The Extraction of Tris(1,10-phenanthroline)ruthenium(II). I. Distribution Studies

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Tris(1,10-phenanthroline)Ru(II) was extracted into various organic solvents with several anions, such as the perchlorate ion, the iodide ion, or the thiocyanate ion. The association constants of ion-pairs were successfully determined by analysis of the extraction curves in the solvents with low polarities. It was found that the ion-pairs were extracted mainly as the associated form and that only the first-step dissociation could slightly occur ($<10^{-7}$) in such solvents; furthermore, the degree of association was considerable even in water. Therefore, the distribution ratio of the complex cation must be governed by both the hydration energy of the counter anion and the solubility parameter of the extraction solvent rather than its dielectric property. An abnormal decrease in the distribution ratio was observed when the tetraphenylborate ion was used as the counter anion. This phenomenon can be explained clearly in terms of the hydrotropism which was often encountered in the solution of an electrolyte with a large ion.

In recent years, the ion-pair extraction systems have been widely investigated, mainly out of analytical interest.[1] However, very few theories which can satisfactorily explain its mechanism have yet been developed. Some authors have successfully tried to discuss the extraction mechanism in connection with the dielectric properties of the solvents.[1,2] On the other hand, Freiser[3] suggested the possibility that the regular solution theory could also be applied to the ion-pair distribution with the organic solvent of a low polarity (≤ 10), much as in the case of chelate distribution.[4] Gibson and Weatherburn[5] have tried to discuss the extraction behavior in connection with the hydration energies of the ions.

In this paper, in order to describe one approach to the systematic investigation of the ion-pair extraction system, tris(1,10-phenanthroline)Ru(II), Ru(II)(phen)$_3$ has been chosen as the extractant to be transferred into various organic solvents in the presence of such anions as the perchlorate ion, the iodide ion, the thiocyanate ion, the tetrafluoroborate ion, and the tetraphenylborate ion. The extraction mechanism can be analysed clearly in the Ru(II)(phen)$_3$ system, because Ru(II)(phen)$_3$ is very substitution-inert so that the interference of the free ligand can be neglected. The distribution ratios were discussed as a function of the bulk character of the solvents and of the hydration energies of the anions. The distribution ratios of sodium perchlorate into chloroform, *o*-dichlorobenzene, *etc.*, which could hardly be determined by direct-extraction measurements, can also be determined indirectly by analyses of the extraction curves of Ru(II)(phen)$_3$. In the extraction of Ru(II)(phen)$_3$ with the tetraphenylborate ion, the decrease in the distribution ratio appeared in the region where the concentration of the tetraphenylborate ion was high. This abnormal phenomenon was explained in terms of the hydrotropism advanced by Neuberg[6] in 1916.

In the next paper,[7] the distribution ratio will be discussed in connection with the solubilities by applying the regular solution theory and the electrostatic theory.

Experimental

Reagents. All the reagents were of a reagent-grade purity. The organic solvents were purified mainly by distillation before use. Sodium perchlorate was used as an anhydrous salt after recrystallization. ^{106}Ru (Lot. No. 1210) was supplied by the Japan Radioisotope Association. The radiochemical purity was checked by means of the γ-ray spectrum. The water was distilled twice with an all-quartz distillation apparatus.

Molar absorptivity of Ru(II)(phen)$_3$. The determination of the molar absorptivity of Ru(II) (phen)$_3$ was carried out by using a ruthenium chloride solution (ruthenium content: 0.07392 mg/ml) in a manner almost identical with that of Banks and ÓLaughlin[8] except that 0.5 M KH_2PO_4–Na_2HPO_4 was used to maintain the pH at 6 during the reaction. The calculated molar absorptivity at 448 nm was 18500 liters per mole-cm. In this series of extraction studies, the concentration of Ru(II) (phen)$_3$ was determined from this value.

Preparation of the ^{106}Ru(II)(phen)$_3$ Solution. A crude aqueous solution of ^{106}Ru(II)(phen)$_3$ was prepared from ^{106}RuCl$_3$ (containing as adequate amount of the carrier) as has been described above except that the NaOH–HCl system was used to adjust the pH to 6. After the reacted mixture has been washed several times with chloroform and then with *n*-hexane, the Ru(II)(phen)$_3$ was extracted with the perchlorate ion into 1,2-dichloroethane. This organic phase was evaporated to dryness and then dissolved with a minimum volume of acetonitrile. If any residue was detected, it was filtered out. This filtrate was dried again and then dissolved in a small amount of water. This resulting solution was passed through the anion-exchanger column in order to convert the counter anions to chloride or sulfate. It is recommended that a labelled complex of a high specific activity should be used immediately after preparation, since serious radiation decomposition was noticed; in a sample of 1 μCi/ml, several percent were found to be decomposed within one week.

Extraction Procedure of Ru(II)(phen)$_3$. An appropriate amount of the ^{106}Ru(II)(phen)$_3$ solution and various amounts of sodium-salt solutions of different anions, such as the perchlorate ion, the iodide ion, and the thiocyanate ion, were placed in a 50 ml glass centrifuge tube equipped with a ground stopper. After sodium chloride or sodium sulfate has been added to keep the ionic strength constant and after the aqueous phase has been diluted up to 10 ml with water, a 10 ml portion of the organic solvent was added. The two phases were shaken vigorously for 30 min in the thermostat at 25 ° and then separated by centrifugation. The net distribution ratio was calculated by measureing the γ-radioactivities of both the phases with a single-channel pulse-height analyser (Osaka Denpa Model LA-3T, or Nuclear-Chicago 1185 series).

Theoretical

The ion-pair extraction equilibrium is independent of the salt which is added in the aqueous phase to keep the ionic strength constant except in the very low concentration region of the counter anion, A^-. Therefore, in the extraction of Ru(II)(phen)$_3$ with various anions, the following concentration constants have been defined in the two phases:

$$k_1 = \frac{[MA^+]_a}{[M^{2+}]_a[A^-]_a} \tag{1}$$

$$k_2 = \frac{[MA_2]_a}{[MA^+]_a[A^-]_a} \tag{2}$$

$$K_D = \frac{[MA_2]_o}{[MA_2]_a} \tag{3}$$

$$K_1 = \frac{[MA^+]_o[A^-]_o}{[MA_2]_o} \tag{4}$$

$$K_2 = \frac{[M^{2+}]_o[A^-]_o}{[MA^+]_o} \tag{5}$$

In these expressions, the subscripts a and o refer to the aqueous and organic phases respectively, M^{2+}, to the complex cation Ru(II)(phen)$_3$, and A^-, to the counter anion.

