The Extraction of the Cesium Ion with Some Nitrophenols into Nitrobenzene. II. Homoconjugation Studies by Means of Conductivity Measurements

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In connection with the liquid-liquid extraction study of alkali metal nitrophenolates, ionic equilibria taking place in the systems were studied by means of conductivity and solubility measurements. It was revealed that the adduct formation of *p*- and *m*-nitrophenolates consisted of homoconjugation, that is, free nitrophenols are attached not to cations, but to the nitrophenolate anions, thus forming the larger anions and being stabilized in the organic phase. Homoconjugation constants of the nitrophenolates, which are independent of the cations present, were measured. The difference in extraction behaviors was interpreted in terms of the solubilities in both aqueous and organic phases and in terms of the homoconjugation constants.

In the previous paper,[1] it was demonstrated that the process of extracting cesium as nitrophenolates could be interpreted in terms of the dissociation of cesium phenolates and in terms of conjugation or adduct formation with free nitrophenols in the nitrobenzene phase. In that study, the interpretation was based on the fact that the experimental data agreed well with the equations which were postulated; no direct evidence has been given for the existence of dissociated forms of extracted species in the nitrobenzene phase. Besides, no confirmation was possible whether anions or cations participate with free nitrophenol molecules.

Kolthoff *et al.*[2-4] have demonstrated a method of estimating anion conjugation constants, in which the solubility product of the slightly soluble salt and the total ionic solubility were measured in the presence of varying concentrations of conjugating reagents.

In the present study, the method[2-4] was applied in order to clarify the ionic equilibria in the organic phase. As a result, it was found that the mono-nitrophenols are conjugated with anions present in the organic phase, whereas di- and tri-nitrophenols are less conjugated, in this order. The conjugation constants and solubilities of several salts in both organic and aqueous phases were determined. The extraction mechanisms and the participation of the solvent are discussed.

Experimental

Reagents. The alkali nitrophenolates were prepared by adding a slight excess of the alkali hydroxide to aqueous solutions of nitrophenols, concentrating the resulting solutions with a rotary evaporator, filtering off the precipitates, and recrystallizing them from acetone or ethanol solutions. The precipitates were dried for about an hour at 50°C *in vacuo* and then stored in a silica-gel desiccator. Nitrophenols and alkali hydroxides used were of reagent grade purity. The nitrobenzene was prepared by vacuum-distilling special-grade nitrobenzene. Titration with Karl-Fisher reagent using dead-stop indication showed a water content of 0.0035 wt% in the nitrobenzene. The nitrobenzene had a specific conductance of *ca.* 4×10^{-9}.

Apparatus. The conductivity measurements were performed in a glass cell equipped with platinized platinum electrodes by the use of a universal bridge, Type BV-Z-13B, supplied by Yokogawa Electric Works, Ltd. During the measurements, the temperature of the cell was controlled at 25±1°C in a thermostat.

Procedure. The ionic mobility of cesium picrate in nitrobenzene was measured by dissolving a standard cesium picrate solution with nitrobenzene; because of the slight solubility, the concentration of the standard solution was of the order of 10^{-4} M (see Fig. 1).

The ionic mobilities of cesium *p*-nitrophenolate (*p*-NP(Cs)), cesium *m*-nitrophenolate (*m*-NP(Cs)), cesium *o*-nitrophenolate (*o*-NP(Cs)), and cesium 2,4-dinitrophenolate (α-DNP(Cs)) were measured in nitrobenzene in the presence of 0.1 M nitrophenol; the salt was dissolved in a 0.1 M nitrophenol solution and diluted with a 0.1 M nitrophenol solution.

The conductivity measurements of a saturated solution in the presence of nitrophenols were carried out as follows; 100—200 mg of salt, which had previously been washed with nitrobenzene, were introduced into the conductivity cell, 10 m*l* of nitrobenzene were added, and the conductance was measured. The nitrophenol dissolved in nitrobenzene was added from a microsyringe, and after each addition of the reagent, the cell and the contents were shaken until the conductance remained constant within a 1% deviation.

The solubilities of nitrophenolates in distilled water were obtained by the use of ^{137}Cs; a labeled salt was saturated in water at 25±1°C, and the concentration was determined by measuring the γ-ray activities of ^{137}Cs.

Theoretical

(1) Dissociation of Cesium Nitrophenolates in Nitrobenzene. The dissociation of cesium nitrophenolates was ascertained by plotting the equivalent conductances, Λ, against the square roots of the concentration, C, of cesium nitrophenolates.

