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ORIGINAL CONTRIBUTION

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Surfacial, liquid sorption and monolayer-forming properties of hydrophilic and hydrophobic Stöber silica particles

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Abstract The surface of silica spheres with a diameter of 500 nm was modified with ethoxysilane. Hydrophilic and partially hydrophobic silica spheres were obtained, suitable for the preparation of two-dimensional monoparticle films at the liquid-air interface. The tendency of these particles to self-assemble is basically dependent on surface hydrophobicity. Liquid sorption excess isotherms were studied in ethanol-cyclohexane and ethanol-chloroform mixtures with the aim of characterizing the adsorption capacity of the particles. Specific surface area and porosity were measured by nitrogen adsorption. The specific surface area determined by liquid sorption was considerably larger than determined by gas adsorption. This is ascribed to penetration of ethanol into the pores and the swelling of the silica particles in ethanol. Surface modification of hydrophilic particles changed the film-forming properties of the particles. The compressibility and the lift-off area of the monolayer films of hydrophobic particles on water were higher than for the films of hydrophilic particles.

Keywords Adsorption · Surface modification · Silica nanoparticles · Adsorption in liquid mixtures

Introduction

The surface properties of porous hydrophilic silica particles can be studied by a variety of adsorption techniques [1, 2, 3, 4, 5, 6, 7, 8]. Several kinds of gas and liquid sorption isotherm analyses are employed for the determination of specific surface area, but usually do not yield identical results. The reason is that in gas adsorption experiments silica particles are aggregated and the measurable (accessible) surface is therefore smaller than the value calculated from the adsorption isotherm in the liquid phase [9, 10, 11, 12, 13]. In addition, Szekeres et al. established [9] that small polar molecules such as methanol and ethanol are preferentially adsorbed in the pores of Stöber silicas.

Hydrophobization affects both gas sorption and liquid sorption. In the former case the silica particles are aggregated by the hydrophobizing alkyl chains. Thus, the surface area calculated from the N_2 adsorption isotherms by the Brunauer, Emmett, and Teller (BET) method is less than the real surface area. In liquid sorption experiments hydrophobization of the silica surface changes the selectivity of adsorption towards the apolar component of the liquid mixture. Thus, Dékány et al. reported [10, 11, 12, 13] that the specific surface area of clay minerals determined by liquid sorption is one order of magnitude higher than that determined by N_2 adsorption experiments. In the case of the hydrophobic non-swelling kaolinite and swelling clay minerals, the surface area obtained from liquid sorption experiments is 2–2.5 and 10 times higher than that determined by N_2 adsorption on the original (hydrophilic) clay minerals. The tendency of the particles to disaggregate in a given binary liquid mixture is the main factor. If wetting of the hydrophobized surface with the apolar organic component is significantly better, a larger heat of immersion is liberated than in poorly wetting liquids. This points to disaggregation and an increase in specific surface area [4].

In view of the above discussion, determination of surface hydrophobization at the liquid-gas interface appears to be an important task, considering that the actual conditions of wetting determine whether the given spherical, partially hydrophobized silica particles will float on the interface [14, 15, 16, 17]. If they are delivered to the surface in a readily wetting liquid or liquid mixture, a stable organosol may be formed, which means that under these conditions it is not possible to produce a two-dimensional film on the surface of the polar liquid.

Our experiments were therefore carried out using hydrophilic and hydrophobized Stöber silica particles. The surface properties of the particles were investigated by nitrogen and liquid sorption methods. The film forming property was studied by measuring the surface pressure vs. area isotherms.

