Preparation and Properties of Some Hydrocarbon-Soluble Cerium and Iron Compounds

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SILICONE LIQUIDS have been stabilized against oxidation and gelation at 300°–325° C., by processing aerated silicone fluids with certain variable-valence rare earth or transitional metal soaps (e.g., cerium or iron) and a chelating agent such as disalicylalpropylenediamine—i.e., disalicylidene-1,2-propanediamine, abbreviated as H_2DSPD (*2, 3*). The work reported here concerns the chemistry of organic compounds of cerium and iron which are possible starting materials or intermediates in the inhibition process. The synthesis of these compounds presents special problems because of the redox nature of the metal ions involved, the ready hydrolysis of some Ce(IV) salts, and because of the tendency of these ions to form coordination complexes with a wide variety of ionorganic and polar organic substances. Hydrocarbon-soluble compounds of cerium and iron were desired; hence, most of the study deals with Ce(IV) and Fe(III) organic compounds, which in general are much more hydrocarbon-soluble than Ce(III) and Fe(II) compounds. The readiness of Ce(IV) to form benzene-soluble covalent complexes is demonstrated by its β-diketone chelates (*11, 12, 18*) and by its alcoholates (*5-9*). Coordination numbers of six and eight are possible, six-coordinate Ce(IV) being more common.

EXPERIMENTAL

The cerium and iron compounds of this study include basic and normal *p*-toluate soaps, alcoholates, and disalicylalpropylenediamine complexes. Preparative methods and assays for the various compounds are given below. Detailed experimental procedures have been published (*4*). Data on molecular weights, solubilities, and melting points are summarized in Table I. Of the ten compounds, nine are new and eight are benzene soluble. Cation determinations were made on all soaps and alcoholates. Formulas assigned the compounds are supported by infrared spectroscopy, analytical assays, molecular weight determinations, and in most instances by stoichiometry of reaction. Infrared observations measured the amount of free acid coprecipitated with certain compounds. The empirical formulas reported correspond to reproducible substances, several of which can be prepared by more than one synthetic method, but in basic soaps shown as containing —OH and —O—, the data given do not permit a definitive assignment of the proportion of each present. The infrared data do establish the presence of substantial amounts of —OH in all compounds for which it appears in the formulas. Cryoscopic measurements were performed in a Beckman apparatus equipped with a drying tube, stirrer, and controlled low temperature bath. Ebullioscopic measurements were performed in a Cottrell apparatus modified to exclude moisture.

Basic Ceric Toluate *A*, Ce(Tol)(OH)(O). Reactions in aqueous media (200 ml.) between sodium *p*-toluate (0.004 mole) and ceric ammonium nitrate (0.004 mole) acidified with nitric acid (0.004 mole) lead to the benzene soluble soap Ce(Tol)(OH)(O), contaminated with about 5% toluic acid (68% yield). Ether extractions reduce the acid content to 2.6%. Redissolving in benzene, filtering and drying gave a pale yellow powder. Anal. calcd. for $Ce(OCOC_6H_4CH_3)(OH)(O)$: Ce, 45.45; C, 31.14; H, 2.62; Found: Ce, 44.9; C, 30.18; H, 2.91.

Basic Ceric Toluate *B*, $Ce(Tol)_{1.5}(OH)_{1.5}(O)_{0.5}$. Metathesis between sodium *p*-toluate (0.12 mole) and ceric ammonium nitrate (0.02 mole) in 80 vol. % alcohol-water solution (700 ml.) precipitates $Ce(Tol)_{1.5}(OH)_{1.5}(O)_{0.5}$ containing 4–5% toluic acid. Alcohol washes reduced the acid content

