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The Liquid-Liquid Extraction of Alkali Metals as Their Poly-Iodides

By Ikuko AKAZA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

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It has been known that alkali metal ions can be extracted into nitrobenzene as their poly-iodides, but the extraction has not been attempted for various salts of alkali metals except in the case of their iodides. In this research ammonium iodide and elemental iodine were preferentially added to the extraction system in order to convert various alkali metal salts into poly-iodides. Ammonium iodide should be larger than the equivalent amount to an alkali metal present in an aqueous solution. The ratio of free iodine to ammonium iodide is an important factor; when the ratio is more than three, a higher distribution ratio is obtained. The ratio of iodine to iodide in the organic phase after the extraction is estimated to be six; therefore, the extracted species seems to be heptaiodide. The extractability of alkali metals increases in the order: Li-Na-K-Rb-Cs, and the distribution ratio decreases with the increase in the amount of metal ions taken in. Back extraction is achieved by shaking the organic phase with 10 M nitric acid. The separation factor between the metals is too low for them to be separated from one another.

Dawson et al. demonstrated at the turn of the century that alkali metal ions could be extracted into nitrobenzene and other solvents with the poly-iodide anion.[1-3] Later Bock and Hoppe[4] investigated the distribution of alkali poly-iodides between aqueous solutions and various organic solvents, and obtained much valuable information on the liquid-liquid extraction of alkali metal ions and their separability from one another. However, in their experiments, metal iodides and iodine were added to the extraction system, and other alkali salts, such as chloride and sulfate, were left outside their scope. Many problems pertinent to the practical application of the method have remained unsolved, e. g., how to convert the chloride or sulfate into iodide easily in an aqueous solution, what distribution ratio is to be established in the presence of diverse ions, and what are the optimum conditions to be kept during the extraction process. The present author has studied the above subjects using nitrobenzene as an extracting solvent. This paper will describe a device for the conversion of other salts of alkali metals into iodides; ammonium iodide is preferred as the reagent for the conversion. Also described will be the relation of the distribution ratio to the concentrations of various alkali salts in the aqueous phase and of the elemental iodine added to the system. It can be concluded that the metals may be divided into two groups: the first, which has lower distribution ratios in

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[1] H. M. Dawson and R. Gawler, *J. Chem. Soc.*, **81**, 524 (1902).

[2] H. M. Dawson, ibid., **85**, 467 (1904); **93**, 1308 (1908).

[3] H. M. Dawson and M. S. Leslie, ibid., **99**, 1601 (1911).

[4] R. Bock and T. Hoppe, *Anal. Chim. Acta*, **16**, 406 (1957).

the nitrobenzene, includes sodium and lithium, while the second, which has higher distribution ratios, consists of potassium, rubidium and cesium. The separation of the metals within each group, even by multiple extraction in the batch system, seems to be difficult because of their low separation factor. The present author aims to accomplish a satisfactory separation of these metals by reversed-phase partition chromatography based on liquid-liquid extraction. The techniques employed and the separability obtained will be described in a following paper.

Experimental

Into a 50-ml. separatory funnel there was put 10 ml. of an aqueous solution containing a known amount of alkali salt and a varying amount of ammonium iodide; then 10 ml. of nitrobenzene was added. After solid iodine in varying amounts had been put into the funnel, the vessel was tightly stoppered and shaken for five minutes with an Iwaki-V-S shaking machine, operating at 230 double strokes per minute. After the phases became disengaged, the lower organic phase was drained into an Erlenmeyer flask, from which 5 ml. of the organic phase was then pipetted into a porcelain crucible. The nitrobenzene and free iodine were driven off by heating them with an infrared lamp. When the residue became white, 1 ml. of 5 M sulfuric acid was dropped onto it and heating was continued under the infrared lamp until the white fumes of sulfuric acid ceased to evolve. The crucible was then put in an electric furnace and heated to 750°C in the cases of potassium and sodium and to 600°C in the cases of lithium, rubidium and cesium. The weight of alkali sulfate was determined in order to calculate the distribution ratio as well as the recovery of the metal. However, in the presence of free iodine, the volumes of the aqueous and organic phases after the equilibration both remarkably differed from that taken initially of the aqueous solution and the nitrobenzene; therefore, the distribution ratio of the metal was computed with the volumes which resulted. The composition of the organic phase was estimated as follows: a part of the phase was taken out and the amount of free iodine was titrated with a standard sodium thiosulfate solution using starch as the indicator. The total iodine content was estimated by titration in hydrochloric acid with a standard potassium iodate solution, as has been described in a general text-book.[5]

