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Distribution Studies of Alkali Metal Picrates

Tadashi IWACHIDO
College of Liberal Arts, Okayama University, Tsushima, Okayama
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Alkali metal picrates are extractable from an aqueous solution into nitrobenzene. The picrates exist mainly as the dissociated form in both the aqueous and the nitrobenzene phases, whereas picric acid exists mainly as the undissociated form in the organic phase. The distribution ratio of the picrates and picric acid at any pH can well be explained in terms of these equilibrium constants. The distribution coefficient of picric acid is evaluated to be $10^{2.63}$.

Polynitroderivatives of phenol and diphenylamine are known as extracting agents of alkali metal cations. However, little is known about the extraction mechanism. Only for alkali metal picrates1) and hexanitrodiphenylaminates,2) the distribution coefficient between aqueous and nitrobenzene phases and the association constants in the aqueous phase have been determined by means of the extraction method. As the association constants of the picrates in nitrobenzene phase, the values obtained by means of conductivity measurements have been cited. Such equilibrium constants show that these salts strongly dissociate in nitrobenzene as well as in the aqueous phase. From these data, it can be concluded that the distribution ratio of alkali metals increases with an increase in the dissociation constant in the organic phase and with a decrease in that in the aqueous phase. The present paper will describe that the introduction of the new constant, that is, the dissociation constant of picric acid in the aqueous phase and the distribution coefficient of the acid made it possible to interpret the dependence of the distribution ratio upon the pH of the aqueous solution.

Experimental

Reagents. All the alkali metal picrates except lithium salt were prepared by dissolving picric acid into an aqueous solution containing alkali metal hydroxide or carbonate. The resultant precipitates were recrystallized thrice from water containing a small amount of the corresponding alkali metal hydroxide or carbonate.

Citric acid-lithium citrate buffers (0.1 M) and 0.1 M phosphoric acid-lithium phosphate buffers were used to adjust the pH of the solution to pH 1.5—5 and pH 6—8 respectively.

Extraction. Into a 50-m*l* separatory funnel, 5 m*l* of a 1.000×10^{-2} M picric acid or alkali metal picrate solution were transferred; then the same volume of the buffer solution of a definite pH was added. The resultant aqueous solution was then shaken with 10 m*l* of nitrobenzene for two hours at 25°C.

Determination of Alkali Metal and Picrate Ions. The concentration of alkali metals extracted into the nitrobenzene was determined using an atomic absorption spectrophotometer (Nippon Jarrell Ash, Type AA-1); the concentration of picrate in the aqueous solution was estimated spectrophotometrically at 353 mμ after diluting the solution 250 times with water, and the pH of the solution was adjusted at pH 12. The nitrobenzene existing as a contaminant in the aqueous solution also shows an appreciable absorbance at the same wavelength, but in such a high dilution as 250 times the interference can be almost extinguished.

After equilibration, the pH of the aqueous solution was measured in order to analyse the distribution equilibrium.

Theoretical

Writing the formulae for picric acid and alkali metal picrates as HR and MR respectively, the reactions involved can be represented schematically as in Fig. 1.

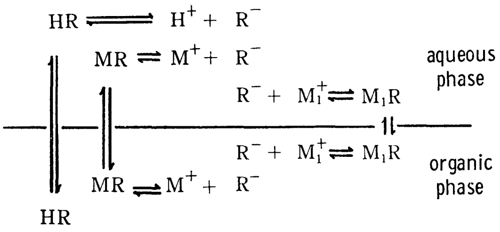

Fig. 1. Schematic representation of the equilibria involved in the extraction.

1) Dissociation of Picric Acid.

$$\mathrm{HR} \rightleftarrows \mathrm{H^+ + R^-} \qquad K_a^{\mathrm{HR}} = \frac{[\mathrm{H^+}]_a[\mathrm{R^-}]_a}{[\mathrm{HR}]_a} \tag{1}$$

2) Association of Alkali Metal Picrates.

$$\mathrm{M^+ + R^-} \rightleftarrows \mathrm{MR} \qquad K_a^{\mathrm{MR}} = \frac{[\mathrm{MR}]_a}{[\mathrm{M^+}]_a[\mathrm{R^-}]_a} \tag{2}$$

$$K_o^{\mathrm{MR}} = \frac{[\mathrm{MR}]_o}{[\mathrm{M^+}]_o[\mathrm{R^-}]_o} \tag{3}$$

$$\mathrm{M_I^+ + R^-} \rightleftarrows \mathrm{M_IR} \qquad K_a^{\mathrm{M_IR}} = \frac{[\mathrm{M_IR}]_a}{[\mathrm{M_I^+}]_a[\mathrm{R^-}]_a} \tag{4}$$

$$K_o^{\mathrm{M_IR}} = \frac{[\mathrm{M_IR}]_o}{[\mathrm{M_I^+}]_o[\mathrm{R^-}]_o} \tag{5}$$

3) Distribution of the Neutral Molecules.

$$D^{\mathrm{HR}} = \frac{[\mathrm{HR}]_o}{[\mathrm{HR}]_a} \quad (6) \qquad D^{\mathrm{MR}} = \frac{[\mathrm{MR}]_o}{[\mathrm{MR}]_a} \quad (7)$$

$$D^{\mathrm{M_IR}} = \frac{[\mathrm{M_IR}]_o}{[\mathrm{M_IR}]_a} \tag{8}$$

In these equilibrium expressions, the a and o subscripts refer to the aqueous and the organic phases respectively; the brackets, to the molar concentration, and $\mathrm{M_I^+}$, to a competing cation. As the competing cation it is desirable to choose a cation which associ-

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1) M. Yamane, T. Iwachido, and K. Tôei, This Bulletin **44**, 745 (1971).

