first or third powers. Thus it would appear that the disproportionation of Pu(IV) is essentially the reverse of the disproportionation of Pu(V) as proposed by Connick.[5] The results of the rate constant measurements as a function of hydrogen ion concentration are given in Table II. In column 4 of Table II are found the products of the specific rate constants and the cubes of the hydrogen ion concentration. The good agreement of this product over a fivefold change in acidity is evidence for the inverse third power hydrogen ion concentration dependence of the specific rate constants for the disproportionation reaction.

The most probable mechanism of disproportionation of Pu(IV) in acid perchlorate solutions is

$$\mathrm{Pu^{++++} + H_2O \rightleftarrows PuOH^{+++} + H^+}$$

$$\mathrm{PuOH^{+++} + H_2O \rightleftarrows Pu(OH)_2^{++} + H^+}$$

$$\mathrm{PuOH^{+++} + Pu(OH)_2^{++} \longrightarrow}$$
$$\mathrm{Pu^{+++} + PuO_2^{+} + H_2O + H^+} \quad \text{(slow step)}$$

$$\mathrm{PuO_2^{+} + Pu^{++++} \rightleftarrows Pu^{+++} + PuO_2^{++}}$$

Since the equilibrium quotient has been shown to be dependent upon the fourth power of the hydrogen ion concentration, and the rate of the forward reaction dependent upon the inverse third power, the reproportionation reaction should exhibit a first power dependence upon the acidity.

In the two experiments at unit ionic strength and at comparable hydrogen ion concentrations, namely, 0.5 and 1.0 *M* perchloric acid, the rate constants found in the present work are in excellent agreement with the results obtained by Connick and McVey's correction of Kasha's data.

Acknowledgments.—The author wishes to express his appreciation to Drs. J. F. Lemons and T. W. Newton of the Los Alamos Scientific Laboratory for helpful discussions pertaining to this research. Private communications have also been exchanged with Dr. Robert E. Connick concerning portions of this paper.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Absorption of Inorganic Salts from Organic Solvents onto Anion Exchange Resins[1]

BY LEONARD I. KATZIN AND ELIZABETH GEBERT[2]

RECEIVED SEPTEMBER 25, 1952

The solutes hydrochloric acid, lithium chloride, lithium nitrate, cobaltous nitrate, cupric chloride and nickelous nitrate have been found to absorb onto anion exchange resins (Dowex A-1) from their solutions in acetone. The absorption is characterized by the molecule as a whole disappearing from the liquid phase, rather than by ions being exchanged. At least the following factors are involved: (a) nature of the anion associated with the cation in solution; (b) nature of the anion associated with the resin; (c) the water content of the starting resin or of the total system. Some discussion is presented of possible mechanisms.

The concentration of inorganic ions from aqueous solutions onto ion exchange resins is a well-known phenomenon. The movement of and separation of inorganic ions in paper chromatography, with the aid of an organic solvent, is also known.[3-5] The only literature on the absorption of salts from organic solutions by ion exchange resins of which the authors are aware was called to their attention during the course of their experimental work, and consists of patents covering the absorption of copper (presumably in organic combination) from petroleum hydrocarbons.[6,7]

In the work to be described, electrolytes such as hydrochloric acid, lithium chloride, lithium nitrate, cobaltous chloride, cobaltous nitrate, cupric chloride and nickelous nitrate have been absorbed from organic solution (principally acetone solution) onto anion exchange resins (principally Dowex A-1). The characteristic feature of the absorption is that one is dealing not with anion exchange, such as characterizes the behavior in water medium, but with removal of the molecule as a whole from the solution onto the resin. This is graphically illustrated in the case of the colored salts by the decrease in color of the solution and the progressive coloration of the solid resin with which it is in contact.

Procedure

Commercial Dowex A-1 resin, chloride form, 250–500 mesh, was treated with aqueous HCl, NaCl or $NaNO_3$, as appropriate, to give a stock resin. The resulting material was washed exhaustively with water and then dried in air to the degree desired. The water content was determined by titration with Karl Fischer reagent with a standard procedure.[8] The chloride content of the resins was determined by bomb ignition, and in the case of the chloride resin, amounts to about 3.1 millimoles per gram of resin.

