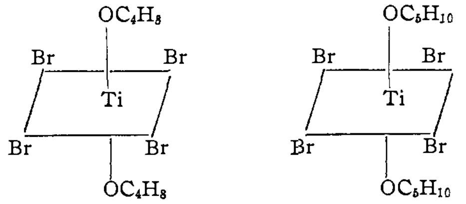
cm.$^{-1}$) is almost completely absent in the spectrum of $TiBr_4 \cdot 2C_4H_8O$. Likewise the C–O–C ring stretching frequency in the tetrahydropyran spectrum is greatly reduced in the spectrum of $TiBr_4 \cdot 2C_5H_{10}O$. No evidence for a C–Br bond was found in the range of 2 to 16 μ.

Cryoscopic measurements on solutions of $TiBr_4 \cdot$ 1,4-dioxane indicate that the compound is monomeric in dioxane solution.

The results of the X-ray diffraction analyses indicate that the three solids are composed of tetragonal crystals. It must be pointed out that there is probably some error in the value for the lattice constants due to the absence of *d*-spacings with θ values between 50 and 85°. Also, the broad diffraction lines reduced the accuracy in the evaluation of the observed *d*-spacings. The very large surface area of the powder samples did not permit accurate pycnometric density measurements in "Ultrasene." Therefore, the precise X-ray evaluation of the addition compounds cannot be made without investigation of single crystals.

On the basis of the above information, one may tentatively propose the following structures for the tetrahydrofuran and tetrahydropyran complexes



The corresponding *cis* forms are also a possibility.

It might be proposed that the bonding could take place between the bromine atoms and ether oxygens instead of between the titanium atoms and oxygen atoms. However, the known lability of complexes formed by halogen to oxygen binding[6] serve to remove any reasonable consideration of such a possibility for these rather stable compounds.

If we assume that the dioxane complex is monomeric in the solid state as well as in dioxane solution the structure in which the two oxygens of dioxane are attached to adjacent positions on the titanium octahedron suggests itself.

[6] Hassel and Hvoself. *Acta Chem. Scand.*, **8**, 873 (1954).

COLUMBUS, OHIO

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

Isopiestic Studies on Aqueous Gallium(III) Perchlorate Solutions[1]

BY C. S. PATTERSON[2] AND S. Y. TYREE, JR.

RECEIVED NOVEMBER 3, 1956

Vapor pressures of gallium perchlorate solutions with from zero to 2.5 hydroxide ions per gallium(III) ion added and over the concentration range from 0.1 to 1.2 *m* were determined by the isopiestic method. The data are interpreted in terms of cationic polymerization with degrees of polymerization ranging from 1.3 at $r = 0.5$ to 84 at $r = 2.0$. The values are in reasonable agreement with those predicted by the oxygen bridging mechanism of Granner and Sillen.

On the basis of potentiometric titrations, Moeller and King,[3] in 1950, proposed that either peptization or polymerization occurs when hydroxide ions are added to gallium(III) salt solutions. In 1952 these same workers reported polarographic data[4] which indicated that polymerization is the important process. Insufficient data were taken to allow any quantitative interpretation of the mechanism.

Experimental

In an attempt to gain some knowledge of the species formed in these solutions, the vapor pressures of aqueous $Ga(ClO_4)_3$ solutions were determined by the isopiestic equilibration technique over a range of concentrations and base-to-gallium ratios. (This is the quantity *r* in Table I and will be subsequently referred to simply as "the ratio.") The apparatus and reagents used have been described previously.[5]

A total of 95 equilibrations were made of KCl or $CaCl_2$ (the reference standard solutions) with seven series of solutions of $Ga(ClO_4)_3$ having from zero to 2.5 moles of OH^- added per mole of Ga^{+3}. Several runs were made at each ratio, the gallium concentration being varied from 0.1 *m* up to about 1.2 *m*. The base was added as NaOH to some solutions and as Na_2CO_3 to others without detectably altering the results.

Results

A large-scale plot was made of the isopiestic ratio *R vs* the gallium concentration *m* for each series of solutions. From them the molalities of KCl isopiestic with round molalities of $Ga(ClO_4)_3$ were calculated. Then from a plot of the relative vapor pressure lowering *vs.* KCl concentration, vapor pressures for the gallium solutions could be read.

The smoothed experimental data, given as equilibrium molalities, isopiestic ratio and the relative vapor pressure lowering, are recorded in Table I for each series of solutions.

