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Ion-Exchange Studies of the Lanthanides and Actinides in Concentrated Mineral Acids

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The absorption of trivalent lanthanide and actinide ions by Dowex-50 ion-exchange resin has been studied in concentrated solutions of perchloric, hydrochloric, hydrobromic, and hydriodic acids. An explanation of the very strong absorption in 12 *M* $HClO_4$ is offered in terms of extraction of metal ion–perchlorate ion-pairs into the resin phase. The order of complexing, $Cl > Br > I > ClO_4$, agreed with the normal order for covalent complexes.

The study of metal complexes which are formed in concentrated electrolyte solutions is hampered by insufficient knowledge of the physical chemistry of such solutions. Since ion-exchange resins provide a medium of greater specificity, they are valuable as a means of investigating the comparative behavior of a series of metal ions in concentrated solutions. Differences in the ion-exchange elution behavior of the metal ions may be interpretable in appropriate cases in terms of their relative complexation. For the actinide elements ion-exchange studies have the added advantage of requiring only tracer levels of radioisotopes.

Previous studies of the behavior of trivalent lanthanide and actinide ions in hydrochloric acid[2] and ammonium thiocyanate[3] solutions by ion-exchange resins have provided evidence for stronger complex formation by the actinide ions than by the lanthanide ions. The necessity for caution in attempting to suggest explanations for the behavior in these poorly understood and complicated systems has been demonstrated by a study of the elution pattern of trivalent plutonium, americium, curium, berkelium, californium, and einsteinium from different batches of Dowex-50.[4] We have investigated the elution behavior from Dowex-50 with perchloric, hydrochloric, hydrobromic, and hydriodic acids of lanthanide, actinide, alkali, and alkaline earth ions to provide the basis for a better understanding of these systems.

Experimental

Dowex-50 4% DVB cation-exchange resin was supplied through the courtesy of the Dow Chemical Company. The original 200–400 mesh stock was graded according to particle size by settling in distilled water and the fraction with a settling rate of 0.5–1.0 cm. per min. (approximately 18–25 μ) was used in these experiments. Prior to use the resin was freed of metal impurities by washing with HCl, NaOH, and again HCl, with distilled water washes between each and after the final HCl wash until absence of chloride ion was ascertained by an $AgNO_3$ solution test. The resin was air-dried to a state of approximately 60% relative humidity and stored in that condition over saturated $NaNO_3$ solution. The resin weights used in the calculations were of the resin in this state.

The reagents were of analytical grade with the exception of hydriodic acid and were used without further purification. Concentrated perchloric (72%), hydrobromic (47%), hydrochloric (49%), and hydriodic (48%) acids were purchased from the J. T. Baker Chemical Company and were diluted to the desired concentrations with distilled water. HBr solutions of 12 *M* concentration were prepared by saturating the commercial reagent with hydrogen bromide gas. It was necessary to remove the phosphoric acid from the commercial hydriodic acid prior to use. This was accomplished by passage of the solution through a Dowex-1 anion-exchange resin column in the iodide form. The column was operated in the dark in a nitrogen atmosphere. The molarities of all solutions were determined immediately prior to use by titration with carbonate-free sodium hydroxide solution which was standardized with potassium acid phthalate primary standard.

The Am^{243} was supplied through the generosity of Drs. Stanley Thompson and Richard Hoff of the Lawrence Radiation Laboratory. The Tb^{160}, Ho^{166}, and Tm^{170} were prepared by neutron irradiation in the Oak Ridge Low Intensity Test Reactor of sub-milligram quantities of the pure metal oxides. The other radioisotope tracers were obtained from the Isotopes Division of Oak Ridge National Laboratory. All the tracer solutions were of sufficiently high specific activity that it was unnecessary to make any corrections for the percentage of the exchange capacity of the resin converted from the hydrogen form.

The Am^{243} was counted in a windowless 2π proportional counter set on the voltage plateau for alpha particles. The remainder of the radioisotopes were counted on either G.M. end-window or NaI scintillation counters as well as

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[1] Based on the Ph.D. dissertation of R. H. D., "Ion Exchange Reactions in Concentrated Strong Acid Solutions," 1960.