Results and Discussion

The Formation and Extraction of Polyiodides.—If alkali chlorides or sulfates only are present in the sample solution, they cannot be extracted with nitrobenzene. Therefore, a method should first be established to convert them into polyiodides. For this purpose a mixture of hydriodic acid and iodine, another of ammonium iodide, sulfuric acid and iodine, and a third of ammonium iodide and iodine were tried separately for the solution containing alkali metal salts. From the results obtained after the extraction in the presence of each mixture, the last one was found to be the best for the conversion of alkali metals into poly-iodides in an aqueous solution, with respect to the stability of the reagents and the ease of maintaining the optimum conditions.

Definite amounts of a potassium sulfate solution and a solution of ammonium iodide, varying in amount from one to five equivalents to the potassium ion, were put into a separatory funnel; the total volume was made 10 ml. Ten milliliters of nitrobenzene were then added, 1.00 to 2.00 g. of solid iodine was thrown into the funnel, and the extraction was attempted according to the standard procedure. As is shown in Table I, the maximum recovery was obtained at the NH_4I : K ratio close to two at a fixed amount of iodine. The recovery of potassium increased with the amount of iodine added and with the ratio of iodine to iodide; when 2 g. of iodine was used the recovery was as high as 93%, while when the iodine was absent scarcely any extraction was accomplished. Thus the extraction seemed to depend upon the amounts of both ammonium iodide and iodine in the system. In other words two variable factors, the NH_4I : K and the $I_2 : NH_4I$ ratios, may be considered to affect the extraction of potassium. Next, the extraction process was carried further, keeping the NH_4I : K ratio at two and varying the $I_2 : I^-$ ratio from unity to five in the reaction system.

Table I. Extraction of potassium as poly-iodide with nitrobenzene in the presence of various amounts of ammonium iodide and iodine

Ammonium iodide taken, mg.	NH_4I : K	Iodine taken g.	Distribution ratio (D)	Recovery %
174.6	1	1.0	5.85	85.4
349.2	2	1.0	9.85	90.8
523.8	3	1.0	2.28	69.6
698.4	4	1.0	2.28	69.6
873.2	5	1.0	3.47	77.6
174.6	1	1.5	2.49	71.3
349.2	2	1.5	4.41	81.5
523.8	3	1.5	4.39	81.5
698.4	4	1.5	1.91	65.6
873.2	5	1.5	3.01	75.1
174.6	1	2.0	4.03	80.1
349.2	2	2.0	14.0	93.3
523.8	3	2.0	5.83	85.4
698.4	4	2.0	2.96	74.7
873.2	5	2.0	2.16	68.3
174.6	1	0.0	0.015	1.5

In each case 47.1 mg. of potassium was taken as 105.0 mg. of potassium sulfate in 10 ml. of an aqueous phase, and 10 ml. of nitrobenzene was used as an extractant.

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[5] I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. 3, Interscience Publ., New York (1957), p. 447.

The larger the amount of iodine added, the larger was the recovery of potassium in the organic phase, as is shown in Table II, and it was also found that as large a recovery as 97% was obtained when the $I_2 : I^-$ ratio was 5.0.

