100. *Solvent Extraction Studies with Polonium.*

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The extraction of polonium from hydrochloric acid solution by dithizone may involve the complex $PoODz_2$, and the complex $PoCl_4,2TBP$ may be formed in the extraction with tributyl phosphate. The dependence of the partition coefficient on the acid concentration of the aqueous phase has been determined for both complex-forming agents.

BOUISSIÈRES and FERRADINI[1] have reported the efficient extraction of tracer polonium from nitric or hydrochloric acid solution at pH 0·2—5 by dithizone (DzH); the polonium was recovered by washing the organic phase with 4N-hydrochloric acid. Ishimori[2] found that the dependence of the partition coefficient on the acid concentration, in the extraction of tracer polonium from nitric acid solution, indicated the formation of a complex containing two dithizonate ions, probably $PoODz_2$, since the polonium, under the reported conditions, would be present in the quadrivalent state.

Karracker and Templeton[3] have reported the extraction of tracer polonium from 6N-hydrochloric acid into a 1 : 4 mixture of tributyl phosphate (TBP) and dibutyl ether, with a partition coefficient of 110 in favour of the organic phase. The polonium can be recovered by back-washing with concentrated nitric acid.[4]

It is difficult to obtain consistent partitions with millicurie amounts of polonium owing to the rapid radiation decomposition of the organic complex-forming agents; in the case of dithizone, the green colour of a $1{\cdot}19 \times 10^{-3}$M-solution in chloroform was completely discharged after 30 minutes' extraction from 10^{-4}M-polonium solution in hydrochloric acid, and the organic phase then contained little polonium; the radiation decomposition is even more rapid in extractions from nitric acid solutions of polonium, or in the presence of hydroxylamine, and consistent results could not be obtained in either case. The partition coefficients obtained by keeping the two phases in contact for 5 minutes were reasonably constant and reproducible within ±4% for both tributyl phosphate and dithizone solution, and all the extractions were therefore carried out for 5 minutes only; it was not possible to approach the equilibrium from both sides as in the procedure of Irving *et al.*[5]

Dithizone Extractions.—When a solution of dithizone, HDz, in an organic solvent immiscible with water is shaken with an aqueous solution of a cation, M^{n+}, so that a metal

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[1] Bouissières and Ferradini, *Analyt. Chim. Acta*, 1950, **4**, 610.
[2] Ishimori, *Bull. Chem. Soc. Japan*, 1954, **27**, 520.
[3] Karracker and Templeton, *Phys. Rev.*, 1951, **81**, 510.
[4] Meinke, American Report AECD-2738, Sec. 84-1, 1949.
[5] Irving, Bell, and Williams, *J.*, 1952, 356.

complex, MDz_n, is formed which is soluble in the organic phase, but not in the aqueous phase, the partition equilibrium can be represented by :

$$(MDz_n)_o/(M^{n+})_w = K_{Po} = C([HDz]_o/\{H\}_w)^n$$

or $\log_{10} K_{Po} = \log_{10} C + n(\log_{10} [HDz]_o + pH)$ (Irving *et al.*[5]). C is a constant and the subscripts o, w refer to the organic and aqueous phases respectively. The results obtained in the present work can be represented graphically as a linear plot of $\log_{10} K_{Po}$ against

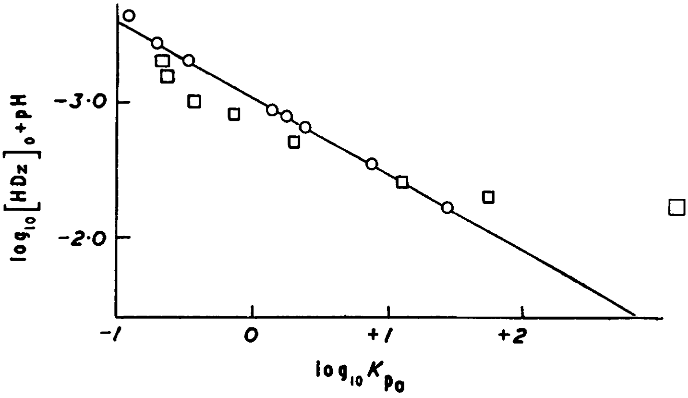


FIG. 1. ○ [HCl] *constant.* □ $[HDz]_0$ *constant* ($3{\cdot}8 \times 10^{-3}$M).

