

## KINETICS OF SILICA CONDENSATION IN BRINES

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Homogeneous nucleation and growth of silica from brines supersaturated in silicic acid has been studied over a range of pH (4.5-6.7), temperature (75°-105°C), salinity, and silicic acid concentration (700 to 1200 ppm as  $\text{SiO}_2$ ). The experimental technique involved analyses for molybdate-reactive silicic acid as a function of time after a supersaturated solution of  $\text{H}_4\text{SiO}_4$  was prepared by mixing aliquots of a stock silicate solution with buffered brine.

The isothermal rate of  $\text{SiO}_2$  condensation is a strong function of supersaturation ( $C/C_{eq}$ ), pH, and salinity. The overall kinetics follow what is expected from the general theory of phase transitions and are adequately described by the Volmer-Becker-Doring expressions for condensation from solution. At supersaturations less than about 3, an induction or transition time is observed. It amounts to several hundred minutes at supersaturations of about 2.0.

The dependence of the condensation rate on silicic acid concentration, after nucleation, suggests that growth is activation controlled, at least initially. The primary nuclei have radii of the order of a few angstroms. Particles of several hundred angstroms are obtained eventually (at equilibrium). Growth kinetics near equilibrium appear to be diffusion controlled.

The substantial effect of brine salinity on condensation rates can be accounted by decreased equilibrium solubility of  $\text{H}_4\text{SiO}_4$  with increasing salt content. In effect, higher salt concentrations increase supersaturation and lead to faster nucleation.

An increase of pH in the range of 4.5 to 6.7 leads to higher nucleation and growth rates. An increase of one pH unit decreases the induction period approximately by a factor of 10. Results on the pH dependence are consistent with the hypothesis that  $\text{SiO}(\text{OH})_3^-$  is one of the reacting species.

Changes of temperature in the range 75°-105°C have little effect on nucleation or growth rates at a fixed initial silicic acid concentration. Since supersaturation decreases with increasing temperature, this result suggests that the increase in rate brought about by increased temperature is essentially counterbalanced by the decrease in supersaturation.

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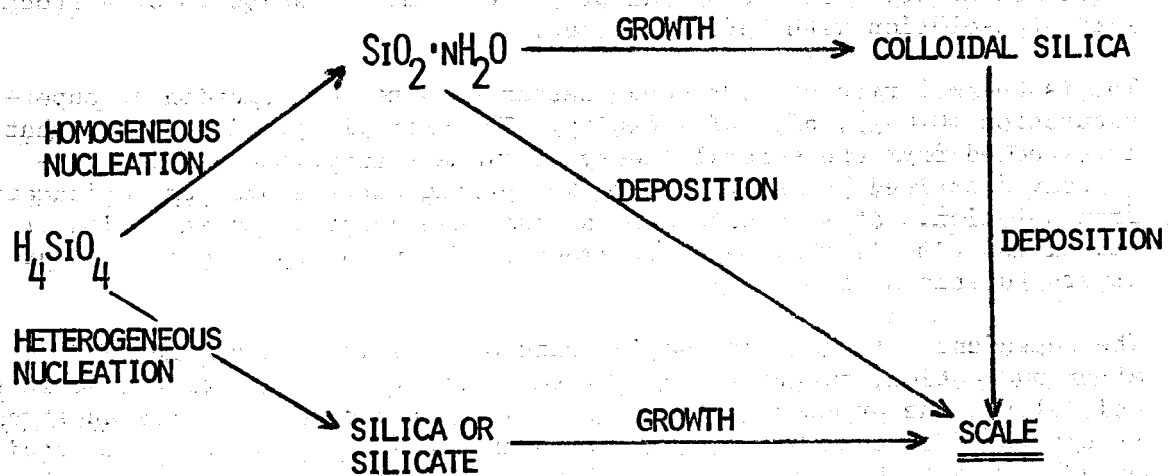


Fig. 1. Homogeneous and heterogeneous pathways for scale formation.

### STANDARD BRINE COMPOSITION

(  $\text{Na}^+$  ) = 0.452 M = 10,400 PPM

(  $\text{K}^+$  ) = 0.065 M = 2,540 PPM

(  $\text{Cl}^-$  ) = 0.315 M = 11,200 PPM

(  $\text{Ac}^-$  ) = 0.202 M = 11,900 PPM

Fig. 2. Composition of standard brine.

