hydrofuran to yield $N_2H_4 \cdot BH_3$ upon removal of solvent. The yield was 79% based on starting borohydride.

The infrared spectrum, melting point, and elemental analyses were identical with that of a known sample.

(2) **$N_2H_4 \cdot BH_3$—Method 2.**—$MgCl_2 \cdot xN_2H_4$ was prepared by adding 4.1 g. of $MgCl_2 \cdot 6H_2O$ to 20 ml. of iced N_2H_4, evaporating under N_2 to a thick clear sirup, and vacuum drying by prolonged pumping at room temperature. The yield (4.5 g.) and nitrogen analysis (50.73 found; 50.03 theory) correspond to $MgCl_2 \cdot 4N_2H_4$, but the material was not characterized further. This solid (1.8 g., 8 mmoles, assuming the tetrahydrazinate) and 0.6 g. (16 mmoles) of $NaBH_4$ were allowed to react in tetrahydrofuran suspension. Hydrogen began to evolve immediately, and, after 8 days, an 83% yield of $N_2H_4 \cdot BH_3$ was isolated from solution. In the hydrogen evolution apparatus, the $H_2:BH_4^-$ ratio was shown to be 1:1.

In neither of the above methods was the actual fate of the magnesium ion determined, although the stoichiometry and material balances lead to the equation

$$MgCl_2 \cdot 4N_2H_4 + 2NaBH_4 \longrightarrow 2(N_2H_4 \cdot BH_3) + 2H_2 + Mg(N_2H_3)_2$$

(3) **$CH_3OHN_2 \cdot BH_3$.**—CH_3ONH_3Cl (0.84 g., 10 mmoles) and $NaBH_4$ (0.38 g., 10 mmoles) yielded 0.26 g. (43%) of soluble product after overnight reaction in tetrahydrofuran suspension. Without any purification other than vacuum drying, the solid melted at 53–58° (dec.) (lit.[5] 55°) and analyzed for $CH_3ONH_2 \cdot BH_3$. (*Anal.* Calcd.: B, 17.6; hydrolyzable H, 4.7. Found: B, 19, hydrolyzable H, 4.9). This material also was sensitive to friction and impact. In the hydrogen evolution apparatus, the $H_2:BH_4^-$ ratio approached 1:1 after several days.

(4) **$(HONBH)_x$.**—Two products always appeared when $HONH_3^+$ salts reacted with borohydrides. The first, soluble in ethers, has been formulated as $(HONBH)_x$; the second, arising from reaction of the first with the solvent, did not give consistent analyses. It is believed to be polymeric, since it was relatively insoluble and small quantities of it formed stable gels with solvents such as tetrahydrofuran. The relative amounts of each product that formed were not completely predictable, although the second was favored if $HONH_3Cl$ was used, or if solutions of $(HONBH)_x$ stood for prolonged periods or were warmed slightly. The following procedure was the most successful for obtaining $(HONBH)_x$. $NaBH_4$ (0.38 g., 10 mmoles) and $(HONH_3)_2SO_4$ (0.82 g.; 5 mmoles) were stirred in 50 cc. of tetrahydrofuran for 3 to 4 days. The solution was filtered, concentrated (N_2 stream) to 5 ml., refiltered, and the product precipitated with 50 ml. of *n*-pentane. Filtration and vacuum drying yielded 0.37–0.45 g. (70–96%) of product. *Anal.* Calcd. for $(HONBH)_x$: B, 25.3 ; N, 32.7; hydrolyzable H, 2.35. Found: B, 24.3, 23.2; N, 30.4, 28.3; hydrolyzable H, 2.33, 2.22, 1.99. Small amounts of carbon always were found, presumably from contamination by the polymer.

The white hygroscopic solid did not melt up to 100° (detonations beyond this temperature). Its density (liquid displacement) was 1.35 ± 0.15 g./cc. Molecular weight determinations (cryoscopic in *p*-dioxane) did not give consistent results. Some values were near 150, but values much higher also were obtained, possibly due to the presence of polymer. The infrared spectrum (mull) showed broad OH, NH, and BH absorptions, but was otherwise ill-defined.

Gas evolution measurements in a wide variety of ethers always gave an $H_2:BH_4^-$ ratio approaching 3:1 at room temperature. At −80°, the evolution rate slowed near 1:1 when tetrahydrofuran, *p*-dioxane, or trimethylene oxide were the solvents. Filtering and removing cold solvent *in vacuo* left a white solid that foamed and gassed when warmed to room temperature, and, except in one case, only $(HONBH)_x$ was isolated. The solid from the trimethylene oxide run had an infrared spectrum slightly different from the usual material and analyzed 3.2% hydrolyzable hydrogen.

