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Light-scattering Studies on Aqueous Aluminum Nitrate Solutions

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Rayleigh turbidities and refractive index increments were measured for solutions of aluminum nitrate with from zero to 2.25 hydroxide ions added per aluminum ion, and over the total aluminum concentration range of 0.1 to 1.0 *M*. The weight average number of aluminum atoms per solute cation has been calculated for each OH/Al ratio and is shown to be in reasonable agreement with number average number of aluminum atoms per solute cation reported by earlier investigators.

The hydrolysis of aqueous aluminum(III) solutions has been studied previously. The initial step, at high H⁺/Al⁺⁺⁺ ratios, is believed to be Al(OH₂)₆⁺⁺⁺ = Al(OH₂)₅OH⁺⁺ + H⁺.²⁻⁴ Jander and Winkel⁵ have demonstrated the existence of higher molecular weight solute species by measuring diffusion coefficients in solutions of basic aluminum salts. Their results are cited as evidence for the aggregation of monomeric hydrolysis products. The effect of basic aluminum nitrate solutions on the freezing point of KNO₃-H₂O eutectic mixtures has been explained by Jahr and Brechlin⁶ in terms of cationic aggregation. The latter authors find the average number of aluminum atoms per aggregate to be a continuous function of the amount of base added, varying from 1 to 9.2 before precipitation of the hydrous oxide occurs.

The light scattering technique is, in principle, capable of measuring the degree of dispersity of a given quantity of matter. It has been used to measure degree of aggregation in a very limited number of inorganic systems.⁷⁻¹⁰ This paper is the first in a series of studies in cationic aggregation using the technique. The treatment follows the

development of Debye for solutions of polymers,¹¹ whereby

$$\frac{Hc}{\tau} = \frac{1}{M} + \frac{2Bc}{RT} \quad (1)$$

and

$$H = \frac{32\pi^3 n_0^2 (dn/dc)^2}{3N\lambda^4} \quad (2)$$

c = concn. expressed in g./ml.

τ = turbidity expressed in cm.⁻¹

*n*₀ = refractive index of the solvent

N = Avogadro's number

λ = wave length of light expressed in cm.

B = interaction constant related to the second virial coefficient

dn/dc = rate of change of refractive index with concn.

M = weight average molecular weight

The turbidity is determined as a function of concentration. The molecular weight is the reciprocal of the intercept at *c* = 0 of a plot of *Hc*/ τ vs. *c*.

Experimental

Materials and Preparation of Solutions.—Merck reagent grade Al(NO₃)₃·9H₂O was recrystallized from dilute nitric acid solution and dried by passing dry nitrogen through the crystals for several hours at 40°. A stock solution of aluminum nitrate was prepared from the crystals. Its aluminum content was determined by precipitation of the hydrous oxide, followed by ignition. The nitrate concentration was determined by the nitron method.¹² The NO₃⁻/Al was found to be 2.986. Baker reagent grade NaNO₂ and Na₂CO₃ were dried overnight at 110° and used without further purification. Baker reagent grade thiophene-free benzene and Baker reagent grade carbon tetrachloride were purified by fractionation in a 15 mm. × 30 cm., vacuum-jacketed column packed with 1/8" helices.

Portions of Na₂CO₃ calculated to give OH/Al ratios of 0.5, 1.0, 1.5, 1.75, 2.0, 2.25 and 2.5 were added to aliquots

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(7) P. Debye and R. V. Nauman, *J. Chem. Phys.*, **17**, 664 (1949).
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TABLE I

OH/Al = Al molarity	$\Delta n \times 10^3$						
	0	0.5	1.0	1.5	1.75	2.0	2.25
1.0	35.605	34.959	34.856	34.254	34.012	33.772	33.442
0.8	28.941	28.413	28.128	27.738	27.566	27.361	27.199
.6	21.852	21.562	21.330	21.081	20.891	20.823	20.686
.4	14.719	14.541	14.366	14.273	14.173	14.103	14.059
.2	7.462	7.317	7.291	7.213	7.205	7.195	7.147
.1	3.768	3.709	3.702	3.642	3.623	3.640	3.619
.05	1.893	1.857	1.835	1.812	1.812	1.826
.025	0.936	0.918	0.914	0.901	0.908	0.910
.0125	0.467	0.465	0.457	0.452	0.456	0.454

of the $\text{Al}(\text{NO}_3)_3$ stock solution. The aliquots were such as to yield (upon dilution) 500 ml. of a new stock solution 1 *M* in total aluminum for each ratio. Dilutions of these new stock solutions were made so as to give 100 ml. each of solutions which were 0.1, 0.2, 0.4, 0.6, 0.7, 0.8, 0.9 and 1.0 molar in aluminum for each OH/Al ratio. A similar set of dilutions was performed on a pure $\text{Al}(\text{NO}_3)_3$ solution, *i.e.*, OH/Al = 0.