Stock solutions of cupric chloride and nickelous nitrate in chemically pure acetone were made by dissolving weighed portions of the hydrated salts. The concentrations of lithium salt solutions were determined by analysis of the solution with the Beckman flame photometer. Solutions of the cobaltous salts were analyzed for cobalt by standard electrodeposition procedures. We are indebted to Mr. Ralph Bane for chloride and lithium analyses, and to Mr. John Ferraro for water and cobalt analyses.

Two milliliters of a salt solution was equilibrated with 0.2 g. of the resin in a glass-stoppered tube for 24–72 hours. In the case of the quantitative studies with the cobaltous

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(1) Presented at Cleveland Meeting of American Chemical Society, April 8–10, 1951.

(2) We are indebted to James C. Sullivan for certain preliminary experiments.

(3) F. H. Burstall, G. R. Davies, R. P. Linstead and R. A. Wells, *Nature*, **163**, 64 (1949).

(4) A. Lacourt, G. Sommereyns, E. de Geyndt, J. Baruh and J. Gillard, *Mikrochem. ver. Mikrochim. Acta*, **34**, 215 (1949).

(5) W. J. Frierson and M. J. Ammons, *J. Chem. Education*, **27**, 37 (1950).

(6) G. P. Ham and R. B. Barnes, Canadian Patent 449,924 (1948).

(7) R. J. Myers, U. S. Patent 2,341,329 (1944).

(8) L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

salts, tracer Co^{60} was incorporated into the stocks, so that the residual concentration of cobalt could be followed even at low cobalt concentrations. In the case of other solutes, *p*H, spectrophotometric and semi-quantitative observations were made appropriate to the particular case.

Results

Cupric chloride was highly absorbed, coloring the resin an olive-yellow. Nickelous nitrate on the nitrate form of the resin colored it green, leaving the supernatant practically colorless. Tests of the water-diluted supernatants with a *p*H meter showed that decolorization of the solution had not been by exchange for hydrogen ion. Tests with hydrochloric acid solution, made by diluting concentrated HCl with acetone, to concentrations of 0.1 *M* and below (to minimize water concentration) showed that HCl itself absorbed on the chloride resin. The *p*H measurements were made by diluting the original acetone solutions 20-fold with distilled water, and measuring the resulting solution with a Beckman *p*H meter. Thus, in representative experiments, an acid solution which gave a *p*H of 2.12 before equilibration with the resin, gave 3.19 afterwards, and one which started at 2.76 gave a *p*H reading of 4.23 at the end of the experiment. Stock acetone, without added HCl, similarly diluted, gave *p*H 5.69 before equilibration, and *p*H 4.74 at the end of the experiment. The particular resin used in these experiments had been prepared by equilibrating commercial chloride resin with 1 *N* HCl for 36 hr., and washing the resin to constant acidity of wash-water (at about *p*H 4.9).

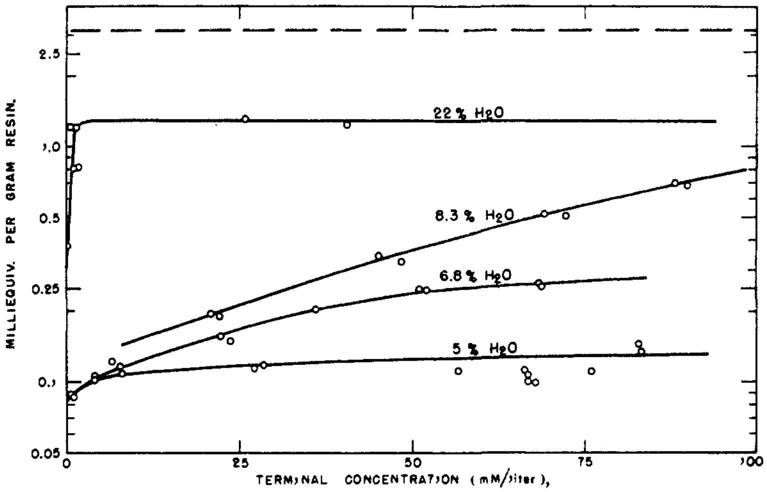

Fig. 1.—Distribution of $CoCl_2$ between acetone solution and Dowex A-1 (chloride form) of varying water contents (2 ml. of solution equilibrated with 0.2 g. of resin).

