BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1746—1751 (1972)

Distribution Studies of the Potassium Salts with Hexanitrodiphenylamine and Analogous Acids

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(Received December 16, 1971)

The association constants of potassium salts with 2,4,6,2′,4′,6′-hexanitrodiphenylamine (hexyl), *N*-(2,4,6-trinitrobenzo)-2,4-dinitro-1-naphthylamine (α-hexyl), and 1,3,7,9-tetranitrophenothiazine-5-oxide (thiohexyl) in the nitrobenzene phase were determined conductometrically. The distribution constants and the association constants of these salts in an aqueous phase were determined simultaneously by means of solvent extraction. The dissociation constants in the aqueous phase and the distribution constants of the acids were estimated from an analysis of the curve obtained by plotting the distribution ratios of the metal or the acids against the pH. The results show that these salts exist mainly in the dissociated form in both phases. The applicability of the proposed distribution mechanism was also discussed.

In a previous paper,[1] the extraction mechanism of the alkali metal picrates into nitrobenzene has been discussed. This paper will show that the distribution of alkali metals or picric acid can well be explained in terms of the association constants of the salts in both the aqueous and the nitrobenzene phases, in terms of the dissociation constant of picric acid in the aqueous phase, and in terms of the distribution constants of the salts.

The distribution ratio of the alkali metals increases with a decrease in the association constant in the nitrobenzene phase and with an increase in that in the aqueous phase. In an earlier work,[2] it has been shown that some amine derivatives have a high extractability for potassium (% E=60 or more), even in the presence of much greater amounts of lithium ions (added as a buffer solution, $[Li^+]/[K^+]=100$—1000), which is quite different from the case of potassium picrates (%E=2, when $[Li^+]/[K^+]=100$). The present paper will describe how the extraction mechanism established for alkali metal picrates is also useful for weak and bulky acids, such as hexyl, α-hexyl, and thiohexyl. The amounts of lithium ions in the aqueous phase are decisive for the determination of the

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[1] T. Iwachido, This Bulletin, **45**, 432 (1972).

[2] T. Iwachido, *ibid.*, **44**, 1835 (1971).

distribution ratio of potassium, especially at an alkaline pH.

Experimental

Reagents. Potassium salt with hexyl was prepared by dissolving commercially-available hexyl into a hot aqueous solution containing potassium carbonate. The resultant precipitates were recrystallized three times from water containing a small amount of potassium carbonate. α-Hexyl was prepared by the nitration of the condensation product of picrylchloride with 1-naphthylamine[3], and thiohexyl, by the nitration of phenothiazine.[4,5] Potassium salts with these acids were prepared by dissolving these substances into a hot mixture of alcohol and water containing potassium carbonate; then the precipitates were recrystallized three times from such a mixture.

Acetic acid-lithium acetate buffers (0.01 M) and 0.01 M phosphoric acid-lithium phosphate buffers were used to adjust the pH values of the solution to pH 4—5.5 and pH 6—8 respectively. More alkaline solutions (pH 9—11) were prepared with a 0.005 M lithium carbonate solution and hydrochloric acid and a pH 12 solution, with a 0.01 M lithium hydroxide solution.

Extraction. Into a 50-m*l* centrifuge tube equipped with a stopper, 10 m*l* of a 0.01 M buffer solution and 10 m*l* of water were transferred; then 20 m*l* of a nitrobenzene solution containing potassium salts of these acids (1×10^{-3} M) was added. The resultant mixture of the aqueous and nitrobenzene solutions was shaken moderately for two hours at 25°C and then centrifuged at the same temperature. The preparation of the aqueous phase was slightly modified when the association constant and the distribution constant in the aqueous phase had been determined: 10 m*l* of an 8×10^{-4} M potassium hydroxide solution was mixed with 10 m*l* of a potassium chloride solution, the concentration ranging from 0 to 2×10^{-3} M. The resultant solutions were then treated as before.

