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Distribution of Alkali Metal Picrates between Water and Methyl Isobutyl Ketone

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As regards the distribution of alkali metal picrates between water and methyl isobutyl ketone, distribution ratios of alkali metals and acid species were determined in the pH range 1.5—8.5. The extraction curves are almost the same for each alkali metal. Association constants of the picrates and the dissociation constant of picric acid in the organic phase were determined conductometrically. The association constants of picrates in the aqueous phase were determined with distribution coefficients by means of a solvent extraction method. The results obtained show that the picrates exist mainly in a dissociated form in both phases, whereas picric acid exists in a weakly dissociated form in the organic phase. The extractability of picrates is discussed on the basis of the extraction parameter proposed and compared with that of the nitrobenzene system.

The results obtained from the previous study on the distribution of alkali metal picrates between aqueous and nitrobenzene phases[1] can be summarized as follows. The extractability of alkali metal picrates can be represented in terms of the extraction parameter $D^{MR}K_a^{MR}/K_o^{MR}$, where K_a^{MR} and K_o^{MR} denote the association constants of the picrates in the aqueous and the organic phases, respectively, and D^{MR} denotes the distribution coefficient. The parameter can also be a good measure of the solvent. Since picrates are strong electrolytes, the ratio D^{MR}/K_o^{MR} is expected to increase with the ionizing power of solvent, giving rise to enhanced extractability.

Acetone and methyl ethyl ketone are known to be ionizing solvents for picrates stronger than nitrobenzene.[2,3] However, they are not suitable for extraction because of their high miscibility with water. Methyl isobutyl ketone (MIBK) was chosen, since it is a dipolar aprotic solvent with high ionizing power yet immiscible with water.

Association constants show that MIBK functions as an ionizing solvent with levelling property, in contrast to the differentiating property of nitrobenzene. The

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

[2] M. B. Reynolds and C. A. Kraus, *J. Amer. Chem. Soc.*, **70**, 1709 (1948).

[3] C. W. Davies, "Ion Association", Butterworths, London (1962) p. 96.

levelling property, commonly observed in acetone and methyl ethyl ketone, becomes conspicuous with the addition of water, which reflects on the extractability of alkali metals. Discussion is made on the basis of equilibrium constants.

Experimental

Reagents. Alkali metal picrates were recrystallized from water except for lithium salt (from an alcohol–water mixture). Sodium and lithium picrates were determined to be monohydrate by measuring the weight loss on heating under reduced pressure. The solvent was purified in the usual way: MIBK previously treated with potassium permanganate was washed with an aqueous solution of sodium carbonate and distilled. The distillate was dried over anhydrous sodium sulfate for two days and distilled again.

Citric acid–citrate buffers (0.01 M) and phosphoric acid–phosphate buffers (0.01 M) were used to adjust the pH of the solutions to pH 2.5—5.5 and pH 6—8, respectively. Strongly acidic solutions (pH below 2.5) were prepared with hydrochloric acid. A series of buffer solutions were prepared with five kinds of alkali metals. All the aqueous solutions were previously saturated with MIBK and all the MIBK solutions with water, in order to avoid volume change on mixing.

Extraction. Dependence of distribution ratios of alkali metals and the acid species on pH was investigated as follows: 10 ml of a 0.01 M buffer solution and 10 ml of a 1×10^{-4} M aqueous alkali metal picrate solution were transferred to a 50 ml centrifuge tube equipped with a stopper. 20 ml of MIBK was then added. The resulting mixture was shaken for two hours at 25 °C. The distribution coefficients and association constants (in the aqueous phase) were determined by modifying the above procedures: 10 ml of an aqueous solution of alkali metal picrate (1×10^{-4} M) was mixed with 10 ml of a buffer solution containing an alkali metal of the same kind to various concentrations (up to 10^{-2} M). The resulting solution was then treated as before.