Lithium chloride, originally 0.2 *M* in the acetone solution, was absorbed on the chloride form of the resin so that the supernatant diluted with water no longer gave a chloride test with silver nitrate. In a more definitive experiment, with analyses for lithium with the flame photometer, 8 ml. of 0.0056 *M* LiCl solution, after equilibration with 0.6 g. of resin for 3 days, showed a reduction in lithium content to less than 2.5% of the starting concentration (limit set by background of the analytical method). Similarly, 8 ml. of 0.0084 *M* $LiNO_3$ solution, equilibrated against 0.6 g. of nitrate resin (see below) showed a terminal concentration of 0.00060 *M*, about 7% of the initial concentration.

Quantitative tests carried out with the cobaltous salts showed that the pattern of absorption of salt by the resin consisted of an essentially quantitative absorption in the low-concentration region, followed by a region in which the concentration of the absorbed salt on the resin changes very slowly, and usually by less than a factor of 2, as the residual concentration in the liquid phase increases. The concentration of the salt on the resin in the region of the transition from quantitative absorption to approximate saturation, and the apparent saturation level of the resin, have been followed to identify the variables involved.

The absorption of cobaltous chloride on the chloride resin is a function of the water content of the resin. A sample of resin containing 22% water absorbs the cobalt to about 1.25 mM./g. Dried to 8.3% water, the shape of the saturation curve is much different (see Fig. 1), the "knee" of the curve is much less sharp, and there is seen a gradually increasing uptake of cobalt by the resin with increasing solution concentration, which conceivably might reach the concentration on the resin of the 22% water case at terminal solution concentrations above 0.1 *M*. With a water content of 6.8%, the curve is flatter, definitely tending to level off at a lower value, and when the water content of the residue has been reduced to 5%, the absorption levels off at a value about 0.1 that of the resin with 22% of water. It is to be understood that the standard conditions, 2 ml. of solution and 0.2 g. of resin, are involved. If 1% by volume of water is added to the acetone solution, the absorption of the resin with 6.8% water is increased to 1.0 mM./g., showing that it is the equilibrium water content of the system that is important, and that drying the resin has not produced a large permanent change in its properties.

If the organic solvent is *t*-butyl alcohol rather than acetone, the absorption of the cobaltous chloride is considerably reduced, with the shape of the absorption curve ($\log_{10}$ residual concentration *vs.* mM./g. resin) considerably altered, in appearance as if the experiment with acetone were performed with resin of lower water content. Thus, for the resin containing the initial 22% of water, the concentration of cobalt on the resin is less than 0.2 mM./g. at a residual concentration of 0.03 *M*, and less than 0.4 mM./g. at 0.06 *M*. For the resin with 6.8% water, the values are 0.02 mM./g. at 0.02 *M* residual solution, and perhaps 0.15 mM./g. at 0.1 *M* residual solution.

Cobaltous nitrate equilibrated with nitrate resin[9] showed a somewhat similar pattern of ab-

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(9) "Nitrate resin," formed by equilibrating chloride resin against concentrated sodium nitrate, and washing with water, still contains up to 10% of the original chloride.

sorption on the resin, with several differences. The "knee" of the curve is more rounded, so that with absorptions approximating 0.9 mM./g., the residual concentration of salt in the acetone may be 0.010–0.015 *M*. There is also a definite slope to the plateau, perhaps related to the rounding of the knee. The most marked difference, however, is the essential independence of the water content of the resin, the absorptions of nitrate onto resin with 4% and 6.8% of water being essentially the same, and equal to that of the chloride on resin of 22% water content. Levels of cobalt on the resin as high as 1.4 mM./g. have been found for solutions of residual concentration 0.11 *M*.