The average agreement between duplicate determinations was within about 0.2% and, in most cases, the agreement was within 0.1%. A few runs at the lowest concentrations gave larger deviations.

Some of the significant features of the results are summarized below.

(i) At high concentrations addition of OH^- decreases the vapor pressure lowering of the solution although no precipitation occurs. However, at low concentrations the reverse is true.

---

[1] Based on a dissertation submitted by C. S. Patterson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of North Carolina in Chapel Hill.

[2] Du Pont Research Fellow, 1953–1954.

[3] T. Moeller and G. L. King, *J. Phys. Colloid Chem.*, **54**, 999 (1950).

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

[5] C. S. Patterson, S. Y. Tyree and Kerro Knox, *ibid.*, **77**, 2195 (1955).

TABLE I

SMOOTHED EXPERIMENTAL DATA

$m_{Ga(ClO_4)_3}$	m_{KCl}	R	$\Delta p/p^0 \times 10^4$
	$r = 0$		
0.1	0.1885	1.885	60
.2	.3994	1.997	129
.3	.6504	2.168	209
.4	.9364	2.341	298
.5	1.2655	2.531	402
.6	1.6356	2.726	520
.7	2.0440	2.920	650
.8	2.4672	3.084	788
.9	2.9691	3.299	954
1.0	3.5020	3.502	1030
1.1	4.0667	3.697	1278
1.2	4.6536	3.878	1476
	$r = 0.500$		
0.1	0.1993	1.993	65
.2	.4274	2.137	140
.3	.6804	2.268	218
.4	.9716	2.429	309
.5	1.2655	2.531	409
.6	1.6296	2.716	518
.7	1.9929	2.847	634
.8	2.3936	2.992	764
.9	2.8170	3.130	903
1.0	3.2690	3.269	1052
1.1	3.7488	3.408	1213
1.2	4.2552	3.546	1385
	$r = 1.038$		
0.1	0.2212	2.212	72
.2	.4634	2.317	149
.3	.7266	2.422	232
.4	1.0108	2.527	322
.5	1.3170	2.634	418
.6	1.6440	2.740	522
.7	1.9929	2.847	634
.8	2.3624	2.953	754
.9	2.7477	3.053	880
1.0	3.1540	3.154	1014
1.1	3.5805	3.255	1156
1.2	4.0284	3.357	1308
	$r = 1.461$		
0.1	0.2368	2.368	77
.2	.4888	2.444	157
.3	.7566	2.522	242
.4	1.0404	2.601	331
.5	1.3390	2.678	425
.6	1.6536	2.756	525
.7	1.9831	2.833	631
.8	2.3272	2.909	742
.9	2.6865	2.985	860
1.0	3.0460	3.046	978
1.1	3.4254	3.114	1104
1.2	3.8160	3.180	1238
	$r = 2.000$		
0.1	0.2549	2.549	83
.2	.5194	2.597	166
.3	.7935	2.645	253
.4	1.0772	2.693	342
.5	1.3695	2.739	435
.6	1.6698	2.783	530
.7	1.9754	2.822	628
.8	2.2856	2.857	729
.9	2.6001	2.889	832
1.0	2.9170	2.917	935
1.1	3.2472	2.952	1045
1.2	3.5832	2.986	1157
	$r = 2.358$		
0.1	0.2695	2.695	88
.2	.5440	2.720	174
.3	.8229	2.743	262
.4	1.1056	2.764	351
.5	1.3920	2.784	442
.6	1.6818	2.803	534
.7	1.9733	2.819	628
.8	2.2656	2.832	723
.9	2.5560	2.844	818
1.0	2.8440	2.860	912
1.1	3.1630	2.876	1018
1.2	3.4680	2.890	1118
	$r = 2.500$		
0.1	0.2760	2.760	90
.2	.5532	2.766	178
.3	.8316	2.772	265
.4	1.1104	2.776	353
.5	1.3900	2.780	442
.6	1.6716	2.786	531
.7	1.9544	2.792	621
.8	2.2368	2.796	713
.9	2.5200	2.800	806
1.0	2.8050	2.808	899
1.1	3.0987	2.817	998
1.2	3.3900	2.825	1093

(ii) The ratio dependence of the vapor pressure lowering of the solutions is linear within experimental error for all concentrations.

(iii) Solutions at 2.5 ratio precipitated after standing for about two weeks. Lower ratios were found to precipitate on longer standing. However, no precipitates were ever noticed in solutions with less than 2.0 OH^- per Ga^{+3}.