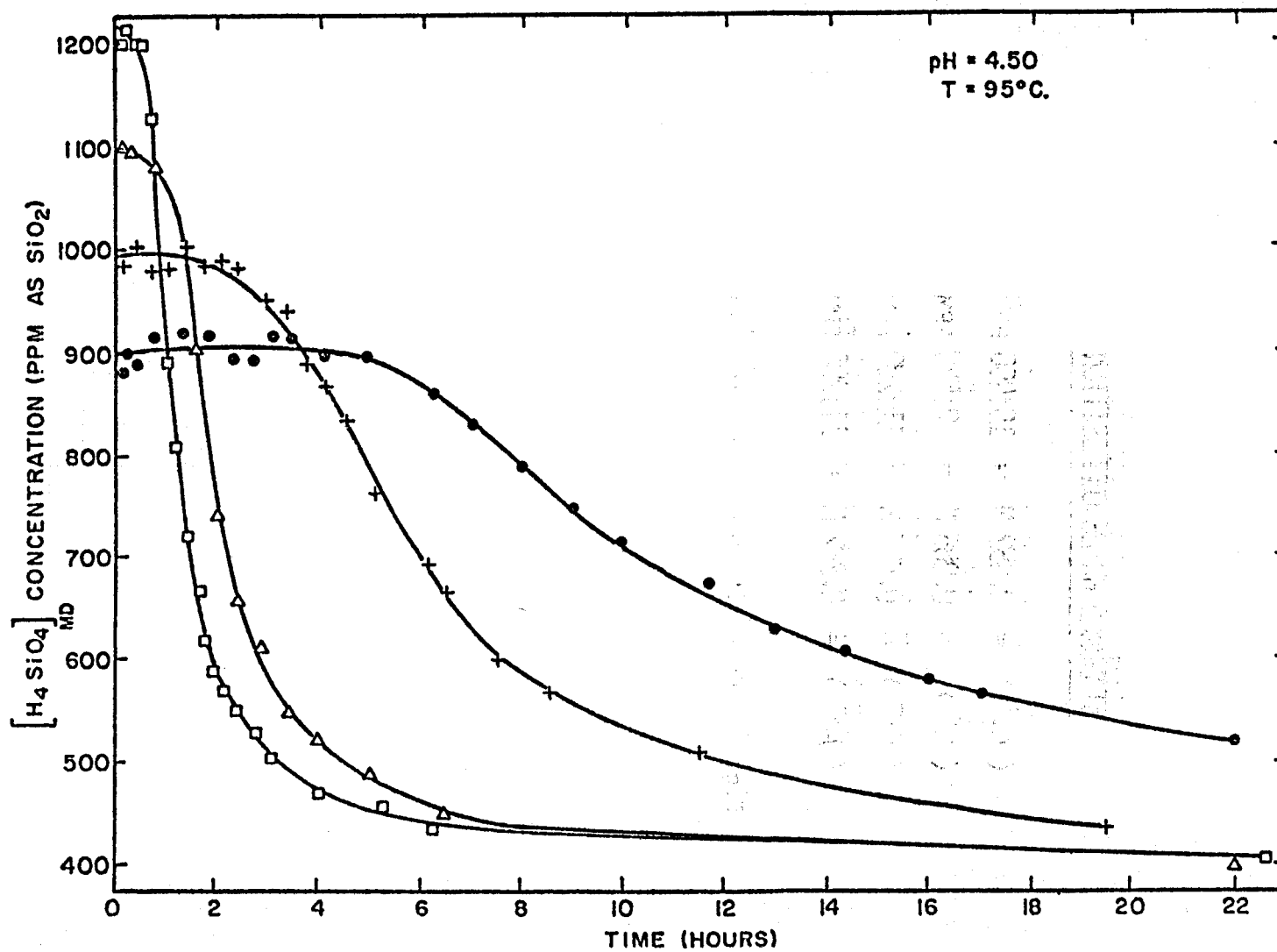


Fig. 3. Silica condensation as a function of time for a series of initial silicic acid concentrations.

