

Evidence that Polywater is a Colloidal Silicate Sol

**WILLARD D. BASCOM, EDWARD J. BROOKS,
AND BRADFORD N. WORTHINGTON, III**

*Surface Chemistry Branch
Chemistry Division*

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**NAVAL RESEARCH LABORATORY
Washington, D.C.**

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13. ABSTRACT A study was made of the "anomalous" condensation of water and its conversion to "polywater" in glass and silica capillaries. The condensate was expelled as a sol-like material that on evaporation frequently gave a particulate appearance. The residue was analyzed using the electron probe and found to contain significant amounts of silicon and sodium. These results suggest that the unusual properties of "polywater" may be due to the presence of silica or silicate. It is further shown that, since alkaline silicate solutions can absorb CO ₂ , the infrared spectra of "polywater" may actually be due, in part, to bicarbonate ion.			

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ABSTRACT

A study was made of the "anomalous" condensation of water and its conversion to "polywater" in glass and silica capillaries. The condensate was expelled as a sol-like material that on evaporation frequently gave a particulate appearance. The residue was analyzed using the electron probe and found to contain significant amounts of silicon and sodium. These results suggest that the unusual properties of "polywater" may be due to the presence of silica or silicate. It is further shown that, since alkaline silicate solutions can absorb CO_2 , the infrared spectra of "polywater" may actually be due, in part, to bicarbonate ion.

Problem Status

This is an interim report; work on this problem is continuing.

Authorization

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EVIDENCE THAT POLYWATER IS A COLLOIDAL SILICATE SOL

INTRODUCTION

Deryaguin and co-workers have presented evidence that a new form of water (anomalous water) is produced when normal water vapor condenses into minute, pristine glass or silica capillaries (1,2). More recently, Lippincott, Stromberg, Grant and Cessac (3), produced water condensate in such capillaries and obtained its infrared and Raman spectra from which they concluded that the condensate contained a high molecular weight polymeric form of water, i.e., "polywater". A distinction should be made between the claims of Lippincott et al. for, "polywater" and those of Deryaguin et al. for anomalous water. The Russian workers do not claim "anomalous water" to be a high molecular weight polymeric water. Furthermore, they were extraordinarily careful in preventing electrolyte contamination of the condensate in many of their experiments. The work reported here indicates that salt contamination is an important consideration in the experiments described by Lippincott et al.

EXPERIMENTAL

Capillaries having internal diameters of 50μ to 5μ were drawn from acid (HNO_3 - H_2SO_4 , 1-1) cleaned Pyrex and silica (GE 204) tubing. In some experiments the capillaries were loosely placed in Pyrex dishes over distilled water in a dessicator evacuated to about 40 mm Hg and held at $25 \pm 1^\circ\text{C}$. This is the procedure used by Lippincott et al. (3). Other condensation experiments were conducted in an apparatus designed to allow the capillaries to be evacuated independently of the water to reduce the chance of spray reaching the capillaries during the pump-down. The apparatus had a chamber for the capillaries separated from the chamber for water by a grease-free vacuum valve. The water chamber was evacuated first, the valve closed and the capillaries introduced into the other chamber. This section was then evacuated, cut off from the pump and opened to the water.

The capillaries were inspected after three to ten days exposure to water vapor. To remove condensate for analysis, the liquid was expelled by air pressure using a gas tight syringe and hypodermic needle. The capillary was sealed into the needle with a drop of melted, purified paraffin. The condensate was expelled onto steel mirror surfaces and the residue examined by light microscopy. For electron probe analysis a pure, low-silicon copper was used instead of steel. The electron probe was an Applied Research Laboratory EMX 200. Infrared spectroscopic determinations were made with a Perkin-Elmer 457 spectrometer.

RESULTS AND DISCUSSION

Condensate was observed in both Pyrex and silica capillaries held over distilled water. For the capillaries in the dessicators the yield (number of capillaries with condensate) was about 50%. In the two-chamber apparatus the yield was 10-25%. Figure 1A illustrates the appearance of condensate columns viewed with a reflected light microscope. When these capillaries were put in an evacuated chamber or left at 40-50% RH for a few hours, most of the condensate evaporated except for a residue with a gel-like appearance. In figure 1B the gel had formed before the liquid phase had fully evaporated.

Much of the condensate evaporated very rapidly when expelled onto steel mirror surfaces, leaving behind minute films of residue. Typical examples of this residue are shown in Figure 2 for condensate from Pyrex capillaries. Note that some of the residues have a particulate appearance. Close examination revealed that many had ridges near the edge indicating a profile such as in Figure 3.

