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A Light-Scattering Study of the Hydrolytic Polymerization of Lead(II) in Aqueous Perchlorate Media[1]

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The hydrolytic polymerization of lead(II) at hydroxyl numbers 0.0 (excess acid), 0.5, 1.0, and 1.33 (incipient precipitation) has been investigated by light-scattering measurements at 25°. Lead(II) concentrations were varied between approximately 0.01 and 0.10 M in solutions maintained 1.00 M in sodium perchlorate. The degree of hydrolysis of the lead(II) ion is shown to have a pronounced effect upon the turbidity, refractive index increment, density, and pH of the series of solutions studied. An unhydrolyzed and uncomplexed lead species with charge +2 is indicated for solutions containing a slight excess of perchloric acid, while species formulated as $[Pb_4(OH)_4(ClO_4)_2]^{2+}$ and $[Pb_6(OH)_8(ClO_4)_3]^+$ are inferred from the data at hydroxyl numbers 1.0 and 1.33, respectively. The degree of polymerization formed for hydroxyl number 0.5 is strongly concentration dependent and suggests a polydisperse system with an average polymerization number of 1.5–2.2 for lead(II) concentrations below 0.05 M. All hydrolyzed solutions yield precipitates in open air which are shown to be basic carbonates of lead rather than hydrolysis products.

Introduction

The early work[3-5] on the hydrolysis of lead(II) was characterized by measurements of the acidity of lead(II) salt solutions with little regard for the nature of the lead-containing species. No evidence was presented for any species other than $[Pb(OH)]^+$ until Reiff and Mueller[6] found by measurements using the lead amalgam electrode that the free lead(II) concentration, in solutions of composition $Pb(OH)ClO_4$, was not negligible and proposed the aggregate $[Pb_2(OH)_2]^{2+}$ which was partly dissociated into Pb^{2+}, $[Pb(OH)]^+$, and $Pb(OH)_2$. Titrations of lead(II) nitrate solutions with sodium hydroxide were later interpreted by Pederson[7] in terms of the successive formation of $[Pb_2(OH)]^{3+}$, $[Pb(OH)]^+$, and $[Pb_4(OH)_4]^{4+}$. Similarly colorimetric,[8] solubility,[9-10] and polarographic[11] studies have been presented as evidence for both monomeric and dimeric lead(II) species.

More recently, pH titrations carried out by Faucherre[12] and Olin[13] in perchlorate media seem to be fairly complete studies of the lead(II) system. Faucherre proposed that $[Pb_4(OH)_4]^{4+}$ was formed at hydroxide-to-lead ratios of less than one and that a nonamer, $[Pb_9(OH)_{12}]^{6+}$, began to form at ratios greater than one. The limit of the titration was the ratio 4:3, above which the basic salt $Pb(ClO_4)_2 \cdot 5Pb(OH)_2$ was precipitated. The same limit of titration was found by Olin, who also proposed a tetramer at hydroxyl number one. A trimer, $[Pb_3(OH)_4]^{2+}$, and a hexamer, $[Pb_6(OH)_8]^{4+}$, were suggested for hydroxyl numbers greater than one. Later studies by the latter[14-15] on more concentrated solutions indicated a dimeric aggregate in addition to the tetramer.

Preliminary ultracentrifuge experiments[16] on the lead system indicated a weight-average polymerization number near four for hydroxyl number one and higher polymers at greater degrees of hydrolysis. This work was completed in 1962 by Esval,[17] who found that the degree of polymerization increased with hydroxyl number, reaching slightly above four at hydroxyl number one and rising to about six at hydroxyl number 1.33. Extensive perchlorate complexing was indicated for all hydrolyzed species in the 1 M $NaClO_4$ medium. In addition, an X-ray diffraction study was carried out on solutions of the tetramer, and the data were explained by assuming a model consisting of four lead atoms at the corners of a regular tetrahedron with hydroxide ions just out from and perpendicular to the centers of each of the four tetrahedral faces.

Due to the similarities in the treatment of light-scattering and ultracentrifuge data, the present investigation was carried out under experimental conditions identical with those employed in the equilibrium ultracentrifugation.[17] Since both methods involve the simultaneous determination of charge and degree of polymerization for hydrolyzed species in the presence of supporting electrolyte, it was thought that the light-scattering study would be an ideal complement to the ultracentrifuge results and further test the evidence derived from the more recent e.m.f. titrations.

