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Ultraviolet Spectra of Aluminum Salt Solutions

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The ultraviolet spectra of various concentrations of $AlCl_3$, $Al(ClO_4)_3$, $Al(NO_3)_3$, and $Al_2(SO_4)_3$ were measured. The objective of this investigation was to establish whether or not structural differences could be observed in aqueous solutions of these salts. (1) An absorption maximum was found at 240 nm for $AlCl_3$, $Al(ClO_4)_3$, and $Al_2(SO_4)_3$. (2) $Al(NO_3)_3$ exhibited a maximum absorption at approximately 303 nm, which was found to be a direct function of the nitrate anion concentration. (3) Chloride and perchlorate anions did not replace inner-sphere groups of Al(III) whereas sulfate caused the maximum at 240 nm to vanish or collapse to a shoulder. (4) No correlation could be made between the molar absorptivity and the apparent absorbing species in solution. Equivalent conductance measurements indicated that sulfate anion, at concentrations higher than 0.50 M, exhibited stronger ion pairing than chloride, nitrate, and perchlorate. This indirectly confirmed the conclusion that sulfate anion substituted into the inner-coordination sphere of Al(III).

Initial studies involved infrared spectroscopic examination of aluminum salt solutions.[1] This report continues the study. Aluminum salt solutions activate aluminum surfaces at a rate peculiar to the individual anion. The immediate objective of this research was to establish structural or composition differences between four aluminum salt solutions.

Electronic transitions in the ultraviolet region are dependent on the nature of the absorbing species and should reveal information about the nature of the ionic atmosphere surrounding the aluminum cation and the nature of the transition responsible for absorption.

There have been few studies of the absorption by aluminum salts in the ultraviolet and apparently none with aqueous solutions in the pH range of 2–4. Investigations by Fairbrother et al.[2] and Eley et al.[3] involved studying the complexing ability of aluminum with olefins and benzene. Ultraviolet measurements of aluminum bromide in benzene show an absorption below about 280 nm which does not obey Beer's law and of which only the absorption edge can be observed. Fairbrother et al.[2] have proposed the following charge transfer scheme responsible for absorption at 280 nm

$$C_6H_6{\cdot}Al_2Br_6 \rightarrow C_6H_6^+{\cdot}Al_2Br_6^- \quad (1)$$

Eley et al.[3] found an intense peak at 297 nm in aluminum iodine–benzene solutions and ascribed this to an iodine–benzene complex of aluminum.

The ternary system of aluminum nitrate–nitric acid–water was studied spectrophotometrically by Henry and Booman.[4] An absorption band found at 295 nm was a direct function of the nitrate concentration.

Several studies by Sato,[5] Brosset,[6] and Brintzinger[7] have been made at higher pHs which involved the spectra of such species as AlO_2^-, $Al(OH)_4^-$, $Al_2(OH)_{10}^{4-}$, and $Al_2O_3(OH)_8^{6-}$. These studies are not pertinent to the present investigation except in so far as they suggest possible charge-transfer reactions.

Jackson et al.[8] and Connick et al.[9] used ^{17}O NMR to distinguish between solvent and coordinated water of various metal cation solutions including Al(III) and found the coordination number of Al(III) to be approximately 6.

Fratiello et al.[10–13] investigated the solution chemistry of Al(III) using ^1H NMR and arrived at a similar conclusion.

Relaxation techniques show that there are two important equilibria pertinent to the present study:

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(OH)(H_2O)_5^{2+} + H^+ \quad (2)$$

and the reaction of sulfate with these two species

$$Al(OH)(H_2O)_5^{2+} + SO_4^{2-} \rightleftharpoons Al(SO_4)(H_2O)_5^+ + OH^- \quad (3)$$

or

$$Al(H_2O)_6^{3+} + SO_4^{2-} \rightleftharpoons Al(SO_4)(H_2O)_5^+ + H_2O \quad (4)$$

These studies are pertinent because they suggest possible charge-transfer reactions.

Experimental Section

The aqueous solutions of $AlCl_3$, $Al(ClO_4)_3$, $Al(NO_3)_3$, and $Al_2(SO_4)_3$ were prepared with reagent grade materials. A concentrated stock solution was first prepared, and less concentrated solutions were made by successive dilution. The concentration of the stock solution was determined by EDTA analytical titrations, as described by Welcher.[14]

A Varian DMS 90 ultraviolet–visible spectrophotometer complete with a base line program correction factor was used to measure the absorbance of the aluminum salt solutions. The base line program stored the amount of absorption due to the solvent and with the base line correction function the base line was automatically subtracted from the spectrum of the solution being analyzed. Beckman 1.0-cm path length cells were used to hold the solution.

Scans were automatically performed between 280 and 215 nm for $AlCl_3$, $Al(ClO_4)_3$, and $Al_2(SO_4)_3$ and between 340 and 225 nm for $Al(NO_3)_3$. Readings were made of the absorbance at 5-nm intervals and plotted against the wavelength; this allowed for an easy method to expand the ordinate and abscissa scales so maxima were easily distinguishable.