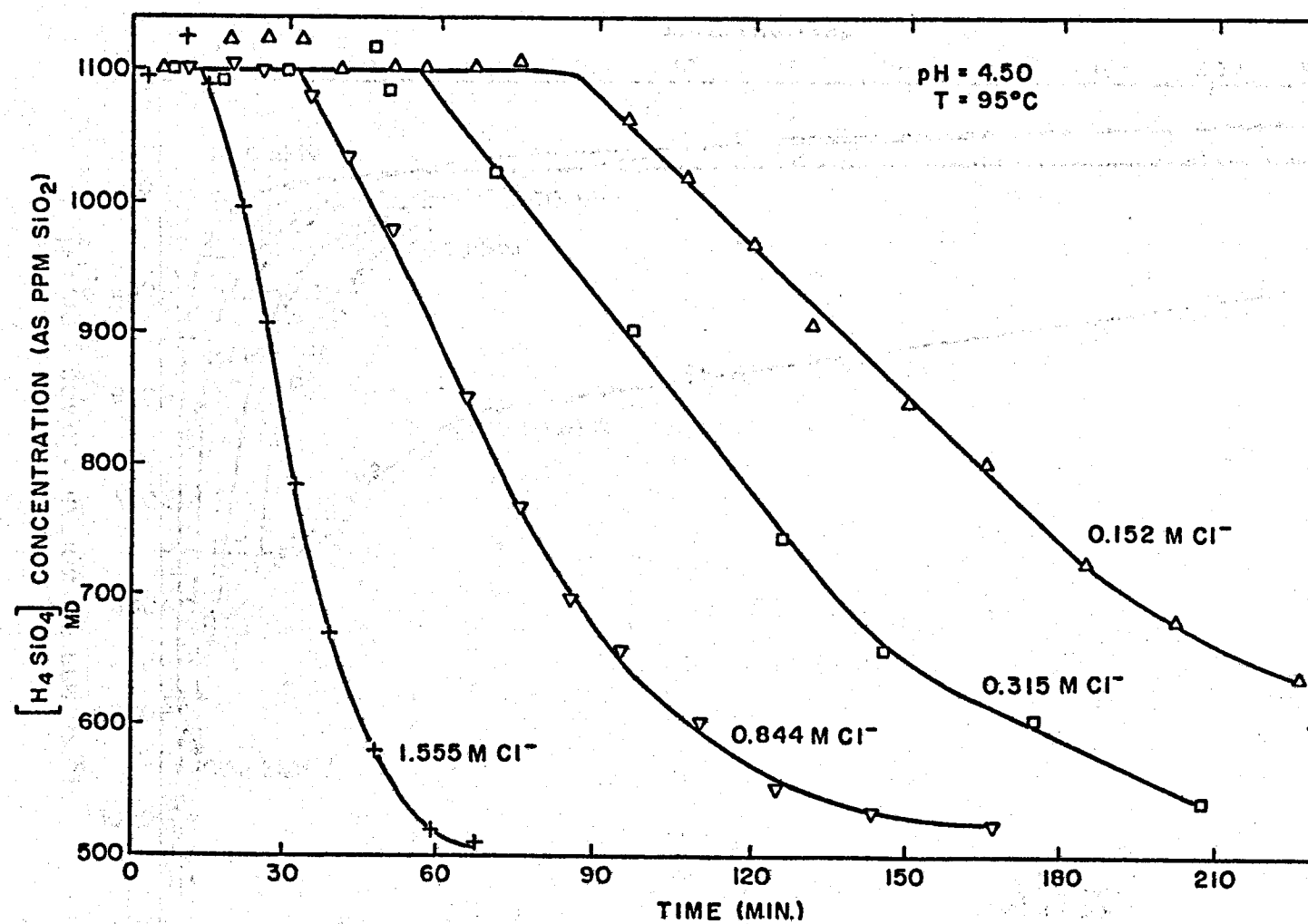


Fig. 4. Silica condensation from a solution of 1100 ppm (as SiO<sub>2</sub>) as a function of time at various salinities.

