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The Extraction of Several Anions by Methyltrioctylammonium into Various Solvents

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The back extraction of methyltrioctylammonium chloride (MTOACl) from ten kinds of organic solvents was investigated as a function of the MTOACl concentration. The chemical species of the ammonium salt in the organic phase were found to be in the form of dissociated ions, of ion pairs, or of dimeric ion pairs, according to the dielectric constant of the solvent. MTOACl was better extracted into more polar and acidic solvents, such as nitrobenzene, 3-methyl-1-butanol, and chloroform. The selectivity coefficients ($K_{X/Cl}$) of MTOA for the exchange of Br^-, I^-, ClO_4^-, *vs.* Cl^- were obtained from the study of the distribution of several organic color reagents; they were found to increase with the anion size, irrespective of the organic solvent used. For all but acidic solvents, the values of $K_{X/Cl}$ were similar to each other. Such acidic solvents as 3-methyl-1-butanol and chloroform, however, reduced the selectivity of the extraction for anions.

Quaternary ammonium salts have been extensively used for metal extractions[1] and more recently have received attention as phase transfer catalysts[2] and exchangers for ion-selective electrodes.[3] However, our knowledge of the properties of substituted ammonium salts in solution is too limited to give a general guide for such applications. Knowledge of their property of extracting simple anions is, above all, most important in understanding many related reactions.

In this paper, the extraction of simple anions, such as chloride, bromide, iodide, and perchlorate, by methyltrioctylammonium (MTOA) into various organic solvents was investigated. MTOA was chosen as a representative long-chain alkylammonium because MTOA and closely related tertiary amine, trioctylamine (TOA) have been commonly used in extraction studies. The organic solvents were selected so as to furnish a wide variation in character. The extraction of chloride was first investigated by the analysis of the distribution of MTOACl between two phases to obtain the general idea of the extraction reaction. The extraction of other anions by MTOA was then indirectly studied through the ion-exchange reaction between the ion to be studied and the anions of several organic reagents, such as thenoyltrifluoroacetone (TTA), tetrabromophenol sulfonephthalein (Bromophenol Blue, BPB), and *p*-nitrophenol (*p*-NP), which coexisted in the system (hereafter, these reagents are referred to as "indicators"). These results were integrated in terms of the selectivity coefficients against chloride and discussed on the basis of various properties of the solvents and anions, as will be described below.

Experimental

Reagents. Methyltrioctylammonium chloride (Capriquat, Dotite reagent) was used as received. The effective concentration of the quaternary ammonium base was determined by acid-base titration in acetic acid.[4] All the other reagents were of a reagent grade and were used without further purification.

Apparatus. A shaker (Takabayashi Rika RL-6) and a centrifuge (Kubota KH-180) were used for the extraction experiment. A pH meter (Tōa Dempa HM-6A) was used for the pH measurements. The absorption spectra were measured with a Hitachi EPS-3 recording spectrophotometer using a quartz cell (1 cm light path).

Procedures. *General Procedure*: Equal volumes (4 cm^3) of an aqueous and an organic solution with the desired compositions were brought into contact in a glass tube and shaken mechanically for 15 min (140 times/min) at room temperature (23±2 °C). If necessary, the phase separation was accelerated by centrifugation. After phase separation, the concentration of the solute of interest was measured by a suitable analytical method. The aqueous phase was used for the pH measurements.

Distribution Ratio of MTOACl: An organic solution containing a definite concentration of MTOACl and an aqueous solution were equilibrated, and the concentration of MTOA in the aqueous phase was determined. The MTOA in the aqueous solution was extracted with BPB into xylene at pH about 11 ($[Na_2CO_3]=0.05$ mol dm^{-3}),[5] then the absorbance of the xylene solution was measured at 607 nm. The concentration of MTOA was calculated from the calibration curve, which obeyed Beer's law over the range from 2.5×10^{-6} to 2.5×10^{-5} mol dm^{-3}. The concentration of MTOA in the organic phase was calculated from the difference between the initial added concentration and the concentration in the aqueous phase after equilibration.

Extraction Exchange Constants: An organic solution containing MTOACl was equilibrated with an aqueous solution containing the desired concentrations of a certain anion (as a sodium salt) and buffer reagents (0.05 mol dm^{-3} of acetic acid, plus a variable concentration of ammonium hydroxide or 0.05 mol dm^{-3} sodium carbonate, depending on the pH of the solution to be studied) in the presence of an indicator which had been added to the organic (TTA) or the aqueous phase (BPB, *p*-NP). When TTA was used as an indicator, the absorption spectrum of TTA in the organic phase was measured to give the ratio of the salt to the acid form of TTA.[6] When BPB or *p*-NP was used as an indicator, the distribution ration was obtained from the measurement of the absorbance of the organic phase (at 600—608 nm for BPB) or the aqueous phase (at 402 nm for *p*-NP).