Additional plots were made of concentration vs. the molar absorptivities of the various salt solutions tested; and, Beer's law plots were also made of concentration against absorbance. In addition to spectroscopic measurements, the conductances of the four aluminum salts at various concentrations were measured. A Jones–Bollinger-type conductivity cell with platinized-Pt electrodes was used for all mea-

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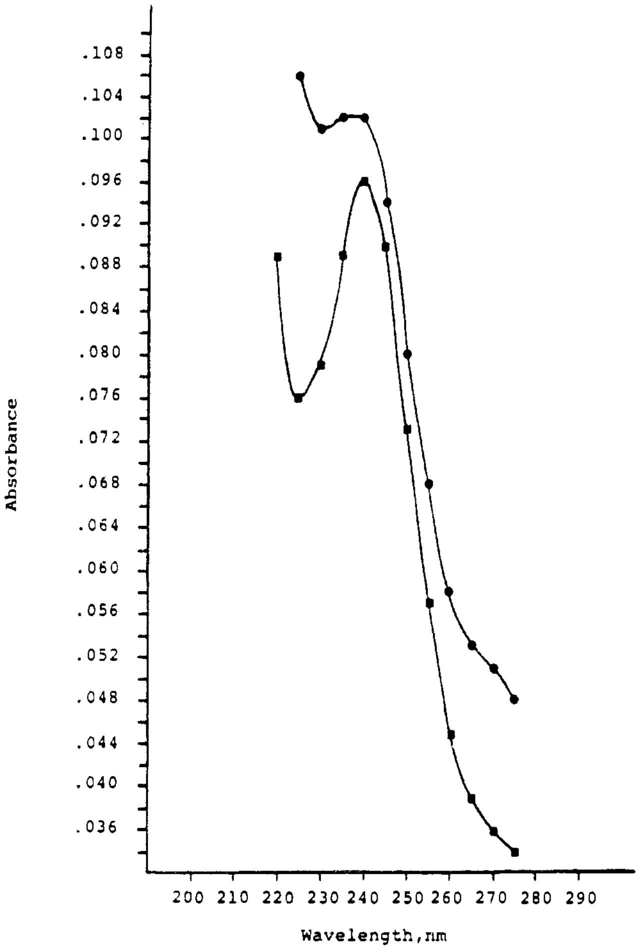

Figure 1. Absorption spectra of aluminum chloride: ●, 0.2130 M; ■, 0.5330 M.

surements. The cell constant was determined at 25 °C with a 0.1000 N KCl solution as 12.5547 cm^{-1}. All conductance measurements were made with an Industrial Instruments conductivity bridge, Model RC 16B2, with the cell thermostated at 25 °C.

Results and Discussion

Representative absorption spectra for $AlCl_3$, $Al(ClO_4)_3$, $Al_2(SO_4)_3$, and $Al(NO_3)_3$ can be seen in Figures 1–5. Tables I–III summarize the data collected and calculated for each salt. The molar absorptivity was calculated from Beer's law (eq 5, where A is the absorbance, b is the cell path length, and C the concentration in moles per liter).

$$\epsilon = A/bC \tag{5}$$

Aluminum Chloride. Typical aluminum chloride spectra are shown in Figure 1. The maximum absorption occurs at 240 nm and was initially attributed to the hexahydrated aluminum cation $Al(H_2O)_6^{3+}$. A Beer's law plot for $AlCl_3$ revealed that adherence to the law was not observed in the 0.01–0.50 M range, and the amount of absorbance as the concentration varied was approximately constant over the concentration range investigated. Even at lower concentrations, 0.00107 and 0.0053 M, the absorbance values were nearly the same as those found at higher concentrations (see Table I for absorbance values at these concentrations). Beer's law failure is attributed to equilibrium reaction 2, which suggests that the concentration of the absorbing species was much different from that calculated from the concentration of aluminum ion as determined by analytical procedures, e.g., EDTA titrations.

Table I. Ultraviolet Absorption Data at 240 nm

salt	concn, mol L^{-1}	absorb	molar absorp
$AlCl_3$	0.00107	0.092	86.22
	0.0053	0.089	16.69
	0.0107	0.093	8.72
	0.0221	0.092	4.16
	0.0533	0.097	1.82
	0.1067	0.095	0.890
	0.213	0.111	0.521
	0.277	0.094	0.339
	0.533	0.097	0.197
$Al(ClO_4)_3$	0.0106	0.090	8.48
	0.0288	0.095	3.29
	0.0530	0.092	1.74
	0.1061	0.094	0.886
	0.1140	0.094	0.824
	0.212	0.096	0.453
	0.285	0.108	0.379
	0.530	0.101	0.190
$Al_2(SO_4)_3$	0.0011	0.083	74.77
	0.011	0.093	8.38
	0.036	0.094	2.59
	0.055	0.108	1.95
	0.110	0.142	1.28
	0.222	0.213	0.959
	0.555	0.379	0.683
	1.110	0.333	0.299