2) S. Motomizu, K. Tôei, and T. Iwachido, *ibid.*, **42**, 1006 (1969).

ates with the picrate ion most weakly in the aqueous solution and most strongly in nitrobenzene. In the present case, the lithium ion suits this purpose.

i) Distribution of Picric Acid. The distribution ratio or the concentration ratio of the reagent species at equilibrium between the two phases can be written as:

$$q^{\mathrm{R}} = \frac{[\mathrm{HR}]_\mathrm{o}+[\mathrm{MR}]_\mathrm{o}+[\mathrm{M_IR}]_\mathrm{o}+[\mathrm{R}^-]_\mathrm{o}}{[\mathrm{HR}]_\mathrm{a}+[\mathrm{MR}]_\mathrm{a}+[\mathrm{M_IR}]_\mathrm{a}+[\mathrm{R}^-]_\mathrm{a}} \tag{9}$$

Each of the last three terms in the numerator can be expressed in terms of the corresponding constants as follows:

$$[\mathrm{MR}]_\mathrm{o} = \frac{D^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{HR}}[\mathrm{M}^+]_\mathrm{a}}{D^{\mathrm{HR}}\quad[\mathrm{H}^+]_\mathrm{a}}[\mathrm{HR}]_\mathrm{o} \tag{10}$$

$$[\mathrm{M_IR}]_\mathrm{o} = \frac{D^{\mathrm{M_IR}}K_\mathrm{a}{}^{\mathrm{M_IR}}K_\mathrm{a}{}^{\mathrm{HR}}[\mathrm{M_I}^+]_\mathrm{a}}{D^{\mathrm{HR}}\quad[\mathrm{H}^+]_\mathrm{a}}[\mathrm{HR}]_\mathrm{o} \tag{11}$$

$$[\mathrm{R}^-]_\mathrm{o} = \frac{D^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{HR}}[\mathrm{M}^+]_\mathrm{a}}{D^{\mathrm{HR}}K_\mathrm{o}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{o}[\mathrm{H}^+]_\mathrm{a}}[\mathrm{HR}]_\mathrm{o} \tag{12}$$

Thus, substituting Eqs. (10), (11), and (12) into Eq. (9) gives the equation:

$$q^{\mathrm{R}} = D^{\mathrm{HR}}\frac{1+\left\{\left(1+\dfrac{1}{K_\mathrm{o}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{o}}\right)D^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{a}+D^{\mathrm{M_IR}}K_\mathrm{a}{}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_\mathrm{a}\right\}\dfrac{K_\mathrm{a}{}^{\mathrm{HR}}}{D^{\mathrm{HR}}[\mathrm{H}^+]_\mathrm{a}}}{1+(1+K_\mathrm{a}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{a}+K_\mathrm{a}{}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_\mathrm{a})\dfrac{K_\mathrm{a}{}^{\mathrm{HR}}}{[\mathrm{H}^+]_\mathrm{a}}} \tag{13}$$

A useful approximation for q^{R} may be obtained from Eq. (13) by making the appropriate assumptions.

(a) If the fourth term in the numerator is assumed to be small enough compared to the second and the third, Eq. (13) can be simplified to:

$$q^{\mathrm{R}} = D^{\mathrm{HR}}\frac{1+\left\{\left(1+\dfrac{1}{K_\mathrm{o}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{o}}\right)\dfrac{D^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{HR}}[\mathrm{M}^+]_\mathrm{a}}{D^{\mathrm{HR}}[\mathrm{H}^+]_\mathrm{a}}\right\}}{1+(1+K_\mathrm{a}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{a}+K_\mathrm{a}{}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_\mathrm{a})\dfrac{K_\mathrm{a}{}^{\mathrm{HR}}}{[\mathrm{H}^+]_\mathrm{a}}} \tag{14}$$

(b) If the alkali metals are absent in this system, Eq. (13) can be further simplified to the well-known equation:

$$q^{\mathrm{R}} = \frac{D^{\mathrm{HR}}}{1+\dfrac{K_\mathrm{a}{}^{\mathrm{HR}}}{[\mathrm{H}^+]_\mathrm{a}}} \tag{15}$$

Equation (13) is the most general expression, but practically Eq. (14) may be the most convenient.

When the aqueous solution is sufficiently acidic, the second and the succeeding terms in the numerator of Eq. (14) may be neglected compared to the first, and in the denominator the first term may be negligible. Thus, Eq. (14) can be simplified to:

$$q^{\mathrm{R}} = \frac{D^{\mathrm{HR}}}{(1+K_\mathrm{a}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{a}+K_\mathrm{a}{}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_\mathrm{a})K_\mathrm{a}{}^{\mathrm{HR}}}[\mathrm{H}^+]_\mathrm{a} \tag{16}$$

The concentration of alkali metals in the aqueous solution can be regarded as constant, because the amounts of these salts extracted into nitrobenzene are very small. Hence, q^{R} becomes a function of pH alone. A plot of log q^{R} *vs.* pH will give a straight line with a slope of -1, and from the intercept we can calculate the ratio of the distribution coefficient to the dissociation constant of picric acid, $D^{\mathrm{HR}}/K_\mathrm{a}{}^{\mathrm{HR}}$. If the constant, $K_\mathrm{a}{}^{\mathrm{HR}}$, is known, D^{HR} can be calculated.