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(1) From a thesis submitted by Forrest C. Hentz, Jr., to the Graduate School of the University of North Carolina in partial fulfillment of the requirements for the Ph.D. degree, 1963.

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Experimental

Stock Lead and NaClO$_4$ Solutions.—Stock lead solutions with hydroxyl number ($\bar{n}$) 1.33 were prepared by dissolving the basic perchlorate,[18] $Pb(OH)_{1.33}(ClO_4)_{0.67}$, in carbonate-free distilled and demineralized water. The stock solution of $\bar{n}$ = 0.5 was prepared by appropriate acidification of the $\bar{n}$ = 1.33 solution with standard 1 *M* HClO$_4$. Solutions of $\bar{n}$ = 1.0 were prepared alternately by acidification of the $\bar{n}$ = 1.33 solution (series 1) and by dissolving dry PbO in standard 1 *M* HClO$_4$ at an acid-to-oxide mole ratio of 1:1. A solution prepared by dissolving PbO in 1 *M* HClO$_4$ at an acid-to-oxide ratio of slightly greater than 2:1 was assumed to represent a solution containing unhydrolyzed lead(II). Due to the instability of the hydrolyzed solutions in the presence of CO$_2$, all manipulations and transfers were performed while maintaining a strong stream of CO$_2$-free nitrogen through the solutions.

Stock NaClO$_4$ solutions were prepared from the salt synthesized by reaction of Na_2CO_3 with HClO$_4$ or from that obtained commercially (G. F. Smith Chemical Company). In either case, the salt was twice recrystallized from water, dissolved and brought to a pH of about 2 with dilute HClO$_4$, and evaporated to the desired concentration under nitrogen. The resulting solutions were adjusted to a pH of about 6 with microdrops of 50% NaOH and sealed in polyethylene bottles. Qualitative tests on these solutions showed no turbidity when treated with BaCl$_2$, AgNO$_3$, and the hydrolyzed lead solutions.

Analyses.—Stock lead solutions were analyzed for total lead(II) by direct titration with EDTA using Eriochrome Black T as indicator.[19] Bound hydroxide was determined by the method employed by Willard and Kassner.[18] Wherever determined, the total perchlorate content of the solutions was obtained by precipitating the lead with excess ammonium carbonate, filtering, and evaporating the filtrate and washings to dryness. The residue dried to constant weight at 110° was weighed as NH$_4$ClO$_4$. Sodium perchlorate stock solutions were analyzed by evaporating to dryness, drying the residue to constant weight at 110°, and weighing as anhydrous NaClO$_4$.

Found: $\bar{n}$ = 1.33 stock (solution 1): lead, 1.700 *M;* bound OH, 2.260 *M;* OH:Pb, 1.329; (solution 2): lead 1.250 *M;* bound OH, 1.689 *M;* OH:Pb, 1.351; pH 7.60. $\bar{n}$ = 1.0 stock, series 1 (solution 1): lead, 0.4314 *M;* bound OH, 0.4337 *M;* OH:Pb, 1.005; (solution 2): lead, 0.2688 *M;* bound OH, 0.2678 *M;* OH:Pb, 0.996; pH 6.10. $\bar{n}$ = 1.0 stock, series 2: lead, 0.8416 *M;* bound OH, 0.8930 *M;* OH:Pb, 1.061; pH 6.65. $\bar{n}$ = 0.5 stock: lead, 0.5482 *M;* bound OH, 0.265 *M;* OH:Pb, 0.484; pH 5.00. $\bar{n}$ = 0.0 stock: lead, 0.7379 *M;* ClO_4^-, 1.497 *M;* ClO$_4$:Pb, 2.029; pH 2.00. NaClO$_4$, stock 1: 5.507 *M;* stock 2, 6.670 *M.*

Experimental Solutions.—For each hydroxyl number, experimental solutions were prepared by taking aliquots of the freshly-filtered and analyzed stock solution and diluting to 100 ml. in volumetric flasks after adding sufficient NaClO$_4$ solution so as to give a final NaClO$_4$ concentration of 1.00 *M*. Calibrated pipets and burets were used in making the dilutions. The solutions were allowed to stand overnight in a room thermostated at 25 ± 1° before saturating with nitrogen and diluting to final volume. After mixing thoroughly, the solutions were immediately subjected to measurements of turbidity and refractive index. Both the stock and experimental solutions of each hydrolyzed series were unstable in the presence of air, becoming slightly turbid on handling due to the absorption of CO$_2$.

