F m$^{-1}$ | C m |
| TMTU | 0.05 | −1.013 | 0.27 | 20 | −33 | 16.7 | 0.71 | 11.9 | −14.7 |
| DMTU | 0.1 | −1.015 | 0.30 | 45 | −30 | 21.0 | 0.71 | 14.9 | −15.2 |
| TMU | 0.5 | −1.282 | 0.24 | 0.011 | −55 | 8.8 | 0.62 | 5.4 | 6.1 |
| DMU | 2.0 | −1.013 | 0.30 | 5.6 | −48 | 15.1 | 0.60 | 9.2 | 1.7 |
| $H_2O$ | — | −1.024 | 0.28 | 1.5 | −58 | 21.3 | 0.31 | 6.6 | — |

a) $C^f_{org}$ and $\alpha^{app}$ mean the concentration corresponding to full coverage and the apparent transfer coefficient, respectively. $\Delta_S^2\phi$, $K_1^i$, $d_1$, $\varepsilon_1$, and $P_1$ are the potential drop across the diffuse layer, the integral inner-layer capacity, the thickness of the inner layer, the permittivity of the inner layer, and the dipole moment of an adsorbed molecule at saturation with the adsorbate, respectively. The double-layer parameters are estimated at each half-wave potential $E_{1/2}$. A positive (negative) value of $P_1$ corresponds to an orientation having the positive (negative) end of dipole directing toward the electrode surface. b) The values for TMTU and DMTU were evaluated from the data obtained by the faraday impedance method, while those for TMU, DMU, and $H_2O$ by d.c. polarography.

One can assume the surface layer formed by adsorbates to be the medium for the electroreduction of $Zn^{2+}$. In general, the permittivity of the surface adsorption layer on the electrode is quite different from that of the bulk.[23] When electrode processes occur in this surface adsorption layer, therefore, we have to use the permittivity of this layer. This permittivity of the surface layer or the inner-layer permittivity at saturation with an adsorbate, $\varepsilon_1$, can be estimated from the integral inner-layer capacity $K_1^i(=\varepsilon_1/d_1)$ and the thickness of the inner layer, $d_1$. The definition of $K_1^i$ is

$$K_1^i = \sigma/(\Delta_2^M\phi_\sigma - \Delta_2^M\phi_{\sigma=0}), \quad (4)$$

where $\sigma$ is the surface charge density on the electrode, and $\Delta_2^M\phi_\sigma$ and $\Delta_2^M\phi_{\sigma=0}$ are the potential drops across the inner layer at an arbitrary charge density and at the zero charge density, respectively. When the reorientation of adsorbate is not so significant, Eq. 4 can be approximated to[24]

$$1/K_1^i = 1/K_1^{i(\text{ion})} - 1/K_1^{i(\text{dipole})}. \quad (5)$$

Since the first term of the right hand side of Eq. 5 is due to the free charges on the electrode and is affected by the electronic polarizability of the adsorbate, and the second term is due to the dipole orientation, Eq. 5 can be reduced to

$$1/\varepsilon_1 = 1/\varepsilon_o - 1/\varepsilon_s, \quad (6)$$

which means that one may obtain $(1/\varepsilon_o - 1/\varepsilon_s)$ from $1/\varepsilon_1$ which can be estimated from the integral inner-layer capacity. The contribution of $\varepsilon_s$ to the inner-layer permittivity has been considered to be minor,[23] which in fact is the case with TMTU.[17]

A plot of ln $k_s^{app}$ against $1/\varepsilon_1$ is shown in Fig. 2. In this figure, no points for U and TU are included for the lack of $\varepsilon_1$ in the literature, and the point for $H_2O$ refers to the surface layer covered with water molecules only, *i.e.*, the surface layer corresponding to the base 0.5 M NaF solution containing no adsorbates.

