

Effect of Various Parameters on the Stability of Silica Dispersions

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Abstract For different practical applications, it is cardinal to maintain the stability of nanoparticles in aqueous suspension. The theoretical impact of pH and ultrasonication time on surface charge, particle size distribution and the dispersion stability of AEROSIL®OX 50 in water were evaluated, and a practical (centrifugal sedimentation analysis) test was used to determine the effects of concentration and molar mass of the polymer polyvinylpyrrolidone (PVP) at different pHs. It was observed that the size distribution of silica remains almost unaffected, but the surface charge increased with ultrasonication time up to 20 min and then leveled off. This increase in surface charge was proportional to the molar mass of the added polymer. The zeta potential increased with the increasing concentration of PVP in the silica suspension. This behavior is attributed to the adsorption of polymer over the surface of the particles. The suspensions were found to be the most stable, up to 36 %, at concentration (1 %) of PVP having higher molar masses. Furthermore, the addition of polymer strengthened the available agglomerates in the dispersion which resulted in the widening of the particles' size distribution.

Keywords Particle size distribution · Ultrasonication · pH · Zeta potential · Surface charge · Molar mass of poly(vinylpyrrolidone) · Stability of silica dispersion

1 Introduction

The stability of colloidal suspensions in the presence of macromolecules is thought to be the result of polymer adsorption on the particle's surface, which imparts steric or

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electrostatic stabilization effects. Hence, the nature of both the polymer and particle's surface play vital roles in the stability of a particular dispersion. Aqueous dispersions of silica have also been of interest for colloidal scientists because of their applications and jarring behavior of aggregation [1]. Among the fused silicas, AEROSIL[®] OX 50 is very useful material because of its high chemical purity, relatively broad particle size distribution, spherical shape, high tapped density, and ability to form highly loaded and stable solid dispersions [2–16]. Owing to these properties, it has applications in sol–gel processing, dental composites, biotechnology, agriculture, medicine and pharmaceuticals. Likewise, water-soluble polymers are extensively used in controlling the stability and other parameters of dispersed systems [17–19]. Among the non-ionic water-soluble polymers, polyvinylpyrrolidone (PVP) is a relatively a new entity that is used as a binding material and pigment dispersant [20]. Owing to the increase in viscosity of its solutions and suspensions, it may cause a stabilizing action for suspensions; therefore it is used as a protective for colloids [21].

In a previous study it was revealed that the stability of aqueous dispersions of inorganic pigment could be increased in the presence of PVP [22].

The impact of mechanical treatment by means of homogenization and/or ultrasonication on the dispersion stability is well known. The effects of ultrasonication on the surface charge, particle size distribution, homogeneity of dispersion and its stability is very important, but little information about the impact of ultrasonication on the degree of dispersion and estimation of stability is available [2, 23].

Therefore, we investigated this problem using various methods for particle characterization such as particle charge determination, laser diffraction (LD) and separation analysis in a centrifugal field (SA).

The objective of this work is to obtain a stable aqueous dispersion of silica in the presence of PVP as a function of molar mass of polymer and ultrasonication time.

2 Experimental

2.1 Materials

AEROSIL[®] OX 50, fumed silica oxide obtained from Degussa, Evonik industries, Germany, was used as a model substrate. Some of the characteristics of AEROSIL[®] OX 50 are presented in Table 1. These properties were also verified by employing a mercury porosity meter (Autosorb-1 der Firma Quanta chrome, USA), pH and LD measurements, and scanning electron microscopy. The specific surface area reported by the manufacturer was 50.15 (m²·g⁻¹) but, when measured, it was 40.72 (m²·g⁻¹) [24].

Three different samples of PVP, also known as Luvitec, was obtained from BASF, Germany. It had three different molar masses and was used as a stabilizer for the silica dispersions. Some of the basic properties of PVP as provided by the manufacturer are listed in Table 2. Water used for the dispersion was obtained from Millipore, GmbH, Schwalbach, Germany, having pH around 6.5 and conductance of 2.5 μS.

2.2 Preparation of the Dispersion

The dispersion was prepared by dispersing 1 g of silica into 100 mL of Millipore water (1 % solid content), using a high intensity ultrasonic processor, UP-200 s operating at 24 kHz, up to 200 W (Dr. Hielscher GmbH), at 22 °C.

