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ORIGINAL CONTRIBUTION

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Surface modification of colloidal silica particles

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Abstract Colloidal silica particles in organic solvents were grafted, using several reagents, in order to make them hydrophobic. The hydrophobicity of the beads could be easily varied. Quasielastic light scattering and transmission electron microscopy experiments showed that no aggregation occurs during the reaction when monofunctional agents are used. Elemental analysis and solid-state NMR measurements gave us the rate of surface modification of the silanol groups. We also studied the rheological behaviour of the grafted particles as a function of the volume fraction in solvents of various hydrophobicity. Hexamethyldisilazane-grafted particles display hard-sphere behaviour in polar solvents such as 2-propanol, but not in alkanes, whereas dimethyldodecylchlorosilane-grafted particles flocculated in polar solvents but could easily be dispersed in apolar solvents.

Key words Hydrophobic particles · Colloidal silica · Rheological behaviour · ^{29}Si solid-state nuclear magnetic resonance

Introduction

Hydrophobised silica surfaces have found applications in many different fields, for instance, hydrophobic silica powders can be used in industry (e.g. as nonblack reinforcing rubber filler, as thickener for oil to make lubricating grease, as reinforcing filler for silicone rubber [1]), silylated gels are commonly used in the field of analytical chemistry (high-performance liquid chromatography, size-exclusion chromatography, gas chromatography), synthetic chemistry (phase-transfer catalyst), and biochemistry (enzyme immobilisation). A lot of work has been done on silica gels and wafers [1, 2], but it is more difficult to find reports of the modification of colloidal silica particles [3]. On the other hand, the stabilisation of hydrophobic particles in water is a very important problem in the fields of inks, paints, etc. We were of the opinion that hydrophobic colloidal particles with well-defined size and shape and with a nearly narrow size distribution could be a powerful tool to better understand the mechanisms of the stabilisation of hydrophobic particles in water with amphiphilic polymers. Silica was chosen because it is possible to get quite monodisperse spherical particles with sizes covering a large range [4] and because the surface modification of this substrate has been investigated intensively. The surface of silica can be hydrophobised by adsorption of organic cations or polycations, by esterification of the surface silanol groups [3, 5], by attaching a living polymer at the surface [6], by growing chains from initiating groups at the surface [7], and by reaction of the surface silanol groups with organosilicon to produce a surface of $\mathrm{Si}\text{–}O\text{–}\mathrm{Si}R_3$ or $(\mathrm{SiO})_2\mathrm{Si}R_2$ groups. Since we wish to study the stabilisation of hydrophobic particles in water, we have to prevent possible hydrolysis of the grafted group and thus the esterification of the surface silanol groups cannot be adopted here because $\mathrm{Si}\text{–}O\text{–}\mathrm{C}$ bonds are easier to break than –Si–C bonds. Here we report the modification of silica particles by substituents of various hydrophobicities, such as hexamethyldisilazane, $(\mathrm{CH_3})_3\mathrm{Si–NH–Si(CH_3)_3}$, (HMDS) dimethyldodecylchlorosilane, $\mathrm{C_{12}H_{25}Si(CH_3)_2Cl}$, (DMDS), and octadecyltrichlorosilane, $C_{18}H_{37}SiCl_3$, (OTS). In the first part of the results, we study the ratio of silanol groups grafted by elemental analysis and NMR, in the second part we check that the size of particles was not changed by transmission electron microscopy (TEM) and quasi-elastic light scattering (QELS), and in the third part we study the rheological behaviour of their concentrated suspensions in solvents of different polarities, which is characteristic of their level of aggregation in these media.

Experimental

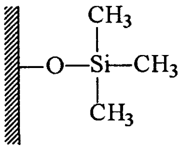
Material

Silica particles dispersed in *N*,*N*-dimethylacetamide (DMAC) were obtained from Nissan Chemical, Japan. According to the supplier, the diameter of the particles is 70–100 nm for the DMAC–ST–ZL silica and 10–20 nm for the DMAC–ST silica. A more detailed characterisation of these particles is presented later. The commercial suspensions and the solvents, i.e. DMAC, heptane, and toluene purchased from Fluka, were dried over molecular sieves (3 Å) before use, the reagents, HMDS, DMDS, and OTS, purchased from Fluka, were used without any further purification.