TABLE II. DEPENDENCE OF RECOVERY ON THE RATIO OF FREE IODINE TO IODIDE IN THE EXTRACTION SYSTEM

$I_2 : I^-$ initially added to system	Recovery of potassium in organic phase %	D	$I : I^-$ in org. phase after extn.	Recovery of NH_4^+ in organic phase %	D
1.0	64.1	1.73	3.9	9.1	0.09
2.0	86.6	6.16	4.7	32.5	0.45
3.0	96.5	25.60	6.0	48.1	0.87
4.0	96.0	21.67	6.6	57.6	1.23
5.0	97.4	33.33	6.4	58.8	1.28

In each case 47.1 mg. of potassium as 105.0 mg. of sulfate and 400 mg. of ammonium iodide were taken in 10 ml. of an aqueous phase. Free iodine was added to nitrobenzene to make the ratio $I_2 : I^-$ in the system as shown in the first column.

In order to examine the composition of the organic phase after the extraction, a part of it was taken out and the amounts of free iodine and iodide were determined volumetrically. From the results shown in the fourth column of Table II, it can be seen that the ratio of iodine to iodide in the organic phase in which the largest recovery of potassium was accomplished was approximately six; therefore, the extracted compound of potassium seemed to be the heptaiodide KI_7, the formation of which has been described by Dawson.[2)] In this process the ammonium ion was also extracted into nitrobenzene as its poly-iodide, as is shown in the last column of Table II. Generally, it may be concluded that when the molar ratio of iodine to ammonium iodide exceeds three, a nearly constant distribution ratio is maintained, and the extracted species is the hepta- or a higher poly-iodide of the metal.

In the extraction the relation between the distribution ratio of the metal and the amount of free iodine added to the system may give information as to the composition of the compound extracted as well as the extraction mechanism in the process. In Fig. 1, the relation is shown in a graph of log D vs. log (I_2); this relation is a straight line with a slope of 2. Taking the results in Table II and Fig. 1 into account, it can be assumed that potassium and ammonium ions form their triiodides readily in the aqueous phase and that two molecules of free iodine subsequently combine with the triiodide to form the heptaiodide.

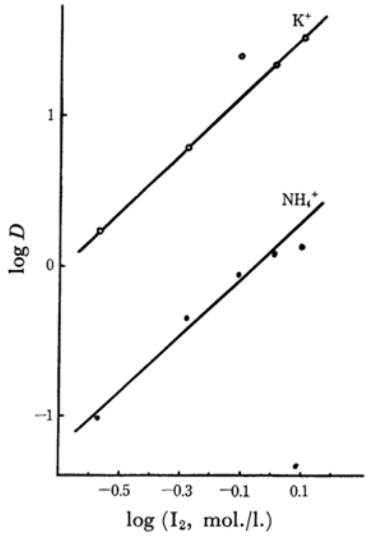

Fig. 1. Relation between distribution ratio and the concentration of iodine added in the system.

In Table III are shown the results of the extraction in which the $I_2 : I^-$ ratio was kept constant while the amount of ammonium iodide was varied. From the results it is clear that if the $I_2 : I^-$ ratio is kept constant at 3.2, the recovery of potassium in the organic phase is also held constant, so the ratio is an important factor, while the amount of ammonium iodide is not. Aqueous solutions containing various amounts of potassium were submitted to extraction by nitrobenzene, as has been described above, at the nearly constant ratio $I_2 : I^-$. The results are shown in Table IV, from which it may be seen that the larger the amount of potassium taken, the lower is the recovery of its poly-iodide; however, the distribution ratio remains constant for a given amount of potassium, even when 20 ml. of the solvent is used. The relation of the distribution ratio to the amount of potassium taken is clearly shown in Fig. 2, in which a straight line with a slope of -1 may be drawn between the distribution ratio and the amount of potassium, both in the logarithmic scale. In these experiments the composition of the organic phase was also examined in the manner shown previously; the extracted species could be identified as potassium heptaiodide, regardless of

TABLE III. EXTRACTION OF POTASSIUM AS POLY-IODIDE WITH NITROBENZENE AT CONSTANT RATIO OF $I_2 : I^-$ IN THE EXTRACTION SYSTEM

Ammonium iodide added mg.	Free iodine added g.	$I_2 : I^-$	Recovery of potassium in org. phase %
349.2	2.0	3.2	96.5
523.8	3.0	3.2	98.3
698.4	4.0	3.2	99.8
873.2	5.0	3.2	96.9

In each case 47.1 mg. of potassium as sulfate was taken in 10 ml. of the aqueous phase, and 10 ml. of nitrobenzene was used.

