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Opalescence of Silicic Acid Gels

BY ALCON C. COPISAROW AND MAURICE COPISAROW

In a Preliminary Note on "Silica and the Liesegang Phenomenon,"[1] brief reference was made to the occasional formation of an opalescent gelatinous silicic acid. Further work on silica revealed a great complexity of reactions and structures—a complexity comparable with that observed in the case of calcium carbonate.[2] The formation of several types of silicic acid gel was observed, ranging from the acidic, beautifully opalescent and elastic poly-silicic acid to the basic, translucent and softer mono-silicic acids. The latter were found to include a whole series of forms, differing in *p*H value and degree of transparency. In accordance with Hurd and his co-workers[3] the alkaline silicic acid gels are termed here as *mono*-silicic more in contrast to the *poly*-silicic acidic gels, than in strict adherence to the actual molecular complexity. Whilst the mono-molecular condition may exist in the aqueous solutions of water glass only, the description adopted in this paper is found useful in differentiating between the comparatively simpler alkaline (ranging in *p*H value between 8.0 and 11.0) and the highly polymerized and closely linked acidic silicic acid gels with a *p*H value below 7.0.

Molecular weight determinations, the gradual lowering of *p*H values with progressive coagulation and the widely accepted conception of gelation as synonymous with polymerization suggest, however, a more apt terminology. The soft, reactive basic gel may be termed as a *primary* or simple polymer of silicic acid, and the elastic, inert acidic form as a *secondary* or complex, closely-linked polymer. Further dehydration by syneresis and external influences, accompanied by a reduction in ionization to a minimum, would lead to the formation of stable *tertiary* polymers of silicic acid, known to us in the form of various minerals of the hydrated silica type.

Experimental

Thirty cc. of concentrated hydrochloric acid was run carefully onto 17 cc. of a 25% by volume (H_2O about 86.5%) solution of commercial water glass,[4] contained in a long tube 15 mm. in diameter, at 11–12°. This led to an immediate formation of a fine network structure of amorphous silica, which soon passed from a translucent to an opaque compact membrane or band at the interface of the two liquids. Within twenty-four hours, 32 mm. precipitate was formed, with many white laminae making up some 12 composite bands. During the next five days the precipitate extended to 80 mm. with further bands of the same type. The product was examined by cutting the test-tube longitudinally and carefully dissecting the stratified formations. The bands were found to be hard and brittle, whilst the inter-band spaces were occupied by yellowish, acidic, gelatinous silicic acid (the color depending upon the type of electrolyte[5]). Below the silica bands a clear and basic viscous mass was formed, followed by an opalescent to translucent viscous region. This opalescence was found to increase downward where it merged with the unreacted water glass. Occasionally, this deepening cloudiness resolved itself into wide bands of increasing intensity. Simultaneously with silica band formation, opalescent gelatinous silicic acid (a 54-mm. column), exhibiting a fine display of colors, was forming above the original membrane in the acid region.

It was further observed that: (1) When the experiment was carried out at 17–18° the upper acidic gel lost its opalescence, becoming clear and refractive to light. The general course of the reaction remained unaltered. At 3° to 5° there was a general slowing down of the reaction. The formation of silica bands below the membrane was sluggish, their outline indefinite with a soft, readily crumbling texture. The silicic acid gel above the membrane was whitish and opaque (translucent when in thin layers).

(2) With higher concentrations of water glass no gelatinous silicic acid appeared above the interface of the two reacting liquids. The silica bands became fewer and thicker, whilst the lower basic silicic acid gel tended to be re-dissolved by the remaining water glass.

(3) In the exhaustive interaction of water glass with acids under conditions specific to the Liesegang phenomenon, an excess of acid completely neutralized the water glass only when the latter was highly diluted or else used in shallow depth (as in a Petri dish). In the usual tube experiments the interaction was frequently brought to a standstill, owing to the obstruction to diffusion exerted cumulatively by the compact and hard silica bands. This was shown by perforating all but the few lower silica bands at the end of the reaction, when the activity was renewed and the basic silicic acid gel below the bands became transformed into further silica formations.

