The Extraction of the Cesium Ion with Some Nitrophenols into Nitrobenzene. I. Distribution Studies

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The liquid-liquid extraction of alkali-metal nitrophenolates was studied by using nitrobenzene as the extracting solvent. Nitrophenol derivatives such as *o*-, *m*-, *p*-nitrophenols, α-dinitrophenol, and picric acid were chosen here in order to examine the effect of their steric characters and p*K* values on the distribution equilibrid. It was concluded that: 1) all the cesium nitrophenolates extracted into nitrobenzene were mainly in the dissociated form; 2) the extraction of *m*- and *p*-nitrophenolates proceeds by the stepwise adduct formation with free phenols, whereas little tendency of adduct formation was observed with the picrate system; 3) α-dinitrophenolate has a character between the other two; 4) the distribution of *o*-nitrophenolate is negligible. A detailed discussion is given of the phenomena in terms of ionic equilibria in both the aqueous and organic phases.

The liquid-liquid extraction of alkali metal ions has received attention not only from the viewpoint of practical analysis, but also from that of a theoretical interest in solute-solvent interaction.

In a previous paper, the present authors reported on the extraction of cesium into nitrobenzene with chromium complexes.[1] Similar extractions have been investigated by many authors using various reagents, such as tetraphenylborate,[2,3] dipicrylamine[4,5] and polyiodide.[6] In all these cases, the subject species are dissociated completely into ions in both the organic and aqueous phases.

On the other hand, Horner *et al.*[7] have shown the possibility of extracting cesium with various phenols as the reagents. Later, many alkyl derivatives of phenol were examined by Konecný and Sistková[8] and the extraction equilibria were discussed by Zingaro *et al.*[9] In the extraction of alkali phenolate, the extracted species are tightly-bounded ion pairs sometimes adducted with reagent acids.

Although the extraction mechanisms and the equilibria are pretty well understood in the case of chelate-extraction systems, the interpretation of the ion-pair extraction has not been completed. The distribution coefficient in the ion-pair system depends not only upon the bulk character of the solvents, such as dielectric constants and/or the solubility parameters, but also upon the particular interactions between solute and solvent, or sometimes between solutes.

The present series of studies were undertaken in order to investigate the influence of the characteristics of reagent anions on the extraction of alkali-metal ions and to estimate the relative degree of solute-solvent interactions.

In these studies, nitrobenzene was chosen as the organic solvent and cesium ions were distributed into both phases, using nitrophenol derivatives as the reagents. The nitrophenol derivatives examined were *ortho*-, *meta*-, *para*-nitrophenol (*o*-NP, *m*-NP, *p*-NP), 2,4-dinitrophenol (α-DNP), and 2,4,6-trinitrophenol (picric acid, PA); they were chosen because they have different acid dissociation constants in water and different steric effects, and are expected to have characters intermediate between those of alkyl phenols and dipicrylamine, tetraphenylborate, and others. In nitrobenzene, which is a strongly ionizing solvent, only dissociated forms are expected, and a difference in anion solvations (homoconjugation) can be observed for each nitrophenol.

The present paper is confined to a study of the ionic equilibria in the extraction processes. In the next paper,[10] the role of anions and the solute-solvent interaction will be discussed with the results obtained through the distribution and conductivity studies.

Experimental

Reagents. All the reagents used were of a reagent-grade purity. The nitrobenzene was vacuum-distilled before use. Carrier-free ^{137}Cs was supplied by the Oak Ridge National Laboratory.

Apparatus. The γ-ray measurements were performed with a single-channel pulse-height analyser (Osaka Denpa-Model LA-3T) equipped with a 1.5″ x 1.5″ NaI(Tl) well-type crystal. The absorbance measurements were carried out with an automatic recording spectrophotometer (Shimadzu-Model SV-5 A) by the use of quartz cells with a 1-cm light path. A pH meter (Horiba Model P) was used for all the pH measurements.

Procedure. In the distribution studies of nitrophenols, the pH of the aqueous phase was controlled by the addition of either a hydrochloric acid or a sodium hydroxide solution. Each nitrophenol solution of a 0.1 M concentration was prepared by dissolving the phenol in nitrobenzene. Four milliliters of the aqueous solution and the same volume of

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[2] T. Sekine and D. Dyrssen, *inid.*, **45**, 433 (1969).

[3] J. Krtil, M. Fojtik, and M. Kyrš, *Collection Czechoslov. Chem. Commun.*, **27**, 2069 (1962).

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[5] S. Motomizu, K. Tôei, and T. Iwachido, This Bulletin, **42**, 1006 (1969).

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[10] T. Fujinaga, M. Koyama, and O. Tochiyama, This Bulletin, to be published.

the nitrobenzene solution were brought into contact and shaken in a glass tube for 30—60 min. at 20±1°C. The distribution ratios of nitrophenols were obtained by measuring their concentrations in the aqueous phase according to the following procedure. An appropriate aliquot of the aqueous phase was taken in a volumetric flask and diluted with a 0.1 M sodium hydroxide solution. The absorbance (*p*-NP; 402 nm, *m*-NP; 392 nm, *o*-NP; 420 nm, α-DNP; 362 nm and PA; 358 nm) was measured in order to determine the concentration of the nitrophenols. The pH of the aqueous phase after the equilibration was also measured and used for the calculation of the distribution ratios. The glass electrode pH meter was found to show pH 0.00, 1.00, 2.00, and 3.00 within an error of ±0.1 in solutions of perchloric acid of 1.0, 0.10, 1.0×10^{-2}, and 1.0×10^{-3} M respectively.

