[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Light Scattering Studies on Aqueous Gallium Perchlorate Solutions

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Rayleigh turbidities and refractive index increments were measured for solutions of gallium perchlorate with from zero to 1.75 hydroxide ions added per gallium ion and over a total gallium concentration range of 0.05 to 0.8 *M*. The weight average number of gallium atoms per aggregate after six weeks aging has been calculated for each OH/Ga ratio. *p*H measurements on solutions with zero to 1.75 hydroxide ions added per gallium ion and over a total gallium concentration range of 0.005 to 0.04 *M* were made and are interpreted in terms of Sillen's core-link hypothesis.

Relatively little work has been published on the hydrolysis of aqueous gallium salts. The most general method of approach used by early investigators[2-5] was the determination of *p*H of dilute solutions as functions of total gallium concentration and base added. The hydrolysis constants calculated on the assumption that only the species $Ga(OH)^{++}$ and $Ga(OH)_2^+$ were present are not consistent. Moeller and King,[6] using a similar technique, found that nearly three moles of base was consumed before permanent precipitation occurred. They agreed that the steady consumption of base indicated that either the hydrous oxide was being peptized or that polymeric gallium-containing species were present in solution. Using a polarographic technique[7] they obtained evidence for polymeric cation formation but were unable to elucidate a mechanism or to indicate the size of the particles being formed. Using the isopiestic technique, Patterson[8] measured the vapor pressure of gallium perchlorate solutions with from zero to 2.5 hydroxide ions added per gallium atom. His data were interpreted in terms of an oxygen-bridging mechanism of hydrolysis, and figures were reported for the average number of gallium atoms per aggregate as a function of OH/Ga.

The present paper is the second in a series on cationic aggregation using the light-scattering technique. We report herewith the data on basic gallium perchlorate solutions. The treatment of the data is identical with that used in the first paper on aluminum solutions.[9]

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

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

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 av. mol. wt.

L. G. Sillen and co-workers have developed an extensive mathematic alanalysis of complex formation based on the hypothesis that the complex can be described as being composed of a core plus numbers of identical links.[10,11] *p*H measurements were made on three series of basic gallium perchlorate solutions and the data analyzed by the Sillen technique.

Experimental

Materials and Preparation of Solutions.—The $Ga(ClO_4)_3 \cdot 6H_2O$ used was prepared and analyzed by the methods previously reported.[12] Since the supply of gallium was insufficient to prepare all of the solutions at the same time, two series of solutions were prepared at a time. After measurement the gallium was recovered, reconverted to the perchlorate and used to make up the next two series. Each lot of $Ga(ClO_4)_3 \cdot 6H_2O$ was analyzed for both gallium and perchlorate. The ClO_4/Ga ratios for the several samples used were 2.963, 3.022, 3.000, 3.022 and 3.010. The average composition corresponded to $Ga(ClO_4)_3 \cdot 5.5H_2O$. J. T. Baker reagent grade sodium carbonate and Merck reagent grade potassium acid phthalate and potassium bitartrate were used without further purification except for drying overnight at 110°.

Portions of Na_2CO_3 calculated to give OH/Ga ratios of 0.0, 0.5, 1.0, 1.5, 1.75 and 2.0 were added to aliquots of $Ga(ClO_4)_3$ stock solutions. Dilutions of these hydrolyzed stock solutions were made to vary the concentration of gallium.

All of the solutions used in the *p*H study were prepared using molar $NaClO_4$ as the solvent. Weights of $Ga(ClO_4)_3 \cdot 6H_2O$ were dissolved in four separate portions of solvent such as to give four stock solutions, 0.04, 0.02, 0.01 and 0.005 *M* in total gallium. Weights of Na_2CO_3 were added to separate portions of each stock solution in order to give solutions with OH/Ga ratios of 0.25, 0.50, 0.75, 1.00, 1.25, 1.50 and 1.75.

Instruments and Measurements.—The differential refractometer and light-scattering photometer were standardized and used as described previously.[9] All measurements were made at 25 ± 2°, using 436 mμ light. No loss of solute was detected during filtration in the most concentrated solution of each series. No angular dependency in the scattering pattern was observed.

Measurements of turbidity were made about six weeks after the solutions had been prepared. At this time the solutions of OH/Ga = 2.0 showed slight precipitates, which were filtered off prior to the measurement of turbidity. The series with OH/Ga = 1.75 gave no precipitate at the time of measurement, but a slight precipitate was observed two weeks later. The series with OH/Ga = 1.50 showed no precipitate until the solutions had been standing about four months. Solutions of lower OH/Ga showed no precipitate during the course of our experiments.

