33. *The Solvent-extraction of Beryllium from Aqueous Solutions of Mineral Acids by Alkyl Esters of Phosphoric Acid.*

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The solvent-extraction of beryllium from aqueous mineral acid solutions by a variety of mono- and di-alkyl esters of phosphoric acid has been studied by using the radioactive isotope ^{7}Be. The distribution coefficient (D_{Be}) has been measured as a function of the equilibration time, the nature and concentration of the aqueous acid, the purity, concentration, and structure of the ester, and the nature of the diluent in the organic phase. The time required to reach equilibrium depends upon the purity and structure of the ester and the concentration of aqueous acid, and varies from 15 min. for di-n-butyl to ~1000 min. with di-2-ethylhexyl hydrogen phosphate. The extraction of beryllium from dilute (<2M-)aqueous acid solution by the dialkyl esters is predominantly as the complex $BeA_2(HA)_2$ [$A = (RO)_2PO{\cdot}O^-$], but at higher aqueous acid concentration complexes containing the anion of the aqueous acid are probably also extracted. The structure of the alkyl group has a slight effect upon the value of D_{Be}, this value decreasing as the degree of branching increases and increasing with chain length. The value of D_{Be} varies considerably with the nature of the diluent and increases in the order chloroform < toluene < benzene < carbon tetrachloride < kerosene. Equilibrium constants for the complexes $BeA_2(HA)_2$ have been calculated for a series of alkyl groups with toluene as diluent. Formation constants for the $BeCl^+$, BeF^+, BeF_2, and BeF_3^- complexes in the aqueous phase have also been calculated from results on the variation of D_{Be} with the concentration of chloride ion and fluoride ion.

In addition to its well-established use as an alloying constituent and in the windows of *X*-ray apparatus, beryllium is used as a moderator in nuclear piles.[1] Beryllium-clad uranium dioxide fuel elements have been proposed for the Advanced Gas-cooled Reactor Experiment in the United Kingdom.[2] Since beryllium is relatively expensive it is of interest to obtain information on its chemical behaviour, particularly that relevant to the processing of the element from its ores to metal, and the recovery of the element from contaminated materials such as irradiated beryllium-clad fuel elements.

Solvent-extraction is a potentially useful method for the purification of beryllium. Many organophosphorus compounds and long-chain organic amines are now widely used for the solvent extraction of uranium and thorium from ore-leach liquors,[3] and of uranium and plutonium from solutions of irradiated fuel elements,[4] and of rare-earths.[5]

We have therefore examined the solvent extraction of beryllium from various aqueous mineral acid solutions by a variety of mono- and di-alkyl esters of phosphoric acid. The radioactive isotope ^{7}Be has been used to facilitate the measurement of the distribution coefficient of the beryllium between the aqueous and the organic phases. The mechanism of extraction of beryllium by these solvents is discussed and compared with that of other metals, and the application of the solvents for the separation of beryllium from other metals is considered.

Experimental

Preparation of Aqueous Solutions containing ^{7}Be.—^{7}Be, formed by irradiation of carbon with protons in the Harwell cyclotron, was obtained from the Isotope Division as a solution in

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[1] "The Metal Beryllium," ed. White and Burke, Amer. Soc. Metals, Cleveland, 1955.

[2] U.K.A.E.A. 5th Annual Report (1958—9), H.M.S.O., London, p. 30.

[3] Brown and Coleman, "Progress in Nuclear Energy," Series III, Pergamon Press, London, 1958, Process Chemistry, Vol. II, Paper 1—2.

[4] "Progress in Nuclear Energy," Series III, Pergamon Press, London, 1958, Process Chemistry, Vol. II, Chapter 7.

[5] Peppard, Mason, and Moline, *J. Inorg. Nuclear Chem.*, 1957, **4**, 141.

approximately M-hydrochloric acid.[6] An aliquot part (0·01 ml.) of this solution was added to the appropriate acid (10 ml.), so that 0·1 ml. of the mixture gave a γ-activity of about 10,000 counts/min. at 5% counting geometry in a standard γ-scintillation counter.

To prepare a 0·1M-beryllium solution with and without ^{7}Be tracer, a weighed excess of metallic beryllium was added to dilute sulphuric acid, and the amount dissolved was determined by weighing the residue. The solution was then diluted with the appropriate concentration of sulphuric acid to give 0·1M-beryllium and 2M-sulphuric acid. In one experiment (section f below) to investigate (*a*) the isotopic exchange in solution of ^{7}Be tracer and macroberyllium and (*b*) the dependence of D_{Be} on beryllium concentration, an aliquot part of the concentrated ^{7}Be tracer solution was added before the dissolution; and in another experiment the tracer was added to the diluted solution after the dissolution stage, and just before the determination of D_{Be}.