Similar procedures were employed for the distribution studies of the cesium ion. The pH of the aqueous phase, however, was adjusted with lithium hydroxide or sodium hydroxide, and the ionic strength was controlled with lithium chloride or sodium chloride.

A cesium chloride solution of an adequate concentration was added to the aqueous phase, and the distribution ratio of the cesium ion was obtained by measuring the γ-ray activities of ^{137}Cs in both the aqueous and organic phases.

Theoretical

(1) Distribution of Nitrophenols. In the extraction of nitrophenol ROH, the following equilibria can be considered in both phases:

$$(\mathrm{RO^-})_a + (\mathrm{H^+})_a \rightleftharpoons (\mathrm{ROH})_a \tag{1}$$

$$(\mathrm{ROH})_a \rightleftharpoons (\mathrm{ROH})_o \tag{2}$$

$$(\mathrm{RO^-})_o + (\mathrm{H^+})_o \rightleftharpoons (\mathrm{ROH})_o \tag{3}$$

where the a and o subscripts refer to the aqueous and organic phases respectively. The concentration constants are expressed by the following equations:

$$K_{a,\mathrm{ROH}} = [\mathrm{RO^-}]_a[\mathrm{H^+}]_a/[\mathrm{ROH}]_a \tag{4}$$

$$K_{D,\mathrm{ROH}} = [\mathrm{ROH}]_o/[\mathrm{ROH}]_a \tag{5}$$

$$K_{0,\mathrm{ROH}} = [\mathrm{RO^-}]_o[\mathrm{H^+}]_o/[\mathrm{ROH}]_o \tag{6}$$

$K_{a,\mathrm{ROH}}$ and $K_{0,\mathrm{ROH}}$ are the dissociation constants of ROH in the aqueous and nitrobenzene phases respectively, and $K_{D,\mathrm{ROH}}$, the distribution coefficient of the neutral ROH.

At the distribution equilibrium between the two phases, the distribution ratio of ROH, D_{ROH}, is written as:

$$D_{\mathrm{ROH}} = \frac{[\mathrm{ROH}]_o+[\mathrm{RO^-}]_o}{[\mathrm{ROH}]_a+[\mathrm{RO^-}]_a} \tag{7}$$

Among these chemical species, $[\mathrm{RO^-}]_0$ can be neglected, because the dissociation of ROH in nitrobenzene is very small. Therefore,

$$D_{\mathrm{ROH}} = \frac{[\mathrm{ROH}]_o}{[\mathrm{ROH}]_a+[\mathrm{RO^-}]_a} \tag{7'}$$

By combining Eqs. (2), (4), (5), and (7′), D_{ROH} is expressed as Eq. (7″):

$$D_{\mathrm{ROH}} = \frac{K_{D,\mathrm{ROH}}}{1+K_{a,\mathrm{ROH}}/[\mathrm{H^+}]_a} \tag{7''}$$

In this equation, D_{ROH} is a function of pH, that is (i) in the lower pH region:

$$D_{\mathrm{ROH}} = K_{D,\mathrm{ROH}} \tag{7''-i}$$

and (ii) in the higher pH region:

$$D_{\mathrm{ROH}} = K_{D,\mathrm{ROH}}[\mathrm{H^+}]_a/K_{a,\mathrm{ROH}} \tag{7''-ii}$$

If the curve of log D_{ROH} *vs.* pH consists of two parts which are represented by Eqs. (7″-i) and (7″-ii), $K_{D,\mathrm{ROH}}$ and $K_{a,\mathrm{ROH}}$ can be calculated from these equations.

The following relationship is obtained between the total concentration of nitrophenol and the concentration of undissociated nitrophenol in nitrobenzene:

$$[\mathrm{ROH}]_{\mathrm{total}} = [\mathrm{ROH}]_o + [\mathrm{ROH}]_a + [\mathrm{RO^-}]_a$$

$$b = [\mathrm{ROH}]_o\left(1+\frac{1}{K_{D,\mathrm{ROH}}}+\frac{K_{a,\mathrm{ROH}}}{K_{D,\mathrm{ROH}}[\mathrm{H^+}]_a}\right) \tag{8}$$

(2) Distribution of the Cesium Ion. In the experiments on the distribution of the cesium ion, the following equilibria must be considered in both the aqueous and organic phases:

$$(\mathrm{Cs^+})_a + (\mathrm{OR^-})_a \rightleftharpoons (\mathrm{CsOR})_a \tag{9}$$

$$(\mathrm{CsOR})_a \rightleftharpoons (\mathrm{CsOR})_o \tag{10}$$

$$(\mathrm{Cs^+})_o + (\mathrm{OR^-})_o \rightleftharpoons (\mathrm{CsOR})_o \tag{11}$$

$$(\mathrm{OR^-})_o + \mathrm{n(ROH)} \rightleftharpoons (\mathrm{OR{\cdot}nROH^-})_o \tag{12}$$

$$K_{a,\mathrm{CsOR}} = [\mathrm{Cs^+}]_a[\mathrm{OR^-}]_a/[\mathrm{CsOR}]_a \tag{13}$$

