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The Adsorption of 2,2′-Bipyridine and Its Ferrous Complex on the the Dropping Mercury Electrode

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The adsorption of 2,2′-bipyridine and its ferrous complex $[Fe(bip)_3]^{2+}$ onto the electrode has been studied both by the electrocapillary method and the impedance-bridge method. Electrocapillary curves were obtained by the drop-time method. A peculiar shape was observed in the electrocapillary curve of $[Fe(bip)_3]^{2+}$, which was corrected for in the further thermodynamic treatment by taking into account the data obtained with an impedance bridge. It was found that 2,2′-bipyridine is adsorbed flat in the more positive region. At more negative potentials, the adsorption is also flat at low concentrations of 2,2′-bipyridine, but becomes perpendicular beyond 2×10^{-3} M. The $[Fe(bip)_3]^{2+}$ adsorption can be accounted for by a Langmuir isotherm. However, the isotherm for 2,2′-bipyridine adsorption varies with the potential, which can be explained in terms of the change in the adsorption structure.

The adsorption of organic compounds at the mercury electrode—solution interface has been studied for many years, mainly by the electrocapillary method and by the impedance-bridge method.[1] Attempts have been made to give a generalized interpretation of the adsorption of simple organic compounds, such as alcohols, and rather successful results have been obtained.[2] However, the adsorption of more complex organic compounds is difficult to interpret by such a generalized theory, and many complicated phenomena have been observed. For instance, certain anionic surface-active substances, such as alkyl sulfate ions, have been found to show three or four peaks in their differential capacity - potential curves.[3] In these cases, the differential capacity during a drop-life changes in a very complicated way.[4] It has also been found that the adsorption isotherms of pyridine and its derivatives vary remarkably with the electrode potential.[2,5–7]

The adsorption of organic compounds can also be studied by a.c. polarography (tensammetry), by which curves similar to the capacity - potential curves measured by the impedance-bridge method can be obtained automatically.[8] Using the a.c. polarographic method, the present author and his co-workers studied the adsorption of oxine and its derivatives and found that they showed peculiar non-faradaic peaks which were not typical of the adsorption - desorption of organic compounds.[9–13] When metal ions, such as copper and zinc, were added to the solution, the peaks disappeared by forming chelates with oxines, showing that the behavior of oxine and its derivatives differed from that of their chelates. This fact was used to detect the end point of titration of very dilute solutions of metal ions with oxines.[9–13] Scarcely a.c. polarographic (tensammetric) studies of the adsorption of chelate compounds have been reported. The present author has studied, in a previous report,[14] the a.c. polarographic behavior of chelates of 2,2′-bipyridine and 1,10-phenanthroline with metal ions, such as iron, zinc, and nickel. He found that, unlike the case of oxine chelates, these chelates

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1) "Electrosorption," ed. by E. Gileadi, Plenum Press, New York (1967).

2) A. N. Frumkin and B. B. Damaskin, "Modern Aspects of Electrochemistry," Vol. 3, ed. by J.O′ M. Bockris, Butterworths, London (1964).

3) K. Eda, *Nippon Kagaku Zasshi*, **80**, 343 (1959).

4) T. Fujinaga, K. Izutsu and H. Sawamoto, *ibid.*, **89**, 759 (1968).

5) L. Gierst and P. Herman, *Z. Anal. Chem.*, **216**, 238 (1966).

6) B. B. Damaskin, *Electrochim. Acta*, **9**, 231 (1964).

7) H. W. Nurnberg and G. Wolff, *Collect. Czech. Chem. Commun.*, **30**, 3997 (1965).

8) B. Breyer and H. H. Bauer, "Alternating Current Polarography and Tensammetry," Interscience Publishers, New York (1963).

9) B. Breyer, *Aust. J. Sci.*, **23**, 225 (1961).

10) B. Breyer, J. W. Hayes, T. Fujinaga, G. Takagi and S. Okazaki, *Bunseki Kagaku*, **14**, 1023 (1965).

11) B. Breyer, T. Fujinaga and H. Sawamoto, *ibid.*, **15**, 487 (1966).

12) T. Fujinaga, K. Izutsu and H. Sawamoto, *ibid.*, **16**, 1188 (1967).

13) T. Fujinaga, K. Izutsu, S. Okazaki and H. Sawamoto, *J. Electroanal. Chem.*, **21**, 187 (1969).

14) T. Fujinaga and H. Sawamoto, in preparation.

show typical adsorption - desorption peaks.