Table 1 Physicochemical properties of AEROSIL[®]OX 50, according to the manufacturer

Model substrate	Source	BET surface area (m ² ·g ⁻¹)	pH at PZC	SiO ₂ content	pH	Primary particle size (μm)	Tapped density (g·L ⁻¹)
AEROSIL [®] OX50	Evonik industries	50 ± 15	3.2	≥99.8	3.8–4.8	0.4	≈ 130

Table 2 Some of the basic properties of PVP as provided by the manufacturer, BASF, Germany

Sample:	PVP1	PVP 2	PVP 3
M _w /kDalton	7–11	45–55	1,200–2,000
M _w /kDalton	1.5–2.5	11–18	300–400
Relative viscosity, 1 % in water	1.075–1.110	1.201–1.291	3.991–6.197

2.3 Characterization of the Dispersion

The dispersion was characterised with respect to particles size and its distribution, using a laser diffractometer, equipped with a He–Ne laser of wavelength 632.8 nm of 2 mW power (Mastersizer, Malvern). The sample stirring was carried out at 2,000 rpm and 22 °C during the measurements.

2.4 Measurement of Surface Charge Density

The charge density of the dispersion was estimated by the colloid titration technique using a PCD 04 particle charge detector (Mütek GmbH, Germany). A solution of sodium polyethylene sulfonate (PES-Na) and polydiallyldimethyl-ammoniumchloride (PDAD-MAC) was used as titrant for cationic and anionic systems, respectively. Charge density (q) in terms of meq·g⁻¹ was calculated according to Eq. 1:

$$q = \frac{C_{\text{titrant}} V_{\text{titrant}}}{Vm}, \quad (1)$$

where C_{titrant} , V , V_{titrant} and m are the concentration of titrant (meq·L⁻¹), volume of titrated solution (L), equivalent titrant volume (L), and content of polyelectrolyte in titrated solution (g·L⁻¹), respectively.

2.5 Electrophoretic Studies

The electrophoretic mobility of the dispersion was measured using a Zeta Sizer 3000 (Malvern, Germany). The concentrations of KCl were kept as 0.1 g·L⁻¹ during the electrophoretic mobility measurements. All the measurements were made after attaining equilibrium in terms of pH.

2.6 Sedimentation Tests/Stability

A centrifugal sedimentation analyzer (LUMiSizer, L.U.M. GmbH Berlin) was used to characterize the storage stability of the dispersion and its dependence on the

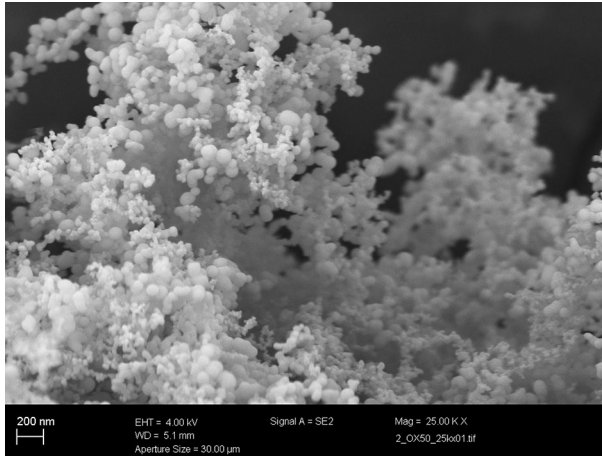


Fig. 1 SEM picture of AEROSIL[®] OX 50

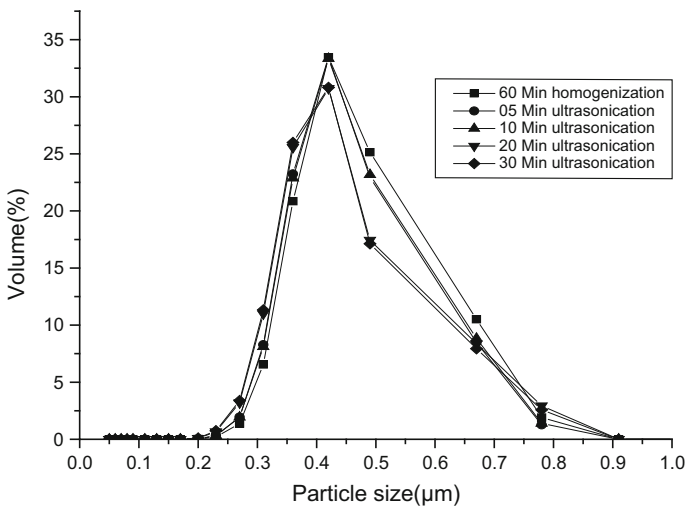


Fig. 2 Particle size distribution of Aerosil OX 50 (1 % aqueous dispersion) under different treatment conditions

