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Studies of mechanism of silica polymerization reactions in the combination of silica sol and potassium sodium waterglass via isothermal heat conduction microcalorimetry

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Abstract Isothermal heat conduction microcalorimetry was adopted as a novel characterization method to investigate the polymerization processes of silica when the combination of silica sol and potassium sodium silicate was stirred at 25.0, 35.0, and 45.0 °C. Thermodynamic and kinetic parameters were simultaneously obtained. The enthalpy change was greater at each higher temperature. The reaction orders (*m*, *n*) instantaneously varied, up and down in an alternate manner. At 25.0, 35.0, and 45.0 °C, the rate constants were different; the maximum rate constant occurred at 25.0 °C. These phenomena reflect a two-stage oligomeric mechanism of silica monomers. The measurements of particle size showed the complex chemical composition of aqueous silicates, which can be qualitatively designated by the particle size distribution in two parts. The results further indicate that the colloidal particles in the mixed silica sol and silicates first dissolved. Then the "active" silica in the silicates redeposited to make a distinct particle size distribution influenced by K^+ and Na^+ ions as well as by temperature.

Keywords Aqueous silicates · Silica sol · Nanoparticle distribution · Microcalorimetry · Thermodynamics · Kinetics

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List of symbols

M	The molar ratio of silica to alkali metal oxide in silicates
Q_T	Total enthalpy change for a mixing reaction when it has gone to completion (J)
ΔH	Changes in enthalpy (kJ mol^{-1})
A_{mol}	The initial number of moles of CH83–125 silica sol (mol)
B_{mol}	The initial number of moles of potassium sodium silicate (mol)
$[A]_0$	The initial molar concentration of CH83–125 silica sol (mol dm^{-3})
$[B]_0$	The initial molar concentration of potassium sodium silicate (mol dm^{-3})
V	The total volume of CH83–125 silica sol and potassium sodium silicate (dm^3)
Φ	Heat flow (mW)
q	Heat output (J)
k	Rate constant ((mol $dm^{-3})^{1-m-n}$ s^{-1})
m	The reaction order of CH83–125 silica sol
n	The reaction order of potassium sodium silicate

Introduction

Aqueous silicates, silica sol, and colloidal silica are the subject of extensive research. All three materials contain silica nanoparticles, silica oligomers, or monomers, and all depend on silica's particle size and distribution, chemical composition, and microstructure. These materials are widely involved in materials science, biology, and ecology [1–5]. As a result of the oligomerization of silica monomers, a variety of complex oligomers form in increasing species; the orders of chemical reaction vary gradually [6].

The kinetics of silica polymerization is usually studied using a colorimetric molybdate method or a rheological measurement [6, 7]. However, the parameters of instantaneous changes in the polymerization process cannot be determined in these two ways. Isothermal heat conduction microcalorimetry is a powerful tool to investigate complex systems [8–10], and this technique has numerous applications [11–15], but has not yet been used in silica polymerization reactions.

Macroscopic properties (e.g., the water resistance of aqueous silicates binder) are determined by the microstructure of silica gels, these properties bear further relation to silica interparticle Si–O–Si bonds [16]. If aqueous silicates are mixed with silica sol, much stronger gels with reinforcing interparticle bonds are obtained and their water resistance is better [17]. Potassium silicate and silica sol have a longer shelf-life than other mixtures [17].

This article discusses the results when the technique of isothermal heat conduction microcalorimetry was used to investigate the mixing process of silica sol and potassium sodium silicate being stirred at 25.0, 35.0, and 45.0 °C. Measurements of particle size in the mixture of silica sol and potassium sodium silicate or silica sol and potassium silicate at 25.0, 35.0, and 45 °C are given.