The present study was undertaken to investigate in more detail the above studies. The adsorption of 2,2′-bipyridine and its ferrous complex in 0.5 M KCl was measured by the impedance-bridge method and by the electrocapillary method. The a.c. polarographic method was used as an auxiliary method. The surface excess and the adsorption isotherms of these adsorbates have been obtained, and their adsorption structures have then been deduced from these results. Special attention was paid to the abnormal shape observed in the electrocapillary curves of $[Fe(bip)_3]^{2+}$ ions.

Experimental

The measurement of the differential capacity with an impedance-bridge has been described previously.[4] The bridge was balanced at the end of the life of a mercury drop. The tensammetric measurement with an a.c. polarograph has also been described previously.[13] Electrocapillary curves were usually obtained by the drop-time method. The drop time was determined by measuring the time of ten drops with a stop watch. The accuracy of the measurement of the drop time was within ±0.01 sec, which corresponds to an interfacial tension of about ±1 dyn/cm at the mercury/electrolyte phase boundary. The reproducibility of the dropping mercury electrode was checked before each measurement in a 0.5 M potassium chloride solution. All the chemicals were of analytical-reagent grades and were used without further purification. Drying 2,2′-bipyridine in a desiccator under reduced pressure caused no weight change. The concentration of the ferrous sulfate solution was determined gravimetrically. $[Fe(bip)_3]^{2+}$ was prepared by mixing equivalent amounts of 2,2′-bipyridine and ferrous sulfate.

Results and Discussion

Electrocapillary Curves. Among the methods for obtaining electrocapillary curves, the measurement with a Lippman electrometer is most reliable for thermodynamic treatment, but it is rather tedious, especially in the presence of organic compounds. Drop time - potential curves usually measured in polarography, on the other hand, can easily be converted to electrocapillary curves by using such relations as are shown by Eqs. (1) and (2) and can be used for further thermodynamic treatment. The relation in Eq. (1) was used by Tate, and that in Eq. (2), by Corbusier and Gierst:[15]

$$\gamma = \frac{\gamma_{\rm ref}}{t_{\rm ref}}t \tag{1}$$

$$\Delta\gamma = K^*\frac{\gamma_{\rm ref}}{t_{\rm ref}}\Delta t = 0.973\frac{\gamma_{\rm ref}}{t_{\rm ref}}\Delta t \tag{2}$$

In these equations, γ and t are the interfacial tension and the drop time respectively. $\gamma_{\rm ref}$ is a known interfacial tension under the conditions chosen as a reference, and $t_{\rm ref}$ is the drop time obtained under the same conditions as $\gamma_{\rm ref}$. $\Delta\gamma$ is equal to $\gamma - \gamma_{\rm ref}$, and Δt, to $t - t_{\rm ref}$. In the present report, the value of the interfacial tension obtained by Devanathan and Peries[16] at a potential of the electrocapillary maximum was used as $\gamma_{\rm ref}$. K^* is a constant; a value of 0.973 was obtained experimentally by Corbusier and Gierst.[15]

The interfacial tension can also be obtained by a double integration of the differential capacity, C:

$$\iint_{E_z}^{E} C\,d^2E = \gamma(E_z)-\gamma \tag{3}$$

where E is the electrode potential, where E_z is the potential of zero charge, and where $\gamma(E_z)$ is the known interfacial tension at E_z.

The electrocapillary curves were obtained in 0.5 M potassium chloride solutions containing various concentrations of 2,2′-bipyridine by using Eqs. (1), (2), and (3); they are compared in Fig. 1. The results obtained from Eq. (3) show slightly larger values than those obtained from Eqs. (1) and (2) in the cathodic potential region. Such differences in the presence of organic compounds have also been reported by Parsons and Zobel.[17]

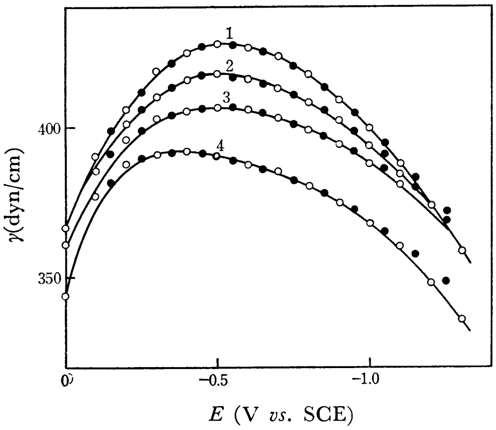

Fig. 1. Comparison of electrocapillary curves of 2,2′-bipyridine in 0.5 M KCl.
2,2′-bipyridine concentration: 1, 0; 2, 10^{-4} M; 3, 10^{-3} M; 4, 10^{-2} M.
Solid line: calculated from Eq. (1)
○: calculated from Eq. (2)
●: calculated from Eq. (3)

The results obtained from Eqs. (1) and (2) coincide well, but in the calculation from Eq. (2) the value of K^* was assumed to be 0.973, as had been obtained experimentally by Corbusier and Gierst;[15]

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[15] P. Corbusier and L. Gierst, *Anal. Chim. Acta*, **15**, 254 (1956).