Solvents.—The esters used (all from Messrs. Albright and Wilson, Oldbury, Birmingham) are given in Table 1. The relative amounts of them in their mixtures were obtained by (i) potentiometric titration with 0·1N-sodium hydroxide of approximately 0·5M-solutions in toluene, and (ii) paper chromatography of the undiluted acids by a technique similar to that described previously.[7] A sample of "crude" di-n-octyl hydrogen phosphate in toluene was freed from the large amount of mono-ester by repeated washing with an equal volume of ethylene glycol, and then with water to remove traces of ethylene glycol.

TABLE 1.

Phosphoric ester	Abbrevn.	Solvent molarity monoester	diester	Phosphoric ester	Abbrevn.	Solvent molarity monoester	diester
Di-n-butyl	HDBP	$<$0·001	0·49	Di-n-decyl	HDNDP	0·007	0·49
Di-2-ethylhexyl	HDEHP	$<$0·001	0·50	Di-isodecyl ...		0·027	0·50
Di-n-octyl	HDNOP	0·10	0·39	Di "dodecyl" *	HDDP	0·006	0·47
Di-n-octyl after purifn.		$<$0·002	0·50	Mono-n-butyl...	H_2MBP	0·50	—
Di-iso-octyl......		0·04	0·50	Mono "dodecyl" *......	H_2MDDP	0·56	—

* "Dodecyl" = 1-isobutyl-3,5-dimethylhexyl.

Determination of the Distribution Coefficient for ^{7}Be.—The solvent and the aqueous phase were equilibrated in glass tubes, except for hydrofluoric acid for which Polythene tubes were used. In the experiments on the time-dependence of the extraction of beryllium the phases were stirred together for the relatively short times (up to 30 min.) and finally shaken mechanically in a stoppered tube. In all the other experiments the phases were shaken together in stoppered tubes. Equal volumes of solvent and aqueous phase (1—2 ml.) were used in distribution experiments, and the phases were separated by centrifugation. The distribution coefficient (D_{Be}) of ^{7}Be between solvent and aqueous phase was measured by γ-counting of aliquot parts of the solvent and aqueous phase after evaporation to dryness on stainless-steel trays (γ-scintillation counter); D_{Be} is defined as the number of counts from the organic phase divided by the number from an equal volume of the aqueous phase in the same time.

RESULTS

Extraction of Beryllium Esters of Phosphoric Acid.—(a) *Dependence of* D_{Be} *on equilibration time.* The dependence of D_{Be} on equilibration time was measured with the ^{7}Be initially in (i) the aqueous phase and (ii) the organic phase (by extraction of the ^{7}Be from an appropriate aqueous solution into the organic phase, and then stripping of the organic phase with fresh aqueous phase). The time required for D_{Be} to reach a constant value (Table 2) varied appreciably with the different solvents, varied slightly with aqueous acid concentration, and was independent of whether equilibrium was approached from the aqueous or the organic phase. All later experiments started with ^{7}Be in the aqueous phase.

The presence of monoester in the diester had a very considerable effect on the time required to reach equilibrium. This is illustrated by comparing (i) the "crude" di-n-octyl ester (containing $\sim$20% of monoester) for which $t_{equil.}$ = 10—15 min., with purified material ($<$0·2%

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[6] Mellish and Payne, A.E.R.E. Report, 1959, I/M 53.

[7] Hardy and Scargill, *J. Inorg. Nuclear Chem.*, 1959, **10**, 323.

of monoester) for which $t_{\text{equil.}}$ = 300—500 min., and (ii) the times required for the monododecyl ester ($t_{\text{equil.}}$ ~30 min.) and the didodecyl ester (containing $<1\%$ of monoester) ($t_{\text{equil.}}$ 250—500 min.). The more detailed work described below was therefore carried out only with dialkyl esters containing $<0{\cdot}5\%$ of monoester.