concentration of added polymer. The intensity of transmitted light was measured as a function of time and position over the entire sample length. Twelve samples were analyzed simultaneously at constant/variable centrifugal force [25]. All the experiments were carried out at 3,000 rpm for 3,600 s at 22 °C using 1.8 mL of the dispersion solution. The integration of the transmission profiles was performed at the middle (between the positions 106 and 124 mm) region of the cell to investigate the sedimentation behavior of the dispersion.

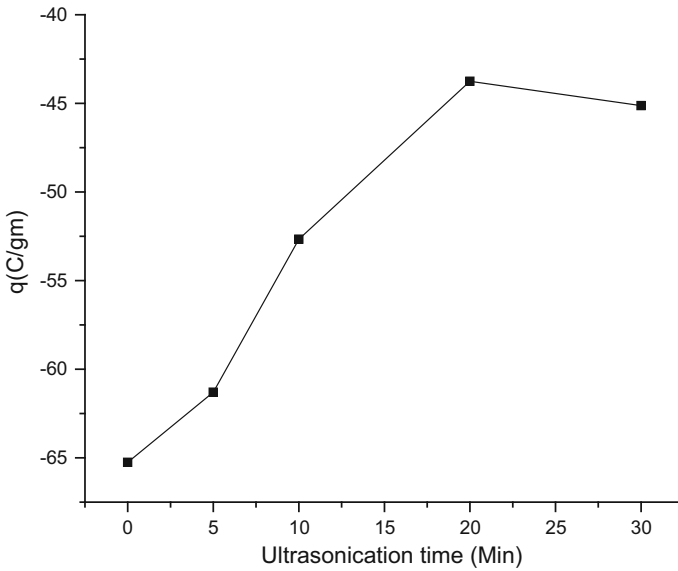


Fig. 3 Effect of ultrasonication time on the surface charge of AEROSIL[®] OX 50 (1 % aqueous dispersion)

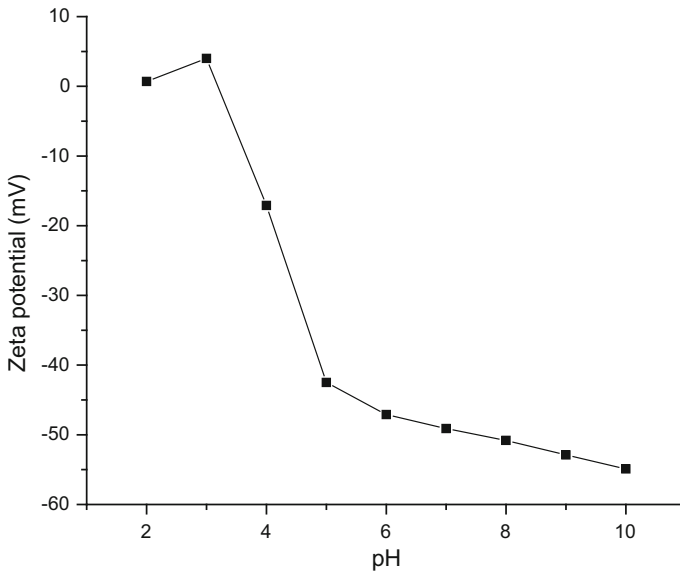


Fig. 4 Zeta potential versus pH profile of AEROSIL[®] OX 50 (1 % aqueous dispersion)