Results and Discussion

Extraction of MTOACl. Since the extracted ammonium salt may be in the form of dissociated ions, of ion pairs, or of still higher ion associations, the concentration of MTOA in the organic phase can be expressed as:

$$C_{Q,o} = [Q^+]_o + [QCl]_o + 2[Q_2Cl_2]_o + \cdots, \qquad (1)$$

assuming that Cl^- is the only anion present. Here, Q^+ denotes the cation of MTOA; square brackets show the concentration of the enclosed species; the subscript o stands for the organic phase; the absence of any subscript indicates the aqueous phase. C is the total (analytical) concentration; in this case, the subscript a stands for the aqueous phase, and the absence of any subscript represents the total of C_o plus C_a. As the electrical neutrality relation in the organic phase,

$$[Q^+]_o = [Cl^-]_o, \qquad (2)$$

holds, Eq. 1 can be transformed into:

$$C_{Q,o} = K_{1/2}([Q^+][Cl^-])^{1/2} + K_1[Q^+][Cl^-] + 2K_2([Q^+][Cl^-])^2 + \cdots, \qquad (3)$$

where $K_{1/2}$, K_1, and K_2 are these concentration quotients:

$$K_{1/2} = ([Q^+]_o[Cl^-]_o/[Q^+][Cl^-])^{1/2}, \qquad (4)$$

$$K_1 = [QCl]_o/[Q^+][Cl^-], \qquad (5)$$

$$K_2 = [Q_2Cl_2]_o/([Q^+][Cl^-])^2. \qquad (6)$$

When no excess anions exist in the system, the relation in the aqueous phase:

$$[Q^+] = [Cl^-], \qquad (7)$$

also holds and Eq. 3 can be expressed as:

$$C_{Q,o} = K_{1/2}[Q^+] + K_1[Q^+]^2 + 2K_2[Q^+]^4 + \cdots. \qquad (8)$$

As it is obvious that

$$C_{Q,a} = [Q^+], \qquad (9)$$

the plot of log $C_{Q,o}$ vs. log $C_{Q,a}$ will show the slopes according to the predominant species in the organic phase: 1 (dissociated ions), 2 (ion pairs), or 4 (dimers). When a large excess of chloride over Q^+ is present in the system, $[Cl^-]$ in Eq. 3 is considered to be constant and the slopes are 1/2 (dissociated ions), 1 (ion pairs), and 2 (dimers). Figures 1—3 show the results obtained in the back extraction of MTOACl from various organic solvents into water or 0.1 mol dm^{-3} of NaCl. The distribution behavior of MTOACl can be grouped into three classes according to the organic solvents used.

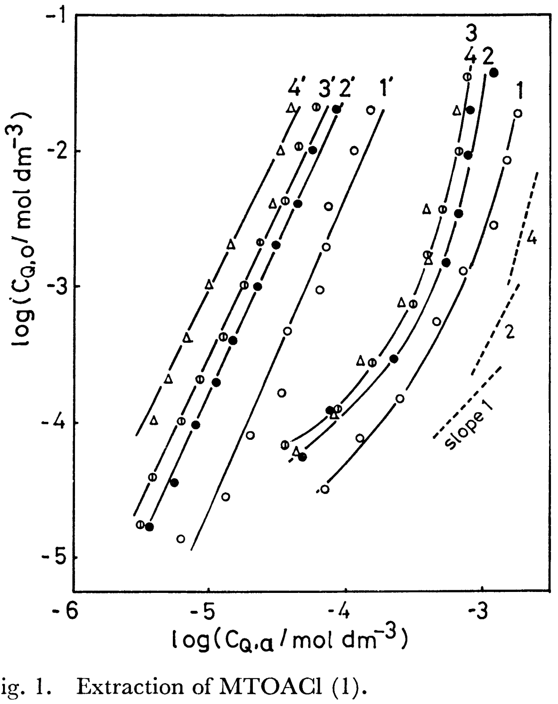

Fig. 1. Extraction of MTOACl (1).
1,1': Hexane, 2,2': xylene, 3,3': carbon tetrachloride, 4,4': benzene, 1—4: vs. water, 1'—4': vs. 0.1 mol dm^{-3} NaCl.

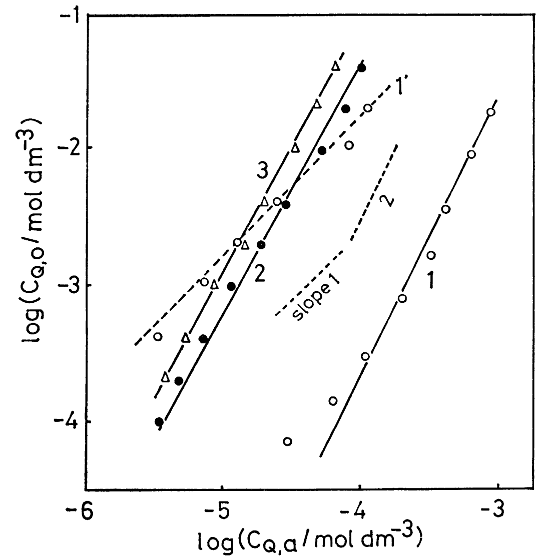

Fig. 2. Extraction of MTOACl (2).
1,1': Butyl acetate, 2: dichloromethane, 3: chloroform, 1—3: vs. water, 1': vs. 0.1 mol dm^{-3} NaCl.