(*b*) *Dependence of D_{Be} on the concentration of nitric acid in the aqueous phase, and on the type of phosphoric ester in the organic phase.* D_{Be} was measured for the available phosphoric esters with 0·25, 2, and 10M-nitric acid (Table 2), and also with 4 and 6M-acid for HDEHP. The values of D_{Be} vary by a factor of only about 3 in the range from di-n-butyl to di" dodecyl." A log–log plot of D_{Be} against $[HNO_3]$ for both mono- and di-esters gives a straight line with a slope of approximately -2 from 0·25 to ~3M-nitric acid, thus indicating an inverse dependence of D_{Be} on $[H^+]^2$. At higher aqueous acid concentrations, D_{Be} is appreciably greater than indicated by this dependence.

TABLE 2. *Distribution of* ^{7}Be *in nitric acid–ester–toluene systems.*

Alkyl ester of H_3PO_4 (0·5M *)	Initial aq. HNO_3 concn. (M)	Time for equilibrn. (min.)	D_{Be}	Alkyl ester of H_3PO_4 (0·5M *)	Initial aq. HNO_3 concn. (M)	Time for equilibrn. (min.)	D_{Be}
Di-n-butyl	0·25	15	34·5	Di-iso-octyl	0·25	30	28·0
	2·0	90	0·74		2·0	~200	0·59
	10·0	~30	0·55		10·0	60	0·30
Di-2-ethylhexyl	0·25	~600	19·0	Di-n-decyl	0·25	45	54·0
	2·0	~1200	0·35		2·0	60	1·02
	10·0	350	0·15		10·0	60	0·61
Di-n-octyl	0·25	10	51·0	Di-isodecyl	0·25	90	30·2
	2·0	15	1·15		2·0	60	0·61
	10·0	10	0·74		10·0	30	0·30
Di-n-octyl	0·25	250	62·0	Di" dodecyl "	0·25	250	60·0
(purified)	2·0	400	0·98		2·0	500	1·20
	10·0	300	0·58	Mono-n-butyl	0·25—10·0	No extraction	
				Mono" dodecyl "	0·25	30	31·4
					2·0	30	0·69
					10·0	10	0·26

* For exact concentration and purity see Table 1.

(c) *Dependence of D_{Be} on phosphoric ester concentration.* Results on the variation of D_{Be} with phosphoric ester concentration are given in Fig. 1 and summarised in Table 3.

TABLE 3.

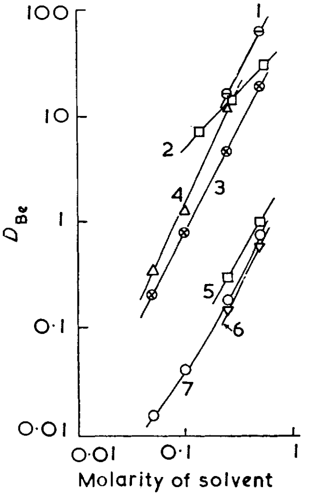
Ester Type	Ester Concn. (M)	Aqueous phase	Slope of log–log plot
HDBP	0·05—0·25	0·25M-HNO_3	2·2
HDBP	0·05—0·5	2M-HNO_3	1·5—2·0
H_2MDDP	0·14—0·56	0·25M-HNO_3	1·0
HDNOP	0·25 and 0·5	0·25, 2, 10M-HNO_3	~2
HDEHP	0·05—0·5	0·25M-HCl	1·9

(d) *Dependence of D_{Be} on acid medium.* (i) General. Values of D_{Be} for 0·5M-di" dodecyl " ester in toluene and 2M-solutions of various acids were H_2SO_4 1·75, $HClO_4$ 1·10, HNO_3 1·00, HCl 0·77, $HClO_4$ + 10^{-2}M-HF 0·65. Because 2M-hydrofluoric acid would have given a very low value of D_{Be} owing to the strong complex-binding of the beryllium cation by the fluoride ion, D_{Be} is given for 10^{-2}M-HF in 2M-$HClO_4$.

(ii) $HClO_4$, HNO_3, and HCl. The variation of D_{Be} with acid concentration for 0·5M-HDEHP–toluene and 0·25—10M-nitric, -hydrochloric, and -perchloric acid is shown in Fig. 2. Within experimental error the results for nitric and perchloric acid in the range 0·25—2M are equal, but those for hydrochloric acid are significantly lower. The lower value of D_{Be} in chloride solution is due to chloride complex-formation with the beryllium ion in the aqueous phase, and from the results the formation constant for the $BeCl^+$ complex has been calculated (see below).