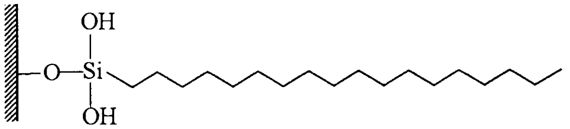
Grafting process

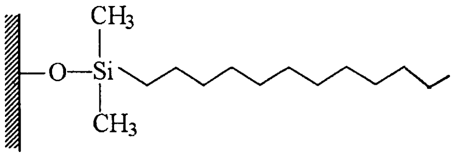
Silica beads were grafted with the reagents HMDS, DMDS, and OTS.

In the case of HMDS grafted on the larger particles (DMAC-ST-ZL), 100 ml silica suspension in DMAC (silica concentration about 10 wt%) was mixed with 10 ml HMDS and mechanically stirred with a magnetic barfor 18 h. The suspension was then centrifuged for 1 h (3,500 *g*), rinsed with DMAC to remove the excess HMDS, centrifuged again and rinsed in tetrahydrofuran then water, and centrifuged (10 min, 550 *g*). The latter procedure was performed twice. The silica was then dried under vacuum and the powder was used without any further purification, and the corresponding particles are referred to in what follows as DMAC–HMDS. When DMAC–ST silica was grafted with HMDS (to give DMAC–ST–HMDS), the process was the same, but the suspension was more dilute (about 2 wt%) and was centrifuged for 5 h at 20,000 *g*. In both cases, this leads to the following groups grafted on the surface:



The procedures followed with OTS and DMDS were quite similar, except that the solvents (DMAC, heptane, and toluene) had to be dried over molecular sieves before use. Only the DMAC–ST–ZL particles were grafted with those reagents (DMAC–OTS and DMAC–DMDS) and the groups grafted on the silica surface were





In a first approach, the ability of the three different types of grafted silica beads to be dispersed in various solvents was checked visually and the results are listed in Table 1.

Finally, from the macroscopic point of view, the hydrophobicity of the particles obtained appears different: DMAC–HMDS particles are stable in polar solvents (DMAC, alcohols), whereas DMAC–DMDS particles flocculate in these solvents and both of these particles look stable in apolar solvents, as confirmed by QELS.

An attempt was also made to prepare silica with mixed grafted chains: the silica was first grafted with DMDS and then with HMDS and is referred to as DMAC–DMDS + HMDS.

Methods

Transmission electron microscopy

TEM experiments were performed with a Jeol side-entry 100 CX II (observation at 100 kV). The samples were prepared as follows: silica particles were first dispersed in water (for nongrafted silica), alcohol (DMAC–HMDS), or dodecane (DMAC–DMDS and DMAC–DMDS), depending on their hydrophobicity, then the suspensions were dropped on a Cu grid coated with a carbon membrane.

QELS measurements

The hydrodynamic radii, R_H, of the unmodified (in water) and the hydrophobically modified silica particles (in an organic solvent: toluene, dodecane, or ethanol) were obtained from photon correlation spectroscopy (using a Malvern PCS 100 goniometer connected to a Malvern K 7025 correlator). The light source was a Spectra Physics laser ($\lambda = 514.5$ nm) and the scattering angles were varied between 150 and 30°. The apparent R_H was calculated after deriving an apparent diffusion coefficient, *D*, from the time constant of the autocorrelation function, using the Stokes–Einstein equation:

$$D = \frac{kT}{6\pi\eta_0 R_H} , \tag{1}$$

where *k* is the Boltzmann constant, *T* the absolute temperature and η_0 the viscosity of the medium. We used the cumulants analysis method, which gives good results when the particles are not too far

Table 1 Stability of three types of silica in different solvents (from visual test). + indicates that the particles are stable, − indicates that they flocculate. The grafting agents were hexamethyldisilazane (*HMDS*), dimethyldodecylchlorosilane (*DMDS*), and octadecyltrichlorosilane (*OTS*)

Grafting agent	Water	*N*,*N*-Dimethyl acetamide	Ethanol	Heptane	Toluene	Dodecane
HMDS	−	+	+	+	+	+
DMDS	−	−	−	+	+	+
OTS	−	−	−	+	+	+

from monodisperse. When the particles are monodisperse, the scattered intensity and correlation time are independent of the scattering angle, whereas they become strongly dependent for polydisperse samples owing to the higher contribution of large objects to the scattering at lower angles. Thus, apparent values of R_H at different scattering angles can give us an idea of the polydispersity of the particles.