At the distribution equilibrium, the distribution ratio, D, of MA_2 is written as:

$$D = \frac{[M^{2+}]_o+[MA^+]_o+[MA_2]_o}{[M^{2+}]_a+[MA^+]_a+[MA_2]_a} \tag{6}$$

By combining Eqs. (1)—(6), D can be expressed as:

$$D = K_D \times \frac{k_1k_2[A^-]_a^2}{1+k_1[A^-]_a+k_1k_2[A^-]_a^2} \times \frac{K_1K_2+K_1[A^-]_o+[A^-]_o^2}{[A^-]_o^2} \tag{7}$$

In the application of Eq. (7), the following four cases can be assumed:

(i) When the dissociation does not occur at all in the organic phase, Eq. (7) can be simplified to Eq. (8):

$$D = K_D \times \frac{k_1k_2[A^-]_a^2}{1+k_1[A^-]_a+k_1k_2[A^-]_a^2} \tag{8}$$

This equation shows that the D values depend only upon $[A^-]_a$. Therefore, the D values are kept constant, even though the concentration of the complex cations changes.

(ii) When the first-step dissociation occurs alone in the organic phase ($K_2=0$), Eq. (7) can be represented as Eq. (9):

$$D = K_D \times \frac{k_1k_2[A^-]_a^2}{1+k_1[A^-]_a+k_1k_2[A^-]_a^2} \times \frac{K_1+[A^-]_o}{[A^-]_o} \tag{9}$$

The electrical neutrality in the organic phase requires the following equation:

$$[MA^+]_o = [A^-]_o \tag{10}$$

In addition, the total concentration of the extracted species, $(C_M)_o$, is represented by Eq. (11):

$$(C_M)_o = [MA^+]_o + [MA_2]_o \tag{11}$$

By combining Eqs. (4), (10), and (11), the next relation is obtained:

$$[A^-]_o = (\sqrt{K_1^2+4K_1(C_M)_o}-K_1)/2 \tag{12}$$

From Eqs. (9), and (12), we obtain Eq. (13):

$$D = K_D \times \frac{k_1k_2[A^-]_a^2}{1+k_1[A^-]_a+k_1k_2[A^-]_a^2} \times \frac{K_1+\sqrt{K_1^2+4K_1(C_M)_o}+2(C_M)_o}{2(C_M)_o} \tag{13}$$

According to Eq. (13), if $[A^-]_a$ is kept constant, the slope of the plot of log D *vs.* log$(C_M)_o$ must be -1 in the low $(C_M)_o$ region, must increase with the increase in $(C_M)_o$, and must finally reach 0 in the high $(C_M)_o$ region. In the region where D is independent of the change of $(C_M)_o$, the third term of Eq. (13) becomes 1 and Eq. (13) is simplified to Eq. (8). Equation (8) can be converted into Eq. (14) by using the method of Sillén:9)

$$(K_D-D)D^{-1}[A^-]_a^2 = k_2^{-1}[A^-]_a + k_1^{-1}k_2^{-1} \tag{14}$$

If K_D is known, k_1 and k_2 can be calculated from the plot of $(K_D-D)D^{-1}[A^-]_a^2$ *vs.* $[A^-]_a$. K_D, here, is experimentally obtained by taking the D value to be equal to K_D in the high $[A^-]_a$ region on the plot of log D *vs.* log $[A^-]_a$, where D becomes constant. If k_1, k_2, and K_D are obtained in this way, K_1 can be estimated from the slope of the plot of D *vs.* $1/(C_M)_o$ in the region where the slope of the plot of log D *vs.* log $(C_M)_o$ becomes -1, because its slope is represented by

$$K_DK_1k_1k_2[A^-]_a^2/(1+k_1[A^-]_a+k_1k_2[A^-]_a^2).$$

(iii) When the first-step dissociation occurs almost completely in the organic phase, that is, when K_1 is very large, Eq. (7) can be written as follows:

$$D = K_D \times \frac{k_1k_2[A^-]_a^2}{1+k_1[A^-]_a+k_1k_2[A^-]_a^2} \times \frac{K_1K_2+K_1[A^-]_o}{[A^-]_o^2} \tag{15}$$

From the electrical neutrality in the organic phase, the following relation can be said to hold:

$$[MA^+]_o + 2[M^{2+}]_o = [A^-]_o \tag{16}$$

Further, $(C_M)_o$ is represented as:

$$(C_M)_o = [MA^+]_o + [M^{2+}]_o \tag{17}$$

By combining Eqs. (5), (16), and (17), the next relation is obtained:

$$[A^-]_o = \{(C_M)_o-K_2+\sqrt{K_2^2+(C_M)_o^2+6K_2(C_M)_o}\}/2 \tag{18}$$

From Eqs. (15), and (18), we obtain:

$$D = K_D \times \frac{k_1k_2[A^-]_a^2}{1+k_1[A^-]_a+k_1k_2[A^-]_a^2} \times \frac{K_1[K_2^2+4K_2(C_M)_o-(C_M)_o^2+\{K_2+(C_M)_o\}\sqrt{K_2^2+(C_M)_o^2+6K_2(C_M)_0}]}{8K_2(C_M)_0^2} \tag{19}$$

According to Eq. (19), if $[A^-]_a$ is kept constant, the slope of the plot of $\log D$ *vs.* $\log (C_M)_O$ must change from −2 in the low-$(C_M)_O$ region to −1 in the high-$(C_M)_O$ region.

(iv) When the first- and second-step dissociations occur to a considerable extent in the organic phase, from Eq. (7) the slope of the plot of $\log D$ *vs.* $\log (C_M)_O$ can be assumed to change from −2 in the low-$(C_M)_O$ region to −1 in the intermediate-$(C_M)_O$ region, finally reaching 0 in the high-$(C_M)_O$ region.

