173. *The Adsorption of Some Anionic Complexes on a Cation-exchange Resin.*

By H. IRVING and G. T. WOODS.

The distribution coefficient, K_D, has been measured for the adsorption of a number of metals on to a cation-exchange resin from concentrated aqueous solutions of alkali-metal or magnesium halides.

With increasing concentration of lithium (or magnesium) iodide the values of K_D for indium first decreased, as expected; they then passed through a minimum and increased, although only anionic complexes must have predominated. The anomalous adsorption was less for bromides and still less for chlorides. Replacement of lithium by sodium or potassium also reduced the effect. With zinc and cadmium K_D decreased rapidly and monotonically with increasing halide concentration. With mercury and lithium chloride there was a small increase. Some analytical applications of these effects are suggested.

THE distribution of an n-valent metal between a cation-exchange resin and an aqueous phase containing ligand ions L^{l-} with which it can form one or more complex ions of formula $ML_j^{(n-jl)+}$ is conventionally described in terms of a distribution coefficient, K_D, defined as follows:

$$K_D = \frac{\text{total concn. of metal on resin (in moles/g. of dry resin)}}{\text{total concn. of metal in soln. (in moles/ml. of soln.)}}$$

Provided there are no changes in activity coefficients over the range of concentrations studied this expression is proportional to $\sum_0^x k_j\beta_j|L|^j/\sum_0^N \beta_j|L|^j$ where the (stoicheiometric) stability constant of the jth species is defined by $\beta_j = [ML_j]/[M][L]^j$. The value of k_j, the distribution coefficient for the jth species, ML_j, decreases rapidly as j increases, *i.e.*, as the positive charge on the complex falls and its size increases: it approaches a small (or zero) value for formally uncharged complexes ($j = n/l = x$). Consequently, as $|L|$ increases with increase in the total concentration of ligand in the aqueous phase, K_D decreases monotonically and approaches zero asymptotically, the more rapidly in systems where large stability constants, β_j, for successive step-complexes favour the formation of species of smaller positive ($j > 0$) or zero charge ($j = n/l$) or of anionic species ($j > n/l$) carrying a formal negative charge. This simple theory satisfactorily describes the behaviour of many systems [1] but it does not predict any extremum in the plot of K_D against $|L|$. A striking example of this phenomenon has recently been studied in some detail by Kraus, Michelson, and Nelson [2] who found that the value of K_D for the adsorption of ferric iron on to Dowex-50 from solutions in hydrochloric acid decreased from approximately 10^4 to a minimum of 2—3 when $[HCl]_{aq.} \sim 4$M but then increased steadily and reached a value of ~ 90 in 10M-acid.

The effect was even more marked when hydrochloric acid was replaced by lithium chloride (Fig. 1) for now K_D approached a value of 10^5 in 12M-solution, *i.e.*, a value greater than that for the aquo-cation itself. Experiments with auric chloride established unequivocally that strong adsorption was proceeding at halide concentrations where the metal could only be present in a complex anion, *i.e.*, where $jl > m$. The behaviour of gallium resembled that of iron(III), and while there was no appreciable "anomalous" adsorption for Mn(II), Co(II), Zn(II), In(III), Bi(III), and Sn(IV), slight adsorption ($1 < \log K_D < 2$) was found for Sb(V) and Tl(III) at high concentrations of chloride. Kraus comments:

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[1] Carleson and Irving, *J.*, 1954, 4390.

[2] Kraus, Michelson, and Nelson, *J. Amer. Chem. Soc.*, 1959, **81**, 3204.

" Interestingly, the same elements may also be readily extracted by ethers from hydrochloric acid solutions, though the connection between these two types of extractions is not clear."

The partition of indium halides between ether and many other organic solvents and halogen acids, HX, has been extensively studied by one of us (H. I.) and shown to increase in the order chloride < bromide < iodide, irrespective of the nature of the immiscible phase into which the solvated acid-complex $HInX_4$ is extracted.[3] We have now examined these systems to see whether the same order holds for " anomalous adsorption " by a cation resin, and have included in our studies several other metal halide systems for which the stability order for metal-complex formation is known to be Cl < Br < I [the reverse of the behaviour for iron(III), gallium, and indium] to see whether this is a significant factor. The work could not be completed, and only the preliminary results are presented here.