Materials and methods

Solid-liquid interfacial adsorption in binary liquid mixtures Based on the relationships postulated by Gibbs' model of S/L interfaces, the *reduced* excess amount normalized to unit mass of adsorbent ($n_1^{\sigma(n)}$) is given by

$$n_1^{\sigma(n)} = n^0\left(x_1^0 - x_1\right)/m = n^0 \Delta x_1/m \qquad (1)$$

The Ostwald-de Izaguirre equation derived from the material balance of the components relates $n_1^{\sigma(n)}$ and the material content of the adsorption layer [10, 11, 12, 13]:

$$n_1^{\sigma(n)} = n_1^s x_2 + n_2^s x_1 = n_1^s - n^s x_1 = n^s\left(x_1^s - x_1\right) \qquad (2)$$

where n^0 is the total material amount of the liquid, x_1^0 and x_1 are the initial and equilibrium molar fractions of component 1 in the liquid phase, m is the mass of the adsorbent, $n^s = n_1^s + n_2^s$, the material content of the adsorption layer and $x_1^s = \left(1 - x_2^s\right) = n_1^s/n^s$, the equilibrium molar fraction of component 1 in the adsorption layer. The material amount of the adsorption layer $n^s = n_1^s + n_2^s$ is calculated by the so-called Schay-Nagy graphical extrapolation method using the linear part of the excess isotherm [7, 18]. If component 1 is preferentially adsorbed compared to component 2, the excess $n_1^{\sigma(n)}$ approximately equals the material amount n_1^s [7, 12, 18]. The adsorption capacity of pure component 1 is

$$n_{1,0}^s \ = \ n_1^s \ + \ r n_2^s, \qquad (3)$$

where $r = V_{m,2}/V_{m,1} = n_{1,0}^s/n_{2,0}^s$ (i.e. the ratio of the molar volumes or the adsorption capacities of the pure components 1 and 2) and $n_{2,0}^s = n_2^s + n_1^s/r$.

The specific surface area (a^s) of the adsorbent can be calculated by $a^s = n^s_{i,0}\ a_{m,i}$ where $a_{m,i}$ is the cross sectional area of the i-th component on the surface and $n_{i,0}{}^s$ is given by Eq. 3

It is impossible in the case of U-shaped excess isotherms to use the graphical extrapolation method. Instead we used the so-called *relative* surface excess representation $n_2{}^{\sigma(n)}/x_1 = f(x_2)$. The section of the isotherm at $x_2 \to 1$ shows then the $n^s{}_{2,0}$ adsorption capacity [7, 10].

Preparation of Stöber silica particles Nearly monodisperse silica particles were prepared by the method of Stöber, Fink and Bohn [19]. Ammonia (25% NH_3 solution, Riedel-de Haëhn) and water (Millipore water, resistivity of 18.2 MΩ cm, MilliQ water purification system) was dissolved in ethanol (analytical grade, Reanal, Hungary). Tetraethyl orthosilicate (TEOS) (BDH Merck) was added to the solution in one step and the mixture was stirred for 24 h. The molar concentrations of ammonia, water and TEOS were 2.0, 6.0 and 0.17 M, respectively. The silica dispersion was centrifuged at 3,000 rpm for 30 min and washed with water six times. The particles were dried at 120 °C overnight. The organophilic silica particles were prepared by adding 0.38 mM N-trimethoxysilyl propyl-N,N,N-trimethylammonium chloride (TMSP) (Gelest, 50% methanolic solution) to the suspension of freshly prepared silica in ethanol and stirring overnight. The particles were washed with water six times. The modified silica was dried at 60 °C.

N_2 adsorption experiments N_2 adsorption isotherms were determined at 77 K in a Micromeritics Gemini 2375 automated sorptometer. Prior to the measurement the samples were dried at 140 °C for 24 h in vacuo (0.133 Pa). The specific surface area was calculated from the adsorption branch of the isotherms in the p/p_0 range 0.05–0.35 with the BET method.