^1H-^{29}Si solid-state NMR

Solid-state NMR is commonly used to characterise grafted silica powders and gels [8, 9, 10]. ^1H-^{29}Si cross-polarisation magic-angle-spinning (MAS) NMR experiments were performed on a Bruker ASX 300 spectrometer. The powder sample was rotated at the magic angle of 54°44′, the MAS frequency was 3500 Hz, the 90° pulse length was 6 μs, and the spectra were typically recorded using a repetition time of 3 s and a contact time of 4 ms.

Rheological measurements

The rheological behaviour of the suspensions was investigated with a Carrimed controlled-stress rheometer (CSR 100) with cone-plate devices and with a low-shear 30 rheometer (Contraves) equipped with a Couette cylinder for the lowest viscosities. The diameter of the cone-plate device used (2, 4 or 6 cm) depended on the range of stress applied to the sample. All the measurements were performed at 25 ± 0.1 °C. The suspensions were prepared as follows: variable amounts of silica powder were mixed with variable amounts of solvent and each suspension was magnetically stirred 2 h before the measurements, in such a way that the results were reproducible.

Results and discussion

Chemical grafting

Elemental analysis

The results are given in Table 2. The elemental analysis allowed us to calculate the number of silanols grafted per square namometre. When HMDS is used, we estimated this number to be 3.5 –OH/nm^2 for the bigger particles and 2.9 for the smaller. This difference between the two types of particles may be due to the determination of the surface area: we derived it from the radius of the particles, and it was very difficult to determine it for the smaller ones because of the polydispersity of the sample. Porosimetry measurements could not be performed; however, we can use the "geometrical" surface of the particles to qualitatively compare the different types of grafting agents.

When DMDS is used, the number of silanols groups grafted per square nanometre is much larger and can be estimated to be roughly 6, which is considerable. At this level, traces of organic solvent could explain these high values. In order to confirm these results, we performed NMR measurements.

When OTS is used, we cannot evaluate the number of silanol groups grafted per square nanometre because of the aggregation of the particles. Values of 2.5 are theoretically expected and are obtained for C_{18} alkyl chains grafted to chromatography silica powder [11]; however, Duvault et al. [12] found values of 2.9 ± 0.1 for silica wafers.

^1H-^{29}Si solid-state NMR

^{29}Si solid-state NMR is currently used to characterise silica gels and powders which are grafted or not [8–10, 13–15]. Three types of silanol groups are usually listed: Q^4 groups (silicon atoms linked to four oxygen atoms), Q^3 groups (silicon atoms linked to three oxygen atoms and one −OH group), and Q^2 groups (silicon atoms linked to two oxygen atoms and two −OH groups). A NMR spectrum of the DMAC–ST–ZL silica is shown in Fig. 1a. The peaks at −91, −101, and −110 ppm are attributed to Q^2, Q^3, and Q^4 groups, respectively, as has already been observed [9, 14, 16, 17]. In the case of DMAC–HMDS and DMAC–DMDS silica, the intensity of the peaks corresponding to Q^2 and Q^3 groups decreased, whereas new peaks (−12, −13 ppm) attributed to $–O–Si(CH_3)_3$ and $–O–Si(CH_3)_2C_{12}H_{25}$ groups [9, 17] appear (Fig. 1b). The ^1H and ^{29}Si results obtained with the different types of silica [18] are consistent with elemental analysis: the number of silanol groups grafted increases when the diameter of the particles decreases (as the specific area of the silica increases), and the more the silica is grafted, the more important the alkyl peaks are. The peaks and relative intensities corresponding to different groups are listed in Table 3. In this table, we arbitrarily normalised Q^4, since this group cannot react (there is no −OH group capable of reacting). For the calculation of the approximate percentage of grafted Q^3, we divided the number of alkylated Si by the number of Q^3 before the reaction. However, Q^2 groups also can react, giving birth to a new Q^3 group and one alkyl peak. We did not take this reaction into account; therefore, the percentage of grafted groups is semiquantitative.

