hydrous halides. Encouraging results have also been obtained through the use of hydrated salts other than acetates, *e.g.*, copper(II) sulfate 5-hydrate and thorium(IV) nitrate 4-hydrate. The exact procedural details for any given case are subject to minor variations depending upon the solubility of the product and the reactivity of the salt employed as the starting material as well as that of the acetyl halide. Acetyl iodide is relatively unstable and should be prepared as needed.[3] Highly covalent halides, such as chromium(III) bromide, that are soluble in benzene may be prepared by this method by boiling off the excess acetyl halide, benzene, and the other reaction products. Alternatively, other organic liquids in which the product halides are less soluble may also be used as the reaction media.

[3] J. Thiele and H. Haakh, *Ann.*, **369**, 145 (1909).

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Studies in Low Concentration Chemistry. X. Further Observations on Yttrium

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RECEIVED JANUARY 5, 1955

Yttrium at concentrations below 10^{-5} *M* in aqueous solution has been the subject of several previous investigations.[1] This paper is a continuation of studies into the radiocolloidal properties of this element and also presents some adsorption and solvent extraction data.

Experimental

Materials.—Strontium-90 in equilibrium with its radioactive daughter yttrium-90 was obtained as the chloride from Oak Ridge National Laboratory. Carrier-free yttrium-90, a β-emitter with a half-life of 65 hr., was separated from the parent element by a slight modification of the method of Schweitzer, Stein and Jackson.[1]

A labeled 10^{-2} *M* yttrium chloride solution was prepared by dissolving yttrium oxide in concentrated hydrochloric acid, adding yttrium-90, and diluting with distilled water. Labeled 10^{-4}, 10^{-5}, and 10^{-8} *M* solutions were prepared by appropriate addition of tracer and dilution of the 10^{-2} *M* stock solution. Norit A Decolorizing Carbon (Pfanstiehl Chemical Co.) was used as an adsorbent. All other chemicals were of C.P. reagent grade quality.

Apparatus.—Centrifugations were carried out in 0.7-ml. Pyrex glass tubes which were rotated in a Misco Microcentrifuge at about 25,000 times gravity. The solvent extractions were performed in a 25-ml. round bottom flask, the contents of which were stirred by a mechanical stirring motor attached to a glass stirrer which rotated in a sleeve of rubber tubing. The rubber tubing was placed in a one-hole rubber stopper which sealed the flask. The liquids in the extraction vessel were maintained at 25.0 ± 1.0° by keeping the vessel partially immersed in a constant temperature bath. Twelve-ml. weighing bottles were employed as sample containers for the adsorption experiments. These bottles were shaken in a Dubnoff Shaking Apparatus at room temperature. All *p*H values were measured by a Beckman Model G-2 Glass *p*H Meter equipped with microelectrodes.

Radioactivity Measurements.—All solutions were sampled by taking 0.100 ml. of liquid with a 0.100-ml. micropipet, placing the liquid on a copper planchet, and then evaporating to dryness under a heat lamp. The activities of the samples were determined with a Nuclear D-34 end-window Geiger tube mounted in a Tracerlab 64-Scaler. All activities were counted for a sufficiently long time to give a maximum standard deviation of 1%.

Centrifugation Experiments.—Ten-ml. portions of the radioactive 10^{-8} *M* yttrium chloride originally 0.1 *N* in hydrochloric acid were adjusted to various *p*H values using hydrochloric acid or sodium hydroxide solution. Three samples at each *p*H value were then placed in separate centrifuge tubes and allowed to stand for 1 hour so that adsorption onto the glass could come to equilibrium. The solutions were sampled and, after centrifugation for 30 minutes, they were resampled and the *p*H values were redetermined. The differences in radioactivities were used to calculate the percentages of yttrium removed. A similar procedure was followed with the labeled 10^{-5} and 10^{-2} *M* solutions.

Solvent Extractions.—Ten-ml. portions of the carrier-free yttrium solution originally 0.1 *N* in hydrochloric acid were adjusted to various *p*H values with hydrochloric acid or sodium hydroxide solution. Three ten-ml. portions at each *p*H value were sampled, placed in the extraction apparatus, and then 12 ml. of acetylacetone was added. The use of these volumes of the two phases gave equal final volumes due to evaporation and mutal solubility. After stirring each sample for 1 hour, the two liquid phases were separated, each phase was sampled, and the *p*H value of the water phase was redetermined. From the radioactivities, the percentage yttrium removed from the water phase was calculated. Similar experiments were performed using the labeled 10^{-8}, 10^{-5} and 10^{-2} *M* yttrium solutions.

