Studies of the Solvent Extraction of Potassium by Nitrobenzene in the Presence of Organic or Inorganic Acids

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Aromatic compounds with an acidic group, such as –OH, –SH, –COOH, –SO_3H, $>$NH, $\geqslant$CH, and $\equiv$B$^-$ (tetraphenylborate) were tested as extracting agents for potassium. The first four acids showed an extractability lower by far than that of the last three. Most inorganic acids exhibited no signs of extraction. Bulky and electron-attracting substituents, such as nitro or halogen group, were proved to be effective in enhancing the extractability. The addition of iodine was also effective. A few kinds of surfactants showed considerably high extractability. Some factors influencing the extraction were speculated upon.

In recent years, the solvent extraction of alkali metals by utilizing ion-pairing agents has attracted growing attention. The first and most extensive works were carried out by researchers engaged in the treatment of radioactive fission products, especially ^{137}Cs. Tetraphenylborate,[1,2] hexanitrodiphenylamine,[3,4] and some phenols[5,6] are typical reagents. Nitrobenzene, a dipolar aprotic solvent with a high dielectric constant, has been frequently used as a solvent of these ion-pairs. However, there has been no systematic explanation of the reasons why these compounds are good for the extraction of alkali metals. This paper will establish some factors affecting potassium extraction by examining a number of organic and inorganic acids and will give some indications on how to obtain good extractions in the future.

Experimental

Reagents. The reagents used were, for the most part, commericial reagents of the purest quality; some were purified when the necessity arose. The amine derivatives were synthesized by a method described in a series of works by Tôei.[7-9] All of the potassium or sodium salts of organic and inorganic acids were dissolved in water to give a 2.5×10^{-2}M aqueous solution. Organic compounds of the acid-form were made up into either a 2.5×10^{-2}M aqueous or a 1.0×10^{-2}M nitrobenzene solution, according to the solubility of the acids. Some of the remaining organic compounds with which a high extractability was obtained were made up into a 10^{-3}M nitrobenzene solution except in a few cases (10^{-4}M).

The pH's of the aqueous solutions were adjusted when necessary by adding a 0.1M citrate buffer (pH 2 and 3), a 0.1M acetate buffer (pH 4 and 5), a 0.1M phosphate buffer (pH 6,7, and 8), or a 0.1M carbonate buffer (pH 9 and 10). The pH of the solution was also adjusted to pH 11 and 12 with 0.1M lithium carbonate and 0.1M lithium hydroxide solutions respectively. The solutions were made so that they all contained equal amounts of lithium ions.

Extraction. Into a 50-m*l* separatory funnel, 1 m*l* of a 0.1M potassium chloride solution was transferred, and then 4 m*l* of a 2.5×10^{-2}M aqueous reagent solution and 5 m*l* of water or a buffer solution were added. The resultant 10 m*l* of a 10^{-2}M potassium solution was gently shaken with 10 m*l* of nitrobenzene for 2 hr at room temperature. Some alterations were made according to the type of stock solution employed, keeping both the molar ratio of potassium to the reagent and the volume ratio of the aqueous to the organic phase at unity. In order to prevent the extraction of lithium ions with the reagent, buffers were not employed except in the cases where reagent anions were expected to hydrolyze to a great extent and where the knowledge of the dependence of the extractability on the pH was necessary for further discussions.

Determination of Potassium. After the extraction mixture had been allowed to stand for half an hour, the nitrobenzene phase was separated and subsequently subjected to atomic absorption spectrophotometry (Nippon Jarrell Ash, Type AA-1). About 0.2×10^{-6}M of potassium was detected.

Results

Extraction Curves. Figure 1 and 2 show the extraction curves obtained with several acids.

With acids having one functional group, the curve will be sigmoidal in shape, but the location of the curve shifts toward a higher or a lower pH region according to the magnitude of the acid dissociation constant and the distribution coefficient of the acid (Fig. 1).