A Beckman Model G *p*H meter was used in the *p*H study. It was calibrated with two standard buffer solutions, freshly prepared saturated potassium bitartrate and 0.05 *M* potassium acid phthalate, *p*H 3.57 and 4.01, respectively. The calibrations were repeated every four measurements. The instrument calibration did not fluctuate by more than 0.02 *p*H unit and the cross check between the two buffers was good to the same tolerance. About three weeks were allowed for the solutions to come to equilibrium. At this

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(1) American Viscose Research Fellow, 1956–1957.

(2) R. Fricke and W. Blenke, *Z. anorg. allgem. Chem.*, **143**, 183 (1925).

(3) R. Fricke and K. Mayring, *ibid.*, **176**, 325 (1928).

(4) E. S. von Bergkampf, *Z. anal. Chem.*, **90**, 333 (1932).

(5) B. N. Ivanov-Emin and Y. I. Rabovil, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 781 (1944).

(6) T. Moeller and G. L. King, *J. Phys. Colloid. Chem.*, **59**, 999 (1950).

(7) T. Moeller and G. L. King, THIS JOURNAL, **74**, 1355 (1952).

(8) C. S. Patterson and S. Y. Tyree, Jr., *ibid.*, **79**, 1821 (1957).

(9) J. K. Ruff and S. Y. Tyree, *ibid.*, **80**, 1523 (1958).

(10) L. G. Sillen, *Acta Chem. Scand.*, **8**, 299 (1954).

(11) L. G. Sillen, *ibid.*, **8**, 318 (1954).

(12) C. S. Patterson, *et al.*, THIS JOURNAL, **77**, 2195 (1955).

time the series with OH/Ga = 2.0 showed a small amount of precipitate and was discarded.

Results and Calculations

pH Study.—Following the treatment of Sillen, the hydroxyl number Z is calculated.

$$Z = \frac{h + H}{m}$$

where $h = [H^+]$, H = OH/Ga, and m = total gallium concentration. Z is plotted *versus* pH for a series of solutions in which the total gallium concentration is constant and the OH/Ga is varied. A set of parallel lines is obtained using our data, indicating that the core-link hypothesis is applicable and that the complexes formed can be represented by the formulas $Ga[Ga(OH)_t]_n$ or $Ga_{n+1}(OH)_{nt}$. The experimental pH values are presented in Table I.

TABLE I

pH VALUES OF HYDROLYZED GALLIUM SOLUTIONS

OH/Ga	m = 0.04	0.02	0.01	0.005
0.25	2.23	2.38	2.52	2.72
.50	2.28	2.43	2.57	2.76
.75	2.31	2.46	2.61	2.78
1.00	2.34	2.48	2.64	2.81
1.25	2.36	2.52	2.68	2.89
1.50	2.40	2.57	2.72	2.97
1.75	2.46	2.63	2.80	

Plotting pH *versus* m at constant Z gives a straight line of slope t. The value of t was found to be 2.1. In order to check this parameter log $m - t \log h$ is plotted *versus* Z, varying the value of t. All of the points should fall on one curve if the correct value of t has been used. Such a plot is shown in Fig. 1, with t = 2.0. No further analysis of the data was attempted since it is felt that the accuracy of the measurements does not warrant it. However from the value of t and the data, an average n ($\bar{n}$) can be calculated for each solution. Z is the average number of hydroxide ions associated with each gallium ion. If the only species present are $Ga_{n+1}(OH)_{2n}$, where n varies from zero to infinity, then $Z = 2\bar{n}/(\bar{n} + 1)$. The calculated values are tabulated as $\bar{n} + 1$ in Table II.

TABLE II

$n + 1$ VALUES OF HYDROLYZED GALLIUM SOLUTIONS

OH/Ga	m = 0.04	0.02	0.01
0.25	1.2	1.3	1.4
.50	1.5	1.5	1.6
.75	1.8	1.9	2.0
1.00	2.3	2.4	2.6
1.25	3.2	3.4	3.8
1.50	4.9	5.4	6.5
1.75	12.5	15.4	22.2

The increase in $\bar{n}$ with decrease in concentration must be attributed to the increasing amount of monomers present, such as $Ga(OH)^{++}$, as would be expected from the mass law. Consequently the apparent values of $\bar{n}$ are likely too large. A plot of $\bar{n} + 1$ *versus* OH/Ga is shown in Fig. 2. Included in the same figure are (1) n, the average number of gallium atoms per aggregate as obtained by Patterson,[8] and (2) n_w, the weight average number of gallium atoms per aggregate obtained in the present light-scattering study.