Adsorption Experiments.—Five-ml. portions of the carrier-free yttrium solution originally 0.1 *N* in hydrochloric acid were adjusted to various *p*H values using hydrochloric acid or sodium hydroxide solution. Three five-ml. portions at each *p*H value were placed in weighing bottles, allowed to stand for 1 hr. to reach adsorption equilibrium, sampled, and then the desired amounts of carbon were added. After shaking for 1 hr., the carbon was allowed to settle, and each portion was resampled. From the radioactivities of the samples, the percentages of yttrium adsorbed onto the carbon could be calculated. A similar procedure was followed using the labeled 10^{-8}, 10^{-5}, 10^{-4} and 10^{-2} *M* yttrium solutions.

Results and Discussion

The results of the centrifugation experiments are presented in Fig. 1, all *p*H values being final ones. These data verify the previous observation that yttrium in very low concentrations forms aggregates under certain solution conditions.[1] It also has been confirmed that as the concentration of yttrium increases, the concentration of hydroxide ion associated with the production of centrifugable

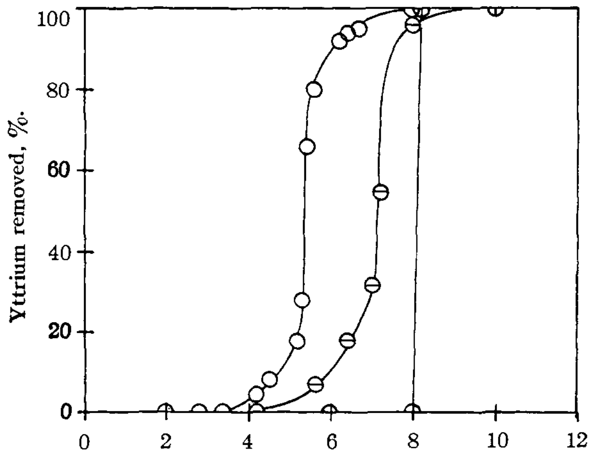

Fig. 1.—Per cent, yttrium removed by centrifugation *versus* *p*H at yttrium concentrations of: 10^{-8} *M*(○); 10^{-5} *M*(⊖); 10^{-2} *M*(⌽).

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[1] J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942); G. K. Schweitzer, B. R. Stein and W. M. Jackson, THIS JOURNAL, **75**, 793 (1953); G. K. Schweitzer and W. M. Jackson, *ibid.*, **76**, 3348 (1954).

yttrium increases. Assuming that the removability of yttrium is due to the presence of some hydroxo form of the cation, these observations are contrary to the solubility product principle. Other investigators have noted a similar behavior in yttrium, as well as other elements.[2]

The results of the solvent extractions from water into acetylacetone are presented in Fig. 2, all *p*H values being final ones. It is apparent that the yttrium concentration has little effect upon the distribution coefficient except at a concentration of 10^{-2} *M*. This effect might be assigned to a self-salting action.[3]

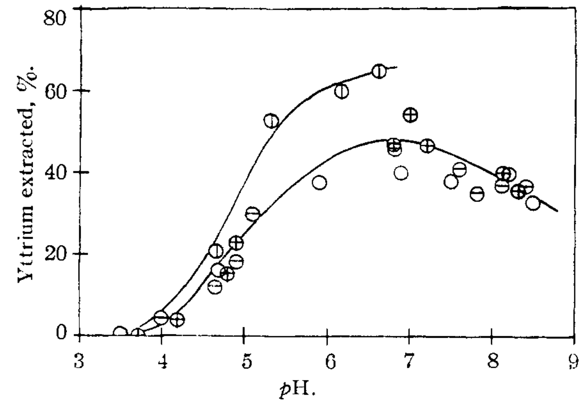

Fig. 2.—Per cent. yttrium extracted from water into acetylacetone *versus* *p*H at yttrium concentrations of tracer (⊕): 10^{-8} *M*; (O), 10^{-5} *M*; (⊖), 10^{-2} *M*(∅).

The results of the experiments involving the adsorption of yttrium onto charcoal at various concentrations, *p*H values, and amounts of charcoal are given in Figs. 3, 4 and 5. As would be expected, the adsorption of yttrium on carbon is strongly dependent upon the hydrogen ion concentration, the yttrium concentrations, and the amount of carbon used. Two factors could be operating to produce

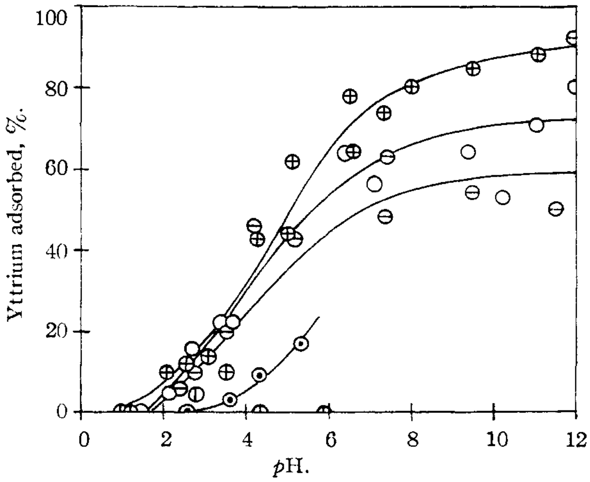

Fig. 3.—Per cent. yttrium adsorbed from water onto 1 mg. of Norit A carbon *versus* *p*H at yttrium concentrations of tracer (⊕): 10^{-8} *M* (O); 10^{-5} *M*(⊖); 10^{-4} *M*(⊙); 10^{-2} *M*(∅).