[2] R. M. Diamond, K. Street, Jr., and G. T. Seaborg, *J. Am. Chem. Soc.*, **76**, 1461 (1954).

[3] J. P. Surls and G. R. Choppin, *J. Inorg. & Nuclear Chem.*, **4**, 62 (1957).

[4] G. R. Choppin and A. Chetham-Strode, *ibid.*, **15**, 377 (1960).

the 2π proportional counter set on the beta plateau. Whenever it was possible to do so, overlapping elution peaks were resolved by counting with appropriate aluminum absorbers.

Column Elutions.—For the experiments using elution techniques, the resin was packed into Pyrex glass columns whose bed dimensions ranged from 1 mm. i.d. by 5 cm. length to 3 mm. i.d. by 16 cm. length. The elution drop volumes were calibrated for each column by catching a number of drops in a weighing bottle and weighing them. The density of each solution was used to calculate the single drop volume (10 to 25 μl.). The resin bed volumes were determined by calibrating the glass column with mercury. The techniques for preparing the column, loading the tracers, and performing the elution have been described previously.[4,5]

Equilibrium Experiments.—These were conducted in the manner described in earlier publications.[4,6]

Results

TABLE I

EQUILIBRIUM DISTRIBUTION FOR Eu(III) IN DOWEX-50 AND $HClO_4$

$HClO_4$ (M)	W_R (mg.)	C_T	C_S	K_d
0.9730	53.8	9,290	1660	423
0.9730	25.2	9,290	2840	453
1.023	25.3	7,460	2460	402
1.023	21.7	7,460	2820	379
3.134	68.5	12,440	8360	35.6
3.134	68.5	12,440	8140	38.5
3.959	66.5	6,440	4860	26.5
3.959	69.9	6,440	4620	28.2
5.550	70.0	13,490	7890	50.6
5.550	54.4	13,490	8920	47.0
6.906	67.1	13,350	5140	119
6.906	63.4	13,350	5500	112
9.046	20.6	12,920	680	4.45×10^3
9.046	11.9	12,920	1070	4.58×10^3
8.879	10.2	16,760	1790	4.10×10^3
8.879	13.8	16,760	1500	3.69×10^3
11.78	5.23	15,650	64	2.3×10^5
11.78	5.68	15,650	65	2.1×10^5
12.05	0.154	13,780	2140	2.80×10^5
12.05	0.177	13,780	1010	2.59×10^5

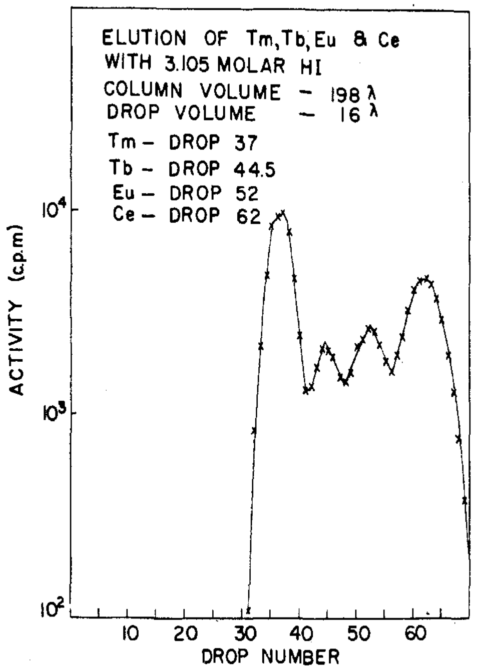

Fig. 1.—Typical elution curve for the lanthanide elements.

The data from a typical equilibrium experiment are presented in Table I. The distribution constant, K_d, was calculated by the expression

$$K_d = \frac{C_T - C_S}{C_S} \cdot \frac{V_S}{W_R}$$

where C_T = counts per minute (c.p.m.) of tracer in a 500-μl. aliquot of the solution before equilibration; C_S = c.p.m. in a 500-μl. aliquot of the solution after equilibration; V_S = volume of solution = 5.0 ml.; and W_R = weight of resin sample (g.). Triplicate samples of each solution were counted to 0.5% probable error and their average value taken for C_T and C_S. The average value of the duplicate K_d values for each acid molarity were used in the curves for the graphs. The complete tabulation of the data is available elsewhere.[1] In Fig. 1 the results of a typical elution are presented. From the column elution data, it is possible to calculate K_d by the equation

$$K_d = \frac{V_m - V_i}{W_R}$$

where V_m = volume of solution (in ml.) to the elution peak maximum for the ion; V_i = volume of solution (in ml.) retained in the interstitial volume of the resin bed; and W_R = weight of resin (in g.) in the column. Figures 2, 3, 4, and 5 summarize the combined results of the equilibrium and elution experiments.