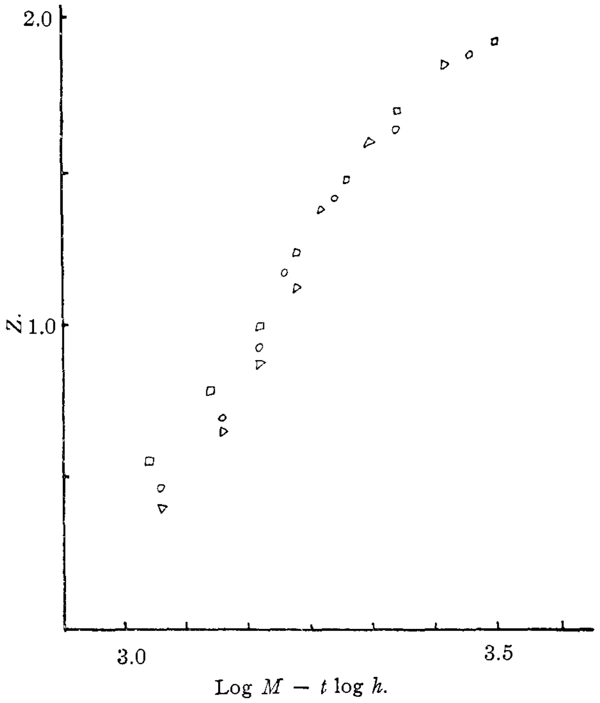

Fig. 1.—Z *vs.* log $m - t \log h$ for t = 2.0: □, for Ga = 0.01 *M;* △, for Ga = 0.04 *M;* ○, for Ga = 0.02 *M.*

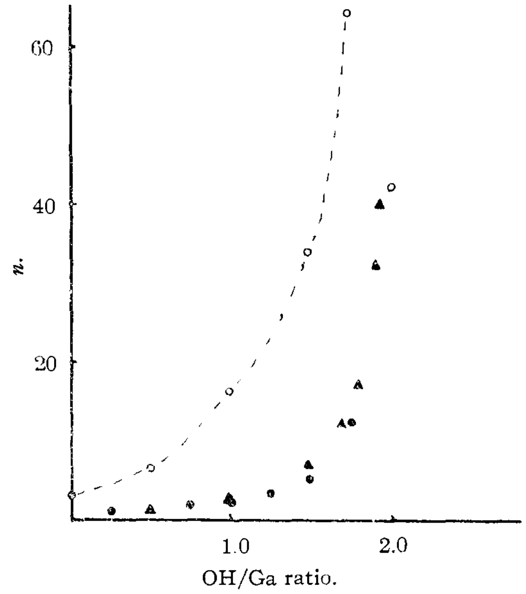

Fig. 2.—$\bar{n}$ *vs.* OH/Ga: ●, calculated from pH data; ▲, from Patterson's work; ○, weight average number from light scattering.

Indices of Refraction and Evaluation of *H*.—The refractive index increment with concentration of $NaClO_4$ is taken as 0.0636 ml./g. from Jenkins.[13] Gross Δn values for the gallium-containing solutions are listed in Table III.

We have assumed that this reaction represents the hydrolysis

$$Ga(OH_2)_6(ClO_4)_3 + r/2Na_2CO_3 = Ga(OH_2)_{6-r}(OH)_r(ClO_4)_{3-r} + rNaClO_4 + r/2CO_2$$

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(13) L. H. Jenkins, Ph.D. Dissertation, Univ. of N. C., 1955.

TABLE III

REFRACTIVE INDEX INCREMENT ($\Delta n \times 10^3$)

Concn. of Ga, *M*	0	0.5	1.0	1.5	1.75	2.0
0.800	29.969	...	...	25.116	...	24.754
.600	...	...	...	...	18.420	...
.500	...	16.236	16.090	...	...	...
.400	13.517	...	...	12.843	12.594	12.676
.300	...	9.766	9.747	...	9.606	...
.250	...	8.165	8.222	...	...	...
.200	6.808	...	...	6.501	6.471	6.422
.150	...	4.936	4.950	...	4.917	...
.125	...	4.321	4.169	...	...	...
.100	3.437	...	...	3.292	3.249	3.241
.075	...	2.547	2.519	...	...	...
.0625	...	2.166	2.110	...	...	...
.0500	...	...	...	1.656	1.630	1.632
.0350	...	...	...	1.143	...	1.140
.0313	...	1.081	1.053	...	...	...
.0250	...	...	...	0.822	0.818	0.815
.0175	...	...	...	0.579	...	0.569
.0125	...	...	...	...	0.410	...

