March, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 745—749 (1971) 745

Studies of the Interaction between the Picrate Ion and Alkali Metal Ions

Mitsuo Yamane, Tadashi Iwachido,* and Kyoji Tôei
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama
* *College of Liberal Arts, Okayama University, Tsushima, Okayama*

(Received November 1, 1970)

Alkali metal picrates in an aqueous solution are extractable by nitrobenzene. The investigations of the equilibria in and between the aqueous and organic phases show that the larger the association constants in the aqueous phase and the dissociation constants in the organic phase, the greater the extractability of the salts. The extremely low extractability of alkali metal picrates can be well explained in terms of such equilibrium constants.

The results of earlier works have suggested that an effective extraction of alkali metals can be achieved by the reagents known as the precipitants of these ions. These reagents are all similar in chemical structure—namely, they are all bulky anions. Polyiodide,[1] tetraphenylborate,[2-4] and perchlorate[4] ions are representative reagents, and these salts with alkali metals are extractable into nitrobenzene. In previous papers,[5-8] it has been shown that alkali metals can be effectively extracted by nitrobenzene in the presence of such polynitroamines as hexanitrodiphenylamine.

Considerations of the equilibrium in and between the aqueous and organic phases show that the greater the extractability of these salts, the larger the association in the aqueous phase and the smaller the association in the organic phase. Phenols,[9] especially nitrophenols, have been known as extractants, though the extractability is much less than that of the polynitroamines. In the present paper, it will also be shown that the low extractability of the picrates can be explained by the equilibrium studies.

Experimental

Reagents. Alkali metal picrates were prepared by dissolving picric acid into an aqueous solution containing a slight excess of each alkali metal carbonate or sulfate. The precipitate was filtered and recrystallized two or three times from ethanol or methanol. The crystals were dried at 70°C for 3 to 5 hr under reduced pressure. Nitrobenzene of a guranteed-grade was dried over anhydrous sodium sulfate for two days. The dried nitrobenzene was then distilled under reduced pressure. The fraction boiling at 75°C/5 mmHg was collected and stored in an ampouple in order to protect it from moisture. The distillate has a specific conductance of about 4×10^{-9} ℧/cm and is satisfactory enough for the conductivity measurement of these salts.

Extraction Procedures. The aqueous solutions of the picrates (4×10^{-2}, 9×10^{-3}, 2×10^{-3}, and 1×10^{-3} M for Na, K, Rb, and Cs respectively) were prepared, 1- to 10-m*l* aliquots were transferred into separatory funnels and diluted with water to make up the volume to 10 m*l*, and then the same volume of nitrobenzene was added to each. The funnels were shaken at 25°C for 30 min and allowed to stand for half an hour. The alkali metals extracted into the organic phase were determined by an atomic absorption spectrophotometer (Nippon Jarrell Ash, Type AA-1).

Conductance Measurements. The apparatus and the procedures of conductance measurements were the same as those described in an earlier paper.[8]

Theoretical

The dissociation constant, K_d, of alkali metal picrates in nitrobenzene were determined by the method of Shedlovsky.[10] The conductances, Λ, were related with the concentration of electrolytes, C, by the following equation:

$$\frac{1}{\Lambda S}=\frac{1}{\Lambda_\infty}+\frac{C\Lambda S f_o{}^2}{K_d \Lambda_\infty^2} \qquad (1)$$

where Λ_∞ refers to the limiting conductance, and f_0, to the mean activity coefficient. S is a function of Z only.

$$S\equiv\left[\frac{Z}{2}+\sqrt{1+\left(\frac{Z}{2}\right)^2}\right]^2 \qquad (2)$$

Z is defined by Eq. (3):

$$Z=\frac{\alpha\sqrt{C\Lambda}}{\Lambda_\infty^{3/2}} \qquad (3)$$

where α is the Onsager coefficient. The picrate anion, R^-, associates with alkali metal cations, M^+, to form the ion-pair:

$$M^+ + R^- \overset{K_a^{MR}}{\rightleftharpoons} MR \qquad (4)$$

and the association constant in nitrobenzene, K_o^{MR} $(=1/K_d)$, is written as:

$$K_o^{MR}=\frac{[MR]_o}{[M^+]_o[R^-]_o f_o{}^2} \qquad (5)$$

where the subscript *o* refers to the nitrobenzene phase and the brackets, to the molar concentration of each species.