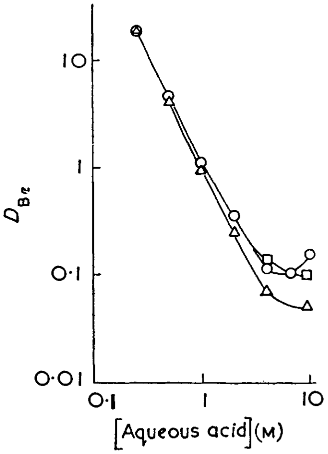
(iii) H_2SO_4. Values of D_{Be} for sulphuric and nitric acid and 0·5M-didecyl ester–toluene are compared in Fig. 3. D_{Be} is higher for sulphuric acid on a molar basis, but when D_{Be} is plotted against the $[H^+]$ therein (calculated from data given by Young [8]), D_{Be} is slightly lower for sulphuric than for nitric acid at equal $[H^+]$ in the range 0·15—1·3M-H^+. The lower values are due to the relatively weak complex-binding of the beryllium ion by the hydrogen sulphate ion. The higher value of D_{Be} at ~6M-$[H^+]$ for sulphuric than for nitric acid is probably due to a combination of stronger sulphate complex-formation (to give $BeSO_4$) than nitrate complex-formation, and also to the extraction of the beryllium sulphate complex by the solvent in a similar way to the extraction of beryllium nitrate.

FIG. 1. *Variation of D_{Be} with concentration of dialkyl and monoalkyl esters.*



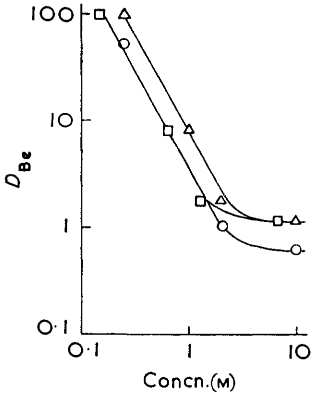
1, HDNOP–0·25M-HNO_3. 2, H_2MDDP–0·25M-HNO_3. 3, HDEHP–0·25M-HCl. 4, HDBP–0·25M-HNO_3. 5, HDNOP–2M-HNO_3. 6, HDNOP–10M-HNO_3. 7, HDBP–2M-HNO_3.

FIG. 2. *Variation of D_{Be} with concentration of aqueous acid for extraction by* 0·5M-HDEHP.



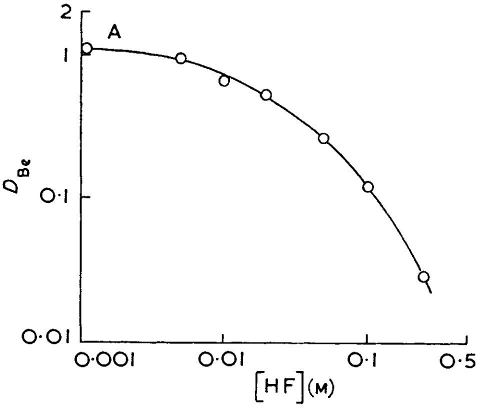
○ HNO_3. △ HCl. □ H_2SO_4.

FIG. 3. *Variation of D_{Be} with concentration of* HNO_3, H_2SO_4, *and* H^+ *in* H_2SO_4, *for extraction by* 0·5M-HDDP.



○ HNO_3. △ HCl. □ H^+ *in* H_2SO_4.

FIG. 4. *Variation of D_{Be} with* HF *concentration in* 2M-$HClO_4$ *for extraction by* 0·5M-HDNDP.



(A = *limit of* [HF] = 0 *in* 2M-$HClO_4$.)

(iv) HF. The variation of D_{Be} with [HF] in the 2M-perchloric acid–0·5M-didecyl ester system is shown in Fig. 4. The shape of the curve can be quantitatively explained on the

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[8] Young, *Rec. Chem. Progr.*, 1951, **12**, 81.

basis of fluoride complex-binding of Be^{2+} to give BeF^+, BeF_2, and BeF_3^-, and formation constants for these complexes are calculated below.

(e) *Variation of D_{Be} with the nature of the diluent.* The variation of D_{Be} with the nature of the diluent is shown in Fig. 5 for 2M-nitric acid and 0·5M-di-n-butyl ester in chloroform, carbon tetrachloride, toluene, benzene, and kerosene. The results are plotted as D_{Be} against $\log_{10} K_2$ (K_2 = dimerisation constant in the organic phase [9]) and are compared with similar results obtained previously with uranium.