It is known that several aqueous complexes are formed in aluminum salt solutions. The first step in the hydrolysis of aluminum chloride can be represented by eq 6. This reaction is followed by the deprotonation of an inner-sphere water molecule (reaction 2).

$$AlCl_3(s) \rightleftharpoons Al(H_2O)_6^{3+} + 3Cl^-(aq) \tag{6}$$

It is likely that the absorption maximum at 240 nm was due to the $Al(OH)(H_2O)_5^{2+}$ complex, which could result in the charge-transfer scheme shown in eq 7.

$$Al^{3+}(OH^-)(H_2O)_5 \rightarrow Al^{2+}(OH)(H_2O)_5 \tag{7}$$

Charge-transfer spectra are most common among the transition-metal complexes that give rise to covalently bonded structures where transfer of charge occurs between the ligand and metal. However, charge-transfer bands can also occur in ion pairs formed by a coordinately saturated complex cation and a polarizable anion. These spectra are commonly known as ion pair charge-transfer bands. According to Balzani et al.,[15] the intensity of these bands depends on the formation constant of the ion pair and on the concentration of the two ions.

The equilibrium constant for reaction 2 is 1.12×10^{-5},[16] and this indicates that the concentration of $Al(OH)(H_2O)_5^{2+}$ is of the order of 10^{-3} M in the concentration range investigated. Experimently it was seen that the intensity of the absorption band at 240 nm was low, which seems to be a direct result of the availability of $Al(OH)(H_2O)_5^{2+}$ for absorption. If $Al(H_2O)_6^{3+}$ was responsible for absorption at 240 nm, then it seems most likely that a more intense absorption band would result since the concentration of $Al(H_2O)_6^{3+}$ exceeds that of $Al(OH)(H_2O)_5^{2+}$. Experimentally this was not observed.

An experiment was conducted by adding 0.75 M sodium sulfate to different volumes of 0.1067 M $AlCl_3$. Figure 2 shows the absorption spectra of two of these solutions. It can be seen that the absorption maximum normally found at 240 nm has been altered and shows up, more or less, as a shoulder and not a distinct maximum. This phenomenon was most likely due to sulfate anion interaction with the inner-sphere groups of aluminum (reactions 3 and 4).

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(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed., Interscience, New York, 1966, p 437.

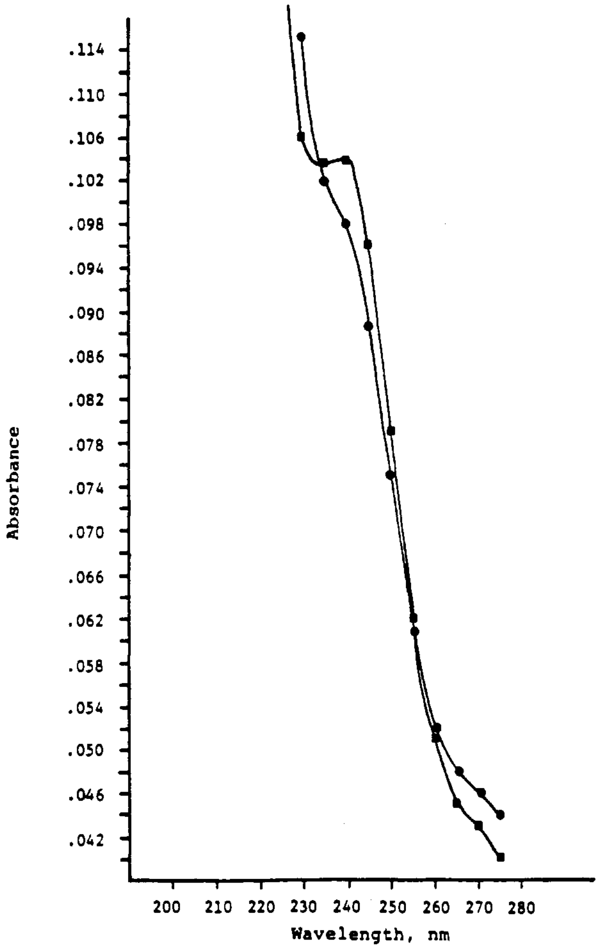

Figure 2. Absorption spectra of $AlCl_3 + Na_2SO_4$: ■, 10 mL of 0.1067 M $AlCl_3$ + 25 mL of 0.75 M Na_2SO_4; ●, 5 mL of 1067 M $AlCl_3$ + 25 mL of 75 M Na_2SO_4.