Different types of extraction curves were obtained with acids having two or more functional groups, as is shown in Fig. 2. The form and the location of the curve may be instructive in estimating what kind of ion-pair is dominantly extractable by nitrobenzene.

Extractability. The values of the percent extractions of many kinds of acids are listed in Tables 1 to 9. The results may be summarized as follows: 1). The highest extraction of potassium was attained with the acids of amine derivatives and tetraphenylborate (8-X), as is shown in Tables 4 and 8. The values of the percent extractions of some typical acids, such as phenols, sulfonic acids, and carboxylic acids (Tables 1 to 3), were all less than 0.1, except for some nitro- or halogeno-substituted acids. Such a situation was also encountered with acids of different types, as is shown in Tables 5 to 9.

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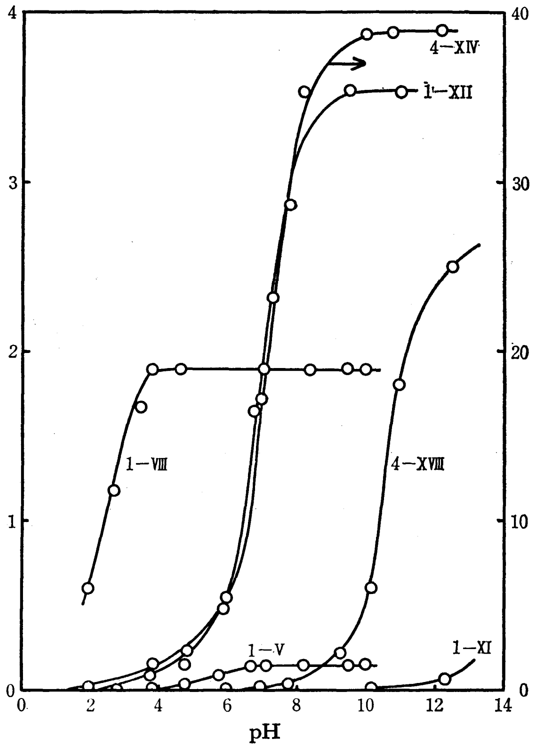

Fig. 1. The effect of pH on the extraction of potassium by some acids in nitrobenzene

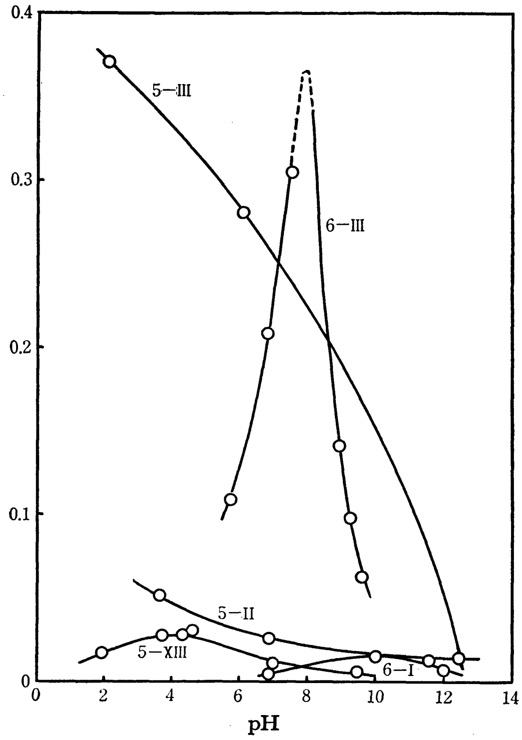

Fig. 2. The effect of pH on the extraction of potassium by some acids in nitrobenzene