$$K_{D,\mathrm{CsOR}} = [\mathrm{CsOR}]_o/[\mathrm{CsOR}]_a \tag{14}$$

$$K_{0,\mathrm{CsOR}} = [\mathrm{Cs^+}]_o[\mathrm{OR^-}]_o/[\mathrm{CsOR}]_o \tag{15}$$

$$\begin{aligned} K_{\mathrm{Cs}}{}^* &= K_{0,\mathrm{CsOR}}K_{D,\mathrm{CsOR}}/K_{a,\mathrm{CsOR}} \\ &= [\mathrm{Cs^+}]_o[\mathrm{OR^-}]_o/[\mathrm{Cs^+}]_a[\mathrm{OR^-}]_a \end{aligned} \tag{16}$$

$$K_n{}^f = [\mathrm{OR{\cdot}nROH^-}]_o/[\mathrm{OR^-}]_o[\mathrm{ROH}]_o{}^n \tag{17}$$

Here, $K_{a,\mathrm{CsOR}}$ and $K_{0,\mathrm{CsOR}}$ represent the dissociation constants in each phase; $K_{D,\mathrm{CsOR}}$, the distribution coefficient of the neutral CsOR; $K_{\mathrm{Cs}}{}^*$, the distribution coefficient of fully-dissociated $\mathrm{Cs^+}$ and $\mathrm{OR^-}$, and $K_n{}^f$, the homoconjugation constant or the adduct formation constant in the organic phase.

When the concentration of cesium ions is sufficiently large as compared with those of other cations in the organic phase, the electrical neutrality in the phase can be written as:

$$\begin{aligned} [\mathrm{Cs^+}]_o &= [\mathrm{OR^-}]_o + [\mathrm{OR{\cdot}ROH^-}]_o \\ &\quad + [\mathrm{OR{\cdot}2ROH^-}]_o + \cdots \\ &= [\mathrm{OR^-}]_o(1+\sum_n K_n{}^f[\mathrm{ROH}]_o{}^n) \end{aligned} \tag{18}$$

On the other hand, the distribution ratio of the cesium ion is:

$$D_{\mathrm{Cs}} = \frac{[\mathrm{Cs^+}]_o+[\mathrm{CsOR}]_o}{[\mathrm{Cs^+}]_a+[\mathrm{CsOR}]_a} \tag{19}$$

When free cesium ions are considered to be the only chemical species of cesium in both the organic and aqueous phases, Eq. (19) can be written as:

$$D_{\mathrm{Cs}} = [\mathrm{Cs^+}]_o/[\mathrm{Cs^+}]_a \tag{19'}$$

By combining Eqs. (13)—(19′), D_{Cs} can be transformed into:

$$D_{Cs} = K_{Cs}^{*1/2}(1+\sum_n K_n^f[ROH]_o^n)^{1/2}\frac{[OR^-]_a^{1/2}}{[Cs^+]_a^{1/2}} \quad (20\text{-i})$$

$$= K_{Cs}^{*1/2}(1+\sum_n K_n^f[ROH]_o^n)^{1/2} \times \frac{K_{a,ROH}^{1/2}[ROH]_o^{1/2}}{K_{D,ROH}^{1/2}[Cs^+]_a^{1/2}[H^+]_a^{1/2}} \quad (20\text{-ii})$$

When most of the cesium ions are present in the form of ion pairs in both phases,

$$D_{Cs} = \frac{K_{D,CsOR}}{K_{a,CsOR}}[OR^-]_a \quad (21\text{-i})$$

$$= \frac{K_{D,CsOR}K_{a,ROH}[ROH]_o}{K_{a,CsOR}K_{D,ROH}[H^+]_a} \quad (21\text{-ii})$$

Eqs. (20) and (21) predict the difference in the dependence of D_{Cs} on $[H^+]_a$ and $[Cs^+]_a$.

Therefore, from the experimental data, whether the chemical form $(Cs^+)_o$ or $(CsOR)_o$ stands in the nitrobenzene phase can be confirmed.

When a considerable amount of NaOR or LiOR is extracted, the electrical neutrality expressed in Eq. (18) is no longer valid; the following relationship must be considered instead:

$$[M^+]_o = [OR^-]_o + [OR\cdot ROH^-]_o + [OR\cdot 2ROH^-]_o + \cdots \quad (18')$$

where M^+ denotes the competing cation, such as Li^+ or Na^+, and where

$$K_{a,MOR} = \frac{[M^+]_a[OR^-]_a}{[MOR]_a} \quad (22)$$

$$K_{D,MOR} = \frac{[MOR]_o}{[MOR]_a} \quad (23)$$

$$K_{o,MOR} = \frac{[M^+]_o[OR^-]_o}{[MOR]_o} \quad (24)$$

$$K_M^* = \frac{[M^+]_o[OR^-]_o}{[M^+]_a[OR^-]_a} \quad (25)$$

From these equations, we obtain:

$$D_{Cs} = [Cs^+]_o/[Cs^+]_a = K_{Cs}^{*1/2}\left(\frac{K_{Cs}^*}{K_M^*}\right)^{1/2}\frac{[OR^-]_a^{1/2}}{[M^+]_a^{1/2}} \times (1+\sum K_n^f[ROH]_o^n)^{1/2} \quad (26)$$

This equation shows that the D_{Cs} values are no longer the function of $[Cs^+]_a$, but the function of $[M^+]_a$, when $[Cs^+]_a \ll [M^+]_a$.