Table II. Absorbance Values for Solutions of 0.1067 M $AlCl_3$ + 3.0 M NaCl

soln comp	Al^{3+} concn, mol L^{-1}	A
1 mL of 0.1067 M $AlCl_3$ + 100 mL of 3.0 M NaCl	0.00107 M	0.096, 0.093, 0.094, 0.094, 0.093
5 mL of 0.1067 M $AlCl_3$ + 100 mL of 3.0 M NaCl	0.00533 M	0.097, 0.093, 0.094, 0.096, 0.094
10 mL of 0.1067 M $AlCl_3$ + 100 mL of 3.0 M NaCl	0.01067 M	0.098, 0.093, 0.094, 0.098, 0.092

The presence of $Al(SO_4)(H_2O)_5^+$ would necessarily reduce the amount of $Al(OH)(H_2O)_5^{2+}$ available for absorption; however, since reaction 3 is an equilibrium process, then enough of the absorbing species is present to give a noticeable shoulder at 240 nm.

The addition of excess Cl^- to solutions of $AlCl_3$ had no effect on the absorption at 240 nm. A 100-mL quantity of 3.0 M NaCl was added to different volumes of 0.1067 M $AlCl_3$ and the absorption spectra measured (see results in Table II). This result confirms that Cl^- does not interact with the inner-coordination sphere waters of aluminum. The effective concentration of each salt after dilution with NaCl is also listed in Table II. $AlCl_3$ solutions of the same concentration were also measured and a comparison was made. As can be seen by inspection of Tables I and II, the absorbance of each solution was nearly the same. There was no apparent change whether $AlCl_3$ solutions were diluted with aqueous NaCl or water.

Aluminum Perchlorate. Aluminum perchlorate spectra are shown in Figure 3. Table I lists all of the absorption data for the aluminum perchlorate solutions tested. The maximum absorption occurs at 240 nm. A comparison between Figures 1 and 3 will reveal that the spectra of aluminum perchlorate and aluminum chloride are nearly identical.

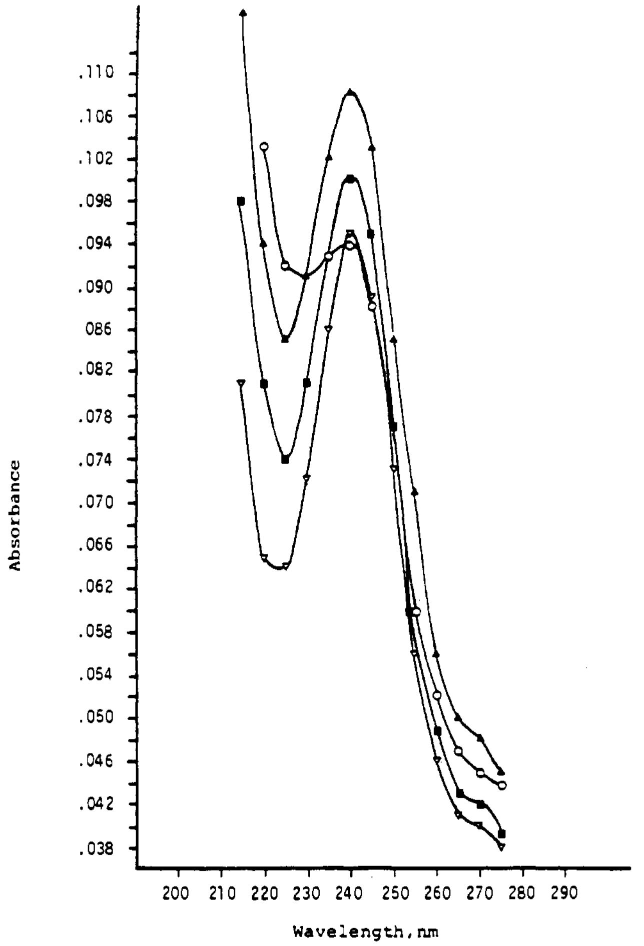

Figure 3. Absorption spectra of aluminum perchlorate: △, 0.0288 M; ■, 0.0570 M; ○, 0.1140 M; ▲, 0.2850 M.

The addition of 0.75 M sodium sulfate to 0.1061 M aluminum perchlorate gave results identical with that of aluminum chloride solutions with excess sodium sulfate added, as shown in Figure 2.

The Beer's law plot for aluminum perchlorate exhibited behavior similar to that of aluminum chloride where the absorbance and concentration were nearly constant, particularly at higher concentration values. The pertinent concentration of absorbing species was obviously different from that used to construct the Beer's law plot. It seems likely that the species $Al(OH)(H_2O)_5^{2+}$ is responsible for absorption at 240 nm rather than the hexahydrated species, $Al(H_2O)_6^{3+}$.

Sulfate anion was assumed to replace the OH of the inner-coordination sphere of aluminum (reaction 3). The production of $Al(SO_4)(H_2O)_5^+$ in solutions of $Al(ClO_4)_3$ and $AlCl_3$ by added SO_4^{2-} resulted in a definite decrease in the absorption maximum at 240 nm. This observation, in turn, confirms the validity of eq 3, suggesting again that the absorbing species is $Al(OH)(H_2O)_5^{2+}$ as postulated for $AlCl_3$ and given by eqation 2.

Aluminum Sulfate. Spectra for $Al_2(SO_4)_3$ solutions are shown in Figure 4. At concentrations below about 0.10 M, the spectra resembled those of $AlCl_3$ and $Al(ClO_4)_3$; however, above 0.10 M the distinct maximum at 240 nm appears as a shoulder.