On the other hand, when the aqueous solution is sufficiently alkaline, the second and the succeeding terms in both the numerator and the denominator of Eq. (14) will become much larger than the first, giving:

$$q^{\mathrm{R}} = \frac{\left(1+\dfrac{1}{K_\mathrm{o}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{o}}\right)D^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{a}}{1+K_\mathrm{a}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{a}+K_\mathrm{a}{}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_\mathrm{a}} \tag{17}$$

If $[\mathrm{M}^+]_0$ is assumed to reach a certain constant value under sufficiently alkaline conditions, q^{R} may become a constant value in such a pH region.

The pH value at the intersection of the two constant-slope portions represented by Eqs. (16) and (17) may be calculated using the following equation:

$$[\mathrm{H}^+]_\mathrm{a} = \left(1+\frac{1}{K_\mathrm{o}{}^{\mathrm{MR}}[\mathrm{M}^+]_\mathrm{o}}\right)\frac{D^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{MR}}K_\mathrm{a}{}^{\mathrm{HR}}[\mathrm{M}^+]_\mathrm{a}}{D^{\mathrm{HR}}} \tag{18}$$

ii) Distribution of Alkali Metals. At equilibrium, the distribution of alkali metals between the two phases can be written as:

$$q^{\mathrm{M}} = \frac{[\mathrm{MR}]_\mathrm{o}+[\mathrm{M}^+]_\mathrm{o}}{[\mathrm{MR}]_\mathrm{a}+[\mathrm{M}^+]_\mathrm{a}} \tag{19}$$

The total concentrations of the reagent, C^{R}, and of alkali metals, C^{M}, are represented as:

$$C^{\mathrm{R}} = [\mathrm{HR}]_\mathrm{a}+[\mathrm{HR}]_\mathrm{o}+[\mathrm{MR}]_\mathrm{a}+[\mathrm{MR}]_\mathrm{o}+[\mathrm{M_IR}]_\mathrm{a}+[\mathrm{M_IR}]_\mathrm{o}+[\mathrm{R}^-]_\mathrm{a}+[\mathrm{R}^-]_\mathrm{o} \tag{20}$$

$$C^{\mathrm{M}} = [\mathrm{MR}]_\mathrm{a}+[\mathrm{MR}]_\mathrm{o}+[\mathrm{M}^+]_\mathrm{a}+[\mathrm{M}^+]_\mathrm{o} \tag{21}$$

The electroneutrality in the organic phase is expressed as:

$$[\mathrm{R}^-]_\mathrm{o} = [\mathrm{M}^+]_\mathrm{o}+[\mathrm{M_I}^+]_\mathrm{o} \tag{22}$$

Combining Eqs. (20), (21), and (22) and solving for $[\mathrm{R}^-]_\mathrm{a}$ gives the following relationships:

$$C^{\mathrm{R}}-C^{\mathrm{M}} = [\mathrm{HR}]_\mathrm{a}+[\mathrm{HR}]_\mathrm{o}+[\mathrm{M_IR}]_\mathrm{a}+[\mathrm{M_IR}]_\mathrm{o}+[\mathrm{R}^-]_\mathrm{a}-[\mathrm{M}^+]_\mathrm{a}+[\mathrm{M_I}^+]_\mathrm{o} \tag{23}$$

$$\frac{1}{[\mathrm{R}^-]_\mathrm{a}} = \frac{1+\dfrac{(1+D^{\mathrm{HR}})}{K_\mathrm{a}{}^{\mathrm{HR}}}[\mathrm{H}^+]_\mathrm{a}+(1+D^{\mathrm{M_IR}})K_\mathrm{a}{}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_\mathrm{a}}{C^{\mathrm{R}}-C^{\mathrm{M}}+[\mathrm{M}^+]_\mathrm{a}-[\mathrm{M_I}^+]_\mathrm{o}} \tag{24}$$

On the other hand, the rearrangement of Eq. (19) gives:

$$q^{\mathrm{M}} = \frac{[\mathrm{MR}]_\mathrm{o}\left(1+\dfrac{1}{K_\mathrm{o}{}^{\mathrm{MR}}[\mathrm{R}^-]_\mathrm{o}}\right)}{[\mathrm{MR}]_\mathrm{a}\left(1+\dfrac{1}{K_\mathrm{a}{}^{\mathrm{MR}}[\mathrm{R}^-]_\mathrm{a}}\right)} \tag{25}$$

The substitution of Eq. (24) into Eq. (25) gives this useful expression:

$$q^{\mathrm{M}} = D^{\mathrm{MR}} \frac{\left\{1 + \dfrac{1}{K_{\mathrm{o}}^{\mathrm{MR}}[\mathrm{R}^-]_{\mathrm{o}}}\right\}}{\left\{1 + \dfrac{1 + (1 + D^{\mathrm{HR}})[\mathrm{H}^+]_{\mathrm{a}}/K_{\mathrm{a}}^{\mathrm{HR}} + (1 + D^{\mathrm{M_IR}})K_{\mathrm{a}}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_{\mathrm{a}}}{K_{\mathrm{a}}^{\mathrm{MR}}(C^{\mathrm{R}} - C^{\mathrm{M}} + [\mathrm{M}^+]_{\mathrm{a}} - [\mathrm{M_I}^+]_{\mathrm{o}})}\right\}} \tag{26}$$