Table I. Properties of Some Organic Cerium and Iron Compounds

Organic Compd and Abbrev.	Formula	Formula Wt.	Mol. Wt. (in benzene)	Soly.[a] Benzene	Soly.[a] EtOH	M.P. °C.
Basic ceric toluate, *A*	$Ce(OCOC_6H_4CH_3)(OH)(O)$	308.27	5000[b]	v.s.	s.	>200[c]
Basic ceric toluate, *B*	$Ce(OCOC_6H_4CH_3)_{1.5}(OH)_{1.5}(O)_{0.5}$	376.37	6700[b]	∞ s.	i.	>200[c]
n-Ceric toluate, $Ce(Tol)_4$	$Ce(OCOC_6H_4CH_3)_4$	680.67	...	0.2% (25° C.)	v.s. (hot)	>230[c]
Cerous toluate, $Ce(Tol)_3$	$Ce(OCOC_6H_4CH_3)_3$	545.54	...	i.	i.	>300[c]
Basic ceric dinonylnaphthalene-sulfonate, $Ce(DNNS)_{3.5}(OH)_{0.5}$	$Ce(C_{28}H_{43}SO_3)_{3.5}(OH)_{0.5}$	1757.04	4000[b]	∞ s.	v.s.	74–84
Ceric isopropoxide solvate, $Ce(O\ Pr\text{-}iso)_4 \cdot Pr\text{-}iso\ OH$	$Ce(OC_3H_7)_4 \cdot C_3H_7OH$	436.57	dimeric[d]	v.s.	...	...
Bis(N,N′-disalicylalpropylene-diamine) cerium (IV), $Ce(DSPD)_2$	$Ce(C_{17}H_{16}N_2O_2)_2$	700.77	730[b]	0.6% (25° C.)	d.s.	326–330
Basic ferric toluate, $(Tol)_2FeOFe(Tol)_2$	$Fe_2O(OCOC_6H_4CH_3)_4$	668.24	1100 ± 200[e]	d.s. (cold) s. (hot)	i	188–192
N,N′-disalicylalpropylenediamine ferritoluate, (DSPD)Fe(Tol)	$Fe(C_{17}H_{16}N_2O_2)(OCOC_6H_4CH_3)$	471.30	550[e]	v.s.	2.1% (25° C.)	193–194
Bis(N,N′-disalicylalpropylene-diamine) ferrioxide (DSPD)FeOFe(DSPD)	$Fe_2O(C_{17}H_{16}N_2O_2)_2$	688.33	...	i.	i.	284–285

[a] Solubility abbreviations: insoluble (i); diffficulty soluble (d.s.); very soluble (v.s.); infinitely soluble (∞ s.). [b] Determined cryoscopically. [c] Decomposes without melting. [d] Ref. (*6*). [e] Determined ebullioscopically.

to 0.6%. Redissolving in benzene and drying gave the product as pale yellow granules (81% yield). Anal. calcd. for $Ce(OCOC_6H_4CH_3)_{1.5}(OH)_{1.5}(O)_{0.5}$: Ce, 37.23; C, 38.29; H, 3.21; Found: Ce, 37.2; C, 39.29; H, 3.40.

Normal Ceric Toluate, $Ce(Tol)_4$. A solution of ceric isopropoxide solvate (0.03569 mole) in benzene (150 ml.) was added during 45 minutes to a refluxing solution of sublimed *p*-toluic acid (0.1428 mole) in benzene (450 ml.). As the benzene-isopropyl alcohol azeotrope distilled under high reflux ratio, the reaction mixture deposited orange-red crystals. Removal of isopropyl alcohol was 98.4% complete after 4 hours. Concentration and freeze-drying of the residual mixture gave orange crystals (100% yield). Moisture must be rigorously excluded from this reaction and the stored product (*4*). Anal. calcd. for $Ce(OCOC_6H_4CH_3)_4$: Ce, 20.59; $CH_3C_6H_4COOH$, 0.0. Found: Ce, 20.64; $CH_3C_6H_4COOH$, 1.5.

Cerous Toluate, $Ce(Tol)_3$. Aqueous solutions of 0.01 molar sodium *p*-toluate (210 ml.) and 0.01 molar cerous chloride (200 ml.) were combined and digested. The precipitate was water washed and dried to obtain a 74.3% yield of white amorphous crystals. Anal. calcd. for $Ce(OCOC_6H_4CH_3)_3$: Ce, 25.69; $CH_3C_6H_4COOH$, 0.0. Found: Ce, 25.45; $CH_3C_6H_4COOH$, 0.0.

Basic Ceric Dinonylnaphthalenesulfonate, $Ce(DNNS)_{3.5}(OH)_{0.5}$. Sodium dinonylnaphthalenesulfonate (0.001 mole) was added to ceric ammonium nitrate (0.009 mole) dissolved in alcohol. Evaporation of the alcohol left a residue which was extracted with benzene. Repeated water washing and drying of the benzene extracts yielded a pale orange solid. Anal. calcd. for $Ce(C_{28}H_{43}SO_3)_{3.5}(OH)_{0.5}$: Ce, 8.0. Found: Ce, 8.1.