The relation between λ and $\sqrt{C}$ can be represented by the following expression:[5]

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[1] T. Fujinaga, M. Koyama, and O. Tochiyama, This Bulletin, **44**, 1591 (1971).

[2] M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **89**, 1582 (1967).

[3] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **91**, 25 (1969).

[4] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **91**, 4621 (1969).

[5] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publishing Corporation, New York, N.Y., (1958) pp. 164, 178, 286.

$$\Lambda = \Lambda^0 - (B_1 \cdot \Lambda^0 + B_2)\frac{\sqrt{\alpha C}}{1 + B\mathring{a}\sqrt{\alpha C}} \tag{1}$$

where B_1, B_2, and B are the constants for the solvent; α, the degree of the dissociation; C, the concentration, and $\mathring{a}$, the distance of the approach of the ions in angstrom units.

The dissociation constants of the salts were obtained by the method of Shedlovsky.[5)]

(2) Homoconjugation of Nitrophenolate Anions. If the chemical form of the species is a free ion in the solvent, the method reported by Kolthoff can be employed to determine the degree of the dissociation and participation of the nitrophenol in nitrobenzene.

The solubility product, $K_{sp,o}$, in nitrobenzene is obtained by measuring the conductivity of the saturated solution of the one-to-one salt MOR:

$$K_{sp,o} = [M^+]_o[OR^-]_o \cdot f^2 \qquad f = f_{M^+} = f_{OR^-} \tag{2}$$

where f is the activity coefficient. When free nitrophenol ROH is added to this solution, the homoconjugation of the anion occurs and the new equilibrium represented below must be considered:

$$(OR^-)_o + n(ROH)_o = (OR \cdot nROH^-)_o \tag{3}$$

$$K_n^f = \frac{[OR \cdot nROH^-]_o}{[OR^-]_o[ROH]_o^n} \qquad f_{OR^-} = f_{OR \cdot nROH^-} \tag{4}$$

The shifts of the equilibrium to the right direction cause a rise in the solubility of the cesium ion, according to the demands of the electrical neutrality relation:

$$\begin{aligned}[M^+]_o &= [OR^-]_o + [OR \cdot ROH^-]_o \\ &\quad + [OR \cdot 2ROH^-]_o + \cdots \\ &= [OR^-]_o(1 + \sum_n K_n^f [ROH]_o^n) \end{aligned} \tag{5}$$

Supposing that $K_{sp,o}$ is constant over the concentration range of the nitrophenol examined, the next expression can be obtained:

$$\begin{aligned} f^2[M^+]_o^2/K_{sp,o} &= 1 + K_1^f[ROH]_o \\ &\quad + K_2^f[ROH]_o^2 + \cdots \end{aligned} \tag{6}$$

This expression means that homoconjugation constants can be estimated from the plots of $f^2[M^+]_o^2/K_{sp,o}$ against $[ROH]_o$.

In the application of Eq. (6), the following assumptions have to be made:

(i) Nitrophenol is considered monomeric, and the activity of nitrophenol is taken to be equal to the equilibrium concentration; this assumption was verified previously by the results of the distribution studies of nitrophenols.[1)]

(ii) Only the unconjugated salt MOR is present in the solid phase, and the solubility product, $K_{sp,o}$, is considered to be constant. The water in the salt and nitrobenzene has little effect on the $f^2[M]_o^2/K_{sp,o}$ value.

(iii) The independent anion conjugation of the nitrophenol is assumed; that is the K_n^f values of anions are independent of the nature of the cations. This assumption was ascertained by the experiments shown in Fig. 3.

(iv) The limiting Debye-Hückel relation was used to evaluate ionic activity coefficients:[5)]

$$\log f_\pm = -A|z_+||z_-|\sqrt{I} \tag{7}$$

$$A = \frac{1.8246 \times 10^6}{(DT)^{3/2}} \tag{8}$$

where D: dielectric constant of nitrobenzene (34.5)
T: Kelvin temperature (273+25)
$|Z_+||Z_-|$: magnitudes of valences of ions (1)
I: ionic strength

(v) The limiting equivalent conductances of the anions, $(OR^-)_o$, $(OR \cdot ROH^-)_o$, and $(OR \cdot 2ROH^-)_o$, are assumed to be equal to the value obtained from Fig. 1. In fact, $\Lambda^0_{OR^-}$, $\Lambda^0_{OR \cdot ROH^-}$, and $\Lambda^0_{OR \cdot 2ROH^-}$ are not equal and the obtained value are mixtures of these values. If, however, $[ROH]_o$ is constant in Eqs. (4) and (5), the ratio of $(OR^-)_o$, $(OR \cdot ROH^-)_o$, and $(OR \cdot 2ROH^-)_o$ remains constant. Therefore, the experimental value can be used in place of each equivalent conductance unless the values, $\Lambda^0_{OR^-}$, $\Lambda^0_{OR \cdot ROH^-}$, and $\Lambda^0_{OR \cdot 2ROH^-}$ differ too much from each other.