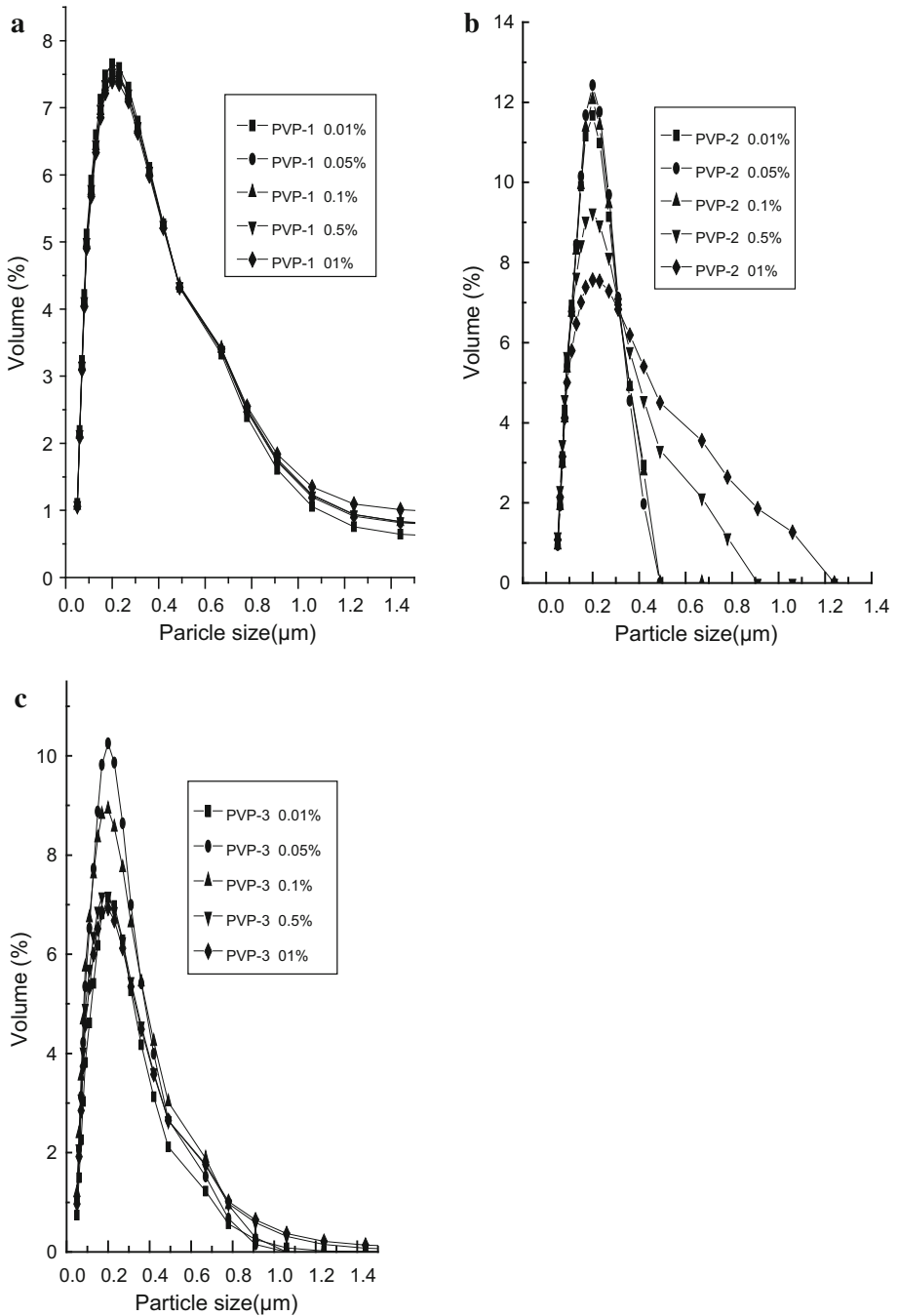


Fig. 5 a, b, c Effects of concentration and molar mass of PVP on the particle size of AEROSIL[®] OX 50 (1 % dispersion)