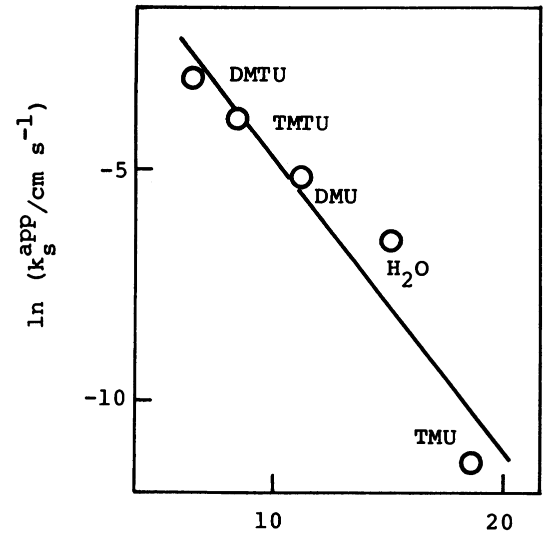

Fig. 2. Plot of ln $k_s^{app}$ for $Zn^{2+}/Zn(Hg)$ against $\varepsilon_1^{-1}$ at saturation with various adsorbates.

The plot in Fig. 2 shows a linear relation, which verifies the validity of Eq. 3. However, the slope gives $R$=1.1 nm on the assumption of $a=R$. This value is rather too large, because $R$ is expected to be 0.3—0.4 nm by taking into account the water layer thickness (0.31 nm) and the ionic radius of $Zn^{2+}$ (0.074—0.088 nm).

Several reasons will be given for the unexpected value of $R$: (i) neglect of the work, $U_i$, for transferring reactants from the solution bulk to the discharge site; (ii) no distinction between two layers with different permittivities; (iii) neglect of the thickness of the adsorption layer, $d_1$; (iv) probable change in $a$ and $R$ during the electrode process. Kharkats[25] discussed effects of two layers with different permittivities and $d_1$ on the solvent reorganization energy $E_s$ and $U_i$, and represented $E_s$ and $U_i$ as functions of $a$, $R$, $d_1$, and permittivity.

In the calculation of $E_s$ and $U_i$, the static permittivity for the adsorption layer is assumed to be 10 times the optical one, and the optical and static permittivities for the water layer adjacent to the adsorption layer are taken as $6.3\times10^{-11}$ and $70\times10^{-11}$ F m$^{-1}$, respectively. When the energies controlling the electrode process are concentrated on $E_s$ and $U_i$, ln $k_s^{app}$ can be given by

$$\ln k_s^{app} = \text{const} - (E_s + U_i)^2/4E_skT. \quad (7)$$

Figure 3 shows the plot of ln $k_s^{app}$ for $Zn^{2+}/Zn(Hg)$ agaist $(E_s+U_i)^2/E_s$, for which 0.4 nm is chosen for $a$ and $R$ so that the experimental slope may agree with the

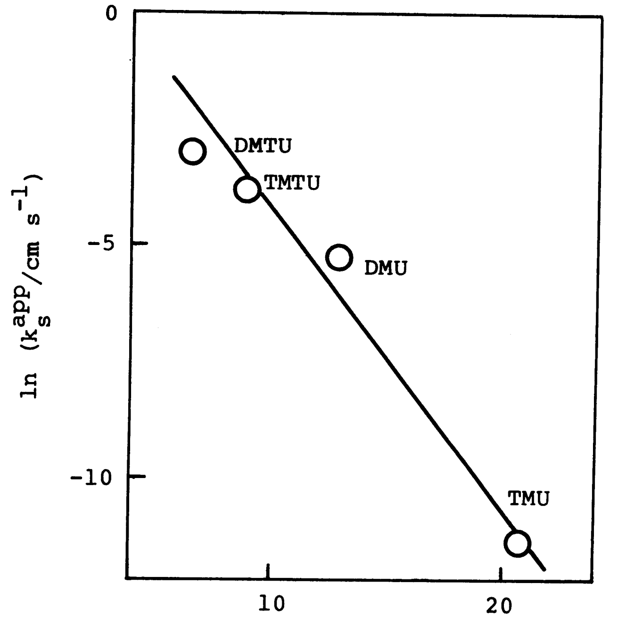

Fig. 3. Plot of ln $k_s^{app}$ for $Zn^{2+}/Zn(Hg)$ against $(E_s+U_i)^2/E_s$ at saturation with various adsorbates.

