

ON THE ORDER IN SILICA GELS WITH SPECIFIC ADSORPTION POWER

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INTRODUCTION

Specifically adsorbing silica gels are obtained by coagulating a silica sol in the presence of an organic substance, the molar ratio of organic substance/SiO₂ being about 1:100¹. After removing all the organic material by extraction with methanol such a gel will adsorb the "printing" substance—or a structurally related substance¹—to a greater extent than a gel coagulated in absence of the organic substance. The higher degree of adsorption on printed gels diminishes for molecules with increasing dissimilarity in structure. The investigations published so far deal with the specificity of adsorption on a given print.

The study presented here is concerned with a probable mechanism leading to a specific structure in the printed gel, which may explain the specific adsorption. Information is obtained by investigating the molecular interrelations of oligo silicic acids and printing substances and by studying the ordering phenomena induced by these.

EXPERIMENTAL

Lepidoid silicic acid by precipitation

A solution of phenanthroline (360 to 40 mg in 1 ml 3*N* HCl) is mixed with 9 ml of a silicic sol (50 ml sodium silicate 40° Bé made up to 110 ml with H₂O is stirred into 140 ml 1/2 conc. HCl). Leave for at least 12 h, then filter.

The remaining solution is analyzed for phenanthroline by diluting with 1*N* HCl and measuring the adsorption at 271.5 nm. The precipitate is dissolved in a little 10% NaOH, then diluted with 3*N* HCl and measured for adsorption at 271.5 nm. The SiO₂ content of the precipitate is determined by ashing and weighing.

Lepidoid silicic acid by freezing a sol

10 ml sodium silicate 40° Bé is diluted with 90 ml H₂O. At 0° 10 ml 1/2 conc. HCl is stirred into this solution, which is dialyzed until free of Cl⁻ and then frozen at -20°. After several minutes it was thawed at room temperature. Printed gels and control gel were synthesized as in ref. 1.

RESULTS

The existence of an interrelationship between oligo silicic acids and 1,10-phenanthroline—a substance known to give good prints in silica gels²—was shown by

the U.V. spectrum of the latter in the presence of increasing amounts of sol. The changes observed are: The shoulder of aqueous phenanthroline at 295 nm decreases while the one at 277.5 nm increases to a maximum; an isosbestic point is observed at 288 nm. The maximum at 271.5 nm decreases to a shoulder in the presence of high SiO_2 concentrations (Fig. 1).

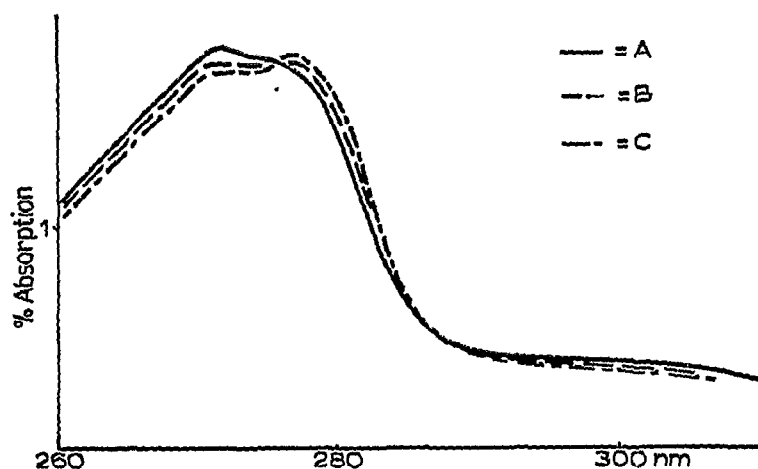


Fig. 1. Spectrum of 1,10-phenanthroline in 1 N HCl (A), in 1 N HCl-silicic acid sol (1 : 1) (B), and in silicic sol (C). See also Experimental.

To get a general idea of the order of the molecules in silicic acid adsorbed to the phenanthroline molecule we worked with more concentrated solutions. Mixing phenanthroline and SiO_2 in a molar ratio of about 1/10 to 1/50 results in a precipitate*. Analyses of several precipitates and of the remaining solutions resulted in the data given in Fig. 2.