In the last two cases, (iii) and (iv), the estimation of the constants by analysis of the extraction curves becomes complicated. Fortunately, however, no such case has been encountered so far, except when a solvent with a relatively high dielectric constant, such as nitrobenzene, has been used.

Results and Discussion

The Extraction of Ru(II)(phen)$_3$ with the Perchlorate Ion into Various Solvents. In Figs. 1 and 2 the relations between $\log D$ and $\log [ClO_4^-]_a$, with several organic solvents, are shown. In these studies the initial concentration, C_M, of the complex cation in the aqueous phase was fixed at 3.15×10^{-6} M, while the ionic strength in the aqueous phase was controlled either at 0.75 with sodium sulfate or at 0.1 with sodium chloride. The extraction curves represented in Fig. 1 are sigmoidal ones which are encountered in oridnary chelate extraction systems with low formation constants. On the other hand, those in Fig. 2 possess inflection points. This phenomenon will be explained by the distribution of sodium perchlorate. From the extraction curves in Fig. 1, the K_D values can be obtained graphically by taking the D values at the high-$[ClO_4^-]_a$ regions, where the slopes of the plots of $\log D$ *vs.* $\log [ClO_4^-]_a$ are 0. These values are shown in Table 1. In Figs. 3—8, $\log D$ is plotted against $\log (C_M)_O$ at the fixed $[ClO_4^-]_i$, where $[ClO_4^-]_i$ shows the initial concentration of the perchlorate ion added to the aqueous phase. As is shown in most of the figures, the slope of the plot of $\log D$ *vs.* $\log (C_M)_O$ changes from −1 in the low-$(C_M)_O$ region to 0 in the high-$(C_M)_O$ region. This result suggests that, in the solvents with low dielectric constants, the extracted Ru(phen)$_3$(ClO$_4$)$_2$ dissociates only at the first step. When $[ClO_4^-]_i$ is kept high, D becomes constant independently of the change in $(C_M)_O$. This tendency is observed in all the solvents examined. This phenomenon can be explained by the fact that,

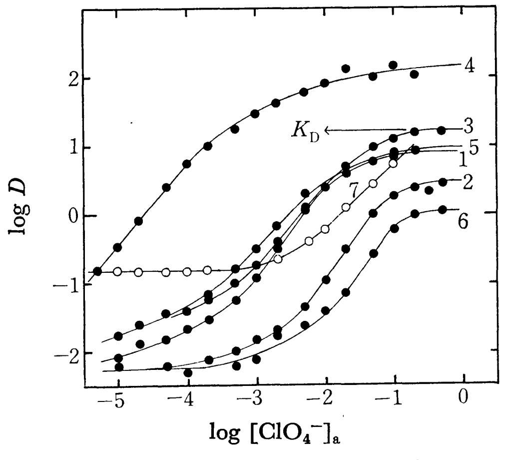

Fig. 1. The extraction of Ru(II)(phen)$_3$ into various solvents. (1) chloroform, (2) chlorobenzene, (3) methyl isobutyl ketone, (4) acetophenone, (5) *o*-dichlorobenzene, (6) *m*-dichlorobenzene, (7) isoamylalcohol. (●) $I=0.75$(Na$_2$SO$_4$), (○) $I=0.1$(NaCl).

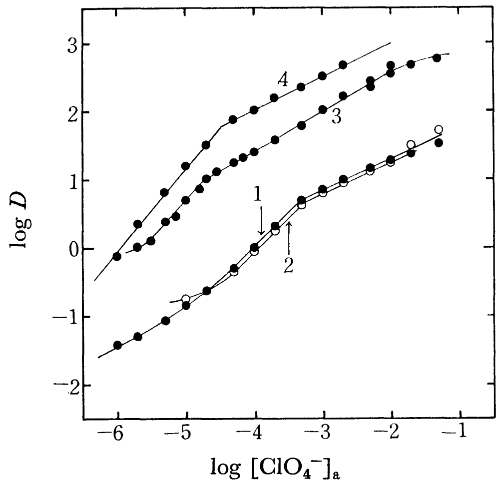

Fig. 2. The extraction of Ru(II)(phen)$_3$ into various solvents. (1) 1,2-dichloroethane, (2) 1,1,2,2-tetrachloroethane, (3) bis(2-chloroethyl) ether, (4) nitrobenzene. $I=0.1$ (NaCl).

TABLE 1. VARIOUS CONSTANTS OF Ru(phen)$_3$(ClO$_4$)$_2$

Solvent	K_D	k_1	k_2	K_1	K_2
	(from extraction)				
Chloroform	8.5	2.4×10^2	5.4×10	5.1×10^{-8}	0
Chlorobenzene	3.0	—	—	9.5×10^{-9}	0
MIBK	16.0	—	—	8.5×10^{-9}	0
Acetophenone	200	2.7×10^5	3.1×10^2	8.2×10^{-10}	0
o-Dichlorobenzene	10.0	—	—	3.0×10^{-7}	0
m-Dichlorobenzene	1.3	—	—	3.0×10^{-8}	0
	(from solubility)				
H_2O	—	2.3×10^3	6.7	—	—

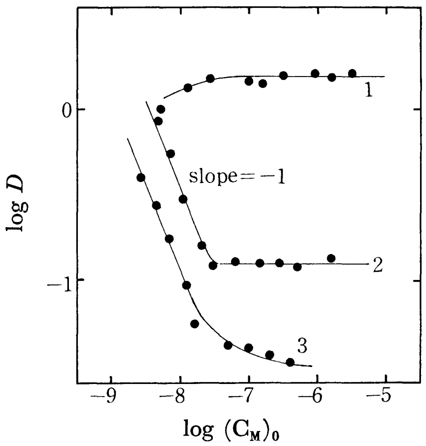

Fig. 3. The relation between $\log D$ and $\log (C_M)_O$ in chloroform. $[ClO_4^-]_i$: (1) 1×10^{-2}M, (2) 1×10^{-3}M, (3) 1×10^{-4}M. $I=0.75$ (Na$_2$SO$_4$).