The values of the mean activity coefficient of the picrates in both the aqueous and organic phases were calculated by means of the following Debye-Hückel limiting law:

---

1) M. Kyrš and S. Podesva, *Anal. Chim. Acta*, **27**, 183 (1962).
2) K. Haruyama and T. Ashizawa, *Bunseki Kagaku*, **14**, 120 (1965).
3) R. C. Fix and J. W. Irvine, Jr., *MIT Lab. Nuclear Science, Annual Progress Report* (Nov. 30, 1955).
4) T. Sekine and D. Dyrssen, *Anal. Chim. Acta*, **45**, 433 (1969).
5) T. Iwachido and K. Tôei, This Bulletin, **37**, 1276 (1964).
6) H. Ueda, T. Iwachido, and K. Tôei, *Nippon Kagaku Zasshi*, **86**, 865 (1965).
7) T. Iwachido, S. Ukai, and K. Tôei, This Bulletin, **40**, 694 (1967).
8) S. Motomizu, K. Tôei, and T. Iwachido, *ibid.*, **42**, 1006 (1969).
9) W. J. Ross and J. C. White, *Anal. Chem.*, **36**, 1998 (1964).
10) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

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

The association constant of the picrates in the aqueous phase, K_a^{MR}, is also represented as follows:

$$M^+ + R^- \overset{K_a^{MR}}{\rightleftharpoons} MR$$

$$K_a^{MR} = \frac{[MR]_a}{[M^+]_a[R^-]_a f_a^2} \tag{7}$$

where the subscript a denotes the aqueous phase. From the atomic absorption measurements, the total quantities of the alkali metal cations in both the aqueous and organic phases, C_a and C_o, were determined.

The ratio of C_o to C_a, or the distribution ratio, is written as follows:

$$q^M = \frac{C_o}{C_a} = \frac{[M^+]_o + [MR]_o}{[M^+]_a + [MR]_a} \tag{8}$$

In considering the $[M^+]_a = [R^-]_a$ relationship, the following equation is derived:

$$\frac{Y}{q^M} = \frac{1}{D^{MR}} + \frac{1}{D^{MR}K_a^{MR}f_a^2[M^+]_a} \tag{9}$$

where D^{MR} refers to the distribution coefficient of an ion-pair.

Y is defined by the following equation:

$$Y = \frac{\sqrt{0.25 + C_oK_o^{MR}f_o^2} + 0.5}{C_oK_o^{MR}f_o^2} + 1 \tag{10}$$

From a plot of Y/q^M *versus* $1/[M^+]_a f_a^2$, the values of D^{MR} and K_a^{MR} can be determined simultaneously.

Results and Discussion

Association Constants and Limiting Conductances of Alkali Metal Picrates in Nitrobenzene. In order to obtain the association constant from a conductance method, it is necessary to get the limiting conductance of the picrates in nitrobenzene.

At first, Z is calculated by using an approximate value of Λ_∞, which is determined graphically by a plot of Λ *versus* $C^{1/2}$ (Fig. 1); this leads to a first approxima-

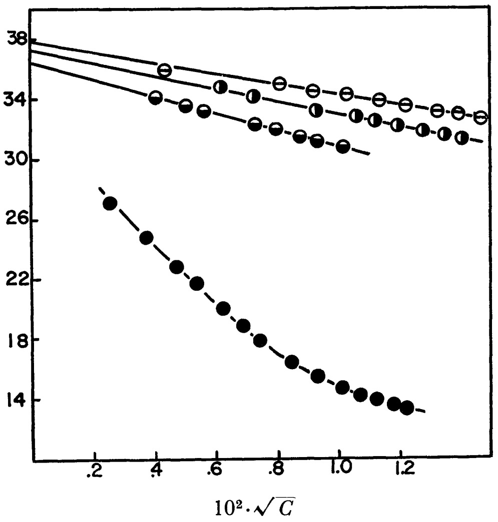


Fig. 1. The Λ-$\sqrt{C}$ curves of alkali metal picrates in dry nitrobenzene.
● Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