Determination of Alkali Metals and the Acid Species. After equilibration the alkali metals in the organic phase were determined with an atomic absorption spectrophotometer (Nippon Jarrell Ash, Type AA-1). The acid species in the aqueous phase was determined spectrophotometrically (Hitachi Ltd., Type 124) by using matched 50 mm cells at 355 nm, at which the absorption of dissolved MIBK is negligible.

The pH of an aqueous solution saturated with MIBK was measured with a pH meter in the usual way. The MIBK dissolved increased the pH value less than 0.02 unit in each case.

Conductance Measurements in the Organic Phase. Conductances of alkali metal picrates in dry and wet (water-saturated) MIBK solutions were measured with a conductometer (Ando Electric Co. Ltd., Universal Bridge, LCR-10). The solution was kept at 25±0.005 °C by circulating thermostated water around the vessel equipped with platinized platinum electrodes and a copper-constantan thermocouple. Specific conductances of the dry and wet solvents were 0.2 and 1.0 $\mu\Omega^{-1}$ cm^{-1}, respectively. Conductivities of the solutions of 0.5×10^{-4}—7×10^{-4} M were measured by a dilution method with a weighing buret.

Theoretical

The equilibria for the picric acid and alkali metal picrates, denoted by HR and MR, respectively, can be written as follows:

1) Dissociation of Picric Acid:

$$\mathrm{HR} \rightleftharpoons \mathrm{H^+ + R^-} \qquad K_\mathrm{a}^\mathrm{HR} = \frac{[\mathrm{H^+}]_\mathrm{a}[\mathrm{R^-}]_\mathrm{a}}{[\mathrm{HR}]_\mathrm{a}} \tag{1}$$

$$K_\mathrm{o}^\mathrm{HR} = \frac{[\mathrm{H^+}]_\mathrm{o}[\mathrm{R^-}]_\mathrm{o}}{[\mathrm{HR}]_\mathrm{o}} \tag{2}$$

2) Association of Alkali Metal Picrates:

$$\mathrm{M^+ + R^-} \rightleftharpoons \mathrm{MR} \qquad K_\mathrm{a}^\mathrm{MR} = \frac{[\mathrm{MR}]_\mathrm{a}}{[\mathrm{M^+}]_\mathrm{a}[\mathrm{R^-}]_\mathrm{a}} \tag{3}$$

$$K_\mathrm{o}^\mathrm{MR} = \frac{[\mathrm{MR}]_\mathrm{o}}{[\mathrm{M^+}]_\mathrm{o}[\mathrm{R^-}]_\mathrm{o}} \tag{4}$$

3) Distribution of the Acid and the Picrates:

$$D^\mathrm{HR} = \frac{[\mathrm{HR}]_\mathrm{o}}{[\mathrm{HR}]_\mathrm{a}} \tag{5}$$

$$D^\mathrm{MR} = \frac{[\mathrm{MR}]_\mathrm{o}}{[\mathrm{MR}]_\mathrm{a}} \tag{6}$$

Subscripts a and o refer to aqueous and organic phases, respectively; molar concentrations are given in brackets.

i) Association Constants in the Organic Phase K_o^MR. Association constants of the picrates in MIBK solutions were determined by the method of Shedlovsky.[4] Conductance Λ is related to the concentration of electrolyte C by the equation

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_\infty} + \frac{K_\mathrm{o}^\mathrm{MR} C\Lambda S f_\mathrm{o}^{\,2}}{\Lambda_\infty^{\,2}} \qquad S \equiv \left[\frac{Z}{2} + \sqrt{1+\left(\frac{Z}{2}\right)^2}\right]^2$$

$$Z = \frac{\alpha\sqrt{C\Lambda}}{\Lambda_\infty^{\,3/2}} \tag{7}$$

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

ii) Association Constants in the Aqueous Phase K_a^MR and Distribution Coefficients D^MR. The distribution ratio of the acid species in a sufficiently alkaline solution can be written as

$$q^\mathrm{R} = \frac{[\mathrm{MR}]_\mathrm{o} + [\mathrm{R^-}]_\mathrm{o}}{[\mathrm{MR}]_\mathrm{a} + [\mathrm{R^-}]_\mathrm{a}} \tag{8}$$