Light-scattering measurements were made as previously described[20] using a photometer calibrated with dry, thiophene-free benzene. The value selected for the absolute value of the turbidity of benzene was that of Kushner[21] and Stamm and Button,[22] 7.71×10^{-4} cm.$^{-1}$. The turbidity of the 1.00 *M* NaClO$_4$ background was approximated by the limiting turbidity of the solution when the lead(II) concentration approached zero; this value agreed well with turbidity measurements on 1.00 *M* NaClO$_4$ alone. This was subtracted from the gross turbidity of the solutions to give the turbidity, τ^*, due to the hydrolyzed lead species.

Solutions were clarified by filtration through 0.45 μ millipore filters directly into the scattering cell blanketed with nitrogen. The saturation of the solutions with nitrogen and filtration under nitrogen were necessary in order to minimize contact of the solutions with the air. Solutions not handled in this manner grew turbid so rapidly as to render meaningful turbidity measurements impossible.

Each value of the turbidity represents the average of 8–12 measurements taken over 6–8 filtrations except for those of the $\bar{n}$ = 1.33 series, where the instability of the solutions was most pronounced. For the latter, the turbidities given are the average of 6–8 measurements over the same number of filtrations.

Turbidity measurements were made with 4358 Å. light using matched 3-cm. square cells. The absence of any dissymmetry of scattering was checked by measurements between angles of 55 and 130° using a special cylindrical cell.

Refractive index increments were determined at 4358 Å. using a Brice-Phoenix differential refractometer calibrated with sucrose solutions.

Density and pH Measurements.—Densities were determined pycnometrically at 25°. The pH of each experimental solution was measured at 25° using a Leeds and Northrup pH indicator standardized with saturated potassium hydrogen tartrate.

Analysis of Precipitates.—The combined precipitates from each series of hydrolyzed lead solutions were collected by filtration after allowing the solutions to stand about 4 weeks following the completion of the light-scattering measurements. They were washed with cold, carbonate-free water, dried *in vacuo* over CaCl$_2$, and weighed. The weights obtained corresponded to an estimated 0.25% of the total lead in solution, assuming a precipitate of PbCO$_3$. Infrared measurements using KBr pellets were performed on the precipitate with a Perkin-Elmer infracord spectrophotometer.

Results and Discussion

For a three-component system consisting of a solvent (component 1), a monodisperse polymer (component 2), and supporting electrolyte (component 3), the degree of aggregation N_z' of the polymer is related to the turbidity due to the polymer, τ^*, by[23]

$$\frac{1}{N_{z'}} = \frac{H''M'\varphi\psi'^2}{\tau^*} - \frac{z'^2M'}{2M_3} \qquad (1)$$

$$H'' = \frac{32000\pi^3n^2}{3N\lambda^4} \qquad (2)$$

In these equations, φ is the volume fraction of the solvent, N is Avogadro's number, n the refractive index of the solution, and λ the wave length of the light. The primed quantities M', z', and ψ' refer to the molarity, charge, and differential refractive index of a "monomeric" component 2, following the method of Scatchard[24] for use in the study of polyelectrolytes. For a hydrolyzed lead species containing $\bar{n}$ hydroxide

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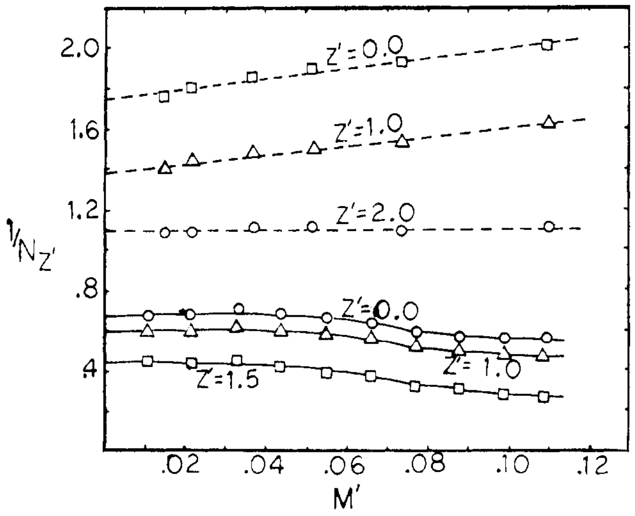