Inspection of Table I reveals that absorbance values were generally higher for $Al_2(SO_4)_3$ than for $AlCl_3$ and $Al(ClO_4)_3$. A plot of absorbance vs. concentration over the concentration

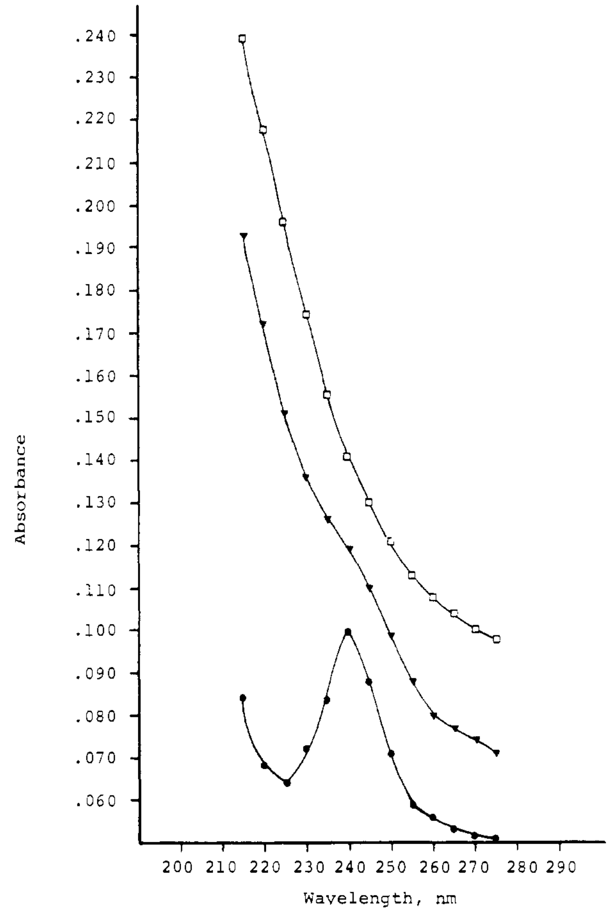

Figure 4. Absorption spectra of aluminum sulfate: □, 0.111 M; ▼, 0.222 M; ●, 0.0111 M.

Table III. Ultraviolet Absorption Data at 303 nm for Aqueous $Al(NO_3)_3 \cdot 9H_2O$

concn, mol L^{-1}	absorb	molar absorp	concn, mol L^{-1}	absorb	molar absorp
0.0010	0.066	63.46	0.0521	1.150	22.07
0.0052	0.083	15.93	0.1040	2.173	20.89
0.0104	0.256	24.61			

range 0.0011–0.555 M is linear, indicating that absorption in aluminum sulfate solutions follows Beer's law as contrasted with the behavior in $AlCl_3$ and $Al(ClO_4)_3$ solutions, suggesting that a different charge-transfer mechanism operates in the sulfate case. The position of the absorption maximum was not altered for $Al_2(SO_4)_3$ but merely reduced to a shoulder at high sulfate concentrations. On the other hand it appears that in the chloride and perchlorate cases, sulfate anion was actually interfering with the major absorbing process.

The absence of a distinct maximum at higher concentrations was most likely due to an increase in the interaction with the inner-coordination sphere to Al(III) by sulfate, as proposed earlier with the addition of Na_2SO_4 to solutions of $AlCl_3$ and $Al(ClO_4)_3$. Excess Na_2SO_4 (0.75 M) added to 0.0111 M $Al_2(SO_4)_3$ resulted in the elimination of the distinct maximum at 240 nm. These results clearly indicated that equilibrium reaction 3 dominanted at higher SO_4^{2-} concentrations with the equilibrium shifting to the right and reducing the concentration of the $Al(OH)(H_2O)_5^{2+}$ absorbing species.

Aluminum Nitrate. Typical spectra for aluminum nitrate are shown in Figure 5, and Table III lists the absorption data at 303 nm. The spectra are dominated by a maximum at 303 nm which was a direct function of the nitrate concentration. The addition of excess nitrate ion, as $NaNO_3$, to solutions of $AlCl_3$ and $Al(ClO_4)_3$ resulted in spectra similar to those for pure $Al(NO_3)_3$ solutions. Absorption increased rapidly below about 260 nm and absorbance values exceeded 2.5, with no maximum being observed. This dependence on nitrate concentration was also observed by Henry et al.[4] at 295 nm for nitrate solutions.

