PROBLEMS WITH THE GELLING
OF EMULSIFIED COLLOIDAL SILICA

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SUMMARY

Important aspects of the rapid gelling of the stabilized silica sols used to produce silica gel have been studied. Rapid gelling is necessary when producing micro-spherical silica gels from stabilized silica sols, because silica sol emulsions are not stable for long periods of time. The effect on rapid gel formation of potassium silicate, added to the silica sol before emulsification, has been studied and the possibility of efficient control of these processes has been investigated. It has been shown that it is possible to control the gelling of silica sol by adding potassium silicate, which not only secures rapid gelling of emulsified silica sols but also ensures introduction of active silica to the silica hydrogel, which reinforces the structure of the gel obtained.

The effect of exchange of intermicellar water in micro-spherical silica hydrogels, by acetic acid, acetone, and ethanol, on the sorption volume of micro-spherical silica gels obtained from stabilized silica sols has been investigated. The use of stabilized silica sols as initial raw material ensures constancy of specific surface area and pore volume, because these primarily depend on the properties of the colloidal particles and their size distribution. Data characterizing the pore structure of the silica gels reveal that exchange of intermicellar water by other liquids of lower surface tension affects the pore volume only.

INTRODUCTION

One of the main demands on chromatographic materials is reproducible physico-chemical properties. This, in turn, is highly dependent on precise control of the technological processes involved, because these determine the structural characteristics of the porous systems obtained. One possible way of regulating the porous structure of silica gels is to use

stabilized silica sols, the particle sizes of which can be regulated when they are prepared as the initial raw material. Regulation of the processes affecting the pore volume of the silica gels obtained is most important, because the porous structure of the silica is determined mainly by the size distribution and average size of the particles in the silica sols [1–5].

In this article means of ensuring controllability of gel-formation when preparing emulsified silica sols and the effect of exchange of inter-micellar liquid by organic solvents on the porous characteristics of micro-spherical silicas obtained are discussed.

Several additional demands are placed on gel-formation processes during the manufacture of micro-spherical silica gels from emulsified stabilized silica sols:

- the gel-formation process must be sufficiently quick (5–10 min);
- the hydrogel must acquire its hardness in a very short time (10–15 min); and
- the hydrogel must be homogenous, hard, and elastic.

Rapid gelling means that stirring of the emulsion must be avoided during the gelling process, i.e. the gelling process must be performed statically to avoid mechanical destruction of the labile micro-spherical hydrogel. Under static conditions, on the other hand, the emulsion slowly becomes laminated and is destroyed. Thus the next important requirement of the hydrogel is rapid acquisition of the required hardness, i.e. the hydrogel must acquire its hardness before lamination of the emulsion and destruction of the hydrogel. If the latter occurs the process of spheroidization will not occur, because if the gel does not acquire its hardness for a long period of time particles of the labile system, owing to destruction of the emulsion, cannot preserve their spherical form and, as a result, silica gels with irregular particles are formed.

The hardness and the elasticity of the hydrogel are highly important in preserving its spherical form when changing from the hydrogel to the xerogel. Because, after gelling, lamination of the emulsion occurs and the gel precipitates to the bottom of the vessel, micro-spherical particles of the hydrogel must have sufficient hardness and elasticity that they are not deformed or destroyed.

Increasing the pH of the system to 9.5–10.0 before gelling is one way of promoting rapid gel formation from stabilized silica sols. It is, however, necessary to remember:

- increasing the pH too far is undesirable, primarily because stabilized silica sols of high pH behave as alkaline metal silicates (liquid glasses).

Such systems are usually more likely to result in precipitation of silica rather than formation of homogenous gels. Reproducibility of the porosity of silica gels obtained from liquid glasses is highly problematic. Another problem if the pH is too high is the need to add stronger and more concentrated gelling agents, which also usually cause precipitation and inhomogenous gel formation; and

- the nature of the agent used to increase the pH is important.

It is known [5,6] that caustic soda and sodium liquid glass are incompatible with stabilized silica sols and cause precipitation of silica from the sols. Ammonia and ammonium silicate are also unsuitable, because of the volatility of ammonia. Not only is ammonium silicate a labile system, the preparation process is very labour-intensive.