Discussion

Since the effects observed in this research are the result of the interactions in a two phase system, interpretation of these observations depends on the ability to separate the effects of each phase. It would be trite to recount the complexity of the physical chemistry of concentrated aqueous solution of electrolytes. The state of the resin phase is at least as complicated. In contact with concentrated electrolyte solutions, the resin phase experiences a significant invasion of non-exchange electrolyte. Thus, for Dowex-50 in 12 M $HClO_4$

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(5) S. G. Thompson, B. G. Harvey, G. R. Choppin, and G. T. Seaborg, *J. Am. Chem. Soc.*, **76**, 6229 (1954).

(6) J. P. Surls and G. R. Choppin, *ibid.*, **79**, 855 (1957).

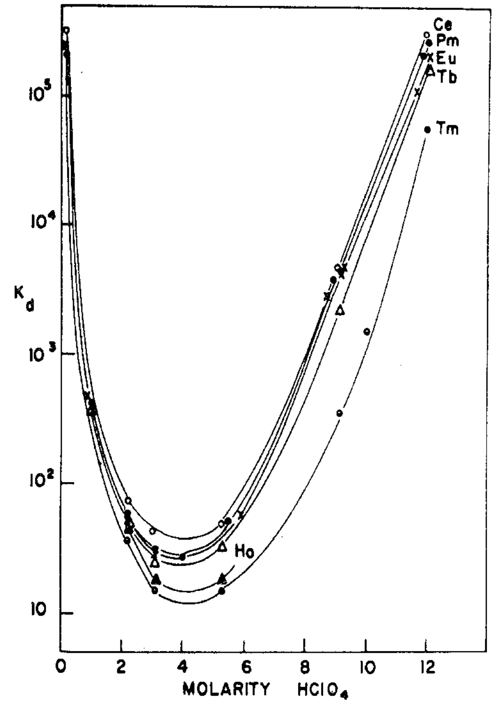

Fig. 2.—K_d of Ce, Pm, Eu, Tb, Ho, and Tm as a function of the molarity of perchloric acid.

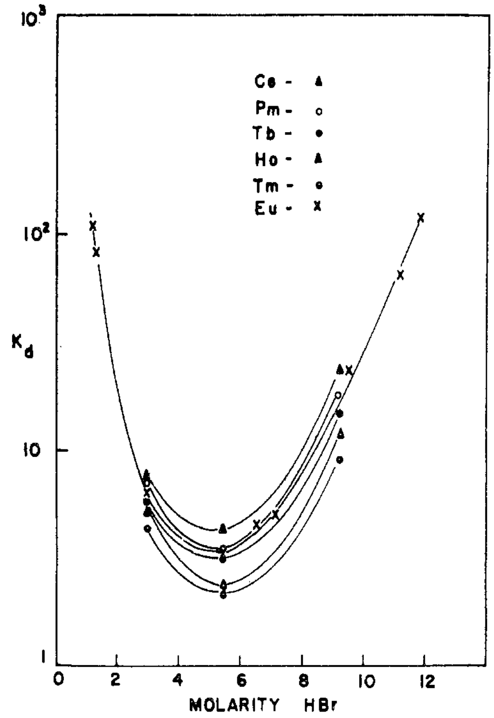

Fig. 3.—K_d of Ce, Pm, Eu, Tb, Ho, and Tm as a function of the molarity of hydrobromic acid.