Ceric Isopropoxide Solvate, $Ce(O\ Pr\text{-}iso)_4 \cdot Pr\text{-}iso\ OH$. The solvate was obtained as yellow needles by a modification of Bradley's procedure (*5*). Anal. calcd. for $Ce(OC_3H_7)_4 \cdot C_3H_7OH$: Ce, 32.1; Pr-iso 0, 67.6; Found: Ce, 32.2; Pr-iso 0, 66.9

Bis(N,N'-Disalicylalpropylenediamine) Ce(IV), $Ce(DSPD)_2$. From basic ceric toluate *B*. A mixture of $Ce(Tol)_{1.5}(OH)_{1.5}(0)_{0.5}$ (0.0153 mole) and H_2DSPD (0.0479 mole) and benzene (1000 ml.) was refluxed 3 hours. Water removed azeotropically amounted to 0.48 gram (theory 0.55 gram). After evaporation of benzene from the reaction mixture, the residue was extracted with chloroform (100 ml.), which was displaced by repeated evaporations with ethyl alcohol. The resulting precipitate was collected, washed with alcohol (2 × 80 ml.) and dried to give 10.0 grams (93% yield) of $Ce(DSPD)_2$ as reddish purple crystals. Anal. calcd. for $Ce(C_{17}H_{16}N_2O_2)_2$: Ce, 20.00; N, 8.00. Found: Ce, 20.03; N, 7.83. From normal ceric toluate. A solution of $Ce(Tol)_4$ (0.00186 mole) in chloroform (50 ml.) was added to a solution of H_2DSPD (0.0056 mole) in chloroform (50 ml.). Formation of the chloroform soluble $Ce(DSPD)_2$ proceeded at room temperature. Displacement of chloroform by repeated boilings with ethyl alcohol precipitated the complex. The precipitate was alcohol washed and dried to furnish 1.26 g. (97% yield) of $Ce(DSPD)_2$. From ceric isopropoxide solvate. A mixture of $Ce(O\ Pr\text{-}iso)_4 \cdot Pr\text{-}iso\ OH$, (0.003 mole), and H_2DSPD, (0.009 mole), and chloroform was reacted and worked up as before to afford a 95% yield of $Ce(DSPD)_2$. From cerous toluate. Air (300 cc./min.) was bubbled for 3 hours through a mixture of benzene (100 ml.), $Ce(Tol)_3$, (0.00183 mole), H_2DSPD, (0.00461 mole), and wet propylenediamine (1.5 grams). Work-up by methods given led to a 93% yield of $Ce(DSPD)_2$. Somewhat lower yields were obtained when ammonia was substituted for propylenediamine.

Basic Ferric Toluate, $(Tol)_2FeOFe(Tol)_2$. Ferric sulfate (0.0184 mole) dissolved in water (300 ml.) was added to sodium *p*-toluate (0.20 mole) dissolved in water (1400 ml.). After digestion, the peach-colored precipitate was collected, water washed and dried. Extractions with toluene (1000 ml.) at 25° C. removed toluic acid and left as a residue 10.9 grams (88.6% yield) of the basic ferric toluate, containing less than 2.0% free toluic acid. Anal. calcd. for $Fe_2O(OCOC_6H_4CH_3)_4$: Fe, 16.72; C, 57.51; H, 4.22. Found: Fe, 16.8; C, 55.1; H, 4.09.

N,N'-Disalicylalpropylenediamine Ferritoluate, (DSPD)Fe(Tol). A charge of $(Tol)_2FeOFe(Tol)_2$, (0.01 mole), H_2DSPD, (0.11 mole), and toluene (300 ml.) was refluxed 2 hours to remove reaction water (0.18 gram). The blood-red reaction mixture was filtered, concentrated to 20 grams and then treated with dry ether (250 ml.) to precipitate the complex. The crude product was dissolved in toluene and reprecipitated with dry ether to yield 7.6 grams (80.6% yield) of the product as fine purplish black crystals. Anal. calcd. for $Fe(C_{17}H_{16}N_2O_2)(OCOC_6H_4CH_3)$: Fe, 11.85; N, 5.94. Found: Fe, 11.80; N, 5.94.

(DSPD)Fe(Tol) was also prepared in somewhat lower yields by an alternate method, due to Pfeiffer (*17*), in which a mixture of disalicylalpropylenediamine ferrioxide, (DSPD)FeOFe(DSPD), and an excess of *p*-toluic acid was reacted in boiling alcohol.