Combination of Eqs. (3), (4), (6), and (8) leads to the following equation:

$$\frac{Y}{q^\mathrm{R}} = \frac{1}{D^\mathrm{MR}} + \frac{1}{D^\mathrm{MR} K_\mathrm{a}^\mathrm{MR} f_\mathrm{a}^{\,2} [\mathrm{M^+}]_\mathrm{a}} \tag{9}$$

$$Y = \frac{\sqrt{0.25 + C_\mathrm{o} K_\mathrm{o}^\mathrm{MR} f_\mathrm{o}^{\,2}} + 0.5}{C_\mathrm{o} K_\mathrm{o}^\mathrm{MR} f_\mathrm{o}^{\,2}} + 1$$

The values of the mean activity coefficient in both aqueous and MIBK solutions were approximated by the Debye-Hückel limiting law

$$-\log f^2 = \frac{3.6494\times10^6\sqrt{I}}{(\varepsilon T)^{3/2}} \tag{10}$$

where I denotes the ionic strength.

iii) Distribution of Acid Species. At equilibrium the distribution ratio of the acid species between the two phases can generally be written as

$$q^\mathrm{R} = \frac{[\mathrm{HR}]_\mathrm{o} + [\mathrm{MR}]_\mathrm{o} + [\mathrm{R^-}]_\mathrm{o}}{[\mathrm{HR}]_\mathrm{a} + [\mathrm{MR}]_\mathrm{a} + [\mathrm{R^-}]_\mathrm{a}} \tag{11}$$

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[4] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

Substitution of the equilibrium constants defined by Eqs. (1)—(6) into Eq. (11) gives

$$q^{\mathrm{R}} = D^{\mathrm{HR}}\frac{1+\left\{\left(1+\dfrac{1}{K_{\mathrm{o}}^{\mathrm{MR}}[\mathrm{M}^+]_{\mathrm{o}}}\right)D^{\mathrm{MR}}K_{\mathrm{a}}^{\mathrm{MR}}[\mathrm{M}^+]_{\mathrm{a}}\right\}\dfrac{K_{\mathrm{a}}^{\mathrm{HR}}}{D^{\mathrm{HR}}[\mathrm{H}^+]_{\mathrm{a}}}}{1+(1+K_{\mathrm{a}}^{\mathrm{MR}}[\mathrm{M}^+]_{\mathrm{a}})\dfrac{K_{\mathrm{a}}^{\mathrm{HR}}}{[\mathrm{H}^+]_{\mathrm{a}}}} \tag{12}$$

iv) Distribution of Alkali Metals. The distribution of alkali metals can also be written as

$$q^{\mathrm{M}} = \frac{[\mathrm{MR}]_{\mathrm{o}}+[\mathrm{M}^+]_{\mathrm{o}}}{[\mathrm{MR}]_{\mathrm{a}}+[\mathrm{M}^+]_{\mathrm{a}}} \tag{13}$$

Total concentrations of the acid species C^{R} and alkali metals C^{M} are represented as

$$C^{\mathrm{R}} = [\mathrm{HR}]_{\mathrm{a}} + [\mathrm{HR}]_{\mathrm{o}} + [\mathrm{MR}]_{\mathrm{a}} + [\mathrm{MR}]_{\mathrm{o}} + [\mathrm{R}^-]_{\mathrm{a}} + [\mathrm{R}^-]_{\mathrm{o}} \tag{14}$$

$$C^{\mathrm{M}} = [\mathrm{MR}]_{\mathrm{a}} + [\mathrm{MR}]_{\mathrm{o}} + [\mathrm{M}^+]_{\mathrm{a}} + [\mathrm{M}^+]_{\mathrm{o}} \tag{15}$$