[16] M. A. V. Devanathan and P. Peries, *Trans. Faraday Soc.*, **50**, 1236 (1954).

[17] R. Parsons and F. G. R. Zobel, *ibid.*, **62**, 3511 (1966).

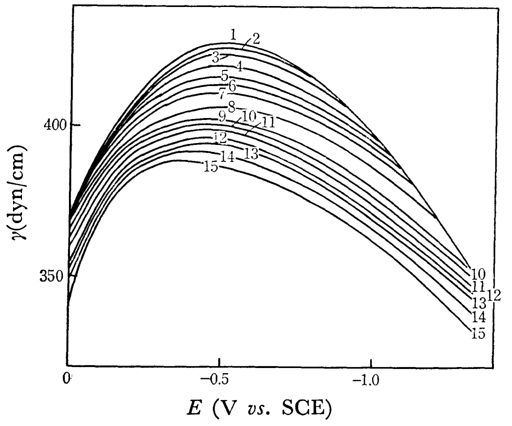

Fig. 2. Electrocapillary curves of 2,2′-bipyridine in 0.5 M KCl.
2,2′-bipyridine concentration: 1, 0; 2, 10^{-5} M; 3, 2×10^{-5} M; 4, 5×10^{-5} M; 5, 10^{-4} M; 6, 2×10^{-4} M; 7, 5×10^{-4} M; 8, 10^{-3} M; 9, 1.4×10^{-3} M; 10, 2×10^{-3} M; 11, 3×10^{-3} M; 12, 5×10^{-3} M; 13, 8×10^{-3} M; 14, 10^{-2} M; 15, 1.4×10^{-2} M

this value may not be applicable to the present dropping mercury electrode. For these reasons, the electrocapillary curves described below were obtained from Eq. (1). More detailed results on the electrocapillary curves in the presence of 2,2′-bipyridine are shown in Fig. 2.

The electrocapillary curves in the presence of $[\mathrm{Fe(bip)_3}]^{2+}$ are shown in Fig. 3. The curves obtained in the concentration range between 5×10^{-5} M and 3×10^{-4} M show a peculiar depression in the cathodic potential range, while those obtained for $[\mathrm{Fe(bip)_3}]^{2+}$ concentrations below 5×10^{-5} M or above 3×10^{-4} M show no such depression and have normal shapes. This appearance of the depression in the electrocapillary curves is a peculiar phenomenon, because the two differentiations of the interfacial tension with respect to the potential causes a negative capacity.

It has been reported that such an abnormal depression of the electrocapillary curves was observed at a dropping mercury electrode at the potential at which the polarographic maximum appeared, but it was not observed with a Lippmann electrometer.[18] When an organic compound is reduced and gives a reductant which is strongly adsorbed onto the electrode surface, a sudden decrease in the interfacial tension is also observed at the potential at which reduction occurs.[19] In the present case, however, no faradaic current was observed in the abnormal region, as is shown in Fig. 4. As to the abnormal depression of the electrocapillary curve in the absence of electrolytic processes, only one example has been observed in anhydrous acetic acid,[20] and none in an aqueous solution.

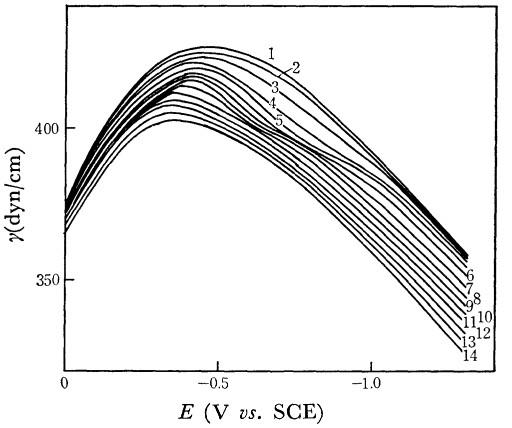

Fig. 3. Electrocapillary curves of $[\mathrm{Fe(bip)_3}]^{2+}$ in 0.5 M KCl.
$[\mathrm{Fe(bip)_3}]^{2+}$ concentration: 1, 0; 2, 2×10^{-5} M; 3, 3×10^{-4} M; 4, 5×10^{-5} M; 5, 7×10^{-5} M; 6, 10^{-4} M; 7, 2×10^{-4} M; 8, 3×10^{-4} M; 9, 5×10^{-4} M; 10, 7×10^{-4} M; 11, 10^{-3} M; 12, 1.4×10^{-3} M; 13, 2×10^{-3} M; 14, 3×10^{-3} M