Results and Discussion

(1) Distribution of Nitrophenols. Figure 1 presents the relationship between the distribution ratios of each nitrophenol at the concentration of 0.1 M and the pH of the aqueous phase after the partition equilibrium has been attained. In these studies, the aqueous ionic strength was not fixed, because the ex-extraction of sodium nitrophenolates could be neglected.

In the figure, there are two parts, representing Eqs. (7″-i) and (7″-ii). From these curves, the $K_{a,ROH}$ and $K_{D,ROH}$ values can be obtained; these values are shown in Table 1. The $K_{a,ROH}$ values are in good agreement with those measured by other method.[11]

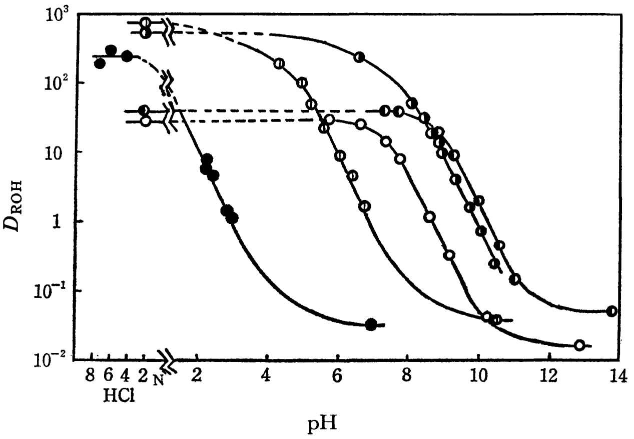

Fig. 1. Distribution of nitrophenols as the function of pH. $[ROH]_{total}=0.1$
○ *p*-NP ◐ *m*-NP ◑ *o*-NP ⦶ α-DNP ● PA

Table 1. Distribution coefficients and dissociation constants obtained by the extraction method

	$K_{D,ROH}$	$K_{a,ROH}$	$K_{a,ROH}$ other methods[11]
p-NP	28.4	6.1×10^{-8}	6.5×10^{-8}
m-NP	40.2	2.2×10^{-9}	5.2×10^{-9}
o-NP	599	1.1×10^{-7}	0.75×10^{-7}
α-DNP	746	0.89×10^{-4}	1.0×10^{-4}
PA	256	2.6×10^{-1}	3.8×10^{-1}

In the higher pH regions, the curves are not as linear as was expected from Eq. (7″-ii), because the extraction of NaOR can not be neglected in these regions.

From the experiment, the relationships between pH and $[ROH]_o$, which are represented by Eq. (8), were obtained and used in the calculation of the distribution of the cesium ion.

(2) Distribution of the Cesium Ion. (2-1) The Relationship between D_{Cs} and pH: In Fig. 2, the dependence of the distribution ratios of the cesium ion on the pH of the aqueous solution is presented. In this study, the total concentration of nitrophenol and the total concentration of the lithium ion were maintained at 0.4 M. However, the distribution of lithium ions in the organic phase was practically

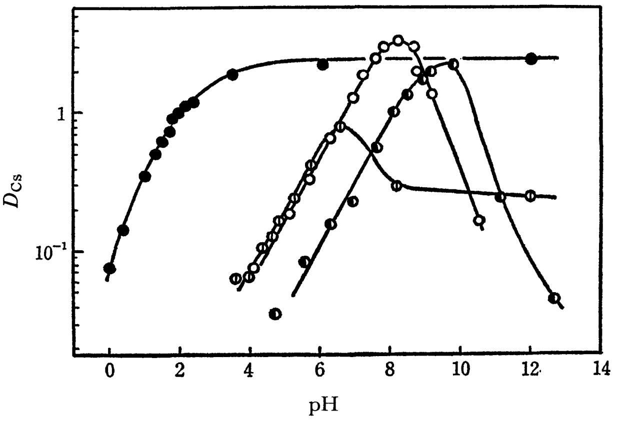

Fig. 2. Distribution of cesium ion as the function of pH. $[ROH]_{total}=0.4$, $[Li^+]_a=0.4$, $[Cs^+]_a=10^{-3}$.
○ *p*-NP ◐ *m*-NP ⦶ α-DNP ● PA

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[11] C. D. Hodgeman, "Handbook of Chemistry and Physics," 42nd Ed., Published by The Chemical Rubber Publishing Co, Cleveland, Ohio (1960).

negligible, and the concentration of lithium ions in the aqueous phase was practically 0.4 M. The distribution ratios have been corrected for the constant aqueous cesium ion concentration (10^{-3} M) according to Eq. (27). This correction is based on Eq. (20), which is derived from the assumption that the chemical species in both organic and aqueous phases are fully dissociated:

$$D_{\mathrm{Cs}}(\text{corrected}) = D_{\mathrm{Cs}}(\text{raw})\left(\frac{10^{-3}}{[\mathrm{Cs}^+]_\mathrm{a}(\text{experimental})}\right)^{1/2} \tag{27}$$

Since, in the case of *o*-nitrophenol, the distribution ratios were found to be below 10^{-3} at all the pH values, no relationship is presented in the figures.