(iv) Solutions which had precipitated were found to agree with freshly prepared duplicates containing no precipitates within little more than the average deviation found for the other duplicate pairs.

(v) Local precipitation could be caused if the base were added too rapidly even at fairly low ratios, but this was reversible, and no permanent precipitate was ever found until after long standing, and then only in the solutions of higher ratio.

Discussion

Any satisfactory quantitative interpretation of the vapor pressure data must be consistent with these qualitative features. In order to determine what type of process is most likely, different mechanisms were assumed, and theoretical lowerings expected for the resulting solutions were calculated. If the deviations of a set of these theoretical values from the experimental ones were sufficiently small, the mechanism could be adopted tentatively.

A set of theoretical lowerings was calculated on the assumption that mononuclear species of the type $Ga(OH)^{++}$ and $Ga(OH)_2{}^+$ are formed as base is added and that these would affect the vapor pressure the same as Zn^{++} and Li^+ ions, respec-

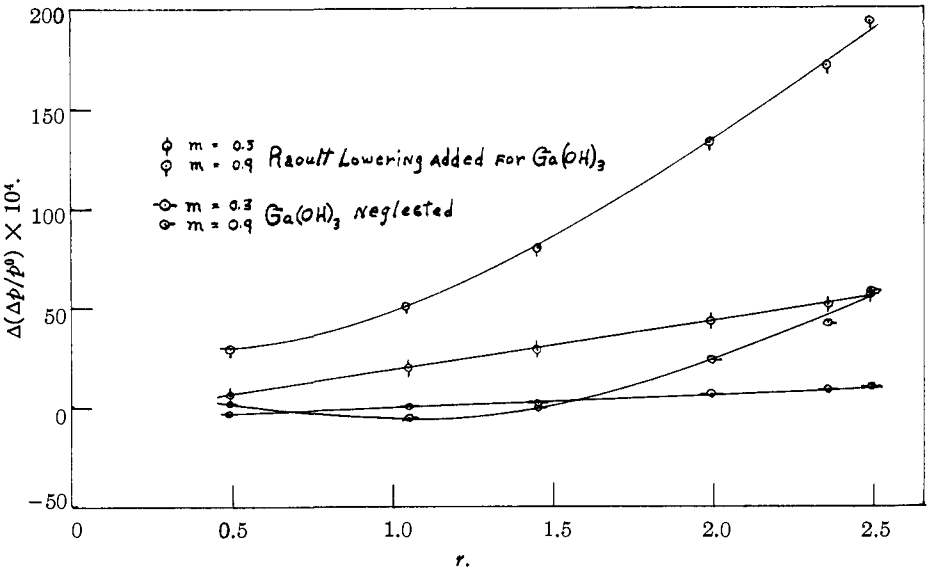


Fig. 1.—Deviation of the peptization theory *vs.* base-to-gallium ratio.

tively. The differences between these theoretical values and the experimental were found to be as much as 30% of the total value of the relative lowering in some cases. In all cases the experimental lowerings were smaller than the theoretical, indicating that species are being formed which contribute considerably less to the vapor pressure lowering than do ordinary monomeric ions of the type considered here. This lends support to the theory of peptization or polymerization proposed by Moeller and King.

A second set of theoretical lowerings was calculated on the assumption that, with the first addition of base, a soluble or peptized form of Ga$(OH)_3$ is formed. Since the nature of this material is not known, two sets of values were calculated. One assumes the $Ga(OH)_3$ to be colloidal and thus not active in lowering the vapor pressure, while the other adds Raoult lowering for it. The second treatment requires a soluble, monomeric and undissociated hydroxide. These two extreme cases may be represented by the equations

$$m\text{Ga}^{+3} + 3m\text{ClO}_4^- + rm\text{Na}^+\text{OH}^- \longrightarrow (1 - r/3)m\text{Ga}^{+3} + (3 - r)m\text{ClO}_4^- + rm\text{Na}^+\text{ClO}_4^- + \text{polymeric Ga(OH)}_3 \quad (1)$$

$$m\text{Ga}^{+3} + 3m\text{ClO}_4^- + rm\text{Na}^+\text{OH}^- \longrightarrow (1 - r/3)m\text{Ga}^{+3} + (3 - r)m\text{ClO}_4^- + rm\text{Na}^+\text{ClO}_4^- + (r/3)m\text{Ga(OH)}_3 \quad (2)$$