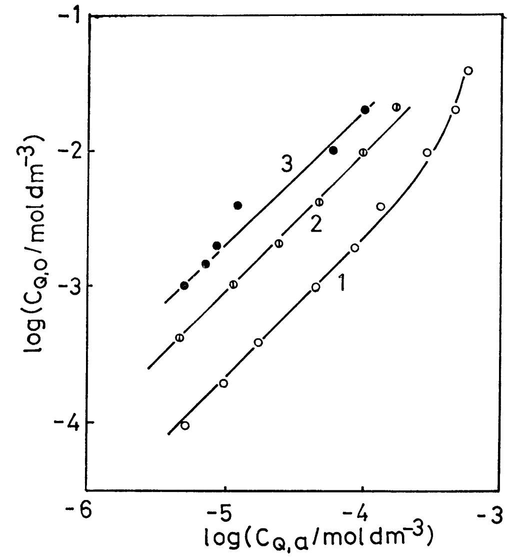

Fig. 3. Extraction of MTOACl (3).
1: 4-Methyl-2-pentanone, 2: nitrobenzene, 3: 3-methyl-1-butanol, 1—3: vs. water.

Figure 1 shows the distribution behavior of MTOACl between water or 0.1 mol dm^{-3} NaCl and four so-called "inert solvents." The slope of 2 obtained for 0.1 mol dm^{-3} NaCl and the maximum slope of 4 for water suggest that MTOACl is in the form of dimers in the organic phase. For water, however, the slope of the curves varies from 1 to 4, depending on the C_Q. As the pH of the aqueous phase was found to decrease slightly after the equilibration, species containing hydroxide

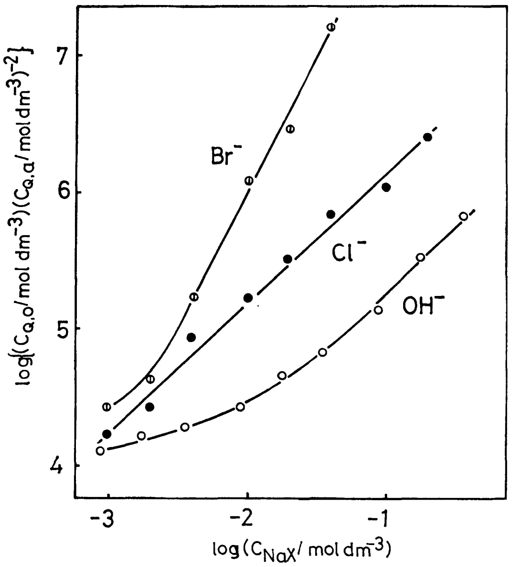

Fig. 4. Effect of anions on the extraction of MTOA into xylene.
$C_Q=8\times10^{-3}$ mol dm^{-3}.

ions may also participate in the extraction of MTOA. If we consider that only dimers are present in the organic phase, it can easily be deduced that the slope of the log $(C_{Q,o}/C_{Q,a}^2)$ *vs.* log $[X^-]$ (X^- denotes anions participating in the extraction) plot will give the mean number of anions in the extracted species. Figure 4 clearly indicates that a mixed dimer such as Q_2ClOH was also extracted along with Q_2Cl_2, while Q_2Br_2 was extracted when a considerable amount of bromide was present. Therefore, the smaller slopes in the lower concentration range of MTOA, shown by Curves 1—4 in Fig. 1, do not mean the extraction of a monomer nor dissociated ions, but the extraction of the mixed dimer. The approximate values of the extraction constants, K_2, were estimated from the data over the concentration range where the slope of Curves 1—4 equals 4, as is shown in Table 1.

Figure 2 shows the results for three solvents which are considered to have intermediate polarity. The slopes of 2 and 1 for the curves obtained for water and for 0.1 mol dm^{-3} NaCl (for butyl acetate) respectively indicate the existence of ion pairs over the concentration range studied. For butyl acetate, however, the contribution of hydroxide ions may not be neglected in the lower concentration range of MTOA.

Figure 3 shows the results for highly polar solvents, such as 4-methyl-2-pentanone, nitrobenzene, and 3-methyl-1-butanol. The slope of 1 observed for these solvents suggests the dissociation of ion pairs, except for 4-methyl-2-pentanone in the higher concentration range of MTOA, where some degree of ion-pair formation is considered to occur since the plots deviate upward from the straight line.