To facilitate intercomparison all measurements of K_D were carried out with the type of resin used by Kraus and his co-workers.[2] The use of radioactive isotopes of indium, zinc, and cadmium enabled low loadings to be used: distribution coefficients for mercury were studied by an absorptiometric procedure using dithizone. Substantial corrections for self-absorption proved necessary in measurements with concentrated solutions of lithium salts but values of the count rate, N_0, corresponding to medium of unit density could be calculated from the measured count rate, N, in solutions of density d, by using the equation

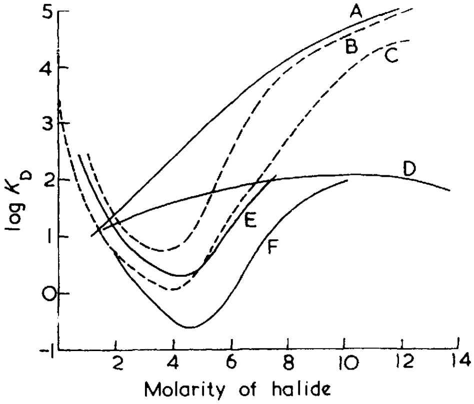

FIG. 1. The adsorption of anionic complexes on the cation resin Dowex-50 from concentrated solutions of hydrochloric acid and lithium chloride. Data from Kraus, Michelson, and Nelson.[2] A, $AuCl_3$–LiCl; B, $GaCl_3$–LiCl; C, $FeCl_3$–LiCl; D, $AuCl_3$–HCl; E, $GaCl_3$–HCl; F, $FeCl_3$–HCl.

$$N_0 = N/[1 - p(d - 1)]$$

where p was determined empirically for each system.

EXPERIMENTAL

Materials.—The radionuclides indium-114 ($t_{\frac{1}{2}}$ = 50 days), zinc-65 ($t_{\frac{1}{2}}$ = 245 days), and cadmium-115^m ($t_{\frac{1}{2}}$ = 44 days) were obtained by irradiating samples of the " Spekpure " metals in Harwell reactors. Stock solutions (9 to 60 × 10^{-4}M) in 0·1M-perchloric acid were diluted as required.

Solutions of lithium halides were made by neutralising freshly distilled halogen acids with lithium carbonate prepared from lithium hydride of good quality. Solutions of magnesium bromide and iodide were prepared similarly from pure magnesium oxide. Magnesium and mercuric chloride and halides of sodium and potassium were of " AnalaR " quality. All solutions of alkali halides were purified from other metals (especially iron and calcium introduced from the sample of lithium hydride) by passage through a column of Amberlite-120, any ensuing acidity being corrected by neutralisation with the appropriate hydroxide.

The resin used was Dowex-50 (10% cross-linked), graded to 100—200 mesh and treated in turn with concentrated hydrochloric acid, 4M-hydrochloric acid, and deionised water to convert

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[3] Irving and Rossotti, *J.*, 1955, 1946.

it into the hydrogen-ion form. All equilibrations were performed with 0·5 g. portions of a large batch of this resin which had been air-dried and was preserved in a tightly stoppered bottle. Loss of weight over phosphorus pentoxide at 64° (4 hr.) = 18·2%.

Measurements of Distribution Coefficients.—(*a*) *Systems containing indium, cadmium, and zinc.* Active indium solution (0·1 ml.) was added to a known weight (~0·5 g.) of the air-dried resin and a solution (15 ml.) of metal halide of known density d, and concentration C_X, contained in a 50 ml. Pyrex tube. The transfer pipette was washed out three times with the same halide solution, 0·25M-perchloric acid (0·5 ml.) was added to prevent hydrolysis, and the tube was stoppered and shaken mechanically (12 hr.). The resin was collected on a sintered-glass filter and the activity of 10 ml. of the filtrate was counted in a Veall-type M-6 liquid counter. The activity of a sample of 0·1 ml. of the stock active indium after dilution to 10 ml. with dilute perchloric acid was measured immediately afterwards. Count rates were corrected for paralysis, background, and (where necessary) decay; the length of a count was sufficient to give a precision of ±1%.

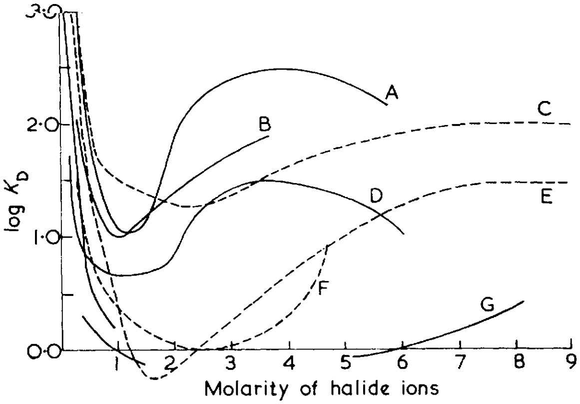

FIG 2. The adsorption on Dowex-50 of indium-114 from solutions of lithium, sodium, potassium, and magnesium halides. A, LiI; B, KI; C, NaI; D, MgI_2; E, LiBr; F, NaBr; G, $MgBr_2$.