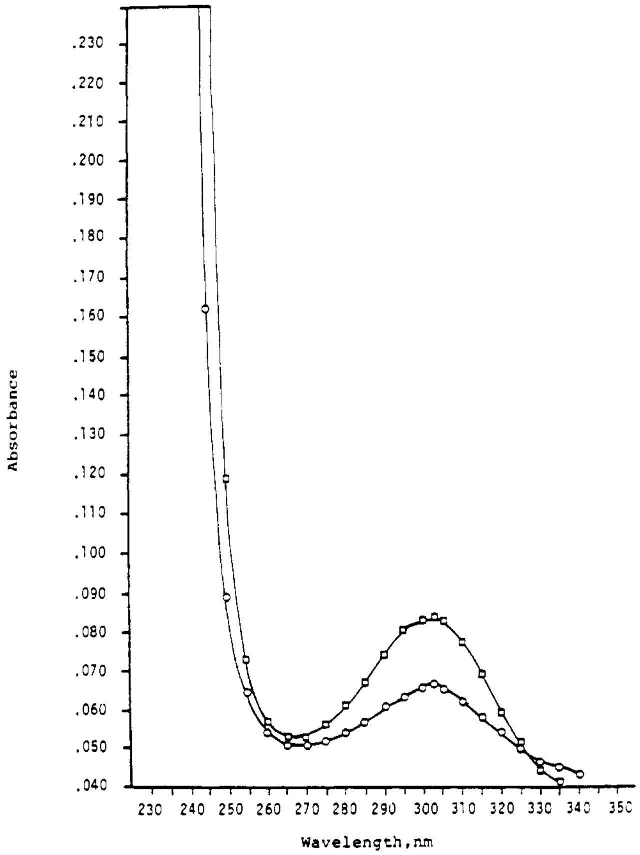

Figure 5. Absorption spectra of aluminum nitrate: ○, 0.0014 M; □, 0.0052 M.

NMR studies[10-13] suggest that nitrate interacts with Al(III) through one water molecule; that is, the ion pair formed is solvent separated. Like $AlCl_3$, $Al(ClO_4)_3$, and $Al_2(SO_4)_3$, $Al(NO_3)_3$ is completely ionized upon dissolution. $Al(H_2O)_6^{3+}$ would most likely give rise to the formation of $Al(OH)(H_2O)_5^{2+}$ which should exhibit an absorption maximum at 240 nm; however, the nitrate ion seems to form a complex wherein NO_3^- interacts or interferes with $Al(OH)(H_2O)_5^{2+}$ and $Al(H_2O)_6^{3+}$. Raman studies by Hester et al.[17] gave evidence for ion pairing in the spectra of nitrate solutions.

Conductivity Measurements. Conductivity measurements were obtained for the four aluminum salts. Since electrolytic conductance is dependent on the number and charge of the current carrying species, ion pair formation will lower the conductivity of a given solution. Spectroscopic results indicated that sulfate anions displaced inner-coordinate sphere water or hydroxide molecules of Al(III). The formation of $Al(SO_4)(H_2O)_5^+$ would be expected to cause a decrease in the conductivity of a given aluminum sulfate solution, and this was observed experimently.

Figure 6 shows a plot of equivalent conductance vs. the square root of the concentration for $AlCl_3$, $Al(ClO_4)_3$, $Al(NO_3)_3$, and $Al_2(SO_4)_3$. The first three salts exhibited linear behavior over the concentration range investigated as expected for strong electrolytes; however, $Al_2(SO_4)_3$ deviated from linearity at higher concentration values, above about 0.555 M, and showed appreciably lower conductances. This deviation was interpreted to be due to an increase in sulfate substitution

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[17] R. E. Hester and R. A. Plane, *Inorg. Chem.* 3, 769 (1964).

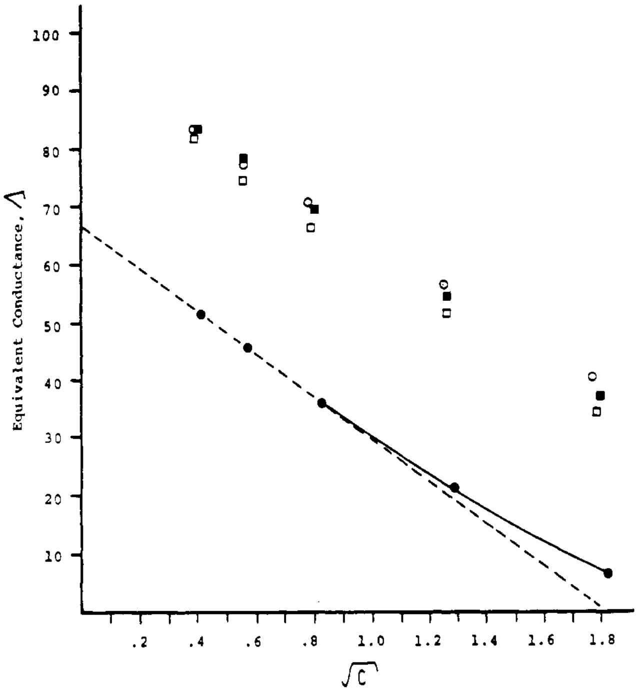

Figure 6. Equivalent conductance vs. the square root of the concentration: ■, $AlCl_3$; □ $Al(ClO_4)_3$; ○, $Al(NO_3)_3$; ●, $Al_2(SO_4)_3$.

