The Separation of Potassium by Solvent Extraction

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Very few investigations of the solvent extraction of potassium have been made because potassium is highly ionic and so it is difficult to extract it by an ordinary solvent immiscible with water. This paper will describe the extraction of the potassium ion in an aqueous solution by nitrobenzene. The potassium ion is extracted in the form of potassium dipicrylaminate (DPA-K) and is stripped from the nitrobenzene layer by shaking it with a hydrochloric acid solution. The potassium ion is then determined gravimetrically with sodium tetraphenylborate (TPB-Na).

Experimental and Discussion

Reagents.—A dipicrylaminate aqueous solution, 0.1 M, was made by dissolving Hexyl Natrium (Mitsubishi Kasei Co., Ltd.) in water, while a 0.05 M dipicrylaminate nitrobenzene solution was prepared by dissolving Hexyl Natrium in nitrobenzene. The potassium chloride and the other reagents were of the analytical grade.

Organic Solvent. — To find out a suitable solvent, one immiscible with water and one which extracts potassium dipicrylaminate from an aqueous solution, the following solvents were tested: nitrobenzene, cyclohexanone, butylacetate and *o*-nitrotoluene. Among these solvents, nitrobenzene was best in extractability, and so it was used in all the extraction procedures.

Extraction. — As is shown in Fig. 1, two procedures were used in this experiment:

Procedure 1: The extraction by nitrobenzene from a solution containing deposited crystals of DPA-K formed by adding the reagent aqueous solution.

Procedure 2: The extraction from a solution containing potassium by adding the reagent nirobenzene solution which is almost saturated

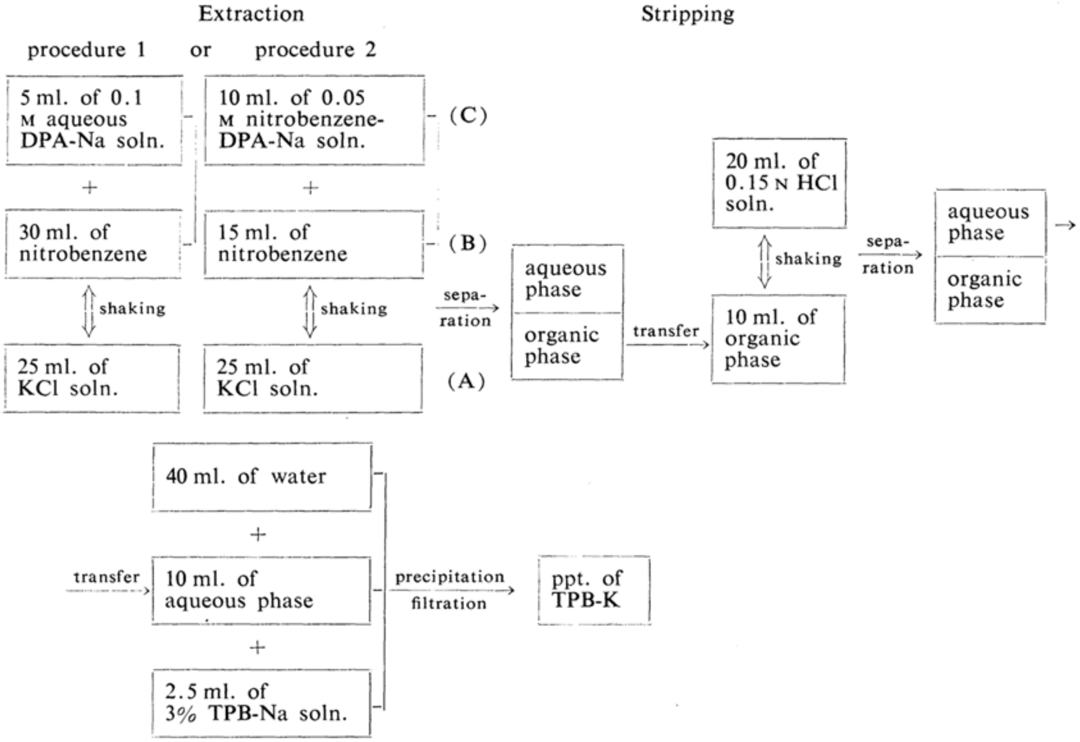

Fig. 1. Scheme of standard procedure.

with DPA-Na (0.05 M).

The molarity of the reagent was kept twice that of potassium throughout this experiment; the concentration of potassium chloride was also kept constant at 0.01023 M, corresponding to the potassium concentration of sea water.