Residues from condensate in silica usually had a more homogeneous appearance (Figure 4) than those from Pyrex. The only particles that could be clearly associated with the silica derived residues are those clustered at the center in Figure 4. Other particles in the photograph are dust.

Electron probe analysis of the residues from Pyrex revealed sodium and silicon in easily detectable amounts. Sodium was most strongly evident in the particulate matter within the residue and the silicon level was highest near the edge. These analyses were not pursued in detail since, as discussed below, the corrosion of pristine glass surfaces is well known and the presence of sodium and silicon was not unexpected.

The residues from condensate in silica were thinner and therefore more difficult to analyze than the residues from Pyrex. Nonetheless, the electron probe revealed significant levels of sodium and silicon in the thicker regions near the edges. Figure 5A shows the secondary electron emission for such a region and 5B shows the silicon x-ray ($\text{SiK}\alpha$ 7.1252) emission from this same region. The silicon level in this residue is about 4 times the background level. The relative intensities for silicon and sodium were approximately equal.

Residues of dilute sodium silicate solutions also showed the annular profile drawn in Figure 3. Analysis of these residues with the electron probe revealed that it was often impossible to detect significant amounts of sodium or silicon in the thin central regions. For example, in Figure 6 the silicon x-ray emission is displayed for a section of a sodium silicate residue left by a 0.1 μ l drop of a 0.1% solution. The arc of the

rim clearly shows emission due to silicon but no significant emission is observed for the central region even though material was visible with the light microscope.

We conclude from the electron probe results that silicon, sodium and possibly other cations are important if not principle constituents of these condensate residues. Failure to detect these elements in earlier work (3) may have occurred because the residues were too thin.

If silicates are part of the condensate, then it is possible to offer an alternate explanation for the infrared spectra of "polywater". Silicate solutions are quite alkaline and are thus capable of absorbing CO_2 from the atmosphere. The principle bands in the "polywater" spectrum are at 1600 cm^{-1} and 1400 cm^{-1} which are close to the frequencies for the antisymmetric and symmetric O-C-O stretching vibrations. To test this idea infrared spectra were obtained for residues left by drops of bicarbonate-silicate solutions on Irtran-2 plates. A typical result is given in Figure 7 for the residue from a solution containing 1.5 gm/l of sodium silicate (mole ratio $\text{SiO}_2/\text{Na}_2\text{O} = 3.3$) and 2.6 gm/l of KHCO_3 . The bands at 1650 , 1400 and 830 cm^{-1} are due to bicarbonate and these same bands can be seen in the polywater spectra (3,4). The broad band at $1200\text{-}1000\text{ cm}^{-1}$ is due to silicate and the one between 3700 cm^{-1} and 2200 cm^{-1} is probably due to residual water.

The spectrum given in Figure 7 differs from the spectra reported for "polywater", just as the "polywater" spectra differ themselves (3,4). After a study of the I.R. spectra of a variety of bicarbonate-silicate mixtures, the reasons for these differences in the spectra became clear. It was found that the band intensities, positions and shapes were a function of (a) total solids concentration, (b) ratio of silicate to bicarbonate, (c) mole ratio of Na_2O and SiO_2 , (d) age of the solution and the residue, (e) the rate and manner in which the solution dries, and (f) the presence of other anions or cations. It is believed that different combinations of these factors gave rise to the observed spectra. For example, the band at 1650 cm^{-1} in Figure 7 does not correspond exactly with the 1600 cm^{-1} band for "polywater" (3,4). However, when the bicarbonate-silicate residues were aged for a few days, there was a detectable shift of the band to 1625 cm^{-1} and sometimes lower.

In these experiments the silicate anion could easily originate from a surface corrosion of the capillary walls. The surface hydrolysis of silicate glasses, especially pristine (freshly formed) surfaces, is well known (5). The process involves the hydration of cationic sites to form an alkaline film capable of hydrolyzing the silicate network. Frazer et al (6) describe water adsorption on the inside of freshly blown glass bulbs and observed a visible condensate which they found to be strongly alkaline. They were also able to show that the alkaline film had left the surface rough and porous.

In the case of condensate from silica capillaries, the electron probe gave clear evidence of sodium as well as silicon which implies contamination since the silica itself does not contain significant amounts of sodium. The principle source of this contamination was probably the glassware holding the capillaries; the formation of a mist or spray from the water during pump-down is believed negligible, especially in the two chamber apparatus. Contamination from the glassware would occur if a water film developed on the walls sufficient to allow surface diffusion or creep of electrolyte onto and into the capillaries. In this connection, it was noted that in all the condensation experiments there was clear evidence of moisture on the walls of the apparatus, formed no doubt during small fluctuations in the room temperature. Also, it was found that if the Pyrex dish holding the capillaries was replaced with a polyethylene dish where the surface creep should be much reduced, the yield dropped from the usual 50% to about 15%.