Instruments and Measurements.—Refractive index increments were determined with a Brice-Phoenix differential refractometer¹³ using light of 436 μ wave length. Calibration of the instrument was accomplished with sucrose solutions and light of 589 μ wave length. Data supplied by the manufacturer¹⁴ permits the calculation of the instrument constant for 436 μ light. Refractive index increments were determined for all aluminum solutions and a series of sodium nitrate solutions.

Turbidities of solutions were determined with a light scattering photometer fabricated in this department,¹⁰ after the design of Brice.¹⁵ All measurements were made at $25 \pm 2^\circ$ using 436 μ light. Benzene was used as a secondary standard.

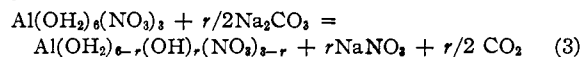
Clarification of the solutions was carried out by filtration, under pressure, through ultra-fine fritted filters, directly into the scattering cells. The latter were inclosed in dust-proof chambers. A determination was made of the refractive index of the most concentrated solution in each series before and after filtration as a check on possible loss of solute during the filtration process. By such a procedure changes in concentration as small as 1×10^{-6} g./ml. can be detected. Since the refractive indices of the solutions before and after filtration were the same, it is assumed that the filtration procedure removed no solute particles.

τ -Values were determined for all of the aluminum-containing solutions except the OH/Al = 2.5 series. No value was accepted unless it was constant through three filtrations. The measurements were made on solutions which had been allowed to age for six months. At that time the OH/Al = 2.5 series of solutions had become colloidal and visibly turbid. No angular dependency was observed in the scattering pattern from any of the aluminum-containing solutions.

Results and Calculations

Indices of Refraction and Evaluation of *H*.

The refractive index increment with concentration of NaNO_3 is constant and equal to 0.1156 cc./g. Gross Δn values for the aluminum-containing solutions are listed in Table I. We have assumed the following reaction as representative of the hydrolysis



where $r = \text{OH}/\text{Al}$. Assuming that no reaction occurs between the NaNO_3 and the aluminum species, the contribution of the NaNO_3 to a given Δn value in Table I can be calculated.¹⁶ Sub-

traction of this value from the gross Δn value gives a Δn value due solely to aluminum-containing species (with associated nitrated anions). It has been assumed that the reaction between $\text{Al}(\text{NO}_3)_3$ and Na_2CO_3 is complete, leaving no carbonate or bicarbonate in solution. A few solutions having OH/Al values of 0.5, 1.0 and 1.5 were prepared using NaOH. τ -Values of these solutions agreed with τ -values of the corresponding solutions prepared with Na_2CO_3 .

It is found that the corrected rate of change of n increases slightly with decreasing aluminum concentration for solutions of the same r . The value levels off to a constant at concentrations below 0.2 *M* total aluminum. Therefore several dilutions were made below 0.1 *M* for each r value studied. The constant value of $(\Delta n/c)_{\text{Al}}$ thus obtained was used to calculate *H* values for use in equation 1. It is our present feeling that the decrease in $(\Delta n/c)_{\text{Al}}$ with increasing aluminum concentration can be explained by assuming that some dissociation of polymeric aluminum species occurs upon dilution even at constant r . It is seen (Table I) that gross Δn values decrease as r increases, for constant total aluminum concentration. The essential difference between a molar solution of aluminum nitrate and a molar solution of basic aluminum nitrate of $r = 2$ is an additional two moles/l. of sodium ions. However the increase in Δn expected from the additional sodium ions is more than offset by a decrease in Δn due to increased aggregation of aluminum. A sample calculation of *H* is reviewed, using data on the solution of $r = 1.5$, 0.1 *M* in Al.