Twenty-five milliliters of an aqueous potassium chloride solution were pipetted into a 100-ml. separatory funnel. In procedure 1, adequate amounts of the reagent aqueous solution and nitrobenzene were added to the potassium solution, or in procedure 2, the reagent nitrobenzene solution and nitrobenzene were added to the solution. After having been shaken for one or two minutes, this solution was allowed to stand overnight in order to separate it completely into two layers. The nitrobenzene solution was drained into a 100-ml. beaker.

Stripping Procedure.—Ten milliliters of the organic phase containing potassium dipicrylaminate was again pipetted into a 100-ml. separatory funnel, and then 20 ml. of 0.15 N hydrochloric acid were added. The two solutions were mixed well by shaking them until the color of the organic phase turned from orange-red to yellow. After the mixture had been allowed to stand for 2 hr., 10 ml. of the colorless aqueous solution was transferred into a 100-ml. beaker.

The Determination of the Potassium.[1]—The aqueous solution was diluted to 50 ml. with water, and then a 3 per cent solution of sodium tetraphenylborate (Kalibor, Dojindo & Co., Ltd.) was added drop by drop, with a gentle swirling. After the solution had cooled for 20 to 30 min. in a refrigerator, the precipitate was filtered through a No. 4 or 5 porosity glass filter, washed well with distilled water, and dried at 125°C for 1 hr. This was cooled in a desiccator and weighed. The precipitate was dissolved in acetone in Soxhlet's apparatus. The amount of potassium was calculated from the loss of weight. All the procedures are shown schematically in Fig. 1.

After 25 ml. of a potassium chloride solution (0.01023 M) had been shaken with the same volume of nitrobenzene, the amount of potassium was determined gravimetrically by means of the above method. The weight of TPB-K was always 0.8 mg. smaller than the calculated value. This negative error is due to the very small amount of TPB-K in a dilute solution (ca. 40 mg./50 ml.).[2]

Extractability. — The extractability, E, was calculated from the following equation, taking the above correction into consideration:

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[1] K. Tamaoku, *J. Japanese Chem.* (*Kagaku-no-Ryoiki*), **17**, 39 (1963).

[2] K. Sporek and A. F. Williams, *Analyst*, **80**, 347 (1955).

$$E=D/(D+V_a/V_o)$$

where D is the distribution ratio, and V_o and V_a are the volumes of the organic and the aqueous layers respectively.

The Effect of the Volume Ratio, V_o/V_a.—Procedures 1 and 2 were compared in extractability under various volume ratios (Fig. 2).

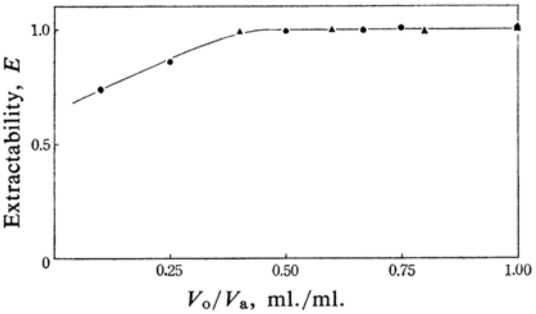

Fig. 2. Dependence of the volume ratios of organic to aqueous phase on extractability.
Sample: 0.01023 M KCl soln.
Procedure:
procedure 1 ($V_o/V_a=1.00$, (A)=25.0 ml.; $V_o/V_a=0.75\sim0.25$, (A)=50.0 ml.): ●
procedure 2 ($V_o/V_a=1.00\sim0.60$, (A)=25.0 ml.; $V_o/V_a=0.40$, (A)=50.0 ml.): ▲

Figure 2 shows that there is no appreciable difference between the two procedures; moreover, in the range of $V_o/V_a>0.5$, the extraction is almost perfect. In the range of $V_o/V_a<0.5$, however, somewhat lower values were obtained.

The Effect of pH.—Sodium in sodium dipicrylaminate will be displaced by hydrogen rather than by potassium in an acidic solution, so the experiment was carried out in a neutral or alkaline solution. The desired basicity was obtained by adding a small amount of a sodium hydroxide solution; the concentration of potassium was kept constant at 0.01023 M. The extractability decreased with the increase in pH, as is shown in Fig. 3. From the results, it must be concluded that the extraction is best in a neutral solution.