If the extraction is carried out when $C^{\mathrm{R}} - C^{\mathrm{M}} = 0$, Eq. (26) reduces to:

$$q^{\mathrm{M}} = D^{\mathrm{MR}} \frac{\left\{1 + \dfrac{1}{K_{\mathrm{o}}^{\mathrm{MR}}([\mathrm{M}^+]_{\mathrm{o}} + [\mathrm{M_I}^+]_{\mathrm{o}})}\right\}}{\left\{1 + \dfrac{1 + (1 + D^{\mathrm{HR}})[\mathrm{H}^+]_{\mathrm{a}}/K_{\mathrm{a}}^{\mathrm{HR}} + (1 + D^{\mathrm{M_IR}})K_{\mathrm{a}}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_{\mathrm{a}}}{K_{\mathrm{a}}^{\mathrm{MR}}([\mathrm{M}^+]_{\mathrm{a}} - [\mathrm{M_I}^+]_{\mathrm{o}})}\right\}} \tag{27}$$

Equation (27) is so complex that the dependence of the q^{M} value upon the pH can not be understood easily from the equation. However, a useful approximation for q^{M} may be obtained from Eq. (27) by making the following assumptions:

a) that the concentration of alkali metals in the aqueous solution is much greater than that of the competing ion in the organic phase: $[\mathrm{M}^+]_{\mathrm{a}} \gg [\mathrm{M_I}^+]_{\mathrm{o}}$;

b) that the distribution coefficient of lithium picrate is negligible compared to 1, whereas that of picric acid is much larger than 1: $1 \gg D^{\mathrm{M_IR}}$ and $D^{\mathrm{HR}} \gg 1$;

c) that the dissociated species are dominant in both phases: $q^{\mathrm{M}} \approx [\mathrm{M}^+]_{\mathrm{o}}/[\mathrm{M}^+]_{\mathrm{a}}$ and

d) that the concentration of metal ions to be tested in the organic phase is much larger than that of the lithium ion: $[\mathrm{M}^+]_{\mathrm{o}} \gg [\mathrm{M_I}^+]_{\mathrm{o}}$. In this manner, Eq. (27) can be simplified to the following expression:

$$(q^{\mathrm{M}})^2 = D^{\mathrm{MR}} \frac{\left([\mathrm{M}^+]_{\mathrm{o}} + \dfrac{1}{K_{\mathrm{o}}^{\mathrm{MR}}}\right)}{\left\{[\mathrm{M}^+]_{\mathrm{a}} + \dfrac{1}{K_{\mathrm{a}}^{\mathrm{MR}}}\left(1 + \dfrac{D^{\mathrm{HR}}}{K_{\mathrm{a}}^{\mathrm{HR}}}[\mathrm{H}^+]_{\mathrm{a}} + K_{\mathrm{a}}^{\mathrm{M_IR}}[\mathrm{M_I}^+]_{\mathrm{a}}\right)\right\}} \tag{28}$$

When the aqueous solution is sufficiently acidic, the third term in the denominator will become by far larger than the residual terms, and the first term in the numerator, much smaller than the second, thus yielding:

$$(q^{\mathrm{M}})^2 = \frac{D^{\mathrm{MR}}K_{\mathrm{a}}^{\mathrm{MR}}K_{\mathrm{a}}^{\mathrm{HR}}}{K_{\mathrm{o}}^{\mathrm{MR}}D^{\mathrm{HR}}} \frac{1}{[\mathrm{H}^+]_{\mathrm{a}}} \tag{29}$$

A plot of log q^{M} *vs.* pH gives a straight line with a slope of 1/2, and the intercept is given by 1/2 log-$D^{\mathrm{MR}}K_{\mathrm{a}}^{\mathrm{MR}}K_{\mathrm{a}}^{\mathrm{HR}}/K_{\mathrm{o}}^{\mathrm{MR}}D^{\mathrm{HR}}$.

Alternatively, when the aqueous solution is kept sufficiently alkaline, the term involving $[\mathrm{H}^+]_{\mathrm{a}}$ can be neglected; hence, Eq. (28) reduces to:

$$(q^{\mathrm{M}})^2 = D^{\mathrm{MR}} \frac{\left([\mathrm{M}^+]_{\mathrm{o}} + \dfrac{1}{K_{\mathrm{o}}^{\mathrm{MR}}}\right)}{\left([\mathrm{M}^+]_{\mathrm{a}} + \dfrac{1}{K_{\mathrm{a}}^{\mathrm{MR}}} + \dfrac{K_{\mathrm{a}}^{\mathrm{M_IR}}}{K_{\mathrm{a}}^{\mathrm{MR}}}[\mathrm{M_I}^+]_{\mathrm{a}}\right)} \tag{30}$$

Since $[\mathrm{M}^+]_{\mathrm{a}}$ and $[\mathrm{M}^+]_{\mathrm{o}}$ remain almost constant, as has been mentioned, a plot of log q^{M} *vs.* pH gives a horizontal line.

The logarithm of the q^{M}-pH curve appears as two constant-slope portions joined by a short curve; the point of intersection can be calculated from Eq. (28) by assuming $[\mathrm{M}^+]_{\mathrm{o}} \ll 1/K_{\mathrm{o}}^{\mathrm{MR}}$:

$$\frac{1}{[\mathrm{H}^+]_{\mathrm{a}}} = \frac{D^{\mathrm{HR}}}{(K_{\mathrm{a}}^{\mathrm{MR}}[\mathrm{M}^+]_{\mathrm{a}} + 1 + K_{\mathrm{a}}^{\mathrm{M_IR}})K_{\mathrm{a}}^{\mathrm{HR}}} \tag{31}$$

Equation (31) shows that the value of $D^{\mathrm{HR}}/K_{\mathrm{a}}^{\mathrm{HR}}$ can be obtained not only from the log q^{R}-pH curve, but also from the log q^{M}-pH curve.