If m is the mass of dry resin, v the initial value of the solution (15·9 ml.), $(C_{In})_R$ the counts/g. of dry resin after equilibration, C_{In}' the counts/ml. of solution before equilibration and C_{In} the counts/ml. after equilibration,

$$K_D = (C_{In})_R/C_{In} \quad \text{and} \quad vC_{In}' = \delta v C_{In} + m(C_{In})_R,$$

where δ is the swelling factor (0·97 in the present instance).

When only a little indium was absorbed on the resin, measurements of K_D by this method were unreliable. In such cases the equilibrated resin was collected on a sintered-glass filter, dried thoroughly by suction, and then washed with a small volume of 0·08M-potassium chloride. Since $K_D \sim 8000$ under these conditions, adsorbed indium is unaffected and only superficially adhering metal is removed. After being dried by suction the resin was shaken mechanically (6 hr.) with 2M-potassium chloride (10 ml.). Since, under these conditions, K_D is negligibly small, the whole of the indium was thus removed and could be determined radiometrically to give an upper limit for the value of K_D. To minimise oxidation, iodide solutions were always protected from the light. Since the observed counting rate, N, of indium-114 was seriously influenced by the concentrated solution of alkali halides in which it was dissolved, the counting rate, N_0, corresponding to pure water of unit density was determined empirically (see later).

Measurements with zinc and cadmium were carried out similarly by using the appropriate radio nuclides.

(*b*) *Systems containing mercury.* The stock solution of mercuric chloride was 0·0M with respect to sulphuric acid; it was diluted as required. The diluted solution (2 ml.), resin (0·5 g.), and lithium chloride solution (8 ml.) were shaken overnight in a stoppered Pyrex test-tube; 5 ml. of the aqueous phase were then withdrawn by a pipette furnished with a small filter, and diluted until the concentration of chloride ion was approximately 1·25M. The concentration of mercury was then determined by the reversion method [4] using calibration curves prepared under comparable conditions.

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[4] Irving, Andrew, and Risdon, *J.*, 1949, 541.

TABLE 1.

Values of p for various halides and indium-114.

	Cl	Br	I		Cl	Br	I
Li	0·2117	0·3033	0·3636	K	0·3354	0·2495	0·3595
Na	0·4154	0·3162	0·3980	Mg	—	0·4688	0·4855

TABLE 2.

Values of K_{D} for the adsorption of indium.

Lithium chloride.

K	0·06	0·17	0·26	0·35	0·52	0·70	0·87	1·04	5·20	11·39
K_{D}	963	1013	134	47·6	8·61	2·35	————very low indeed————			

Lithium bromide.

M	0·11	0·19	0·28	0·37	0·56	0·75	0·93	1·12	1·61	1·88	2·62	3·02
K_{D}	4830	1840	415	139	24·4	6·7	5·6 *	~1·5 *	~0·5 *	~0·7 *	~1·4 *	~3·3 *
M	3·63	4·53	5·65	6·33	6·52	7·52	7·36	8·16	9·07	9·79	10·04	
K_{D}	~3·3 *	~7·8 *	12·4	20·3	33·6 *	33·2	31·1	34·6	19·7	25·6	26·6	

* Obtained by removing indium activity from the equilibrated resin by shaking with 2M-potassium chloride (6 hr.) as described in the text.

Lithium iodide.

M	0·15	0·30	0·45	0·60	0·75	0·90	1·00	1·20	1·56
K_{D}	~10,000	950	276	82·1	38·2	16·7	14·6	10·1	15·3
M	1·80	2·00	2·50	3·00	3·93	4·37	4·83	5·30	5·75
K_{D}	38·0	82·3	173·4	256·3	291	281	260	138	154

Sodium bromide.

M	0·29	0·48	0·72	0·56	1·43	1·91	2·38	2·86	3·75
K_{D}	45·8	8·41	1·3 *	1·0 *	1·0 *	v. low	1·1 *	1·0 *	1·6 *
M	4·04	4·27	4·43	4·52	4·65				
K_{D}	1·6 *	2·6 *	3·5 *	~4·5	7·5				

Sodium iodide.