Determination of adsorption isotherms in binary liquid mixtures Ethanol (1)-cyclohexane (2) and ethanol (1)-chloroform (2) mixtures were prepared of analytical grade solvents (Reanal, Hungary). Equilibrium composition was determined in a Zeiss differential interferometer at 25 ± 0.1 °C, using a calibration curve. The adsorption excess isotherms of the liquid mixtures were determined at 25 °C on dried Stöber silica. The adsorption excess was calculated by the equation $n_1{}^{\sigma(n)} = n^o\ \Delta x_1/m$, where n^o is the total molar amount of the liquids, Δx_1 is the change in the molar fraction of component 1 due to adsorption and m is the mass of adsorbent. The adsorption capacity of pure components 1 and 2 was used to calculate the specific surface area (Schay-Nagy extrapolation method [7, 10, 18]).

Light scattering experiment for particle size and zeta potential determination The particle size distribution was measured by dynamic light scattering using a Zetasizer 4 (Malvern, UK) instrument. The mean particle diameter was 550 ± 10 nm. The same instrument was used for the electrophoretic mobility determination of TMSP-modified silica during addition of sodium dodecylsulfate (SDS) (Sigma) to the aqueous suspension in 0.01 M KCl background electrolyte.

Surface pressure-area isotherms and film deposition Compression isotherms of the silica films at the air/water interface were measured in a Langmuir trough (Nima 611, Nima Technologies, Coventry, England) at 25 ± 0.5 °C. The films were compressed at 20 cm^2/min barrier speed. Films were deposited on glass substrates at surface pressures below the collapse pressure, 4 mN/m for hydrophilic and 10 mN/m for hydrophobic particle films. The deposition of the silica films and their subsequent investigation are described in detail in [20].

Electron microscopic imaging The size distribution of the silica particles was checked using transmission electron microscopy (TEM) (OPTON 920, Carl Zeiss, Jena, Germany). The deposited particle films were examined by scanning electron microscopy (SEM) (Philips SEM 515).

Results and discussion

The Stöber particles were uniform spherical particles with a diameter of 500 nm with a standard deviation of

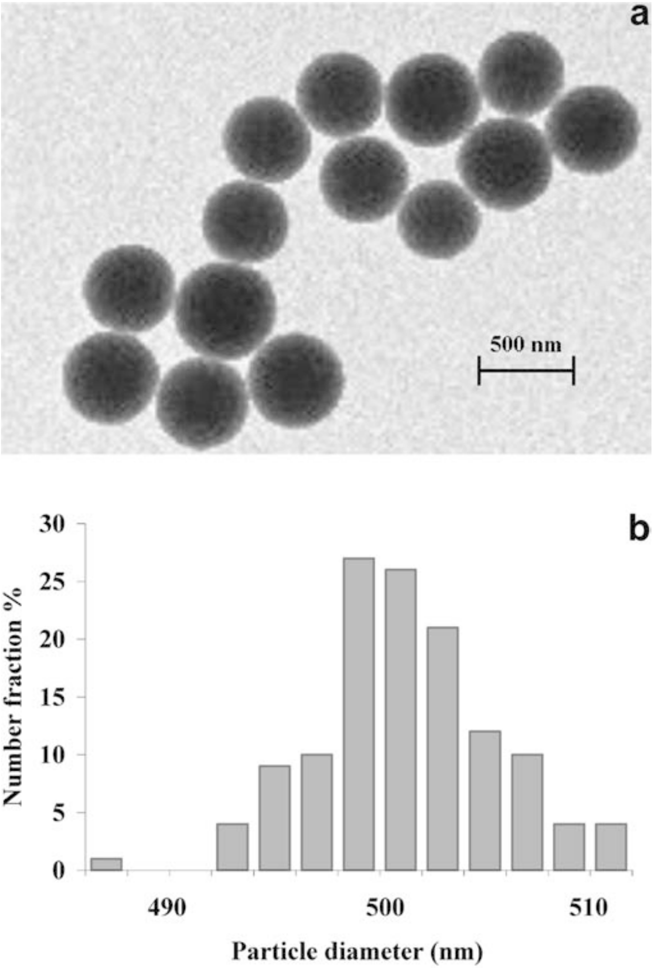

Fig. 1a Transmission electron microscopy (TEM) picture of spherical Stöber silica particles. **b** Particle size distribution of the silica particles based on TEM pictures