Determination of Potassium, Lithium, and the Acids. The concentration of potassium remaining in the aqueous phase after equilibration and that of lithium extracted into nitrobenzene were determined using an atomic absorption spectrophotometer (Nippon Jarrell Ash, Type AA-1); the concentrations of the acids in the aqueous phase were determined spectrophotometrically (Hitachi Ltd.; Spectrophotometer, Type 124) using matched 50-mm cells at 425, 445, and 463 mμ for hexyl, α-hexyl, and thiohexyl respectively, while the solution was kept sufficiently alkaline (pH 13) to avoid the hydrolysis of the salts. The pH of the aqueous solution was also measured in order to analyse the distribution equilibria.

Conductance Measurements in the Nitrobenzene Solution. Nitrobenzene of a guaranteed-grade was washed with an aqueous solution of sodium carbonate and then distilled water, and subsequently dried over calcium chloride for two days. The nitrobenzene was then distilled under reduced pressure. A fraction boiling at 75°C/5 mmHg, with a specific conductance of 0.02 μ℧/cm, was collected. The specific conductance of the water-saturated or wet nitrobenzene was about 20 times that of the dry nitrobenzene. The conductance of the nitrobenzene solution placed in a jacketted vessel equipped with platinized platinum electrodes and a thermometer (a thermocouple; Cu-Con.) was measured by using a conductometer (Ando Electric Co. Ltd., LCR-10, Universal Bridge), while the temperature of the solution was kept at 25±0.005°C by circulating the thermostated water. In order to obtain the $\Lambda-\sqrt{C}$ plot, a dilution method using a weighing buret was adopted.

Theoretical

By writing the formulae for the hexyl, α-hexyl, and thiohexyl acids and the potassium salts of these acids as HR and MR respectively, the equilibria involved can be represented schematically as in Fig. 1:

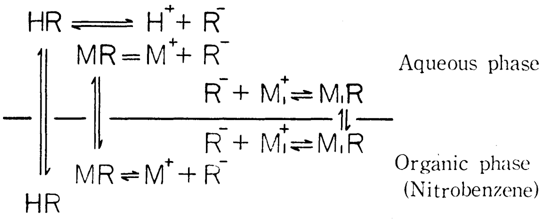

Fig. 1. Schematic representation of the equilibria involved in the extraction.

1) Dissociation of the Acids:

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

2) Association of Potassium Salts:

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

$$\mathrm{M}^+ + \mathrm{R}^- \rightleftharpoons \mathrm{MR}$$

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

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

$$\mathrm{M_I^+} + \mathrm{R}^- \rightleftharpoons \mathrm{M_IR}$$

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

3) Distribution of the Neutral Molecules:

$$D^{\mathrm{HR}} = \frac{[\mathrm{HR}]_o}{[\mathrm{HR}]_a} \tag{6}$$

$$D^{\mathrm{MR}} = \frac{[\mathrm{MR}]_o}{[\mathrm{MR}]_a} \tag{7}$$

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

In these equilibrium expressions, the subscripts a and o 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 the lithium ion, because the extractability of the lithium salts with the acids is much lower than that of the potassium salts.

i) Association Constant, K_o^{MR}. The association constants of these salts in a nitrobenzene solution were determined by the method of Shedlovsky.[6] The conductances, Λ, were related to the concentration of the electrolytes, C, by the following equation:

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_\infty} + \frac{K_o^{\mathrm{MR}} C \Lambda S f_o^2}{\Lambda_\infty^2} \qquad S \equiv \left[\frac{Z}{2} + \sqrt{1+\left(\frac{Z}{2}\right)^2}\right]^2 \qquad Z = \frac{\alpha\sqrt{C\Lambda}}{\Lambda_\infty^{3/2}} \tag{9}$$

where Λ_∞ refers to the limiting conductance; f, to the mean activity coefficient, and α, to the Onsager

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3) K. Tôei, *Nippon Kagaku Zasshi*, **76**, 106 (1955).

4) A. Bernthsen and H. Sattler, *Ann.*, **230**, 116 (1885).

5) F. Kehrmann and F. Ringer, *Ber.*, **46**, 3018 (1913).

6) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

coefficient.

ii) Association Constant, K_a^{MR}, and Distribution Constant, D^{MR}. The distribution ratio of the acid, q^R, in a sufficiently alkaline solution can be written as:

$$q^R = \frac{[MR]_o + [R^-]_o}{[MR]_a + [R^-]_a} \tag{10}$$

In this case only, the pH of the solution was adjusted by the use of potassium hydroxide instead of the lithium buffers. Hence, the terms of lithium in neither phase appears in the expression (cf. Eq. (13)).

The combination of Eqs. (2), (3), and (7) leads to the following equation:

$$\frac{Y}{q^R} = \frac{1}{D^{MR}} + \frac{1}{D^{MR} K_a^{MR} f_a^2 [M^+]_a}$$

$$Y = \frac{\sqrt{0.25 + C_o K_o^{MR} f_o^2} + 0.5}{C_o K_o^{MR} f_o^2} + 1 \tag{11}$$

The values of the mean activity coefficient, f, in both the aqueous ($\varepsilon = 78.54$) and the nitrobenzene ($\varepsilon = 34.8$) phases were approximated by the Debye-Hückel limiting law:

$$-\log f^2 = \frac{3.6494 \times 10^6 \sqrt{I}}{(\varepsilon T)^{3/2}} \tag{12}$$

where I denotes the ionic strength.

iii) Distribution of the Acids. The distribution ratio of the acid at equilibrium between the two phases can be written as:

$$q^R = \frac{[HR]_o + [MR]_o + [M_IR]_o + [R^-]_o}{[HR]_a + [MR]_a + [M_IR]_a + [R^-]_a} \tag{13}$$

The substitution of the equilibrium constants defined by Eqs. (1) to (8) into Eq. (13) gives this equation:

$$q^R = D^{HR} \frac{\left[1 + \left\{\left(1 + \frac{1}{K_o^{MR}[M^+]_o}\right) D^{MR} K_a^{MR} [M^+]_a + D^{M_IR} K_a^{M_IR} [M_I^+]_a\right\} \frac{K_a^{HR}}{D^{HR}[H^+]_a}\right]}{\left\{1 + \left(1 + K_a^{MR}[M^+]_a + K_a^{M_IR}[M_I^+]_a\right) \frac{K_a^{HR}}{[H^+]_a}\right\}} \tag{14}$$

iv) Distribution of Potassium. At equilibrium the distribution of potassium between the two phases can be written as:

$$q^M = \frac{[MR]_o + [M^+]_o}{[MR]_a + [M^+]_a} \tag{15}$$

The total concentrations of the reagent, C^R, and of potassium, C^M, are represented as:

$$C^R = [HR]_a + [HR]_o + [MR]_a + [MR]_o + [M_IR]_a + [M_IR]_o + [R^-]_a + [R^-]_o \tag{16}$$

$$C^M = [MR]_a + [MR]_o + [M^+]_a + [M^+]_o \tag{17}$$

The electroneutrality condition in the organic phase is expressed as:

$$[R^-]_o = [M^+]_o + [M_I^+]_o \tag{18}$$

Combining Eqs. (16), (17), and (18) and solving for $[R^-]_a$ gives:

$$\frac{1}{[R^-]_a} = \frac{1 + \frac{1 + D^{HR}}{K_a^{HR}}[H^+]_a + (1 + D^{M_IR}) K_a^{M_IR} [M_I^+]_a}{C^R - C^M + [M^+]_a - [M_I^+]_o} \tag{19}$$

On the other hand, the rearrangement of Eq. (15) gives:

$$q^M = D^{MR} \left(\frac{1 + \frac{1}{K_o^{MR}[R^-]_o}}{1 + \frac{1}{K_a^{MR}[R^-]_a}} \right) \tag{20}$$

The substitution of Eq. (19) into Eq. (20) gives this useful expression:

$$q^M = D^{MR} \frac{\left(1 + \frac{1}{K_o^{MR}([M^+]_o + [M_I^+]_o)}\right)}{\left\{1 + \frac{1 + (1 + D^{HR})[H^+]_a / K_a^{HR} + (1 + D^{M_IR}) K_a^{M_IR} [M_I^+]_a}{K_a^{MR}(C^R - C^M + [M^+]_a - [M_I^+]_o)}\right\}} \tag{21}$$

It must be noted that all the experiments were carried out under such a condition as $C^R - C^M = 0$, which can easily and exactly be realized by the use of the salt as the source of the reagent and the metal species. This is also advantageous in simplifing Eq. (21).