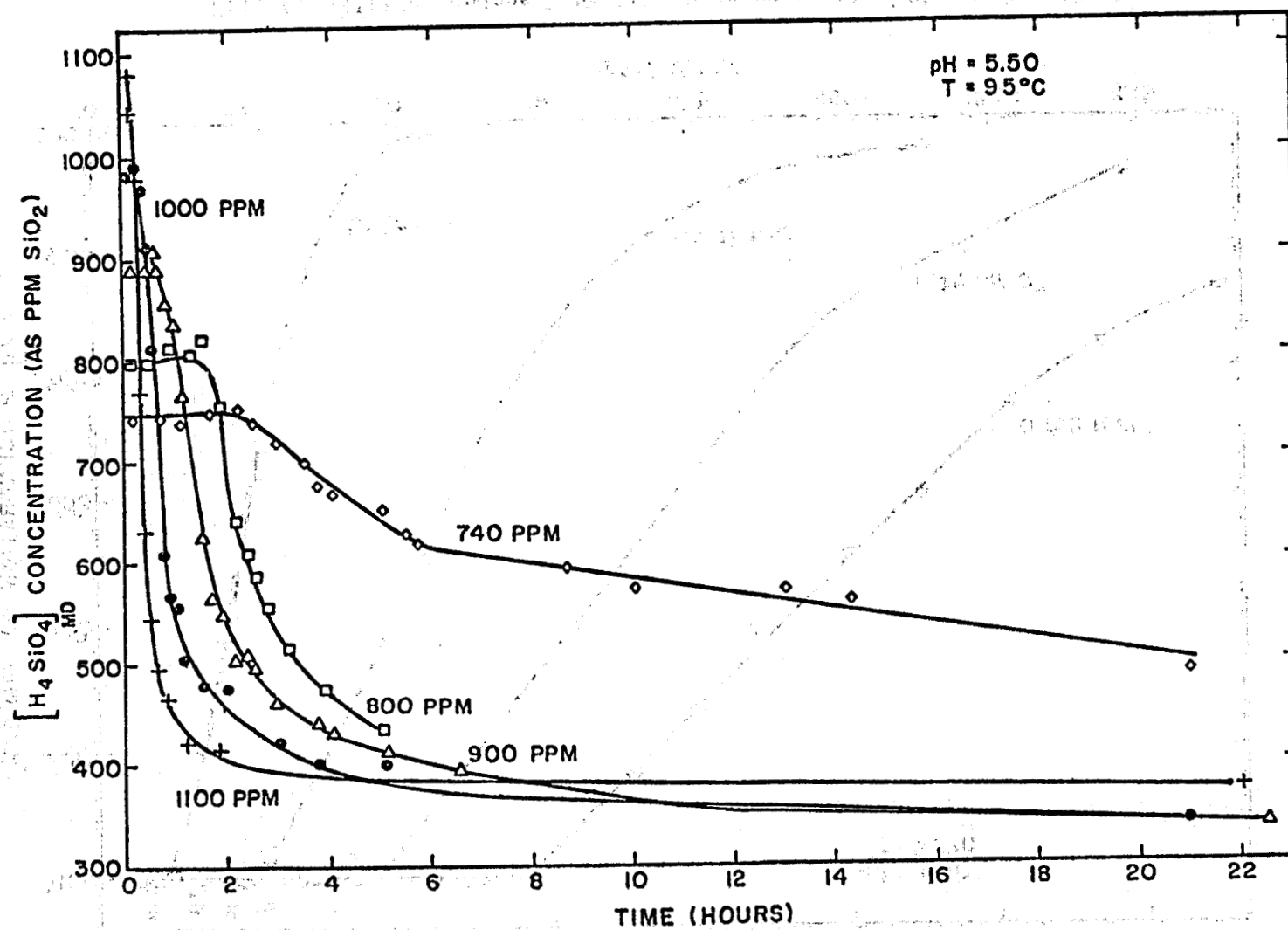


Fig. 5. Silica condensation as a function of time for a series of initial silicic acid concentrations.