$$\text{Concn. NaNO}_3 = \frac{r \times M \times \text{mol. wt.}}{1000} = \frac{1.5 \times 0.1 \times 85}{1000} = 12.75 \times 10^{-3} \text{ g./ml.}$$

$$\Delta n \text{ due to NaNO}_3 = 0.1156 \times 12.75 \times 10^{-3} = 1.474 \times 10^{-3}$$

$$\Delta n \text{ due to Al species} = (3.642 - 1.474) \times 10^{-3} = 2.168 \times 10^{-3}$$

$$\text{Mol. wt. Al}(\text{OH})_{4.5}(\text{OH})_{1.5}(\text{NO}_3)_{1.5} = 226.5$$

$$(\Delta n/c)_{\text{Al}} = \frac{2.168 \times 10^{-3}}{226.5 \times 10^{-4}} = 9.57 \times 10^{-2} \text{ ml./g.} = dn/dc$$

$$H = \frac{32 \times (3.14)^3 \times (1.34)^2 \times (9.57 \times 10^{-2})^2}{3 \times 6.02 \times 10^{23} \times (436 \times 10^{-7})^4} = 2.50 \times 10^{-6}$$

Turbidity Values.—It is assumed that the τ values for the several solutes in a solution are additive. Table II and Table III give the necessary τ -values. The τ -value due to aluminum

(13) B. A. Brice and M. Halwer, *J. Opt. Soc. Am.*, **41**, 1033 (1951).

(14) Phoenix Precision Instrument Co., 3803 N. Fifth St., Philadelphia 40.

(15) B. A. Brice, *et al.*, *J. Opt. Soc. Am.*, **40**, 768 (1950).

(16) T. G. Berg, *Z. anorg. allgem. Chem.*, **273**, 291 (1943).

species in a given solution was obtained by subtracting the τ for water and the τ for the appropriate concentration of NaNO_3 from the uncorrected τ -value. Corrected τ -values are reported in Table III.

Obsd. τ (cm. ⁻¹)	Molar concn.	Substance
6.19×10^{-5}	..	Water
7.71×10^{-5}	..	Benzene (436 $m\mu$) ¹⁷
10.45×10^{-5}	2.0	Aq. sodium nitrate
9.55×10^{-5}	1.6	Aq. sodium nitrate
8.78×10^{-5}	1.2	Aq. sodium nitrate
8.52×10^{-5}	1.0	Aq. sodium nitrate
7.61×10^{-5}	0.8	Aq. sodium nitrate
7.49×10^{-5}	.6	Aq. sodium nitrate
7.10×10^{-5}	.4	Aq. sodium nitrate
6.58×10^{-5}	.2	Aq. sodium nitrate

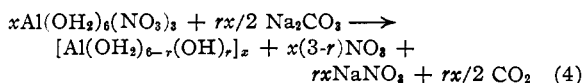
OH/Al = τ = Al molarity	$\tau \times 10^{14}$ (cm. ⁻¹)						
	0	0.5	1.0	1.5	1.75	2.0	2.25
1.0	7.22	8.89	13.9	21.5	25.9	28.7	31.6
0.9	6.84	8.77	13.3	20.1	24.0	26.3	28.7
.8	6.34	8.25	12.4	18.2	21.5	24.1	26.9
.7	6.08	7.61	11.2	16.4	19.2	21.7	24.2
.6	5.57	7.22	10.1	14.6	17.0	19.2	21.5
.4	4.43	5.93	7.48	10.3	11.6	13.0	14.2
.2	2.03	3.35	4.00	5.54	5.67	6.32	6.83
.1	1.01	1.93	2.58	2.71	3.09	3.35	3.35

Estimation of Aggregation.—Figure 1 is a plot of Hc/τ vs. c for the several series of solutions. The decrease in slope as τ increases is to be expected. The slope depends on B , an interaction parameter, and, if for no other reason, the amount of interaction should fall off as the concentration of indifferent electrolyte (NaNO_3) builds up. In addition the charge density on the solute species is probably decreasing as τ increases. When plotted on a larger scale, it is noted that the curves turn upward slightly at very low concentrations. It is possible that this effect is the result of dissociation of the aggregates upon dilution. If so, then the molecular weights obtained are not only an average of the species present at a given concentration but also an average of the species present over a concentration range.

The reciprocal of the intercepts in Fig. 1 gives weight average molecular weights, defined as

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

where n_i is the number of particles of weight M_i . Table IV gives values of M_w calculated from Fig. 1. Using equation 4 the weight average number



of aluminum atoms associated with each polymeric cation is given by the relationship

$$X_w = \frac{M_{\text{exp}}M - (3-r)M^2\text{NO}_3}{M^2 \text{cation}}$$

(17) L. M. Kushner, *J. Opt. Soc. Am.*, **44**, 155 (1954).