Results and Discussion

i) Equilibria Involved in the Extraction System. The equilibria shown in Fig. 1 are fundamental ones. Certainly, some other equilibria also exist in the two phases, such as the dissociation of the acids in nitrobenzene, the homoconjugation reaction (as has been mentioned in connection with picric acid in nitrobenzene),[7] the dimerization of the acids in both phases, *etc.* Lin[8] has suggested that the polymerization of hexylate ions in the aqueous phase does not occur until the concentration of hexylate exceeds 10^{-2} M.

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7) I. M. Kolthoff, D. Stŏcesocá, and T. S. Lee, *J. Amer. Chem. Soc.*, **75**, 1834 (1953).

8) Z. F. Lin, *J. Chinese Chem. Soc.*, **9**, 115 (1962).

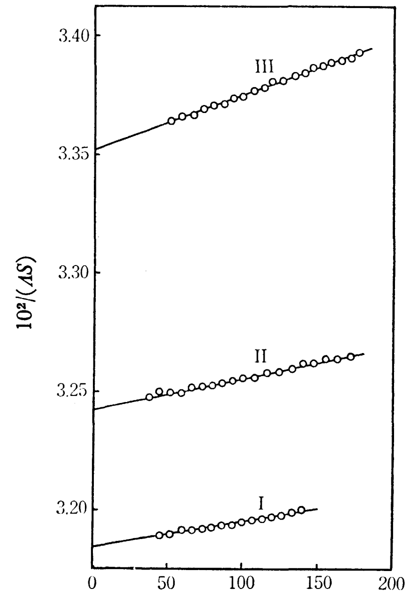

Fig. 2. Shedlovsky plot of the potassium salts in wet nitrobenzene,
I: Hexyl, II: α-Hexyl, III: Thiohexyl.

The present studies of the distribution of potassium or the acids between the aqueous and the nitrobenzene phases show that the neglect of the reactions mentioned above does not cause any trouble in explaining the experimental results. This fact supports the idea that these equilibria are of minor importance.

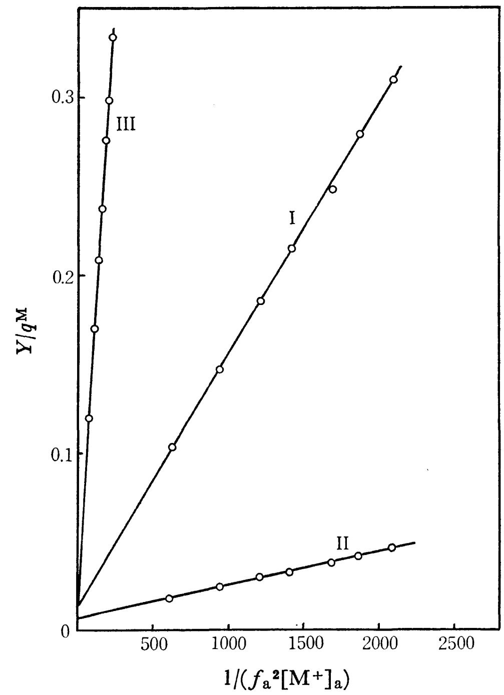

Fig. 3. The plot of Y/q^M *vs.* $1/f_a^2[M^+]_a$,
I: Hexyl, II: α-Hexyl, III: Thiohexyl.