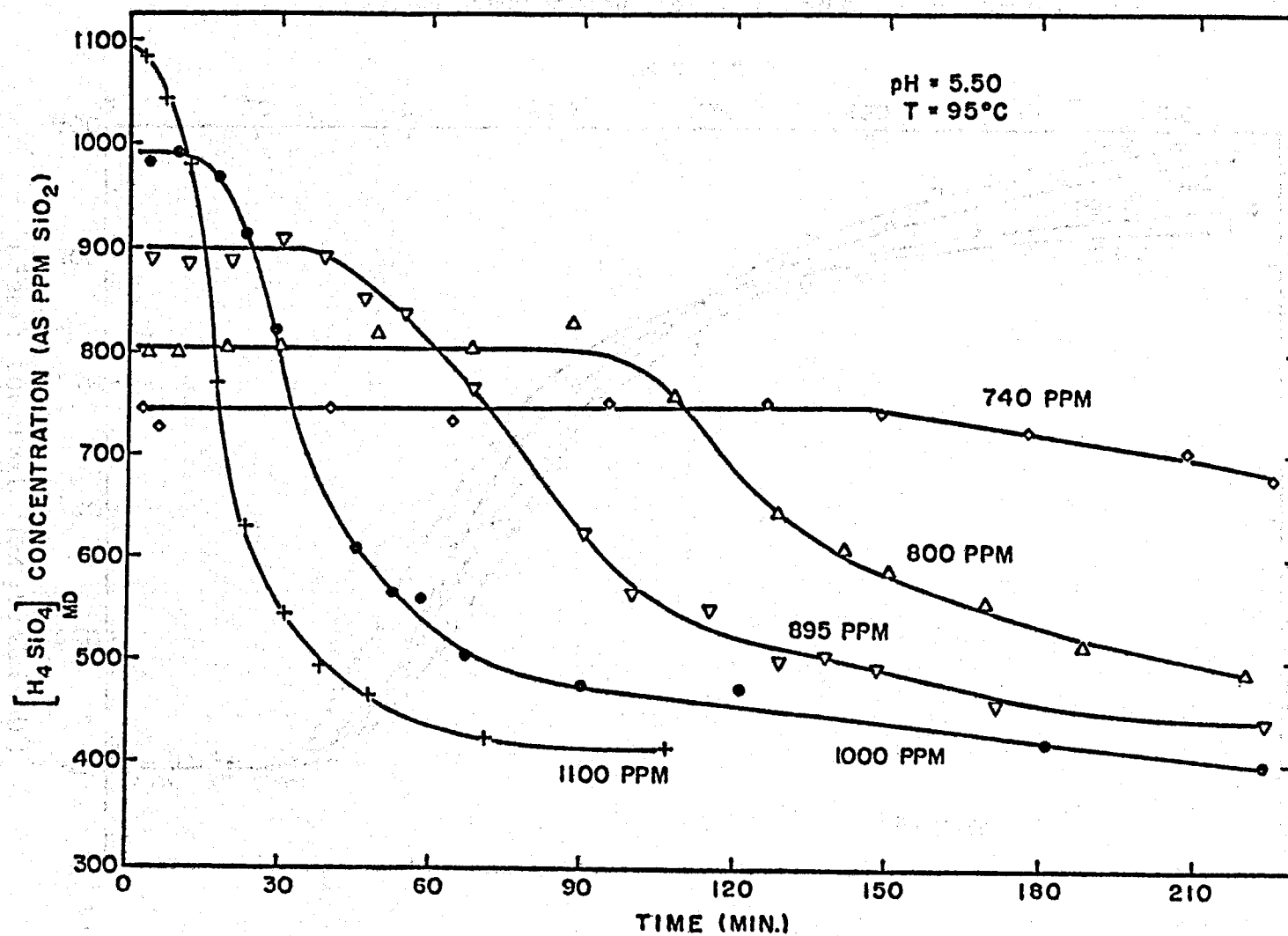


Fig. 6. Silica condensation as a function of time for a series of initial silicic acid concentrations.