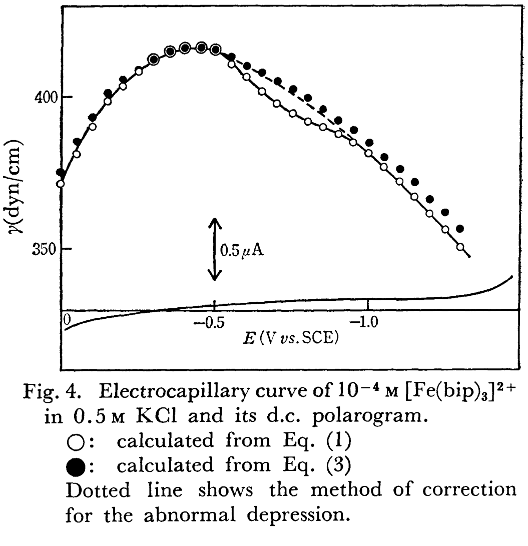

Fig. 4. Electrocapillary curve of 10^{-4} M $[\mathrm{Fe(bip)_3}]^{2+}$ in 0.5 M KCl and its d.c. polarogram.
○: calculated from Eq. (1)
●: calculated from Eq. (3)
Dotted line shows the method of correction for the abnormal depression.

In order to test the effect of the sulfate ion introduced as $\mathrm{FeSO_4}$ in 0.5 M potassium chloride, ferrous chloride was used instead of ferrous sulfate. As this electrocapillary curve showed the same abnormality, the effect of the sulfate ion can be disregarded.

The electrocapillary curve in the presence of both 2,2′-bipyridine and $[\mathrm{Fe(bip)_3}]^{2+}$ also showed an abnormality at 2,2′-bipyridine concentrations above 10^{-4} M. This fact might show that the presence of both 2,2′-bipyridine and $[\mathrm{Fe(bip)_3}]^{2+}$ is

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[18] J. Heyrovsky and J. Kuta, "Principles of Polarography," Academic Press, New York (1966), p. 23.

[19] "Polarography," ed. by I. Tachi, Iwanami Shoten, Tokyo (1954), p. 312.

[20] G. B. Bachman and M. J. Astle, *J. Amer. Chem. Soc.*, **64**, 2177 (1942).

the cause of the abnormal phenomena, and that the species obtained as a result of the dissociation of $[Fe(bip)_3]^{2+}$ might be responsible for it. However, from the calculation of the dissociation of $[Fe(bip)_3]^{2+}$ previously described,[13,21] it was found that $[Fe(bip)_3]^{2+}$ is not so dissociated as to affect the electrocapillary curves. Though the electrocapillary curve of the mixture of $[Fe(bip)_3]^{2+}$ and 2,2′-bipyridine coincides with that of $[Fe(bip)_3]^{2+}$, their C - E curves differ markedly from each other, showing that the causes of the abnormalities are not identical.

From these results, it can be concluded that the abnormality of the electrocapillary curves in the presence of $[Fe(bip)_3]^{2+}$ is not due to the presence of both $[Fe(bip)_3]^{2+}$ and 2,2′-bipyridine resulting from the dissociation of the complex in solution, though the real cause of this abnormality is still uncertain.

The electrocapillary curves calculated from Eq. (3) using the data of the impedance-bridge measurements showed no abnormality, as is shown in Fig. 4. Therefore, a correction shown by a dotted line in Fig. 4 will be made in the following discussion for the abnormality.

Adsorption Structure. The surface excess, Γ, of an adsorbed species can be obtained from the Gibbs adsorption equation:

$$\Gamma = -\left(\frac{\partial \gamma}{\partial \mu}\right)_{E,T} = -\frac{1}{2.303\boldsymbol{RT}}\left(\frac{\partial \gamma}{\partial \log c}\right)_{E,T} \tag{4}$$

where μ and c are, respectively, the chemical potential and the concentration of the adsorbate in solution; R, the gas constant, and T, the absolute temperature. The value of $(\partial \gamma/\partial \log c)_{E,T}$ can be obtained by graphically differentiating the γ-log c curve as is shown in Fig. 5.