(4) The *acidic* silicic acid gels, clear (when formed at 17–18°), opalescent (11–12°), opaque (3–5°) and as found in the interband spaces were firm and elastic and must be regarded as fundamentally identical with the acidic polysilicic acid gels recorded by Hurd and his co-workers[3]—differing, however, from one another in the amount and state of dispersion of by-products and possibly impurities.

(5) The *basic* silicic acid gels, intermediate in the transition of silicic acid sol to its acidic gel, were softer and less elastic than the acidic forms. These basic gels, produced by the interaction of acid and base (with their gradation of concentrations in opposite directions) were taken to be identical with the basic mono-silicic acid hydrogels investigated by Hurd, *et al.*, and likewise ranged in *p*H value and degree of opalescence or rather cloudiness.

(6) The appearance and general properties of the opalescent and other acidic gels were not affected by previous boiling and cooling *in vacuo* of the water glass and the redistillation of the hydrochloric acid. These features of acidic silicic acid gels, therefore, were governed by osmosis and temperature conditions, rather than the presence of dissolved air in the reagents. In this respect a close analogy may be found in the rhythmic forms, especially the opacity bands, of calcium carbonate.[2] In both cases the cloudiness or opalescence was due to finely divided matter in a state of high dispersion. In the present in-

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(1) A. C. Copisarow and M. Copisarow, *Nature*, **149**, 413 (1942).

(2) M. Copisarow, *J. Chem. Soc.*, 222 (1927); *Kolloid. Z.*, **47**, 60 (1929); *Nature*, **129**, 400 (1932); **132**, 67 (1933); **138**, 509 (1936); *Protoplasma*, **30**, 258 (1938).

(3) Hurd, Pomatti, Spittle and Alois, THIS JOURNAL, **66**, 388 (1944).

(4) The water glass was the 140° Tw. solution manufactured by Messrs. Joseph Crosfield & Sons, Ltd., of Warrington. It contained 46% approx. of water, with a *p*H value of 10.7 for a 0.2% solution.

(5) Hurd and Barclay, *J. Phys. Chem.*, **44**, 847 (1940).

stance amorphous silica was probably orientated within the network structure of the polymerized silicic acid gel.

(7) Unlike the inert acidic gels the basic opalescent forms were transitory in character. On gradually altering the *p*H value of the basic form by the addition of very dilute hydrochloric acid the passage of the gel through all degrees of opalescence could be attained, culminating in the partial or complete clearing and finally in an acidic gel. Acid extracts of such triturated basic gels were found on analysis to contain traces of iron, calcium and aluminum. Although the non-availability of pure water glass prevented the reproduction of the basic opalescent bands solely by the separation of amorphous silica, it may be assumed that the opalescence of the basic silicic acid from commercial water glass represented the combined effect of amorphous silica and mineral impurities. However, no such "salting out" of silica occurred with water glass, differing in the ratio of sodium to silicon. Thus, the acid-treated gels, when dissolved in the minimum quantity of pure sodium hydroxide and then subjected to the process of rhythmic re-gelation, yielded (in addition to the acidic gels) *clear* basic gelatinous silicic acid entirely free from cloudiness. Similarly non-opalescent basic gels were obtained by redissolving the clear poly-silicic acid gel from the upper acid region. The varying cloudiness of basic gels therefore appeared to be due to the impurities present in commercial water glass, namely, metallic hydroxides, and *not* the separation of amorphous silica. This conclusion is confirmed by the milkiness of the basic gels produced by the interaction of water glass with sulfuric acid.[5]