The equilibrium solutions would therefore contain a mixture of unchanged $Ga(ClO_4)_3$ of concentration $(1 - r/3)m$, $NaClO_4$ of concentration rm, and, in the second case, $Ga(OH)_3$ of concentration $rm/3$. The total lowerings of such mixtures were calculated as follows. Values of the relative lowerings per mole were plotted *vs.* ionic strength for each electrolyte assumed to be present in the solution. From these plots values of $\Delta p/mp^0$ could be read off at the ionic strength predicted for the mixture, and from this value the theoretical vapor pressure lowering due to any particular species could be obtained. The $\Delta p/p^0$ values obtained for the several solutes were summed and compared with the measured value. The assumption is therefore made that the relative lowering per mole for an electrolyte is a function of the total ionic strength of the solution and not of its own concentration.

In general the deviation from experiment of the peptization theory, as expressed by eq. 1 and 2, is found to increase with increasing concentration for each method of treating the $Ga(OH)_3$. The behavior with change in ratio may be seen by reference to Fig. 1. For comparison, curves at two representative concentrations are included for each treatment of the hydroxide.

The sharp increase in deviation above $r = 1$ indicates that, at high ratios, even neglecting the hydroxide's lowering altogether gives theoretical lowerings which are too large. In this range the calculated lowering of the remaining $Ga(ClO_4)_3$ alone is larger than that found experimentally.

The magnitude of these deviations indicates rather strongly that formation of mononuclear $Ga(OH)_3$ is not a process of any importance. Furthermore, the results beyond a ratio of unity indicate that even the assumption that the hydroxide is completely condensed would not effect a reasonable agreement between theory and experiment. Therefore the formation of a soluble polymeric hydroxide also seems unlikely. These conclusions are in agreement with those of Moeller and King derived from polarographic data.[4]

The results of a qualitative examination of the data have indicated that, upon addition of base, the $Ga(ClO_4)_3$ must be replaced by some products which affect the vapor pressure to a much lesser degree as ratio of base to gallium increases. The linear nature of the relation between the vapor pressure lowering and ratio indicates some process which is the same throughout the entire range of ratios rather than some discontinuous or stepwise process. A number of polymerization mechanisms could be devised which would qualitatively fit both of these requirements.

The interpretation here adopted treats the data in terms of such a polymerization theory. Rather than assume some mechanism at the outset it is simply assumed that all the OH^- added combines with Ga^{+3} and that the resulting complex ions form aggregates with an average of n gallium atoms per ion. This results in polymers of the general type $\mathrm{Ga}_n(\mathrm{OH})_{rn}^{+(3-r)n}$ and the general reaction for their formation may be written as

$$m\mathrm{Ga}^{+3} + 3m\mathrm{ClO_4}^- + rm\mathrm{Na^+OH^-} \longrightarrow (m/n)\mathrm{Ga}_n(\mathrm{OH})_{rn}^{+(3-r)n} + (3-r)m\mathrm{ClO_4}^- + rm\mathrm{Na^+ClO_4}^- \quad (3)$$

The first step in treating the data by this method is to correct for the $\mathrm{NaClO_4}$, leaving the lowering due to the "gallium polymer perchlorate." In this case the ionic strength of the solution is not immediately defined by the assumptions, as was the case with the peptization theory. Therefore the correction for $\mathrm{NaClO_4}$ is made on the basis of the ionic strength which would have resulted if the base had reacted to form monomeric rather than polymeric ions. This should not lead to serious error since $\Delta p/mp^0$ for $\mathrm{NaClO_4}$ is not very strongly concentration dependent. Furthermore, the error is in such a direction as to lead to a slight underestimation of the degree of polymerization. Column 2 in Table II gives the values so obtained for the "polymer perchlorate."