The electroneutrality condition in the organic phase is expressed by

$$[\mathrm{R}^-]_{\mathrm{o}} = [\mathrm{M}^+]_{\mathrm{o}} + [\mathrm{H}^+]_{\mathrm{o}} \tag{16}$$

Combining Eqs. (14), (15), and (16) and solving for $[\mathrm{R}^-]_{\mathrm{a}}$ gives

$$\frac{1}{[\mathrm{R}^-]_{\mathrm{a}}} = \frac{1+\dfrac{(1+D^{\mathrm{HR}})}{K_{\mathrm{a}}^{\mathrm{HR}}}[\mathrm{H}^+]_{\mathrm{a}}}{C^{\mathrm{R}}-C^{\mathrm{M}}+[\mathrm{M}^+]_{\mathrm{a}}-[\mathrm{H}^+]_{\mathrm{o}}} \tag{17}$$

On the other hand, rearrangement of Eq. (13) gives

$$q^{\mathrm{M}} = \frac{[\mathrm{MR}]_{\mathrm{o}}\left(1+\dfrac{1}{K_{\mathrm{o}}^{\mathrm{MR}}[\mathrm{R}^-]_{\mathrm{o}}}\right)}{[\mathrm{MR}]_{\mathrm{a}}\left(1+\dfrac{1}{K_{\mathrm{a}}^{\mathrm{MR}}[\mathrm{R}^-]_{\mathrm{a}}}\right)} \tag{18}$$

Substitution of Eq. (17) into Eq. (18) gives the useful expression

$$q^{\mathrm{M}} = D^{\mathrm{MR}}\frac{\left\{1+\dfrac{1}{K_{\mathrm{o}}^{\mathrm{MR}}([\mathrm{M}^+]_{\mathrm{o}}+[\mathrm{H}^+]_{\mathrm{o}})}\right\}}{\left\{1+\dfrac{1+(1+D^{\mathrm{HR}})[\mathrm{H}^+]_{\mathrm{a}}/K_{\mathrm{a}}^{\mathrm{HR}}}{K_{\mathrm{a}}^{\mathrm{MR}}(C^{\mathrm{R}}-C^{\mathrm{M}}+[\mathrm{M}^+]_{\mathrm{a}}-[\mathrm{H}^+]_{\mathrm{o}})}\right\}} \tag{19}$$

It should be noted that all the experiments were carried out under conditions where the value of C^{M} is about 100 times that of C^{R}.

Results and Discussion

Equilibria Involved in the Extraction System. Fundamental equilibria are shown by Eqs. (1)—(6). MIBK is a solvating solvent like water, but little is known about the solvates of the picrates both in wet MIBK solution and MIBK-saturated aqueous solution. The solvates in both phases are represented by the simplest symbols. The equilibrium constants obtained should be distinguished from those defined in a pure medium.

Interactions between alkali metal cations and the citrate anions added as buffers should be considered. The values of the ion-pair formation constants of the alkali metal citrates obtained by Rechnitz and Zamochnick⁵⁾ are 6.8, 5.0, 3.9, 3.1, and 2.1, in going from lithium to cesium at constant initial metal and citric acid concentration of 0.1 M and pH 8.3. The values are about a quarter of those of respective picrates. Under the present experimental conditions, however, the influence of the citrate ions are negligible below pH 5.5, when the acid dissociation constant of citric acid ($\mathrm{p}K_3=6.396$)⁶⁾ is taken into account.

The dissociation constant of picric acid in the wet MIBK solution is determined conductometrically to be 3.00×10^{-5}. This indicates that the dissociation of the acid can no longer be neglected as compared with other equilibria. This is quite different from the case of the nitrobenzene system. Introduction of the acid dissociation complicates theoretical treatments, but without this the extraction curve especially the acidic parts can not be explained.