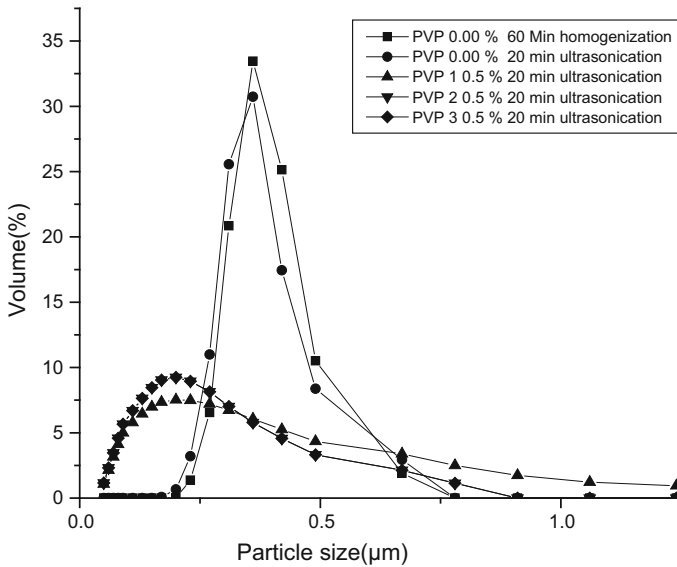


Fig. 6 Effects of concentration and molar masses of PVP and different conditions of preparation on the particle size of Aerosil OX 50 (1 % dispersion)

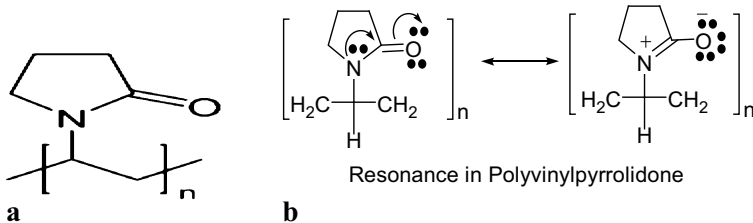


Fig. 7 **a** Schematic structure of Poly(vinylpyrrolidone). **b** Resonance in PVP

3 Results and Discussion

3.1 Effect of Ultrasonication on the Size and Size Distribution of the Particles

SEM images of the particles after ultrasonication for 30 min are displayed in Fig. 1. The figure indicates mono dispersity in the size of the particles; however, some aggregates are visible in the images. The particle sizes obtained in the aqueous dispersed phase for the samples sonicated for different times ranged from 220 to 900 nm with an average of 400 nm, as is displayed in Fig. 2. These plots also show mono dispersity to some extent while the polydispersity is attributed to aggregates that are present in the system. Furthermore, these observations are in accord with information provided by the manufacturer. The figure also indicates that the sonication time has an almost negligible impact on the size and size distribution. However, the degree of dispersity first decreased and then increased when the sonication time was longer than 20 min. This trend is attributed to the balance between shear and colloidal forces. This phenomenon is further supported by

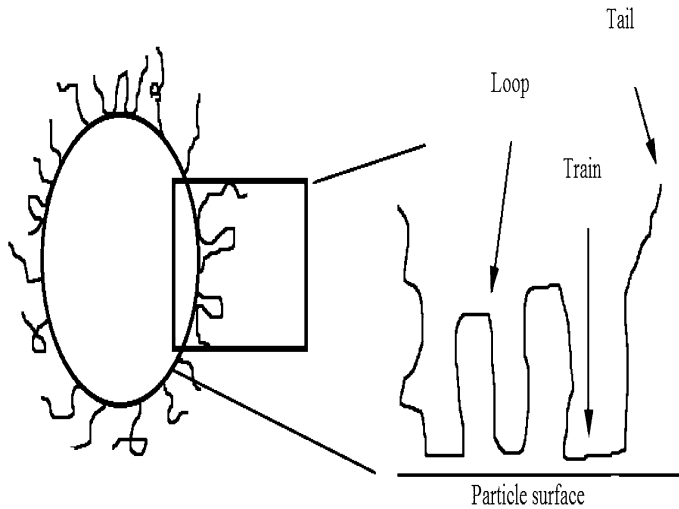


Fig. 8 Schematic representation of polymer absorbed on a particle surface [25, 26]

Eq. 2, which states that aggregate formation or disintegration depends upon the critical shear rate. It is important to note that the shear rate is directly proportional to the ratio of the continuous media/dispersed media viscosities [26]:

$$\gamma_c = f\left(\frac{s\sigma}{\eta_A a}\right). \quad (2)$$

Here γ_c is the critical shear rate, s is the ratio of particle-to-medium viscosities, σ is interfacial tension, η_A the droplet viscosity and a is the size of the particle.