Results and Discussion

i) Equilibria Involved in the Extraction System. The equilibria shown in Fig. 1 are fundamental ones. Of course, these simple expressions are used for convenience to represent the possible complex equilibria in which the solvent molecules participate. Some other equilibria, such as:

$$2\mathrm{HR} \rightleftarrows (\mathrm{HR})_2$$

$$\mathrm{RHR}^- \rightleftarrows \mathrm{HR} + \mathrm{R}^- \qquad K_{\mathrm{o}}^{\mathrm{RHR}^-} = \frac{[\mathrm{HR}]_{\mathrm{o}}[\mathrm{R}^-]_{\mathrm{o}}}{[\mathrm{RHR}^-]_{\mathrm{o}}}$$

$$\mathrm{HR} \rightleftarrows \mathrm{H}^+ + \mathrm{R}^- \qquad K_{\mathrm{o}}^{\mathrm{HR}} = \frac{[\mathrm{H}^+]_{\mathrm{o}}[\mathrm{R}^-]_{\mathrm{o}}}{[\mathrm{HR}]_{\mathrm{o}}}$$

may exist. As has been pointed out by Moore[3] and Brønsted,[4] the dimerization of picric acid need not be considered in the aqueous phase or even in the organic phase. Kolthoff[5] and his collaborators have mentioned that a homoconjugation reaction of picrate anions may be expected to exist in a nitrobenzene solution, and that the dissociation constant evaluated from the solubility measurements is above 10^{-2}. In the same paper, he has also estimated spectrophotometrically the dissociation constant for picric acid in nitrobenzene to be 3.5×10^{-8} at 25°C. Judging from the magnitude of the constants, these reactions were assumed not to be taken into account under the present experimental conditions.

The association constants and the distribution coefficients of the alkali metal picrates are listed in Table 1. It must be noted that $K_{\mathrm{o}}^{\mathrm{MR}}$ in this table is used to designate the association constant of the picrates in water-saturated nitrobenzene in place of the $K_{\mathrm{o}}^{\mathrm{MR}}{}_{(\mathrm{H_2O})}$ in the original paper.[1]

ii) Distribution of Picric Acid. Plots of log-q^{R} *vs.* pH are shown in Figs. 2 to 6. Each curve gives a straight line with a slope of exactly -1 in a suf-

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[3] T. S. Moore, E. Shepard, and E. Goodall, *J. Chem. Soc.*, **1931**, 1447.

[4] J. N. Brønsted and R. P. Bell, *J. Amer. Chem. Soc.*, **53**, 2478 (1931).

[5] I. M. Kolthoff, D. Stŏcesocá, and T. S. Lee, *ibid.*, **75**, 1834 (1953).

TABLE 1. ASSOCIATION AND DISTRIBUTION CONSTANTS FOR ALKALI METAL PICRATES

Constants	Picric acid	Li-Pic	Na-Pic[1]	K-Pic[1]	Rb-Pic[1]	Cs-Pic[1]
K_a^{MR}	$10^{-0.42}$ [6] [a]	$10^{1.13}$ [b]	$10^{1.38}$	$10^{1.64}$	$10^{1.94}$	$10^{2.07}$
K_o^{MR}	$10^{-7.46}$ [a]	$10^{5.80}$ [5]	$10^{3.67}$	$10^{2.92}$	$10^{2.65}$	$10^{2.43}$
D^{MR}	$10^{2.63}$	$10^{-3.05}$ [b]	$10^{-2.55}$	$10^{-1.85}$	$10^{-1.68}$	$10^{-1.17}$

a) Dissociation constants. b) Estimated values.

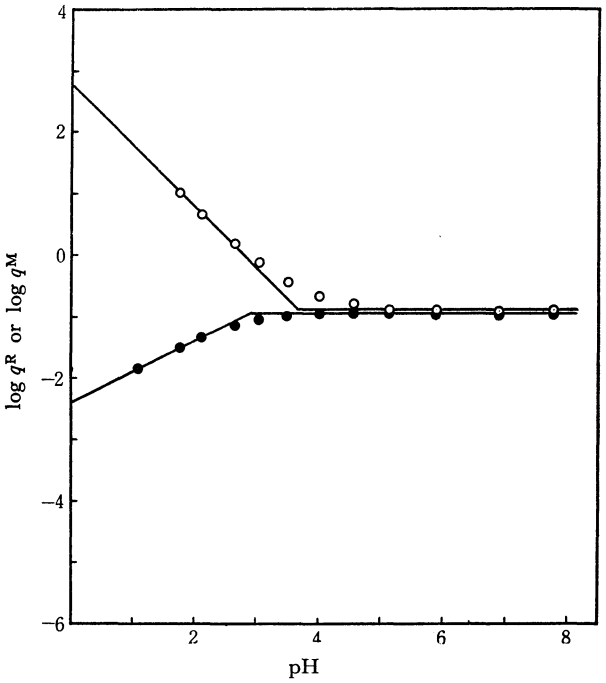

Fig. 2. The distribution of cesium picrate.
log q^R - pH, open circles; log q^M - pH, solid circles.
q^R: open circles, q^M: solid circles