7% (Fig. 1a, b). The nitrogen adsorption isotherms (Fig. 2) are type-II isotherms. There is a slight hysteresis between adsorption and desorption branches of the isotherm of hydrophilic silica, which is absent for TMSP-modified silica. This is indicative of some mesoporosity in the hydrophilic silica. The specific surface

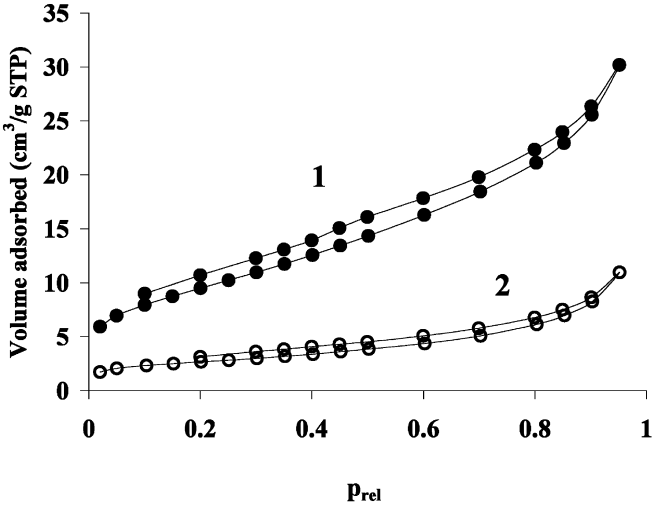

Fig. 2 Adsorption and desorption isotherms of N_2 at 77 K on hydrophilic (*1*) and hydrophobized (*2*) Stöber silica

areas are 28 m^2/g and 9 m^2/g for silica and TMSP-modified silica (Table 1). The calculated specific surface area of spherical particles with $d = 500$ nm diameter is 6.67 m^2/g assuming a density of 1.8 g/cm^3. The experimental surface area of TMSP-modified silica is close to the theoretical lower value of 6.67 m^2/g. This is an indication for a smooth surface and absence of porosity. In the case of hydrophilic silica the 28 m^2/g indicates a rough surface and/or some porosity accessible to N_2.

Liquid sorption measurements on hydrophilic silica particles dispersed in ethanol-cyclohexane mixtures are shown in Fig. 3. The isotherm is of type II according to the Schay-Nagy classification thus, ethanol is preferentially adsorbed on the surface and in the pores of the hydrophilic silica. The adsorption capacity for ethanol was $n_{1,0}^s = 1.1$ mmol/g ($n_1^s = 1.1$, $n_2^s = 0$) and the equivalent surface area $a^s_{eq} = 132\ m^2/g$ (Table 1). After hydrophobization, the excess isotherm in the ethanol-cyclohexane mixture is an S-shaped type IV isotherm (Fig. 4). The adsorption capacity determined by the Schay-Nagy extrapolation method is more than twice as high as the value measured on the hydrophilic surface. Linear extrapolation leads to $n_1^s = 1.15$ and

Table 1 Specific surface area determination from N_2gas adsorption and liquid mixture adsorption experiments on hydrophilic and hydorphobized Stöber silica

Stöber silica	d_{TEM} nm	a^s_{geom}[a] m^2/g	a^s_{BET} m^2/g	a^s_{eq} m^2/g	$n_{1,0}^s$ mmol/g	a^s_{eq} m^2/g	$n_{2,0}^s$ mmol/g
			From gas adsorption	From ethanol/cyclohexane		From ethanol/chloroform	
Hydrophilic	500 ± 20	6.7	28	132	1.10	-	-
Hydrophobized	500 ± 20	6.7	9	358	2.59	405	2.68

[a]The geometric surface area was calculated with particle density of 1.8 cm^3/g [20].

