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Note

Distribution coefficients of 52 elements on a strongly basic anion-exchange resin in aqueous solutions of orthophosphoric acid

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Since the early work of Kraus and Nelson[1], systematic determinations of distribution coefficients of elements between a strongly basic anion exchanger and aqueous acidic solutions have been made by various workers for most mineral acids and some organic acids and acid mixtures[2,3]. Surprisingly, only very limited and incomplete data are available on the anion-exchange behaviour of elements in orthophosphoric acid solutions[4–9].

In this paper preliminary results on this topic are reported. Weight distribution coefficients, λ (amount per gram of dry resin (phosphate)/amount per millilitre of the solution), were determined by the batch equilibration method[3] with the use of radioactive tracers at room temperature and loadings not exceeding 1 % of the resin capacity, at H_3PO_4 concentrations from 0.1 to 14 *M*. The results are given in Table I. Care was taken to prepare tracer solutions free from halide ions. In some instances, however, this was not possible. Elements originally present as chloride complexes are marked with an asterisk in Table I.

Examination of the results in Table I enables one to draw the following conclusions.

(1) Adsorbabilities of elements on Dowex 1-X8 resin in H_3PO_4 solutions show marked differences (also for elements in the same group of the Periodic Table).

(2) With few exceptions, the distribution coefficients decrease proportionally with increase in acid concentration.

(3) Three main groups can be distinguished:

(a) Elements that show no or low adsorbability ($\lambda < 10$) over the whole concentration range of the acid: alkali metals, alkaline earth metals, Cu(II), Zn(II), Cd(II), Se(IV), Tl(I), Y(III), Pr(III), Ge(IV), Mn(II), Co(II) and Ni(II). These elements apparently do not form or form only very weak anionic phosphate complexes.

(b) Elements that have distribution coefficients with values from tens to a few hundreds at low H_3PO_4 concentrations: Ag(I), La(III), Gd(III), Tm(III), Lu(III), Ga(III), In(III), Hf(IV), Sn(II), As(III), Sb(III), Cr(III), Cr(VI), W(VI), Fe(III) Rh(III), Ir(IV) and Np(VI). For most of these elements, there is evidence for the formation of complex anions with phosphates[10].