The most suitable agents for increasing the pH of silica sols without silicon dioxide precipitation are potassium silicates [5,6]. In these the value of the silicate module M, $= [SiO_2]/[K_2O]$, can vary over wide range – from 3 to 24. An important aspect of the use of potassium silicates is ensuring the silicates are added to the hydrogels at the same time as the pH is increased; this reinforces the hydrogels which, in turn, results in a structure with the required hardness and elasticity. Another important aspect of the gelling of emulsified silica sols is the nature and quantity of gelling agent added – the optimum quantity depends on the amount of potassium silicate added to the silica sol. When large amounts of potassium silicate are added, stronger and more concentrated gelling agents (organic acids or their anhydrides) must be used, as mentioned above [7]. Application of such gelling agents, as also indicated above, leads to precipitation of the silicon dioxide. Use of dilute gelling agents leads, on the other hand, to general dilution of the system. This might be immaterial during gelling of silica sols to produce silica gel particles of irregular form, but such dilution becomes essential when the silica sol gelling process is performed on an emulsion. The presence of phase bonding surface in the emulsion makes rapid distribution of the gelling agent throughout the whole system even more difficult.

Another problem when a large amount of aqueous phase (gelling agent solution) is introduced into the sol is that the emulsion begins rebuilding, because the ratio of the aqueous and organic phases in the reverse emulsion (water/oil) changes sharply. Such rebuilding of the system leads to an increase in the size of the micro-spheres, and again leads to the formation of deformed and/or shapeless micro-particles during gel formation. Use of large volumes of gelling agent does not usually lead to the formation of hard, homogenous, and elastic silica hydrogels.

The porosity (a measure of the pore volume) of silica gel is mainly determined during the change from hydrogel to xerogel. During this process contraction of the silica gel framework occurs until mechanical strains arising in the xerogel cannot resist the pressure acting on the structure owing to surface tension [5,6]. Iler [5] believes that silica gels with high porosity are obtained when gel contraction is avoided during removal of the intermicellar liquid. This can be achieved by:

- strengthening the silica gel by means of additives hardening the structure; this increases the strength of bonds between particles which thus resist the forces causing the contraction;
- heating of gel filled with liquid at a pressure higher than the critical point;
- creation of silica with a hydrophobic surface; and
- substitution of water by any polar liquid with a lower surface tension.

The sorption volume of silica gel decreases when the heat of wetting of silica gel increases, and vice versa, the sorption capacity increases with decreasing energy of interaction of intermicellar liquid with the silica surface. If trustworthy chromatographic data are to be obtained exchange of intermicellar water by organic liquids must be performed thoroughly and completely. If exchange of water by the liquid of lower surface tension is complete the sorption volume of the structure of the xerogel obtained is maximum. By analogy, if exchange is partial a series of structures can be obtained which differ in sorption volume and pore size but with similar specific surface area.

The efficacy of action of intermicellar liquid depends not only on its nature but also on the state of the inside of the gel, the amount of particle aggregation, and the strength of bonds between the elements of its structure [5]. It has been shown [6] that for slow drying the gels undergo almost no compression if the diameter of the pores exceeds 300 Å, i.e. for capillaries of such sizes the capillary forces of water are so weak they cannot cause contraction of the hydrogel structure during drying. Usually, however, silica gels obtained by sol–gel technology have pores with sizes <300 Å. For such systems, therefore, exchange of water by organic liquids is a possible means of regulating the porous structure of silica gels obtained from stabilized silica sols.

EXPERIMENTAL

All reagents used were chemically pure or 'for chromatography' grade.

The investigation was performed on stabilized silica sol particles of pH 8.5 and 9.0 obtained according to a technique described elsewhere [8]. The concentration of SiO_2 in the silica sols was 20% by mass. Potassium silicate with silicate module $M = 4.0$ containing 20% by mass silicon dioxide was used. It was prepared by dissolving the appropriate amount of silica gel in a 1.22 mol L^{-1} boiling solution of potassium hydroxide, with continuous stirring.

Micro-spherical hydrogels of these silica sols mixed with known amounts of potassium silicate were obtained by means of their emulsification in toluene in the presence of sorbitan monostearate (Span 60) with subsequent gelling by addition of ammonium nitrate solution. The gel obtained was then aged at room temperature.

During the experiments direct substitution of intermicellar water was performed by using organic liquids which were highly soluble in water (i.e. acetic acid, acetone, and ethanol). Direct exchange of water in the gel by other liquids is possible as a result of their mutual solubility. After ageing the micro-spherical gels were separated from toluene, placed in acetone, exposed for 3–4 h, filtered, and the corresponding organic liquid was then added. After exposure to the liquid for 2–3 h the micro-spherical gel was isolated by filtration and placed in liquid in which the gel was finally exposed for 1, 2, 5, 8, or 10 days.