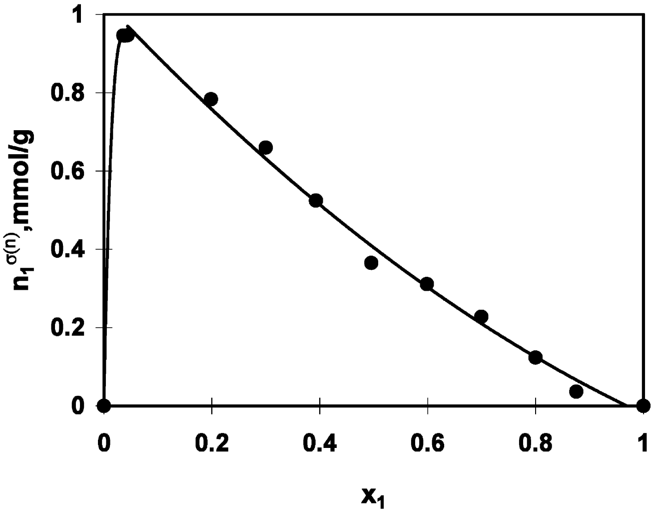

Fig. 3 Reduced adsorption excess isotherm on hydrophilic Stöber silica in ethanol (1)-cyclohexane (2)

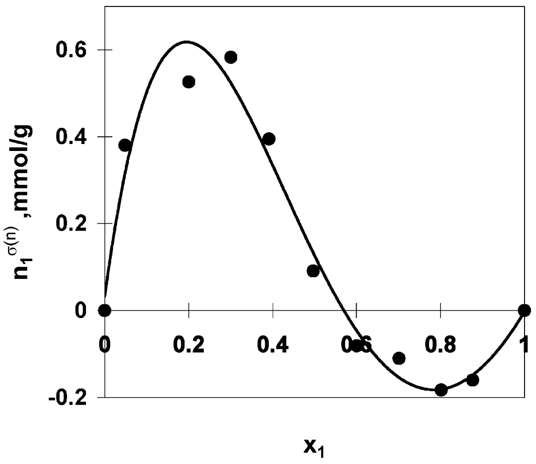

Fig. 4 Reduced adsorption excess isotherm on hydrophobized Stöber silica in ethanol (1)-cyclohexane (2)

$n_2^s = 1.05$ mmol/g for ethanol and cyclohexane respectively, and the adsorption capacity of ethanol is $n_{1,0}^s = 2.59$ mmol/g (Table 1). This result shows that the area of the polar surface of the hydrophobized silica, available for ethanol adsorption, is equal to that of the hydrophilic silica (n_1^s is equal to 1.1 and 1.15 for the hydrophilic and hydrophobized silica respectively). Thus, cyclohexane adsorbs only on the alkyl chains of the hydrophobizing agent. The data also suggest that ethanol does not adsorb at the hydrophobic domain of the silica surface. The equivalent areas of the hydrophilic and hydrophobic domains are 138 and 220 m^2/g, respectively. The equivalent specific surface area of the hydrophobized silica is 358 m^2/g, the sum of the areas of the two domains.