ii) Association Constants of Potassium Salts in Nitrobenzene, K_o^{MR}. The conductance measurements were carried out with a cell devised for dilution runs, the concentrations ranging from about 0.5×10^{-4} to 7×10^{-4} M. A plot of Λ *vs.* $\sqrt{C}$ gives good straight lines, the intercepts on the Λ-axis for potassium salts with hexyl, α-hexyl, and thiohexyl being 31.42, 30.89, and 29.90 respectively, and the slope giving a value almost equal to Onsager's coefficient for each salt. The Shedlovsky plot (Fig. 2) was obtained by the the following calculations. First, z (Eq. (9)) is calculated from the Λ_∞ evaluated approximately by extrapolating the above linear $\Lambda-\sqrt{C}$ plot to the Λ-axis, and then the Shedlovsky plot is made by the help of Eq. (12). The reciprocal of the intercept of the plot on the $1/(\Lambda S)$-axis gives the second approximation for Λ_∞. The process is repeated until the Λ_∞ thus obtained is no longer altered. The final plots are shown in Fig. 2. The values of Λ_∞ and K_o^{MR} can be determined simultaneously from the plot. The value of K_o^{MR} in the wet nitrobenzene solution is calculated in the same manner, because the saturation of water (about 0.1 M) does not alter the dielectric constant of nitrobenzene (34.8) practically. Table 1 shows that the saturation of water causes about a 1.5-hold increase in Λ_∞ and a large decrease in K_o^{MR}. Taking into consideration the fact that the Λ_∞ values of potassium picrate are 34.7 and 40.3 for dry and the wet nitrobenzene solutions respectively, the sequence of Λ_∞ may well account for the bulkiness of the conjugate base, R^-.

iii) Distribution Coefficients, D^{MR}, *and Association Constants of Potassium Salts in the Aqueous Phase,* K_a^{MR}. The pH values of the aqueous solution were kept at pH 10.46±0.03, 10.14±0.02, and 11.67±0.01 for hexyl, α-hexyl, and thiohexyl respectively. A plot of Y/q^M *vs.* $1/(f_a^2[M^+]_a)$ (Fig. 3) shows a line in accordance with the theoretical requirements. However, the enlarged plot for thiohexyl shows that the line curves slightly downwards at the upper part.

For potassium picrate, it has been reported that the values of K_a^{MR} and D^{MR} are 44 and 0.014 respectively.[1] A comparison of the present results with those of the picrates shows that the structural difference (for example, in a functional group or bulkiness) be-

TABLE 1. SEVERAL CONSTANTS OBTAINED WITH HEXYL, α-HEXYL, AND THIOHEXYL

Compound	Soln.	Λ_∞	K_o^{MR}	K_a^{MR}	D^{MR}	$K_a^{MR}D^{MR}/K_o^{MR}$	K_a^{HR}/D^{HR}	K_a^{HR}
Hexyl	Dry	29.72	32.65					
	Wet	31.41	10.32	112.5	78.55	$10^{1.466}$	$10^{-8.573}$	$10^{-4.75}$
α-Hexyl	Dry	29.27	31.29					
	Wet	30.84	12.48	418.4	160.5	$10^{1.865}$	$10^{-11.151}$	$>10^{-7}$
Thiohexyl	Dry	28.46	46.68					
	Wet	29.83	20.47	12.86	69.76	$10^{0.821}$	$10^{-11.481}$	$>10^{-9}$

tween the picrates and the acids much more significantly influences the value of D^{MR} than that of K_a^{MR}. It may, however, be difficult to point out such a correlation between K_a^{MR} or D^{MR} and the structural factors among these three acids.

iv) Distribution of Potassium, q^{M}. Figures 4, 5, and 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 slope exactly 1/2, and the other, a horizontal line independent of the pH.

The appearance of the horizontal line can be explained from Eq. (21) by assuming that the potassium or lithium concentration in both phases attains a certain constant value characteristic of the acids in a sufficiently high pH region. The $(1+D^{\mathrm{HR}})[\mathrm{H^+}]_a/K_a^{\mathrm{HR}}$ term is, of course, much smaller than unity and smaller than the $(1+D^{\mathrm{M_IR}})[\mathrm{M^+}]_a$ term. If the $[\mathrm{M^+}]_a$ term can be assumed to be much larger than $[\mathrm{M_I^+}]_o$, Eq. (21) reduces to a much simpler expression, as has been pointed out in the case of alkali metal picrates,[1] as:

$$(q^{\mathrm{M}})^2 = \frac{K_a^{\mathrm{MR}}D^{\mathrm{MR}}}{K_o^{\mathrm{MR}}} \tag{22}$$