Table 1. Percent extraction of potassium with phenolates

Compound	No.	pK_a	pH	%E
Phenol	1-I	9.98	12	0
—, 2-Nitro-	1-II	7.22	12.2	0
—, 3-Nitro-	1-III	8.40	13.2	0.005
—, 4-Nitro-	1-IV	7.15	13.2	0.005
—, 2,4-Dinitro-	1-V	4.02	10.0	0.150
—, 2,5-Dinitro-	1-VI	5.32	13.2	0.060
—, 2,6-Dinitro-	1-VII	3.71	13.2	0.103
—, 2,4,6-Trinitro- (Picric acid)	1-VIII	−0.22	10.1	1.89
—, 2,4,6-Tribromo-	1-IX		13.2	0.125
—, Pentachloro-	1-X		10.5	1.05
1-Naphthol	1-XI	9.30	12.6	0.062
—, 2,4-Dinitro-	1-XII		9.50	3.54
8-Hydroxyquinoline	1-XIII	9.81	12	0.003

Table 2. Percent extraction of potassium with carboxylates

Compound	No.	pK_a	pH	%E
Benzoic acid	2-I	4.20	10.0	0
—, 2-Nitro-	2-II	3.49	10.1	0
1-Naphthoic acid	2-III	3.69	12.6	0.011
Acetic acid	2-IV	4.76	7.0	0
—, 1-Naphthyl-	2-V	4.24	12.5	0.003
Anthraquinone-2-carboxylic acid	2-VI	3.37	10.5	0.008
Methyl Red	2-VII	4.84	12.4	0.007
Nicotinic acid	2-VIII	4.81	12	0.003

Table 3. Percent extraction of potassium with sufonates

Compound	No.	pK_a	pH	%E
Benzenesulfonic acid	3-I	−0.70	1.8	0.006
—, 2,4-Dinitro-	3-II		6.90	0.10
1-Naphthalene-sulfonic acid	3-III	−0.17	6.10	0.021
2-Naphthalene-sulfonic acid	3-IV		4.3	0.035
1,2-Naphthoquinone-4-sulfonic acid	3-V		2.75	0.060
Anthraquinone-2-sulfonic acid	3-VI	−0.38	6.24	0.11

It is of much interest to compare the values of percent extraction obtained with acids having a benzene or naphthalene nucleus in common: 2,4-dinitrophenol (0.150)>2,4-dinitrobenzenesulfonic acid (0.10); 1-naphthol (0.062)>1-naphthalenesulfonic acid (0.021)> 1-naphthoic acid (0.011). The sequence is the reverse of that which can be observed between 2-naphthyl mercaptan (8-IX) and 1-naphthol (1-XI); this might be due to the hydrolysis of the former in the aqueous phase. Mercaptans (8-VII, -VIII) showed much higher extractabilities than imidazoles (8-IV, -V), although all of them are similar in size.

2) Acids having a bulky nucleus were desirable as extraction agents. This was well shown by sulfonic acids as follows: Anthraquinone-2-sulfonic acid (0.11) >2-naphthalenesulfonic acid (0.035)>benzenesulfonic acid (0.006). The same sequence was also observable with phenols and carboxylic acids (Tables 1 and 2). The insertion of a CH_2 group between the nucleus and the functional group reduced the effect, as was shown with 1-naphthylacetic acid (2-V).

3) The introduction of a bulky, electron-attracting

TABLE 4. PERCENT EXTRACTION OF POTASSIUM WITH AMINE DERIVATIVES (10^{-3} M)

Compound	No.	pH	%E
Aniline	4-I	12	0[a]
—, 2-Nitro-	4-II	12.5	0[a]
—, 2,4-Dinitro-	4-III	12.5	0[a]
2,4,5,7-Tetranitroacrydone	4-IV	12.8	45.4
1,3,7,9-Tetranitrophenothiazine-5-dioxide	4-V	12.8	65.3
Phenoxazine, 1,3-Dinitro-	4-VI	12.8	0.09
—, 1,3,7,9-Tetranitro-	4-VII	11.8	3.40
1,3,6,8-Tetranitrocarbazole	4-VIII	12.8	7.30
Diphenylamine, 2,4-dinitro-	4-IX	12.5	0
—, 2,4,2′,4′-Tetranitro-	4-X	12.8	40.8
—, 2,4,6,2′,4′,6′-Hexanitro-	4-XI	13.2	58.3[b]
2-Naphthylamine, 2,4-Dinitrobenzo-	4-XII	12.8	0
—, 2,4,6-trinitrobenzo-	4-XIII	12.8	1.63
1-Naphthylamine, *N*-(2,4,6-trinitrobenzo)-2,4,-dinitro-	4-XIV	12.2	39.1[b]
2,4,6-Trinitrophenylamine, *N*-(1-anthraquinolino)-	4-XV	12.8	5.87
—, *N*-(2-nitro-1-anthraquinolino)-	4-XVI	12.8	42.7
N-(2,4,6-trinitrobenzo)-benzene-sulfamide	4-XVII	12.8	16.2
Diphenylpicrylhydrazine	4-XVIII	12.5	2.50[a]