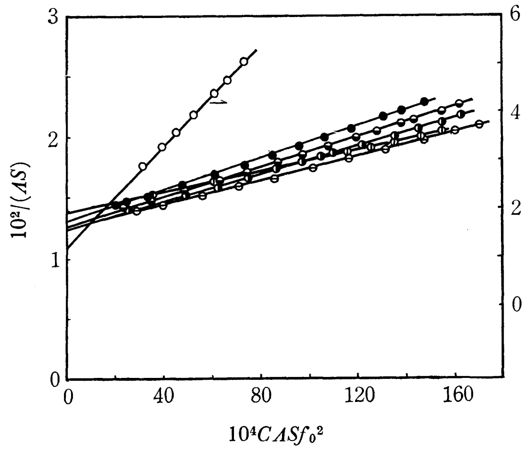

Fig. 1. Shedlovsky plot of the alkali metal picrates in wet MIBK ○: H-Pic, ⦶: Li-Pic, ●: Na-Pic, ◒: K-Pic, ◑: Rb-Pic, ⊖: Cs-Pic.

Association Constants $K_{\mathrm{o}}^{\mathrm{MR}}$. Conductance measurements were carried out with dry and wet MIBK solutions. A plot of Λ *vs.* $C^{1/2}$ gives a curve characteristic of a weak electrolyte. The value of Λ_∞ evaluated graphically is used for the first Shedlovsky plot. The data required for the plot are given in Table 1. The reciprocal of the intercept on $1/(\Lambda S)$-axis gives the second approximation for Λ_∞. The Shedlovsky plot is repeated until Λ_∞ gives a constant value. The final plots are shown in Fig. 1, the values of Λ_∞ and $K_{\mathrm{o}}^{\mathrm{MR}}$ being determined simultaneously (Table 2).

The levelling property of MIBK is reflected on the limiting conductances and all the equilibrium constants as seen from Table 2. The water added emphasizes the property. The strong levelling power of water has

TABLE 1. DIELECTRIC CONSTANT (ε), VISCOSITY (η), AND SPECIFIC GRAVITY (SG) AT 25 °C

Medium	ε	η (cP)	SG
Dry MIBK	12.66	0.546	0.79515
Wet MIBK	13.63	0.5766	0.79918
Water	78.54		
Water (MIBK satd.)	75.73		

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5) G. A. Rechnitz and S. B. Zamochnick, *Talanta*, **11**, 1061 (1964).

6) R. G. Bates and G. D. Pinching, *J. Amer. Chem. Soc.*, **71**, 1274 (1949).

Table 2. Constants obtained with the MIBK system

Comp.	Soln.	Λ_∞	K_0^{MR}	K_a^{MR}	D^{MR}	$K_a^{MR}D^{MR}/K_0^{MR}$ I	$1+A/[M]_a$ II	q^M_{calc} $(I\times II)^{1/2}$	q^M_{meas}	q^R_{calc} $1/q^M_{calc}$	q^R_{meas}
H–Pic	Dry										
	Wet	80.68	0.000030	0.381	500						
Li–Pic	Dry	76.10	80100								
	Wet	73.46	2390	30	0.19	0.0024	0.00609	0.0038	0.00386	0.63	0.634
Na–Pic	Dry	83.86	36100								
	Wet	78.08	4120	18	0.38	0.0017	0.00656	0.0033	0.00334	0.52	0.510
K–Pic	Dry	81.85	11700								
	Wet	79.80	3930	13	1.00	0.0033	0.00557	0.0043	0.00431	0.77	0.783
Rb–Pic	Dry	82.06	9140								
	Wet	80.29	3700	13	0.83	0.0029	0.00565	0.0040	0.00411	0.73	0.726
Cs–Pic	Dry	83.02	8350								
	Wet	81.22	3330	15	0.71	0.0032	0.00573	0.0043	0.00421	0.74	0.729