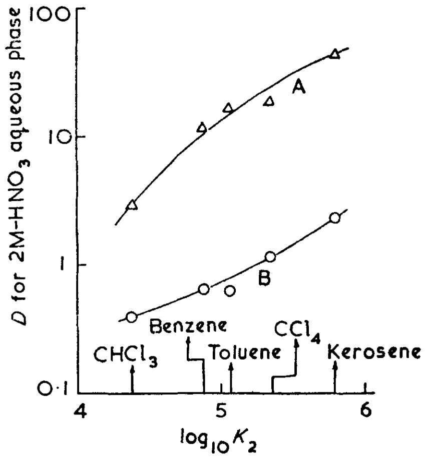

FIG. 5. *Correlation of D_{Be} and D_U with $\log_{10} K_2$ for the HDBP–2M-HNO$_3$ system.*
A, Uranium–0·05M-HDBP. B, Be–0·5M-HDBP

(f) *Dependence of D_{Be} on the beryllium concentration.* This is illustrated in Table 4. The conditions were—organic phase: 0·5M di-n-decylphosphoric acid/toluene; aqueous phase: 2M-H_2SO_4; varying equilibration times until equilibrium was reached.

Solution	Equilibrn. time (hr.)	D_{Be}
(i) ^7Be alone	1 (equil.)	1·02
(ii) 0·1M-Be + ^7Be (added at time of dissolution)	1	0·62
	3 (equil.)	1·00
(iii) 0·1M-Be + ^7Be (added immediately before equilibrn.)	1	0·54
	3 (equil.)	0·95

The conclusions from these experiments are: D_{Be} is independent of beryllium concentration in the range from tracer level to 0·1M-Be; the time to reach equilibrium depends upon the beryllium concentration (1 hr. for tracer, ~3 hr. for 0·1M); and ^7Be reaches isotopic equilibrium with 0·1M-Be in <60 min.

Calculation of the Equilibrium Constants for the Chloride and Fluoride Complexes of Beryllium.—(a) *Formation constant for the* $BeCl^+$ *complex.* The significant lowering of D_{Be} for hydrochloric compared with perchloric and nitric acid solutions (Fig. 2) is due to chloride complex-binding of the Be^{2+} ion in the hydrochloric acid solution.

The equilibrium constant, K_1, for the $BeCl^+$ complex formed by the equilibrium $Be^{2+} + Cl^- \longrightarrow BeCl^+$ is defined by:

$$K_1 = [BeCl^+]/[Be^{2+}][Cl^-]$$

The value of D_{Be} in the absence of chloride ions is given by

$$D_{Be} = [Be]_{org}/[Be]_{aq} = [BeA_2(HA)_2]_{org}/[Be^{2+}]_{aq}$$

in which A represents ester ion. In the presence of chloride ions D'_{Be} is given by:

$$D'_{Be} = [BeA_2(HA)_2]_{org}/([Be^{2+}]_{aq} + [BeCl^+]_{aq})$$

It follows that $K_1 = (x - 1)/[Cl^-]_{aq}$ where $x = D_{Be}/D'_{Be}$. Values of K_1 obtained from

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[9] Hardy and Scargill, *J. Inorg. Nuclear Chem.* 1959, **11**, 128.

the comparison of distribution coefficients in perchloric and hydrochloric acid respectively (Fig. 2) are:

	HDEHP				HDDP
$[HCl]_{aq}$ (M)	0·5	2	4	9·4	2
K_1 (mole^{-1})	0·22	0·20	0·25	0·20	0·21

The mean value of $K_1 = 0{\cdot}22 \pm 0{\cdot}03$ mole^{-1} is obtained, and is independent of ionic strength in the above range within experimental error.

(b) *Equilibrium constants for the fluoride complexes of beryllium.* The gross equilibrium constants for

$$Be^{2+} + nHF \rightleftharpoons BeF_n^{(2-n)+} + nH^+ \quad (n \leqslant 3)$$

defined by

$$^*\beta_n = [BeF_n][H^+]^n/[Be^{2+}][HF]^n$$

can be calculated from the variation of D_{Be} with [HF] in perchloric acid (Fig. 4).

$$\text{Total } [Be]_{aq} = C_M = [Be^{2+}] + [BeF^+] + [BeF_2] + [BeF_3^-] = [Be^{2+}]x$$

where

$$x = 1 + {}^*\beta_1\frac{[HF]}{[H^+]} + {}^*\beta_2\frac{[HF]^2}{[H^+]^2} + \cdots\cdots$$