Sampling for determination of pore volume was performed during this period. For this measurement a new portion of liquid was added to the filtered gel and samples for determination of pore volume were dried at 100°C for 3–4 h. The drying temperature was reached gradually over a period of 60 min. After drying the temperature was increased to 600°C and the samples were heated for 5 h. The porosity of the samples of silica gel obtained was determined by the BET method on an AccuSorb 2300E apparatus (Micromeritics). Pore volume was determined by benzene vapour sorption.

RESULTS AND DISCUSSION

Because gelling processes for such systems take a long time it is impossible to perform rapid neutralization of the initial silica sols. During

the gelling process homogenous silica gels acquire their hardness during an extremely long period of time (15–20 h). This gelling procedure is unsuitable for preparation of micro-spherical silica gels. Silica gels obtained without use of potassium silicate have pores of comparatively low sorption volume (from 0.50 to 0.53 cm^3 g^{-1}). The dependence of the duration of the gelling process on the amount of potassium silicate in the silica sol–potassium silicate system is depicted in Fig. 1. The main characteristics of gel
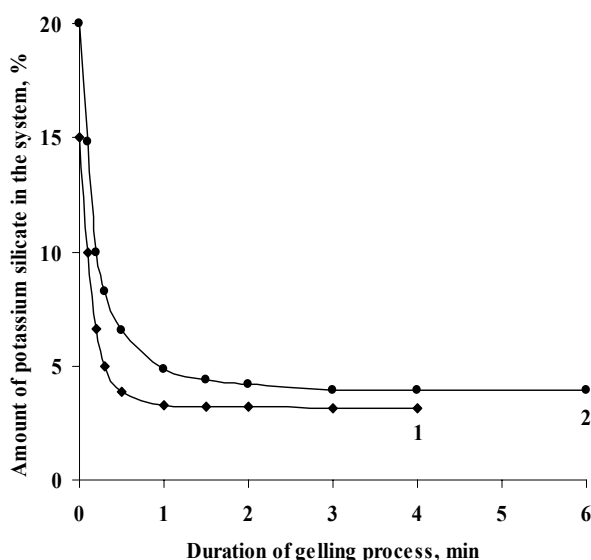
Fig. 1

Correlation between the amount of potassium silicate and duration of system gelling

formation in the silica sol–potassium silicate system are listed in Table I. It follows from Fig. 1 and Table I that it is possible to control gel-formation by adding potassium silicate to the stabilized silica sol. During the gelling process homogenous, hard, and elastic hydrogels are usually obtained in very few minutes. Whether concentrated (3.0 mol L^{-1} NH_4NO_3, curve 2 in Fig. 1) or comparatively dilute (1.5 mol L^{-1}, curve 1 at the Fig. 1) gelling agents are used, if the amount in the system is >0.35 mol L^{-1} local precipitation of hydrogels occurs. Such phenomena are observed when the potassium silicate content of the system exceeds 20% by mass.
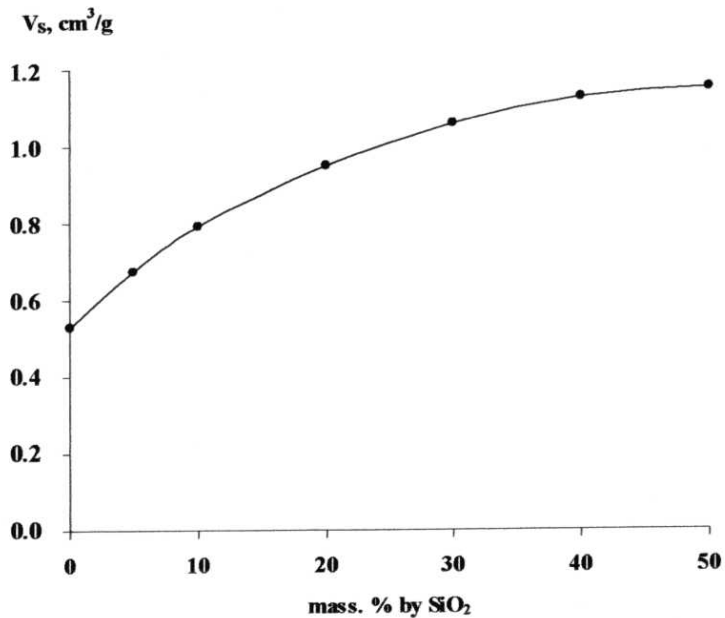
The dependence of silica gel pore volume on the quantity of potassium silicate added to silica sol with 10-nm particles is presented in Fig. 2.