In Fig. 2, the slope of the ascending part of the curve is 1/2 in every case, and Eq. (20) applies well. In these parts, $[\mathrm{ROH}]_\mathrm{o}$ can be considered constant in Eq. (20-ii), because the third term in Eq. (8) can be neglected in the low pH regions, as is demonstrated in Fig. 1. In the case of picric acid, the slope deviates from 1/2 and approaches to 1 in the lower pH region. This deviation can be attributed to the increase of $[\mathrm{H}^+]_\mathrm{o}$ caused by the extraction of picric acid and/or of hydrochloric acid. If the hydrochloric acid is extracted and the electrical neutrality is expressed as $[\mathrm{H}^+]_\mathrm{o}=[\mathrm{Cl}^-]_\mathrm{o}$, the relation between D_{Cs} and $[\mathrm{H}^+]_\mathrm{a}$ can be represented by Eq. (27):

$$D_{\mathrm{Cs}} = \frac{K_{\mathrm{Cs}}^*}{K_\mathrm{H}^*}K_{\mathrm{HCl}}^{*1/2}\frac{[\mathrm{Cl}^-]_\mathrm{a}^{1/2}}{[\mathrm{H}^+]_\mathrm{a}^{1/2}} \tag{27}$$

where:

$$K_\mathrm{H}^* = \frac{[\mathrm{H}^+]_\mathrm{o}[\mathrm{OR}^-]_\mathrm{o}}{[\mathrm{H}^+]_\mathrm{a}[\mathrm{OR}^-]_\mathrm{a}} \tag{25'}$$

$$K_{\mathrm{HCl}}^* = \frac{[\mathrm{H}^+]_\mathrm{o}[\mathrm{Cl}^-]_\mathrm{o}}{[\mathrm{H}^+]_\mathrm{a}[\mathrm{Cl}^-]_\mathrm{a}} \tag{28}$$

According to Eq. (27), the slope of the plot of log D_{Cs} *vs.* pH must remain 1/2, even in the lower pH region. If $[\mathrm{H}^+]_\mathrm{o}$ is mainly created by the dissociation of the picric acid extracted and if, therefore, the electrical neutrality is expressed as $[\mathrm{H}^+]_\mathrm{o}=[\mathrm{OR}^-]_\mathrm{o}$, Eq. (26′), which is derived from Eq. (26) by replacing $[\mathrm{M}^+]$ by $[\mathrm{H}^+]$, applies to the relation between D_{Cs} and $[\mathrm{H}^+]_\mathrm{a}$. This equation shows that the slope must be 1 in the lower pH region:

$$D_{\mathrm{Cs}} = K_{\mathrm{Cs}}^{*1/2}\left(\frac{K_{\mathrm{Cs}}^*}{K_\mathrm{H}^*}\right)^{1/2}(1+\sum_n K_n{}^f[\mathrm{ROH}]_\mathrm{o}{}^n)^{1/2} \times \frac{K_{\mathrm{a,ROH}}^{1/2}[\mathrm{ROH}]_\mathrm{o}^{1/2}}{K_{\mathrm{D,ROH}}^{1/2}[\mathrm{H}^+]_\mathrm{a}} \tag{26'}$$

Therefore, the increase of the slope which is observed in the lower pH region can be attributed to the extraction and dissociation of picric acid, and not to the extraction of hydrochloric acid.

The increase in pH also causes a loss of $[\mathrm{ROH}]_\mathrm{o}$ according to Eq. (8). In the high pH regions, the concentration of nitrophenol in nitrobenzene can be presented as:

$$[\mathrm{ROH}]_\mathrm{o} = [\mathrm{ROH}]_{\mathrm{total}}\left(1+\frac{1}{K_{\mathrm{D,ROH}}}+\frac{K_{\mathrm{a,ROH}}}{K_{\mathrm{D,ROH}}[\mathrm{H}^+]_\mathrm{a}}\right)^{-1} = \frac{K_{\mathrm{D,ROH}}}{K_{\mathrm{a,ROH}}}[\mathrm{H}^+]_\mathrm{a}[\mathrm{ROH}]_{\mathrm{total}} \tag{8'}$$

Therefore, Eq. (20) comes to Eq. (20′):

$$D_{\mathrm{Cs}} = K_{\mathrm{Cs}}^{*1/2}\frac{[\mathrm{ROH}]_{\mathrm{total}}^{1/2}}{[\mathrm{Cs}^+]_\mathrm{a}^{1/2}} \times \left\{1+\sum_n K_n{}^f\left(\frac{K_{\mathrm{D,ROH}}}{K_{\mathrm{a,ROH}}}[\mathrm{H}^+]_\mathrm{a}[\mathrm{ROH}]_{\mathrm{total}}\right)^n\right\}^{1/2}$$

where $[\mathrm{ROH}]_{\mathrm{total}}$ and $[\mathrm{Cs}^+]_\mathrm{a}$ are constant. This equation shows that the slopes of log D_{Cs} *vs.* pH approach $-n/2$ in the high pH regions. Although few data are available for the high pH regions because the solution is not well-buffered in those regions, *p*- and *m*-nitrophenols show a decrease in D_{Cs} with an increase in the pH. In contrast, the system with picric acid shows no decrease in D_{Cs} with an increase in the pH. This means that the $K_n{}^f$ value is negligibly small and that simple ion pairs are the predominant species in the extract. In the case of α-dinitrophenol, the slope of the descending part reaches zero as the pH increases. This can be explained by using Eq. (20′). In the region where D_{Cs} decreases as the pH increases, the second term:

$$\left(K_1{}^f\frac{K_{\mathrm{D,ROH}}}{K_{\mathrm{a,ROH}}}[\mathrm{H}^+]_\mathrm{a}[\mathrm{ROH}]_{\mathrm{total}}\right)$$

plays a more important role than the first term, 1. On the other hand, in the region where the slope reaches zero, the second term becomes less important. Thus with the system of α-dinitrophenol, non-conjugated ions are extracted in the higher pH region, and both conjugated and non-conjugated ions are extracted in the lower pH region.