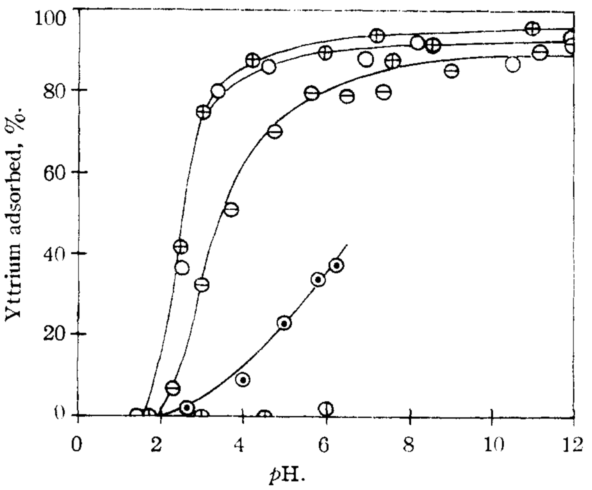

Fig. 4.—Per cent. yttrium adsorbed from water onto 10 mg. of Norit A carbon *versus* *p*H at yttrium concentrations of tracer (⊕): 10^{-8} *M*(O); 10^{-5} *M*(⊖); 10^{-4} *M*(⊙); 10^{-2} *M*(∅).

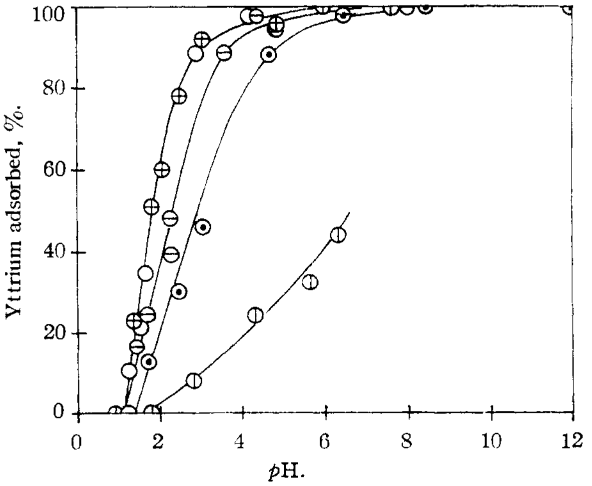

Fig. 5.—Per cent. yttrium adsorbed from water onto 100 mg. of Norit A carbon *versus* *p*H at yttrium concentrations of tracer (⊕): 10^{-8} *M*(O); 10^{-5} *M*(⊖); 10^{-4} *M*(⊙); 10^{-2} *M*(∅).

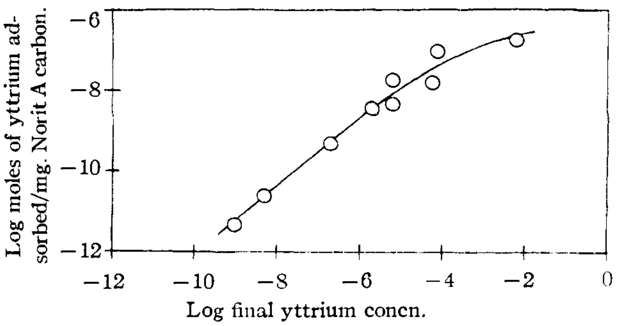

Fig. 6.—Moles of yttrium adsorbed per mg. of Norit A carbon *versus* final yttrium concentration.

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[2] C. Chamie and M. Haissinsky, *Compt. rend.*, **198**, 1229 (1934); J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942); M. H. Kurbatov and J. D. Kurbatov, *J. Chem. Phys.*, **13**, 208 (1945); J. D. Kurbatov and A. M. Silverstein, *J. Phys. Colloid Chem.*, **54**, 1250 (1950).

[3] N. H. Nachtrieb and R. E. Fryxell, THIS JOURNAL, **70**, 3547, 3552 (1948); G. K. Schweitzer and W. N. Bishop, *ibid.*, **75**, 6330 (1953); G. K. Schweitzer and W. N. Bishop, *ibid.*, **76**, 4321 (1954).

an increased adsorption of the yttrium as the *p*H value is increased: firstly, there are fewer hydrogen ions competing for sites on the carbon surface and, secondly, the aggregates may be the major adsorbing entity.