a) The extraction of potassium was carried out with the reagent of 10^{-2}M.

b) Reagent concentration, 10^{-4}M.

substituent, such as a nitro group or halogen atoms, was highly effective in improving the extractability. In general, the extractability increases rapidly with the number of the substituents. The effect was obvious with phenols (Table 1) and amine derivatives (Table 4).

4) Compounds which have two or more functional groups in a molecule showed a characteristic extraction curve. With phthaleins (6-I, -III) and sulfonphthaleins (6-XI) we obtained a curve with a maximum at a certain pH value, and with alizalinsulfonic acid (5-III), a monotonously-descending curve. In both cases, the percent extraction begins to decrease at a somewhat higher pH value than that to be expected from the first dissociation constant of the acid. The fact may show that, among the possible species existing in the aqueous phase, the neutral ion-pair composed of equimolecular amounts of potassium and the monovalent, reagent anion is dominantly extractable by nitrobenzene. Styphnic acid (5-I) may be a good illustration. Molybdate (9-VIII) and tungstate (9-IX) may be the same.

5) The addition of iodine greatly improved the extractability (Tables 6 and 9). It is well known that the iodine combines with iodide to form a bulky I_3^- anion. Therefore, it seems likely that the KI_3, ion-pair, is extractable by nitrobenzene. For the other cases encountered, a different explanation must be given.

6) A few surfactants showed quite good results, whereas polyvinylsulfate (8-XIII) exhibited no extraction. It must be noted that the separation of the nitrobenzene phase from the aqueous phase becomes increasingly difficult as the amount of the surfactant used increases. This may prevent their practical use.

7) Many kinds of inorganic compounds were tested by varying the pH of the aqueous solution, but only a few were capable of extracting only a small amount of potassium. Bulky, monovalent peroxyacid anions were the best; divalent anions were all incapable of extracting potassium, except for a few compounds which are known as precipitants of potassium.

Extractability and Solubility. In Fig. 3 the solubility of potassium salts in water, *S*, is plotted against the distribution ratio, *q*, of these compounds between

TABLE 5. PERCENT EXTRACTION OF POTASSIUM WITH COMPOUNDS HAVING TWO OR MORE FUNCTIONAL GROUPS

Compound	No.	pK_a or pH Range	pH	%E
2,4,6-Trinitroresorcinol	5-I		2.4	1.73
			12.7	0
Alizalin	5-II	5.5—6.8	3.7	0.052
Alizalin-3-sulfonic acid	5-III	5.45	2.1	0.371
		11.01		
2,4-Dinitro-1-naphthol-8-sulfonic acid	5-IV		1.7	0.107
			12	0.013
4,5-Dihydroxy-2,7-naphthalenedisulfonic acid	5-V	5.36	3.9	0.003
		15.6		
2,3-Dihydroxy-6-naphthalenesulfonic acid	5-VI		2.1	0
			5.5	0
1-Nitrobenzene-3,5-disulfonic acid	5-VII		7.5	0.029
1-Naphthylamine-8-sulfonic acid	5-VIII		12	0.035
1-Napthylamine-4,8-disulfonic acid	5-IX		2.6	0.003
Tartaric aicd	5-X	3.04	4.3	0
		4.36		
Phthalic acid	5-XI	2.95	3.8	0.007
		5.41	7.0	0
Aurintricarboxylic acid	5-XII		5.2	0.059
Salicylic acid	5-XIII	2.75	3.8	0.028
		12.4		