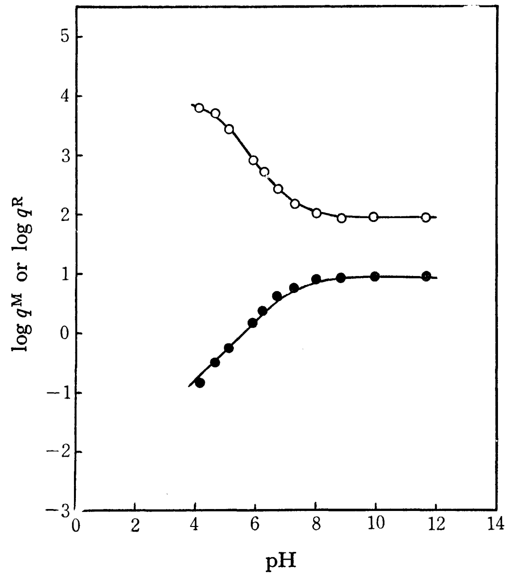

Fig. 4. The distribution of the potassium salt with hexyl, Open circles: log q^{R}–pH curve Solid circles: log q^{M}–pH curve.

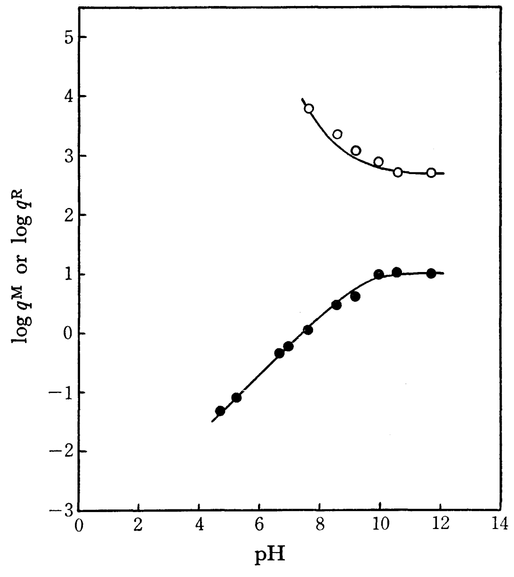

Fig. 5. The distribution of the potassium salt with α-hexyl, Open circles: log q^{R}–pH curve Solid circles: log q^{M}–pH curve.

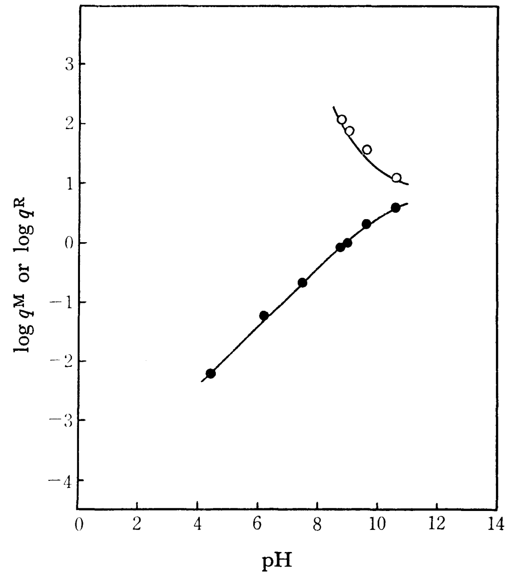

Fig. 6. The distribution of the potassium salt with thiohexyl, Open circles: log q^{R}–pH curve Solid circles: log q^{M}–pH curve.