Adsorption values were read from Figs. 3, 4 and 5 at a *p*H value of 5.5 and a Freundlich isotherm plot which is given in Fig. 6 was obtained. From the equation determined from this plot, it was estimated that the concentration of the tracer yttrium solution was about 10^{-10} or 10^{-11} *M*.

Acknowledgment.—The authors wish to express their gratitude to the U. S. Atomic Energy Commission for the grant of funds which made this work possible.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

Relative Stabilities of Chelate Compounds of Pyrrole Pigments[1]

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RECEIVED JULY 6, 1954

The importance of dielectric constant in the determination of the relative stabilities of complexes with metals has been illustrated. From competition and exchange reactions, it was observed that increasing the electron-attracting power of methenes and porphyrins results in an increase in affinity for copper and a decrease in affinity for magnesium.

Porphyrins and closely related compounds are used in the physiological processes of plants and animals in the form of chelate compounds, usually with either magnesium or iron. While the bonding to magnesium is probably ionic[2] the bonding to either ferrous or ferric iron may be either ionic or covalent.[3]

Barnes and Dorough[4] have compared the relative stabilities of various metalloporphyrins and found the general over-all stability to be small divalent > large divalent > alkali.

In our studies, the relative stabilities and rates of formation of the chelate compounds were considered from the following points of view: (1) influence of the medium on chelation, (2) influence of the nature of the metal to nitrogen bond (covalent or ionic) and (3) the effect of the electron-attracting power of the chelating group. Copper was chosen as an example of a metal which readily forms covalent bonds in porphyrin systems and magnesium as one which preferentially forms ionic bonds.[5] The dipyrrylmethenes require two molecules for equivalence to one atom of metal, the porphyrin, one molecule to an atom. The experiments were of two kinds: (1) competition of one equivalent of each of two dipyrrylmethenes for one equivalent of metal and (2) exchange of metal between preformed metal–chelate and a free chelating agent. If the metal exchanges with difficulty, experiments of the first type give information about relative rates of reaction. If the metal exchanges with ease, experiments of this type give information about stabilities. To test for the ease of exchange, and hence for stabilities instead of rates, experiments of the second type were performed.

Discussion of Results

Effect of Medium on Relative Stability.—In their classical studies on the hydrolysis of alkyl halides, Gleave, Hughes and Ingold[6] called attention to the fact that electron-donating alkyl groups could diminish the rate of the reaction if the transition state involved only the breaking and forming of covalent bonds, while in the case that the reaction involved ionization as the rate-determining step, electron-donating alkyl groups would speed the reaction. In only the latter case would an increase in the dielectric constant of the medium cause a marked increase in rate. Because of the numerous cases in which it can be shown that rates and equilibria are parallel,[7] the results of the British investigators create a presumption that cases will be found in which a given type of substitution will also produce opposite effects upon stabilities, depending upon whether the bond affected is ionic or covalent. For the same reason, it also is to be presumed that cases should be found in which a change in dielectric constant should produce reversal of relative stabilities.

In the case of copper compounds, it has been pointed out earlier[8] that the nature of the medium is of critical importance in determining the relative stabilities of bonds to oxygen and nitrogen. In a medium of low dielectric constant, oxides are more stable than nitrides, while in high dielectric constant the ammine is more stable than the hydrate.[9] Recently, Irving[10] reported that the order of stability can change with a change in solvent.

We now have found that when water and pyridine are allowed to compete for copper, the stability of the pyridine complex relative to the aquo complex in dioxane is increased by the addition of

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[1] Porphyrin Studies. XIII. Paper XII, W. S. Caughey and A. H. Corwin, THIS JOURNAL, **77**, 1509 (1955). This paper was presented at the Atlantic City Meeting of the American Chemical Society, September, 1952, and is from the doctoral dissertation of Marjorie H. Melville.

[2] J. W. Barnes and G. D. Dorough, THIS JOURNAL, **72**, 4047 (1950).

[3] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 117.

[4] J. W. Barnes and G. D. Dorough, THIS JOURNAL, **72**, 4045 (1950).

[5] Ward V. Evans and R. Pearson, *ibid.*, **64**, 2867 (1942).

[6] J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 238 (1935).

[7] L. P. Hammett, THIS JOURNAL, **59**, 96 (1937).

[8] A. H. Corwin in "A Symposium on Copper Metabolism," W. C. McElroy and B. Glass, Editors, The Johns Hopkins University Press, Baltimore, Md., 1950, pp. 10–11.

[9] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford University Press, Oxford, 1950, p. 156.

[10] H. Irving, Discussion of a paper by H. Freiser, *The Analyst*, **77**, 841 (1952).