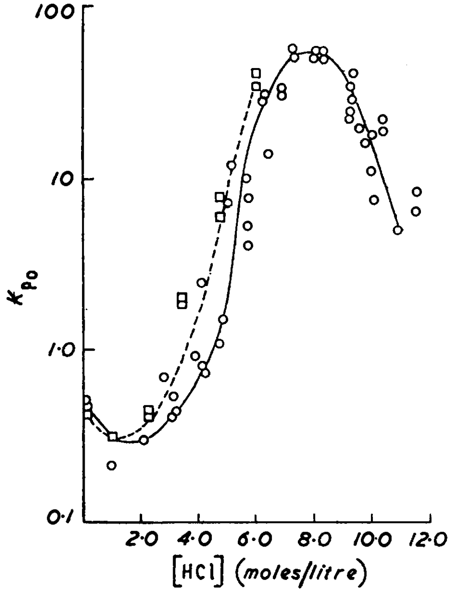


FIG. 2. ○ 10% v/v *Tributyl phosphate in decalin.* □ 10% v/v *Tributyl phosphate in odourless kerosene.*

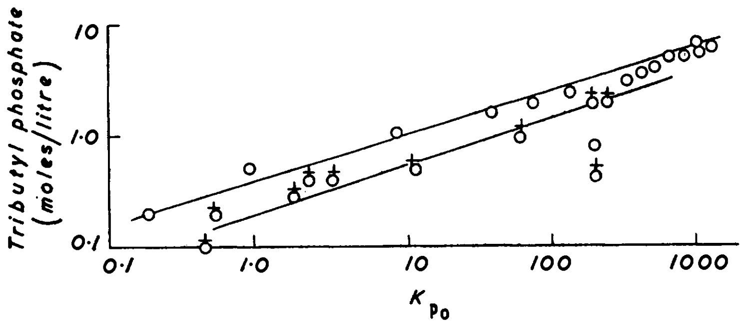
($\log_{10} [HDz]_o$ + pH), the value of n being 1·8; it should be noted that the values obtained at a constant pH of 0·1 (N-HCl) and varying dithizone concentration give a better straight line than the results for constant dithizone concentration and varying pH (Fig. 1). The complex is therefore probably $PoODz_2$, since the polonium remains in the quadrivalent state under the conditions of these experiments and it appears that at least a part of the polonium is present as the polonyl (PoO^{++}) ion.

The complex is bright red in concentrated solutions in chloroform and it can also be prepared as a red solid by shaking a suspension of polonium " hydroxide " with an alkaline solution of dithizone. It was not possible to determine the melting and boiling points of the complex, or to analyse it, since it charred rapidly as a result of the intense α-bombardment.

The extractions from <0·05N-acid were extremely inconsistent owing to the hydrolysis of the polonium tetrachloride, and consequently the partition data could be obtained only in regions of high acidity, which is unsatisfactory since extensive complex-ion formation occurs under these conditions; buffered solutions could not be used for the same reason. The absorptiometric determination of the excess of dithizone remaining in the organic phase could not be carried out owing to the rapid radiation decomposition, and the recorded concentrations refer to the original dithizone concentration less an allowance for the polonium complex. No allowance could be made for the dithizone decomposed by the α-radiation; in some of the experiments this might amount to about 10% of that present. Determinations of the solubility of polonium tetrachloride were also made, but these were inconclusive.

Extractions with Tributyl Phosphate.—The variation of the partition coefficient, $K_{Po}(= [Po]_o/[Po]_w)$, with hydrochloric acid concentration is shown in Fig. 2 and the dependence on tributyl phosphate concentration is shown in Fig. 3. In the latter the plot is approximately linear and of slope 3, suggesting the formation of a yellow complex with 3 molecules of the phosphate. This result is probably fortuitous and determinations of the solubility of solid polonium tetrachloride in solutions of the phosphate in decalin indicate the formation of a yellow complex $PoCl_4,2TBP$: $PoCl_4 + 2TBP \rightleftharpoons PoCl_4,2TBP$, for which the equilibrium constant $K_c = [PoCl_4,2TBP]/[TBP]^2$ is about 0·04 at 22° (see Table).

FIG. 3.



○ 6N-HCl. ♁ 8N-HCl.