Therefore, the rest of the study was performed on dispersions ultrasonicated only for 10 min. It is interesting to note that the surface charge of the particles increased with the increase in ultrasonication time (Fig. 3). The cavitation phenomenon is concluded to appear in liquids by propagation of intense sound waves creating new active surfaces [27, 28]. This process was found to be active only up to 20 min and thereafter it had no effect. We conclude that the dispersion will be most stable after sonification for 20–30 min; at high surface charge density the repulsion among the particles will be greater. The charge density of the particles measured at various pH values is plotted in Fig. 4. It is observed that the charge increases with increase in pH and this is attributed to adsorption of OH^- ions over the surface of the particles.

3.2 Effect of PVP on the Size and Size Distribution of the Particles

The effect on size and size distribution of the system from added PVP is depicted in Fig. 5. The addition of PVP decreased the mean particle size and narrowed the distribution. The impact is more pronounced for high molar mass/concentrations of polymer. This trend is attributed to the formation of a uniform and stable dispersion through the adsorption of polymer over the surface of the particles. However, the degree of dispersity increased when the low molar mass polymer was added. Also, the addition of relatively high molecular mass polymer (PVP2) reduced both the degree of dispersity and the size. When the

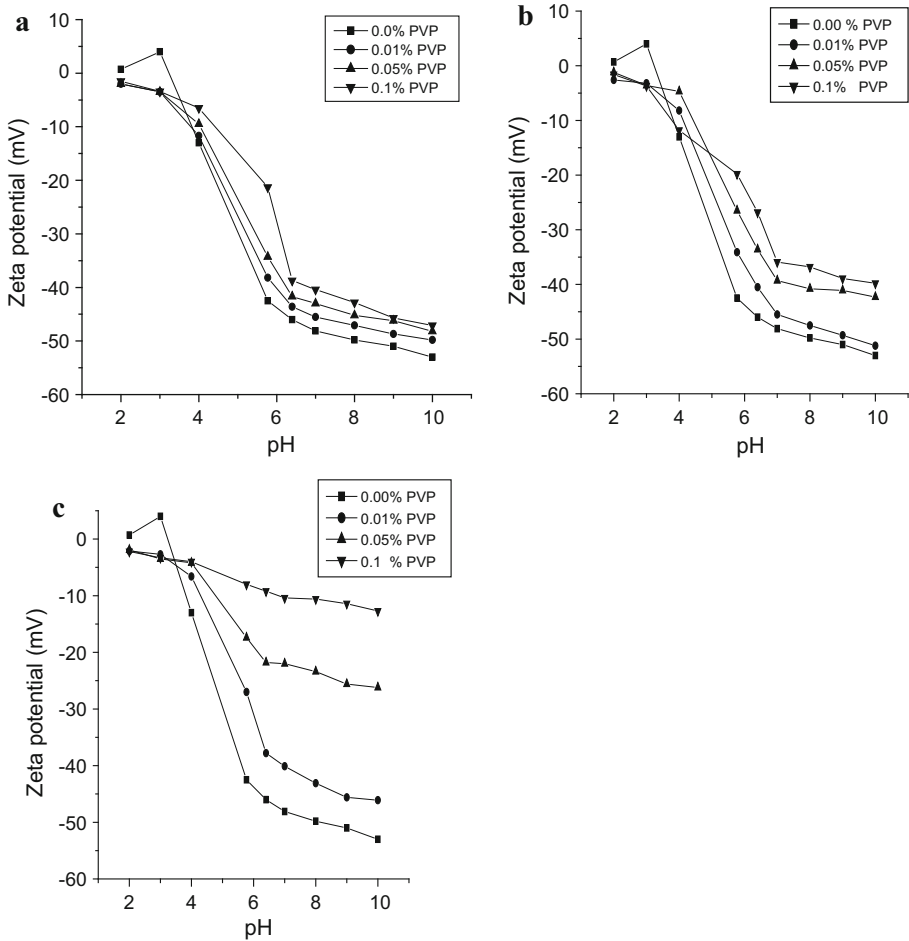


Fig. 9 Zeta potential pH profiles: effects of polymer type **a** PVP 1 **b** PVP 2 **c** PVP 3 and concentration (0.01, 0.05 and 0.1 %)

concentration was increased, the average particle size and degree of dispersity increased. This trend is attributed to the high viscosity, which creates resistance to the disintegration of aggregates [21]. There seemed to be no visible effect of concentration and the particles had a small size with narrow distribution (Fig. 5c) for the very high molar mass polymer (PVP 3). The polymer with long chains had a conformation that did not allow the aggregates to disintegrate when shear forces are applied [21, 29].