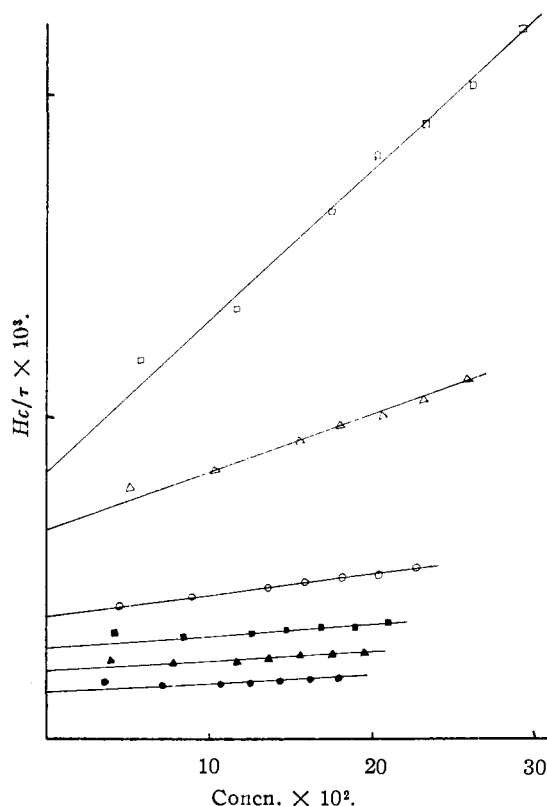


Fig. 1.—Concentration expressed in grams/ml. $\times 10^2$: \square , OH/Al = 0.5; Δ , OH/Al = 1.0; \circ , OH/Al = 1.5; \blacksquare , OH/Al = 1.75; \blacktriangle , OH/Al = 2.0; \bullet , OH/Al = 2.25.

where M_{exp} = the value calculated from Fig. 1, M = mol. wt. un-ionized species $\text{Al}(\text{OH}_2)_{6-r}(\text{OH})_r(\text{NO}_3)_{3-r}$, M_{cation} = mol. wt. of the cation $\text{Al}(\text{OH}_2)_{6-r}(\text{OH})_r$, M_{NO_3} = mol. wt. of nitrate ion. Figure 2 shows X_w plotted as a function of τ .

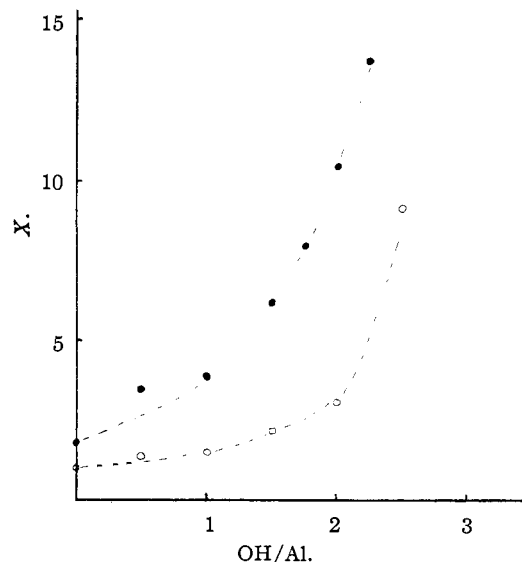


Fig. 2.— \bullet , X_w ; \circ , X_n .

For comparison, X_n (number average number) is plotted using data from Jahr and Brechlin.⁶

It should be noted that if the aluminum ion is not considered to have a constant coordination number

of six, quite different values of X_w are obtained; in fact X_w for pure $\text{Al}(\text{NO}_3)_3$ comes out to be about 10 if all calculations are based on anhydrous salts.

OH/Al	M_w	OH/Al	M_w
0	138	1.75	715
0.5	256	2.0	1000
1.0	308	2.25	1430
1.5	526		

Discussion

τ -Values were obtained on freshly prepared solutions as a function of time in order to be sure that our data do represent equilibrium conditions. In the case reported, Na_2CO_3 was added to a solution of $\text{Al}(\text{NO}_3)_3$ in sufficient quantity to give an OH/Al of 1.5. Hydrous oxide precipitated immediately, but the solution cleared upon shaking for ten minutes. Following two filtrations τ was measured until no further change could be detected after waiting several hours. From the data presented in Table V, it is clear that equilibrium is established in about a week. It would appear that the dissolution of hydrous oxide to form small solute aggregates (basic salts) is much slower than the precipitation reaction.^{18,19} It is considered likely that some unprecipitated aluminum species reacts with hydrous oxide, forming large but soluble aggregates. These aggregates are then hydrolytically cleaved to smaller aggregates or are attacked by more of the unprecipitated aluminum species. Such a mechanism is considered as the most likely explanation of the decrease in scattering with time.