Table IV. Conductance Data at 25 °C

salt	concn, N	conduct, Ω^{-1}	specific conduct Ω^{-1} cm^{-1}	equiv conduct	$C^{1/2}$
$AlCl_3$	0.160	0.00106	0.0134	83.56	0.40
	0.320	0.00199	0.0250	78.25	0.56
	0.640	0.00352	0.0442	69.08	0.80
	1.600	0.00691	0.0863	54.26	1.26
	3.201	0.00961	0.1207	37.60	1.80
$Al_2(SO_4)_3$	0.166	0.00069	0.0087	52.16	0.41
	0.333	0.00122	0.0153	46.01	0.57
	0.666	0.00194	0.0244	36.60	0.82
	1.665	0.00287	0.0361	21.66	1.29
	3.333	0.00185	0.0233	6.98	1.82
$Al(ClO_4)_3$	0.159	0.00104	0.0130	81.63	0.39
	0.318	0.00193	0.0242	74.65	0.56
	0.636	0.00351	0.0441	66.08	0.79
	1.590	0.00704	0.0884	51.71	1.26
	3.183	0.01000	0.1255	34.39	1.78
$Al(NO_3)_3$	0.156	0.00103	0.0129	83.39	0.39
	0.312	0.00189	0.0237	77.53	0.56
	0.624	0.00335	0.0420	70.66	0.78
	1.563	0.00655	0.0822	56.56	1.25
	3.120	0.00872	0.1094	40.24	1.77

with inner-sphere higher concentrations.

Table IV gives the conductance data. It should be pointed out that the concentration range studied was substantially higher than that covered by theoretical laws, e.g., Debye–Hückel–Onsager up to 0.01 M and the Davies equation up to 0.1 M. Extrapolation to infinite dilution, according to theory, to achieve a limiting conductance value must be made in the dilute range. However, the ratio of the equivalent conductance at a given concentration to the theoretical Λ_0 can be considered as a qualitative measure of ion pairing or at least a measure of the total effect of the ion atmosphere.

A theoretical Λ_0 can be calculated by using Kohlrausch's law of independent migration (eq 8). Values for Cl^-, ClO_4^-,

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- \qquad (8)$$

NO_3^-, and SO_4^{2-} are available from the literature:[18] 76.35, 68.00, 71.44, and 159.62 respectively; and the λ_0^+ for Al(III) as determined by Frink et al.[19] is 59.70.

From these conductance measurements it is concluded that $AlCl_3$ and $Al(ClO_4)_3$ solutions have $Al(OH)(H_2O)_5^{2+}$ and $Al(H_2O)_6^{3+}$ as the principal charge carriers whereas $Al_2(SO_4)_3$ solutions will have $Al(SO_4)(H_2O)_5^+$ as well. If $Al(SO_4)(H_2O)_5^+$ predominates over $Al(OH)(H_2O)_5^{2+}$, then the conductance will be significantly lower for $Al_2(SO_4)_3$ solutions. Experimentally this was observed.

Conclusion and Summary

The wavelength of maximum absorption for $AlCl_3$, $Al(ClO_4)_3$, and $Al_2(SO_4)_3$ was located at 240 nm. $Al(NO_3)_3$ exhibited a maximum absorption at approximately 303 nm; it also absorbed in the 240 nm range, but no maximum was observed because absorbance values were above 2.5.

Sato's[5] investigation of sodium aluminate solutions revealed an absorption maximum at 230 nm which was attributed to the hydrated aluminum cation $Al(H_2O)_6^{3+}$. The solutions tested in this investigation were at pH values below those solutions investigated by Sato. And after consideration that pH strongly affects the nature of complexes, a slight shift in the hydrated aluminum cation absorption maximum is not surprising.

The absorption spectra for $AlCl_3$ and $Al(ClO_4)_3$ were nearly identical, and all the experimental evidence indicates that Cl^- and ClO_4^- ions do not interact with the inner-coordination sphere of aluminum. Conductance measurements support this conclusion.

$Al_2(SO_4)_3$ solutions, particularly at high concentrations, differed from $AlCl_3$ and $Al(ClO_4)_3$ solutions in that SO_4^{2-} replaced an inner-sphere group according to eq 3. The formation of $Al(SO_4)(H_2O)_5^+$ reduced the absorption maximum at 240 nm to a shoulder, and eventually at high enough concentrations of SO_4^{2-} the maximum vanished. The formation of $Al(SO_4)(H_2O)_5^+$ was supported by conductance data. Not only were the equivalent conductance values lower than the values observed for the other three salts at comparable concentrations, but at higher concentrations of SO_4^{2-} the conductance decreased below values observed for lower concentrations. This result was most likely due to the reduced charge of the $Al(SO_4)(H_2O)_5^+$ complex as compared to charge carriers such as $Al(H_2O)_6^{3+}$ and $Al(OH)(H_2O)_5^{2+}$. The absorption spectra for $Al_2(SO_4)_3$ at low concentrations was very similar to that of $AlCl_3$ and $Al(ClO_4)_3$.