(c) Elements that show high adsorbability with distribution coefficients of the

TABLE I

WEIGHT DISTRIBUTION COEFFICIENTS OF INORGANIC IONS IN THE SYSTEM DOWEX 1-X8 (PO_4^{3-})–H_3PO_4

Ion	*H_3PO_4 concentration (moles/l)*							
	0.1	*1*	*3*	*5*	*7*	*9*	*12*	*14*
Zr(IV)	$>10^4$	$>10^3$	77	30	0	0	—	3
Tc(VII)	$1.6\cdot10^4$	584	330	458	167	242	94	54
Hg(II)	$9.4\cdot10^3$	$2.0\cdot10^3$	542	379	122	142	50	67
S(VI)	$6.3\cdot10^3$	116	36	33	30	12	17	12
Mo(VI)	$3.7\cdot10^3$	211	87	30	23	0	3	3
Pt(IV)*	$3\cdot10^3$	$3\cdot10^3$	$3\cdot10^3$	$3\cdot10^3$	$1.4\cdot10^3$	—	463	289
Nb(V)	$3\cdot10^3$	$3.5\cdot10^3$	81	19	13	0	0	0
I(I)	$1.8\cdot10^3$	$1.0\cdot10^3$	515	318	176	—	235	65
Sc(III)	$1.4\cdot10^3$	147	23	12	4	4	3	3
Br(I)	$1.0\cdot10^3$	114	86	91	68	95	20	18
Pd(II)*	889	802	686	729	537	—	347	198
Pu(IV)	629	187	6	0	—	0	0	0
Ta(V)	625	309	178	138	23	37	38	5
Re(VIII)	559	238	140	79	36	57	21	8
Au(III)*	471	625	440	310	—	371	154	68
Os(IV)*	400	286	293	264	232	251	148	137
Fe(III)	368	31	3	2	~1	~1	~1	0
Ir(IV)*	328	130	95	65	57	66	29	34
Sb(III)	261	22	43	55	17	11	0	0
Lu(III)	205	34	6	2	7	0	0	0
Ag(I)	143	205	61	26	16	28	10	3
Hf(IV)	102	226	56	41	2	16	9	—
Tm(III)	62	7	0	0	0	0	0	0
In(III)	54	10	6	0	—	0	—	—
Np(IV)	48	76	22	10	7	3	6	3
Rh(III)*	46	21	9	5	6	2	—	0
Cr(VI)	43	9	0	0	9	3	6	~1
Sn(II)	32	132	140	68	88	72	0	0
As(III)	31	6	5	4	5	0	—	—
W(VI)	29	24	15	11	8	2	0	0
Cr(III)	26	17	14	9	8	—	9	14
Ga(III)	19	0	0	0	0	0	0	0
La(III)	15	6	2	0	0	0	0	0
Gd(III)	14	~1	—	~1	~1	0	0	0
Mn(II)	8	4	7	6	8	5	8	—
Cs(I)	7	2	~1	~1	~1	~1	~1	—
Zn(II)	4	3	2	2	2	2	4	—
Cd(II)	4	2	2	2	1	2	—	0
Se(IV)	4	~1	0	0	0	0	6	8
K(I)	3	<1	<1	<1	—	0	—	—
Na(I)	~1	~1	~1	<1	<1	<1	<1	<1
Rb(I)	<1	<1	<1	<1	<1	<1	<1	<1
Tl(I)	0	0	0	0	0	0	0	0
Ca(II)	0	0	0	0	0	0	0	0
Sr(II)	0	0	0	0	0	0	0	0
Ba(II)	0	0	0	0	0	0	0	0
Cu(II)	0	2	~1	4	2	0	0	—
Co(II)	0	0	0	0	0	0	0	0
Ni(II)	0	0	0	0	0	0	0	0
Y(III)	0	0	0	0	0	0	0	0
Pr(III)	0	0	0	0	0	0	0	0
Ge(IV)	0	0	0	0	0	0	0	0

* Elements originally present as chloride complexes.

order of 500 or more in dilute H_3PO_4 solutions. These include Zr(IV), Nb(V), Ta(V), Mo(VI), S(VI), Tc(VII), Re(VII), Br(I), I(I), Pd(II), Os(IV), Pt(IV), Pu(IV), Au(III), Hg(II) and Sc(III). It can be seen that these are mostly elements that exist as simple anions, oxyanions, heteropolyacids or anionic halide complexes in solutions. Sc(III) apparently forms stable anionic complexes with phosphates (*cf.* also ref. 10).