(2-2) The Relationship between D_{Cs} and $[Cs^+]_a$: The relationship between the distribution ratios of cesium ions and the cesium-ion concentration in equilibrium is shown in Figs. 3—6. The aqueous ionic strength, which was adjusted with sodium or lithium chloride (before the equilibration), was considered to be unchanged during the extraction process. The pH of the aqueous phase was adjusted so as to be constant in each experiment.

The slope of log D_{Cs} *vs.* log $[\mathrm{Cs}^+]_\mathrm{a}$ is $-1/2$ unless the concentration of cesium ions is relatively small. This value shows that the cesium ion in the nitrobenzene phase is a free ion and that Eq. (20) holds quite well.

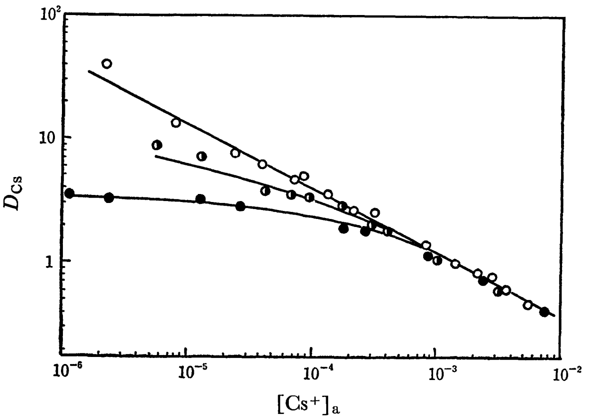

Fig. 3. Distribution of cesium ion as the function of cesium concentration (*p*-NP).
$[\mathrm{ROH}]_{\mathrm{total}}=0.4$, pH 7.0
○ $[\mathrm{Li}^+]_\mathrm{a}=0.008$, ◑ $[\mathrm{Li}^+]_\mathrm{a}=0.2$, ● $[\mathrm{Na}^+]_\mathrm{a}=0.32$

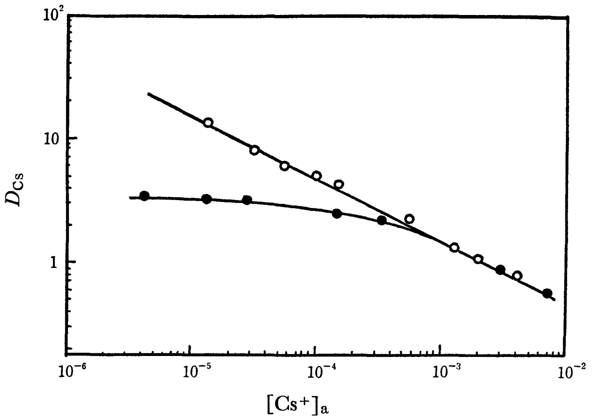

Fig. 4. Distribution of cesium ion as the function of cesium ion concentration (*m*-NP).
$[ROH]_{total}=0.4$, pH 8.7
○ $[Li^+]_a=0.02$, ● $[Na^+]_a=0.27$

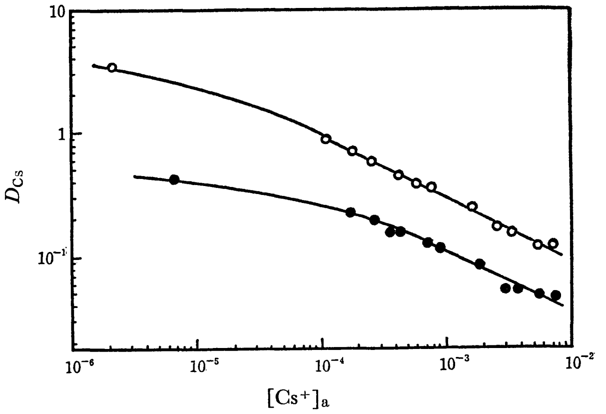

Fig. 5. Distribution of cesium ion as the function of cesium ion concentration (α-DNP).
○ $[ROH]_{total}=0.4$, pH 5.3, $[Li^+]_a=0.02$
● $[ROH]_{total}=0.2$, pH 12.5 $[Li^+]_a=0.25$