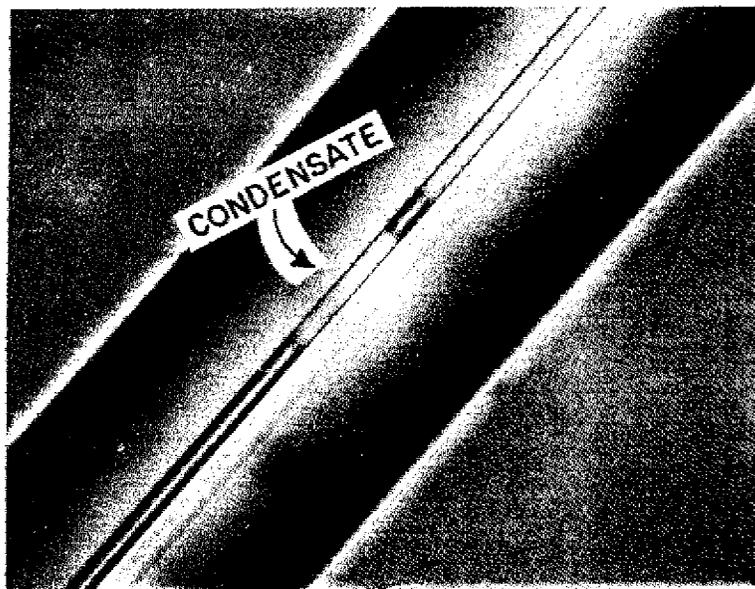
Undoubtedly, the contaminating salts can contribute to the corrosion of the pristine silica surface but, even with silica, such contamination may not be essential. Silica surfaces offer Si-OH groups for water adsorption and at monolayer coverage and higher ($P/P_0 > 0.4$) the film is mobile (7). This film is also acidic since conductivity studies indicate the charge carrier is H^+ or H_3O^+ (7). Therefore, an acid-catalyzed surface corrosion may occur, especially on a pristine surface in which many Si-O-Si bonds are strained.

Initially, the corrosion product of silica or Pyrex would be silicic acid (or metal silicate) which would condense quickly into a colloidal silicate sol and ultimately to a colloidal gel if the solution is dried. Many of the properties attributed to "polywater", such as the gel-like appearance (3,8) and the birefringence (8,9) of the condensate residues certainly suggest silicate. Also, the high refractive indices reported for polywater (9) are consistent with silicate solutions containing high proportions of metal cation (10).

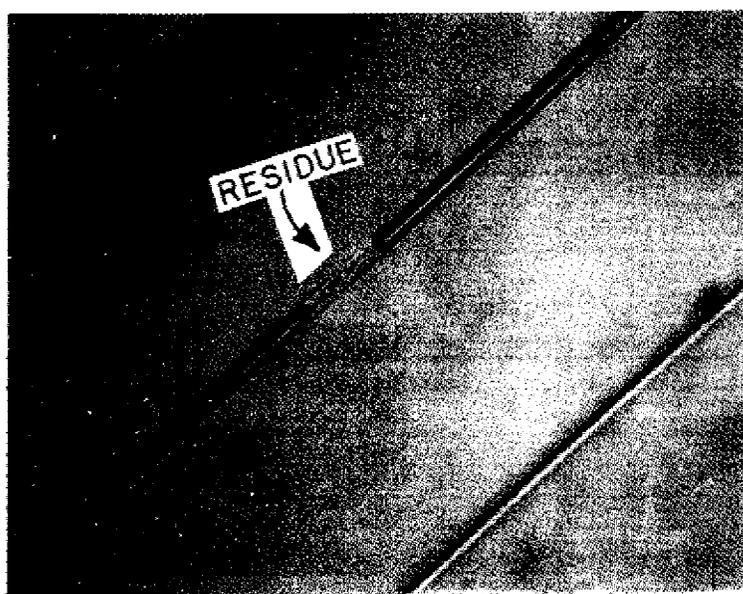
The results reported here offer alternate explanations for the "polywater" phenomena. Samples of "anomalous water" prepared by the technique of Deryaguin and co-workers have not yet been studied. They obtained condensate in very pure silica capillaries held in a platinum fixture with distilled water as the source of vapor (1). This experiment would seem to remove any possibility of contamination by electrolyte. However, an acid-catalyzed corrosion of pristine silica by adsorbed water alone may lead to a silica sol which could explain many of the anomalous properties they observed. Work is underway here to repeat these experiments and analyze the condensate.