In view of these experiments the general course of the reaction could be reconstructed as follows: The contact of the acid with the alkaline surface led to the passage of the mobile silicic acid sol to a reactive basic mono-silicic acid gel (*p*H value 8.0–11.0),[3] which rapidly disintegrated into amorphous silica and water. The cloudy mass of silica particles became orientated to form radial and concentric patterns of the membrane structure, which aggregated ultimately into bands. In the meantime the locally liberated water created conditions favorable to peptization, and this resulted (in an acid medium) in the polymerization of some of the basic gel into inert acidic gelatinous silicic acid (*p*H value below 7.0).[3] Further diffusion brought about a repetition of conditions prevailing in the formation of the first silica membrane and this was again succeeded by peptization. Thus, the interaction of the acid with water glass under conditions specific to the Liesegang phenomenon produced an alternation of an anhydrous and hydrated state, in which the silica bands were separated by acidic poly-silicic acid gel. Yet this sequence of formations was maintained only under the limited experimental conditions given earlier. Consequently increased peptization, conditioned either by the exhaustion of the acid above the interface of the two liquids or by the impermeability of the growing number of silica bands, led to the permanency of basic gelatinous mono-silicic acid below the bands. With concentrations of water glass above 25% by volume the compact silica network formed a semi-permeable membrane through which no gelatinous silicic acid (though of lower specific gravity than the medium) could pass into the upper acid region; it thus remained in the interband spaces. With 25% solutions of water glass the silica bands became sufficiently porous to allow some of the silicic acid gel to rise into the acid region, where, at 17–18°, it coalesced into a clear, refractive, elastic poly-silicic acid gel (a case of thixotropy[6]). At 11–12°, however, the degradation of the basic silicic acid gel to silica and the orientation and consolidation of the latter were retarded, with the result that the upward current of poly-silicic acid carried with it a multitude of finely divided silica particles. These, orientating within its lattice structure, imparted an opalescence to the gel. By lowering the temperature to 3–5° the reaction was still further retarded, leading to an increased proportion of the dispersed silica to be carried away in the upward current of the silicic acid gel and giving rise to the opaque colloid. The difference between the opalescence and opaque gel must be attributed to one or more of such factors as number, size and orientation of silica particles.

Summary

In the present investigation the simpler basic-silicic acid gels, differing in *p*H value (between 8.0 and 11.0) and intensity of opalescence, are automatically reproduced as a rhythmic series under the conditions of the Liesegang Phenomenon.

The synthesis of the opalescent, opaque and clear polysilicic acid gels, recorded in this paper, is significance as a possible basis for the formation of opalite and hyalite.

(6) Pauli and Valkó, *Kolloid. Z.*, **38**, 289 (1926); Freundlich, *ibid.*, **46**, 289 (1928); Hurd and Thompson, Jr., *J. Phys. Chem.*, **45**, 1263 (1941).

MANCHESTER 16, ENGLAND RECEIVED MAY 24, 1945

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Coulometric Analysis

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Recent experiments in this Laboratory have shown that it is relatively easy to attain 100% current efficiency in the electrolytic reduction of various metal ions,[1] and certain organic compounds,[2] when the electrolysis is performed with a mercury cathode whose potential is controlled precisely These results suggested the possibility of basing an electroanalytical method on the measurement of the quantity of electricity that must be passed through an electrolysis cell to achieve quantitative reaction at one of the electrodes of the substance being determined. The experiments described in the present paper demonstrate that such a procedure is feasible, and capable of general application, when the electrolysis is carried out with a mercury cathode at controlled potential.

A similar method of "coulometric analysis" has already been described by Szebelledy and Somogyi,[3] but it differs in several important respects from the method described herein. Szebelledy and Somogyi employed an electrolysis cell with two platinum electrodes, and electrolyzed

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(1) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 147 (1944).

(2) J. J. Lingane, C. G. Swain and M. Fields, THIS JOURNAL, **65**, 1348 (1943).

(3) L. Szebelledy and Z. Somogyi, *Z. anal. Chem.*, **112**, 313, 323, 332, 385, 391, 395, 400 (1938).