



# Variation of surface area of silica monoliths by controlling ionic character/chain length of surfactants and polymers



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## ABSTRACT

To achieve maximum pore diameter and surface area of porous silica monoliths different structure directing agents (SDAs) (Cationic/anionic/neutral/mixture) were used. BET study showed alteration of SDA's chain length, composition or concentration have a cumulative effect on controlling the surface area and pore size. PEG in combination with other SDAs like CTAB, SDS, BTMAC, Triton-X100 etc. controlled internal agglomeration along with particles size. The maximum amount of surface area was observed by using maximum chain length of PEG and CTAB.

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## 1. Introduction

Nowadays, mesoporous monoliths/structures have gained an immense interest for their usefulness in catalytic activity, adsorption, water purification etc. [1,2]. Pores of silica gels are heterogeneous in nature and range from <2 nm (micropore) to 2–50 nm (mesopore). The porosity of the gels gets determined by its preparation conditions. Silica monoliths prepared by sol-gel-process are known to have a trimodal distribution of pore size [3,4]. Modifications of the sol-gel process along with phase separation result in the formation of meso/macro/mix porous silica monoliths [5]. Pore size, pore volume, and surface area of these monoliths can be tuned by critical use of SDAs [1,2]. Different SDAs (cationic/anionic/non-ionic and mixed) have different effects on the pore size and distribution of monoliths. Use of cationic surfactant in various combinations during synthesis results in the formation of lamellar mesoporous silica structures [6]. Use of nonionic SDAs such as Pluronic-p123 showed the formation of ordered bimodal pore size distribution with hierarchical network structures [7]. Anionic SDAs showed the formation of amorphous structure [8]. Again; water soluble polymers such as (PEGs) determines the degree of polarity and flexibility of mesoporous structures [9]. Due to their amphoteric properties, PEG increases the solubility of the materials

[10,11]. PEG improves the porosity of inner and outer surfaces of mesoporous particles. In spite of substantial studies in this field very little is known about the effect of charge distribution of surfactant on the properties of porous silica monoliths. Moreover; very little is known about the effect of chain length of hydrophilic polymer on the porous structure of silica monolith. Viscosity, hydroxyl group content and polarity are the determining properties of SDAs which control the characteristics such as pore size of silica monoliths. Therefore; various porous silica monoliths were synthesized using a sol-gel method by critical tuning SDAs composition and investigated for their surface linked properties.

## 2. Experimental

Material and instrument information are given in [supporting information](#).

### 2.1. Synthesis of silica monolith

Tetraethylorthosilicate (TEOS) 8.5 ml was added to a mixture of HNO<sub>3</sub> (30% v/v) and PEG (6.25% w/v) solution and stirred at room temperature (~10 min) until a translucent sol was obtained. Thereafter, the calculated amount of C<sub>n</sub>TAB was added to the sol and continued stirring until the surfactant dissolved completely. For sol to gel formation and aging of gel around 90 h (minimum 12 h for sol to transition and 72 h for aging) was required at

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40 °C. Due to the variation of surfactant; gelation time and size of silica monolith differed. To increase condensation and stability of silica monolith; the solvent exchange was performed. For hardening; silica monolith were soaked in (1 M)  $\text{NH}_4\text{OH}$  ( $10\times$  volume) solution at 90 °C for 9 h. Later, the solutions of silica monolith were acidified using  $\text{HNO}_3$  (0.1 M). Before calcination at 550 °C (5 h with 1 K/min heating ramp), silica monolith was washed thoroughly with deionized water and dried for 5 days at 40 °C.

### 3. Results and discussion

#### 3.1. Effect of PEG chain length

Silica monoliths were prepared at constant CTAB:TEOS:PEG 0.9:1:0.003 M ratios with increasing PEG chain length. PEG is the

main component for sol-gel forms of interconnected macropores silica monolith [12]. Upon use of different PEG (MW – 400–35,000  $\text{g mol}^{-1}$ ), silica monolith rods with interconnected mesoporous structures were obtained (Fig. 1). The increment resulted in the faster polymerization of silica gel. Due to interaction with silica gel volume fraction of polymer increased with the increase of PEG chain length. It also resulted in the steric stabilization and interconnected colloid formation process which leads to the formation of higher textural mesopore size due to an increase of particle volume fraction. Fig. 2A shows  $\text{N}_2$  sorption isotherms of silica monolith made of different MW PEG. With increasing, PEG MW increase in the  $\text{N}_2$  adsorption happened. The increase in PEG MW caused an increase of surface area from 638 to  $760 \text{ m}^2 \text{ g}^{-1}$  ( $\pm 30 \text{ m}^2 \text{ g}^{-1}$ ) and increase of the textural mesopore size (Fig. 2B). On the other hand, a pore volume of silica monolith significantly