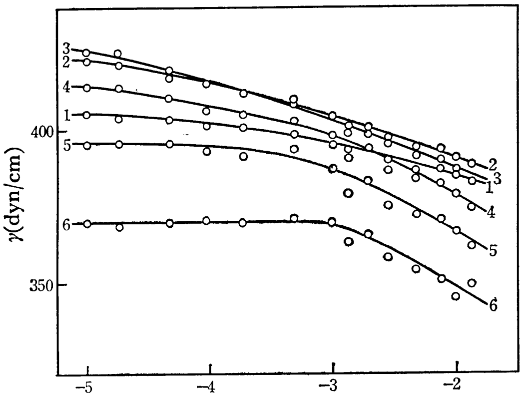

Fig. 5. Effect of 2,2′-bipyridine concentration on interfacial tension.
Potentials: 1, −0.2 V; 2, −0.4 V; 3, −0.6 V; 4, −0.8 V; 5, −1.0 V; 6, −1.2 V

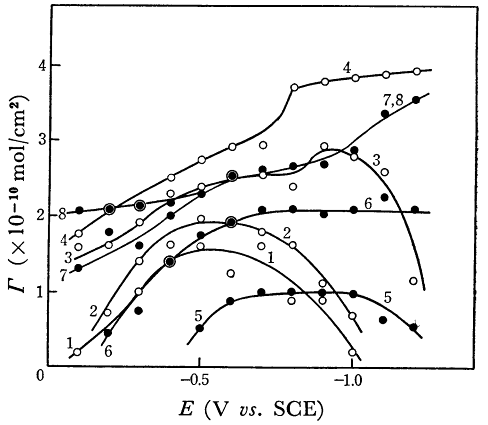

Fig. 6. Variation of surface excess with electrode potentials at different concentrations of (a) 2,2′-bipyridine and (b) $[Fe(bip)_3]^{2+}$ in 0.5 M KCl.
(a): 1, 2×10^{-5} M; 2, 10^{-4} M; 3, 10^{-3} M
4, 3×10^{-3} M
(b): 5, 2×10^{-5} M; 6, 10^{-4} M; 7, 10^{-3} M
8, 3×10^{-3} M

The variation of the surface excess with the electrode potential is shown in Fig. 6 for 2,2′-bipyridine and $[Fe(bip)_3]^{2+}$. At low concentrations of 2,2′-bipyridine, the curves are almost symmetrical, as in the case of typical neutral molecules (curves 1 and 2). The surface excess is at its maximum at the point of zero charge and decreases almost to zero at sufficiently anodic or cathodic potentials. However, as the concentration increases, asymmetrical curves are obtained whose maximum is located at a considerably negative potential (curves 3 and 4). If the 3.9×10^{-10} mol/cm² obtained from curve 4 in Fig. 6 is assumed to be the saturated surface excess for the monolayer adsorption of 2,2′-bipyridine, the area occupied by its single molecule can be calculated as 42.5 Å²/mol. The area of the electrode occupied by a molecule of α-naphthol, which is considered to be smaller than that of 2,2′-bipyridine, has been reported[22] to be 66 Å² when it is adsorbed in parallel to the electrode and 26 Å² when adsorbed perpendicularly. This shows that, at negative potentials, 2,2′-bipyridine cannot be adsorped in parallel to the electrode if a monolayer is assumed. Therefore, the adsorption of 2,2′-bipyridine at negative potentials (about −1.0 V) seems to be in multilayers or perpendicular to the electrode in a monolayer.

$[Fe(bip)_3]^{2+}$ at low concentrations is not adsorbed at sufficiently positive potentials (curves 5 and 6). At high concentrations, however, it is adsorbed in all the potential regions investigated, and the surface excess is especially large in negative regions (curves 7 and 8). This shows that [Fe-

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[21] L. G. Sillen and A. E. Martell, "Stability Constant of Metal-Ion Complexes," Spec. Publ., **17**, Chem. Soc., London (1964).

[22] S. G. Meibuhr, *Electrochim. Acta*, **10**, 215 (1965).

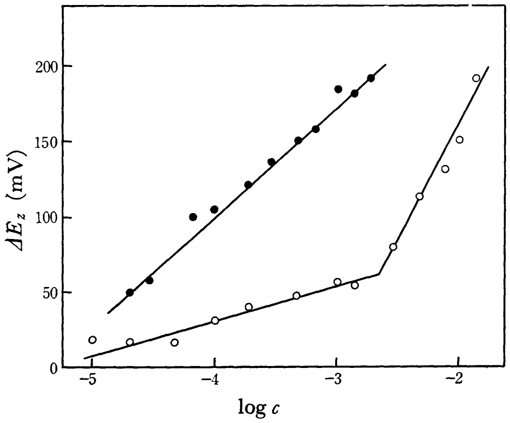

Fig. 7. Shifts of the potential of zero charge with the logarithms of adsorbate concentration in 0.5 M KCl.