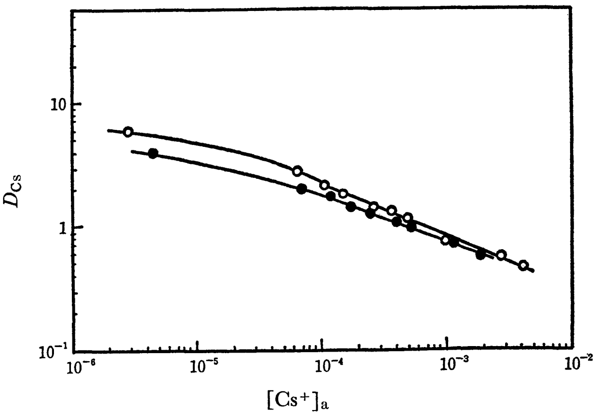

Fig. 6. Distribution of cesium ion as the function of cesium ion concentration (PA).
○ $[ROH]_{total}=0.4$, pH 1.6
● $[ROH]_{total}=0.2$, pH 12.3 $[Li^+]_a=0.25$

In Figs. 3—6, the effect of the aqueous ionic strength can be seen when the concentration of lithium or sodium ions is quite large. When the concentration of cesium ions is quite small, Eq. (26) shows the relationship between D_{Cs} and $[Cs^+]_a$. The equation indicates that D_{Cs} is no longer the function of $[Cs^+]_a$ but the function of $[M^+]_a$. The relationship between D_{Cs} and $[M^+]_a$ when the cesium-ion concentration is quite small is shown in Fig. 7. The slope of $\log D_{Cs}$ *vs.* $\log [M^+]_a$ is $-1/2$. This shows that Eqs. (18′) and (26) are valid in this case.

The extraction behavior with picric acid is shown in Fig. 6. The slope of $\log D_{Cs}$ *vs.* $\log [Cs^+]_a$ deviates a little from the slope of $-1/2$, although no metal ions are present except cesium ions. In this case, the cation competing against the cesium ion in the organic phase is a proton which is derived from the dissociation of picric acid in the organic phase (the dissociation constant, pK_o, of picric acid in nitrobenzene is 7.5[12]). From the assumption that $[H^+]_o=[OR^-]_o$ is valid, the concentration of protons in the organic phase can be calculated as *ca.* 10^{-4} M by using Eq. (6). Accordingly, in the region where the concentration of cesium ions in the organic phase is lower than 10^{-4} M, D_{Cs} is no longer dependent on $[Cs^+]_a$, but on $[H^+]_o$. With an increase in the concentration of cesium ions beyond 10^{-4} M, D_{Cs} becomes more dependent on the concentration of cesium ions.

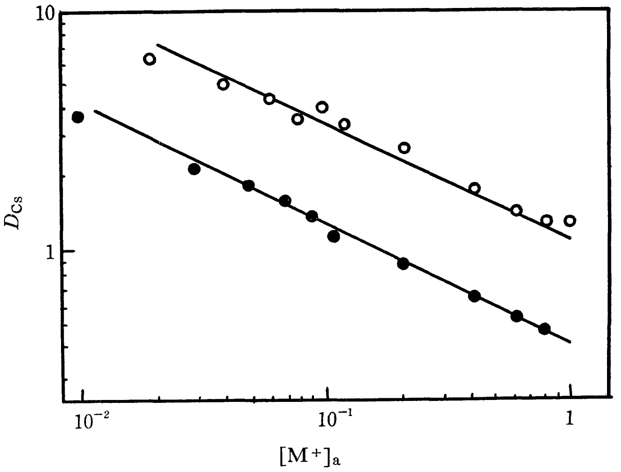

Fig. 7. Distribution of cesium ion as the function of sodium ion concentration or lithium ion concentration (*p*-NP).
$[ROH]_{total}=0.1$, $[Cs^+]_a=10^{-5}$
○ M=Li, pH 8.2, ● M=Na, pH 7.6

(2-3) The Relationship between D_{Cs} *and* $[ROH]_{total}$: Figure 8 shows the dependence of the distribution ratios of the cesium ion on the total concentration of nitrophenol. In this study, the experimental values have been corrected to the value at the constant pH and at the constant aqueous cesium-ion concentration. The correction has been made according to the following equation:

$$D_{Cs}(\text{corrected}) = D_{Cs}(\text{raw}) \times \left\{\frac{[Cs^+]_a(\text{corrected})[H^+]_a(\text{corrected})}{[Cs^+]_a(\text{raw})[H^+]_a(\text{raw})}\right\}^{1/2}$$

In this experiment, no cations were present in either the organic or aqueous phase except proton and cesium ions.

At a constant pH, the term

$$(1 + 1/K_{D,ROH} + K_{a,ROH}/K_{D,ROH}[H^+]_a)$$

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[12] I. M. Kolthoff, D. Stcoesoća, and T. S. Lee, *J. Amer. Chem. Soc.*, **75**, 1834 (1953).

TABLE 2. EXTRACTION OF CESIUM ION WITH SOME NITROPHENOLS

Reagent	Slope of log D_{Cs} plot			Principal species in org. phase	K_{Cs}* or K_{Cs}*$K_n{}^f$	K_{Cs}*/K_{Na}*
	pH	log $[Cs^+]_a$	log $[ROH]_t$			
p-NP	1/2	−1/2	3.3/2	Cs^+ $OR\cdot 2ROH^-$	$K_{Cs}*K_2{}^f=1.2$	2.3×10^3
m-NP	1/2	−1/2	3/2	Cs^+ $OR\cdot 2ROH^-$	$K_{Cs}*K_2{}^f=1.1$	1.3×10^3
o-NP	—	—	—	—	—	—
α-DNP	1/2	−1/2	2/2	Cs^+ $OR\cdot ROH^-$ Cs^+ OR^- (alkaline)	$K_{Cs}*K_1{}^f=2.1\times10^{-2}$ $K_{Cs}*=7.4\times10^{-5}$	1.3×10^3
PA	1/2	−1/2.4	1.3/2	Cs^+ OR^-	$K_{Cs}*=2.4\times10^{-3}$ $K_{Cs}*K_1{}^f=3.6\times10^{-2}$	5.0×10^3