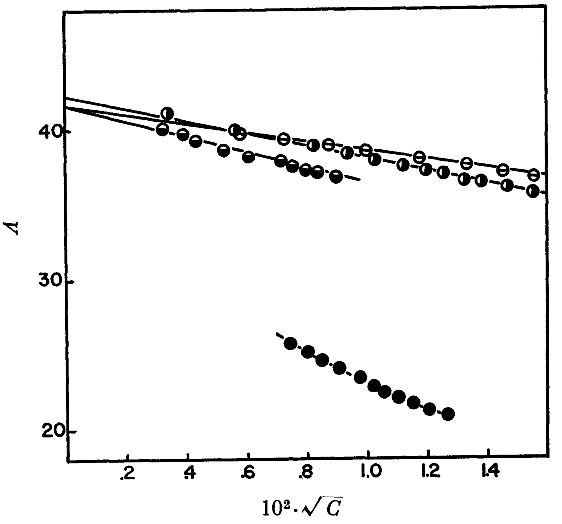


Fig. 2. The Λ-$\sqrt{C}$ curves of alkali metal picrates in nitrobenzene saturated with water.
● Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

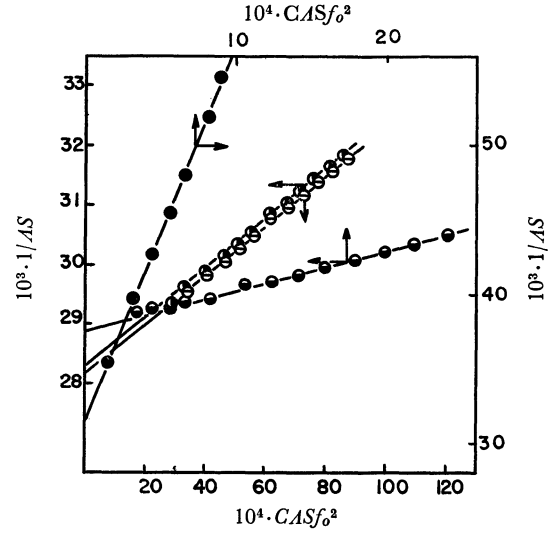


Fig. 3. Shedlovsky plot of the picrates in dry nitrobenzene.
● Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

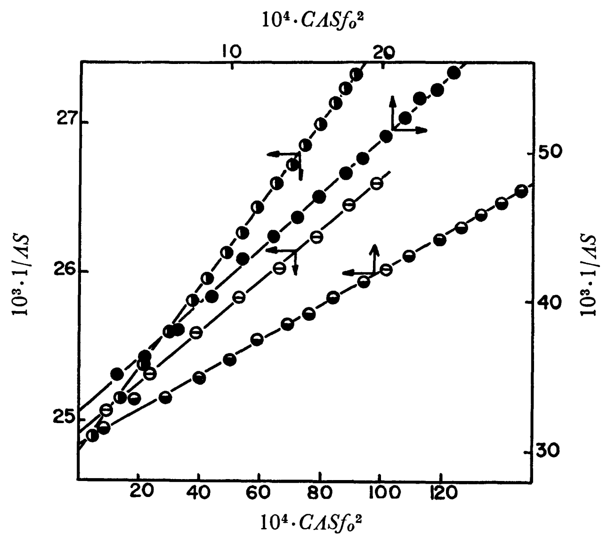


Fig. 4. Shedlovsky plot of the picrates in nitrobenzene saturated with water.
● Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

tion for S. A first approximation for f_o is calculated from the Debye-Hückel limiting equation (6). These values are applied to Eq. (1) for all the values of C, and the plot of $1/\Lambda S$ *versus* $C\Lambda Sf_o^2$ gives the second approximation of Λ_∞. The process is repeated two or three times until Λ_∞ is no longer altered. The constants, Λ_∞ and K_o^{MR}, were calculated from the intercept and the slope of the linear extrapolation by means of the least-squares method (Fig. 3). Association constants in nitrobenzene saturated with water, $K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$, are calculated in the same manner by assuming that the dielectric constant and the viscosity of the water-saturated nitrobenzene are equal to those of dry nitrobenzene (Figs. 2 and 4).