Assuming that no reaction occurs between the gallium species and the $NaClO_4$ formed, the contribution of the $NaClO_4$ to a given Δn value in Table III can be calculated. Subtraction of this from the gross Δn value gives a Δn value due solely to the gallium-containing species and associated perchlorate anions. The same increase in $(\Delta n/c)_{Ga}$ with a decrease in concentration was found in this study that was reported in the first study.[9] Accordingly several dilutions were made below 0.1 *M* for each ratio in order to obtain the constant $(\Delta n/c)_{Ga}$ for the calculation of *H*. *H* was calculated in the same manner as was used in the aluminum case.[9]

Turbidity Values.—The τ-value due to gallium species in a given solution was obtained by subtracting the τ for water and the τ for the appropriate concentration of $NaClO_4$ from the observed τ of the solution. Corrected values of τ are reported in Table IV.

TABLE IV

CORRECTED TURBIDITIES EXPRESSED AS $\tau \times 10^5$ (CM.$^{-1}$)

Concn. of Ga, *m*	OH/Ga = 0	0.5	1.0	1.5	1.75	2.0
0.80	3.80	...	...	41.2	...	63.4
.60	...	...	...	...	51.7	...
.50	...	6.49	16.2	...	...	...
.40	2.91	...	...	24.2	45.6	38.1
.30	...	5.17	11.9	...	36.0	...
.25	...	4.39	10.7	...	...	...
.20	1.77	...	...	16.4	30.4	21.2
.15	...	3.23	7.44	...	24.4	...
.125	...	2.71	6.54	...	...	...
.10	0.76	...	...	9.56	15.4	12.0
.075	...	1.42	4.13	...	...	...
.05	...	...	...	5.04	...	6.33

Estimation of Aggregation.—Plots of Hc/τ *versus c* for the several series of solutions are shown in Fig. 3. The decrease in slope as the OH/Ga ratio increases is to be expected for reasons stated previously.[9] The weight average molecular weight M_w obtained from the intercept is an average over concentration as well as over the distribution of species present, we believe. Values of M_w, calculated from Fig. 3, are given in Table V.

TABLE V

OH/Ga	M_w	OH/Ga	M_w
0.0	200	1.5	3330
0.5	500	1.75	6670
1.0	1430	2.0	4760

The low value reported at OH/Ga = 2.0 will be discussed later. The weight average number of gallium atoms per aggregate (n_w) can be calculated if we assume that the polymeric aggregates ionize in accordance with equation 3.

$$nGa(OH_2)_6(ClO_4)_3 + nr/_2Na_2CO_3 = [Ga(OH_2)_{6-r}(OH)_r]_n{}^{n(3-r)} + n(3-r)ClO_4^- + rnNaClO_4 + rn/2CO_2 \quad (3)$$

$$n_w = \frac{M_{exp} \cdot M - (3-r)M^2{}_{ClO_4}}{M_c{}^2}$$

M_{exp} = experimental mol. wt.
M = $(3-r)M_{ClO_4} + M_c$
M_{ClO_4} = mol. wt. of ClO_4
M_c = mol. wt. of $Ga(OH_2)_{6-r}(OH)r$

n_w is plotted as a function of OH/Ga in Fig. 2. As was found in the aluminum case, if the assumption of a coördination number of six for the gallium cation is not made, all values of n_w are increased by nearly a factor of ten.

Discussion

The evidence suggests that, unlike the aluminum nitrate case, the solutions of gallium perchlorate have not reached true equilibrium. As a test of this hypothesis a time study was performed. A solution 0.5 *M* in gallium, with OH/Ga = 1.0, was converted to a solution 0.2 *M* in gallium, with OH/Ga = 2.0, by the addition of Na_2CO_3 and dilution. The turbidity was followed as a function of time immediately subsequent to the conversion. The results are plotted in Fig. 4. A precipitate formed immediately upon the addition of the Na_2CO_3, but it dissolved with ease on shaking. The solution was filtered twice, sealed in a scattering cell and placed on the photometer. The initial drop in turbidity was found in the aluminum study also. We feel that it is due probably to the attack of solute gallium species on the precipitated hydrous oxide, forming large but soluble aggregates which are subsequently depolymerized. The sustained upward trend in turbidity is certainly due to a continuous increase in the size of the aggregates until a critical size is reached and precipitation takes place. The precipitate forms on the sides of the scattering cell so that turbidity values beyond this point are not representative of the solution, which remains clear. Concentrated acids will not dissolve the precipitate, but they are soluble in strong base.