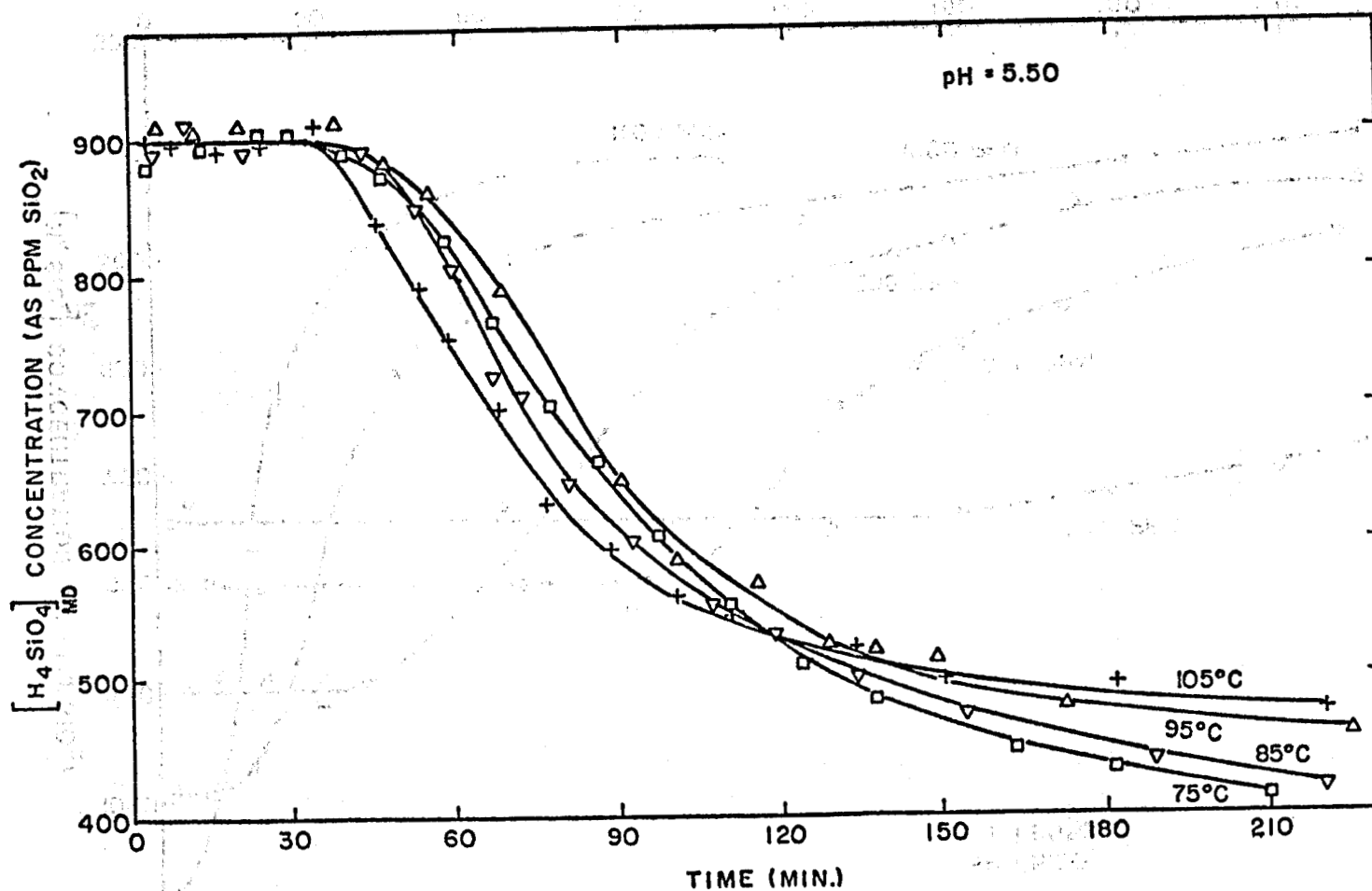


Fig. 7. Silica condensation from a solution of 900 ppm (as  $SiO_2$ ) as a function of time at various temperatures.