REFERENCES

1. Deryaguin, B. V., Talaev, M. V., and Fedyaikin, N. N., Dokl. Phys. Chem. (USSR) 165, 807 (1965).
2. Deryaguin, B. V., Discussion Faraday Soc., 42, 109 (1966).
3. Lippincott, E. R., Stromberg, R. R., Grant, W. H. and Cessac, G. L., Science 164, 1482 (1969).
4. Page, T. F., Jakobsen, R. J. and Lippincott, E. R., Science 167, 51 (1970).
5. Holland, L., The Properties of Glass Surfaces, Wiley, New York, 1964, Chapter 3.
6. Frazer, J. C. W., Patrick, W. A., and Smith, H. E., J. Phys. Chem. 31, 897 (1927).
7. Fripiat, J. J., Jelli, A., Poncelet, G. and Andre, J., F. Phys. Chem., 69, 2185 (1965).
8. Willis, E., Rennie, G. K., Smart, C., and Pethica, B. A., Nature 222, 159 (1969).
9. Castellion, G. A., Grabar, D. G., Hession, J., and Burkhard, H., Science 167, 865 (1970).
10. Debye, P. and Nauman, R., J. Phys. Chem. 65, 8 (1961).



A



B

Fig. 1 - Appearance of water condensate in a silica capillary immediately after removal from a dessicator (A) and after most of the condensate had evaporated (B). The inner diameter of the capillary is about 30μ .



Fig. 2 - Residues left by condensate formed in Pyrex capillaries and expelled onto a steel mirror



Fig. 3 - Residue profile



Fig. 4 - Residue left by condensate formed in a silica capillary and expelled onto a steel mirror

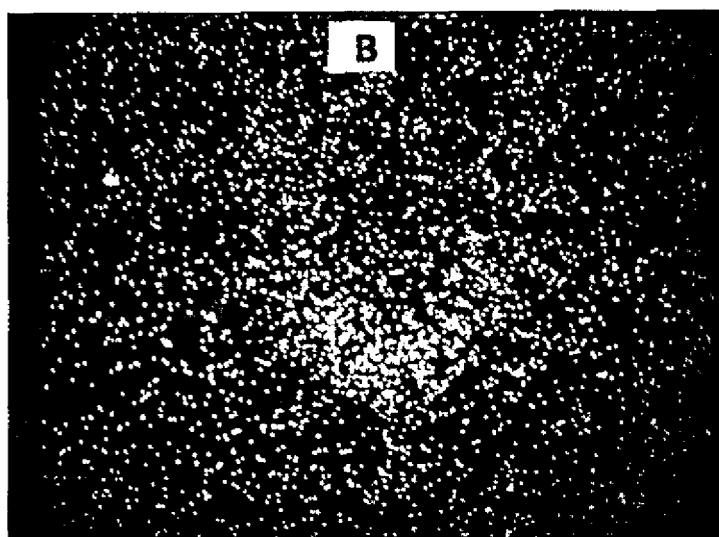
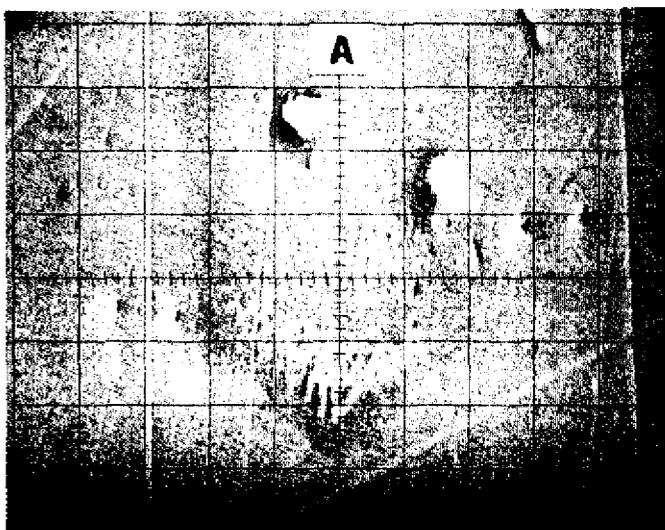


Fig. 5 - Electron probe secondary emission (A) and silicon x-ray emission (B) for a residue of condensate from a silica capillary (Cu substrate)