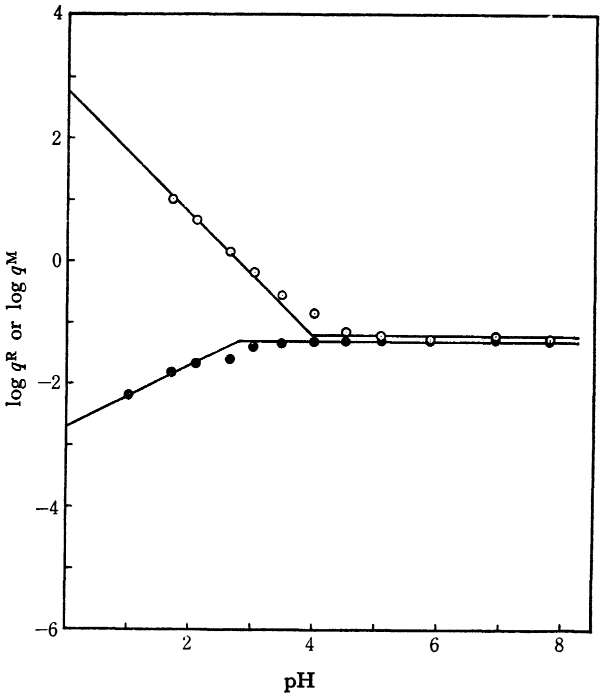

Fig. 3. The distribution of rubidium picrate.
log q^R - pH, open circles; log q^M - pH, solid circles.

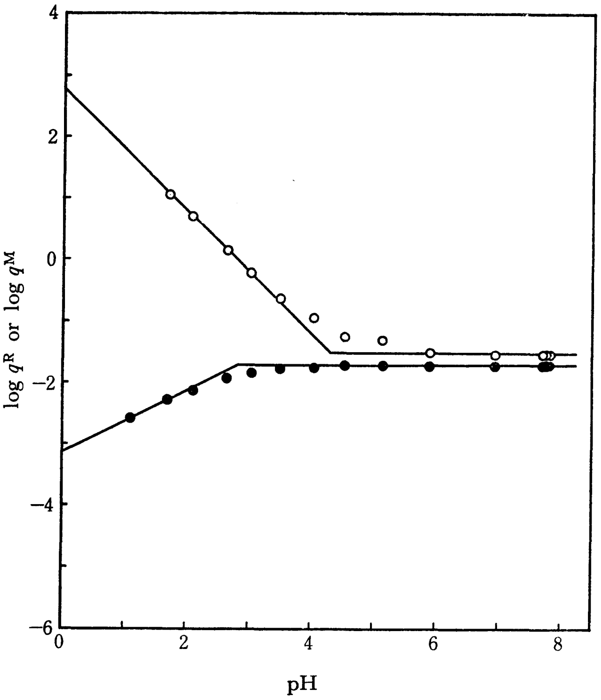

Fig. 4. The distribution of potassium picrate.
log q^R - pH, open circles; log q^M - pH, solid circles.

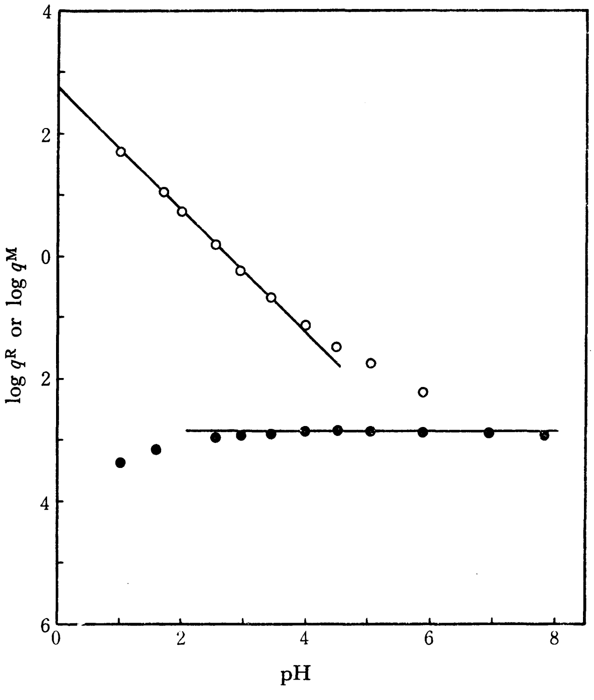

Fig. 5. The distribution of sodium picrate.
log q^R - pH, open circles; log q^M - pH, solid circles.

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[6] H. v. Halban and M. Seiler, *Helv. Chim. Acta*, **21**, 385 (1938).

Table 2. Constants characteristic of log q^R-pH curves

Salts	Intercept at pH=0	D^{HR}/K_a^{HR}	D^{HR}	pH-independent q^R values		$[H^+]_a$ values at the intersection	
				(Meas.)	(Calcd.)	(Meas.)	(Calcd.)
Li-Pic	$10^{2.78}$	$10^{3.00}$	$10^{2.58}$				
Na-Pic	$10^{2.77}$	$10^{3.02}$	$10^{2.60}$		$10^{-2.20}$		
K-Pic	$10^{2.74}$	$10^{3.02}$	$10^{2.60}$	$10^{-1.43}$	$10^{-1.64}$	$10^{-4.19}$	$10^{-4.48}$
Rb-Pic	$10^{2.77}$	$10^{3.09}$	$10^{2.67}$	$10^{-1.19}$	$10^{-1.33}$	$10^{-3.93}$	$10^{-4.13}$
Cs-Pic	$10^{2.77}$	$10^{3.12}$	$10^{2.70}$	$10^{-0.88}$	$10^{-0.83}$	$10^{-3.68}$	$10^{-3.60}$