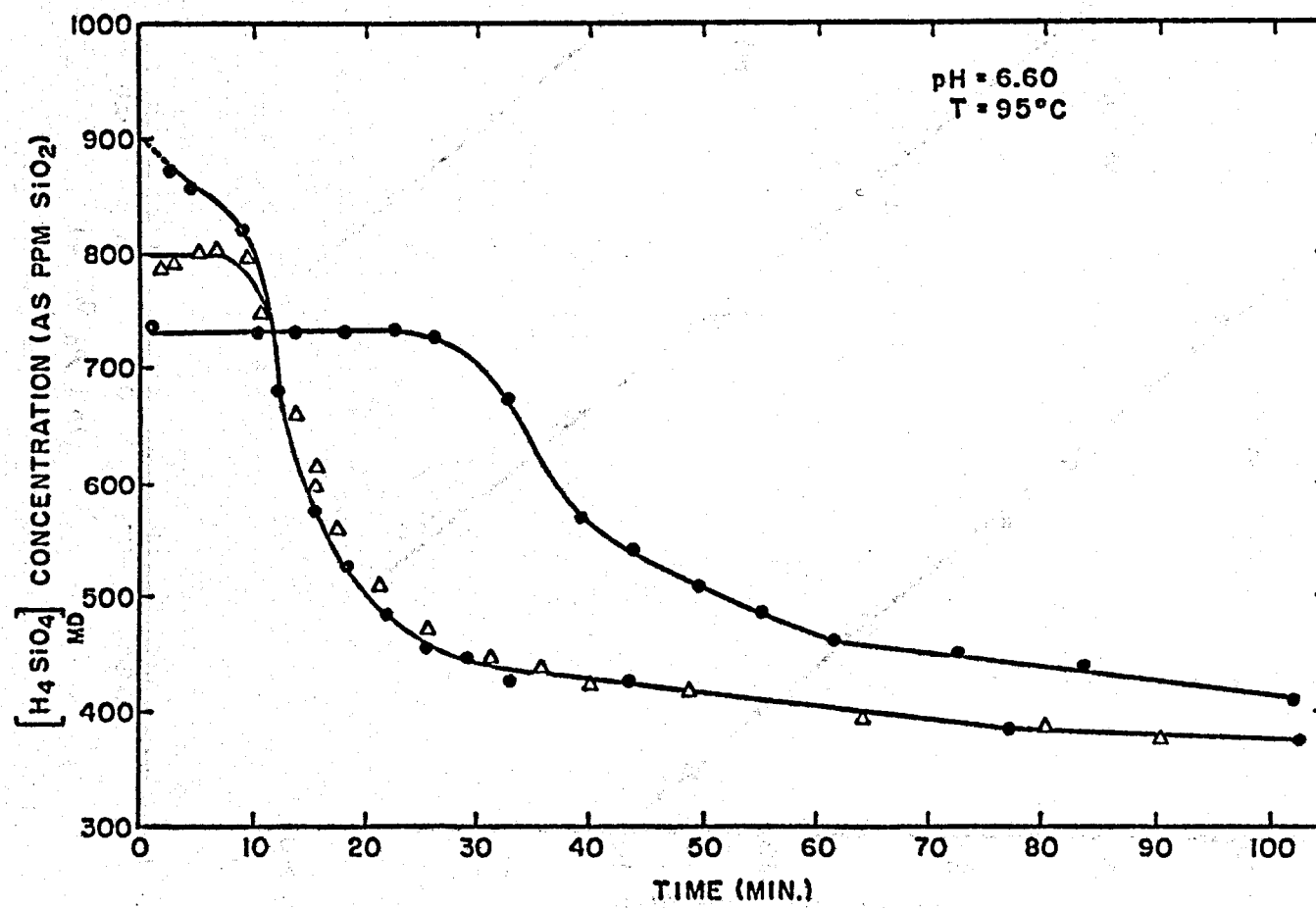


Fig. 8. Silica condensation as a function of time for a series of initial silicic acid concentrations.

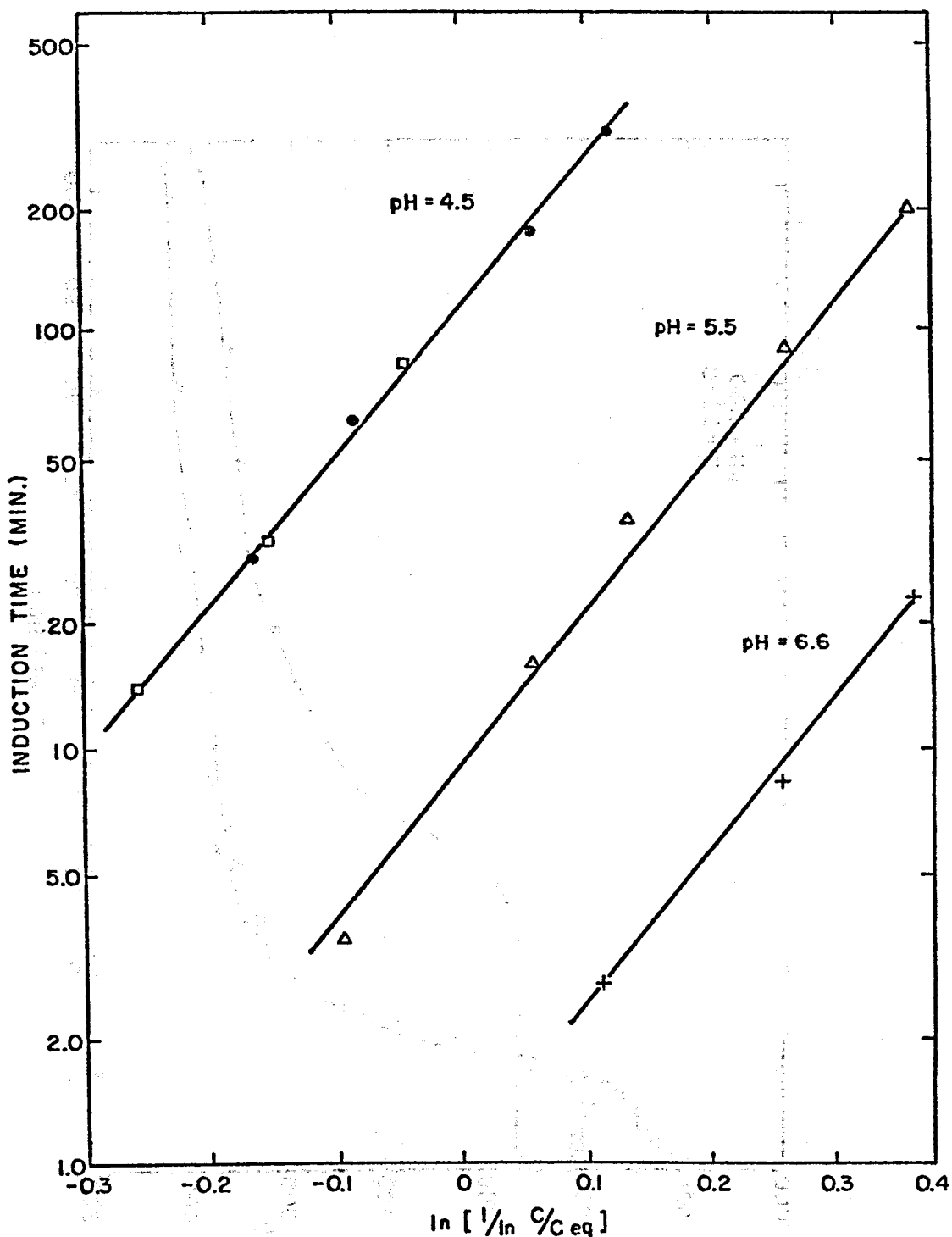


Fig. 9. Induction times as a function of supersaturation at 95°C and a series of pH values. Results at pH 4.5 include condensation in standard brine (●) and in brines of various salinities at a fixed initial silicic acid concentration of 1100 ppm (as SiO<sub>2</sub>) (□).