Figures 4 and 5 show that the q^{M} values measured at sufficiently high pH values are considerably smaller than those to be expected from Eq. (22), as shown in Table 1. Such a result can well be understood by taking into account the effect of the concentration of the lithium extracted, $[\mathrm{M_I^+}]_o$. In fact, the results of the atomic absorption spectrophotometric measurements show that the extractabilities of potassium salts by these acids are so high that the concentration of potassium in the aqueous phase, $[\mathrm{M^+}]_a$, decreases to about 10^{-4} M. The value is only slightly larger than that of the lithium extracted, $[\mathrm{M_I^+}]_o$, though the extractability of lithium ions still remains much lower than that of potassium. Therefore, the neglect of the $[\mathrm{M_I^+}]_o$ term compared to the $[\mathrm{M^+}]_a$ term causes a large deviation between the measured q^{M} values and q^{M} values estimated by means of the much simpler expression. An atomic absorption spectrophotometric method might not always be satisfactory in finding out such a small difference.

Thiohexyl reveals no horizontal line below pH 11.5. With a more alkaline solution (pH 12.69), a slightly small q^{M} value was obtained (log $q^{\mathrm{M}}=0.356$). The decrease in q^{M} value can also be explained from Eq. (21) by taking into account the increased value of $[\mathrm{M_I^+}]_o$. The log q^{M} value thus obtained is 0.3564. The good agreement between the measured and calculated q^{M} values may prove the usefulness of Eq. (21).

On the other hand, when the aqueous solution is acidic, potassium as well as lithium ions will remain almost unextracted in the aqueous phase to satisfy the condition $[\mathrm{M}^+]_\mathrm{a} \gg [\mathrm{M}_\mathrm{I}^+]_\mathrm{o}$. Accordingly, under such a condition a useful approximation for q^M may be obtained from Eq. (21) by making the following assumptions:

$$[\mathrm{M}^+]_\mathrm{o} \gg [\mathrm{M}_\mathrm{I}^+]_\mathrm{o},\ D^{\mathrm{M_IR}} \ll 1,\ D^{\mathrm{HR}} \gg 1, \text{ and } q^\mathrm{M} \approx \frac{[\mathrm{M}^+]_\mathrm{o}}{[\mathrm{M}^+]_\mathrm{a}}$$

In this manner, Eq. (21) can be simplified to the following expression:

$$(q^\mathrm{M})^2 = \frac{[\mathrm{M}^+]_\mathrm{o} + \dfrac{1}{K_\mathrm{o}^{\mathrm{MR}}}}{[\mathrm{M}^+]_\mathrm{a} + \dfrac{1}{K_\mathrm{a}^{\mathrm{MR}}}\left(1 + \dfrac{D^{\mathrm{HR}}}{K_\mathrm{a}^{\mathrm{HR}}}[\mathrm{H}^+]_\mathrm{a} + K_\mathrm{a}^{\mathrm{M_IR}}[\mathrm{M}_\mathrm{I}^+]_\mathrm{a}\right)} \tag{23}$$

Under sufficiently acidic conditions, Eq. (21) is further simplified, yielding:

$$(q^\mathrm{M})^2 = \frac{D^{\mathrm{MR}}K_\mathrm{a}^{\mathrm{MR}}K_\mathrm{a}^{\mathrm{HR}}}{K_\mathrm{o}^{\mathrm{MR}}D^{\mathrm{HR}}} \cdot \frac{1}{[\mathrm{H}^+]_\mathrm{a}} \tag{24}$$

A plot of log q^M *vs.* pH gives a straight line with a slope of 1/2; the intercept on the Y/q^M-axis is given by $1/2(\log K_\mathrm{a}^{\mathrm{MR}}D^{\mathrm{MR}}K_\mathrm{a}^{\mathrm{HR}}/K_\mathrm{o}^{\mathrm{MR}}D^{\mathrm{HR}})$. In Figs. 4, 5, and 6, it is shown that the above relation holds well in the acidic region. The solid line in each figure was drawn by means of Eq. (21) so as to fit well with the experimental values (solid circles) by choosing an appropriate value for $K_\mathrm{a}^{\mathrm{HR}}/D^{\mathrm{HR}}$ (Table 1).

v) Distribution of the Acids, q^R. The dependence of the distribution ratio of the acid upon pH is expressed by Eq. (14). This equation may well be understood by dividing it into two equations on the basis of appropriate assumptions; that is, an equation which holds in a sufficiently alkaline pH:

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

and one which holds in a sufficiently acidic pH:

$$q^\mathrm{R} = D^{\mathrm{HR}} \tag{26}$$

When the aqueous solution is sufficiently alkaline, the amounts of potassium in both phases attain a certain constant value, as has been mentioned before. Accordingly, from Eq. (25) it can be expected that log q^R will also attain a certain constant value. Figures 4 and 5 show that Eq. (25) holds well in such an alkaline solution. Thiohexyl (Fig. 6) does not show such a constant portion below pH 11.5.