The values of Λ_∞, $\Lambda_{\infty(\mathrm{H_2O})}$, K_o^{MR}, and $K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$ thus obtained are listed in Table 1. The light alkali metal picrates behave like weak electrolytes; especially is this true for lithium ($K_o^{\mathrm{LiPic}}=10^{7.2}$ after Witschonke and Kraus).[11]

Table 1. THE LIMITING CONDUCTANCES AND ASSOCIATION CONSTANTS FOR ALKALI METAL PICRATES

MR	Λ_∞	$\log K_o^{\mathrm{MR}}$	$\Lambda_{\infty(\mathrm{H_2O})}$	$\log K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$
Na-Picrate	33.9	4.48	31.9	3.67
K-Picrate	34.7	3.06	40.3	2.92
Rb-Picrate	35.1	2.81	40.7	2.65
Cs-Picrate	36.4	2.81	40.4	2.43

A plot of log K_o^{MR} *versus* the ionic potential (the ratio of the charge to the crystal radius, z/r) of the alkali metal cation clearly shows that, in both nitrobenzene and the water-saturated nitrobenzene, the larger the radius, the smaller the association constant (Figs. 5 and 6).

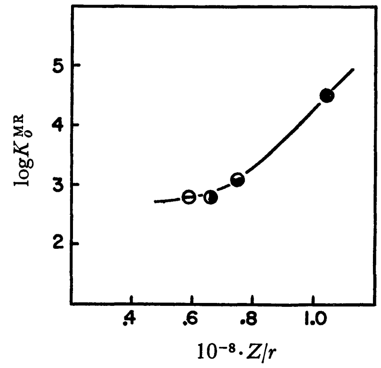


Fig. 5. The plot of $\log K_o^{\mathrm{MR}}$ *vs.* z/r.
●Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

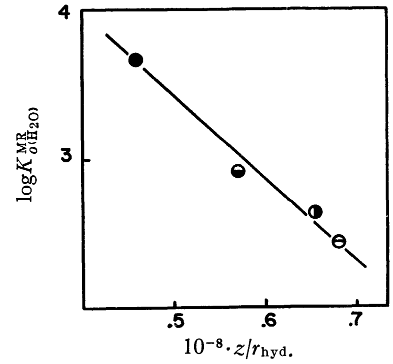


Fig. 6. The plot of $\log K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$ *vs.* z/r_{hyd}.
● Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

Association Constant in an Aqueous Solution. The association constant in an aqueous solution, K_a^{MR}, is obtainable by Eq. (9) from the slope of the lines in Fig. (7). First approximate values, K_a^{MR} and D^{MR}, are calculated by substituting the analytical concentration of the alkali metal, C_a, for the concentration of the free metal-cation, $[\mathrm{M}^+]_a$. The association constant thus obtained leads to a more accurate value of $[\mathrm{M}^+]_a$. These procedures were repeated two or three times until the value of K_a^{MR} did not alter any more upon further refinement. The values of log K_a^{MR} increase gradually in proceeding from Na to Cs, as is shown in Table 2 and Fig. 8.

The Role of Hydration. If the ion-pairing arises from the coulombic force, it will be greatly affected by the radius of the alkali metal cation. An ion of the small effective radius should associate with the oppo-

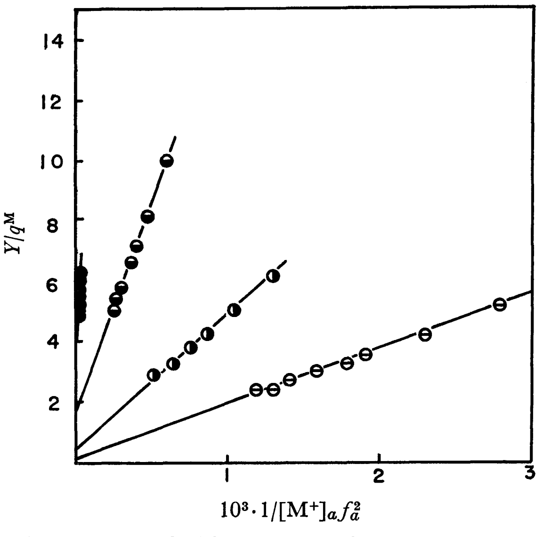


Fig. 7. The plot of Y/q^{M} *vs.* $1/[\mathrm{M}^+]_a f_a^2$.
● Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

Table 2. THE CONSTANTS OF K_a^{MR}, D^{MR}, q^{M} AND $(D^{\mathrm{MR}}\,K_a^{\mathrm{MR}}/K_{o(\mathrm{H_2O})}^{\mathrm{MR}})^{1/2}$ FOR ALKALI METAL PICRATES, ALONG WITH THE IONIC RADII, r, AND THE RADII OF HYDRATED IONS, r_{hyd}