TABLE II

m	$(\Delta p/p^0)$ pol. per.	$(\Delta p/p^0)$ pol. cat.	$(\Delta p/mp^0)$ pol. cat.
	$r = 0.500$		
0.1	49	12	120
.2	108	30	150
.3	169	47	160
.4	244	82	205
.5	327	123	246
.6	420	172	290
.7	518	229	327
.8	631	299	374
.9	752	375	417
1.0	883	461	461
1.1	1026	558	507
1.2	1179	665	554
	$r = 1.038$		
0.1	38	6	60
.2	82	18	90
.3	131	36	120
.4	187	60	150
.5	249	89	178
.6	319	127	212
.7	396	171	244
.8	481	223	279
.9	571	279	310
1.0	669	343	343
1.1	774	413	375
1.2	890	494	412
	$r = 1.461$		
0.1	29	4	40
.2	62	12	60
.3	100	25	83
.4	142	42	105
.5	188	63	126
.6	240	90	150
.7	297	121	173
.8	359	157	196
.9	427	199	221
1.0	495	241	241
1.1	570	289	263
1.2	653	345	288
	$r = 2.000$		
0.1	17	1	10
.2	36	4	20
.3	59	11	33
.4	83	18	45
.5	111	30	60
.6	140	43	72
.7	172	58	83
.8	207	76	95
.9	243	96	107
1.0	278	114	114
1.1	320	139	126
1.2	363	164	137
	$r = 2.358$		
0.1	11	0.5	5
.2	21	1	5
.3	33	2	7
.4	46	4	10
.5	60	8	16
.6	75	13	22
.7	91	17	24
.8	107	23	29
.9	123	28	31
1.0	144	39	39
1.1	163	47	43
1.2	182	55	46
	$r = 2.500$		
0.1	8	0	..
.2	16	0	..
.3	22	−2	..
.4	29	−3	..
.5	37	−3	..
.6	44	−5	..
.7	51	−6	..
.8	60	−5	..
.9	69	−5	..
1.0	78	−4	..
1.1	91	0	..
1.2	100	+1	..

It remains to determine the nature of this average species. An estimate of the degree of ionization is needed before any conclusion can be reached with regard to the ions formed. The very slight ion pair formation in pure $\mathrm{Ga(ClO_4)_3}$[5] suggests that the assumption of 100% ionization in the case of these polymer perchlorates would not be in serious error. This is substantiated by the data in Table II. Column 2 gives $\Delta p/p^0$ values which might be considered as those of undissociated gallium polymer perchlorate. Except at the highest ratios these values are considerably larger than Raoult lowering would be for the corresponding concentration of undissociated monomeric molecules, $\mathrm{Ga(OH)}_r(\mathrm{ClO_4})_{(3-r)}$.

On the assumption that the $\mathrm{ClO_4}^-$ ions are completely ionized, a further subtraction was made for them, giving the lowering due solely to the polymer cations. Since the relative molal lowering of the vapor pressure of individual ions cannot be measured, it was further assumed that one-half the

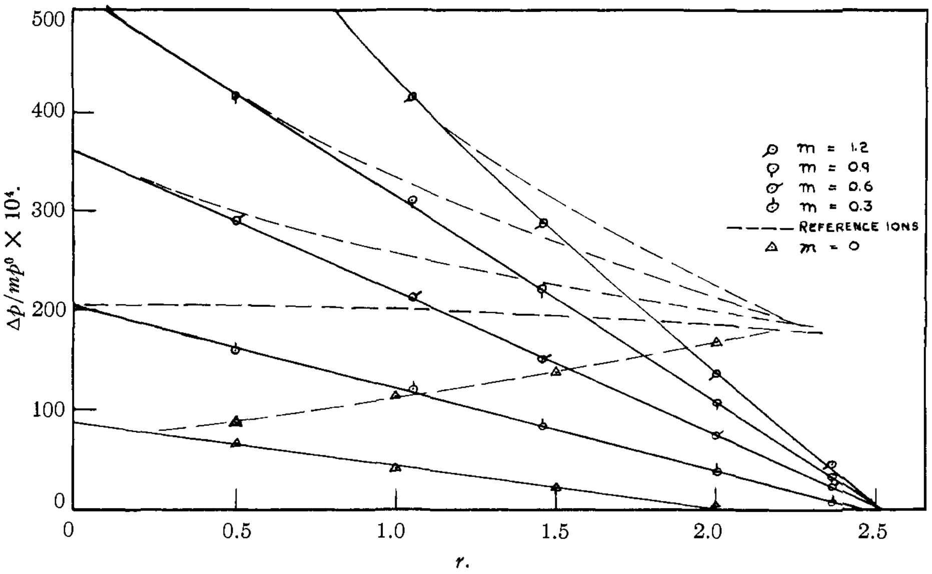


Fig. 2.—Relative molal lowerings of cations calculated from experimental data assuming polymerization plotted *vs.* base-to-gallium ratio.

lowering of $NaClO_4$ is due to ClO_4^- ions and the amount to subtract was calculated from this assumption in each case. For example, if the ClO_4^- ion concentration were 1.0 *m* its lowering was taken as equal to that which 0.5 *m* $NaClO_4$ would have in a solution of the same ionic strength. The assumption must again be made that the relative lowering per mole for an electrolyte is determined by the total ionic strength and not by its own concentration.