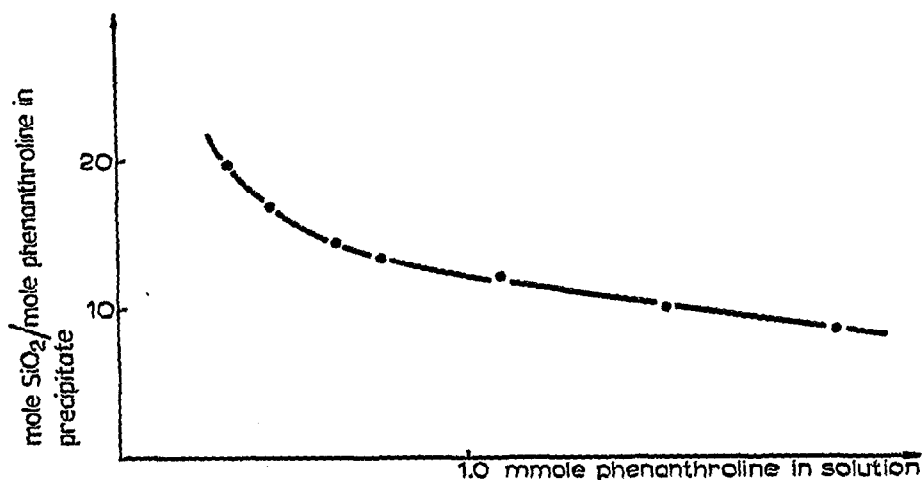


Fig. 2. Molar ratio SiO_2 -phenanthroline in precipitate of constant amounts of silicic acid sol and increasing amounts of phenanthroline.

* Similar precipitates are obtained with 3,4-; 5,6-; 7,8-benzoquinoline and acridine. Because of the lower solubility of these compounds in aqueous HCl, the reaction can only be studied at low concentrations. The smaller printing molecules of quinoline, aniline, *p*-aminobenzoic acid, α,α -bipyridine, antipyrine, and nicotine gave no such precipitates under the conditions chosen.

The molar ratio of phenanthroline/SiO₂ in the precipitate increases for very small concentrations of printing substance. It reaches asymptotically a value of about 1:9. This indicates that 9 moles of Si in some polymeric silica structure adsorb preferentially one mole of phenanthroline. The nearly constant molar ratio in the precipitate suggests a regularly structured silicic acid which adsorbs the printing molecules. In order to characterize this structure X-ray spectra were made. The spectra given in Figs. 3a and b also indicate, because of the sharp lines, a regularly

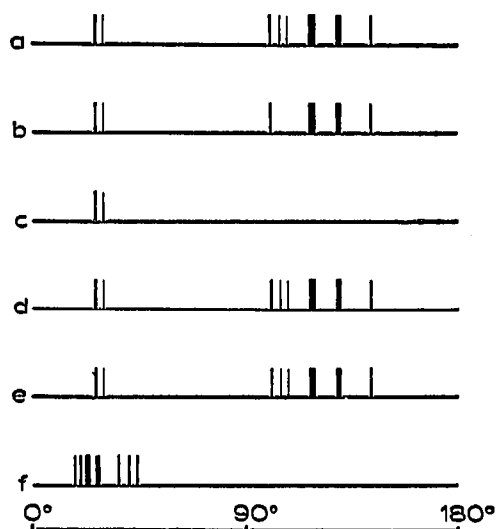


Fig. 3. Debye-Scherrer spectra of: (a) Precipitate of phenanthroline and silicic acid; (b) same precipitate after extraction of phenanthroline; (c) silicic acid gel; (d) "lepidoid silicic acid"³; (e) silicic acid gel printed with phenanthroline (Fe-lamp, exposure 8 to 10 h); (f) phenanthroline (3 h).

structured silicic acid. It was found by calculation that a molar ratio of phenanthroline to SiO₂ of 1:9 or 1:10 corresponds to a complete coverage of the surface of a two-dimensional layer of silicate with phenanthroline molecules. We therefore concluded that the precipitate obtained is a "lepidoid silicic acid"³ consisting of flaky two-dimensional silicic acid crystals, the hydrophilic side of which is covered with phenanthroline. Lepidoid silicic acid was then synthesized according to KAUTSKY AND SAUKEL³ and a Debye-Scherrer diagram was obtained (Fig. 3d). It was identical with the diagrams of the silica structures obtained by precipitation.

To obtain information concerning the order of the molecules in specifically adsorbing gels, *i.e.* the structure of printed sites, an X-ray spectrum was taken of a gel printed with phenanthroline (molar ratio phenanthroline/SiO₂ = 1:100, coagulation 5 days, methanol extraction leaving pure SiO₂). The spectrum was identical with that of lepidoid silicic acid, suggesting that part of the gel structure is formed by phenanthroline during coagulation.

DISCUSSION

1,10-Phenanthroline—or perhaps more generally a molecule with three fused aromatic rings—is a matrix for regular two-dimensional silicic acid crystals. The formation of specifically adsorbing sites in gels is due to the adsorption of several oligo silicic acids on the surface of a 1,10-phenanthroline molecule, and subsequent

condensation to a regular two-dimensional silicic acid crystal. As there is no order-inducing reagent in the neighbourhood further condensation is irregular, thereby restricting the two-dimensional silicic acid structure to a "footprint", ready to adsorb the printing molecule "specifically".

ACKNOWLEDGEMENT

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SUMMARY

The "footprints" in silica gels with specific adsorption power—obtained by coagulation of a silicic sol in the presence of a larger organic molecule with subsequent elimination of these molecules by extraction—are shown to consist of a geometrically restricted two-dimensional silicic acid structure.

REFERENCES

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