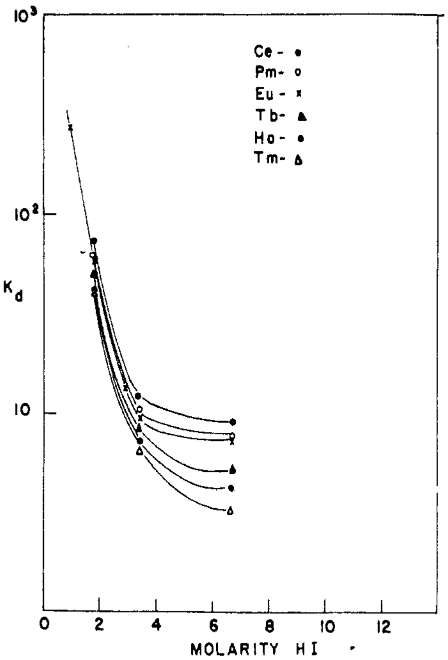

Fig. 4.—K_d of Ce, Pm, Eu, Ho, Tb, and Tm as a function of the molarity of hydriodic acid.

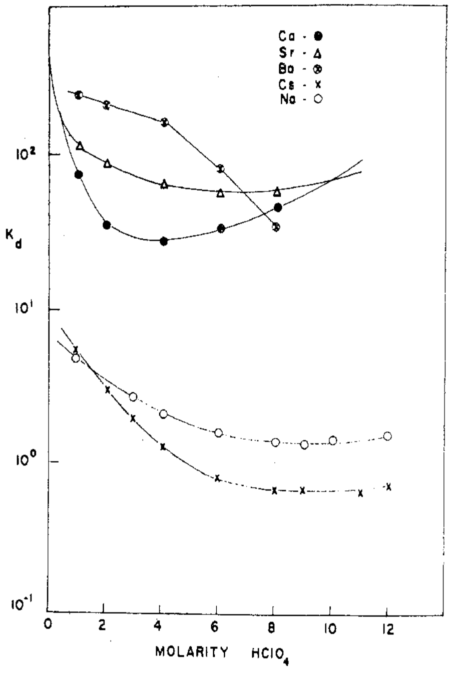

Fig. 5.—K_d of Na, Cs, Ca, Sr, and Ba as a function of the molarity of perchloric acid.

solution, there are in the resin phase approximately equal numbers of equivalents of the hydrogen resinate and of $HClO_4$. Accompanying this invasion by electrolyte is a decrease in the water content of the resin phase—from 18 moles of water per resinate equivalent in pure water to 2.3 moles of water per resinate equivalent in 12 *M* $HClO_4$.[1] The extensive organic network of the resin also results in a low effective dielectric constant in the resin phase. As a result of these three factors—high electrolyte concentration, dehydration, and low dielectric constant—the resin phase is expected to be favorable to complex and/or ion-pair formation. It has been suggested by Horne[7] (following a suggestion by R. M. Diamond) that ion-pair formation is more favored in the resin phase than in the solution phase. This results in resin phase absorption by a mechanism very similar to that of solvent extraction.

For the alkali metal ions in Dowex-50–hydrochloric acid systems, Diamond[8] has offered an explanation for the reversal of the Na^+ and Cs^+ curves in terms of dehydration of the metal ions. Such dehydration would reverse the order of their effective radii. We observed reversals of the Na^+ and Cs^+ elution sequence in $HClO_4$, HCl, and HBr with the reversals occurring at 1–2 *M* $HClO_4$, 5–6 *M* HBr, and 6–7 *M* HCl. In Fig. 6 the separation factors ($\alpha = K_{d\text{Cs}}/K_{d\text{Na}}$) are plotted as a function of the activity of the water, A_{H_2O}, in the acid solutions. Dehydration in the aqueous phase would be expected to be related directly to the aqueous activity; thus the occurrence of $\alpha = 1$ at different values of A_{H_2O} is taken to indicate that solution phase dehydration is not the important factor. Since perchloric acid has a greater dehydrating effect on the resin phase than hydrochloric acid,[9] the simplest interpretation of the curves in Fig. 6 is that the alkali ions are dehydrated in the resin phase at lower aqueous phase $HClO_4$ concentrations than for HCl or HBr. The similarity of the curves for the 3 acids, other than the concentration at which reversal occurs, may indicate that ion-pair formation is not a dominating factor, since differences would be expected for ClO_4^-, Br^-, and Cl^-.