TABLE IV. EXTRACTION OF POTASSIUM OF VARIOUS AMOUNTS

Potassium taken mg.	Potassium recovered %	Distribution ratio D	I : I$^-$ in org. phase	Condition of extraction
17.9	98.8	74.0		(1) and (3)
26.9	98.1	48.5		
44.8	96.0	22.2		
62.8	94.6	16.2		
71.7	92.4	11.1		
89.7	89.9	8.2		
0.0	—	—	6.4	(2) and (3)
50.0	95.4	14.4		
75.0	95.1	13.3	6.2	
100.0	92.7	8.8		
125.0	90.1	6.3	5.9	
150.0	90.7	6.7		
175.0	86.4	4.4	6.0	
25.0	100.0	infin.		(2) and (4)
75.0	96.2	17.3		
100.0	94.2	6.7		
125.0	93.5	5.7		
150.0	92.6	4.6		
175.0	93.5	5.6		
200.0	92.4	4.4		

Extractions were carried out with potassium taken as sulfate and under the following conditions.

(1) 0.40 g. NH_4I and 2.80 g. I_2 were put into the system.
(2) 1.48 g. NH_4I and 9.08 g. I_2 were put into the system.
(3) 10 ml. of nitrobenzene was used as an extractant.
(4) 20 ml. of nitrobenzene was used as an extractant.

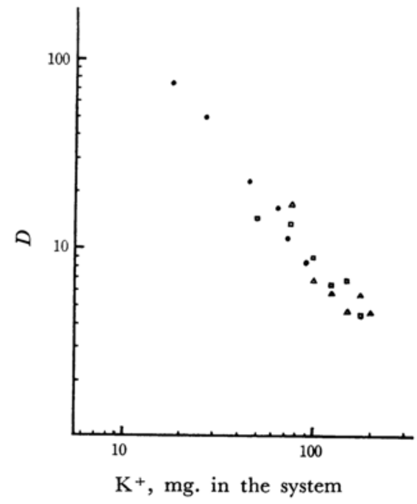

Fig. 2. Dependence of distribution ratio on the amount of potassium taken in the system. Condition of extraction (1), (2), (3) and (4) are shown in Table IV.
• (1) and (3), □ (2) and (3), △ (2) and (4)

the amount of potassium in the original solution.

The extraction procedure was also applied to an aqueous solution containing various kinds of potassium salt, as is shown in Table V; satisfactory recoveries were obtained, even when their amount present was large. Therefore, this procedure must be applicable to solutions containing neutral potassium salts. Other alkali metal ions, lithium, sodium, rubidium and cesium, were subjected to extraction under the same conditions as for potassium, but the detailed results will be omitted here, since these ions behaved exactly like potassium. The summarization in Fig. 3 shows the behavior of individual metal ions when extracted with nitrobenzene from an aqueous solution containing the corresponding chloride. The same results were obtained for their sulfates. Cesium was the most easily extractable in both cases, followed by rubidium, potassium, sodium, and lithium in that order. Because the distribution ratios of cesium, rubidium and potassium are

TABLE V. EXTRACTION OF POTASSIUM FROM AQUEOUS SOLUTION CONTAINING VARIOUS KINDS OF POTASSIUM SALT

Potassium salt kind	Potassium salt taken mg.	Potassium taken mg.	Distribution ratio (D)	Recovery of K$^+$ %
KNO_3	323.0	125.0	6.58	86.8
KSCN	311.0	125.0	7.62	88.4
K_2CO_3	221.0	125.0	8.69	89.7
KH_2PO_4	435.0	125.0	6.62	86.9
KBr	381.0	125.0	6.76	87.1
KCl	238.0	125.0	7.39	88.1
KI	531.0	125.0	10.40	91.2
K_2SO_4	279.0	125.0	7.50	88.1

In the above experiment 1.48 g. of NH_4I and 9.0_8 g. of iodine were added to each extraction system.