○: 2,2′-bipyridine
●: $[Fe(bip)_3]^{2+}$

(bip)$_3$]$^{2+}$ has a character of the organic cation.

The shifts of the potential of zero charge (ΔE_z) with the logarithms of the concentrations of the adsorbates in 0.5 M KCl are shown in Fig. 7. In Fig. 7, $\Delta E_z = E_z^0 - E_z$, and E_z^0 is the potential of zero charge of the 0.5 M KCl solution, while E_z is that in a solution containing 2,2′-bipyridine or $[Fe(bip)_3]^{2+}$. The potentials of zero charge were determined from the electrocapillary curves. The change in E_z with the change in the concentration of an inorganic anion can be explained by the Esin and Markov effect,[23] which predicts that E_z will vary linearly with the logarithm of the activity of the anion. Barradas *et al.*[24] studied this effect with uncharged organic molecules and got linear relations between E_z and the logarithms of the concentrations of the organic molecules. In Fig. 7, E_z in the presence of $[Fe(bip)_3]^{2+}$ varies linearly with the logarithm of its concentration, as in the case of other inorganic ions, while the $E_z - \log c$ curve in the presence of 2,2′-bipyridine consists of two lines with different slopes. The lines cross each other at about 2×10^{-3} M, indicating a change in the structure of the adsorbed layer at this concentration.

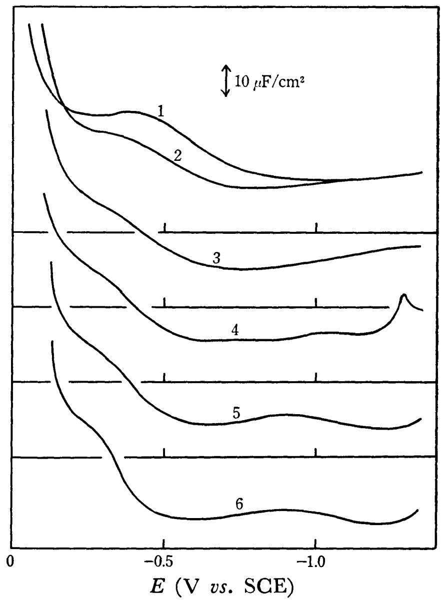

Fig. 8. Differential capacity - potential curves of 2,2′-bipyridine in 0.5 M KCl.
1, 0; 2, 5×10^{-5} M; 3, 2×10^{-4} M; 4, 2×10^{-3} M; 5, 5×10^{-3} M; 6, 10^{-2} M

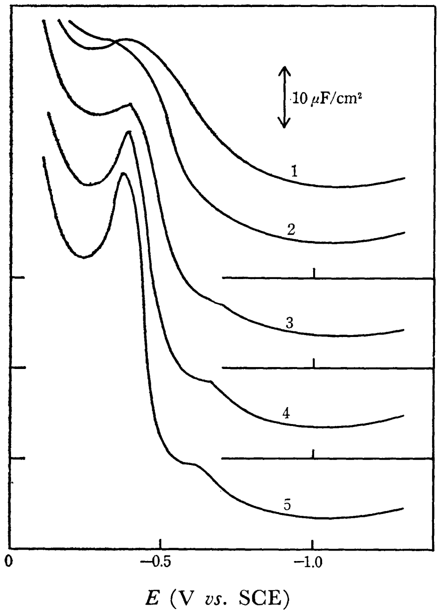

Fig. 9. Differential capacity - potential curves of $[Fe(bip)_3]^{2+}$ in 0.5 M KCl.
1, 0; 2, 5×10^{-5} M; 3, 2×10^{-4} M; 4, 5×10^{-4} M; 5, 10^{-3} M

The differential capacity - potential curves in the presence of 2,2′-bipyridine, shown in Fig. 8, do not show typical peaks, but the depression of the curves from that of the base solution indicates that 2,2′-bipyridine is adsorbed in this potential region. Above 2×10^{-3} M of 2,2′-bipyridine, a hump is observed in the adsorption region, indicating that two different adsorption structures exist on the two sides of the hump. The deep depression of the differential capacity in the potential region more negative than the hump indicates a strong adsorption; this is in agreement with the results from the electrocapillary data shown in Fig. 6. The differential capacity - potential curves of $[Fe(bip)_3]^{2+}$

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[23] O. A. Esin and B. F. Markov, *Acta Physicohim. URSS*, **10**, 353 (1939).

[24] R. G. Barradas, P. G. Hamilton and B. E. Conway, *J. Phys. Chem.*, **69**, 3411 (1965).