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Complexes of the Rare Earths. IV. Electrophoretic Examination of the Hydrolysis of N-Hydroxyethylethylenediaminetriacetic Acid Chelates

BY LARRY C. THOMPSON AND JAMES C. NICHOL

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In a recent note Gupta and Powell[1] have reported on the interaction between the rare earth–N-hydroxyethylethylenediaminetriacetic acid (HEDTA) chelates and an equivalent amount of base and have concluded that species of the form $RChOH^-$ exist in such solutions. We have confirmed their results with a titration technique[2] and have found formation constants in good agreement with theirs.

We also have performed electrophoresis experiments on solutions containing the hydrolysis products of lanthanum, neodymium, dysprosium, and ytterbium chelates. We believe that the results are worth presenting since they are consistent with the behavior expected of solutions containing principally a neutral complex and a single negatively charged species, as inferred from the titration experiments, and provide good supporting evidence by an independent method for the correctness of conclusions drawn from the titration data.

Experimental

Electrophoresis experiments were performed at 1.00° with a Spinco Model H electrophoresis apparatus. An 11-ml. quartz Tiselius cell with reference paths was used, and schlieren and interference fringe photographs were taken simultaneously. Fringe displacements and mobilities were calculated as described previously.[3] Conductances were measured at 0°, using a Jones bridge and a conductance cell of the Jones and Bollinger type.

In all experiments the rare earths, at a total molar concentration of about 0.0018, adjusted to the desired pH with 0.1 *M* potassium hydroxide, were studied in 0.1 *M* potassium nitrate as supporting electrolyte. The details of solution preparation have been described elsewhere.[4] The experimental situation is analogous to the commonly encountered electrophoresis of proteins in a buffer, the complex species and the potassium nitrate corresponding to the protein and buffer components, respectively Fig. 1). Above pH 10, the concentration of free hydroxide ion becomes appreciable and should be indicated as KOH in the appropriate phases.

Results and Discussion

In all experiments at pH values where significant hydrolysis would be expected (as shown by the acid dissociation constant of the chelates) a single moving boundary, proceeding toward the anode, was observed

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[1] A. K. Gupta and J. E. Powell, *Inorg. Chem.*, **1**, 955 (1962).

[2] The entire run of our titration was less than 1 hr., whereas Gupta and Powell equilibrated their samples at each point for 100 hr.

[3] J. C. Nichol, E. B. Dismukes, and R. A. Alberty, *J. Am. Chem. Soc.*, **80**, 2610 (1958).

[4] L. C. Thompson and J. A. Loraas, *Inorg. Chem.*, **2**, 89 (1963).

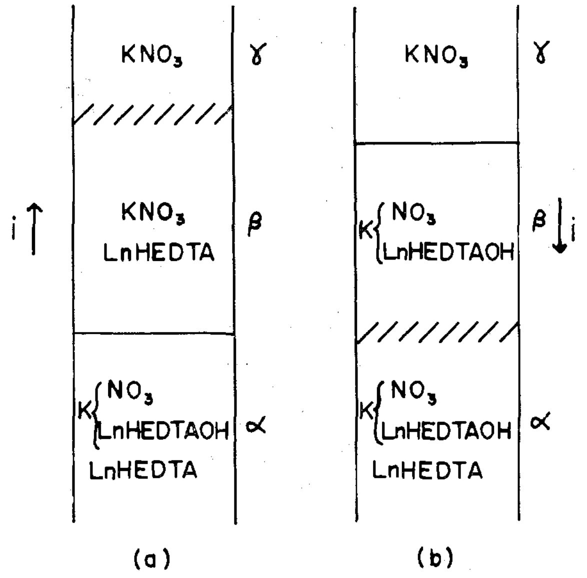

Fig. 1.—(a) Diagram of the descending moving boundary system obtained upon electrophoresis of a rare earth–HEDTA complex in KNO_3 as supporting electrolyte, in the pH range in which hydrolysis occurs. (b) Corresponding ascending system. The α- and γ-phases are the original solutions, and the β-phases are formed upon electrophoresis. It is assumed that the complex species present are the neutral molecule LnHEDTA and the anion $LnHEDTAOH^-$. The arrows indicate the direction of positive current, the boundaries remaining near the initial boundary positions are indicated by ////, and the moving boundaries are indicated by ——.

in both the descending and ascending limbs. This is illustrated for ytterbium in Fig. 2. The mobilities calculated from boundary velocities and conductances of the appropriate solutions are about 1×10^{-4} cm.^{2} volt^{-1} sec.$^{-1}$ for the four chelates studied. No boundaries moving toward the cathode were observed at any pH investigated. These results are consistent with the conclusion drawn from titration data calculations that the neutral complexes hydrolyze principally to a negatively charged monomer. The experiments provide no information as to the composition or the magnitude of the charge on the hydrolyzed ion.