It is apparent from this figure that the pore volume of micro-spherical silica gels increases as the quantity of potassium silicate added to the silica sols is increased.

Table I

Main characteristics of the gel-formation process in the system stabilized silica sol–potassium silicate

No.	Silica sol volume (mL)	Potassium silicate solution volume (mL)	Volume of gelling agent solution (NH₄NO₃) (mL)		Final content of gelling agent in hydrogel (mol L⁻¹)		Duration of the gelling process (s)		pH of the hydro-gel
			1.5 M	3.0 M	1.5 M	3.0 M	1.5 M	3.0 M	
1	97.5	2.5	20.0	10.0	0.250	0.272	360	80	7.5
2	95.0	5.0	22.5	11.0	0.276	0.297	65	20	7.5
3	92.5	7.5	25.0	12.5	0.300	0.333	25	15	7.5
4	90.0	10.0	27.5	15.0	0.323	0.391	18	10	7.5
5	85.0	15.0	30.0	17.5	0.346	0.446	8	5	7.5
6	80.0	20.0	35.0	20.0	0.389	0.500	0	0	8.0

Fig. 2

Dependence of the pore volume of micro-spherical silica gels on the quantity of potassium silicate added to the system

The pore-size distribution for micro-spherical silica gels obtained from silica sols with 8, 12, and 17-nm particles is presented in Fig. 3. To obtain these results micro-spherical silica hydrogels, after ageing for 2 days and filtering, were rinsed with acetone, then with 1:1 (*v/v*) acetone–water, filtered, dried at 150°C for 3 h, and heated at 600°C for 4 h. It follows from Fig. 3 that silica gels obtained from silica sol with 8-nm colloidal particles have a wider pore-size distribution, which testifies indirectly to the poly-dispersity of the silica sol. Curves 3b and 3c indicate that colloidal particles of the corresponding silica sols were more homogenous in size.
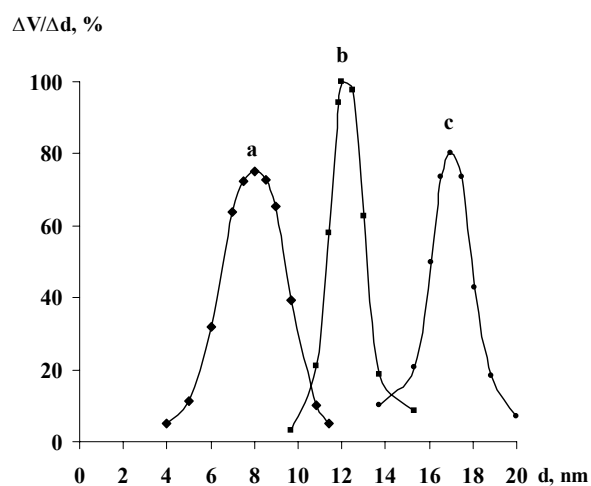
Fig. 3

Pore-size distribution for micro-spherical silica gels obtained from silica sols with (a) 8-nm, (b) 12-nm, and (c) 17-nm particles