MR	$\log K_a^{\mathrm{MR}}$	D^{MR}	q^{M}	$(D^{\mathrm{MR}}K_a^{\mathrm{MR}}/K_{o(\mathrm{H_2O})}^{\mathrm{MR}})^{1/2}$	r	$r_{\mathrm{hyd.}}$
Na-Picrate	1.38	0.0028	0.0035	0.0038	0.97	2.17
K-Picrate	1.64	0.014	0.025	0.027	1.33	1.75
Rb-Picrate	1.94	0.022	0.061	0.066	1.52	1.53
Cs-Picrate	2.07	0.068	0.18	0.17	1.70	1.47

---

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

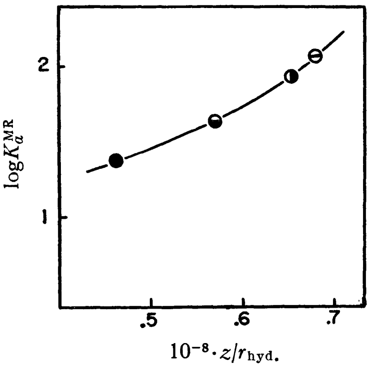


Fig. 8. The plot of logK_a^{MR} *vs.* z/r_{hyd}.
● Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

sitely-charged ion to form a stable ion pair. Generally, the effective radius of an ion is largely influenced by the hydration. The crystal radius of the alkali metal cation increases gradually from lithium to cesium; the order of the effective radius is completely reversed in an aqueous solution. The sequence of K_o^{MR} in dry nitrobenzene (Table 1) and of K_a^{MR} in an aqueous solution (Table 2) is coincident with the above consideration.

If a hydrated alkali metal cation and a picrate anion form an ion-pair in the water-saturated nitrobenzene, $K_{o(H_2O)}^{MR}$ should increase gradually from sodium to cesium, because the effective radius of the cation decreases from sodium to cesium. However, the sequence of the $K_{o(H_2O)}^{MR}$ values are completely inverse. This implies that the ion pairs formed in the water-saturated nitrobenzene and in the aqueous phase are somewhat different in a hydration state; that is, the hydrated water molecules in the nitrobenzene phase are not effective in the reversal of the order of the crystal radii of cations. It might be attributed to the nature of the picrate anion, which is relatively small and whose charge is not distributed to the whole of the anion, but fairly well to the phenolic oxygen atom.

The sequence of Λ_∞ (Table 1) should decrease from sodium to cesium, because the radius of the ion increases with the atomic weight. However, the results obtained are the inverse of this. It implies that a hydration of ions occurs even in the dry nitrobenzene solution. The evidence proves that the freshly-distilled nitrobenzene contains a small amount of water, the amount determinable by the Karl-Fisher method. The order of the tendency to dissolve the picrates in the dry nitrobenzene is as follows: Cs>Rb>K<Na<Li. The hydrated water molecules loosen the bonding between the cation and the picrate anion, and so enhance the dissociation of the ion pair. Therefore, the unexpected high solubility of sodium and lithium picrates is another evidence of the presence of the hydrated species in the dry nitrobenzene, because they are apt to be hydrated among alkali metal cations.

The values of K_o^{MR} are very consistent with the results of Witschonke and Kraus. They have mentioned that the association constant of lithium picrate in dry nitrobenzene ($10^{7.2}$) is decreased 1/25 fold ($10^{5.8}$) on the addition of 0.03M water. The same tendency was observed in the present case. The water promotes the dissociation of alkali metal picrates, and so $K_{o(H_2O)}^{MR}$ becomes smaller than K_o^{MR}. The tendency decreases from lithium to cesium, and all the $K_{o(H_2O)}^{MR}$ values tend to be convergent.