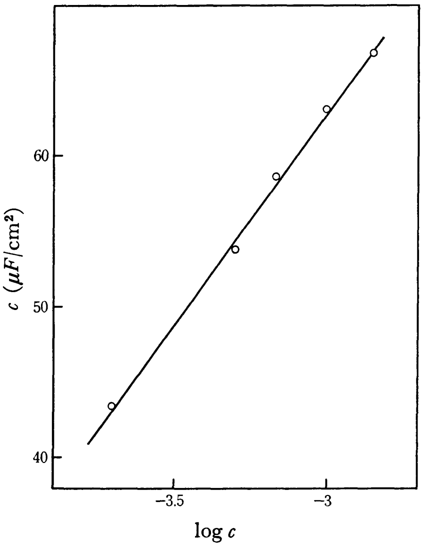

Fig. 10. Dependence of the height of capacity peak on concentration of $[Fe(bip)_3]^{2+}$.

are shown in Fig. 9. When compared with the curves in Fig. 8, distinct peaks are observed at about—0.4 V, and the capacity in the adsorption potential region is smaller in this case. As is shown in Fig. 10, the peak height varies linearly with the logarithm of the concentration. This is a characteristic trend of the adsorption - desorption peak.[2)]

On the basis of the above studies, the adsorption structure can be deduced. It is preferable to assume a monolayer if there is no sure evidence for multilayers, as has been found in the case of the adsorption of certain anionic surface-active substances.[3,4)] In low concentrations, 2,2′-bipyridine is adsorbed flat throughout the adsorption regions. Beyond 2×10^{-3} M, though it is still adsorbed flat in the more positive region, in the more negative region it is adsorbed perpendicularly to the electrode, probably because of the specific adsorption of nitrogen atoms onto the mercury electrode. The boundary of the two adsorption regions is not very distinct, so a hump is observed instead of a peak in the differential capacity - potential curves. Although the reason for the abnormal behavior of the electrocapillary curves of $[Fe(bip)_3]^{2+}$ is not yet certain, it is supposed to have only one adsorption region. As the chemical structure of $[Fe(bip)_3]^{2+}$ is almost symmetrical, the change in the orientation of the adsorbed ion cannot be considered as in the case of 2,2′-bipyridine.

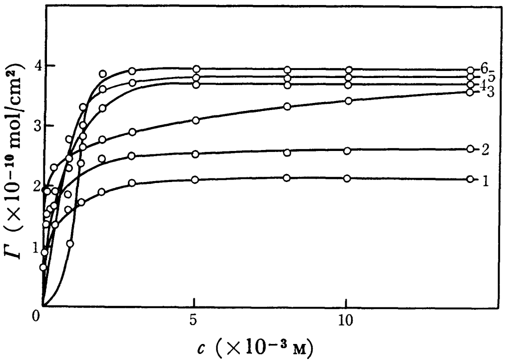

Fig. 11. Adsorption isotherms of 2,2′-bipyridine in 0.5 M KCl.
Potentials: 1, −0.2 V; 2, −0.4 V; 3, −0.8 V; 4, −0.8 V; 5, −1.0 V; 6, −1.2 V

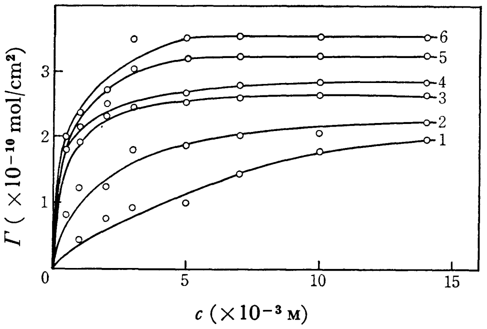

Fig. 12. Adsorption isotherms of $[Fe(bip)_3]^{2+}$ in 0.5 M KCl.
Potentials: 1, −0.2 V; 2, −0.4 V; 3, −0.6 V; 4, −0.8 V; 5, −1.0 V; 6, −1.2V

Adsorption Isotherms. The surface excesses Γ of 2,2′-bipyridine and $[Fe(bip)_3]^{2+}$ at various potentials were plotted against their concentrations in the bulk of the solution. The results are shown in Figs. 11 and 12. From the figures, the isotherm for $[Fe(bip)_3]^{2+}$ is found to be of the Langmuir type, while that for 2,2′-bipyridine is not so simple and varies considerably with the electrode potential, as has been found in the case of pyridine and its derivatives.[2,5–7)]