Table 1 summarizes the results of the extraction of MTOACl. To compare the extractability of organic solvents for MTOACl, the logarithms of the distribution ratios of MTOA, log D_Q=log $(C_{Q,o}/C_{Q,a})$, at $C_Q=2\times10^{-3}$ mol dm^{-3} are also given. The general features of the extraction of MTOACl are quite similar to those of hydrohalic acids by tridodecylamine (TDA), as investigated by Müller and Diamond.[8] The dielectric constant of the organic solvents directly affects the degree of association or dissociation of ion pairs. In the extraction of TDAHX ($X^-=Cl^-$, Br^-, I^-, SCN^-), the presence of ion pairs (in chloroform), ion pairs and higher ion aggregates (in benzene, carbon tetrachloride, and cyclohexane), and ion pairs and free ions (in nitrobenzene) have been reported. In the extraction of MTOACl, however, the existence of only one chemical form for one solvent was verified under the experimental conditions adopted; dimers alone in benzene, carbon tetrachloride and hexane, ion pairs in chloroform, and free ions alone in nitrobenzene. The difference in the results for nitrobenzene between TDAHX and MTOACl may be attributable to the presence of the hydrogen bond in the ion pairs. The dielectric constant of the solvents plays an important role also in determining the extractability; polar solvents are favorable for the

TABLE 1. EXTRACTION CONSTANTS OF MTOA CHLORIDE

Species in organic phase and solvent	ε[a]	*AN*[b]	Extraction constant	log D_Q[d]
Q_2Cl_2 (or Q_2ClOH)			log (K_2 mol^3 dm^{-9})	
Hexane	1.89	0	8.9	0.2
Xylene	2.37	—	10.1	0.5
Carbon tetrachloride	2.24	8.6	10.5	0.6
Benzene	2.28	8.2	10.6	0.6
QCl			log (K_1 mol dm^{-3})	
Butyl acetate	5.01	—	4.35	0.79
Dichloromethane	9.08	20.4	6.76	2.03
Chloroform	4.81	23.1	7.07	2.18
$Q^+ + Cl^-$			log $K_{1/2}$	
4-Methyl-2-pentanone	13.11	—	1.32	1.32
Nitrobenzene	34.82*	14.8	1.97	1.97
3-Methyl-1-butanol	14.7*	(33.5)[c]	2.30	2.30

a) Relative dielectric constant at 20 °C or 25 °C (marked by *) from Ref. 7. b) Acceptor number from Ref. 9; for water, *AN*=54.8. c) Value for 2-propanol. d) At $C_Q=2\times10^{-3}$ mol dm^{-3}.

extraction of MTOACl and TDAHX. Furthermore, it is certain that the acidic properties of the solvents influence the extraction, as evidenced by the correlation between the extraction constants and the acceptor numbers which have been introduced by Gutmann[9] as a measure of the acidity of electrophilic solvents. As a whole, MTOACl is better extracted by the more polar and acidic (as a Lewis acid) solvents.

Ion-exchange Selectivity of MTOA. As has been discussed above, the extraction of MTOACl shows complex features depending upon the solvents and upon the concentrations of MTOA and anions. In order to compare the extraction of various anions by MTOA, therefore, it is preferable to apply a method which can simplify both the experimental and theoretical treatments. For this purpose, we have studied the exchange property of MTOA for several anions. If we assume that the concentration of exchangeable counter anions in the organic phase governs the equilibrium,[10] the exchange reaction may be described as follows:

$$(\cdots\mathrm{Y}^{m-})_\mathrm{o} + m\mathrm{X}^- = m(\cdots\mathrm{X}^-)_\mathrm{o} + \mathrm{Y}^{m-}, \qquad (10)$$

where Y denotes the anion with the charge m and where $(\cdots\mathrm{Y}^{m-})_\mathrm{o}$ and $(\cdots\mathrm{X}^-)_\mathrm{o}$ indicate the exchangeable anions in the organic phase; *i.e.*,

$$[\cdots\mathrm{X}^-]_\mathrm{o} = C_{\mathrm{X,o}}, \qquad (11)$$

$$[\cdots\mathrm{Y}^{m-}]_\mathrm{o} = C_{\mathrm{Y,o}}, \qquad (12)$$

when the charge of these anions balances with that of MTOA cations in the organic phase. The constant for the exchange reaction (10) is defined as:

$$(K_{\mathrm{X/Y}})^m = (C_{\mathrm{X,o}})^m[\mathrm{Y}^{m-}]/C_{\mathrm{Y,o}}[\mathrm{X}^-]^m. \qquad (13)$$

When $m=1$, Eq. 13 can be written as follows according to the predominant species of MTOA salt in the organic phase:

(*i*) For free ions,

$$K_{\mathrm{X/Y}} = [\mathrm{X}^-]_\mathrm{o}[\mathrm{Y}^-]/[\mathrm{Y}^-]_\mathrm{o}[\mathrm{X}^-], \qquad (14)$$

(*ii*) for monomers,

$$K_{\mathrm{X/Y}} = [\mathrm{QX}]_\mathrm{o}[\mathrm{Y}^-]/[\mathrm{QY}]_\mathrm{o}[\mathrm{X}^-], \qquad (15)$$

(*iii*) and for dimers,

$$K_{\mathrm{X/Y}} = \frac{(2[\mathrm{Q_2X_2}]_\mathrm{o}+[\mathrm{Q_2XY}]_\mathrm{o})[\mathrm{Y}^-]}{(2[\mathrm{Q_2Y_2}]_\mathrm{o}+[\mathrm{Q_2XY}]_\mathrm{o})[\mathrm{X}^-]}. \qquad (16)$$