Experimental

Materials

CH83–125 silica sol (25.24 mass/% SiO_2), GHSK potassium silicate (20.63 mass/% SiO_2, SiO_2/K_2O molar ratio $M = 4.09$) and potassium sodium silicate (potassium sodium waterglass, 24.96 mass/% SiO_2, 3.89 mass/% K_2O, 7.76 mass/% Na_2O, molar ratio $M = 2.5$) are all commercially available materials. Potassium silicate solution (molar ratio $M = 2.5$) was prepared by mixing GHSK potassium silicate ($M = 4.09$) with KOH (analytical purity grade).

Mixture preparation

The SiO_2 mass fraction in the mixture of silica sol (75 mass/% fraction in total in the mixture) and potassium sodium silicate (25 mass/% fraction in total in the mixture) was the same as the SiO_2 mass fraction in the mixture of silica sol (75 mass/% fraction in total in the mixture) and potassium silicate (25 mass/% fraction in total in the mixture). Three batches of the mixture of silica sol and potassium sodium silicate and three batches of the mixture of silica sol and potassium silicate were prepared at 25, 35, and 45±1 °C, respectively. All mixtures were made at the same stirring rate in a water bath, and silicates were added into silica sol in drops. The mixed samples were immediately measured for particle size by using a Zetasizer (Nano-S, ZEN 1600, Malvern Instruments Limited).

Particle size measurements

Manual measurement settings	
Cell type	DTS0012—disposable sizing cuvette
Material name	Polystyrene latex
Dispersant name	Water
Temperature	25.0, 35.0, and 45.0 °C (corresponding to the temperature of mixture preparation, respectively)
Temperature equilibration time	1 min
Measurement duration	Automatic
Result calculation	General purpose

The results of size quality reports meet quality criteria. The figures of particle size distributions in the text are obtained from size statistics reports by intensity via OriginPro 7.5.

Isothermal heat conduction microcalorimetry

A Thermometric 3114/3236 TAM Air Isothermal Calorimeter (made in Sweden, equipped with a minitype stirrer and two 1.00-mL injection tubes) was used in the experiments. Silica sol was in a 20-mL glass ampoule, and potassium sodium silicate was in an injection tube. The 5.00-mL distilled water sealed in a 20-mL glass ampoule was used as a reference solution placed in the channel B of microcalorimeter. The microcalorimeter was housed in an air-conditioned room (25 ± 1 °C). Several hours or a night was needed to stabilize the baseline. The stirrer was then switched on and continued running until the mixing reaction ended. With the stirrer running, the injection tube operation began after the baseline was stable for at least 30 min. The sample in the injection tube was slowly injected into the glass ampoule. For more information about the TAM operation procedure and data collection and data process please refer to Ref. [18–22].

Results and discussion

Determination of thermodynamic and kinetic parameters

The main problem for calculating the enthalpy change is to find a point in time for a mixing reaction which has gone to completion. The reaction goes on for about 3 h or more [23], at a certain point in time; the power–time curve levels out (as shown in Fig. 1). The time period of the curve parallel to time

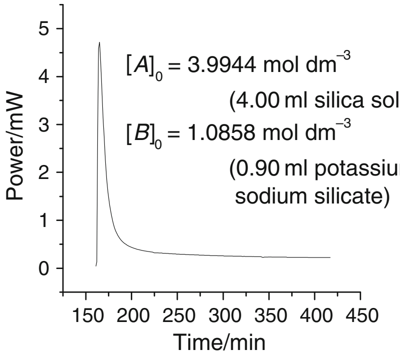

Fig. 1 The power–time curve of the mixture of silica sol (*A*) and potassium sodium silicate (*B*) under stirring at 25.0 °C

line is more than 20 min. The total area contained by the curve from the start point of mixing reaction to the point in time where the curve first levels out is Q_T (the total enthalpy change for the mixing reaction when it has gone to completion, $\Delta H = Q_T/B_{mol}$, where B_{mol} is the initial number of moles of potassium sodium silicate) [24–26]. The resulting enthalpy change was greater, the higher the temperature (see Table 1). The determination of kinetic parameters was made using following equation [25, 26]:

$$\Phi = \frac{dq}{dt} = kV\Delta H\left([A]_0 - \frac{1}{V}\frac{q}{\Delta H}\right)^m\left([B]_0 - \frac{1}{V}\frac{q}{\Delta H}\right)^n \qquad (1)$$

where *V* is the total volume of CH83–125 silica sol (*A*) and potassium sodium silicate (*B*). Since the reaction orders varied gradually, and by the linear fitting and non-linear fitting, the microcalorimetric data can not be calculated correctly, the calculation method described by Beezer et al. was applied [27–29]. This method is given by Eq. 2:

$$\Delta X = \frac{\Phi_1}{\Phi_2} - \left(\frac{A_{mol}\Delta H - q_1}{A_{mol}\Delta H - q_2}\right)^m \cdot \left(\frac{B_{mol}\Delta H - q_1}{B_{mol}\Delta H - q_2}\right)^n \qquad (2)$$

The highest peak of the power–time curve is the base and start point (Φ_1); the next points (Φ_2, Φ_3 …) follow along the curve in a downward direction (Fig. 1). The degree of error (ΔX) of Eq. 2 is ±0.00001. The calculated results (see Table 1) indicate that the reaction orders (*m*, *n*) instantaneously varied, up and down in an alternate manner: (*m*, *n*), (0.3, 1.4), (2.4, 1.3), (5.3, 0.9), (7.2, 0.7), (1.3, 2.3), (3.4, 2.0), (1.5, 2.6), (1.7, 2.7), (9.0, 1.2), (1.0, 3.1) when the microcalorimeter ran in the first 166–175 min at 25.0 °C (Fig. 1). Similar to the trends reported by Bishop and Bear [30], the rate constant varied with reaction order

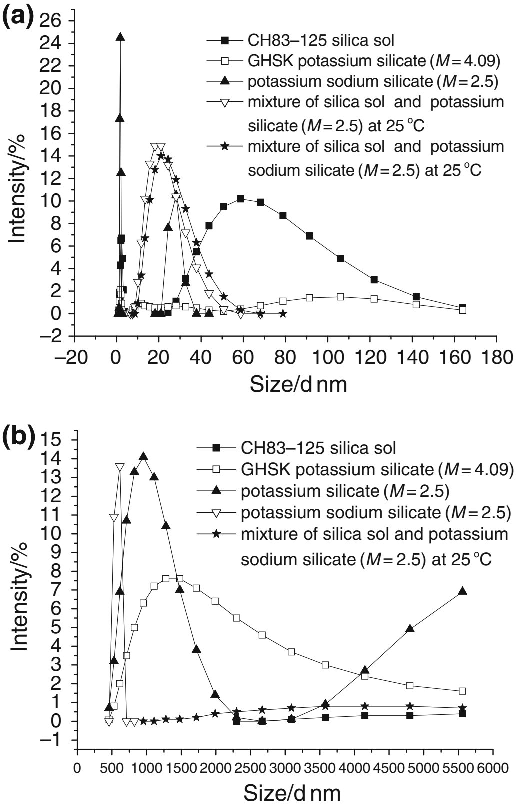

Fig. 2 The front part (**a**) and the latter part (**b**) of particle size distributions of silica sol, potassium silicate, potassium sodium silicate and their mixtures by intensity at 25.0 °C

Table 1 Thermodynamic and kinetic parameters of the mixture of potassium sodium silicate and silica sol under stirring at 25.0, 35.0, and 45.0 °C

	Microcalorimeter running temperature/°C					
	25.0		35.0		45.0	
Curve peak height/mW	4.6776		6.8556		8.618	
Reaction time to go to completion/min	256		288		633	
Q_T/J	6.217		10.87		23.45	
ΔH/kJ·mol^{-1}	1.169		2.043		4.408	
Reaction orders of the first minute after peak	*m*	*n*	*m*	*n*	*m*	*n*
	0.3	1.4	3.4	0.7	2.8	3.0
The rate constant of the first minute after peak	$k = 5.5676 \times 10^{-4}$/ (mol dm^{-3})$^{-0.7}$ s^{-1}		$k = 6.5513 \times 10^{-6}$/ (mol dm^{-3})$^{-3.1}$ s^{-1}		$k = 7.8034 \times 10^{-6}$/ (mol dm^{-3})$^{-4.8}$ s^{-1}	

and temperature, and the maximum rate constant occurred at 25.0 °C.