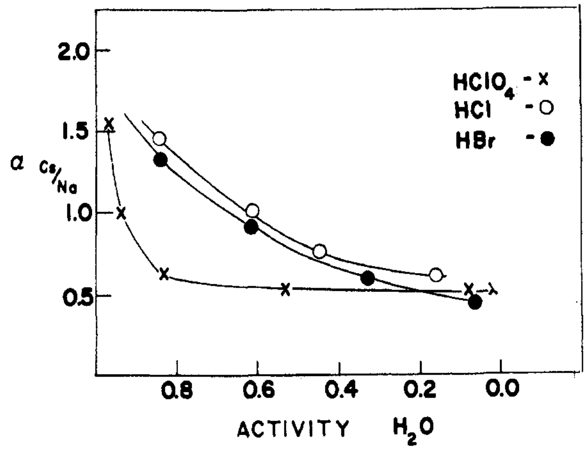

Fig. 6.—Separation factor of Cs with respect to Na as a function of aqueous activity in perchloric, hydrochloric, and hydrobromic acids.

The reversals in the curves for Ca^{2+}, Sr^{2+}, and Ba^{2+} may be interpreted satisfactorily in the same manner as in the previous paragraph. Of course, detailed interpretation of these curves would involve a great many factors which we have ignored and emphasizing the reversal of the elution sequence provides a qualitative estimate of the importance of only one effect, that of ionic dehydration.

In Fig. 2, 3, and 4 no reversals of the elution sequence for the lanthanide ions are observed as the acid concentrations increase. The absence of reversal in these curves could be interpreted to mean that the high charge-to-volume ratio of these trivalent ions is sufficient to retain a significant fraction of the hydration sphere even in the resin phase. However, it also is possible to account for the absence of reversal by assuming the formation of complexes of the lanthanides since the K_d order Ce > Pm > -- >Tm is exactly that expected if complexes are formed.

It has been suggested[10] that Ce(III) and perchlorate ion in the 1–2 *M* concentration region do form a very weak complex of the outer type in which hydrogen bonds are formed between two or more oxygen atoms of the perchlorate ligand and the hydrogen atoms of the water molecules coördinated with the Ce(III) cation. Later investigations of absorption[11] and Raman[12] spectra have indicated that the claim for such a complex at that concentration was incorrect due to erroneous interpretations of spectral shifts whose origins lie in solvent medium effects rather than complex formation. In agreement with these latter two reports are the observations that the character of the absorption bands of Am(III)[13] and Cm(III)[14] are not significantly changed as the perchloric acid concentration is increased from 0.1 to 6.0 *M*. The evidence seems convincing that perchlorate complexes are negligible or non-existent for the trivalent lanthanide and actinide ions in perchloric acid solutions up to 6 *M* concentration, while in solutions of higher acid concentration there is fair evidence from the spectral effects of some type of

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(7) R. A. Horne, *J. Phys. Chem.*, **61**, 1651 (1957).

(8) R. M. Diamond, *J. Am. Chem. Soc.*, **77**, 2978 (1956).

(9) G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

(10) L. J. Heidt and J. Berestecki, *J. Am. Chem. Soc.*, **77**, 2049 (1955).

(11) P. Krumholz, *J. Phys. Chem.*, **63**, 1313 (1959).

(12) M. M. Jones, E. A. Jones, D. F. Harmon, and R. T. Semmes, *J. Am. Chem. Soc.*, **83**, 2038 (1961).

(13) G. N. Yakolev and V. N. Kosyakov, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, **7**, 363 (1956).

(14) W. T. Carnall and P. R. Fields, *J. Am. Chem. Soc.*, **81**, 4445 (1959).

weak interaction between the metal cations and the perchlorate anions. In the resin phase, such interactions might be expected much sooner due to the reasons discussed previously.

The ion-pair formation–extraction process of Diamond and Horne would seem to account qualitatively for the curves in perchloric acid. The lanthanide ions would have a much stronger tendency to ion-pair formation and to retention of hydration than the alkali ions. If the hydrated ions formed ion-pairs in the resin phase, providing thereby the driving force for extraction, the order of extraction would be Ce > Pm > -- > Tm (since the Ce(III) hydrated ion is smaller than the Tm(III) hydrated ion resulting in a more stable Ce-$(H_2O)_x{}^{+3}$-$ClO_4{}^-$ ion-pair). The increase in K_d of 4 orders of magnitude between 4 and 12 *M* $HClO_4$ is more readily understandable by this extraction process than by simple Donnan invasion by nonexchange electrolyte. If similar ion-pair formation of the hydrated lanthanide ions occurs in the solution phase, it would tend to reverse the elution sequence and lower the K_d. The lack of reversal and large increase in K_d is indicative of the greater importance of ion-pair formation in the resin phase. Ion-pair formation between the metal ions and the resin sulfonate groups also is a possibility. This should occur to approximately the same extent in all the acid systems. The curves in Fig. 7 are the basis for considering ion-pairing with perchlorate to be more important than with the sulfonate groups.