Distribution Coefficient and Distribution Ratio. The distribution coefficient of the picrate is obtained from the reciprocal of the intercept of the line in Fig. 7. The values of $K_{o(H_2O)}^{MR}$ and K_a^{MR} show the presence of the ion pairs both in the aqueous and nitrobenzene phases, although the amounts of it are not great. Accordingly, the following relation can be obtained by neglecting the formation of the ion pair and the hydrolysis of the picrate ion in both phases:

$$q^M \approx \frac{[M^+]_o}{[M^+]_a} = \sqrt{\frac{D^{MR}K_a^{MR}}{K_{o(H_2O)}^{MR}}} \qquad (11)$$

The distribution ratio of the metal cation, q^M, is expected from Eq. (11) to be constant. Therefore, the ratio of the total concentration of metal in the aqueous phase, C_a $(=[M^+]_a+[MR]_a)$, to that in nitrobenzene, C_o $(=[M^+]_o+[MR]_o)$, should be constant. The circles in Fig. 9 represent the experimental data, while the lines show the experimental mean values of q^M. The calculated values of $(D^{MR}K_a^{MR}/K_{o(H_2O)}^{MR})^{1/2}$ are very coincident with the experimental values of q^M, as is shown in Table 2. If there is a reagent which can be highly dissociated in both phases, namely, $[M^+]\gg[MR]$ and $[M^+]=[R^-]$ in each phase, the extractability could be calculated directly from the values of K_a^{MR}, $K_{o(H_2O)}^{MR}$ and D^{MR}. The complete extraction would be achieved by the use of the reagent with the largest D^{MR} and K_a^{MR} values and the smallest $K_{o(H_2O)}^{MR}$ value.

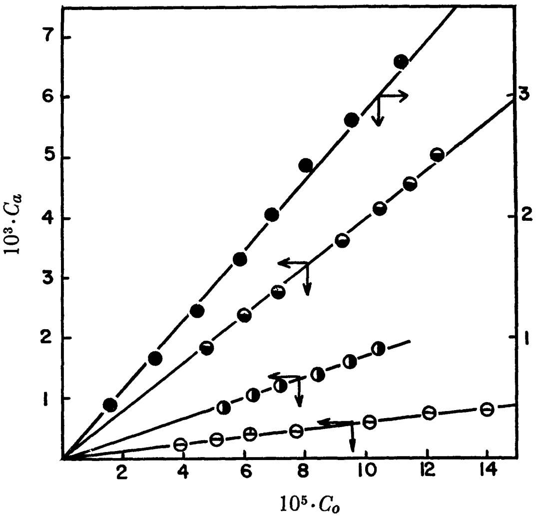
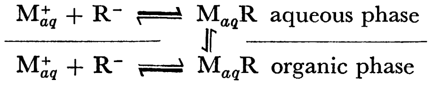


Fig. 9. The plot of concentrations of alkali metal ions in an aqueous phase. C_a, *vs.* those of an organic phase, C_o.
● Na-Picrate, ◒ K-Picrate, ◑ Rb-Picrate, ⊖ Cs-Picrate

Conclusion

The extraction of alkali metals by nitrobenzene in the presence of a bulky organic anion may be classified as an ion-association system. However, the present extraction system is somewhat different from the ordinary one in that the ion pair extracted extensively dissociates in the organic phase as well as in the aqueous phase. The mechanism of the extraction may well be visualized by the following scheme:



$$\begin{array}{lcll} M^+_{aq} + R^- & \rightleftharpoons & M_{aq}R & \text{aqueous phase} \\ \hline & \downarrow\uparrow & & \\ M^+_{aq} + R^- & \rightleftharpoons & M_{aq}R & \text{organic phase} \end{array}$$

With regard to the number of hydration in the organic phase, there is no direct evidence, but from the analogy with the case of polynitroamine (Hexyl[8]) and from the other indirect evidences, it seems to be reasonable to consider the coextraction of water molecules into nitrobenzene by means of the above scheme.

A high extractability is attainable with a reagent which allows the equilibrium to shift in the direction shown by the bold-faced arrows. From this point of view, the very low extractabilities of the picrates as compared with those of the Hexyl salts can be explained by the facts that the D^{MPic} values are smaller than D^{MHexyl}, and the $K^{\mathrm{MPic}}_{o(\mathrm{H_2O})}$ values are larger than $K^{\mathrm{MHexyl}}_{o(\mathrm{H_2O})}$, while the K^{MPic}_{a} and K^{MHexyl}_{a} values remain almost the same.

Apart from the equilibrium discussion, it is also of much interest to know with what kind of anions the highest extractability can be obtained. The simple and correct answer is hard to obtain, because the factors affecting the extraction are too complex to elucidate, but it is shown that the size and the charge distribution of anions used may have a great effect on the extractability.

The present work has been supported in part by a Grant for Scientific Research from the Ministry of Education.