Table 1 indicates that the polymerization reactions of silica were in an induction period and oligomerization processes which can be divided into two distinct stages. The first stage was mainly reflected in the 25–35 °C region, and the second one was done in the 35–45 °C region. The first one gave priority to the formation of linear and branched oligomers with a fast reaction rate. However, ring structure and larger oligomers were dominant products in the second one which was accompanied by a relatively slow rate and by larger changes in enthalpy due to the factors of hydrogen bonding and activation barrier in an anionic mechanism [31, 32]. The formation of ring oligomers was favorable at higher temperature. Corresponding variation tendencies of reaction orders ($m + n$) and the dimensionless of rate constant with increasing temperature exhibit complex reaction mechanisms from reactants to products because the reaction time to go to completion was longer at higher temperature. Moreover, at each different temperature in the same time, the reaction mechanism was different from one another. Therefore, the oligomerization process of silicic acid from monomer to dimmer, trimer, etc., larger oligomer was not the only one throughout the polymerization reactions of silica.

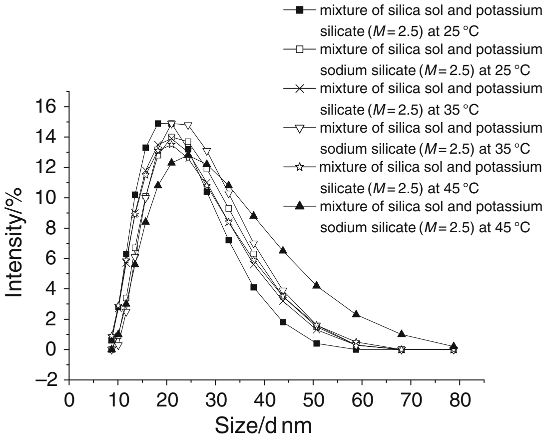

Fig. 3 Effects of the K^+ and Na^+ on the particle size and distributions of the mixtures at 25.0, 35.0, and 45.0 °C

Particle size and distribution

Complex reaction orders are a consequence of the complex chemical reactions and chemical composition of aqueous silicates [33–35]. Different silica/alkaline molar ratios and the nature of alkaline ions offer distinct distributions of silicate species [36, 37]. Figure 2 shows that in potassium silicate (silica/alkaline molar ratio, $M = 4.09$), there was the existence of colloidal particles while in potassium silicate ($M = 2.5$), there existed major monomers and oligomers. However, potassium sodium silicate ($M = 2.5$) contained mainly colloidal species. CH83–125 silica sol was mainly composed of two peaks from colloidal species. When silica sol was mixed with silicates, the chemical reactions occurred immediately. In the reaction the concentration of each component of silicate species changed, the pH value of both silica sol and silicates also changed. Both the small and large colloidal particles of silica sol dissolved, then the "active" silica in the silicates redeposited to make a distinct particle size distribution. Therefore, the mechanism of particle size measurements observed was different from that of the oligomerization of silicic acid in microcalorimetric experiments. The mechanisms following the oligomerization of silicic acid were silica solution, and then redeposition and growth (see also [17], p. 507, [38, 39]).