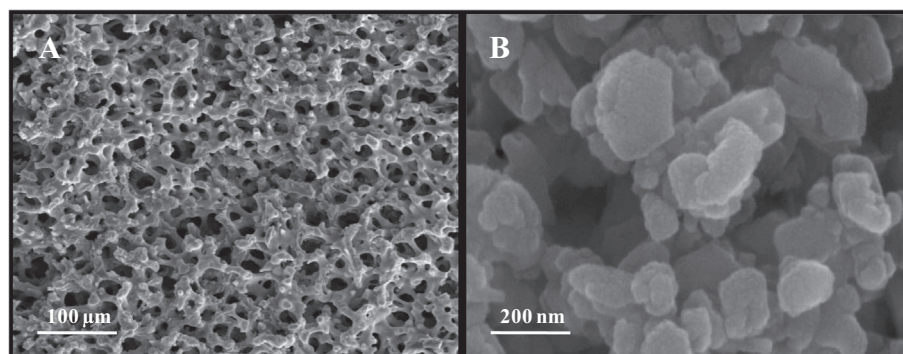


Fig. 1. SEM image of porous silica monolith (S-350) showing the textural porosity.

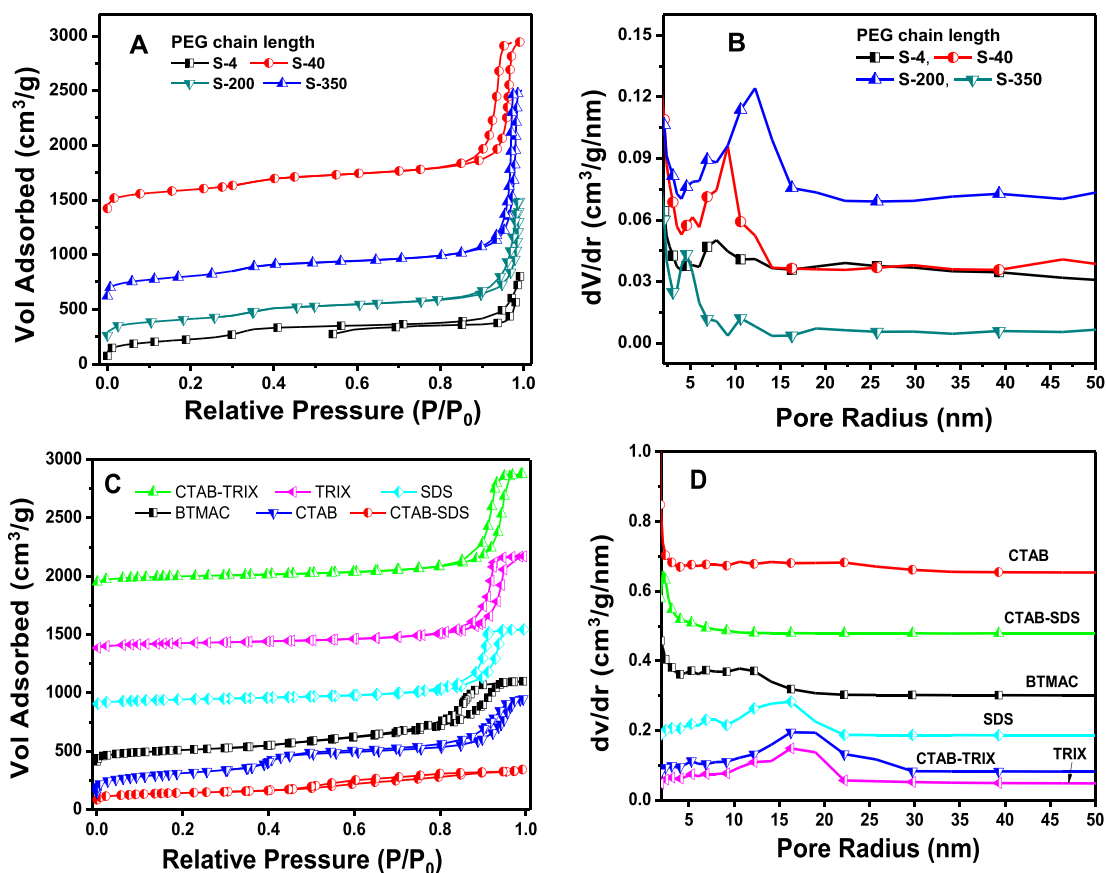


Fig. 2. Nitrogen sorption isotherm plots for silica monolith with different A) PEG chain length, C) surfactants; differential pore volume distribution using BJH plots for silica monolith with different B) PEG chain length, D) surfactants. (In case of, Fig. A–B surfactant used:  $\text{C}_{16}\text{TAB}$  and C–D polymer used: PEG-35,000  $\text{g}/\text{mol}$ ).