Fig. 1.—$1/N_{z'}$ *vs.* M' with z' as a parameter; hydroxyl numbers ($\bar{n}$) 0.0 and 0.5: --------, $\bar{n}$ = 0.0; ———, $\bar{n}$ = 0.5.

ions bound per lead atom, the "monomeric" component 2 is

$$\left[\mathrm{Pb(OH)}_{\bar{n}}(\mathrm{ClO_4})_{\nu}{}^{(2-\bar{n}-\nu)+} + (2 - \bar{n} - \nu)\mathrm{ClO_4}^- - \left(\frac{2 - \bar{n} - \nu}{2}\right)\mathrm{NaClO_4}\right]$$

where

$$z' = (2 - \bar{n} - \nu);\ \psi' = \frac{\partial n}{\partial M'} - \frac{z'}{2}\frac{\partial n}{\partial M_3};\ M_3 = 1.00 + \frac{z'}{2}M'$$

Refractive Index Increments, Densities, and pH of Solutions.—Since the $NaClO_4$ and lead concentrations were known accurately from solution make-up, the subtraction of the $NaClO_4$ contribution from the gross Δn of the solution gave Δn for the lead-containing electrolyte. The slope of a plot of the resultant Δn as a function of M gave the differential refractive index, $\partial n/\partial M'$. Values for $\partial n/\partial M_3$ necessary for calculation of ψ were taken from the data of Goehring.[25]

Solvent volume fractions for each solution were calculated from the density data using the reported values[26] for $\bar{V}_1$ in aqueous $NaClO_4$ solutions. In each series φ varied only slightly with lead concentration and was about 0.95 for all solutions.

The turbidities and refractive index increments for the lead species and the pH and solvent volume fractions for the solutions are given in Table I. Values for $\partial n/\partial M'$ are tabulated in Table II.

Degrees of Polymerization and Estimated Charges for the Lead Species.—Figures 1 and 2 show plots of $1/N_{z'}$ as a function of M' using z' as a parameter. For the $\bar{n}$ = 0.0 series, a degree of polymerization of *ca.* 0.9 is found for a lead solute with charge +2. It is concluded that the lead(II) exists in these solutions as an unhydrolyzed ion which is not complexed by the perchlorate gegenions. A polydisperse system is indicated for the $\bar{n}$ = 0.5 solutions with an approximate degree of polymerization between 1.5 and 2.2 for lead concentrations below about 0.05 *M*. The sharp drop in $1/N_{z'}$ beyond this point is perhaps due to the growth of a larger aggregate at higher concentrations. The calculations of Esval[17] using the data of Olin[13] qualitatively support these findings.

Both series of solutions at $\bar{n}$ = 1.0 agree remarkably well in view of the different modes of preparation of the stock solutions. A degree of aggregation of about 4

TABLE I

EXPERIMENTAL TURBIDITIES (4358 Å.), REFRACTIVE INDEX INCREMENTS, SOLVENT VOLUME FRACTIONS, AND pH OF THE LEAD(II) SOLUTIONS AS A FUNCTION OF HYDROXYL NUMBER