Table 3. Constants obtained with the nitrobenzene system[a)]

Comp.		Λ_∞	K_0^{MR}	K_a^{MR}	D^{MR}	$(K_a^{MR}D^{MR}/K_0^{MR})^{1/2}$	q^M_{meas}
H–Pic	Wet		3.47×10^{-8}	0.381	427		
Li–Pic	Wet		6.31×10^{5}	13.5	8.9×10^{-4}	0	
Na–Pic	Dry	33.9	30200				
	Wet	31.9	4680	24.0	0.0028	0.0038	0.0035
K–Pic	Dry	34.7	1150				
	Wet	40.3	832	43.7	0.014	0.027	0.025
Rb–Pic	Dry	35.1	646				
	Wet	40.7	447	87.1	0.022	0.066	0.061
Cs–Pic	Dry	36.4	646				
	Wet	40.4	269	117	0.068	0.17	0.18

a) taken from Refs. 1 and 8.

also been observed in the nitrobenzene system (Table 3). Association of the picrates in dry MIBK solutions is only a case that shows a definite correlation with the sizes of the cations concerned, though not so conspicuous as in the nitrobenzene system.

With dry ketones (acetone, methyl ethyl ketone, and MIBK), the $1/\varepsilon$ law is verified. The distance of closest approach is calculated to be about 4 Å on the basis of the theory by Denison and Ramsey.[7] This suggests that the main factor in determining the extent of the ion association is an electrostatic force.

Distribution Coefficients D^{MR} and Association Constants K_a^{MR}. Measurements of these constants were carried out under conditions in which aqueous solutions were sufficiently alkaline (pH about 7.5) not to allow the presence of HR. A plot of Y/q^R *vs.* $1/(f_a^2[M^+]_a)$ shows a straight line in accordance with theoretical requirements (Fig. 2). The values of the intercept on the ordinate are so close to zero that the values of K_a^{MR} and D^{MR} are less accurate than those obtained with the nitrobenzene system.

For sodium picrate the value of K_a^{MR} is also determined potentiometrically to be about 20 by using a sodium-sensitive glass electrode. The value is in fair agreement with that given in Table 3, indicating the validity of the present method.

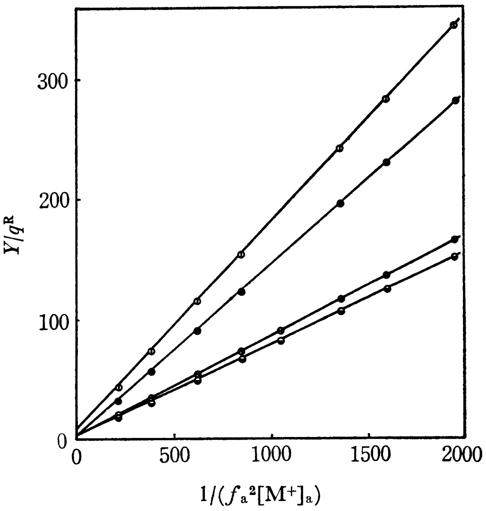

Fig. 2. The plot of Y/q^R *vs.* $1/(f_a^2[M^+]_a)$
The symbols used are the same as those in Fig. 1.

The D^{MR} values obtained show that MIBK dissolves larger quantities of the picrates than nitrobenzene. It is also shown that MIBK acts as a levelling solvent for the distribution and association of the picrates.

The value of D^{HR} is evaluated in such a way that the q^M and q^R curves calculated for five kinds of picrates

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[7] J. T. Denison and J. B. Ramsey, *J. Amer. Chem. Soc.*, **77**, 2615 (1955).