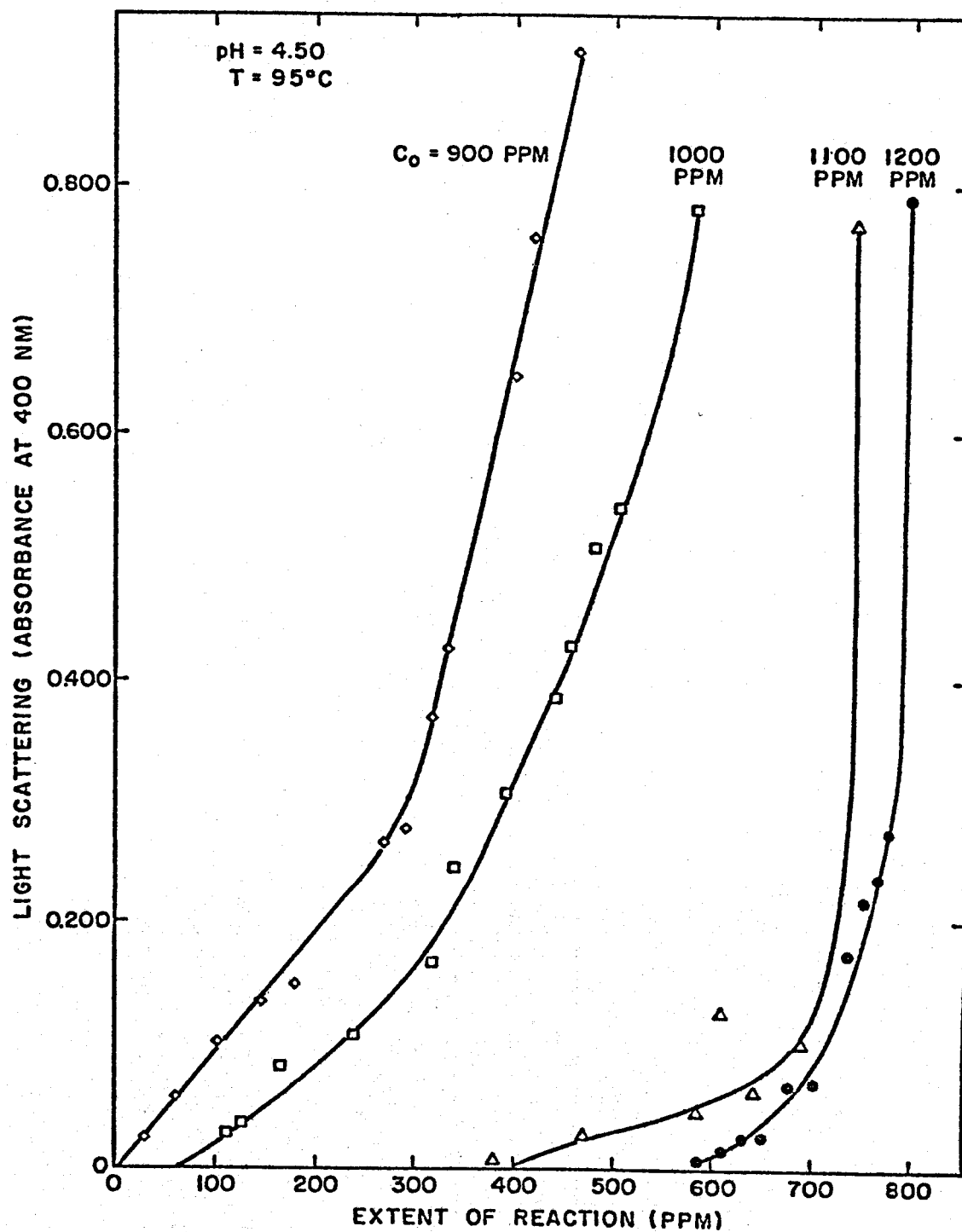


Fig. 10. Light scattering by acidified aliquots of solutions during condensation.