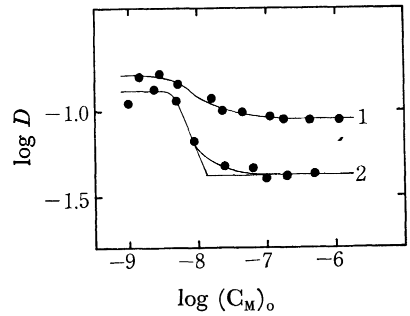

Fig. 4. The relation between log D and log $(C_M)_o$ in chlorobenzene. $[ClO_4^-]_i$: (1) 1×10^{-2}M, (2) 5×10^{-3}M. I=0.75 (Na_2SO_4).

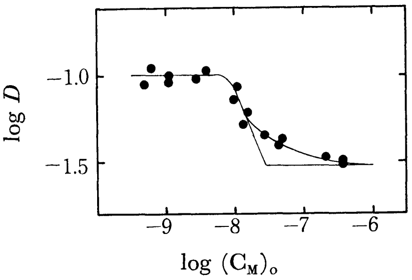

Fig. 5. The relation between log D and log $(C_M)_o$ in *m*-dichlorobenzene. $[ClO_4^-]_i=1\times10^{-2}$M. I=0.75 (Na_2SO_4).

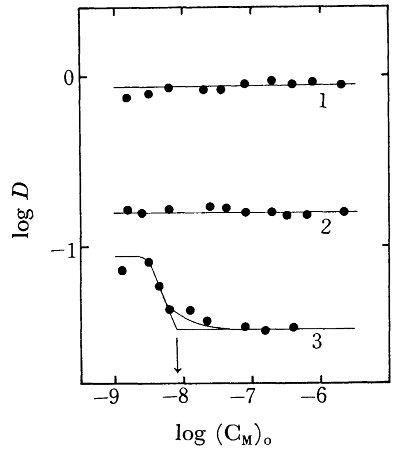

Fig. 6. The relation between log D and log $(C_M)_o$ in MIBK. $[ClO_4^-]_i$: (1) 5×10^{-3}M, (2) 1×10^{-3}M, (3) 1×10^{-4}M. I=0.75 (Na_2SO_4).

in the high-$[ClO_4^-]_i$ region, the $[A^-]_0$ in the third term of Eq. (9) is no longer determined by the dissociation of $Ru(phen)_3(ClO_4)_2$, but by the dissociation of the sodium perchlorate present in the organic phase; the sodium perchlorate in the organic phase begins to act as an anion buffer. This phenomenon can be used in the estimation of the distribution coefficient of sodium perchlorate.

The Determination of the Association and Dissociation Constants. If chloroform is used as the extraction solvent, the third term of Eq. (9) can be taken as 1 in the region where $(C_M)_O$ is more than 10^{-7} M. (See Fig. 3) Therefore, the extraction curve can be analysed according to Eq. (8) in the range where D is above 3.3×10^{-2}. Figure 9 demonstrates the plot of $(K_D-D)D^{-1}[ClO_4^-]_a^2$ *vs.* $[ClO_4^-]_a$ in that region; it shows a good linearity. k_1 and k_2, as calculated from the slope and the intercept on the $(K_D-D)D^{-1}[ClO_4^-]_a^2$ axis in Fig. 9, are 2.4×10^2 and 54 respectively.

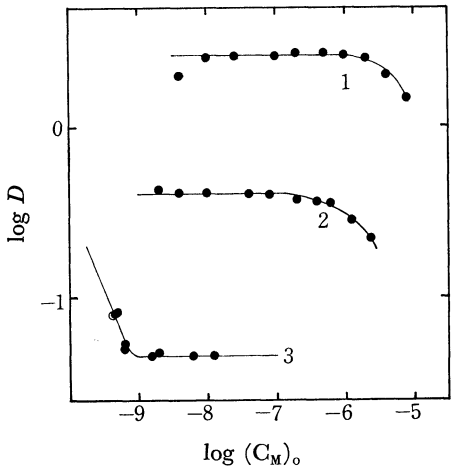

Fig. 7. The relation between log D and log $(C_M)_o$ in acetophenone. $[ClO_4^-]_i$: (1) 5×10^{-5}M, (2) 1×10^{-5} M, (3) 1×10^{-6}M. I=0.75 (Na_2SO_4).

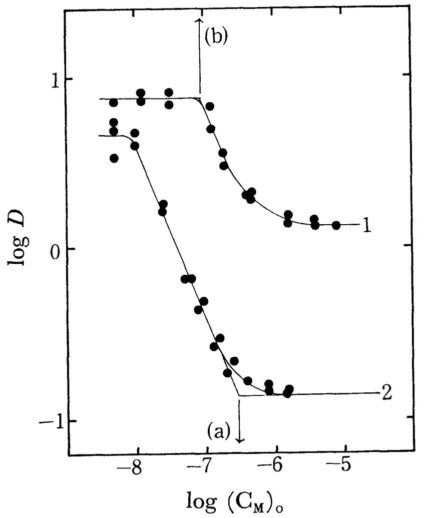

Fig. 8. The relation between log D and log $(C_M)_o$ in *o*-dichlorobenzene. $[ClO_4^-]_i$: (1) 1×10^{-2}M, (2) 1×10^{-3}M. I=0.75 (Na_2SO_4).

In order to calculate K_1, D was plotted as a function of $1/(C_M)_O$ in the region where the slope of the plot of log D *vs.* log $(C_M)_O$ is −1 in Fig. 3. (See Fig. 10) From the slope of the plot in this figure, the estimation of K_1 can be made by using the k_1 and k_2 values calculated previously. For determining K_1, the slope (1) at 1×10^{-3} M $[ClO_4^-]_i$ was used, since the effect of sodium sulfate, added in the aqueous phase to maintain the ionic strength constant, and other experimental errors are minimized in that region.