Table 6. Percent extraction of potassium with phthaleins or sulfonphthaleins

Compound	No.	pH Range	pH	%E
Phenolphthalein	6-I	8.0—9.8	10.0	0.015
—, 3′,3″-Dimethyl-	6-II	8.2—9.8	12.5	0.017
—, 3′,3″-Dinitro-	6-III	6.8—8.2	7.5	0.305
3′,5′,3″,5″-Tetrabromophenolphthalein ethyl ester	6-IV		10.0	10
Fluorecein	6-V		8.6	0.008
—, 2,4,5,7-Tetrabromo-	6-VI		7.0	0.468
—, 2,4,5,7-Tetraiodo-	6-VII		6.7	0.23
			8.0	0.094
	(+equiv. I_2)		6.7	5.59
	(+excess I_2)		6.2	67.1
Phenolsulfonphthalein	6-VIII	6.8—8.4	7.2	0.107
			8.0	0.108
—, 3′,3″-Dimethyl-	6-IX	0.4—2.2	1.1	0.028
		7.2—8.8	8.3	0.102
—, 3′,3″-Dinitro-	6-X	2.9—4.8	4.5	0.333
			12.4	0.010
—, 3′,5′,3″,5″-Tetrabromo-	6-XI	3.0—4.6	1.2	0.270
			4.5	0.845
			9.0	0.351
—, 3′,5′,3″,5″-Tetraiodo-	6-XII		3.9	2.33
			11.6	0.047
	(+equiv. I_2)		4.9	7.43

Table 7. Percent extraction of potassium with phenyl derivatives of some oxyacids

Compound	No.	pK_a	pH	%E
Phenylarsonic acid	7-I	3.47	2.0	0
		8.48	3.8	0
			6.9	0
			8.7	0
			12.2	0
—, 2-Nitro-	7-II	3.37	1.9—12.2	0—0
		8.54		
Phenylboric acid	7-III	8.86	12.5	0

Table 8. Percent extraction of potassium with miscellaneous compounds

Compound	No.	pK_a	pH	%E
5-Nitrobarbituric acid	8-I		1.6	0.003
			12	0
Picrolonic acid	8-II		12	1.07
Phthalimide	8-III	8.3	6.5	0
Benzimidazole	8-IV	5.3	7.9	0
		12.3		
—, 2-Methyl-	8-V		7.9	0
Hexanitrotriphenylmethane	8-VI		12.8	2.58[a]
2-Mercaptobenzoxazole	8-VII		12.9	0.044
2-Mercaptobenzothiazole	8-VIII		12.9	0.125
2-Naphthyl mercaptan	8-IX		12.7	0.029
Tetraphenylboric acid	8-X		7.4	76.6[b]
Laurylbenzensulfonic acid	8-XI		6	0.43
Sodium lauryl sulfate	8-XII			1.0
Polyvinyl potassium sulfate	8-XIII		6.1	0

a) Reagent concentration, 10^{-3}M.
b) Reagent concentration, 10^{-4}M.

Table 9. Percent extraction of potassium with inorganic compounds

Anion	No.	pK_a	pH	%E
IO_4^-	9-I		6.2	0.115
ClO_4^-	9-II		6.5	0.120
MnO_4^-	9-III		7	0.331
BF_4^-	9-IV		4.0	0.045
SCN^-	9-V	−0.85	6.8	0.025
I^-	9-VI		6.2	0.012
I^- (+equiv. I_2)	9-VII		5.7	15.9
MoO_4^{2-}	9-VIII	$pK_2=6$	1.0	0.084
			4.9	0.012
			7.4	0
WO_4^{2-}	9-IX	$pK_1+pK_2=7$	1.0	0.232
			5.1	0.018
			8.0	0
$PtCl_6^{2-}$	9-X		1.0	0.004
			2.8	0.009
Uranyl Zinc Acetate	9-XI		4.6	0.021
$Co(NO_2)_6^{3-}$	9-XII		1.0	0.017
			3.9	0.014