If, as the titration data suggest, the moving boundary system involves no significant concentration of species other than the neutral and singly charged forms of the complex, along with the ions of the supporting electrolyte, a fairly simple situation exists, and it is possible to predict, at least qualitatively, the electrophoretic behavior to be expected of the system. This is the case even if the neutral and charged forms of the complex are in rapid reversible equilibrium in the original solution, provided that upon electrophoresis one of the forms is left behind in an environment unfavorable to the re-establishment of equilibrium, or else migrates ahead into such an environment.[5] The phase compositions to be expected are shown in Fig. 1. In the descending limb, the complex anion would be expected to migrate downward, leaving the neutral complex behind in an environment too low in hydroxide ion concentration to restore the original equilibrium. In an experiment involving ytterbium chelate the predicted presence of ytterbium in the β-phase was demonstrated by the formation of a white precipitate upon addition of oxalic acid. Furthermore, the pH was lower than that of the starting solution, as would be expected if the anion form had migrated out of the region. In the ascending limb, the complex anion should migrate upward, again leaving the neutral complex behind. Addition of oxalic acid to the ascending β-phase for the ytterbium experiment gave a white precipitate, and the pH of the solution was higher than that of the original solution, as would be expected if the neutral chelate were left behind. If the migration is into a solution of negligible hydroxide ion concentration, there is the possibility that the ion will react to produce some neutral complex in the β-phase. However, there is no indication that such a reaction is significant in the present experiments (see below). In any event, in either limb, the higher the pH, the greater will be the fraction of the complex in the ionic form, and the larger should be the fringe displacement and area under the schlieren pattern corresponding to the moving boundary across which the charged form disappears. Correspondingly, the stationary boundary will become smaller because of the drop in concentration of the neutral complex.

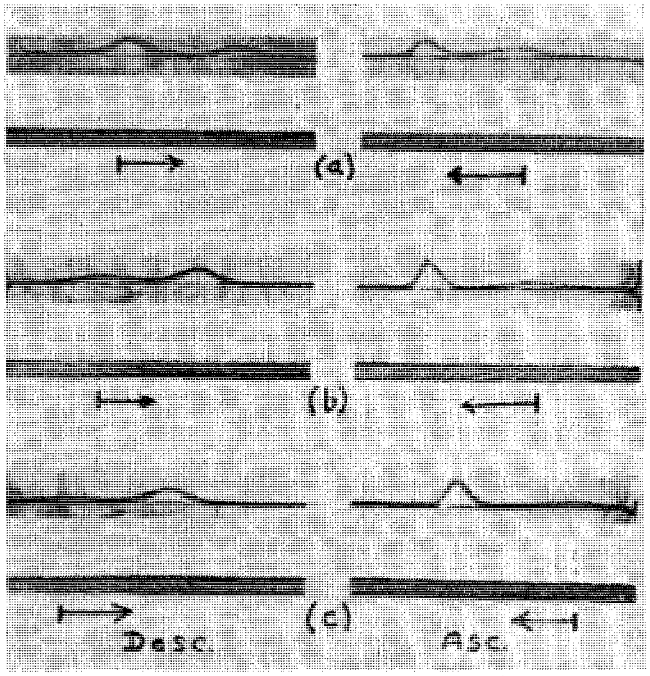

Fig. 2.—Descending and ascending electrophoresis patterns of ytterbium–HEDTA complexes in 0.1 *M* KNO_3 after about 100 min. at 13 ma. current. (a) The initial boundary consisted of 0.1 *M* KNO_3 layered over 0.1 *M* KNO_3–0.0018 *M* YbHEDTA at pH 9.0. (b) and (c) These are the same as (a), except that the pH was adjusted to 9.8 in (b), and to 10.0 in (c).

The patterns of Fig. 2 and the corresponding experimental data in Table I for the ytterbium–HEDTA system are clearly consistent with the above picture.

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[5] J. C. Nichol, *J. Am. Chem. Soc.*, 2367 (1950); Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., 1959, p. 5-S.

There is a marked increase in the fraction of the total fringe displacement contributed by the moving boundary in each limb as the pH is increased, and a corresponding decrease in the contribution from the stationary boundary. These changes are sufficiently large to be evident upon visual inspection of the schlieren patterns of Fig. 2.