Another example is shown in the case of acetophenone. As is shown in Fig. 7, the third term of Eq. (9) could be taken as 1 in the region where $(C_M)_O$ is more than 10^{-7} M, much as in the case of chloroform. Therefore, from the plot of Eq. (14), we can calculate

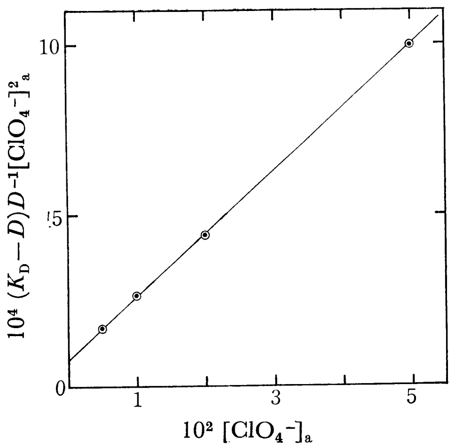

Fig. 9. Linear plot between $(K_D-D)D^{-1}[ClO_4^-]^2_a$ and $[ClO_4^-]_a$ in chloroform.
Slope $=k_2^{-1}=1.84\times10^{-2}$, Intercept $=k_1^{-1}k_2^{-1}=7.7\times10^{-5}$.

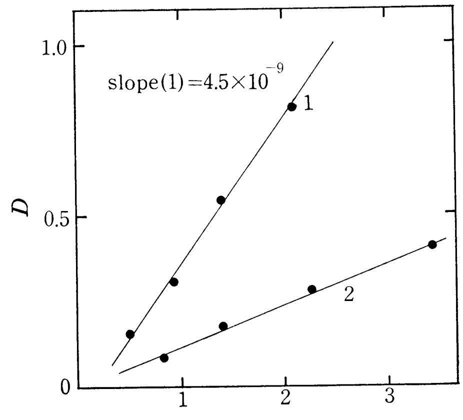

Fig. 10. The relation between D and $1/(C_M)_o$. $[ClO_4^-]_i$: (1) 1×10^{-3}M, (2) 1×10^{-4}M.

k_1 and k_2. The k_1 and k_2 values thus obtained are 2.7×10^5 and 3.1×10^2 respectively, which are considerably larger than those obtained in the chloroform system. Perhaps this difference is caused by the apparent decrease in the dielectric constant of the aqueous phase, since acetophenone is more soluble in chloroform than water. The ionic equilibrium in the acetophenone phase is governed by sodium perchlorate, which is extracted in a small amount. Therefore, the slope of -1 in the plot of log D *vs.* log $(C_M)_O$ does not appear until $[ClO_4^-]_i$ gets down as low as 1×10^{-6} M under the experimental conditions employed, as is shown in Fig. 7. As can be seen from Curve (3) in Fig. 7, the concentration of the perchlorate ion in the aqueous phase should be constant, because the concentration of the perchlorate ion which is extracted with Ru(II)(phen)$_3$ into the organic phase is negligible. Therefore, the plot of D *vs.* $1/(C_M)_O$ in the region where the slope of the plot of log D *vs.* log $(C_M)_O$ shows -1 can be utilized for the calculation of K_1. The K_1 thus calculated was 8.2×10^{-10}.

In the other solvents the plot of Eq. (14) did not show a good linearity. Therefore, the precise values of k_1 and k_2 in these systems could not be estimated on the basis of the theoretical analysis. Therefore, in such systems K_1 was assumed to be equal to $(C_M)_O$ at the inflection point (for example, point (a) in Fig. 8), which appears between the slope of -1 and 0 in the plot of log D *vs.* log $(C_M)_O$.

As has been shown, in the system where the solvent has a low dielectric constant (<20), the calculation of those constants can be done either by fitting numerical values to the equations or by graphical analysis. On the other hand, in the system where a solvent with a high dielectric constant is used, such analysis becomes impossible, because sodium perchlorate is considerably extracted into the organic phase and, furthermore, K_D can not be estimated from the extraction curves. In addition, to make the k_1 and k_2 values obtained from the extraction studies more reliable, those values were reexamined from the point of view of solubility. The solubility product, K_{sp} in water, which was defined as $K_{sp}=[M^{2+}][ClO_4^-]^2$, was calculated at 1.52×10^{-10} at 25°.

All the constants are summarized in Table 1. From these results, Ru(phen)$_3$(ClO$_4$)$_2$ can be said almost to be associated with the solvents with low dielectric constants. When ketones are the extraction solvents, the K_D values are fairly much larger than those in the other solvents. This can be explained by the tendency of Ru(II)(phen)$_3$ to solvate with ketones, since Ru(II)(phen)$_3$ has considerable electron affinity because of its double positive charge, although it is a very large cation. The distribution to the solvent with a high dielectric constant (>20) is also promoted by the dissociation in the organic phase. Our data on both the extraction and the solubility show that Ru(phen)$_3$(ClO$_4$)$_2$ is considerably associated in water. This is contradictory to the conclusion of Yamamoto[1] in a similar study with Fe(phen)$_3$(ClO$_4$)$_2$; they concluded that this ion-pair is completely dissociated in water and in nitrobenzene. In Fig. 1, the distribution ratio into isoamyl alcohol is relatively higher than that into other solvents in the low-$[ClO_4^-]_a$ region. This can be explained by the high solubility of chloride in alcohol; this phenomenon was confirmed by the solubility measurements, which will be reported in the next paper.[7]

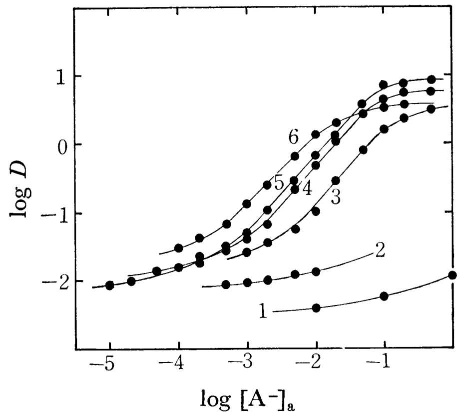

Fig. 11. The extraction of Ru(II)(phen)$_3$ into chloroform with various anions.
(1) Cl$^-$, (2) NO$_3^-$, (3) BF$_4^-$, (4) SCN$^-$, (5) I$^-$, (6) IO$_4^-$. $I=0.75$ (Na$_2$SO$_4$).