Potassium can not be extracted by the following reagent.
IO_3^-, ClO_3^-, BrO_3^-, NO_3^-, NO_2^-, F^-, Cl^-, Br^-, N_3^-, OCN^-, CrO_4^{2-}, SO_4^{2-}, HPO_4^{2-}, SeO_4^{2-}, TeO_4^{2-}, $HAsO_4^{2-}$, CO_3^{2-}, SiF_6^{2-}, $S_2O_7^{2-}$, $S_2O_8^{2-}$, $H_2Sb_2O_7^{2-}$, $B_4O_7^{2-}$, $Cr_2O_7^{2-}$, BO_3^-, BiO_3^-, VO_3^-, AlO_2^-, AsO_2^-, $Fe(CN)_5NO^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$

the aqueous and nitrobenzene phases. Because of the lack of the solubility data, most of the results obtained can not be shown in this figure. This figure indicates that the solubility is closely related to the extractability. It is of much interest to note that this relation holds not only for nitro compounds, which are similar in chemical constitution to nitrobenzene, the solvent, but also even for inorganic compounds. Such a correlation will be helpful for further extractions.

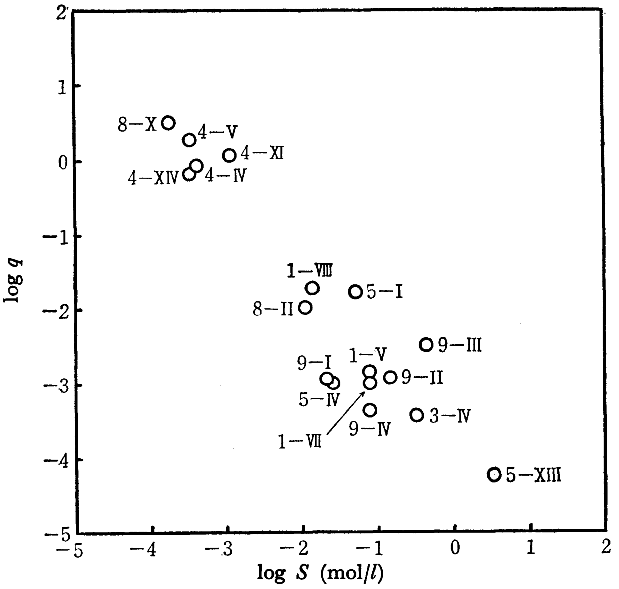

Fig. 3. The relation between the distribution ratio of potassium and the solubility of potassium salts in water
q: The distribution ratio of potassium salts
S: The solubility of potassium salts in water

Discussion

In a previous paper,[10] it has been reported that the extraction of alkali metals with organic acids into nitrobenzene can be well understood by recognizing that nitrobenzene helps the ionic dissociation of the ion-pairs extracted. The paper also has stated that the extractability of the ion-pair increases with the association constant in the aqueous phase and with the dissociation constant in nitrobenzene.

Some chemical constitutional factors influencing such equilibria will be considered below.

Ion Size. Ion association in organic solvents has been extensively studied by Kraus and his collaborators by means of conductometry.[11] As might be expected from a long-range electrostatic force, ion association generally increases with a decrease in the ion size. This may be true for a simple binary electrolyte. The estimation of the energy of charge separation, however, becomes increasingly more difficult as the structural complexity of the anions increases. In general, large anions from loosely associated ion-pairs, and the resultant ion-pairs can easily be dissociated in nitrobenzene.