varied due to the variation of mesopore size ( $1.1\text{--}3.1\text{ cm}^3\text{ g}^{-1}$ ). BET-surface area along with pore volume and pore size in relation with PEG chain lengths is listed in Table S1.

### 3.2. Effect of ionic characters of surfactant

To check the effect of nature of surfactants on the pore size and surface area; cationic (CTAB, BTMAC), anionic (SDS), neutral (TRIX) and a mixture of (cationic-anionic and cationic-neutral) surfactants were used to prepare silica monolith. The molar ratio of batches was  $\text{H}_2\text{O}:\text{HNO}_3:\text{TEOS}:\text{PEG}$  (MW 35,000 g/mol):  $\text{CTAB} = 8.2:0.53:2.2:9.54 \times 10^{-4}:0.2$ , in which either a single surfactant or an equimolar mixture of surfactants were used. Nitrogen adsorption-desorption isotherm for silica monolith with different surfactants are shown in Fig. 2C and textural characteristics are shown in Table S2. Because of charge neutralization between cationic surfactant (CTAB) and negatively charged silica particles (TEOS) become more hydrophobic in nature. Chain-chain interactions by surfactant adsorption resulted in an increment in micelle size and as a result pore size increased (Fig. 2D). SDS formed negatively charged micelles with small mesoporous size and upon addition of TEOS (negatively charged) strong electrostatic repulsions forces generated which resulted in a decrease of pore size and surface area in comparison with the cationic surfactant. Due to low electrostatic force in nonionic surfactant intermediate surface area formed. Similarly, due to electro-neutrality of an equimolar mixture of CTAB-SDS; upon interaction with TEOS; a weak electrostatic attraction generated which increased surface area and critical aggregation concentration [13]. In cationic-nonionic mixture posi-

tively charged, micelle neutralized the negative charges of TEOS leading decrease in surface area.

### 3.3. Effect of surfactant concentration

The concentration of surfactants strongly influenced the textural and morphological properties of mesoporous monoliths. Surface area was also found to be directly proportional to the molar concentration of CTAB (Fig. 3A). The BET area increased from  $316$  to  $994\text{ m}^2\text{ g}^{-1}$  with an increase of the molar concentration of CTAB ( $0.1\text{--}0.5\text{ M}$ ). Some physical parameters (surface area, pore size, and pore volume) are summarized in Table S3.

The critical micelle concentration (CMC) of CTAB in aqueous solution is  $0.9\text{--}1\text{ mM}$  [14]. Above the CMC transition of spherical shape to rod-like structures occurs. Therefore at higher concentration of CTAB; positively charged, larger mesoporous, rod-like micelles formed. The increase in the concentration of CTAB caused strong electrostatic attraction with the TEOS resulting in an increment of pore size (Fig. 3B) and surface area.

### 3.4. Effect of chain length of CTAB

The chain length of CTAB also influenced the textural and morphological properties of silica monolith. The molecular weight of CTAB is directly proportional to surface area of monoliths (Fig. 3C). Alteration of physical parameters like surface area, pore size and pore volume in respect to CTAB chain length are summarized in Table S4. Smatt et al. (2003) synthesized silica monoliths by varying chain length of CTAB and found all were giving similar surface area ( $755 \pm 30\text{ m}^2\text{ g}^{-1}$ ) [3]. But we found an increase in the