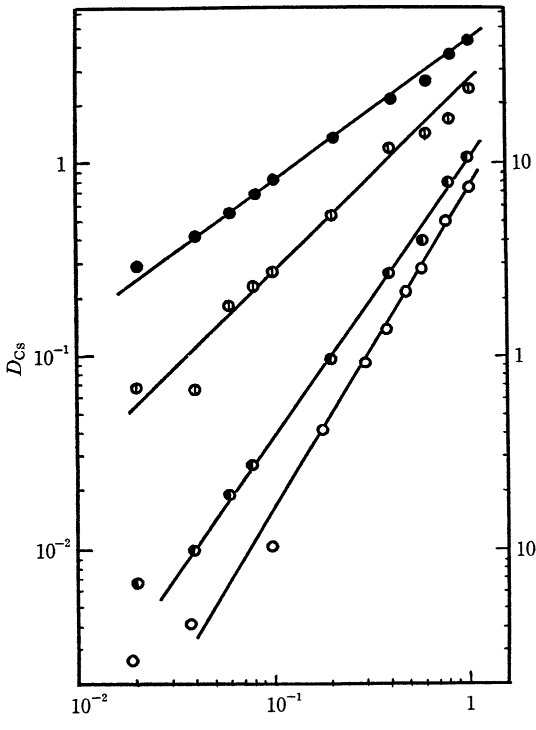

Fig. 8. Distribution of cesium ion as the function of nitrophenol concentrations.
○ *p*-NP, pH 7, $[Cs^+]_a=10^{-3}$ (right-hand scale)
◐ *m*-NP, pH 6, $[Cs^+]_a=10^{-5}$ (right-hand scale)
⦶ α-DNP, pH 5, $[Cs^+]_a=10^{-5}$ (left-hand scale)
● PA, pH 2, $[Cs^+]_a=2\times10^{-4}$ (left-hand scale)

is constant in Eq. (8). Therefore, the slope of log D_{Cs} *vs.* log $[ROH]_{total}$ is the same as that of log D_{Cs} *vs.* log $[ROH]_o$. The slopes correspond to $(n+1)/2$ in Eq. (20-ii). From the experiment shown in Fig. 8, the n values obtained were 0.3 with picric acid, 1 with α-dinitrophenol, 2 with *m*-nitrophenol, and 2.3 with *p*-nitrophenol. The number, n, of the adduct molecules increases as the number of substituted nitrogroups decreases. This observation is also supported by the results shown in the experiments on the relationship between D_{Cs} and pH.

(2-4) Conclusions: The results of the above experiments are summarized in Table 2. In this table, no clear relations can be found in the case of *o*-nitrophenol, because the distribution ratios were below 10^{-3} in every experiment. The reason for this difference from the cases of *p*- and *m*-nitrophenols can not be explained by these experiments alone, though the obstruction of the formation of the CsOR ion-pair, the difficully of the formation of the conjugated ion $(OR\cdot nROH^-)_o$, and some other causes can be considered.

In all cases, the chemical form of cesium ions is concluded to be dissociated ions. The participation of free nitrophenols was observed in the distribution of cesium ions. Through distribution studies, however, no information can be obtained on whether free nitrophenols interact with anions or with cations. Nevertheless, in the present study, we assumed that free nitrophenols interact only with anions. The reason for this assumption will be discussed in the next paper,[10] which will deal with the results of the conductivity measurements. The adduct formation (homoconjugation) of free nitrophenols with anions is seen in the cases of mono- and di-substituted nitrophenols. These cases correspond with the cases of other alkyl-substituted phenols. The extraction of picrate resembles those of dipicrylaminate, tetraphenylborate, reineckate, and other ion-pairs.

The extraction constants were calculated from the data; the values were obtained; as K_{Cs}* or K_{Cs}*$K_n{}^f$. In the cases of picric acid and α-dinitrophenol, both K_{Cs}* and $K_{Cs}K_1{}^f$ were obtained, K_{Cs}*, from the data when pH is very high, and K_{Cs}*$K_1{}^f$, from the data when pH is low. As can be seen from the slopes of the curves of log D_{Cs} *vs.* log $[ROH]_{total}$ in Table 2, the n values can not be determined exactly. Therefore, the extraction constants obtained in this experiment include some uncertainty.

The exchange constants, K_{Cs}*/K_M*, are also shown in Table 2. The values were obtained from the data when $[M^+]_a \gg [Cs^+]_a$ or from the log D_{Cs} *vs.* log$[Cs^+]_a$ curves, which are shown in Figs. 3—6.

In this paper, all the experimental data are plotted as a function of the concentration, and all the constants are calculated by using the concentration, no special attention being paid to the activity coefficients in the two phases. However, the ionic strength in the aqueous phase was maintained constant in most of the experiments. No meaningful deviation is noticeable in the explanation of the experimental results.

The relationship between these extraction constants and solubilities will be discussed in the next paper.[10]