Selected data from Fig. 5 have been plotted in Fig. 6 for comparison purpose. It was noted that when the polymer was added the size decreased whereas the degree of dispersity increased. The aggregate formation due to polymers and their entanglement can be explained according to Eq. 2. Addition of a polymer increases the viscosity of the continuous media and hence the shear forces are increased during ultrasonication. These shear forces result in the disintegration of aggregates. Once the aggregates have disintegrated the particles thus formed are coated immediately with the available polymer in the system.

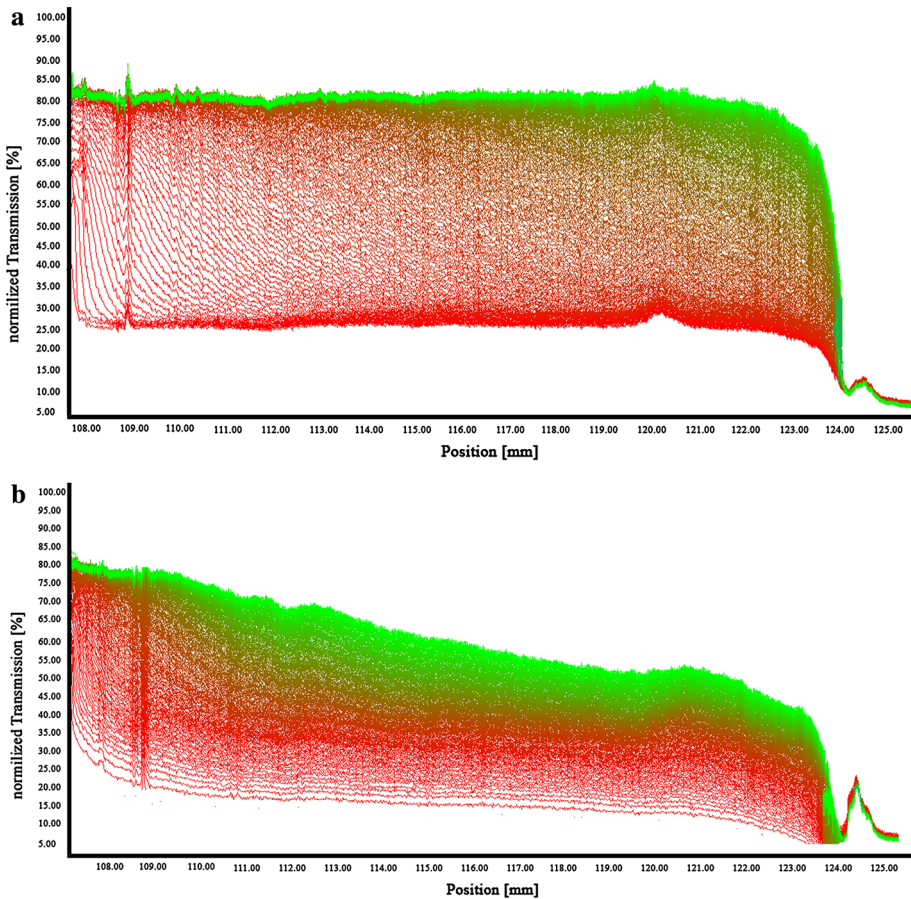


Fig. 10 **a** Transmission profile of a pure silica dispersion, **b** Transmission profiles of a silica dispersion in the presence of 1 % PVP with high molar mass (PVP 3); solid content is 1 %

Hence, they are not able to aggregate again due to steric stabilization as well as electrostatic repulsions. The structure of PVP shows that a negative charge can be created through a resonating structure (Fig. 7). If the concentration and molar mass of the polymer are high then aggregates/micelles can be formed. When the interactions between the polymer–polymer molecules are weaker than the interactions between polymer molecules and silica particles, this results in disruption of the PVP molecules’ agglomeration (Fig. 8) [21].