Column 3 in Table II gives the lowerings obtained for these polymer cations by this method. Column 4 gives the magnitude of this quantity per mole of Ga^{+3} originally added.

Figure 2 shows a plot, *vs.* ratio, of the relative lowerings per mole for the polymer cations (column 4 of Table II) for four concentrations. The dotted curves were obtained by plotting the lowerings of lithium,[6] zinc[7] and gallium[5] ions at ratios 2, 1 and zero, respectively. These values were calculated from the lowerings of the corresponding salts by subtracting for ClO_4^- in exactly the same way that the values for the polymer cations were calculated. These reference curves may be considered as theoretical values for systems with no polymerization, *i.e.*, with $n = 1$. Although no monomer reference ion exists which corresponds to $r = 0.5$ or any other fractional *r* value (since this would require a fractional valence), this situation does exist for the polymer species. There should, therefore, be no objection to drawing the smooth curves through the Li^+, Zn^{+2} and Ga^{+3} values and taking the value at any point of this curve to be that of the reference ion of the corresponding valence.

It is noteworthy that the experimental curves are very nearly linear at all concentrations whereas the reference curves are not. Also the polymer curves decrease to zero at about $r = 2.5$ for all concentrations, while the theoretical curves decrease with *r* only at high concentrations. Furthermore the experimental values fall below the corresponding reference monomer curves in all cases and become progressively farther below them with increasing *r*.

All of these differences are in such a direction as to be explained by polymerization. Furthermore, if it be assumed that the differences are due solely to polymerization, then the ratio of reference values to experimental gives a measure of the degree of polymerization. Due to non-ideality this assumption holds only at infinite dilution where Raoult's law is valid. Therefore, in order to estimate the degree of polymerization, it is necessary to extrapolate the $\Delta p/mp^0$ values for monomers and polymers to zero concentration and compare the resulting values. Such an extrapolation was made by reading off values of the relative molal lowerings at round ratios from Fig. 2 for both reference and polymer cations. These were plotted *vs.* concentration and the intercepts determined. The lowest curve in Fig. 2 for both reference and experimental ions is for these extrapolated values.

According to Raoult's law

$$\Delta p/p^0 = N_2 \cong m\text{M}_1/1000 \qquad (4)$$

where N_2 is the mole fraction of solute, *m* is the molality of solute and M_1 is the molecular weight of the solvent. Thus for aqueous solutions the theoretical limit of $\Delta p/mp^0$ for any single component of a solution should be 0.01802 (or 180.2 on the scale used here). The fact that the reference electrolyte ions all give curves which hit below their respective theoretical limits indicates that there is deviation from the monomeric theory other than that due to polymerization. We can only assume that all these non-ideality effects except those due to polymerization will cancel, which seems reasonable since reference and experimental values were determined by making the same approximations.

If the experimental values are too low because of polymerization, it is because we have used the wrong *m* in calculating $\Delta p/mp^0$, the value having

---

(6) R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(7) R. H. Stokes, *ibid.*, **44**, 295 (1948).

been used for monomers. The true molality, which will be designated as m_n, will be of such magnitude as to give the expected theoretical relative molal lowering at $m = 0$. This expected value will be taken as the limit found for the corresponding reference monomer ions.

Now the experimental intercept is given by $\Delta p/mp^0$ whereas the theoretical is given by the expression, $\Delta p/m_np^0$. Furthermore, if the difference is due solely to polymerization of n molecules of monomer, then $m = nm_n$ whence

$$n = \frac{\text{reference ion intercept}}{\text{experimental intercept}} \qquad (5)$$

Several values of n were calculated by this relation from the data in Fig. 2. Figure 3 shows a plot of these experimental degrees of polymerization as the solid line.

The values of n in Fig. 3 indicate that polymerization becomes significant beyond a ratio of 0.5 and increases rapidly as base is added. The fact that the experimental $\Delta p/mp^0$ curves (Fig. 2) go to zero at about 2.5 ratio indicates that at this ratio the polymerization has become so extensive that the contribution of the polymer species to the vapor pressure lowering has become immeasurably small.