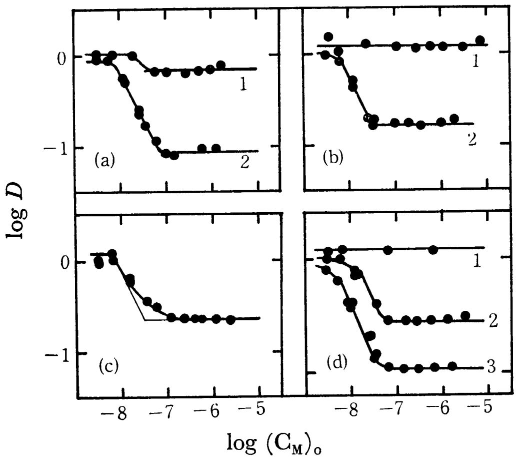

Fig. 12. The extraction of Ru(II)$(phen)_3$ into chloroform with various anions as a function of $(C_M)_o$. (a) with iodide ion: (1) 1×10^{-2}M, (2) 2×10^{-3}M. (b) with thiocyanate ion: (1) 2×10^{-2}M, (2) 5×10^{-3}M. (c) with periodide ion: 2×10^{-3}M. (d) with tetrafluoroborate ion: (1) 5×10^{-2}M, (2) 2×10^{-2}M, (3) 1×10^{-2}M. I=0.75 (Na_2SO_4).

Table 2. Constants of $Ru(phen)_3A_2$ in chloroform

Anion	K_D	k_1	k_2
BF_4^-	3.6	4.9×10	8.9
SCN^-	5.7	6.3×10^2	10.5
I^-	9.2	3.8×10^2	9.8
ClO_4^-	8.5	2.4×10^2	54.0
IO_4^-	3.7	2.9×10^3	43.0

Extraction of Ru(II)$(phen)_3$ into Chloroform with Various Anions. Ru(II)$(phen)_3$ was extracted into chloroform with several anions; the relations between log D *vs.* log $[A^-]_a$ are shown in Fig. 11. In Fig. 12, the extraction behavior on changing counter anions is shown by plotting log D as a function of log $(C_M)_o$. The constants, K_D, k_1, and k_2, which were obtained by means of the theoretical analysis described in the previous sections, are summarized in Table 2.

By examining the extraction curves shown in Fig. 12, it becomes obvious that the ion-pairs extracted into chloroform dissociate only at the first step, and that the calculated values of K_1 were present in the $10^{-8}\leq K_1\leq10^{-7}$ region in all the systems. Therefore, these ion-pairs exist mostly as associated molecules in chloroform. The order of extractability as a measure of half-extraction $[A^-]_a$ is as follows: $B(C_6H_5)_4^- \gg IO_4^- \sim ClO_4^- > I^- > SCN^- > BF_4^- \gg NO_3^- > Cl^- \sim OH^- \gg SO_4^{2-}$. This sequence suggests that the enthalpy of the hydration of the anion is the major factor determining the distribution ratio, because, in this system, the enthalpy of the hydration of the cation is negligible compared with that of the anion. Strongly hydrated ions, such as SO_4^{2-} and F^-, are scarcely extracted at all. This result is in good agreement with those obtained by Gibson and Weatherburn[5] with the quaternary phosphonium and arsonium, by Biswas and Mandal[10] with surfactant cations, and by Diamond *et al.*[11,12] with ammonium. As is shown in Fig. 11, the great change in the distribution ratio appears between NO_3^- and BF_4^-. This observation also agrees with that obtained by Gibson and Weatherburn;[5] the distribution ratio increases remarkably when the enthalpy of hydration of the anions is below 70—80 kcal/mol. This phenomenon can be explained successfully by the equation derived by Ionin and Kurina,[13] assuming that the distribution ratio is determined solely by changes in the enthalpies of the hydration of the anion. Moreover, as is shown in Table 2, the association constants, k_1 and k_2 increase with the decrease in the enthalpy of the hydration of the anion and with the increase in the size of the anion. It is also noticeable that the ratio of k_1 to k_2 becomes larger with the increase in the size of the anion. This tendency can be understood in terms of the repulsion between the anions which combine with Ru(II)$(phen)_3$. When quite large anions such as ClO_4^- are used, k_1 and k_2 become larger than would be expected from the electrostatic theory. Therefore, the concept of water structure-enforced ion-pairing should be applied.[14]

On the basis of the above discussion, the distribution ratio is mainly determined by both the degree of association of the ion-pair in the aqueous phase and the distribution of the associated ion-pair when the solvent, whose dielectric constant is low and whose solvation power is weak, is used for ion-pair extraction. The former depends on the enthalpy of the hydration of ion, and the latter, on the solubility of the associated ion-pair in the extraction solvent, which might be correlated with the solubility parameter.

It should be mentioned that the above discussion is not applicable to a system with a strong basic or acidic solvent; in such a system the distribution of ion-pairs is influenced not only by the solubility of the associated form, but also by the dissociation due to the ion-solvent interaction in the organic phase.

The Extraction of Ru(II)$(phen)_3$ with the Tetraphenylborate Ion. Ru(II)$(phen)_3$ was extracted into chloroform, ethyl acetate, MIBK, or nitrobenzene with the tetraphenylborate ion. The relations between log D *vs.* log $[B(C_6H_5)_4^-]_i$ in chloroform and MIBK respectively are shown in Figs. 13 and 14. An abnormal

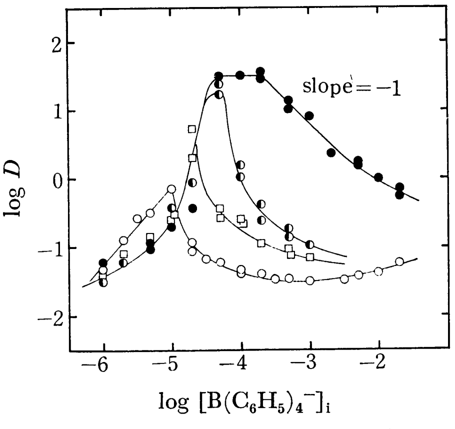

Fig. 13. The extraction of Ru(II)$(phen)_3$ into chloroform as a function of $[B(C_6H_5)_4^-]_i$.
concn of chloride ion in the aqueous phase: (○) in the absence of NaCl, (□) 1×10^{-3}M, (◐) 1×10^{-2}M, (●) 1×10^{-1}M.