$\bar{n}$	M'	$10^5\tau^*$	$10^3\Delta n$	φ	pH
0.0	0.0075	0.17	0.285	0.952	2.50
	0.0147	0.28	0.559	0.952	2.50
	0.0221	0.41	0.843	0.951	2.47
	0.0368	0.66	1.377	0.950	2.40
	0.0515	0.90	1.906	0.949	2.33
	0.0736	1.28	2.667	0.947	2.21
	0.1104	1.79	4.000	0.945	2.00
	0.1471	2.56	5.296	0.942	1.90
	0.1842	3.09	6.666	0.937	1.77
0.5	0.0108	0.45	0.357	0.954	5.98
	0.0219	0.89	0.699	0.953	5.81
	0.0329	1.28	1.119	0.952	5.69
	0.0440	1.79	1.441	0.951$_5$	5.58
	0.0549	2.30	1.787	0.950	5.50
	0.0659	2.82	2.151	0.950	5.51
	0.0767	3.58	2.497	0.949	5.43
	0.0880	4.22	2.820	0.948	5.44
	0.0988	4.86	3.194	0.947	5.34
	0.1093	5.50	3.498	0.947	5.32
1.0	0.0053	0.38	0.150	0.953	6.72
(Ser. 1)	0.0134	0.89	0.319	0.952	6.61
	0.0268	1.78	0.719	0.951	6.51
	0.0536	3.58	1.425	0.949	6.35
	0.0670	4.47	1.832	0.949	6.29
	0.0804	5.49	2.193	0.948	6.26
	0.1072	6.91	2.947	0.947	6.21
	0.1340	8.70	3.686	0.945	6.18
1.0	0.0083	0.63	0.223	0.953	6.78
(Ser. 2)	0.0167	1.15	0.385	0.952	6.70
	0.0252	1.78	0.644	0.952	6.60
	0.0337	2.42	0.846	0.951	6.52
	0.0421	3.06	1.105	0.950	6.48
	0.0507	3.58	1.314	0.949	6.41
	0.0675	4.72	1.790	0.949	6.39
	0.0844	6.26	2.251	0.948	6.38
	0.0925	6.77	2.487	0.947	6.35
	0.1007	6.91	2.707	0.947	6.31
1.33	0.0124	1.00	0.346	0.954	7.72
	0.0249	2.04	0.593	0.953	7.80
	0.0374	3.06	0.925	0.952$_5$	7.82
	0.0501	4.09	1.212	0.951	7.78
	0.0625	5.24	1.545	0.951	7.75
	0.0754	6.26	1.793	0.950	7.73
	0.0877	7.53	2.114	0.949	7.71
	0.1002	8.68	2.391	0.949	7.69
	0.1124	9.97	2.704	0.948	7.70
	0.1246	11.39	2.982	0.947	7.66

TABLE II

DIFFERENTIAL REFRACTIVE INDICES OF THE LEAD(II) SPECIES AT 4358 Å.

$\bar{n}$	$10^2(\partial n/\partial M')$, l. mole^{-1}	Av. $\Delta n/M'$ × 10^2, l. mole^{-1}
0.00	3.59	3.66
0.5	3.25	3.27
1.0	2.77	2.71
1.33	2.40	2.42

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and a monomeric charge of near +0.5 is found in both cases, giving a fairly well-defined tetramer, $[Pb_4(OH)_4(ClO_4)_2]^{2+}$, as the major lead-containing species in this concentration range.

At $\bar{n}$ = 1.33, the results are somewhat concentration dependent. The degree of polymerization is near six and the charge on the aggregate is considerably diminished by perchlorate complexing. The species is therefore formulated as $[Pb_6(OH)_8(ClO_4)_3]^+$, consistent with the ultracentrifuge[17] and e.m.f. titration[13] results. No evidence for any polymerization number greater than six can be inferred from the data.

Of the measurements directly associated with the calculation of $1/N_{z'}$, those of turbidity are the least certain. This is due mainly to two factors: (1) the uncertainty in the absolute turbidity of the calibrating liquid, benzene,[27] and (2) the low turbidities encountered with inorganic polymers compared to that of the background. The latter effect has been minimized in this work by smoothing of the turbidity data at low solute concentrations. The calculated degrees of polymerization found in this work are believed to be accurate to within ±10% and probably are even more certain. This is about the same order of accuracy as that obtained in the ultracentrifugation of similar systems. Since small degrees of polymerization were found, this maximum uncertainty does not significantly alter the conclusions drawn from this work.

The pH measurements made on the solutions justify the assumption that $\bar{n}$ is constant over the concentration range studied. The systems are in every case at equilibrium. No time effects due to hydrolytic processes were noted in any of the physical measurements made.