(vi) In order to calculate the true conjugation constants, the following mathematical treatments have been made.

First, the relationship between $f^2[M^+]_o^2/K_{sp,o}$ and the total concentration of added nitrophenol, $[ROH]_t$, is obtained experimentally.

Then the relationship between $[ROH]_t$ and $[ROH]_o$ described below is used for the calculation of the concentration, $[ROH]_o$, of free nitrophenol.

$$\begin{aligned}[ROH]_t &= [ROH]_o + [OR \cdot ROH^-]_o \\ &\quad + 2[OR \cdot 2ROH^-]_o + \cdots \\ &= [ROH]_o + [OR^-]_o \sum_n nK_n^f [ROH]_o^n \end{aligned} \tag{9}$$

As the first approximation, the values of K_n^f are estimated from Eq. (6), assuming that $[ROH]_t$ is equal to $[ROH]_o$. By using the K_n^f value thus obtained, $[ROH]_o$ can be calculated according to Eq. (9). The new relationship between $f^2[M^+]_o^2/K_{sp,o}$ and the calculated $[ROH]_o$ gives improved K_n^f values. This procedure was repeated until the calculated value settles to give a converged curve which can be taken to represent a true $f^2[M^+]_o^2/K_{sp,o}$ against $[ROH]_o$.

Results and Discussion

(1) Dissociation of Cesium Nitrophenolates in Nitrobenzene. The relationships between the equivalent conductance and the square root of the concentration of cesium nitrophenolates are shown in Fig. 1. In the experiment, cesium nitrophenolates were dissolved and diluted in a 0.1 M free nitrophenol solution except in the case of cesium picrate. When the concentration of a dissolved salt is quite small compared with that of 0.1 M free nitrophenol, $[ROH]_o$ can be considered to be constant in Eq. (6).

This means that the ratio of the free anion $(OR^-)_o$ and the conjugated anions $(OR \cdot nROH^-)_o$ is constant in the experiment. Under these conditions, the limiting conductances, Λ^0, were estimated by the following relationship:[5)]

$$\Lambda = \Lambda^0 - A\sqrt{C}, \tag{1'}$$

The results are shown in Table 1.

In the case of cesium picrate, no picric acid was added in nitrobenzene, and the dissociation constant

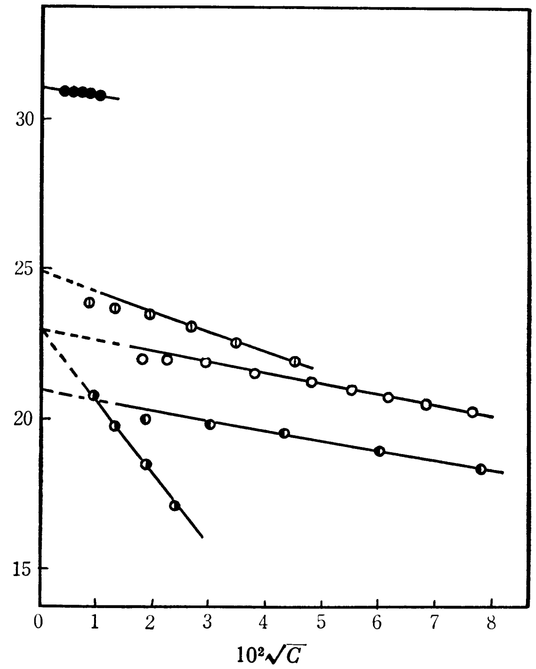

Fig. 1. Λ—$\sqrt{C}$ Plots of cesium nitrophenolates in nitrobenzene.
○ *p*-NP, ◐ *m*-NP, ◑ *o*-NP, ⦶ α-DNP, ● PA

TABLE 1. DISSOCIATION CONSTANTS AND LIMITING EQUIVALENT CONDUCTANCES.