Also, when no fluoride is present we have:

$$D_{Be} = [BeA_2(HA)_2]_{org}/[Be^{2+}]$$

and

$$D'_{Be} = \frac{[BeA_2(HA)_2]_{org}}{([Be^{2+}] + [BeF^+] + [BeF_2] + [BeF_3^-])} = \frac{[BeA_2(HA)_2]_{org}}{[Be^{2+}]x}$$

provided that no fluoride-complex of beryllium is extracted. Hence $x = D_{Be}/D'_{Be}$ and a plot of $(x - 1)/[HF]$ against [HF] will give a straight line at low values of [HF], *i.e.*, where the BeF_3^- complex is not present in significant amount. At higher values of [HF], a curve will be obtained if the BeF_3^- complex becomes significant. In the straight-line region the slope gives $^*\beta_2/[H^+]^2$ and the intercept on the $(x - 1)/[HF]$ axis gives $^*\beta_1/[H^+]$. Substitution of $^*\beta_1$ and $^*\beta_2$ in the general equation for higher values of [HF] enables the value of $^*\beta_3$ to be calculated.

An approximate straight line is obtained up to 0·1M-hydrofluoric acid, and values of $^*\beta_1 = 97$ and $^*\beta_2 = 1290$ are obtained. Substitution of these values in the general equation gives $^*\beta_3 = 3100$. From these three constants the value of D'_{Be} has been calculated for each [HF] in Fig. 4, and these values are compared below with the experimental values. The agreement is very good.

[HF] (M)	0·005	0·01	0·02	0·05	0·10	0·25
D'_{Be} (calc.)	0·88	0·72	0·52	0·26	0·12	0·028
D'_{Be} (expl.)	0·95	0·65	0·52	0·26	0·12	0·028

For comparison of $^*\beta_n$ with other published constants see below.

DISCUSSION

The extraction of metals from aqueous solution by dialkyl hydrogen phosphates (HA) has been studied in detail recently by a number of workers [3,5,10-15] and has usually been described by the principal reaction:

$$M_{aq}^{n+} + n(HA)_{2,\,org} \rightleftharpoons MA_n(HA)_{n,\,org} + nH^+_{aq}$$

for low concentrations of the metal and an excess of the ester HA. The predominant complex in the organic phase is usually the monomer $MA_n(HA)_n$; however, the presence of the complex MA_n has been confirmed by Dyrssen and Krasovec [10] for U(VI)–HDBP–$HClO_4$

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[10] Dyrssen and Krasovec, *Acta Chem. Scand.*, 1959, **13**, 561.

[11] Baes, Zingaro, and Coleman, *J. Phys. Chem.*, 1958, **62**, 129.

[12] Hardy, A.E.R.E. Report, 1959, R-3267.

[13] Dyrssen and Liem Djiet Hay, *Acta Chem. Scand.*, 1960, in the press.

[14] Dyrssen, *Acta Chem. Scand.*, 1957, **11**, 1277.

[15] Hardy and Scargill, A.E.R.E. Report, 1959, R-2945.

at low concentrations of HDBP in the diluent hexone (isobutyl methyl ketone). With increasing metal concentration, polymers are formed, for example, $HA_2UO_2A_2UO_2\ldots A_2UO_2A_2H$ in the U(VI)–HDEHP–$HClO_4$ system.[11]

Other extraction reactions are possible from aqueous solutions in which the anion (*e.g.*, nitrate, chloride) of the mineral acid can form complexes with the metal cation. The importance of the extraction of uranyl nitrate by HDBP relative to the extraction of the uranyl ion has been discussed in detail by Hardy,[12] and equilibrium constants for the following reactions have been calculated:

$$UO_{2,aq}^{2+} + 2(HDBP)_{2,org} \longrightarrow UO_2(DBP)_2(HDBP)_{2,org} + 2H_{aq}^{+}:\ K = 3{\cdot}6 \times 10^4$$

$$UO_{2,aq}^{2+} + 2NO_{3,aq}^{-} + (HDBP)_{2,org} \rightleftharpoons UO_2(NO_3)_2(HDBP)_{2,org}:\ K = 46\ \text{moles}^{-3}$$

The extraction of beryllium from nitrate, chloride, and sulphate solution by dialkyl hydrogen phosphates follows the same pattern as the extraction of uranium from nitrate solution, *i.e.*, D_{Be} decreases with increasing $[H^+]$ at low ($<$3M-)aqueous acid concentration, and increases with aqueous acid concentration at $> \sim$6M. It is therefore very likely that from $>$3M-aqueous acid nitrate, chloride, and sulphate complexes are extracted in addition to the $BeA_2(HA)_2$ complex.