Among the many isotherms proposed up to now,[25)] the Langmuir isotherm (Eq. (5)) is most commonly been used;

$$Bc = \frac{\theta}{1-\theta} \tag{5}$$

where B is the constant of the adsorption equilibrium; c, the concentration of the organic compound, $\theta=\Gamma/\Gamma_m$, the fraction of the coverage, and Γ_m, the limiting value of Γ at $c\to\infty$. Recently, however, the following Frumkin isotherm[2)] has often been used:

$$Bc = \frac{\theta}{1-\theta}\exp(-2a\theta) \tag{6}$$

where a is the attraction constant, a quantity characterizing the interaction between the adsorbed particles. If a is equal to zero, Eq. (6) is converted to Eq. (5). A comparison of the experimental results with the theoretical expectations becomes much easier when Eq. (6) is modified as Eq. (7):

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25) P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers, New York (1965), p. 83.

$$\frac{c}{c_{\theta=0.5}} = \frac{\theta}{1-\theta}\exp\left[a(1-2\theta)\right] \qquad (7)$$

where $c_{\theta=0.5}$ is the concentration at which θ becomes equal to 0.5. Supposing that the Γ_m of 2,2′-bipyridine is 3.9×10^{-10} mol/cm^2 and that the Γ_m of $[\mathrm{Fe(bip)_3}]^{2+}$ is 3.5×10^{-10} mol/cm^2, the relations of $c/c_{\theta=0.5}$ and θ were calculated; they are plotted in Figs. 13 and 14. The value of a determined from these figures is between 0 and -3 for $[\mathrm{Fe(bip)_3}]^{2+}$, while that for 2,2′-bipyridine changes from -5 at -0.2 V to $+2.5$ at -1.2 V. Damaskin[26] explained the adsorption of pyridine by using the Frumkin isotherms, but he did not explain why a changed considerably with the electrode potential.

Now, from the results of the investigation of the adsorption structure of 2,2′-bipyridine, the change in a with the potential can be explained in the following way, by means of the change in the adsorption structure with the potential. In the more positive potential regions, 2,2′-bipyridine is adsorbed flat onto the electrode surface as a result of the π-electron - electrode interaction. In this case, the isotherm shown by curve 1 in Fig. 13 is obtained, and a negative attraction constant is obtained from it. In the more negative potentials, however, 2,2′-bipyridine at low concentrations is scarcely adsorbed because of the repulsion between the π-electron and the electrode. However, when the concentration is increased, it is adsorbed in a large amount perpendicularly to the electrode, resulting in an adsorption isotherm with a positive attraction constant, as in curve (8) of Fig. 13. As one adsorption structure changes in relation to another with an electrode potential, the isotherm changes between the two extreme cases with the electrode potential.

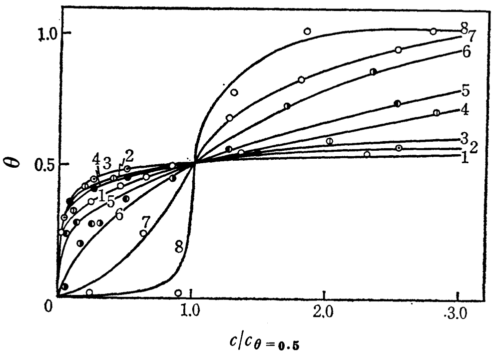

Fig. 13. Frumkin isotherms of 2,2′-bipyridine in 0.5 M KCl.
Potentials: 1, -0.2 V, $a=-5.0$; 2, -0.4 V, $a=-2.5$; 3, -0.6 V, $a=-1.0$; 4, -0.8 V, $a=-0.3$; 5, -0.9 V, $a=0.0$; 6, -1.0 V, $a=1.0$; 7, -1.1 V, $a=1.7$; 8, -1.2 V, $a=2.5$.

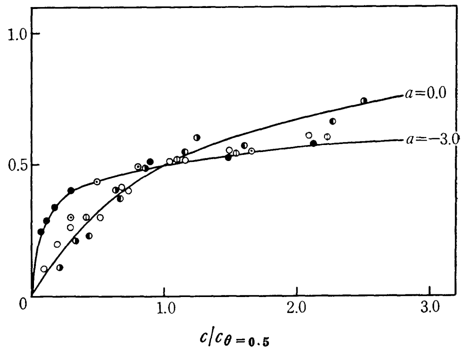

Fig. 14. Frumkin isotherms of $[\mathrm{Fe(bip)_3}]^{2+}$ in 0.5 M KCl.
Potentials: ○: -0.2V; ●: -0.4 V; ⊙: -0.6 V; ⦶: -1.0 V; ◐: -1.1 V; ◑: -1.2 V

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[26] B. B. Damaskin, *Electrochim. Acta*, **9**, 231 (1964).