Figure 7 shows the comparison of the ion-exchange behavior of the trivalent actinides and lanthanides in $HClO_4$, HCl, HBr, and HI. In solutions of lower concentrations the behavior is similar for all four systems, which is in agreement with the assumption[2] that the predominant factor in this region (below 2 *M*) is the exchange between hydrogen ions and trivalent ions for these four strong acids. In the more concentrated solutions, the pattern is more complex. However, the similarity in K_d for Eu(III) and Am(III) in strong perchloric acid is in agreement with the suggestion in the previous paragraph that purely electrostatic ion-pair formation is involved since the radii for Eu(III) and Am(III) are very similar.

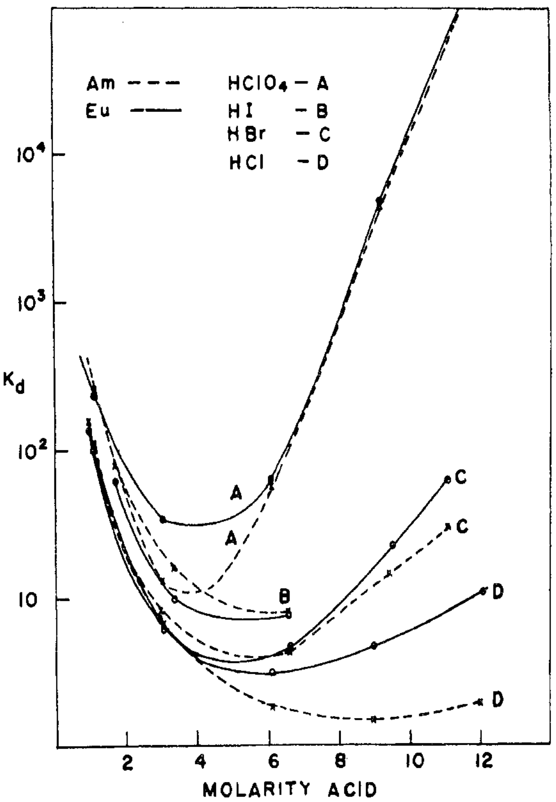

Fig. 7.—K_d of Eu and Am as a function of molarity of perchloric, hydriodic, hydrobromic, and hydrochloric acids.

Studies with cation resin[2] and anion resin[15] have been interpreted to indicate the formation of chloro complexes with considerable covalent character for these elements. The order of complexing expected in the aqueous phase is Cl > Br > I > ClO_4, which would agree with the observed K_d order in Fig. 7. The order of complex strength for the ions would be Tm > Ho > Tb >--> Ce, which agrees with the K_d order in Fig. 3 and 4. However, possible resin phase effects must be considered before it can be concluded that the correlation between K_d order and complex order is significant.

Recently, evidence has been offered that an ion-exchange resin may function as a differentiating medium to imbibed acids.[16] The absorption of HCl would result in a relatively low concentration of chloride ions in the resin phase due to the association of HCl. This would be true also but to an increasingly lesser extent for HBr, HI, and $HClO_4$. If this is correct, then complex formation in the resin phase would be less important than in the aqueous phase. In addition, the extraction process would decrease in importance in the order ClO_4 > I > Br > Cl, which would combine with the order of solution phase complex formation to give the K_d order of Fig. 7. Therefore, we conclude that the data in Figs. 3, 4, and 7 reflect the

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(15) E. K. Hulet, R. G. Gutmacher, and M. S. Coops, *J. Inorg. & Nuclear Chem.*, **17**, 350 (1961).

(16) B. Chu and R. M. Diamond, *J. Phys. Chem.*, **63**, 2021 (1959).

order of solution phase complex formation for the lanthanide ions.