TABLE 2. KINETIC DATA FOR $Eu^{3+}/Eu^{2+}$ AND DOUBLE- LAYER PARAMETERS AT $E_{1/2}$ [a)]

| Adsorbate | $C_{org}$ | $E_{1/2}$ | $\alpha^{app}$ | $k_s^{app} \times 10^5$ [b)] | $\theta$ | $\Delta_S^2\phi$ | $K_1^i$ | $d_1$ | $\varepsilon_1 \times 10^{11}$ | $P_1 \times 10^{30}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | M | V *vs.* SCE | | $cm\ s^{-1}$ | | mV | $\mu F\ cm^{-2}$ | nm | $F\ m^{-1}$ | C m |
| $H_2O$ | — | −0.665 | 0.33 | 26 | 1 | −31 | 25.5 | 0.31 | 7.9 | — |
| TMU | 0.005 | −0.661 | 0.33 | 26 | 0.27 | −29 | | | | |
| | 0.01 | −0.663 | 0.33 | 28 | 0.52 | −29 | | | | |
| | 0.05 | −0.676 | 0.35 | 22 | 0.78 | −33 | | | | |
| | 0.1 | −0.690 | 0.51 | 15 | 0.89 | −35 | | | | |
| | 0.2 | −0.696 | 0.52 | 14 | 1 | −37 | 12.5 | 0.61 | 7.6 | 8.1 |
| TMTU | 0.001 | −0.741 | 0.46 | 0.93 | 0.60 | −21 | | | | |
| | 0.005 | −0.807 | 0.48 | 0.065 | 0.86 | −19 | | | | |
| | 0.01 | −0.840 | 0.42 | 0.062 | 0.94 | −20 | | | | |
| | 0.05 | −0.910 | 0.32 | 0.055 | 1 | −27 | 17.0 | 0.71 | 12.1 | −15.4 |

a) $C_{org}$ and $\theta$ represent the concentration and surface coverage of adsorbate, respectively. The meanings of the other notations are the same as those in Table 1. b) All the values were evaluated from data obtained by d.c. polarography.

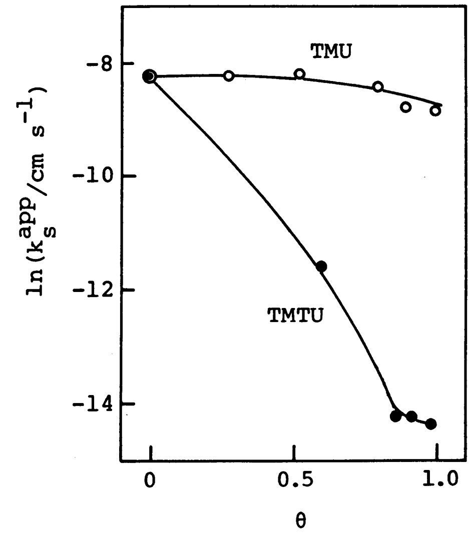

Fig. 4. Variation of ln $k_s^{app}$ for $Eu^{3+}/Eu^{2+}$ with surface coverage at TMU and TMTU.

theoretical one ($1/4kT$). The above value $a=R=0.4$ nm is in fair agreement with the expected value of 0.3—0.4 nm. However, the point for $H_2O$ is excluded from the plot in Fig. 3, because $(E_s+U_i)^2/E_s$ calculated for $H_2O$ was an unreasonable value. Probably, the discharge site would be located just outside the water adsorption layer, and the selected values might be different from those for the bulk water.