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

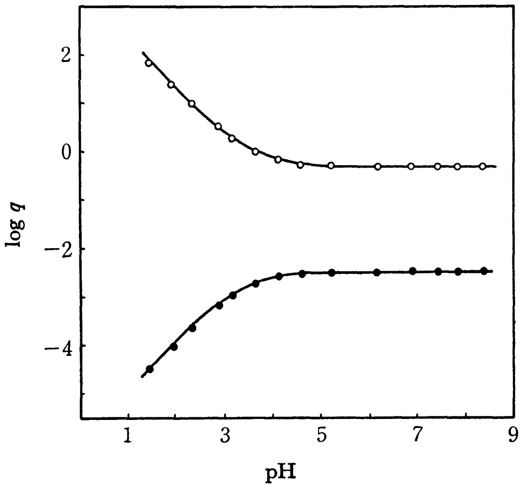

Fig. 3. The distribution of sodium picrate
○: q^R, ●: q^M

fit the observed ones. The best fit (Fig. 3, solid lines) is attained by choosing the value of 500, which is comparable to that obtained with the nitrobenzene system.

A value of 0.381[9] obtained in pure water is chosen for K_a^{HR} by neglecting a possible effect of the MIBK dissolved.

Distribution of Alkali Metals q^M. A typical plot of log q^M *vs.* pH for sodium picrate is shown in Fig. 3 by solid circles. The curves for the other picrates are not shown, since they were almost the same. The q^M and q^R values in Table 2 can serve as a measure of the slight differences in the curves among the picrates.

Appearance of a horizontal line can be explained by means of Eq. (19) as follows: When the aqueous solution is kept sufficiently alkaline, Eq. (19) can be rearranged into the following by neglecting $[H^+]_o$ and the terms containing $[H^+]_a$

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

$$C^R - C^M = A$$

This is further simplified to

$$(q^M)^2 = \frac{D^{MR}K_a^{MR}}{K_o^{MR}}\left(1+\frac{A}{[M^+]_a}\right) \tag{21}$$

where $[M^+]_a/[M^+]_o$ is approximated by $1/q^M$. The concentrations of alkali metals remain practically constant over the whole pH range studied, since the concentrations of the picrates are much smaller than those of the alkali metals added as buffers. The values of q^M, therefore, become constant.

In the acidic region, on the other hand, circumstances are not so simple as in the alkaline region, since the term $[H^+]_o$ can not be neglected. Since no direct method for determining the $[H^+]_o$ values is known, the values are calculated from the pH:

$$[H^+]_o = \frac{K_o^{HR}K_o^{MR}D^{HR}[M^+]_o}{K_a^{HR}K_a^{MR}D^{MR}[M^+]_a}[H^+]_a \tag{22}$$

Introduction of this term makes it difficult to estimate a simple relationship between the values of log q^M and pH, as has been shown in the nitrobenzene system.

Distribution of the Acid Species q^R. The dependence of the distribution ratio upon pH is calculated from Eq. (12). This equation can be simplified under sufficiently alkaline conditions as

$$q^R = \frac{D^{MR}K_a^{MR}}{K_o^{MR}}\left(K_o^{MR}[M^+]_a+\frac{1}{q^M}\right) \tag{23}$$

This is further simplified to

$$q^R = \frac{D^{MR}K_a^{MR}}{K_o^{MR}}\cdot\frac{1}{q^M} \tag{24}$$

showing that q^R values are independent of pH. The equation also shows that the q^M values are smaller than the q^R values by a factor of $(1+A/[M^+]_a)$. When the initial concentrations of C^M and C^R are equal ($A=0$), the values of q^M and q^R become the same, as in the nitrobenzene system.

In the acidic region, on the other hand; the q^R values vary almost linearly with pH, though the slope is slightly smaller than −1.

It has been comfirmed that the distribution of the picrates can be explained by means of six kinds of equilibria. The validity of such treatments may be proved indirectly by the fact that the K_a^{MR} value obtained with sodium picrate agrees well with that determined potentiometrically. No successful application to the mutual separation of alkali metals can be expected for the MIBK system because of its high levelling property.

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