One may also absorb chloride on nitrate resin, and nitrate on chloride resin. Thus, absorption of cobaltous chloride on nitrate with 8.4% water resin may be as high as 1.5 mM./g. with a residual concentration of 0.05 *M*. The absorption on resin with only 4% water is depressed to about 0.72 mM./g. at 0.025 *M* residual concentration. Cobaltous nitrate in acetone, on chloride resin, with 22% water, shows absorption to 0.5 mM./g. at 0.05 *M* residual concentration, 1.0 mM./g. at 0.1 *M* and 1.5 mM./g. at 0.15 *M* residual concentration. Against the resin with 6.8% water, the level is about 0.1 mM./g. resin at 0.015–0.03 *M* residual concentration, significantly less.

Chlorides have been shown to be capable of forming complexes with cobaltous chloride in acetone.[10] The effects of lithium chloride on the absorption of cobaltous chloride from acetone have not been demonstrable with any certainty, and the same may be said of pyridinium chloride. Lithium nitrate likewise shows no clear effect on the absorption of cobaltous chloride or nitrate. These statements are to be understood to apply to a concentration range up to about 0.2 *M* in the added salt. Pyridine, which also associates with the cobaltous salts in acetone solution, and which is able, in at least some cases, to displace coördinated chloride,[10] does have a strong effect on the absorption of the cobalt salts. Thus, 1.5–3 equivalents of pyridine almost completely inhibit the absorption of 0.07 *M* cobaltous nitrate on nitrate resin, while 0.4–0.9 equivalent of pyridine will reduce the absorption of cobaltous chloride on the same resin to some 20% or so of the value with pyridine absent.

In summary, therefore, it is seen that substances as diverse as HCl, LiCl and the chlorides and nitrates of the divalent transition elements can be absorbed from acetone solution onto anion exchange resins, the molecule as a whole disappearing from solution. A single mechanism, it is conceivable, may cover all the cases; it is possible, on the other hand, to point to possible specific (and different) factors in several of the cases. Thus, for HCl, the hypothesis is tenable that a large factor at least in its absorption is the presence of weakly basic nitrogen groups in the resin which dissociate acid in the procedures of washing the resin with water, but take it up again from the (undoubtedly) high activity acetone solutions. The transition element salts are known to participate in equilibria in which higher complexes are formed with anions, and therefore a mechanism for their absorption may be written in terms of the equilibrium

$$R^+X^- + MX_2 = R^+(MX_3)^-$$

in which R^+ represents the resin cation. Lithium chloride does not obviously follow either of these two explanations, and therefore represents a potential third class, though it is conceivable that its absorption may represent evidence for complexes of the type $(LiCl_2)^-$ and $(Li(NO_3)_2)^-$, and perhaps even the HCl case may be due in part to an analogous phenomenon.

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[10] L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5464 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Infrared Spectra of Heavy Water Adsorbed on Silica Gel

BY GEORGE C. PIMENTEL, CARL W. GARLAND* AND GEORGE JURA

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A technique has been developed for the determination of the infrared absorption spectrum of adsorbed D_2O. The experiments were performed with D_2O adsorbed on silica gel. In the 1900–3400 cm.$^{-1}$ region, the spectra of samples with surface coverages from 0.35 to 1.8 monolayers are similar to the spectrum of D_2O in the liquid phase. Exchange of the adsorbed D_2O with the H_2O in the gel has been observed.

I. Introduction

Spectroscopic studies of adsorbed materials provide information which aids in understanding the properties of surfaces as well as the nature of processes occurring at interfaces.[1] Some studies have been made using visible and ultraviolet light,[1,2] but the results have been limited by experimental difficulties peculiar to adsorption systems: insufficient adsorbate to provide definitive spectra or excessive light scattering by the adsorbent. These experimental difficulties are encountered in infrared spectroscopy; in addition, there is the problem of putting the sample in a suitable form for infrared study while maintaining a known surface coverage. Apparently the only studies of this kind in the infrared spectral region are those of Kurbatov and Neuĭmin.[3] Their technique is such that the surface coverage is not known. The present work indicates experi-

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* AEC Predoctoral Fellow 1951-53.

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