$Al(NO_3)_3$ solutions were characterized by an absorption at 303 nm, which was a function of the NO_3^- concentration. At all concentrations of $Al(NO_3)_3$, it was observed that no absorption maximum occurred at 240 nm; however, absorbance readings were found to exceed 2.5. Experimental results gave no evidence for NO_3^- substitution into the inner-coordination sphere of Al(III). NMR studies[10-13] indicated that NO_3^- interactions are limited to solvent separated ion pairs. But, this does not explain the absence of the 240-nm absorption peak, in the same manner as aluminum sulfate. Conductance data supported the postulate that aluminum sulfate was substituting into the inner-coordination sphere of Al(III); however, the same results were not found for NO_3^-; in fact, aluminum nitrate behaved like aluminum chloride and perchlorate.

The results of this investigation suggest the following:

(1) The charge-transfer reaction

$$Al^{3+}(OH^-)(H_2O)_5 \rightarrow Al^{2+}(OH)(H_2O)_5$$

is responsible for absorption at 240 nm.

(2) Sulfate anion replaces an inner-sphere group of aluminum to give the $Al(SO_4)(H_2O)_5^+$ complex, causing a reduction of the absorption maximum at 240 nm.

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(3) Aluminum nitrate spectra are dominated by the 303-nm absorption peak, which is a direct function of NO_3^- concentration. No maximum at 240 nm is observed.

(4) Cl^- and ClO_4^- do not replace inner-sphere groups.

(5) Equivalent conductance measurements support the conclusions of the spectroscopic investigation.

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Registry No. $AlCl_3$, 7446-70-0; $Al(ClO_4)_3$, 14452-39-2; $Al_2(SO_4)_3$, 10043-01-3; $Al(NO_3)_3$, 13473-90-0.

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Photooxidation of 1,2-Dithiolene Complexes of Nickel, Palladium, and Platinum in Chloroform

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The photochemistry of the following 1,2-dithiolene complexes has been investigated. $M(S_2C_2R_2)_2^z$: M = Ni, Pd, Pt, R = CN, z = 2–, 1–; M = Ni, Pt, R = C_6H_5, z = 0; M = Ni, R = C_6H_5, z = 1–. These complexes were not light sensitive in most solvents such as acetonitrile. Those complexes which are oxidized at potentials between $E_{1/2}$ = 0.1 and 0.5 V vs. SCE (M = Ni, Pd, Pt, R = CN, z = 2–; M = Ni, R = C_6H_5, z = 1–) were photooxidized in $CHCl_3$ with light of wavelengths between 300 and 350 nm. The other complexes which are oxidized at higher potentials are not light sensitive in $CHCl_3$. It is suggested that the reactive excited state is of the charge-transfer-to-solvent (CTTS) type. The energy of this state depends only on the redox potentials of the complex and the solvent. When $CHCl_3$ as solvent was replaced by the stronger oxidant CCl_4, the photoactive wavelength region was shifted to the red. It was blue shifted when the weaker oxident CH_2Cl_2 was used. The CTTS states may be reached by internal conversion from higher intramolecular excited states. Direct light absorption by CTTS bands is not necessary to initiate the photooxidation.

Introduction

The photooxidation of coordination compounds may occur by quite different mechanisms. Bimolecular electron transfer from electronically excited transition-metal complexes to reducing agents has been extensively investigated recently.[1,2] Another example is the photooxidation of certain cyanide complexes in aqueous solution accompanied by the production of solvated electrons.[3,4] However, the majority of photooxidations of a great variety of transition-metal complexes has been observed in halocarbon solvents; where solvent molecules act as electron acceptors.[5-10] Although charge-transfer-to-solvent (CTTS) states may be important in some cases,[5,6,9] the nature of the photoactive excited states does not seem to be very clear. The present study may contribute to a better understanding of these photooxidations.

For our investigation we selected 1,2-dithiolene complexes[11] of Ni, Pd, and Pt. This choice was guided by the following considerations. By a variation of the metal, the dithiolene ligand, and the charge of the complex, its electronic structure can be altered to a great extent. It was expected that such changes would influence the photochemical behavior considerably and lead to a correlation between electronic structure and photoreactivity.

Another interesting aspect of the present study is the growing interest in coordination compounds with sulfur-coordinating ligands[12] due to their importance in biological systems. So far only a few investigations of the photochemistry of sulfur-containing complexes have been carried out[8,9,13] although such complexes are known to participate in photosynthesis.[12]

Experimental Section

Materials. The complexes $[N(C_2H_5)_4]_2\{M[S_2C_2(CN)_2]_2\}$, with M = Ni,[14] Pd,[15] and Pt,[14] $\{M[S_2C_2(C_6H_5)_2]_2\}$, with M = Ni, Pt,[16] and $[N(C_2H_5)_4]\{Ni[S_2C_2(C_6H_5)_2]_2\}$[17] were prepared according to published procedures. Their electronic absorption spectra agreed well with those reported previously.[16-19] All solvents used in the photochemical

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