Disalicylalpropylenediamine Ferrioxide, (DSPD)FeOFe(DSPD). A slurry of (DSPD)Fe(Tol), (2.0 grams), and wet ether (200 ml.) was stirred for 20 minutes. The insoluble residue was separated, washed with benzene and dried. This was dissolved in pyridine, filtered, and reprecipitated with alcohol. Washing with petroleum ether and drying gave a 60% yield of orange-red crystals. Anal. calcd. for $Fe_2O(C_{17}H_{16}N_2O_2)_2$: Fe, 16.22; N, 8.14. Found: Fe, 16.02; N, 8.08.

RESULTS AND DISCUSSION

Basic Ceric Toluates. Ce(IV) toluates precipitated from aqueous media are extensively hydrolyzed. Significant properties of the basic Ce(IV) soaps obtainable by variations in stoichiometry are indicated below.

Ce(Tol)(OH)(O). The soap has a molecular weight of 5,000 in benzene, possibly as a result of the formation of micelles or polynuclear complexes. Physical properties of the soap are given in Table I.

$Ce(Tol)_{1.5}(OH)_{1.5}(O)_{0.5}$. Analytical and stoichiometric data support the formula given. Further evidence for the formula assigned is that the chelating agent, disalicylalpropylenediamine, reacts quantitatively with the soap to displace the amount of toluate ion and water indicated. The presence of ol groups (or aquo or hydroxo groups), as evidenced by infrared studies, excludes fully oxolated formulas such as $Ce(Tol)_{1.5}(O)_{1.25}$. The formula assigned is consistent with analytical, spectroscopic, and reaction data, but the possibility of closely related formulas such as $Ce(Tol)_{1.5}(OH)_{2.5}$ or $Ce(Tol)_{1.5}(O)_{1.25} \cdot H_2O$ cannot be excluded. This basic soap is infinitely soluble and micellar in benzene (MW 6700; i.e., about 18 monomer units per micelle). Its properties are given in Table I. Micelles are the characteristic state of aggregation of oil-soluble soaps of alkali and alkaline earth carboxylates and sulfonates in hydrocarbon solvents (*19*). Basic aluminum dilaurate is strongly associated in hydrocarbons to form extended polymer structures containing hundreds of units. The basic ceric toluate $Ce(Tol)_{1.5}(OH)_{1.5}(O)_{0.5}$, on the other hand, gives a relatively small micelle, much like those formed by dinonylnaphthalenesulfonates and some arylstearates. Because of the unusual opportunities for coordinative intermolecular linking through ol or oxo units, the micellar system deserves further study for the light it may throw on the theory of micellar association in nonpolar solvents.

$Ce(Tol)_3(OH)$. This soap precipitates along with 26.3% of toluic acid, when sodium toluate and acidified ceric ammonium nitrate are reacted in 4 to 1 molar ratios. The mixture is soluble in ether and alcohol, and attempts to extract the acid from the salt failed. No detailed study of properties was made on this mixture.

Normal Ceric Toluate, $Ce(Tol)_4$. The alcoholate route furnishes $Ce(Tol)_4$ low in toluic acid (1.5 wt. %) and parallels the synthesis of normal aluminum fatty acid soaps (*10, 15, 16*) and certain zirconium soaps (*13, 14*).

Like the aluminum and zirconium normal soaps, $Ce(Tol)_4$ is extremely sensitive to hydrolysis. It is soluble with difficulty in aromatic solvents at room temperature, somewhat more soluble in boiling toluene, but readily soluble in boiling xylene. The low solubility in benzene may reflect intermolecular linking through carboxyl groups in the solid state. The comparatively low solubility in boiling benzene hampered molecular weight studies. Properties of the normal Ce(IV) soap are given in Table I.

Normal Cerous Toluate, $Ce(Tol)_3$. In contrast to the Ce(IV) normal toluate, the Ce(III) toluate can be prepared by metathesis in aqueous media. The salt is not readily hydrolyzed. It is insoluble in aromatic solvents and in alcohol (Table I). Cerous toluate reacts in the presence of oxygen and H_2DSPD to form benzene-soluble $Ce(IV)(DSPD)_2$. The addition of a suitable amine (or ammonia) greatly accelerates the reaction. The tendency of Ce(III) to oxidize to Ce(IV) during complex formation has also been observed by other investigators. The oxidation reaction is favored by the formation of stable covalent complexes (*11, 18*).