Finally, if the concentrations and molar refractions of the different substances present in the various phases could be determined, the refractive index changes, and from them the fringe displacements across the various boundaries, could be predicted, and compared with the experimental values. The compositions of the original solutions may be calculated with the aid of the acid dissociation constants evaluated from the titration data. The β-phase compositions then may be estimated from the original phase compositions and appropriate conductance and boundary velocity data, using strong electrolyte moving boundary theory, which holds approximately for systems of this type.[5] The molar refractions may be determined from fringe displacement measurements across boundaries involving only potassium nitrate and across the initial boundaries in the various experiments. Values predicted in this fashion for the ytterbium experiments are listed in Table I. The reasonably good agreement between the observed and predicted values provides qualitative confirmation for the correctness of the titration curve value of K for ytterbium. (The difference of about one and one-half fringes in the total fringe displacement between the pH 10 run and the other two arises from the fact that 0.102 M rather than 0.100 M potassium nitrate was used as the top solution.) The fact that the agreement for the ascending displacements is as good as that for the descending suggests that the formation of neutral complex in the ascending β-phase is not extensive.

TABLE I

INTERFERENCE FRINGE DISPLACEMENTS ACROSS BOUNDARIES FOR YTTERBIUM–HEDTA

	Fig. 2a (pH 9.0)		Fig. 2b (pH 9.8)		Fig. 2c (pH 10.0)	
	Obsd.	Pred.	Obsd.	Pred.	Obsd.	Pred.
Descending SB[a]	5.91	5.2	3.50	3.2	1.78	1.6
Descending MB[a]	3.96	4.7	6.27	6.6	6.37	6.6
Total	9.87		9.77		8.15	
Ascending SB	5.10	5.6	3.63	3.1	2.06	1.4
Ascending MB	4.75	4.3	6.14	6.6	6.14	6.8
Total	9.85		.77		8.20	

[a] SB = stationary boundary (*i.e.*, the boundary remaining near the site of the initial boundary position); MB = moving boundary.

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The Effect of Metal Ion Chelation on the Acid Dissociation of the Ligand 4-(2-Pyridylazo)-resorcinol

BY ALFIO CORSINI, QUINTUS FERNANDO, AND HENRY FREISER

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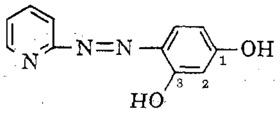
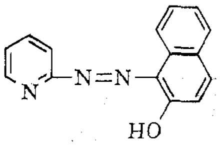
There has been a growing interest, recently, in the effect of metal ion chelation on the chemical properties of the ligand. Of particular interest is the effect of chelation on the acidity of ligand substituents. Investigations to date have shown, without exception, that chelation substantially increases the dissociation constants of acid substituents in the bound ligand, relative to the free ligand.[1-3]

This note is concerned with changes, caused by chelation, in the acidity of the 1-hydroxy group in 4-(2-pyridylazo)-resorcinol (PAR). The metal chelates of PAR are stable and, with the exception of the Mn(II) chelate, form at low pH.[4] These observations provided some promise that the pH range of chelate formation and of dissociation of the 1-hydroxy group in the bound ligand would not overlap appreciably.



PAR



PAN

Experimental

Materials.—The preparation and purification of all the materials used in this work have been described previously.[4]

Potentiometric Measurements.—To determine the dissociation constants of the PAR chelates, titrations were conducted as follows. Fifty ml. of water, purified by passing distilled water through an ion-exchange column, 1 to 5 ml. (depending on the solubility of the PAR chelates) of a standard (0.01 M) solution of metal perchlorate, and 25 ml. of a freshly prepared standard ($\sim 10^{-3}$ M) solution of PAR in 1,4-dioxane were added to a jacketed titration vessel maintained at 25.0 ± 0.1°. A further quantity of dioxane was added to obtain, initially, a 50% v./v. aqueous dioxane solution. The quantities of metal perchlorate and PAR added were such that the metal:ligand ratio was 1:2 for Mn, Zn, Ni, and Co and 1:1 for Cu. The dissociation constants of the hydroxy groups in the reagent PAR were determined by titration in the absence of the metal ion.

A standard solution (0.01 M) of carbonate-free sodium hydroxide was added in small increments together with equal volumes of dioxane to the stirred solution. All pH measurements were made as previously described.[4]

The Ni, Co, Zn, and Mn titrations were repeated substituting the reagent PAR with 1-(2-pyridylazo)-2-naphthol (PAN).

The pK values in Table I are average values of two or three replicate titrations.

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(1) T. R. Harkins and H. Freiser, *J. Am. Chem. Soc.*, **78**, 1143 (1956).

(2) G. I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, 2745 (Part I), 2750 (Part II) (1962).

(3) S. P. Bag, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **1**, 887 (1962).

(4) A. Corsini, I. M. Yih, Q. Fernando, and H. Freiser, *Anal. Chem.*, **34**, 1090 (1962).