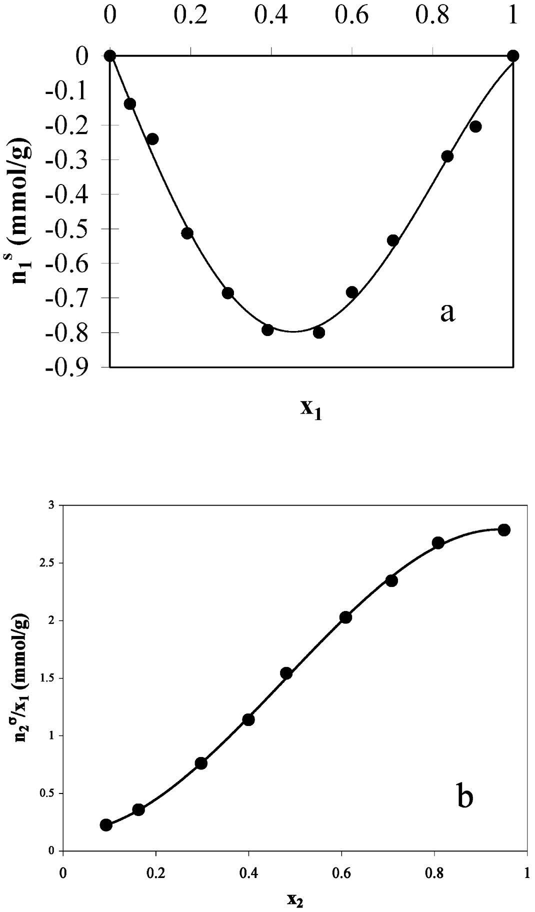

Fig. 5 **a** Reduced adsorption excess isotherm on hydrophobized Stöber silica in ethanol (1)-chloroform (2). **b** Relative adsorption excess isotherm on hydrophobized Stöber silica in ethanol (1)-chloroform (2)

Ethanol-chloroform mixtures are very suitable for the preparation of two-dimensional particle monolayer films on water surface [17, 20]. Therefore, the adsorption of ethanol (1)-chloroform (2) mixtures was examined on the hydrophobic Stöber silica (Fig. 5a, Table 1). In this case the excess isotherm is U-shaped and the adsorption capacity cannot be calculated by the linear extrapolation method. Instead, the relative excess isotherm, $n_2^{\sigma(n)}/x_1 = f(x_1)$ was used to calculate the specific surface area from the plateau of this representation [7,10,18] (Fig. 5b). We obtained $n_{2,0}^s = 2.68$ mmol/g for chloroform, and $a^s_{eq} = 402$ m^2/g.

A comparison of the specific surface areas obtained from gas and liquid adsorption (Table 1) clearly shows that a large fraction of the surface area, present in the pore system of Stöber silica, is not accessible for N_2. TMSP modification decreases the BET surface area, clogging the pore system, but increases the equivalent surface area from liquid adsorption due to additional adsorption sites for chloroform in the hydrophobic parts

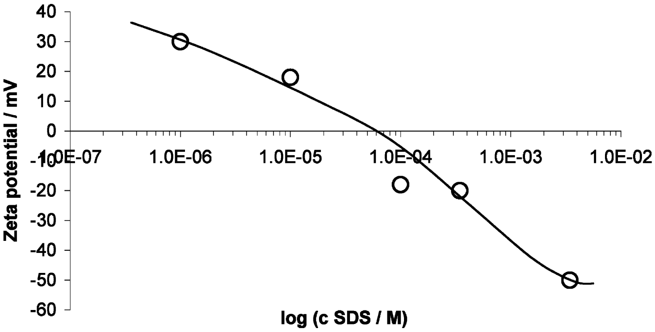

Fig. 6 Changes in the zeta potential of the TMSP-modified Stöber silica by addition of sodium dodecyl sulfate (*SDS*) in aqueous dispersion

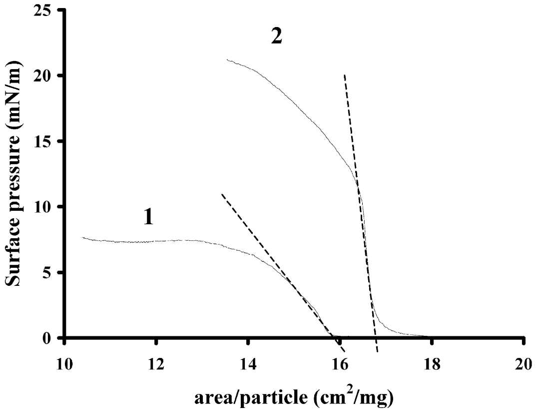

Fig. 7 Pressure-area diagrams of hydrophilic Stöber silica (*1*) and TMSP-modified Stöber silica (*2*) films on the water surface