Reactions of H_2DSPD with Ce(IV) Toluates and Alcoholates. All of the benzene soluble basic ceric soaps react with excess H_2DSPD to form $Ce(DSPD)_2$, toluic acid and water. Yields of $Ce(DSPD)_2$ exceed 90% with all but the most basic soap Ce(Tol)(OH)(O). Quantitative studies of the reaction of $Ce(Tol)_{1.5}(OH)_{1.5}(O)_{0.5}$ and excess H_2DSPD in refluxing toluene provide supporting evidence for the formula assigned the former. The following equation satisfactorily accounts for the products and the stoichiometry:

$$Ce(Tol)_{1.5}(OH)_{1.5}(O)_{0.5} + 2H_2DSPD \rightarrow Ce(DSPD)_2 + 1.5HTol + 2H_2O) \uparrow$$

Both normal ceric toluate and ceric isopropoxide solvate react with excess H_2DSPD to provide anhydrous routes to $Ce(DSPD)_2$. The reactions proceed quantitatively, according to the following equations:

$$Ce(Tol)_4 + 2H_2DSPD \xrightarrow[\text{or chloroform}]{\text{benzene}} Ce(DSPD)_2 + 4HTol$$

$$Ce(O\ Pr\text{-}Iso)_4 \cdot Pr\text{-}iso\ OH + 2H_2DSPD \rightarrow Ce(DSPD)_2 + 5Pr\text{-}iso\ OH$$

$Ce(DSPD)_2$, isolated as reddish purple crystals, melts at 326–330° C., and is monomeric in benzene. Its properties are summarized in Table I. The nonformation of micelles by this compound is in keeping with the fact that the covalent coordination with DSPD radicals allows little ionic character in the complex and at the same time fills every available coordination site on the ceric ion, thus blocking interactions between molecules to form micelles.

Infrared spectra of $Ce(DSPD)_2$ were obtained for the 2 to 15 μ region using a Perkin-Elmer Model 21 spectrometer, employing KBr discs. The complex does not contain detectable amounts of free H_2DSPD, basic ceric toluate, free toluic acid (HTol) or coordinated toluate ion (Tol). In the infrared spectra of $Ce(DSPD)_2$, the peaks identifiable with the DSPD ligand are nearly identical in frequency and intensity with similar peaks in the spectra of the Fe(III) DSPD complexes described in this report.

A formal analogy exists between $Ce(DSPD)_2$ and the monomeric acetylacetonates—i.e., $M^{IV}(C_5H_7O_2)_4$, where M is Ce, U, Po, Th, Zr, or Hf. In all of these cases the central metal atom is apparently eight-coordinate. Such coordination would allow the DSPD to function as a tetradentate ligand. Uranium (IV), which like Ce(IV), has the *f* orbitals required by theory for eight-coordination, has been shown to form an eight-coordinate acetylacetone complex (*1*). While the coordination number of six is more common for Ce(IV) compounds than that of eight, in the case of $Ce(DSPD)_2$ the eight-coordinate arrangement allows the DSPD to appear in its characteristic role as a tetradentate ligand. Several spatial arrangements can be suggested for eight-coordinate complexes which offer two sets of geometrically identical sites, and such a structure is plausible if both oxygen and nitrogen atoms participate in the formation of the complex. Additional evidence that the Ce(IV) ion coordinates DSPD as a tetradentate ligand is given by the close spectral similarities observed between $Ce(DSPD)_2$ and certain Fe(III) DSPD complexes. In the case of the Fe(III) compounds, coordination of DSPD as a tetradentate ligand is generally recognized.

Basic Ceric Dinonylnaphthalenesulfonate. This basic soap is soluble in alcohol, pentane, and aromatic solvents. Its molecular weight (4000 in benzene) indicates the presence of two cerium atoms in the predominant solute species. The data at this point do not exclude the possibility that the solute unit involves an oxo linkage between two cerium atoms. In benzene solution the basic soap reacts slowly with H_2DSPD to form $Ce(DSPD)_2$. Proton acceptors such as propylenediamine facilitate displacement of the tightly bound DNNS ligands by DSPD ligands. Properties of the sulfonate are given in Table I.