In Fig. 7 it is seen that the difference in K_d between Am(III) and Eu(III) increases from $HClO_4$ to HBr to HCl, which would seem to indicate that Am(III) forms stronger complexes with chloride and bromide ions than does Eu(III). The data on the $HClO_4$, HI, and HBr systems are not in disagreement nor do they add any substantial weight to the theory offered from an earlier study[2] with HCl that 5f orbitals can be used by the actinide ions to form more stable halide complexes.

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Substituted Metal Carbonyls with Ligands Having Sulfur as the Donor Atom[1a]

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The preparation and properties of the first substituted metal carbonyls containing ligands which coördinate through bicovalent sulfur are reported. By direct reaction of the ligands, L, with cycloheptatrienemolybdenum tricarbonyl, the five compounds, $MoL_3(CO)_3$, with L representing $(CH_3)_2S$, $(C_2H_5)_2S$, $(CH_2)_4S$, $(NH_2)_2CS$, and CH_3CSNH_2, have been prepared. All are yellow crystalline solids ranging in stability in air from very unstable to moderately stable. The frequencies of the C–O stretching modes show that the dialkyl sulfides have a substantial tendency to function as pi acceptors though not so much as analogous phosphines and arsines, while the two C═S compounds have only a small (though definite) tendency to do so.

Introduction

It perhaps is surprising that although a great deal of effort has been devoted to the synthesis and spectroscopic study of metal carbonyl molecules in which one or several of the carbon monoxide groups are replaced by other ligands, especially amines, phosphines, and arsines, until very recently[1a] there was no report of the preparation of compounds in which the substituents have bicovalent sulfur as the donor atom.

This paper reports in detail the preparation and properties of five such compounds, all of the type $MoL_3(CO)_3$ in which the ligands, L, are $(CH_3)_2S$, $(C_2H_5)_2S$, $(CH_2)_4S$, $(H_2N)_2CS$, and CH_3CSNH_2. It was originally our intention, on finding that the compounds reported here were stable enough to encourage further study, to extend the work to similar substituted carbonyls, especially those containing chelate ligands where stability should be even greater. Upon the appearance of our preliminary note, however, we were informed by Professor G. Wilkinson that he and Miss Christina Mannerskantz already had succeeded in preparing several compounds with chelate ligands, and we therefore have concluded our own efforts in this area with the work reported here.

Experimental

For the preparation of the new compounds, the starting material was cycloheptatrienemolybdenum tricarbonyl which we prepared according to the procedure of Abel, *et al.*,[2] but using dry *n*-butyl ether as a solvent. In our experience the employment of this ether reduces the reaction time and increases the product yield.

Tricarbonyltris(tetramethylene sulfide)molybdenum.—One g. (0.012 mole) of tetramethylene sulfide was added, under nitrogen, to a solution of cycloheptatrienemolybdenumtricarbonyl (0.8 g. = 0.003 mole) in benzene (5 ml.). After a few minutes the red color of the cycloheptatriene complex had completely disappeared. The benzene then was distilled off in vacuum. The dry residue, dissolved in methylene chloride, was filtered under nitrogen, and precipitated by addition of petroleum ether. The product, pale yellow crystals, was filtered under nitrogen, washed with petroleum ether, and dried in high vacuum. It was stable in nitrogen atmosphere but in the presence of air it darkened rapidly owing to decomposition. *Anal.* Calcd. for $MoC_{15}H_{24}S_3O_3$: C, 40.53; H, 5.44; Mo, 21.59. Found: C, 39.94; H, 5.12; Mo, 21.0.

Tricarbonyltris(dimethyl sulfide)molybdenum.—This compound was prepared in much the same way as was the analogous tetramethylene sulfide derivative from dimethyl sulfide (0.75 g. = 0.012 mole) and cycloheptatrienemolybdenumtricarbonyl (0.8 g. = 0.003 mole) and

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(1) (a) Part of this work has been summarized earlier in a preliminary Communication, *Chem. & Ind.* (London), 1219 (1960). (b) Alfred P. Sloan Foundation Fellow. (c) On leave from Istituto di Chimica Generale dell' Università di Milano, 1959–60.

(2) E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).