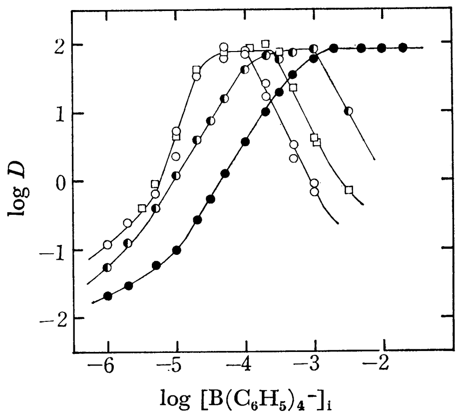

Fig. 14. The extraction of Ru(II)(Phen)$_3$ into MIBK as a function of $[B(C_6H_5)_4^-]_i$.
concn of chloride ion in the aqueous phase: (○) in the absence of NaCl, (□) 1×10^{-3}M, (◐) 1×10^{-2}M, (●) 1×10^{-1}M.

decrease of D at the higher concentrations of sodium tetraphenylborate was more or less observed in every solvent so far examined. Moreover, the extraction behavior is largely dependent upon the concentration of sodium chloride in the aqueous phase. In the extraction, the adsorption of Ru(II)(phen)$_3$ on the wall of the glass tube and on the interface was observed at low concentrations of sodium chloride. Therefore, it seems that the ion-pair is difficult to dissolve in both the phases. Such results have not been observed in the systems with anions other than the tetraphenylborate ion.

In order to compare this abnormal tetraphenylborate system with another anion system, the behavior of sodium tetraphenylborate itself should be considered. For this purpose, its distribution into chloroform or MIBK was examined by using the tracer technique (see Fig. 15); furthermore, its association in both the phases was also measured on the basis of the conductivity by applying the Shedlovsky method[15] (see Table 3).

By correcting for the behavior of sodium tetraphenylborate, it becomes clear that the tetraphenylborate ion possesses a very high extractability compared with the other anions such as ClO_4^- and I^-. This observation can be explained by the facts that the tetraphenylborate ion has a very low enthalpy of hydration and a very hydrophobic structure, and that the ion-pairing with such anions is promoted by the structure-making force of water. Moreover, in the MIBK system, the extraction behavior is influenced greatly in the low $[B(C_6H_5)_4^-]_i$ region by the presence of sodium chloride in the aqueous phase; the decrease is caused by the high distribution of sodium tetraphenylborate into the organic phase because of the addition of sodium chloride. On the other hand, the partition of sodium tetraphenylborate into chloroform is so rare that the extraction curves have not been influenced by the addition of sodium chloride to the aqueous phase, as would be expected. Therefore, its influence on the distribution ratio of Ru(II)(phen)$_3$ must be due to the salting-out effect, which will be described later.

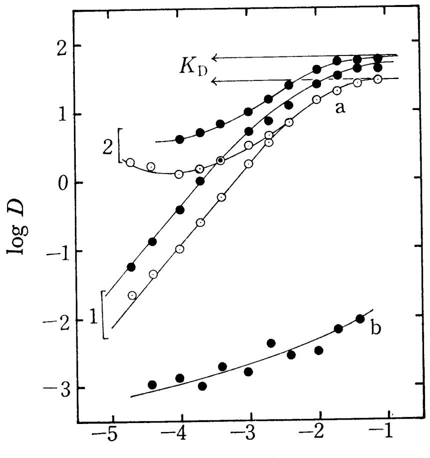

Fig. 15. The extraction of $NaB(C_6H_5)_4$ into chloroform (b) and into MIBK(a). (●) pH is adjusted about 6 by adding $NaHCO_3$, (○) pH is not adjusted. (1) in the absence of NaCl in the aqueous phase, (2) 2×10^{-3} M NaCl is added in the aqueous phase.

Table 3. Association constants of sodium tetraphenylborate at 25°

Solvent	ε	K(association)
H_2O	78.304	8.46
H_2O saturated with MIBK	76.922	10.92
MIBK	13.11	4.03×10^2 $(3.21\times10^2)^{a)}$
MIBK saturated with H_2O	14.65	2.55×10^2

a) The value calculated from the Fuoss equation, $K(\text{diss.})=(3000/4\pi a^3N)\exp(-e/a\varepsilon kT)$, $a=7.5$(Å).

It has been described how the distribution of sodium tetraphenylborate into the organic phase influences the extraction curve of Ru(II)(phen)$_3$. However, as far as the abnormal phenomenon is concerned, it can not be explained by this correction. Accordingly, in order to elucidate this phenomenon, the following three possibilities were examined; (1) an anion such as Cl^- or OH^- might be involved in the associated species; this seems probable judging from the fact that the associated ion-pair has a low solubility in the organic phase in spite of its hydrophobicity; (2) this phenomenon might be explained by selecting appropriate values of the constants, k_1, k_2, K_1, and K_2, or (3) the distribution constant of the associated ion-pair might decrease greatly as a result of the change in the bulk properties of both the phases in the high $[B(C_6H_5)_4^-]_i$ region, or as a result of the increased solubility of molecules due to solubilization in a surfactant solution.

The first possibility was examined by the extraction study of $^{36}Cl^-$, which was added in an equivalent amount to Ru(II)(phen)$_3$ in the presence of various concentrations of sodium tetraphenylborate. As a result, no uptake of chloride into the organic phase was observed at all. In addition, the extraction behavior of Ru(II)(phen)$_3$ in the presence of sodium fluoride or sodium sulfate exhibits a pattern similar to that in the presence of sodium chloride in spite of the fact that the hydration energies of the fluoride ion and the sulfate ion are much larger than that of the chloride ion.

Therefore, it is not feasible to consider that the associated ion-pair contains an anion other than the tetraphenylborate ion.