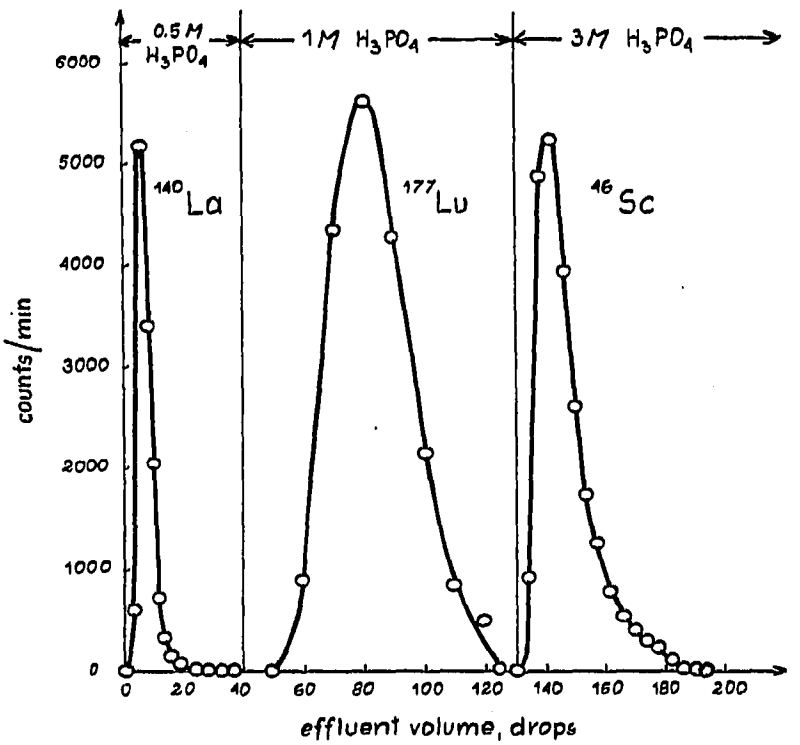

Fig. 1. Separation of lanthanum, lutetium and scandium. Column: 3.0 cm × 0.035 cm² Dowex 1-X8 (PO_4^{3-}) (24 μm < (particle diameter) < 42 μm). Temperature: 34°. Flow-rate: 1.7 cm/min.

The high adsorbability of Hg(II) is of interest especially when it is considered that recently reported R_F values on DEAE-cellulose in H_3PO_4 solutions[11] do not suggest the existence of anionic phosphate complexes of mercury. Irrespective of the mechanism of the pronounced sorption of Hg(II) on Dowex 1 resin, it may be of importance in practical separations.

Differences in the adsorbabilities of elements on Dowex 1 in H_3PO_4 medium offer many possibilities for the separation of elements by ion-exchange chromatography. Some of these separations are illustrated in Figs. 1 and 2. Further work including the effect of temperature and resin cross-linking on anion-exchange separations in this system is in progress.

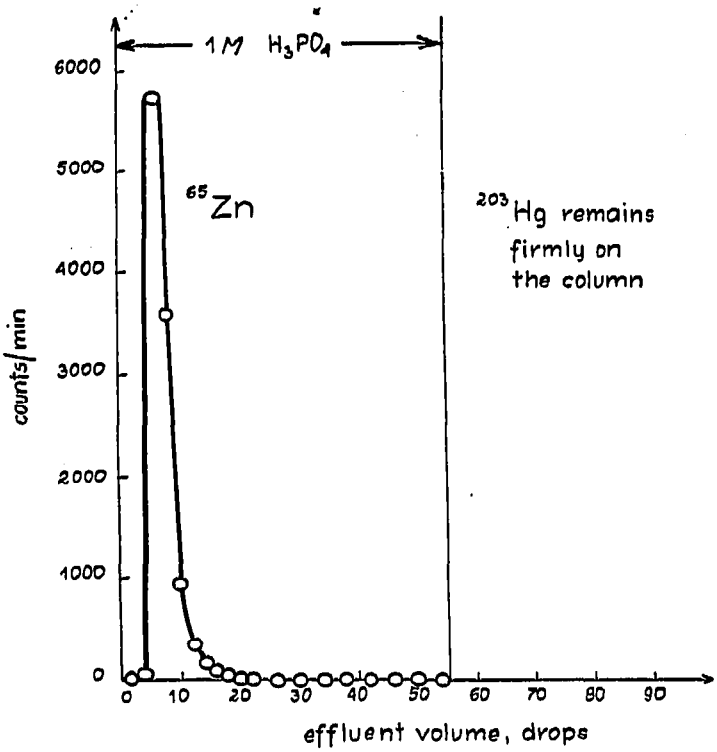

Fig. 2. Separation of zinc and mercury. Column: 3.0 cm × 0.035 cm^2 Dowex 1-X8 (PO_4^{3-}) (24 μm ≤ (particle diameter) ≤ 42 μm). Temperature: 25°. Flow-rate: 1.7 cm/min.

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