Hydrocarbon-Soluble Ferric Compounds. Aqueous reaction between excess sodium toluate and ferric sulfate yields the basic ferritoluate $(Tol)_2FeOFe(Tol)_2$, which is soluble and dimeric in boiling benzene, but only sparingly soluble in cold benzene. The oxolated structure is substantiated by infrared studies, which show the absence of OH groups. Mixtures of the basic ferritoluate and excess H_2DSPD in refluxing toluene give quantitative yields of water, toluic acid, and the very soluble N,N′-disalicylalpropylenediamine ferritoluate, (DSPD)Fe(Tol), which is monomeric in benzene. The crystalline complex, (DSPD)Fe(Tol), hydrolyzes to the insoluble bis(N,N′-disalicylalpropylenediamine) ferrioxide, (DSPD)FeOFe(DSPD), which in turn reacts with excess toluic acid to regenerate (DSPD)Fe(Tol). Properties of the various ferric compounds are given in Table I.

$$H_2O + Fe_2(SO_4)_3 + 6NaTol \rightarrow (Tol)_2FeOFe(Tol)_2 + 2HTol + 3Na_2SO_4$$

$$(Tol)_2FeOFe(Tol)_2 + 2H_2DSPD \rightarrow 2(DSPD)Fe(Tol) + 2HTol + H_2O \uparrow$$

$$2(DSPD)Fe(Tol) + H_2O \rightleftarrows (DSPD)FeOFe(DSPD) + 2HTol$$

Disalicylalethylenediamine homologs of our ferric compounds were prepared by Pfeiffer, using different synthetic routes (*17*). Our compounds correspond spectrally and analytically to the types prepared by Pfeiffer.

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Acidity Functions for Acid-Salt Mixtures: HCl-AlCl$_3$ and HCl-KCl

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THROUGH STUDIES of electron transfer reactions in acid solutions (*1*) we have become interested in measuring the acidity function, H_o, (*2*) in acid-salt mixtures. To begin with we selected HCl-KCl and HCl-AlCl$_3$ mixtures, at several ionic strengths, because acid activities in these mixtures are known and because these mixtures conform to Harned's rule (*3, 5*).

EXPERIMENTAL

Stock solutions of constant boiling hydrochloric acid were used as the source of HCl in preparing the acid-salt mixtures. Weighed portions of these solutions were analyzed by titration with 0.1*N* sodium hydroxide solutions, which were first standardized against potassium acid phthalate.

Stock solutions of aluminum chloride were prepared from reagent grade $AlCl_3 \cdot 6H_2O$ and then weighed portions of solutions were analyzed by potentiometric titration with standard silver nitrate solutions. The aluminum content was taken as one-third the chloride content.

The potassium chloride stock solution was prepared from reagent grade KCl and was standardized gravimetrically by precipitation of AgCl from a weighed portion of the stock solution.

Two indicators, 4-nitroaniline and 2-nitroaniline, were purchased from Aldrich Chemical Co. Solutions of these indicators in HCl were prepared, and the HCl content was determined by titration of weighed samples with standardized NaOH.

The solutions of acid-salt mixtures were prepared from the stock solutions by delivering weighed amounts of each stock solution, including the indicator, and an appropriate weight of water to make solutions of the desired ionic strength and (molal) concentration of each component.

Acidity functions of the mixtures were then determined by means of a Beckman, model DU, spectrophotometer. Readings were made at the maxima corresponding to the basic forms of the indicators: 4-nitroaniline and 380 mμ; 2-nitroaniline, 410 mμ. The acidity functions of the solutions were calculated as

$$H_o = pK + \log \frac{(D - D_{BH^+})}{(D_B - D)}$$

where pK refers to the appropriate indicator and D, D_{BH^+} and D_B are the absorbancies of the mixture, tha acid and basic forms of the indicator (at equal total indicator concentrations), respectively. Measurements were made at 25.5 ± 0.5°. The solutions were stored in a water bath, and the cell compartment of the spectrophotometer was controlled by circulation of the water from the thermostated bath through the thermospacers.

RESULTS AND DISCUSSION

Results from measurements of the acidity functions of AlCl$_3$-HCl mixtures are given in Table I. Mixtures at two ionic strengths (1 and 3) were studied. In Table II, the results obtained for KCl-HCl, with μ = 3, are recorded.

For all solutions studied, graphs of H_o *vs.* log (H^-) or *vs.* log $(H^-)\,\gamma_\pm$ gave good straight lines. All three of these systems obey Harned's rule for mixed electrolytes (*4*). In preliminary studies made by means of a Dubosq colorimeter, BiCl$_3$-HCl mixtures and SrCl$_2$HCl mixtures (μ =