Next, if k_1 and k_2 are very large and if K_1 is much larger than K_2, then the extraction curve will exhibit the pattern shown in Figs. 13 and 14, according to Eq. (9). Although those theoretical conditions could be fulfilled provided the theory of Diamond[14] is applied, $\log K_D$ in this system would then have to become a negative value. This is very improbable, because the $Ru(phen)_3(B(C_6H_5)_4)_2$ has a very hydrophobic property and the K_D values in the systems of the other anions have large positive values.

The last possibility was examined as follows: the solubilities of $Ru(phen)_3(B(C_6H_5)_4)_2$ were measured in two systems; in one system the precipitates of $Ru(phen)_3(B(C_6H_5)_4)_2$ were added to an aqueous sodium tetraphenylborate solution (1% sodium bicarbonate has been added), while in the other system an aqueous sodium tetraphenylborate solution (1% sodium bicarbonate has been added) was added to a $\sim 10^{-6}$ M $Ru(phen)_3Cl_2$ solution. This means that both the crystallization and dissolution processes were cross-checked. As a result, it was found that the presence of sodium chloride (0.01—0.1 M) accelerates the rate of attaining the equilibrium between the precipitate and the solution; therefore, the solubilities have been measured both in the presence and in the absence of sodium chloride. The absorbance or the radioactivity was measured after equilibriating for 2 days' shaking in a thermostat at 25°; sodium tetraphenylborate decomposes after longer standing. The results obtained with the two systems are in good agreement with each other except when sodium chloride was not added; in the absence of sodium chloride, in the latter system equilibrium was not attained completely.

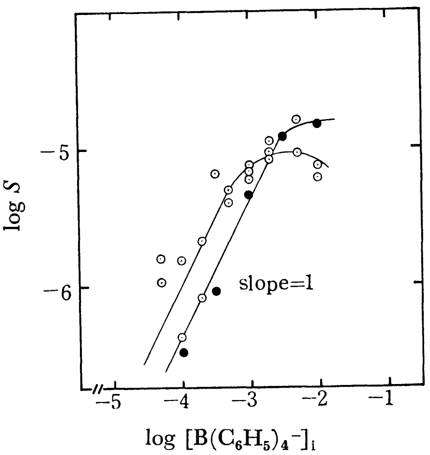

Fig. 16. The solubility of $Ru(phen)_3(B(C_6H_5)_4)_2$ in the sodium tetraphenylborate solution at 25 °C. (○) in the absence of NaCl, (●) 0.1 M NaCl is added.

In Fig. 16, $\log S$ is plotted against $\log [B(C_6H_5)_4^-]_i$. The solubility of $Ru(phen)_3(B(C_6H_5)_4)_2$ increases remarkably with the increase in the concentration of sodium tetraphenylborate, and the slope of the plot of $\log S$ *vs.* $\log [B(C_6H_5)_4^-]_i$ becomes about 1. This phenomenon can be explained on the assumption that the increase in the solubility is due to the formation of a large anion, $[Ru(phen)_3(B(C_6H_5)_4)_3]^-$, which is produced as a result of the addition of one more $B(C_6H_5)_4^-$ to the neutral ion-pair. This assumption seems probable if the concept of water structure-enforced ion-pairing can be extended to this system. $Ru(phen)_3(B(C_6H_5)_4)_2$ and $B(C_6H_5)_4^-$ are alike with respect to their hydrophobic and poorly hydrated character. Therefore, it is much more probable for $Ru(phen)_3(B(C_6H_5)_4)_2$ and $B(C_6H_5)_4^-$ to form one large anion, which causes only one disturbance of the water structure, instead of surviving as two species which produce two disturbances.

Another possible assumption is that the increase in the solubility is to be explained not by the formation of a rigid anion such as $[Ru(phen)_3(B(C_6H_5)_4)_3]^-$, but by a solubilization similar to that with surfactant solutions. However, the micelle formation can not be considered, because the tetraphenylborate ion has no long alkyl chain in its structure and is a spherical ion. Therefore, this solubilization must be a kind of hydrotropism, an idea which was advanced by Neuberg[6] in 1916. Hydrotropism[16] is the general term for the phenomenon in which many nonelectrolytes, mostly polar but including nonpolar ones, are salted in by salts with large ions, such as tetraalkylammonium chloride and sodium *p*-toluenesulfonate.

In order to examine which assumption is more suitable to explain the present system, two additional investigations were performed—paper-electrophoresis and dialysis. The electrophoresis on paper strips (17—46 V/cm, 1—5 hr, 5 mA) revealed that $Ru(II)(phen)_3$ did not migrate at all in the 10^{-2}—10^{-1} M sodium tetraphenylborate solution. The dialysis was carried out by using a cellulose tube which had holes of 15—20(Å) and which was permeable for molecules with molecular weights below 10000—20000. $Ru(II)(phen)_3$ was dialyzed for two days against a 1×10^{-2} M sodium tetraphenylborate solution or against a 1×10^{-2} M sodium chloride solution. However, no $Ru(II)(phen)_3$ was dialyzed into the sodium tetraphenylborate solution, although the dialysis equilibrium was achieved within several hours in the sodium chloride solution.

In addition to the results presented above, the solubilized $Ru(phen)_3(B(C_6H_5)_4)_2$ solution often became colloidal. The addition of excess salts to this solution induced a salting-out effect. Therefore, the latter assumption seems to explain more satisfactorily the phenomenon of the present system, and we believe that $Ru(phen)_3(B(C_6H_5)_4)_2$ is solubilized by forming such an anionic colloid as $[Ru(phen)_3(B(C_6H_5)_4)_2]_n$-$[B(C_6H_5)_4^-]_m$. The actual structure is assumed to be that of aggregated molecules, *i.e.*, $[Ru(phen)_3(B(C_6H_5)_4)_2]_n$ surrounded with $B(C_6H_5)_4^-$. The aggregation numbers, *n* and *m*, are expected to be almost equal, because, as is shown in Fig. 16, the slope of the plot of $\log S$ *vs.* $\log [B(C_6H_5)_4^-]_i$ is almost 1.

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