Due to the M^+ ion pairing effect, other experiments showed that K^+ and Na^+ ions had a different influence on the particle size in the different mixtures (Figs. 3, 4, 5). At all three temperatures, the particle size was larger in the Na^+ mixture than in the K^+ mixture. For the same mixture, the higher the temperature, the larger the particle size, the wider the particle size distribution. Higher temperatures favored the formation of larger particles. This view was further evidenced by the distribution of silicate species in

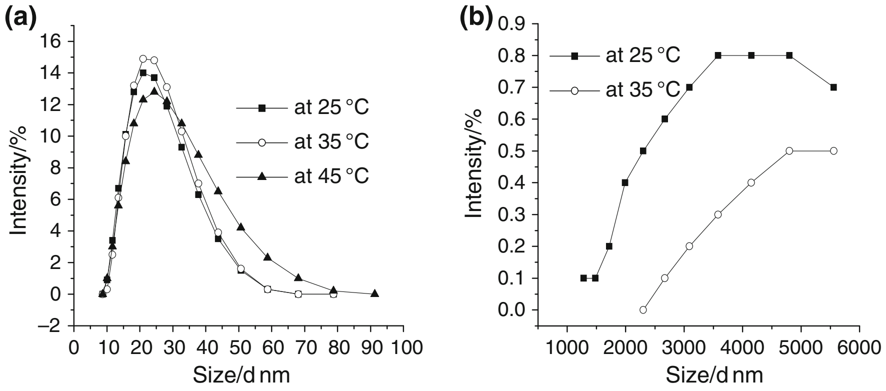

Fig. 4 The front part (**a**) and the latter part (**b**) of particle size distributions of mixtures of silica sol and potassium sodium silicate (SiO_2/M_2O molar ratio $M = 2.5$) at 25.0, 35.0, and 45.0 °C

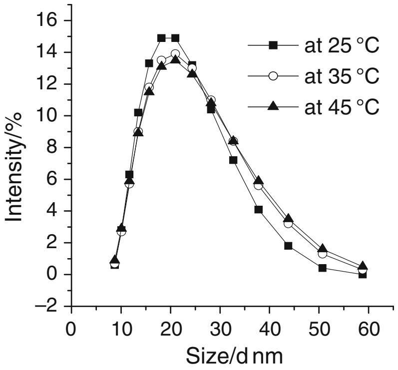

Fig. 5 Particle size distributions of mixtures of silica sol and potassium silicate (SiO_2/M_2O molar ratio $M = 2.5$) at 25.0, 35.0, and 45.0 °C

two parts: one is colloidal particles smaller than 100 nm as shown in Fig. 4a, the other is monomers and oligomers as shown in Fig.4b. Particularly at 45 °C, Fig. 4 clearly shows a wider peak shape than the other temperatures (Fig. 4a), but mainly in colloidal particles but not monomers and oligomers (Fig. 4b) which had grown into large colloidal particles. Figure 5 also shows that the particles were larger at 35.0 and 45 °C than at 25 °C.

Conclusions

Isothermal heat conduction microcalorimetry was a novel means to determine simultaneously both thermodynamic and kinetic parameters in silica polymerization reactions. This technique has obvious advantages over the colorimetric molybdate method. In addition, with regard to the present research work, there are two novelties. One is the data processing method, namely, the calculation method described by Beezer et al. was utilized for silica polymerization reactions in microcalorimetric experiments. The other is that measurements of particle size can serve to designate the chemical composition of aqueous silicates. Different chemical composition of aqueous silicates displays different particle size distributions in two parts influenced by K^+ and Na^+ ions as well as by temperature. The polymerization reaction of silica is characterized by constantly changing reaction orders. The complexity of reaction orders results from the complexity of the chemical composition of aqueous silicates, and from the silica polymerization processes involved in mechanisms of the oligomerization of monomers in two stages, silica solution, and then redeposition and growth. On the one hand, from the perspective of kinetics, different temperature regions (25–35 °C region and 35–45 °C region) have different effects on the formation mechanism of oligomers. And at each different temperature in the same time, the reaction mechanism is different from one another. The formation of ring structure oligomers is favorable at higher temperature. On the other hand, from thermodynamics, reaction time to go to completion, and particle size measurement point of view, the mechanisms of silica solution, and then redeposition and growth can be observed.

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