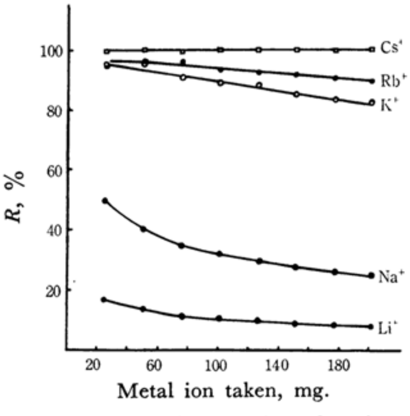

Fig. 3. Recovery of extraction of various metal chlorides as poly-iodides in nitrobenzene. In each case 1.483 g. of NH_4I, 10 ml. of nitrobenzene and 9.09 g. of free iodine were present in the system.

approximately equal, these metals may be included in one group, while sodium and lithium may be put in another for the same reason. Because of the marked difference in distribution ratio between potassium and sodium, these ions may be separated from each other by the method of continuous extraction.

The Effect of Acids on the Extraction.—If a free acid is present in the aqueous solution, it may affect the extraction of alkali poly-iodides. As an example, the data found in the case of perchloric acid are given in Table VI. It may be concluded that the stronger the acid, the less satisfactory the extraction.

TABLE VI. EFFECT OF ACIDS ON THE EXTRACTION

a) Perchloric acid:

$HClO_4$ in aq. phase M	Extraction of Na		Extraction of K	
	D	Recovery %	D	Recovery %
0.00	0.471	32.0	8.90	89.0
0.02	0.429	30.0	11.00	91.7
0.06	0.410	29.1	9.75	90.7
0.10	0.404	28.8	9.53	90.5
0.20	0.412	29.2	9.64	90.6
0.40	0.377	27.4	6.69	78.3
0.50	0.357	26.3	2.01	66.8
1.00	0.280	22.4	0.48	32.8

b) Organic acids:

Acid, 100 mg. equivalent	pH of aqueous phase before extraction	Extraction of Na	
		D	Recovery %
Citric acid	1.95	0.464	31.7
Oxalic acid	0.90	0.477	32.3
Succinic acid	2.32	0.456	31.3
Tartaric acid	1.61	0.473	32.1
Without org. acid	6.18	0.471	32.0

In the above experiment 1.48 g. of ammonium iodide and 9.08 g. of iodine were put into the system, and 100 mg. of sodium or potassium ion was taken in each case.

The Back-extraction of the Metals from the Organic Phase.—The organic phase can be readily stripped, by the following method, of the metal it has taken up. The organic phase separated with a separating funnel was mixed with an equal volume of 10 M nitric acid; the free iodine separating out as a solid by the oxidative action of the acid was then filtered off with a sintered-glass-filter and washed well with water. In the filtrate and washings, two layers of liquid were seen; one of them was nitrobenzene, and the other, a solution of the nitrate of the metal. The organic layer was rejected, and the aqueous phase was evaporated to dryness under an infrared lamp. Thus the alkali metal in the nitrobenzene layer was isolated as its nitrate. The residual iodine on the filter was found to have adsorbed a small quantity of the metal. The yield in the stripping process reached 97.0%.

Summary

The author has described how alkali metal ions in an aqueous solution can be extracted as their hepta- or higher poly-iodides into nitrobenzene in the presence of ammonium iodide in an aqueous solution and in the presence of free iodine in an organic solvent. The extractability of the metals increased in the order; Li–Na–K–Rb–Cs. The equivalence ratio of free iodine to ammonium iodide was an important factor in the satisfactory extraction of the metallic poly-iodide; the ratio had to be kept above three. Acids in the aqueous phase inhibited the extraction, and the removal of metals from the nitrobenzene could be achieved by shaking it with 10 M nitric acid.

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