	pK_o	λ_+^0	λ_-^0
p-NP(Cs)	—	23.0 (0.1 M HOR)	
m-NP(Cs)	—	21.0 (0.1 M HOR)	
o-NP(Cs)	—	23.0 (0.1 M HOR)	
α-DNP(Cs)	—	25.0 (0.1 M HOR)	
PA(Cs)	2.24	31.5	
PA(K)	3.15⁶⁾	17.8⁶⁾	16.0⁶⁾
PA(Na)	4.55⁶⁾	16.3⁶⁾	
PA(Li)	7.2⁶⁾		
PA(H)	7.4⁷⁾	23.0⁸⁾	

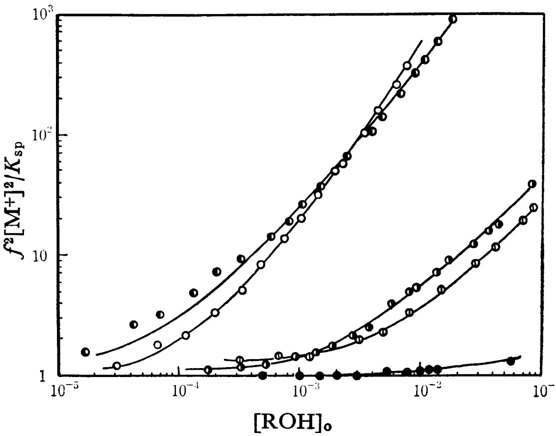

Fig. 2. $f^2[M^+]_o^2/K_{sp,o}$ *vs.* $[ROH]_o$ plots of cesium nitrophenolates in nitrobenzene.
○ *p*-NP, ◐ *m*-NP, ◑ *o*-NP, ⦶ α-DNP, ● PA

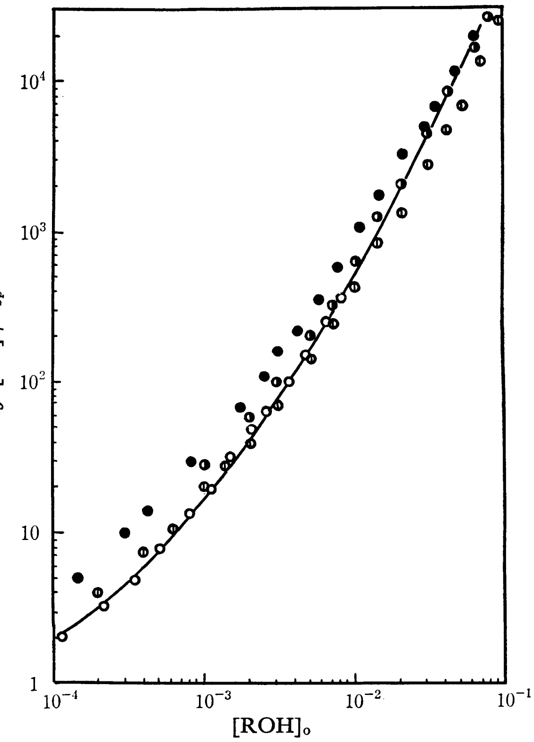

Fig. 3. $f^2[M^+]_o^2/K_{sp,o}$ *vs.* $[ROH]_o$ plots of alkali *p*-nitrophenolates in nitrobenzene.
○ Cs, ● K, ◑ Na, ⦶ Li
curve; $K_1^f=10^4$ $K_2^f=5\times10^6$

was determined from the results to be $pK_o=2.2$. This value is compared with the dissociation constants of other alkali picrates given by Kraus.⁶⁾ In Fig. 1, the Λ *vs.* $\sqrt{C}$ plots of cesium *p*-nitrophenolate, cesium *m*-nitrophenolate, and cesium α-dinitrophenolate present fairly gentle slopes. This may perhaps be attributed to the formation of larger conjugated anions, thus giving the larger $\mathring{a}$ value in Eq. (1).

The dissociation of all cesium salts in nitrobenzene can be concluded from these data.

(2) Homoconjugations of Nitrophenolate Anions. Plots of $f^2[M^+]_o^2/K_{sp,o}$ *vs.* $[ROH]_o$ on a logarithmic scale are presented in Figs. 2 and 3, where f is the activity coefficient of the dissociated metal ions in nitrobenzene. $[ROH]_o$ is the concentration of the added nitrophenol minus the concentration of the conjugated nitrophenol. $K_{sp,o}$ represents the solubility product, which was calculated from the conductance of the saturated solution and the limiting equivalent conductance. The $K_{sp,o}$ values of metal nitrophenolates were calculated on the assumption that the Λ^0 value of metal nitrophenolates were equal to those of cesium nitrophenolates. The $K_{sp,o}$ values and homoconjugation constants obtained from Figs. 2 and 3 are summarized in Table 2. The results shown in the table give some suggestions for extraction studies; the $K_{sp,o}$ values increase in the order Na<K<Cs in any nitrophenolate. This difference is the cause of the difference in the distribution behavior. On the contrary, the values do not differ much among cesium nitrophenol-

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6) C. R. Witschonke and C. A. Kraus, *J. Amer. Chem. Soc.*, **69**, 2472 (1947).