The porosity characteristics of the micro-spherical silica gels obtained are presented in the Table II and the dependence of pore sorption volume, for micro-spherical silica gels prepared from silica sol with 8-nm particles, on the duration of exposure of the silica hydrogels to acetic acid, acetone, and ethanol is presented in Fig. 4. It follows from Table II that the pore sorption volume increases from 0.64 cm^3 g^{-1} to 1.10 cm^3 g^{-1} when acetic acid is used to substitute intermicellar water in micro-spherical silica gel obtained from silica sol with 8-nm colloidal particles. The volume increases to 1.06 cm^3 g^{-1} when acetone is used. The maximum pore sorption
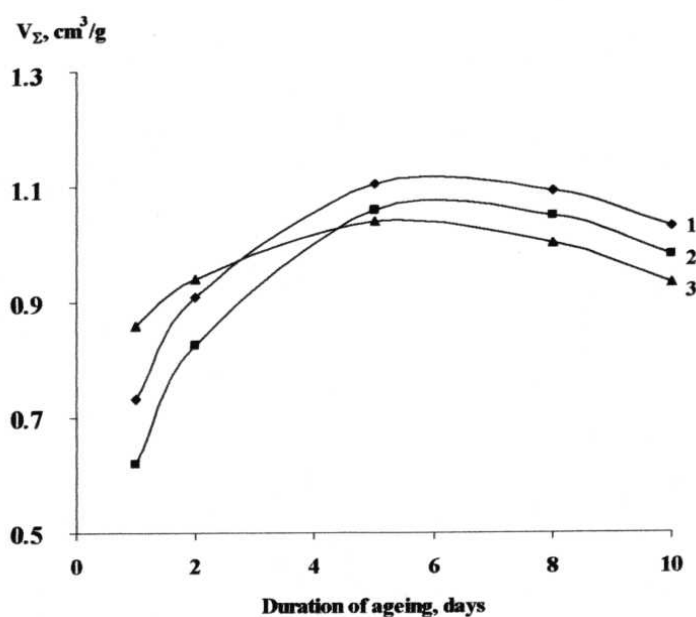
volume is observed when the hydrogel is exposed for 4–5 days; after this time the volume decreases slightly.

Table II

Porous characteristics of micro-spherical silica gels prepared from silica sols with 8, 12, and 17-nm colloidal particles

Sample	Size of silicasol colloidal particles, determined by the Sears method (nm)	Specific surface area $(m^2 g^{-1})$	Sorption volume of pores $(cm^3 g^{-1})$		Average pore diameter (nm)
			Ageing for 3 days	Ageing for 4 days in CH_3COOH	
1	8	280	0.64	1.10	8
2	12	200	0.55	0.78	12
3	17	150	0.50	0.70	16

Fig. 4

Dependence of the pore volume of micro-spherical silica gels on the duration of ageing in acetic acid (1), acetone (2), and ethanol (3).

This relatively large increase in sorption volume as a result of substituting intermicellar water by organic liquids is because the pores formed are comparatively small (average pore size $d_{av} \approx 80$ Å) and during the conver-

sion from hydrogel to xerogel the capillary forces of water are very strong, which leads to severe compression of the hydrogel framework. Less compression of the framework is observed when water is exchanged for an organic liquid of lower surface tension, so silica gels with a larger pore volume are obtained. As remarked above, it follows from Fig. 4 that microspherical silica gel obtained from a silica sol with 8-nm particles is characterized by a wider pore size distribution. This testifies to the polydispersity of the particles of this silica sol. It is known [5] that polydispersed silica sols form structures with greater porosity during conversion from hydrogel to xerogel, and that they counteract capillary forces to a greater extent, resulting in less contraction. It is supposed that changes of pore volume obtained by substitution of intermicellar water by liquids of lower surface tension will be greater for poly-dispersed systems than for more systems with more homogenous particle-size distribution.

It follows from Table II that as the size of the colloidal particles of the silica sols increases, the effect on sorption pore volume of substituting intermicellar water by acetic acid in micro-spherical silica gels (MSG) will decrease. Whereas the difference between the pore volumes before and after ageing of micro-spherical silica gel formed from silica sol with 8-nm diameter particles is $0.46 \ cm^3 \ g^{-1}$ for similar silica gel prepared from 12-nm particles the difference is $0.23 \ cm^3 \ g^{-1}$ and for silica gel prepared from sol with 17-nm particles it is only $0.20 \ cm^3 \ g^{-1}$.

CONCLUSIONS

It is possible to control gelling processes by addition of potassium silicate to stabilized silica sols before the gelling process is started. In the presence of potassium silicate the gelling process proceeds very quickly.

Although the gelling process is rapid, it is possible to obtain homogenous, hard, and elastic hydrogels. The sorption volume of the silica gels obtained decreases as the amount of potassium silicate added to the silica sols is increased.

It is possible to increase the sorption volume of the silica gel sorbents obtained by exchanging intermicellar water for organic liquids such as acetic acid, acetone, and ethanol in silica hydrogels obtained from stabilized silica sols. The increase in the pore sorption volume is greatest for polydispersed samples and less for fine-porosity homogenous samples.

The increase in the pore sorption volume obtained by substitution of intermicellar water with organic liquids decreases with increasing size

of the colloidal particles in the silica sols used as initial raw material for preparing the silica hydrogel.

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