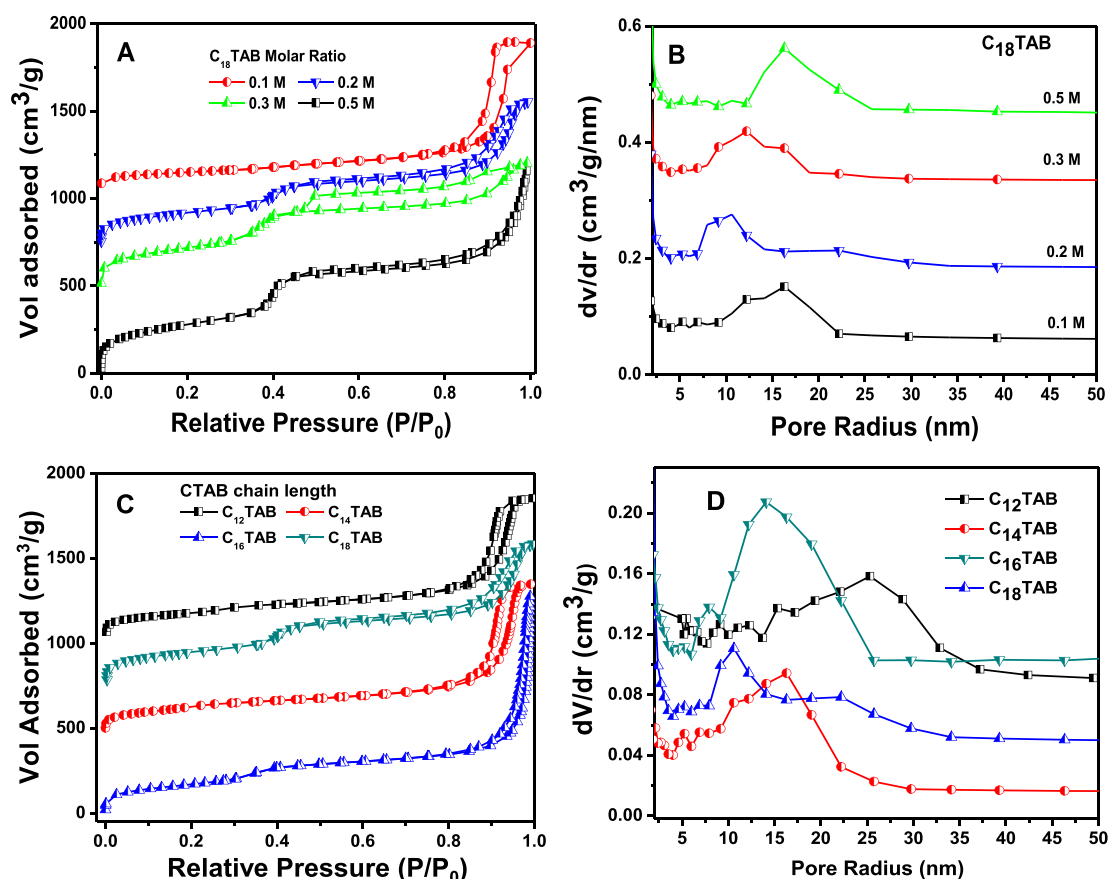


Fig. 3. Nitrogen sorption isotherm plots for silica monolith with different A) molar ratio of  $\text{C}_{18}\text{TAB}$ , C) CTAB chain length; differential pore volume distribution using BJH plots for silica monolith with different B) molar ratio of  $\text{C}_{18}\text{TAB}$ , D) CTAB chain length. (In all cases polymer used: PEG-35,000 g/mol).

BET surface areas from 528 to 782.54 m<sup>2</sup> g<sup>-1</sup> with an increase of chain length of C<sub>n</sub>TAB (n = 12–18). The increase in chain length of CTAB resulted in a decrease of the textural mesopore size (Fig. 3D).

Cationic surfactants can form a long worm-like micelle in combination with TEOS by forming packed entanglement network with enhanced viscoelasticity. Primarily, during the synthesis process; CTAB got completely dissolved in a mixture of TEOS-PEG and resulted in small micelle formation. While the increase in hydrocarbon chain length of surfactants (C<sub>n</sub>TAB, n = 12–18), spherical micelle converted into uniaxial micellar close-packed structure due to the mass-action effects. The increase of the diameter of micelles leads to increase in osmotic compressibility due to increased surface area in compact micelle system [15].

#### 4. Conclusion

The effect of chain length of PEG on network structure, packing along with the effect of different surfactants (cationic, anionic, neutral or mixture) over the formation of silica monolith has been presented in detail. The findings suggested that surfactant and/ or PEG reaction with silica nanoparticles leads to the formation of a composite with architectural pore network system. Controlling of internal structure and agglomeration of particles can be possible by changing the chain length of PEG. In combination with PEG, surfactants interacted with silica monolithic system resulting in the formation of enlarged interconnected pores. It has also been found macropore diameters of the monoliths were tunable by controlling types and concentration of surfactants. Alteration of chain length

or composition along with the concentration of surfactant showed a synergistic effect on the surface area and pore size of monoliths.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.matlet.2017.02.074>.

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