The structure of the alkyl group in ester has a slight effect on the magnitude of D_{Be} at a given concentration of ester and aqueous acid. The values of D_{Be} relative to HDEHP = 1 (Fig. 1, 0·25M-HNO_3) and the order of extraction on a mole basis are:

Di-2-ethylhexyl	1	Di-n-butyl	1·82
Di-iso-octyl	1·47	Di-n-octyl	2·68
Mono" dodecyl "	1·58	Di-n-decyl	2·84
Di-isodecyl	1·58	Di" dodecyl "	3·15

The value of D_{Be} is therefore lower the greater the degree of branching of the alkyl groups for a given carbon number, *e.g.*, 2-ethylhexyl < iso-octyl < n-octyl. Also D_{Be} increases with chain length for n-alkyl groups, *e.g.*, n-butyl < n-octyl < n-decyl.

The rate of attainment of equilibrium depends upon the purity and structure of the ester, and upon the concentration of mineral acid in the aqueous phase. The importance of purity on the rate has been illustrated for the di-n-octyl ester but the absolute value of D_{Be} is not appreciably affected. Comparison of HDBP, HDEHP, and HDNOP, all $>$99·8% pure, indicates that the rate of attainment of equilibrium is lower the longer the alkyl chain and the more branched the chain. These effects are probably due to steric hindrance to the attachment of a number of molecules of ester HA or ion A^- round such a small cation as beryllium (the same esters reach equilibrium much more rapidly with a large cation such as uranyl [3,12]) and also to the need to displace the strongly bound water in the primary hydration sheath.

The extraction of beryllium by mono" dodecyl " dihydrogen phosphate (H_2A) is proportional to the first power of its concentration and to $[H^+]^{-2}$ at $<$3M-aqueous acid. The simple equation $Be_{aq}^{2+} + H_2A_{org} \rightleftharpoons BeA_{org} + 2H_{aq}^{+}$ can therefore be used to represent equilibrium in the absence of further information on the exact nature of H_2A in the system studied, *e.g.*, dimerisation or polymerisation. The rate of extraction of beryllium by the mono" dodecyl " ester is higher than for the diester, probably owing to the greater ease of complex-formation for the small beryllium ion by one monoester molecule (2 replaceable hydrogen atoms in OH groups attached to the same phosphorus atom) than by two diester molecules, the first of which may sterically hinder the second.

The nature of the diluent has a considerable effect on the extraction of beryllium by the esters. The highest value of D_{Be} was obtained with kerosene, and if the values of D_{Be} for other diluents are expressed relative to it the following reduction factors are obtained:

Diluent	Kerosene	CCl_4	C_6H_6	$CHCl_3$
Reduction factor	1	2·0	3·5	5·8

This effect has also been found for uranium(VI),[12] and has been studied by Dyrssen and Liem Djiet Hay[13] for europium(III) and americium(III). Extraction of the metal ion increases as the extent of interaction of the diester monomer with the diluent decreases, and the extent of interaction is indicated by the value of K_d, the distribution coefficient of the HA monomer between the two phases (and also by the value of K_2, the dimerisation constant of HA in the diluent, since K_2 increases as K_d decreases).

Equilibrium constants for beryllium–diester complexes have been calculated from the overall equations:

$$\mathrm{Be_{aq}}^{2+} + 2(\mathrm{HA})_{2,\mathrm{org}} \rightleftharpoons \mathrm{BeA_2(HA)_{2,org}} + 2\mathrm{H_{aq}}^{+}$$

$$\log_{10} K = \log_{10} D_{\mathrm{Be}} + 2 \log_{10} [\mathrm{H}^{+}]_{\mathrm{aq}} - 2 \log_{10} (C_{\mathrm{A}}/2)$$

in which C_{A} is the total molar concentration of HA in the system. Values of $\log_{10} K$ for 0·25M-nitric acid and toluene are: Bu^{n} 1·55, 2-ethylhexyl 1·28, iso-octyl 1·45, n-octyl 1·71, isodecyl 1·48, n-decyl 1·73, and " dodecyl " 1·78.