(18) W. D. Treadwell and M. Zurcher, *Helv. Chim. Acta*, **15**, 980 (1933).

(19) W. D. Treadwell and J. E. Boner, *ibid.*, **17**, 774 (1934).

Note that the equilibrium τ -value agrees well with the value recorded for the same solution in Table III. It is believed that all values recorded in Table III are representative of true equilibrium conditions.

Time (hr.)	$\tau \times 10^4$ in cm.^{-1} ($r = 1.5, 0.4 M \text{ Al}$)	Time (hr.)	$\tau \times 10^4$ in cm.^{-1} ($r = 1.5, 0.4 M \text{ Al}$)
1	75.5	29	14.8
1.5	72.1	77	11.9
4	60.7	181	10.6
7	50.8	270	10.7
10	41.8	450	10.6

The interpretation of the existing data in terms of an exact hydrolysis mechanism is, of course, impossible. However, we are inclined to the view that there exists in a given solution a distribution of aluminum atoms among a number of aggregates, the average of which increases with increasing OH/Al ratio. Sillen²⁰ suggests that $\text{Al}_6(\text{OH})_{15}^{+3}$ is the most important species over the entire range of basicity, although he admits that his interpretation is not final. The values of X_w and X_n for the high OH/Al ratios indicate numerous aggregates containing more than six atoms of aluminum. Furthermore if one calculates X_w and X_n for the hydrolysis of bismuth²¹ based on the assumption of a continuous aggregation mechanism and compares the relative shape of the two curves to those in Fig. 2, reasonable agreement is found. Of course, the curves for bismuth are displaced toward lower values of OH/Bi.

(20) L. G. Sillen, *Acta Chem. Scand.*, **8**, 1917 (1954).

(21) L. G. Sillen and F. Graner, *ibid.*, **1**, 331 (1947).

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Vapor Pressures of Aluminum Chloride, Aluminum Bromide and the Mixed Halide Phase $\text{Al}_2\text{Br}_2\text{Cl}_4$

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Vapor pressures of Al_2Cl_6 , Al_2Br_6 and $\text{Al}_2\text{Br}_2\text{Cl}_4$ have been measured between 0 and 40° by the effusion method. The mixed halide vapor pressure is about thirty times larger than that of the chloride and one quarter of that of the bromide at room temperature. No dependence of pressures (within experimental error) on cell geometry could be detected.

At room temperature hydrogen chloride reacts with anhydrous aluminum bromide liberating hydrogen bromide; the resulting chlorine containing aluminum compounds and aluminum bromide form a solid solution until the chlorine content reaches *ca.* 18 mole %. Further reaction produces a mixed halide phase with composition near that of $\text{Al}_2\text{Br}_2\text{Cl}_4$ (65–69 mole % chloride). The characteristics of this halogen exchange reaction and of the aluminum chloride–aluminum bromide system have been discussed in some detail in an earlier paper¹; at room temperature the mixed halide phase is quite resistant to reaction with hydrogen chloride and it has been postulated that the remaining bromine

atoms are in the bridge positions of dimeric aluminum halide molecules. Structural evidence (from X-ray powder patterns) indicates that the mixed halide phase is isomorphous with aluminum chloride,² $C2/m$; the existence of molecular dimers in crystals of aluminum chloride is not as pronounced as in aluminum bromide which has a different crystal structure,³ $P2_1/a$.

Continuing a study of the mixed halide phase we have measured its vapor pressure and that of aluminum chloride and aluminum bromide at temperatures from 0 to 40°, using the effusion technique. Vapor pressures of aluminum chloride and aluminum

(1) J. D. Corbett and N. W. Gregory, *THIS JOURNAL*, **75**, 5238 (1953).

(2) J. A. A. Ketelaar, C. H. MacGillavry and P. A. Renes, *Rec. trav. chim.*, **66**, 501 (1947).

(3) P. A. Renes and C. H. MacGillavry, *ibid.*, **64**, 275 (1945).