In the case of (*i*) or (*ii*), it can be easily seen that $K_{\mathrm{X/Y}}$ gives a constant value. On the other hand, in the case of dimers, it is doubtful if the right-hand side of Eq. 16 gives a constant value. It is clear that the combination of the extraction constant for pure dimers,

$$K_{2,\mathrm{X}} = [\mathrm{Q_2X_2}]_\mathrm{o}/([\mathrm{Q}^+][\mathrm{X}^-])^2, \qquad (6')$$

$$K_{2,\mathrm{Y}} = [\mathrm{Q_2Y_2}]_\mathrm{o}/([\mathrm{Q}^+][\mathrm{Y}^-])^2, \qquad (6'')$$

leads to the following relationship:

$$K_{2,\mathrm{X}}/K_{2,\mathrm{Y}} = [\mathrm{Q_2X_2}]_\mathrm{o}[\mathrm{Y}^-]^2/[\mathrm{Q_2Y_2}]_\mathrm{o}[\mathrm{X}^-]^2. \qquad (17)$$

The assumption made for Eq. 10 means that the two exchange sites in dimers do not interact with each other; in other words, the dimerization from QX and QY to $\mathrm{Q_2X_2}$, $\mathrm{Q_2Y_2}$, or $\mathrm{Q_2XY}$ occurs statistically. Therefore, the concentration of each species in the organic phase can be described as:

$$[\mathrm{Q_2X_2}]_\mathrm{o} = (C_{\mathrm{X,o}})^2/2(C_{\mathrm{X,o}}+C_{\mathrm{Y,o}}) = (C_{\mathrm{X,o}})^2/2C_{\mathrm{Q,o}}, \qquad (18)$$

$$[\mathrm{Q_2XY}]_\mathrm{o} = C_{\mathrm{X,o}}C_{\mathrm{Y,o}}/(C_{\mathrm{X,o}}+C_{\mathrm{Y,o}}) = C_{\mathrm{X,o}}C_{\mathrm{Y,o}}/C_{\mathrm{Q,o}}, \qquad (19)$$

$$[\mathrm{Q_2Y_2}]_\mathrm{o} = (C_{\mathrm{Y,o}})^2/2(C_{\mathrm{X,o}}+C_{\mathrm{Y,o}}) = (C_{\mathrm{Y,o}})^2/2C_{\mathrm{Q,o}}. \qquad (20)$$

The substitution of these equations into Eq. 17 gives the relationship as:

$$K_{2,\mathrm{X}}/K_{2,\mathrm{Y}} = (C_{\mathrm{X,o}})^2[\mathrm{Y}^-]^2/(C_{\mathrm{Y,o}})^2[\mathrm{X}^-]^2 = (K_{\mathrm{X/Y}})^2. \qquad (21)$$

Therefore, we can now understand that Eq. 16 gives a constant value, which may in turn be written as:

$$\begin{aligned} K_{\mathrm{X/Y}} &= [\mathrm{Q_2XY}]_\mathrm{o}[\mathrm{Y}^-]/[\mathrm{Q_2Y_2}]_\mathrm{o}[\mathrm{X}^-] \\ &= [\mathrm{Q_2X_2}]_\mathrm{o}[\mathrm{Y}^-]/[\mathrm{Q_2XY}]_\mathrm{o}[\mathrm{X}^-]. \qquad (22) \end{aligned}$$

Hence, we can conclude that Eq. 13 holds regardless of the form of the predominant species in the organic phase if the dimer formation occurs statistically. Furthermore, Eq. 13 can be applied when monomers coexist with dimers. When free ions and monomers coexist, however, Eq. 13 no longer holds as long as QX and QY differ in the dissociation constant in the organic phase. The assumption made here was warranted by the fact that Eq. 13 could be successfully applied to the experimental results, as will be described later. Therefore, we can simply compare the extraction of various anions by MTOA under the notion of the exchange reaction, Eq. 10, except when free ions coexist with monomers.

From Eq. 13, the distribution ratio of Y can be represented as follows:

$$\begin{aligned} D_\mathrm{Y} &= C_{\mathrm{Y,o}}/[\mathrm{Y}^{m-}] \\ &= (1/K_{\mathrm{X/Y}})^m(C_{\mathrm{X,o}}/[\mathrm{X}^-])^m. \qquad (23) \end{aligned}$$