It has been suggested[14] that aqueous solutions of Cr undergo a very slow hydrolysis upon the addition of base, leading to the formation of hydrous chromium(III) oxide, and that the resulting build-up of hydrogen ion concentration not only represses further precipitation but reverses the reaction so that smaller aggregates are formed. The amount of precipitate and the average size of the remaining

[14] J. A. Laswick and R. A. Plane, private communication.

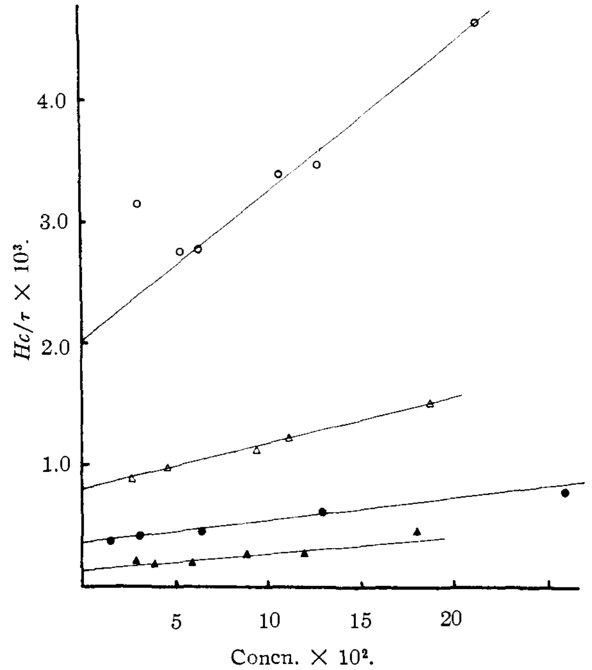

Fig. 3.—Hc/τ vs. c: ○, for OH/Ga = 0.5; △, for OH/Ga = 1.0; ●, for OH/Ga = 1.5; ▲, for OH/Ga = 1.75.

solute aggregates will, of course, vary with the OH/Cr.

Our solution of OH/Ga = 2.0 which was 0.8 *M* in total gallium gave a precipitate in approximately 21 days after its preparation. The solution was filtered and the other solutions at this ratio were prepared from the filtered solution by dilution. Each was allowed to stand 35 days before measurement. The original precipitate contained not more than 1% of the total gallium initially present. The weight average molecular weight and the weight average number of gallium atoms per aggregate are seen to be lower than those found for the series with OH/Ga = 1.75. This behavior is very similar to that of the chromium solutions. The explanation offered by Plane and Laswick is preferred by us also.

Since it is felt that equilibrium had not been established in all of the solutions studied, the molecular weights obtained indicate only the order of magnitude of aggregation. Obviously, the kinetics of the hydrolysis must be studied.

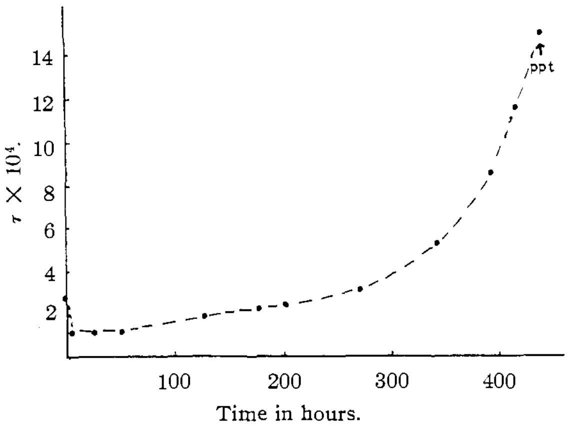

Fig. 4.—τ vs. time.

Two doubtful points arise in the treatment of the light-scattering data. The solutes are strong electrolytes. Ionization is instantaneous, in contrast with the aggregation processes which are shown to be slow. As such the activity coefficients must vary with concentration since the ionic strength was not maintained constant. However, for solutions of high OH/Ga, the amounts of sodium perchlorate formed were such as to maintain a large relative amount of indifferent electrolyte. Under such conditions the activity coefficients should remain more nearly constant and the activities more nearly proportional to concentration. In addition as OH/Ga increases the average charge per gallium atom decreases and the solute behavior deviates from that of a 3–1 electrolyte toward that of 2–1 and 1–1 electrolytes, which is known to show much less variation of activity coefficient with concentration. Thus for two reasons the Hc/τ curves for high OH/Ga solutions are not so much affected by activity coefficient variation as are those for low OH/Ga solutions. The slopes of the curves in Fig. 3 decrease as OH/Ga increases, in support of the foregoing discussion.

The second doubtful point consists of the more fundamental question of how to interpret light-scattering data from solutions of electrolytes. The answer to this is uncertain as yet. It is a problem that we hope to report on within a year.

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