M	0·35	0·70	1·05	1·73	2·19	2·83	3·34	3·75	4·48
K_{D}	561	37·4	28·4	22·1	18·3	23·6	26·9	41·9	48·6
M	5·28	5·81	6·47	7·10	7·66	8·46			
K_{D}	66·0	82·2	89·1	102	104	107			

Potassium chloride.

M	0·07	0·15	0·25	0·50	0·75	0·89	2·11 to 3·74
K_{D}	7850	201	22·5	9·8	6·4	6·5	v. low

Potassium bromide.

M	0·32	0·65	0·97	1·59	1·80	2·51 to 3·47
K_{D}	535	38·4	1·25 *	0·8 *	0·9 †	~0·8 *

Potassium iodide.

M	0·19	0·34	0·48	0·67	1·01	1·23	1·51	2·02	2·62	3·02	3.48
K_{D}	620	83·5	35·2	16·1	9·3	13·2	17·0	23·0	32·5	57·0	64·5

Magnesium chloride.

No detectable change in K_{D} over the range of 0·6—5·2M.

Magnesium bromide.

M	0·17	0·50	0·88	1·75	2·57	3·05	3·53	4·0
K_{D}	2·28	1·30	v. low		0·3 *	1·2 *	2·0 *	~2·1 *

Magnesium iodide.

M	0·13	0·26	0·38	0·64	0·82	1·00	1·11	1·28
K_{D}	29·2	5·02	4·84	4·34	4·97	6·10	12·6	18·8
M	1·55	1·92	2·28	2·65	2·80	3·01		
K_{D}	28·5	31·4	26·2	20·6	21·1	11·4		

When most of the mercury was adsorbed on the resin phase ([LiCl] $\geqslant$ 7M) its initial concentration in the aqueous phase was increased.

Time to Attain Equilibrium.—Samples were equilibrated for 16 hr. and experiments with 2·83M-sodium iodide showed that equilibrium was reached in a quarter of that time. With the most concentrated solutions of halides the full time was needed.

Determination of the Density Correction.—The counting rate, N, was determined for a series of solutions of alkali (or alkaline-earth) halides whose density, d, had been determined at 18—21° and which all contained the same quantity of active indium. On the assumption that a plot of N against d could be represented by the equation $N = N_0[1 - p(d - 1)]$, where N_0 is the counting rate in pure water of density 1·000 and p is a constant for each halide used, the values of p were determined by a least-squares treatment and are given in Table 1.

Typical measurements of K_D for various molarities, M (calculated from the measured densities with the aid of data in International Critical Tables), are reported in Tables 2 to 5. Some of the results are plotted in Fig. 2.

TABLE 3.

Adsorption of zinc-65 from lithium halides.

Lithium chloride.

M	0·44	1·09	3·28	6·76	9·82
K_D	250	31	1·25 *	0·58 *	0·64 *

Lithium bromide.

M	0·46	1·14	3·41	5·18 to 8·71	
K_D	157	17·4	0·9 *	0·6 *	

Lithium iodide.

M	0·36	0·90	2·71	4·38	5·22
K_D	242	37·4	2·3 *	1·7 *	0·5 *

TABLE 4.

Adsorption of cadmium-115^m from lithium halides.

Lithium chloride.

M	0·07	0·50	1·09	3·28	6·76	9·82
K_D	591	201	2·8 *	1·0 *	1·0 *	1·0 *

Lithium bromide.

M	0·09	1·14	2·29	3·41	5·51	6·94	8·71
K_D	271	1·4 *	1·4 *	1·0 *	1·1 *	1·2 *	1·2 *

Lithium iodide.

M	0·06	0·15	0·45	0·90	1·80	2·71	2·85	3·0
K_D	529	5·60	2·1 *	1·3 *	1·00 *	0·88 *	0·86 *	0·93 *
M	3·14	3·75	4·78	5·82				
K_D	0·98 *	1·18 *	1·14 *	1·04 *				

TABLE 5.

Adsorption of mercury(II) from lithium chloride.

M	0·012	0·06	0·24	0·90	1·50	2·40	3·68	4·15
K_D	very low					0·12	0·77	0·95
M	5·33	6·40	7·08	7·81	8·44			
K_D	1·03	1·27	1·39	1·57 [a]	1·60 [a]			

[a] The initial concentration of mercury was increased 2·5 times for these experiments.