Values for the apparent molar volumes of the monomeric unit, ϕ_{mon}, were calculated from the density data by the equation

$$\phi_{mon} = \frac{1.0000 - n'_{H_2O}V^{\cdot}_{H_2O} - n'_3\phi_3}{M'/1000} \qquad (3)$$

where n'_{H_2O} and n'_3, respectively, refer to the number of moles of water and $NaClO_4$ per ml. of solution and $V^{\cdot}_{H_2O}$ = 18.070 ml. is the molar volume of pure water. The apparent molar volume of $NaClO_4$, ϕ_3, was estimated from the data of Wirth and Collier[26] by assuming its value in 1 *M* $NaClO_4$, 44.8 ml. n'_{H_2O} was obtained by subtracting from the density of the solution the weights of the lead species and $NaClO_4$ contained per ml. and dividing the remainder by the molecular weight of water. ϕ_{mon} was found to vary somewhat regularly with $\bar{n}$: for $\bar{n}$ = 0.0, ϕ_{mon} = 70–75 ml. mole^{-1}; $\bar{n}$ = 0.5, ϕ_{mon} = 65–70 ml. mole^{-1}; $\bar{n}$ = 1.0, ϕ_{mon} = 55–60 ml. mole^{-1}; and $\bar{n}$ = 1.33, ϕ_{mon} = 50–55 ml. mole^{-1}. The decrease in ϕ_{mon} with increasing hydroxyl number is presumed to be due mainly to the elimination of perchlorate anions from the monomer as the hydroxyl number increases.

The experimental solutions were found to be transparent from about 3000 Å. to 4600 Å.; however, from 1900 Å. to near 3000 Å. even the most dilute solutions were completely opaque, even with measurements using 1-mm. cells. The solutions were not studied spectrophotometrically as a function of dilution and no calculations were made as to the average extinction coefficients of the lead species; however, it is possible that a careful spectrophotometric study of these solutions would serve the purpose of confirming Olin's[13] scheme. Qualitatively, it was noted that the solutions absorbed at longer wave lengths as $\bar{n}$ increased, in agreement with reported observations.[12,28]

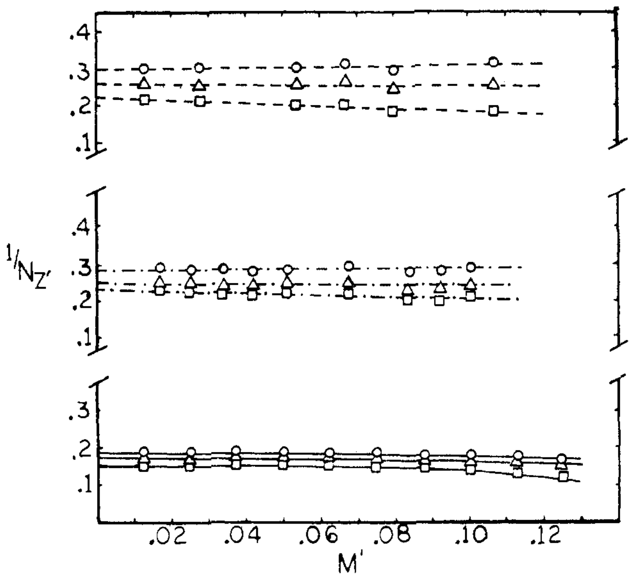

Fig. 2.—$1/N_{z'}$ *vs.* M' with z' as a parameter; hydroxyl numbers ($\bar{n}$) 1.0 and 1.33. ---------, $\bar{n}$ = 1.0, series 1: O, z' = 0.0; Δ, z' = 0.5; □, z' = 1.0. —·—·, $\bar{n}$ = 1.0, series 2: O, z' = 0.0; Δ, z' = 0.5; □, z' = 1.0. ——, $\bar{n}$ = 1.33: O, z' = 0.0; Δ, z' = 0.25; □, z' = 0.50.

The infrared spectra of the minute amounts of precipitates obtained from the hydrolyzed solutions after long standing were found to agree qualitatively with the spectrum of the solid obtained by adding Na_2CO_3 to $Pb(ClO_4)_2$ solutions. Each spectrum showed the strong carbonate absorption at 1430 cm.$^{-1}$ accompanied by several bands between 700 and 1100 cm.$^{-1}$, characteristic of basic carbonates.[29] In addition, the band at approximately 3300 cm.$^{-1}$, which is attributed to the bonded OH groups in basic salts,[29] was apparent. The over-all features of the spectra tended to agree with those found by Hunt, *et al.*,[30] for $Pb_3(OH)_2(CO_3)_2$. Perchlorate[31] bands were not found in the spectra. It was concluded that the visible turbidity which developed in the hydrolyzed solutions is due to carbon dioxide absorption rather than to the formation of insoluble products of further hydrolysis and aggregation.

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