7) I. M. Kolthoff, D. Stŏcesocă, and T. S. Lee, *ibid.*, **75**, 1834 (1953).

8) "Kagaku Binran," Maruzen Co., Tokyo (1966).

Table 2. Solubility constants, solubilities, and conjugation constants of alkali nitrophenolates

		p-NP	m-NP	o-NP	α-DNP	PA
$K_{sp,o}$	Li	6.7×10^{-12}	2.9×10^{-13}	1.5×10^{-10}	8.9×10^{-10}	1.6×10^{-8}
	Na	1.1×10^{-10}	1.1×10^{-10}	1.0×10^{-10}	1.0×10^{-10}	7.4×10^{-9}
	K	7.5×10^{-9}	3.0×10^{-8}	1.3×10^{-9}	2.2×10^{-8}	4.1×10^{-8}
	Cs	6.4×10^{-7}	1.0×10^{-6}	2.0×10^{-7}	7.5×10^{-7}	5.5×10^{-7}
S_a	Na	3.5×10^{-1} [9]			1.9×10^{-1} [9]	1.57×10^{-1} [9]
	Cs	1.55			9.7×10^{-2}	1.5×10^{-2}
K_n^f	K_1^f	1.0×10^{4}	2.0×10^{4}	4.5×10^{2}	2.4×10^{2}	$<10^{2}$
	K_2^f	5.0×10^{6}	2.0×10^{6}	—	—	—

ates of different kinds. Only cesium o-nitrophenolate gives a little smaller value. This similarity must be caused by the fact that nitrobenzene is a basic solvent and, therefore, combines with cations, but not with anions.

A bare anion which has a localized charge can be stabilized by homoconjugation. Figure 3 shows that the degree of the conjugation is independent of the species of cations.

This fact demonstrates that only the anion conjugation expressed by Eq. (4) takes place preferentially and that free nitrophenols have little capability of interacting with cations in nitrobenzene. In Table 2, it is shown that p-and m-nitrophenols have homoconjugation constants of considerable extents. *Ortho*-substituted phenols are, however, poor hydrogen-bond donors and form only monoconjugates $(\mathrm{OR\cdot ROH^-})_o$, whereas p- and m-nitrophenols can form higher conjugates, *e.g.*, $(\mathrm{OR\cdot 2ROH^-})_o$. This seems to be the main reason why there is less possibility of extracting cesium with o-nitrophenol.

(3) A Comparison of Solubility Measurements with Extraction Studies. Cesium nitrophenolates which are present as one-to-one salts are not extracted appreciably into nitrobenzene except in the case of cesium picrate, as is reported previously.[1] In the expression of the extraction of cesium:

$$D_{\mathrm{Cs}} = K_{\mathrm{Cs}}^{*1/2}(1+\sum_n K_n^f[\mathrm{ROH}]_o{}^n)^{1/2}\frac{[\mathrm{OR^-}]_a{}^{1/2}}{[\mathrm{Cs^+}]_a{}^{1/2}} \qquad (10)$$

n was obtained from the slope of log D_{Cs} *vs.* log $[\mathrm{ROH}]_{\mathrm{total}}$, and $K_{\mathrm{Cs}}^*\ K_n^f$ was also calculated as the extraction constant.

These values are shown in Table 3. It was also shown in the previous paper that cesium ions are extracted to a considerable extent with picric acid or α-dinitrophenol, whereas the conductivity experiments have shown that both have small K_n^f values and that their cesium salts show values of $K_{sp,o}$ similar to those of other nitrophenolates.