On the other hand, when the aqueous solution is sufficiently acidic, it can be expected from Eq. (26) that the log q^R value will also attain a constant value. Only hexyl reveals incompletely the presence of such a constant. The distribution behavior in a more acidic region can be shown only when more sensitive methods than spectrophotometry are available for the determination of the acid in the aqueous phase.

When the pH value of the solution is comparable with that of p$K_\mathrm{a}^{\mathrm{HR}}$ ($K_\mathrm{a}^{\mathrm{HR}}/[\mathrm{H}^+]_\mathrm{a} \approx 1$), no terms (except lithium terms) can be neglected. Therefore, it is impossible to make such an illustrative statement about the distribution curves.

When appropriate values for $K_\mathrm{a}^{\mathrm{HR}}$ and D^{HR} are chosen, a theoretical q^R—pH curve which fits well with the experimental values should be obtained. In Figs. 4, 5, and 6 the calculated curves are shown by solid lines. The fit is the best for the hexyl salt. In the remaining two salts, the experimental q^R values are so few that the $K_\mathrm{a}^{\mathrm{HR}}$ and D^{HR} values can not be determined exactly, because the data on q^R in the acidic region (which are lacking in the experiment) are dominant in determining these values. This can easily be understood from the fact mentioned above; that is, the q^R values in the alkaline region do not depend upon $K_\mathrm{a}^{\mathrm{HR}}$ or D^{HR} (cf. Eq. (25)). The $K_\mathrm{a}^{\mathrm{HR}}$ value thus obtained for hexyl agrees well with that reported by Lin[9] (pK_a=5.4). It is noticeable, however, that the $K_\mathrm{a}^{\mathrm{HR}}$ values reported by Grunwald,[10] Glover,[11] and O'Donnell[12] are much larger than that of the present work.

vi) Association Constants, $K_\mathrm{a}^{\mathrm{M_IR}}$, and Distribution Constants, $D^{\mathrm{M_IR}}$, for the Lithium Salts. The values of $K_\mathrm{a}^{\mathrm{M_IR}}$ and $D^{\mathrm{M_IR}}$ for these salts have not been reported, except in the case of hexyl salt ($K_\mathrm{a}^{\mathrm{M_IR}}$=8.9, $D^{\mathrm{M_IR}}$=0.5[13]). The atomic absorption spectrophotometric measurements proved that the distribution ratio of lithium was almost the same for hexyl and α-hexyl and was considerably smaller for thiohexyl. This fact supports the idea that the terms containing these constants are negligibly small, as is the case with hexyl. Therefore, for α-hexyl and thiohexyl the theoretical q^R—pH and the q^M—pH curves are calculated by means of Eqs. (14) and (21) respectively, disregarding these terms.

In conclusion, the present work has made it clear that the distribution mechanism proposed for alkali metal picrates is valid also for the acids which show a high extractability. However, it must be noted that the application of this method suffers some limitations from the properties of the acid used. The acids favorable for such distribution studies are sufficiently acidic in nature to prevent the hydrolysis of the salts in wet nitrobenzene. The hydrolysis makes it impossible to determine the association constant of the salt by conductometry. Another important requirement is that the acids must have a moderate q^R or q^M value. For example, with an acid having an extremely high q^R value the method fails to determine a dissociation constant and a distribution constant, as has been mentioned in connection with α-hexyl and thiohexyl.

The author wishes to express his gratitude to Professor Kyoji Tôei for his guidance throughout the course of this work.

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