*Effects of Adsorbates on Electrode Kinetics of $Eu^{3+}/Eu^{2+}$.* Figure 4 shows the variation of ln $k_s^{app}$ for $Eu^{3+}/Eu^{2+}$ with the adsorption of TMU and TMTU. The kinetic data and double-layer parameters at each $E_{1/2}$ are summarized in Table 2. The effect of TMU and TMTU on the reduction rate of $Eu^{3+}$ is in quite a contrast to that on the reduction rate of $Zn^{2+}$; TMTU increases the reduction rate of $Zn^{2+}$ but lowers the rate of $Eu^{3+}$ significantly. The nearly constant values of ln $k_s^{app}$ at higher coverages suggest a tunneling transition[26] through the adsorption layer to the strongly hydrated $Eu^{3+}$ ion.[27] The estimate of ln [$k_s^{app}$ (TMU)/ $k_s^{app}$ (TMTU)] on the basis of the tunneling transition,[28] however, is 0.6, which is rather a small value as compared with the experimental value of 5.6. The Frumkin correction for the surface concentration of $Eu^{3+}$ cannot explain the above experimental value, either. As a matter of course, the permittivity effect predicts an opposite result to the experimental one. It is most likely that the adsorbate's dipole charges located at the solution side affect the surface concentration of $Eu^{3+}$, because such charges are positive for TMTU and negative for TMU as can be seen from the value, $P_1$, of dipole moment of an adsorbed molecule in Table 2.

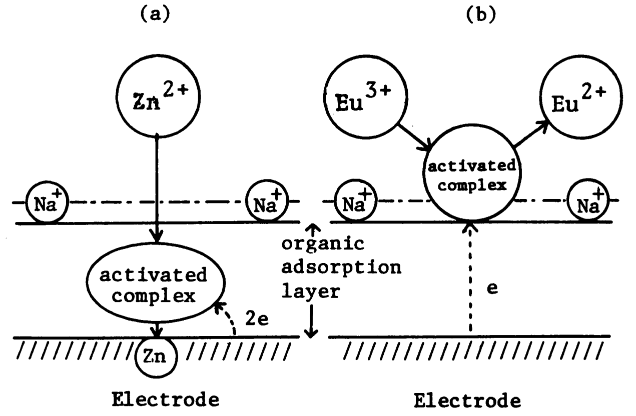

Fig. 5. Reaction paths elucidated for the reductions of (a) $Zn^{2+}$ and (b) $Eu^{3+}$.

*Reaction Paths.* A comparison of the two types of electrode reactions has led us to assign the reaction paths shown in Fig. 5 to the reductions of $Zn^{2+}$ and $Eu^{3+}$. In Fig. 5, the locations where the activated complex is formed are different: (a) Inside the adsorption layer for $Zn^{2+}$ and (b) just outside the layer for $Eu^{3+}$.

The hydration structure of $Zn^{2+}$ in 0.5 M aqueous NaF solution is considered to be $[ZnF(H_2O)_3]^+$.[29] We could detect no clear complex formation of $Zn^{2+}$ with the ureas or thioureas used as adsorbates, because no change was caused in the UV-visible spectrum for the $1.0 \times 10^{-3}$ M $Zn^{2+}$+0.5 M NaF solution by addition of the adsorbates. This result does not deny the possibility that the complex is formed during the transfer of $Zn^{2+}$ into the surface adsorption layer. When thioureas formes a strong complex with a reacting ion such as $Cu^{2+}$ or $Cd^{2+}$, however, it is well known that the reduction rate of these ions is caused to decrease.[2] These results suggest that any complexation of $Zn^{2+}$ occurs with the thioureas or ureas neither in the solution bulk nor in the adsorption layer.

The characteristics of the UV-visible spectrum for the case of $Eu^{3+}$ are similar to those for $Zn^{2+}$. Since water molecule also is a ligand, we believe that $Eu^{3+}$ in a dilute aqueous solution of any one of the thioureas and ureas will form no complex with them.

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