3.3 Electrophoretic Mobility in the Presence of PVP

The charge of particles can be changed by adding a polymer and by varying the pH or ionic strength of the solution. The use of polymers like PVP is more effective in this regard because of their direct absorption on the surface of the particles. Therefore, the zeta potential can be a good tool to measure the adsorption of different polymers on solid surfaces [21, 29]. The results of zeta potential as functions of pH and polymer OX 50 concentration is displayed in Fig. 9. The zeta potential decreases with the increase in pH

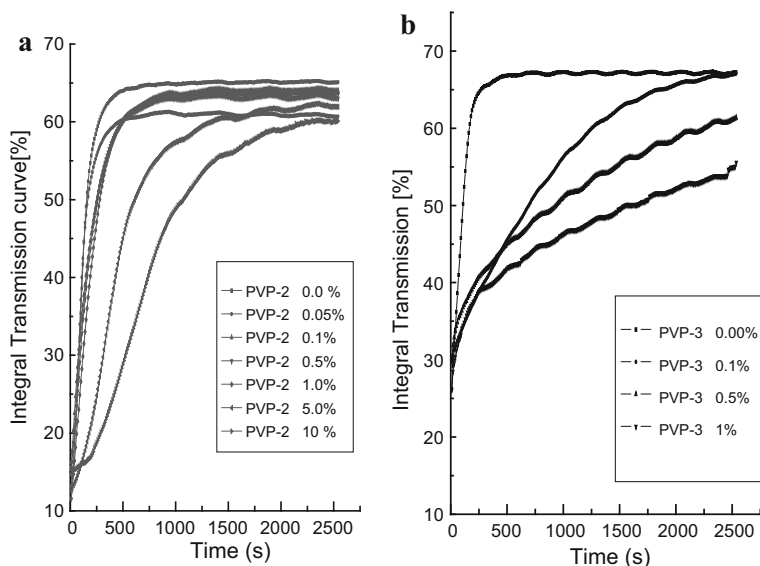


Fig. 11 Integrated transmissions of silica dispersions in the presence of PVP with low (PVP-2) (a) and high molar mass (PVP-3) (b)

and ultimately levels off as noted earlier, and the Zero Charge Point (ZCP) corresponds to pH 3.2. From the addition of polymer the zeta potential increased in the investigated range of PVP concentration at a particular pH. The effect is more pronounced for high molar mass polymers and high pH as noted for other systems [22, 30, 31]. This was attributed to adsorption of H^+ and OH^- ions as stated earlier. Similarly, the surface charge increased with the increase in polymer concentration due to adsorption of polymer on the particle's surface. The figure also shows that the pattern of variation of charge with the variation in pH remained the same, irrespective of the polymer concentration, leading to the conclusion that the adsorption of H^+ or OH^- ions was not affected by the polymer.

3.4 Stability in the Presence of PVP

Figure 10 displays the light transmission profile of silica dispersions obtained through the centrifugation experiment. The results indicate that the dispersion became more stable as the concentration of polymer increased [27, 31]. For example, the light transmission for the pure silica dispersion without polymer was 87 % and with polymer was 55 % at position 117 mm after the measuring time, indicating a 36 % increase in stability with the addition of polymer (Fig. 10b). The integrated light transmission curves of the same experiment are displayed in Fig. 11. The slopes of the integrated transmission curves represent the stability of the dispersion that is lower in the presence of PVP than in water. The transmission profiles recorded during centrifugation at 1,000 rpm indicate that, if the integral transmission is lower, the sedimentation will be less. Thus, the slopes of the curves displayed in Fig. 11 indicate that the sedimentation velocity was highest for the pure silica dispersion and decreased with the addition of polymers. The highest stability was achieved by the addition of polymer with the highest molar mass. The most stable dispersion was the dispersion with 1 % PVP having the highest molar mass (PVP-3).

4 Conclusions

Silica dispersions have been investigated with respect to particle size, size distribution, surface charge and their stability as a function of ultrasonication time, and the molar mass and concentration of added polymer. The ultrasonication has no significant effect over the particle size or its distribution. However, the surface charge increased with ultrasonication up to 20 min but then became constant. The addition of polymer had a noticeable effect upon the size and distribution of the dispersion. The particle size decreased whereas the distribution widened. The surface charge and zeta potential dramatically increased with increase in concentration and molar mass of the polymer. The stability of the silica dispersion is not only dependent on the polymer concentration but also depends upon the molar mass of the polymer. The stability of the dispersion increased due to an increase in repulsive forces and steric hindrance.

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