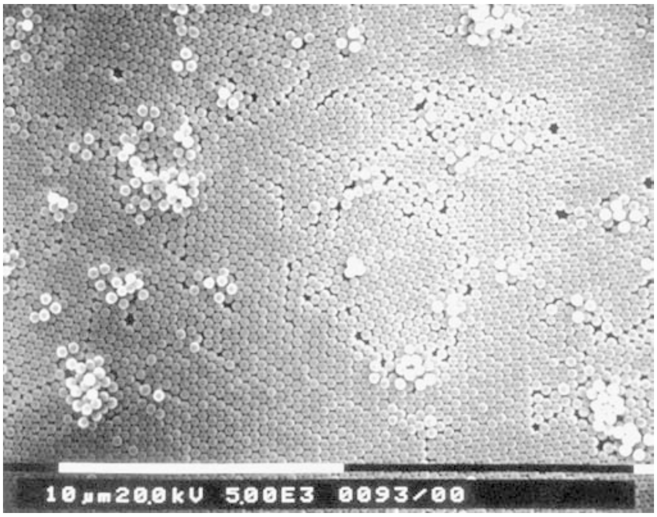

Fig. 8 Scanning electron microscopy picture of a Stöber silica particle monolayer

of the silica particles. It should be noted that chloroform is preferentially adsorbed from the mixture with ethanol on the hydrophobized surface. Little ethanol is present in the adsorption layer of hydrophobic particles (Fig. 5a). The preferential adsorption of the apolar component (chloroform) in the binary mixture ensures that particles with modified surfaces do not submerge into the water subphase during film formation in a Langmuir-Blodgett trough. Naturally, the binary mixture will evaporate during spreading and the two-dimensional film will finally assemble on the surface of water, with the particles floating on the surface.

The surface charge of the silica particles covered with TMSP is positive due to quaternary ammonium end groups. The interparticle electrostatic interactions also play a role in the stabilization of the particle monolayer arrangement on the liquid-air interface. The change in the zeta-potential during addition of SDS to the TMSP-modified silica suspension is shown in Fig. 6. Charge reversal occurs with the isoelectric point at 5×10^{-5} mol/dm^3 SDS concentration.

Particle monolayer films on the water surface were prepared from both hydrophilic and hydrophobic silica particles [19, 20]. The hydrophobic silica particle films collapsed at considerably higher surface pressures than the films of hydrophilic particles (Fig. 7). This suggests that the stability of the two dimensional monolayer against collapse increases due to the electrostatic and steric repulsion between the particles in the presence of the hydrophobizing TMSP layer. The calculated surface areas per particle in the compressed films are 1.99×10^5 nm^2 for hydrophilic and 1.88×10^5 nm^2 for the hydrophobized silica. The structure of the particle monolayers can be visualized by SEM pictures (Fig. 8). Crystalline domains of hexagonally close-packed silica spheres are separated by small disordered aggregates that are randomly distributed.

To conclude, nearly monodisperse hydrophilic silica particles were modified with N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride to render the surface hydrophobic. The adsorption capacity increases considerably after surface modification and ethanol penetrates into the micropores of the silica particles. These micropores are not accessible for N_2 molecules at 77 K. Adsorption isotherms from chloroform/ethanol mixtures were determined on the hydrophobized silica, because this liquid mixture is suitable as spreading solvent in preparation of Langmuir monolayers of the particles on water surface. Chloroform adsorbs preferentially and a colloidally stable particle dispersion forms in chloroform/ethanol. Spreading of the particles on the water surface from the stable dispersions promotes particle ordering and reduces random particle aggregation.

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