When D_Y is obtained for an indicator Y, $C_{\mathrm{X,o}}$, and $[\mathrm{X}^-]$ can be calculated from the respective initial concentrations as follows:

$$C_\mathrm{Y} = C_{\mathrm{Y,o}} + [\mathrm{Y}^{m-}], \qquad (24)$$

$$\begin{aligned} C_\mathrm{Q} &= mC_{\mathrm{Y,o}} + C_{\mathrm{X,o}} \\ &= mC_\mathrm{Y}(1+1/D_\mathrm{Y})^{-1} + C_{\mathrm{X,o}}, \qquad (25) \end{aligned}$$

$$C_\mathrm{X} = C_{\mathrm{X,o}} + [\mathrm{X}^-]. \qquad (26)$$

Then the exchange constant of X against Y can be obtained from the plot of log D_Y *vs.* log $C_{\mathrm{X,o}}/[\mathrm{X}^-]$. When TTA is used as an indicator, the constant, $K'_{\mathrm{X/T}}$ was obtained from the next relationships:

$$K'_{\mathrm{X/T}} = ([\mathrm{HT}]_\mathrm{o}/[\cdots\mathrm{T}^-]_\mathrm{o})(C_{\mathrm{X,o}}/[\mathrm{H}^+][\mathrm{X}^-]), \qquad (13')$$

$$D'_\mathrm{T} = [\cdots\mathrm{T}^-]_\mathrm{o}/[\mathrm{HT}]_\mathrm{o} = (1/K'_{\mathrm{X/T}})(C_{\mathrm{X,o}}/[\mathrm{H}^+][\mathrm{X}^-]), \qquad (23')$$

$$C_\mathrm{T} = [\cdots\mathrm{T}^-]_\mathrm{o} + [\mathrm{HT}]_\mathrm{o} + [\mathrm{T}^-], \qquad (24')$$

$$C_\mathrm{Q} = [\cdots\mathrm{T}^-]_\mathrm{o} + C_{\mathrm{X,o}}, \qquad (25')$$

$$C_\mathrm{X} = C_{\mathrm{X,o}} + [\mathrm{X}^-]. \qquad (26)$$

The distribution ratios of BPB or *p*-NP, or the ratios of the salt to the acid form of TTA in the organic phase, were measured at various concentrations of NaX or at various pH values. From the experimental plots thus obtained, some of which are shown in Figs. 5—7, the exchange constants were estimated to be as is shown in Tables 2—4. HT, $\mathrm{H_2B}$, and HR denote the acid forms of TTA, BPB, and *p*-NP respectively. The straight lines obtained by the method of least squares have the slopes to be expected from the number of acidic hydrogen in the indicators, that is, close to 1 for the TTA and *p*-NP systems and 2 for the BPB system. In some exceptional cases, however, the slopes deviate somewhat from

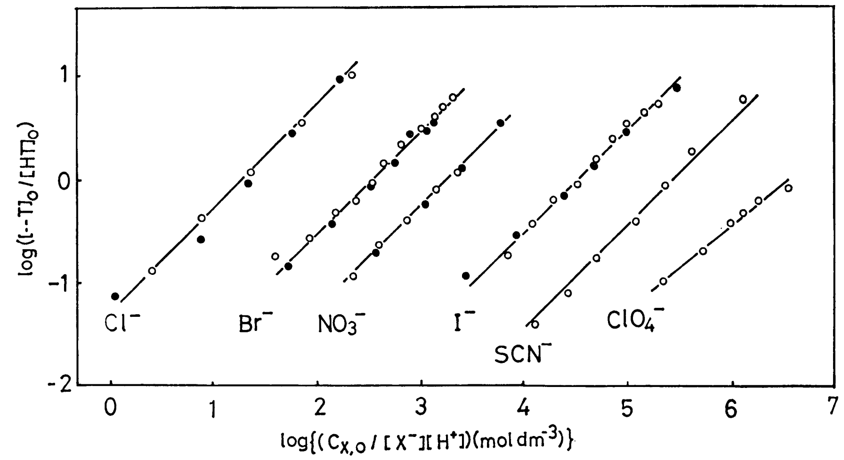

Fig. 5. Plot of Eq. 23′ for TTA-xylene system.
○: Obtained by varying C_{NaX} (at pH 4—6), ●: obtained by varving pH (at C_X=0.01—0.1 mol dm^{-3}), C_Q=(5—10)×10^{-5} mol dm^{-3}, C_T= 6×10^{-5} mol dm^{-3}.

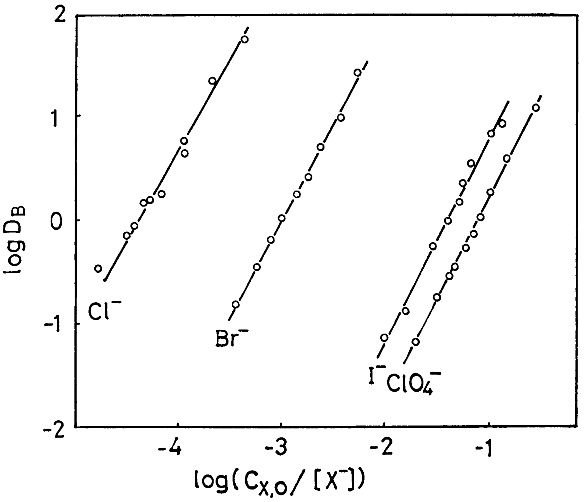

Fig. 6. Plot of Eq. 23 for BPB-chloroform system. C_Q=4×10^{-5} mol dm^{-3}, C_B=10^{-5} mol dm^{-3}.