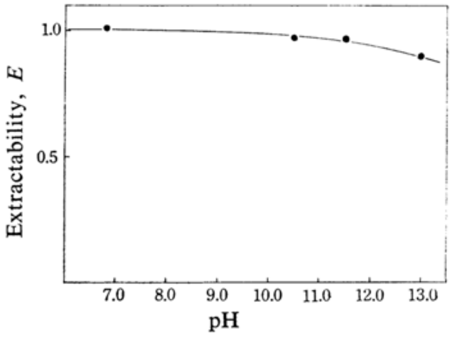

Fig. 3. Effect of pH.
Sample: 0.01023 M KCl soln. (+NaOH)
Procedure: standard procedure 1

The Effect Sodium Ions.—When an aqueous solution containing only potassium chloride was extracted by the reagent nitrobenzene solution, no turbidity was found in the organic phase, but in the presence of both sodium and potassium ions in a solution, the organic phase was turbid, even after standing overnight. In order to eliminate this turbidity, the solution was filtered through a dry filter paper or centrifuged at 2000 r. p. m. for 10 min. These two methods were compared in extractability by varying the time of standing in the stripping procedure. In these experiments, it was found that the extractability does not depend upon the stripping time; moreover, no significant difference between these two procedures was observed.

From Table I and Fig. 4, it is clear that the extractability decreases with the increase in the ratio of sodium to potassium ions, and that, thus, the co-existence of sodium hydroxide should similarly decrease the extractability (Fig. 3). The turbidity in the organic phase increases with the quantity of sodium ions.

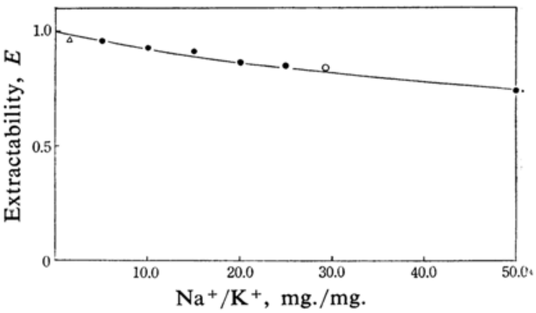

Fig. 4. Effect of sodium ion.
Sample: Mixture of KCl and NaCl: ●
Bittern : △
Sea water : ○
Procedure: procedure 2

For rapidity and convenience of experimentation, procedure 2 and the method of the elimination of turbidity by filtration were adopted for the following experiments.

The Separation of Potassium from Sea Water and Bittern by Solvent Extraction.—The extractabilities obtained with bittern (Table II) and sea water are shown in Table III. In Fig. 4, these values are plotted with open symbols against the ratio of sodium to potassium ions.

From Table III it may be concluded that, among all the ions which disturb the extraction, sodium ion has the most undesirable effect, but the co-existence of even a large

TABLE I. EFFECT OF SODIUM ION

A* Na+K soln. ml.	B ml.	C ml.	Na^+/K^+ mg./mg.	TPB-K found mg.	TPB-K** corr. mg.	E
25.0	15.0	10.0	5.0	16.7	17.5	0.955
25.0	15.0	10.0	10.0	16.1	17.0	0.925
25.0	15.0	10.0	15.0	15.8	16.6	0.907
25.0	15.0	10.0	20.0	14.9	15.7	0.857
25.0	15.0	10.0	25.0	14.5	14.7	0.845
25.0	15.0	10.0	50.0	12.6	13.5	0.734

* The concentration of potassium was kept constant at 0.01023 M.

** The calculated value of TPB-K is 18.32 mg.

TABLE II. COMPOSITION OF BITTERN* (g./l.)

Be^1	Temp.** °C	pH	$MgSO_4$	$MgBr_2$	$MgCl_2$ g./l.	KCl	NaCl
32.0	13.6	7.28	72.32	3.79	209.55	41.34	74.98

* By courtesy of Mr. M. Komatsu (Kinkai Engyo Co., Ltd.).

** For extraction, supernatant solution at this temperature was used.

TABLE III. EXTRACTION OF POTASSIUM FROM SEA WATER AND BITTERN*

	Sample soln. ml.	B ml.	C ml.	V_o/V_a ml./ml.	Na^+/K^+ mg./mg.	TPB-K found mg.	TPB-K corr. mg.	E
Sea water**	25.0	15.0	10.0	1.0	29.3	13.5	14.3	0.841
Bittern	2.0	0	40.0	20.0	1.36	49.0	49.9	0.960

* The direct determination of potassium gave the results of 34.05 mg./10 ml. for sea water and 19.96 mg./10 ml. for bittern (diluted ten times with water).

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amount of magnesium ions has a negligible effect on the extractability.

In conclusion, by solvent extraction using sodium dipicrylaminate and nitrobenzene, the quantitative separation of potassium was not attained when sodium ions were also present. When sodium ions are absent, however, potassium can be quantitatively separated from the other ions.

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