Table 3. Extraction constants and extraction exchange constants (25°C)

		p-NP	m-NP	α-DNP	PA
$K_{\mathrm{Cs}}^*K_n^f$	$n=0$	—	—	4.7×10^{-5}	2.8×10^{-3}
	$n=1$	—	—	1.6×10^{-2}	4.6×10^{-2}
	$n=2$	1.4	0.83	—	—
$K_{\mathrm{Cs}}^*/K_{\mathrm{Na}}^*$		1.1×10^{3}	1.3×10^{3}	2.2×10^{3}	5.0×10^{3} (20°C)

These facts imply that cesium picrate and cesium α-dinitrophenolate have a very small solubility in water if the distribution equilibria are determined solely according to the ratio of the solubilities of the solutes in both organic and aqueous solutions. In Table 2, the solubilities, S_a, of sodium or cesium nitrophenolates in water are shown. The S_a values of cesium salts were obtained by the use of $^{137}\mathrm{Cs}$, while those of sodium salts were taken from the literature.[9]

From the solubility and conjugation data, the extraction constants can be estimated according to the following equation.

$$K_{\mathrm{M}}^{**} = S_o{}^2/S_a{}^2,\ S_o{}^2 = K_{sp,o}/f^2 \qquad (11)$$

Table 4. Calculated distribution coefficients and exchange constans

		p-NP	α-DTP	PA
K_{Cs}^{**}	$n=0$	2.7×10^{-7}	8.1×10^{-5}	2.3×10^{-3}
K_{Na}^{**}		9.0×10^{-10}	2.8×10^{-9}	3.0×10^{-7}
$K_{\mathrm{Cs}}^{**}K_n^f$	$n=1$	—	1.9×10^{-2}	—
	$n=2$	1.4	—	—
$K_{\mathrm{Cs}}^{**}/K_{\mathrm{Na}}^{**}$		3.0×10^{2}	2.9×10^{4}	7.7×10^{3}

The values of K_{Cs}^{**}, $K_{\mathrm{Cs}}^{**}K_n^f$, K_{Na}^{**}, and $K_{\mathrm{Cs}}^{**}/K_{\mathrm{Na}}^{**}$ which are the constants calculated from the solubility and conjugation data, are shown in Table 4. These values can be compared with those shown in Table 3, which were obtained from the extraction studies. In the case of p-nitrophenol, only $K_{\mathrm{Cs}}^*K_2^f$ $(n=2)$ can be obtained from the extraction studies, while in the cases of α-dinitrophenol and picric acid, both $K_{\mathrm{Cs}}^*K_1^f$ $(n=1)$ and K_{Cs}^* $(n=0)$ were obtained from the data when the pH was small and when the pH was very large $([\mathrm{ROH}]_o=0)$, respectively. In Tables 3 and 4, K_{Cs}^* and K_{Cs}^{**}, $K_{\mathrm{Cs}}^*K_n^f$ and $K_{\mathrm{Cs}}^{**}K_n^f$, are in good agreement. For example, in the case of α-dinitrophenol, K_{Cs}^* was obtained as 4.7×10^{-5} from the extraction study when the pH was very large. This value is in fairly good agreement with the value of $K_{\mathrm{Cs}}^{**}=8.1\times10^{-5}$ obtained as the square of the ratio of the solubilities of one-to-one cesium α-dinitrophenolate in the organic and aqueous phases.

When the pH was quite small, $K_{\mathrm{Cs}}^*K_1^f$ was obtained as 1.6×10^{-2}. This value indicates the distribution constant of one-to-two cesium α-dinitrophenolate CsORROH; the value is also in good agreement with

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[9] W. M. Fischer, *J. Physik. Chem.*, **92,** 581 (1918).

$K^{**}_{\mathrm{Cs}}K^{f}_{1}=1.9\times10^{-2}$, which is the product of $K^{**}_{\mathrm{Cs}}=8.1\times10^{-5}$ and $K^{f}_{1}=2.4\times10^{2}$. These facts suggest that water molecules distributed in the nitrobenzene phase have little effect on the distribution of cesium ions. The $K^{*}_{\mathrm{Cs}}/K^{*}_{\mathrm{Na}}$ values and $K^{**}_{\mathrm{Cs}}/K^{**}_{\mathrm{Na}}$ values are different in the cases of *p*-nitrophenol and α-dinitrophenol. This disagreement may be attributed to the difference between K^{*}_{Na} and K^{**}_{Na}; the fairly high solubility of sodium salt in water and the very slight solubility of the salt in nitrobenzene seem to have given unsatisfactory data; the extracted water in nitrobenzene affects the solubility seriously.

The agreement of extraction constants and of the *n* value obtained from the extraction experiments with those obtained from the conductivity measurements indicates that Eq. (10) and Eq. (6) are equally meaningful and correlate with each other. Therefore, it must be emphasized that both methods offer equivalent information about the chemical interaction in organic solvents.