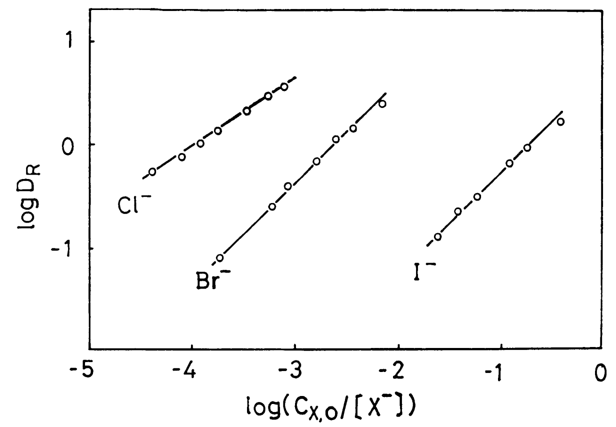

Fig. 7. Plot of Eq. 23 for *p*-NP-MIBK system. C_Q=10^{-4} mol dm^{-3}, C_R=5×10^{-5} mol dm^{-3}.

these values; the reason for this is not clear, but the difference in the degree of dissociation of ion pairs, or the extraction of some other species, such as QHB, QNaB, and QHR$_2$, may be considered to be responsible. As long as the slopes are similar for a certain pair of anions, however, it is possible for us to obtain the selectivity coefficient for the pair because the method adopted is based on the comparison of the concentrations of anions which give D_Y (or D'_T)=1 for the distribution of the indicator. The standard deviations for the values of the exchange constants in Tables 2—4 were around 0.06. They amounted to about 0.1 for exceptional cases where the experimental conditions were such that it was difficult to obtain the data with a satisfactory accuracy. From Tables 2—4, the logarithm of the selectivity coefficient for X_1 *vs.* X_2 can be estimated by means of the following equation:

Table 2. Exchange constants of MTOA salt (TTA)[a]

Solvent	log $K'_{X/T}$ (Eq. 13′)					
	Cl	Br	I	ClO$_4$	NO$_3$	SCN
Hexane	1.18 (0.9)[b]	2.09 (1.0)	3.90 (1.0)	5.41 (1.1)		
Xylene	1.26 (1.0)	2.49 (1.0)	4.51 (1.0)	6.57 (0.8)	3.25 (1.0)	5.44 (1.0)
	1.30*(1.0)	2.61*(1.0)	4.49*(0.9)		3.25*(0.9)	
Benzene	1.45 (0.8)	2.84 (1.0)	5.03 (1.0)	7.06 (0.9)		
Chloroform	4.22 (1.0)	5.60 (1.0)			5.48 (1.0)	6.84 (1.2)

a) Obtained from data at various C_X values at a constant pH (4—6), except for values marked with *, which were obtained from data at various pH values at a constant C_X (0.01—0.1 mol dm^{-3}), both at C_Q=(5—10)×10^{-5} mol dm^{-3} and C_T=5×10^{-5} mol dm^{-3}. b) Numbers in parentheses indicate the slope, *m*, obtained by the method of least squares.

TABLE 3. EXCHANGE CONSTANTS OF MTOA SALT (BPB)[a)]

Solvent	$\log K_{X/B}$ (Eq. 13)			
	Cl	Br	I	ClO_4
Xylene			−3.00(2.0)[b)]	−1.32(1.7)
Benzene			−2.84(2.0)	−1.20(2.0)
Carbon tetrachloride			−2.61(2.1)	−1.90(2.0)
Butyl acetate		−4.04(1.8)	−2.27(2.1)	−0.43(2.0)
Dichloromethane	−4.90(1.4)	−3.30(2.0)	−1.41(2.1)	−0.12(1.9)
Chloroform	−4.37(1.8)	−3.00(1.9)	−1.42(2.0)	−1.13(2.0)
4-Methyl-2-pentanone	−4.72(1.2)	−3.24(1.8)	−1.36(2.0)	1.26(1.4)
Nitrobenzene		−3.67(2.4)	−1.47(2.2)	0.71(1.7)
3-Methyl-1-butanol[c)]	−2.56(1.2)	−2.10(1.3)	−1.36(1.4)	−1.11(1.3)

a) Obtained from data at various C_X values at $C_Q=4\times10^{-5}$ mol dm^{-3} and $C_B=10^{-5}$ mol dm^{-3}. b) See Note b) in Table 2. c) Obtained at $C_Q=2\times10^{-4}$ mol dm^{-3} and $C_B=1.5\times10^{-5}$ mol dm^{-3}.

TABLE 4. EXCHANGE CONSTANTS OF MTOA SALT (*p*-NP)[a)]

Solvent	$\log K_{X/R}$ (Eq. 13)		
	Cl	Br	I
Carbon tetrachloride	−2.40(0.8)[b)]	−0.76(0.9)	1.53(0.8)
Butyl acetate	−3.72(0.6)	−2.50(0.8)	−0.79(0.8)
4-Methyl-2-pentanone	−3.98(0.7)	−2.64(1.0)	−0.73(1.0)
Nitrobenzene	−3.75(0.9)	−2.10(1.0)	0.16(1.0)

a) Obtained from data at various C_X values at $C_Q=10^{-4}$ mol dm^{-3} and $C_R=5\times10^{-5}$ mol dm^{-3}. b) See Note b) in Table 2.