TABLE 6.

The effect of loading on the adsorption of indium from 1·59M-potassium iodide.

Loading (g. indium per g. dry resin)	$5·85 \times 10^{-6}$	$2·34 \times 10^{-5}$	$5·85 \times 10^{-5}$	$1·17 \times 10^{-4}$	$2·3 \times 10^{-4}$	$4·68 \times 10^{-4}$
K_D	16·7	17·8	17·2	16·4	16·5	15·9
Loading	$1·17 \times 10^{-3}$	$2·50 \times 10^{-3}$	$1·01 \times 10^{-2}$	$2·50 \times 10^{-2}$	$5·01 \times 10^{-2}$	$1·01 \times 10^{-1}$
K_D	15·7	14·1	13·8	8·25	3·76	1·83

DISCUSSION

The present, incomplete, study of metal halide systems has not produced results suitable for a quantitative theory of anomalous adsorption of anionic species on to cation-exchange resins from solutions of high ionic strength. Kraus's report [2] that indium(III) is not adsorbed significantly from hydrochloric acid or lithium chloride is confirmed by the present work. On the other hand, there is appreciable adsorption of complex indium bromide anions starting from ~1·5M from either lithium or magnesium bromides and ~2·5M from sodium bromide. With the iodides the effect is very clear-cut and the minimum in the plot of log K_D against halide-ion concentration occurs sooner at 1·0—1·5M for iodides of lithium, potassium, and magnesium; here again the use of the sodium salt gives a later and broader minimum. It must be emphasised that, unlike the behaviour of gold, iron, and gallium (Fig. 1), the values of K_D for indium in concentrated halide solutions never exceeded, and indeed failed to regain, the value for pure water.

Now, the stabilities of the halides of zinc, cadmium, and mercury are high and they increase in the order $Cl < Br < I$. In consequence their adsorption on an anion-exchange resin is high at quite low halide-ion concentrations and decreases rapidly as the anionic complexes are displaced with increasing halide-ion concentration.[5] That zinc shows no tendency, and cadmium and mercury only a slight tendency to invade a cation exchange resin even from very concentrated solutions of halides, confirms Kraus's observation:[2] " it appears that strong adsorption of negative species by cation exchangers is confined to those complexes which are extremely strongly adsorbed by anion exchangers from concentrated chloride solutions."

The anomalous adsorption with indium halides cannot depend primarily on the stability of the metal halide complexes, which decrease in the order $Cl > Br > I$, but more closely follows the order in which they are extractable from halogen acids by donor solvents ($HCl < HBr < HI$).[3] This reflects the increasing size of the complex anions, InX_4^- and their tendency to form ion-pairs. On this basis iron(III) and gallium, which extract less well from hydrobromic than from hydrochloric acid, would be expected to show the anomalous behaviour to a lesser extent than that shown in Fig. 1 if lithium chloride were replaced by lithium bromide; on the other hand, the behaviour of gold should be much the same, whilst that of thallium(III) ($K_D = 42$ for 10M-lithium chloride) might increase. It is noteworthy that zinc, cadmium, and mercury cannot be extracted from halogen acids. If strong adsorbability on an anion-exchange resin at high halide-ion concentration is indeed the best guide to prediction of abnormal behaviour on cation-exchange resins, zirconium, hafnium, vanadium(V), protactinium, molybdenum(VI), uranium-(IV) and -(VI), and possibly germanium(IV) and tellurium(IV), might exhibit the anomaly at high chloride-ion concentrations. Of these ions molybdenum(VI) can also be extracted effectively from hydrochloric acid into ether.

By using a cation-exchange resin we have separated indium from concentrated solutions of zinc, cadmium, and mercury (1—2M) after adding lithium chloride to bring the halide-ion concentration within the range 2·5—4·5M. The indium was retained quantitatively on the column. However, the value of K_D decreases rather rapidly with loading when $[In^{3+}] > 10^{-4}$M (see Table 6) so that breakthrough occurs after only a few column volumes have been added, unless the concentration of indium is quite low. However the method is good for the separation of active indium from an irradiated cadmium target. Other analytical possibilities for rather specific separations may well be discovered when the invasion of cation resins by anionic species has been investigated from concentrated solutions of thiocyanates, carbonates, and halides other than chloride.

THE INORGANIC CHEMISTRY LABORATORY,
THE UNIVERSITY OF LEEDS.

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[5] Irving, *Chem. Soc. Special Publ.* No. 13, 1959, 13.