Comparative values for other metals calculated from data obtained under similar conditions are:

Metal	Alkyl group and diluent	$\log_{10} K$	Ref.
U(VI)	n-butyl/toluene	4·55	12
U(VI)	n-butyl/$CHCl_3$	3·58	10
Y(III)	n-butyl/$CHCl_3$	3·20	14
La(III)	2-ethylhexyl/hexane	−2·52	5

The extraction of Be^{2+} relative to other cations is illustrated for the HDBP–diluent–dilute nitric acid system, Hardy's value[15] for zirconium(IV) and Dyrssen's[13] for the other metals being used: Zr(IV) > Sc(III) > U(VI) > Y(III) > Be(II) > Eu(III) > Am(III) > La(III) > Ca(II) > Sr(II). It will therefore be possible to extract and separate selectively Zr(IV), Sc(III), and U(VI), from solutions containing Be(II) in dilute nitric acid, and to extract Be(II) from solutions containing La(III), Ca(II), and Sr(II).

The extraction of beryllium by dialkyl hydrogen phosphates can be contrasted with the extraction by tri-n-butyl phosphate (TBP) from nitric and perchloric acid solution.[16] With perchloric acid D_{Be} has the same general trend with $[HClO_4]$ as uranium(VI),[17] and it seems likely that the beryllium exists in the organic phase in the form of hydrated ions which are solvated by TBP, *e.g.*, $Be^{2+}(H_2O)_x(TBP)_2$, rather than as neutral molecules such as $Be(NO_3)_2(TBP)_2$ or $Be(ClO_4)_2(TBP)_2$. The rate of extraction by TBP is much higher than by dialkyl hydrogen phosphates (which generally have to displace the strongly bound water of hydration to form a chelate complex) as would be expected if the TBP molecules are co-ordinated through phosphoryl-oxygen groups to the water molecules around the Be^{2+} ion.

Beryllium can be placed in the following order of extraction from 2M-nitric acid by 100% TBP relative to the many other elements which have been studied:[18,19] U(VI) > Pu(VI) > Th(IV) > Am(III) > Ce(III), Zr(IV), Y(III) > Be(II) > Zn(II) > Co(II).

It is comparatively easy to separate uranium(VI) and plutonium(IV) from beryllium(II) by extraction with tributyl phosphate from the solution which would be obtained by dissolution of an irradiated beryllium-clad nuclear fuel element in nitric acid. The beryllium(II) would be discarded with the fission products in the highly active aqueous waste solution from the solvent-extraction process. It would, however, be very difficult to recover the beryllium(II) selectively from this waste solution by extraction with tributyl phosphate or with dialkyl hydrogen phosphates because many of the fission products [*e.g.*, zirconium(IV), yttrium(III)] have higher extraction coefficients than beryllium(II).

Equilibrium constants have been calculated (see Results) for the $BeCl^{+}$ complex, and

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[16] Hardy, Greenfield, and Scargill, A.E.R.E. Report, 1960, R-3316.

[17] Hesford and McKay, *J. Inorg. Nuclear Chem.*, 1960, **13**, 165.

[18] McKay and Healy, " Progress in Nuclear Energy," Series III, Pergamon Press, London, 1958, Vol. II, Appendix III.

[19] Hardy, unpublished work on the TBP extraction of Zn(II) and Co(II).

for the first three fluoro-complexes of Be^{2+}. The values for the *consecutive* fluoro-equilibrium constants, $*K_n$, defined by

$$*K_n = [BeF_n][H^+]/[BeF_{n-1}][HF]$$

are compared below with other published values.[20] No other value for the chloro-complex has been published.

Complex	Method †	Ionic strength and medium	Temp.	n in $\log_{10} *K_n$ 1	2	3	4	Ref.
$BeCl^+$	A	0·5—6, HCl	20°	$-0{\cdot}66$(K_1, not $*K_1$)				This work
$BeF_n^{(2-n)+}$ ...	A	2, $HClO_4$	20	1·99	1·12	0·38	—	This work
	B	0·5, $NaClO_4$	25	2·11	0·90	$-0{\cdot}17$	—	*a*
	B	0·5, $NaClO_4$	25	2·12	0·84	0·03	—	*b*
	C	Various	?	2·89	1·94	0·56	$-1{\cdot}0$	*c*

† A, Solvent extraction; B, e.m.f. with redox electrode; C, calorimetry, etc. Refs.: *a*, Yates and Dodgen, Amer. Chem. Soc. 122nd Meeting, Sept. 1952, Abs. 18P; *b*, Yates, Thesis, State Coll., Washington, 1955, Univ. Microfilms 15,662. *c*, Kleiner, *Zhur. obshchei Khim.*, 1951, **21**, 18.

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[20] " Stability Constants," Part II, Inorganic Ligands, *Chem. Soc. Spec. Publ.* No. 11, London 1958.