TBP (moles per l. of decalin)	Solubility of $PoCl_4$ (c/l.)	$PoCl_4$ (10^{-6} mole/l.)	K_c
0·037	52	55·5	0·0405
0·055	112	119	0·0395
0·074	220	235	0·0428

The solvent-extraction results obtained with tributyl phosphate were not very reproducible and any calculation to determine the species involved would be speculative. It may be significant that the maximum on the K_{Po}–[HCl] curve (Fig. 2) occurs at 7N-hydrochloric acid, which is in the region where the undissociated acid was extracted into the organic phase. If the tributyl phosphate forms complexes with the extracted acid (*e.g.*, TBP,*n*HCl), its concentration available for complexing with the polonium will fall, producing an effect similar to that observed in Fig. 2.

EXPERIMENTAL

Dithizone.—Dithizone was purified by Sandell's method [6] and the normal precautions required for the preparation of the reagents used for work with dithizone were observed (see,

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[6] Sandell, "Colorimetric Determination of Traces of Metals," New York, Interscience Publ. Inc. 1944, p. 89.

e.g., Irving *et al.*[5]). The concentration in the final chloroform solution (10^{-2}M) was determined by extractive titration against 0·01N-silver nitrate solution;[7] the change in the dithizone concentration in the organic phase was followed with a Spekker absorptiometer (1 cm. cell; Ilford orange filter No. 607; tungsten lamp). The method eliminates the final evaporation of the chloroform solution which frequently results in the loss of a part of the purified dithizone owing to its thermal instability. The reproducibility of the method is better than 1%. The extinction coefficients of dithizone in solution in chloroform at 440, 505, and 605 mμ were measured in order to check the titration results, the values being in good agreement with previous work.[8] A Hilger Uvispek spectrophotometer was used for these measurements.

Estimation of polonium dithizonate by α-counting requires care since tracer amounts of the dithizonate vaporise at about 120°.[9] This was confirmed in the present work when it was found that considerable losses of polonium occurred on evaporation of aliquot parts of the dithizonate solution on a hot-plate, even after hydrogen peroxide, chlorine water, or concentrated nitric acid had been added in an attempt to decompose the polonium dithizonate. Consistent results were obtained by allowing aliquot parts of the chloroform solution to evaporate at room temperature.

Tributyl Phosphate.—Equal volumes of tributyl phosphate and N-sodium hydroxide were boiled until about half of the aqueous layer had distilled; the tributyl phosphate was then separated and dried at 60° in a current of dry air.[10] Since the density of the ester is close to that of water, good phase separation can be achieved only by diluting it with a water-immiscible solvent of markedly different density. This diluent must not extract polonium under the conditions of the experiment. Ethers should be avoided since they tend to form peroxides under the intense α-bombardment.

Determinations of Partition.—Preliminary experiments with the tributyl phosphate–polonium tetrachloride–hydrochloric acid system were made with solutions of the tetrachloride which contained small amounts of lanthanum as carrier; the results were unsatisfactory since the effect of the additional chloride ion (from the lanthanum trichloride) was uncertain. Later work with both complex-forming agents was carried out with pure carrier-free polonium tetrachloride, prepared as described previously.[11] About 30 μg. (~100 mc) of polonium tetrachloride were used for each experiment. In each determination, equal volumes (3 ml.) of the polonium solution and of the organic phase were placed in a 10 ml. centrifuge tube and agitated by means of an air-pulsing device.[12] The phases were finally separated by centrifugation and assayed for polonium by α-counting.

Solubility Determinations.—The techniques used for the determination of the solubility of polonium tetraiodide [13] were used in this work, all of which was carried out in a dry-box in order to minimise the hazards involved in the handling of large amounts of polonium.[7]

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[7] Bagnall and Robertson, British Report AERE C/R 1935, 1956.

[8] Cooper and Sullivan, *Analyt. Chem.*, 1951, **23**, 613; Landry and Redondo, *ibid.*, 1954, **26**, 732; Irving and Bell, unpublished work.

[9] Kimura and Mabuchi, *Bull. Chem. Soc. Japan*, 1955, **28**, 535.

[10] Grimley, personal communication.

[11] Bagnall, D'Eye, and Freeman, *J.*, 1955, 2320.

[12] Bagnall and Miles, *J. Sci. Instr.*, 1953, **30**, 172.

[13] Bagnall, D'Eye, and Freeman, *J.*, 1956, 3385.