TABLE 5. COMPARISON OF SELECTIVITY COEFFICIENTS OBTAINED BY DIFFERENT REAGENTS

Solvent	X_1	X_2	$\log K_{X_1/X_2}$ (Eq. 27)		
			HT	BPB	*p*-NP
Xylene	ClO_4	I	2.07	1.68	
Benzene	ClO_4	I	2.03	1.64	
Butyl acetate	I	Br		1.77	1.71
Chloroform	Br	Cl	1.38	1.37	
4-Methyl-2-pentanone	Br	Cl		1.48	1.34
	I	Br		1.88	1.91
Nitrobenzene	I	Br		2.20	2.26

TABLE 6. SUMMARY OF SELECTIVITY COEFFICIENTS OF MTOA SALT[a)] AND TDAH SALT[b)]

Solvent	$\log K_{X/Cl}$				
	MTOA			TDAH	
	Br	I	ClO_4	Br	I
Hexane	0.91	2.72	4.23		
Cyclohexane				0.96	2.40
Xylene	1.27	3.22	5.1		
Carbon tetrachloride	1.64	3.93	4.64	1.19	3.44
Benzene	1.39	3.58	5.4	1.00	2.48
Butyl acetate	1.22	2.96	4.80		
Dichloromethane	1.60	3.49	4.78		
Chloroform	1.37	2.95	3.24	0.80	1.75
4-Methyl-2-pentanone	1.41	3.31	5.93		
Nitrobenzene	1.65	3.88	6.06	0.92	2.22
3-Methyl-1-butanol	0.46	1.20	1.45		
Dowex-1[c)]	0.48	1.00	1.48		

a) When values obtained by different reagents disagreed, mathematical means were adopted. b) Calculated from K_{app} in Ref. 8. $K_{app}=C_{TDAH,o}/C_{TDA,o}a_{HX}$ at a total TDAHX concentration of 0.1 mol dm^{-3}. c) Ref. 11.

$$\log K_{X_1/X_2} = \log K_{X_1/Y} - \log K_{X_2/Y}. \tag{27}$$

As is shown in Table 5, the values obtained through the use of different indicators agreed with each other within the limits of experimental error, except for the cases of $\log K_{ClO_4/I}$ in xylene and benzene. These last two disagreements are beyond the limits of experimental errors, and further experiments must be carried out to understand the reason for these disagreements.

The selectivity coefficients of MTOA for the exchange of anions *vs.* Cl^- are summarized in Table 6, as are those of Dowex-1X8—10[11)] for purposes of comparison. The table indicates that the values of $\log K_{X/Cl}$ increase in the order $Br^- < I^- < ClO_4^-$ and are similar to each other for most of the solvents used in spite of the marked difference in their extraction power and in the chemical species of MTOACl in these solvents.

However, it is interesting to note that the solvent with a higher acceptor number has a lower selectivity for anions; such acidic solvents as 3-methyl-1-butanol and chloroform are inferior in selectivity to other solvents. Because of the specific interaction of alcohols in alkylammonium systems,[12)] 3-methyl-1-butanol is a good solvent for the extraction of MTOA salts, but its selectivity for anions is inferior to that of other solvents (about the same degree as solid-ion exchangers). Carbon tetrachloride and chloroform have abnormally small $\log K_{ClO_4/I}$ values. One possible explanation is the specific reaction of alkylammonium salt with halogenated hydrocarbons,[13] for example, the deprotonation of chloroform producing CCl_3^- anions and finally dichlorocarbene in a strongly alkaline solution, which is the important reaction in phase-transfer catalysis.[2]

MTOA salts and trialkylammonium salts, $(alkyl)_3NH^+X^-$, resemble each other in the general features of these selectivity. In Table 6, the selectivity coefficients of tridodecylammonium for the exchange of anions *vs.* Cl^- are also shown; they were estimated from the apparent extraction constant of TDAHX obtained by Müller and Diamond.[8] On the whole, the selectivity of MTOA for anions is higher than that of TDAH; the difference increases with both the polarity of the solvents and the size of the anions. These findings are compatible with the common understanding[1] that the higher substituted alkylammonium have higher selectivities.

In conclusion, a better extraction of MTOA salts can be obtained by the use of polar and acidic solvents; in the case of acidic solvents, however, there should be a low selectivity for anions. Therefore, in the extraction of anionic complexes of metal ions in the presence of a large excess of such acids as HCl and HNO_3, aromatic solvents will meet the requirement of selectivity at the cost of extractability. On the other hand, acidic solvents such as chloroform and alcohols may be used for the extraction of chelate complexes of metal ions from aqueous solutions at the sacrifice of selectivity. Polar, aprotic solvents, such as nitrobenzene and 4-methyl-2-pentanone, are considered to be the best, although they have other disadvantages in practical use.

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