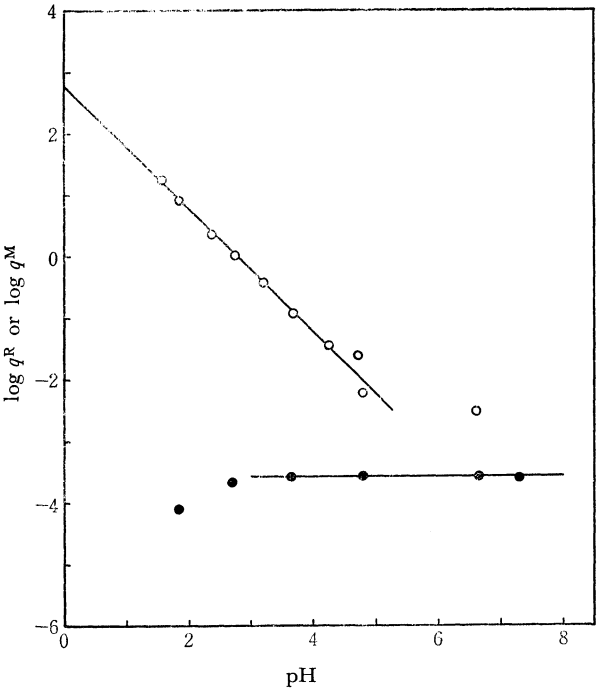

Fig. 6. The distribution of lithium picrate.
log q^R - pH, open circles; log q^M - pH, solid circles.

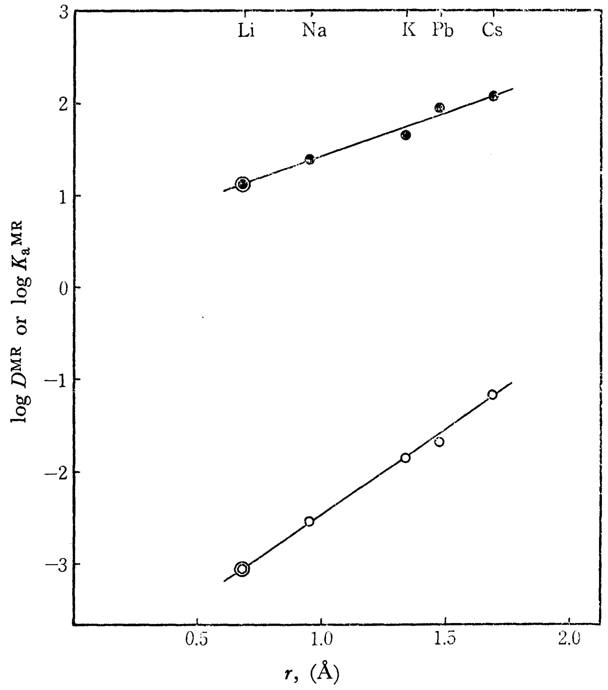

Fig. 7. The evaluation of the distribution constant and the association constant of lithium picrate in aqueous solution.
Distribution constant: open circle
Association constant: solid circle

ficiently acidic solution. A horizontal line was observed only in the extraction of potassium, rubidium, and cesium picrates, which is in accord with the expectation based on Eq. (17). As the errors inherent in the spectrophotometric method are of the order of 1 per cent, small distribution ratios below 10^{-2} can not be determined accurately. Therefore, the values of q^R below $10^{-2.5}$ are not shown in these figures. This is the case for lithium and sodium picrates.

The values of D^{HR}/K_a^{HR} are estimated to be approximately $10^{3.05}$. The evaluation of D^{HR} requires the dissociation constant for picric acid in water saturated with nitrobenzene. For the lack of available data on K_a^{HR}, the constant was replaced by the one obtained in an aqueous solution. The D^{HR} values thus obtained are listed in the fourth column of Table 2. These five values are close to each other within the limits of experimental error, and the mean value, $10^{2.63}$, is in fairly good agreement with $10^{2.41}$.[7] The totals concentration of the picrate ions existing in both phases at a sufficiently high pH were 4.96×10^{-3}, 4.98×10^{-3}, 4.95×10^{-3}, 4.97×10^{-3}, and 4.94×10^{-3} M for lithium, sodium, potassium, rubidium, and cesium picrates respectively. This shows that the accuracy of the experiments is satisfactory.

iii) Estimation of $K_a^{M_IR}$, D^{M_IR}, *and* $K_o^{M_IR}$.
Due to the very low extractability of lithium picrate, $K_a^{M_IR}$ and D^{M_IR} can not be determined by the extraction method.[1] For the other alkali metal picrates, a plot of log K_a^{MR} or log D^{MR} *vs.* the ionic radii of these cations helps in the evaluation of these values for lithium picrate. The linear extrapolation of each line to r=0.68 Å gives the approximate values of $K_a^{M_IR}$ and D^{M_IR} (Fig. 7). However, the validity of such an approximation is difficult to justify.