On the other hand, in an aqueous solution Bjerrum's theory[12] is not always helpful for the study of ion-pairing. According to the theory, the distance of the closest approach of free ions is 3.57 Å for 1:1 electrolytes in water at 25°C. This distance roughly corresponds to that of potassium iodide. Hence, anions which are larger than iodide should not make stable ion-pairs in the aqueous solution. Diamond[13] has indicated the formation of an ion-pair of a different type between bulky and poorly hydrated ions, the distance of the separation being much greater than 3.57 Å. He also suggested that, with regard to such ion-pairs, the hydrogen-bonded structure of water enforces the association of the oppositely-charged ions to minimize the disturbance of the water structure. This type of ion-pairing or the water structure-enforced ion-pairing has a dependence on the distance of charge separation the reverse of that of the ion-pairing of the Bjerrum type. From the above considerations of the behavior of ion-pairs in both the aqueous and nitrobenzene phases, it might be expected that ion-pairing between large organic anions and a potassium cation is facilitated in the aqueous phase and suppressed in the nitrobenzene phase. Accordingly, it can be concluded that large anions favor the extraction.

Steric Factors. In tetraphenylborate (8-X), hexanitrotriphenylmethane (8-VI), and diaryl-substituted amines (Table 4), a formal, negative charge is located on the boron, carbon, and nitrogen atoms respectively, and they are all sterically hindered by large, bulky phenyl groups from coming in contact with the potassium cation. Nitro-group or halogen atoms also help to keep the oppositely-charged ions apart.

On the other hand, anions with no steric hindrance can contact the potassium cation directly, even though they have a residual bulky group. This results in a strong ion-pairing. The fact that the association constant of potassium picrate in nitrobenzene[10] is 1200, about 120-times than that of hexanitrodiphenylamine,[14] can be considered as a good illustration of the effect. Such examples may easily be seen in the remaining compounds.

Charge Dispersal. The concept of charge dispersal has been developed on the basis of the discussion of the acid-base strength. Electrons in an extended π bond are free to move anywhere within the region of the charge cloud; this promotes the delocalization of electrons through a π-molecular orbital system. Thus, the negative charge located at first on the atom from which the hydrogen atom is released as the hydrogen ion is delocalized or dispersed on the whole molecule. As a consequence, the resultant anions are stabilized by the amount corresponding to the delocalization energy. The stabilization of anions will result in the enhancement of the acidity of the corresponding conjugate acids. A similar effect might be expected as well in the case of ion-association; that is, the charge dispersion of anions weakens the interaction with cations and helps the dissociation of such ion-pairs in the organic phase. If atoms of a high electronegativity are assumed to resist the dispersion of the charge located on them, it can be expected that the anions suitable for potassium extraction by nitrobenzene are such that the negatively-charged atoms are less electronegative. The electronegativities of the atoms in question decrease in the following order: O>N>C, S>B. Therefore, the ion-pair of tetraphenylborate should strongly dissociate, and oxy-acids or phenols

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in nitrobenzene should weakly dissociate. Such a sequence has already been verified with tetraphenylborate[15] and picrate.[10] The sequence may also be supported by the fact that, in liquid ammonia, the dissociation constant decreases in the following order:

$$\mathrm{NaSPh} > \mathrm{NaNHPh} > \mathrm{NaOPh},^{11)}$$

where Ph denotes the phenyl radical.

Inductive Effect. The introduction of substituents which can attract electrons away from the negatively-charged atoms decreases the electron density on them. As the nitro group and halogen atoms will exert an electron-attracting inductive effect, it can be expected that, with these compounds, a highly enhanced extractability will be obtained. It is, however, difficult to discuss the effect of ion size and the inductive effect separately, because these substituents are very bulky themselves. Acrydone (4—IV) and phenothiazine (4-V) can clearly be differentiated from phenoxazine (4-VII). This fact may also suggest the inductive effect of $>$C=O, $>$SO$_2$, and $>$O groups.

Conclusion

From the above discussion and the experimental results, it can be concluded that bulky, charge-dispersible anions with electronegative groups in adjacent positions of the functional group are the best for the extraction of potassium by nitrobenzene.

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15) Unpublished work.