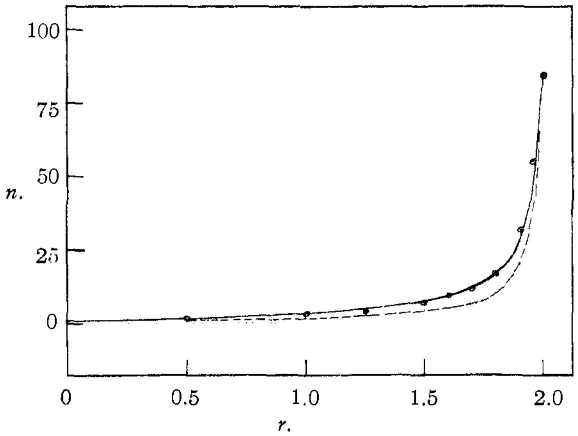


Fig. 3.—Polymerization numbers *vs.* base-to-gallium ratio: O, experimental; - - -, oxygen bridging theory.

It may be shown easily that our use of the ionic strength of monomer solutions in making correction for $NaClO_4$ leads to minimum values of n. This follows from the fact that the polymer solutions would have larger ionic strengths than the corresponding monomer solutions. The error will not be large since $\Delta p/mp^0$ for $NaClO_4$ is a relatively insensitive function of the ionic strength. On the other hand the negative values of $\Delta p/mp^0$ at r = 2.5 (Table II) indicate that other errors must be involved. The most important of these are probably the assumption that the lowering of $NaClO_4$ may be divided equally between Na^+ and ClO_4^- ions and the linear extrapolation of the relative molal lowering curves to zero. The former probably is responsible for the negative $\Delta p/mp^0$ values (n too large) while the latter would lead to minimum values of n in the range in which it is most important.

Granner and Sillen[8] found that a polymerization mechanism, which they called oxygen bridging, could be made to fit the experimental data for the hydrolysis of the Bi^{+3} ion. The general equation for this process is

$$Bi_nO_{n-1}{}^{+(n+2)} + HOH + Bi^{+3} \longrightarrow Bi_{n+1}O_n{}^{+(n+3)} + 2H^+ \qquad (6)$$

If the hydrolysis of Ga^{+3} may be represented by such a mechanism, then the ratio of oxygen to gallium in the polymer ions must be $(n - 1)/n$, as predicted by eq. 6. Furthermore, if the average number of gallium atoms per ion is n, then the average charge per ion must be $(n + 2)$ as indicated. The formula $Ga_nO_{rn/2}^{+(3-r)n}$ may be written for the average ion assumed to be present in the gallium solutions, which differs from the notation of eq. 3 only in the degree of hydration. Comparison of the cation charges or the oxygen subscripts for these ions will show that, if the gallium polymer ions have been formed by the oxygen bridging mechanism, then the number of gallium atoms per polymer ion is given, as a function of the ratio, by the expression

$$n = 2/(2 - r) \qquad (7)$$

Values of n calculated by means of this equation for several values of the ratio are plotted as the dotted line in Fig. 3. Agreement in the low ratio range is good, and both curves show a very marked ratio dependence, the values of n becoming very large near r = 2.0 in each case. It should be pointed out that the oxygen bridging mechanism cannot be extended beyond a ratio of 2.0, since unity is the limit of the ratio of oxygen to gallium in ions formed by this process because

$$\lim_{n \to \infty} \left[\frac{n-1}{n}\right] = 1$$

As stated by Granner and Sillen, this means that there must be effective, in the range above r = 2.0, another mechanism which can lead to $Ga(OH)_3$ as the final product. This seems to be in line with the experimentally observed fact that long standing produced precipitates in solutions with ratios greater than 2, but did not at lower ratios.

Also the extremely high values of n near r = 2.0 would explain the unusual agreement found above this ratio between duplicates with and without precipitates. The explanation is simply that the polymer's lowering has become so small at this point that its presence is practically indetectable by the isopiestic method, and hence its removal as precipitate has no appreciable effect on the vapor pressure.

Acknowledgment.—The generous gift of 10 g. of gallium metal from the Eagle-Picher Company and the invaluable help of Anne Patterson are hereby acknowledged.

GREENVILLE, SOUTH CAROLINA

---

[8] F. Granner and L. G. Sillen, *Acta Chem. Scand.*, **1**, 631 (1947).