Witschonke and Kraus[8] have reported that the dissociation constant of lithium picrate in nitrobenzene containing 0.03 M water is $10^{5.80}$. The dissociation constant tends to increase with the water content in nitrobenzene. Therefore, a somewhat greater value than $10^{5.80}$ might be expected with water-saturated (0.1 M)

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

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

TABLE 3. CONSTANTS CHARACTERISTIC OF log q^M-pH CURVES

Salts	Intercept at pH=0		pH-independent q^M values				$[H^+]_a$ values at the intersection	
	(Meas)	(Calcd)	(Meas)	(Calcd by Eq. (32))	(Calcd by Eq. (30))	(Calcd by Eq. (27))	(Meas)	(Calcd)
Na-Pic	10^{-4}	$10^{-3.91}$	$10^{-2.85}$	$10^{-2.42}$	$10^{-2.54}$	$10^{-2.71}$	10^{-2}	$10^{-2.77}$
K-Pic	$10^{-3.11}$	$10^{-3.08}$	$10^{-1.73}$	$10^{-1.57}$	$10^{-1.69}$	$10^{-1.69}$	$10^{-2.80}$	$10^{-2.74}$
Rb-Pic	$10^{-2.68}$	$10^{-2.74}$	$10^{-1.30}$	$10^{-1.18}$	$10^{-1.33}$	$10^{-1.37}$	$10^{-2.76}$	$10^{-2.77}$
Cs-Pic	$10^{-2.39}$	$10^{-2.33}$	$10^{-0.94}$	$10^{-0.77}$	$10^{-0.91}$	$10^{-0.85}$	$10^{-2.92}$	$10^{-2.77}$

nitrobenzene; however, because of the lack of a way to estimate the extent of the effect, $K_o^{M_IR}$ is approximated by $10^{5.80}$ in the present paper.

iv) Distribution of Alkali Metal Picrate. Figures 2 to 6 show a plot of log q^M *vs.* pH by means of solid circles. Each curve consists of two constant-slope portions; that is, one is a line with a constant slope of 1/2, and the other, a horizontal line independent of the pH. These results are in good accord with the expectations based on the formulation.

The q^M values at the intercepts of the log q^M-pH curves agree well with those to be expected from Eq. (29), as is shown in Table 3. For sodium and lithium picrates, the q^M values below pH 2 were so erroneous that the values measured in this pH region are shown without drawing a line.

The pH-independent q^M values obtained and calculated by means of Eq. (30) are listed in the fourth and the sixth columns of Table 3 respectively. The values increased in proceeding from sodium to cesium, and the agreement between the observed and the calculated values was satisfacotry. It must be noted that the such q^M values can also be approximated by the following equation:

$$(q^M)^2 = \frac{D^{MR}K_a^{MR}}{K_o^{MR}} \tag{32}$$

The fifth column of Table 3 shows that such a simple relationship is still valid for potassium, rubidium, and cesium picrates.

Figures 2 to 4 show that, in both the log q^M-pH and the log q^R-pH curves, the q^M and q^R values tend to approach each other in the high pH region. The situation can be well understood by rewriting Eq. (17) as follows:

$$q^R = \frac{\left(1+\frac{1}{K_o^{MR}[M^+]_o}\right)D^{MR}K_a^{MR}[M^+]_a}{1+K_a^{MR}[M^+]_a+K_a^{M_IR}[M_I{}^+]_a} \tag{17}$$

$$= D^{MR}\frac{\left(\frac{1}{K_o^{MR}}+[M^+]_o\right)}{\left(\frac{1}{K_a^{MR}}+[M^+]_a+\frac{K_a^{M_IR}}{K_a^{MR}}[M_I{}^+]_a\right)}\frac{[M^+]_a}{[M^+]_o} \tag{17a}$$

The approximation of $[M^+]_a/[M^+]_o$ by $1/q^M$ gives:

$$q^Rq^M \approx D^{MR}\frac{\left(\frac{1}{K_o^{MR}}+[M^+]_o\right)}{\left(\frac{1}{K_a^{MR}}+[M^+]_a+\frac{K_a^{M_IR}}{K_a^{MR}}[M_I{}^+]_a\right)} \tag{33}$$

The term on the right-hand side of the above equation is identical with $(q^M)^2$ (cf. Eq. (30)), so Eq. (33) reduces to:

$$q^R \approx q^M \tag{34}$$

Such a relationship can also be directly derived from Eq. (9) in a somewhat different manner. If the aqueous solution is kept sufficiently alkaline, the hydrolysis of the picrate ions can be neglected. Thus, Eq. (9) reduces to:

$$q^R = \frac{[M_IR]_o+[MR]_o+[R^-]_o}{[M_IR]_a+[MR]_a+[R^-]_a} \tag{35}$$

If $[M_IR]_a$ and $[M_IR]_o$ are assumed to be negligibly small, $[R^-]_a$ and $[R^-]_o$ in Eq. (35) can be replaced by $[M^+]_a$ and $[M^+]_o$ respectively, because C^R and C^M are kept equal in the present case. This leads to the same relationship:

$$q^R \approx q^M$$

The eighth column in Table 3 shows that the pH value at the intersection of these two constant-slope portions is characteristic of all the picrates, as is to be expected from Eq. (31). The agreement between the observed and the calculated values is very good. This means that, from the intersect, the D^{HR}/K_a^{HR} value can be calculated correctly in the opposite sense.

v) Corrections for the Competing Ions. In the above treatments, the lithium ions in the organic phase have been neglected. Since appreciable amounts of lithium picrate are also extractable by nitrobenzene, as is shown in Fig. 6, the effect of the lithium ions must be taken into account when a stricter treatment is required. Equation (27) is useful for this purpose. The pH-independent q^M values as corrected by the equation are shown in the seventh column of Table 3. As might be expected, the corrections are larger for sodium picrate; this results in a marked improvement of the agreement between the observed and the calculated values. These facts may indicate the validity of the values ($K_a^{M_IR}$ and D^{M_IR}) estimated by the graphical method.

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