Table 2 Elemental analysis of the products synthesised

Product	DMAC–HMDS	DMAC–OTS	DMAC–DMDS	DMAC–DMDS[a]	DMAC–DMDS + HMDS
%C	0.55	1.90	3.22	0.64	2.68
%H	0.44	0.63	0.91	0.45	0.81

[a] This corresponds to the first step of the synthesis of DMAC–DMDS + HMDS: the amount of DMDS introduced is smaller than for DMAC–DMDS

These spectra enable us to confirm that DMAC–HMDS silica is roughly 1.5 times less grafted that DMAC–DMDS.

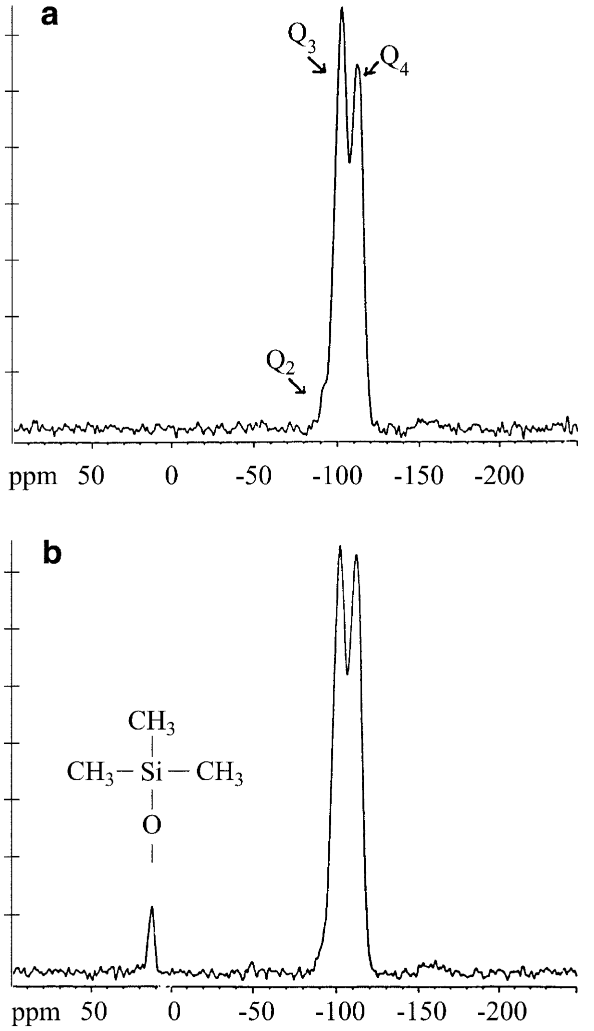


Fig. 1 ^{29}Si solid-state NMR spectrum of **a** *N,N*-dimethylacetamide (*DMAC*)–ST–ZL silica particles and **b** DMAC–ST–hexamethyldisilazane (*HMDS*) silica particles. The peaks are attributed on the spectra

Size

Transmission electron microscopy

TEM experiments on DMAC–ST–ZL silica allowed us to determine the histogram of the population of the particles (Fig. 2) and a mean radius of 50 nm. The grafting process was not found to aggregate the silica modified with HMDS and DMDS (Fig. 3a, b), which was not the case when the silica was grafted with OTS. Pictures taken by TEM (Fig. 3c) show that the silica particles are embedded in a matrix of polymerised OTS. This can be easily explained if we consider the mechanisms proposed for this grafting by Sagiv [19] and more recently by Silberzan et al. [20] and Flinn et al. [21]. They assume that the layer of OTS molecules is not linked to the surface by all the individual molecules but rather forms a net where molecules are linked to each other; and this net would be bonded to the surface by only a few bonds. The first step would be the strong and quick adsorption of a water film, which would be followed by the silane physisorption on this film. Then, the chemical reaction itself would take place on it,

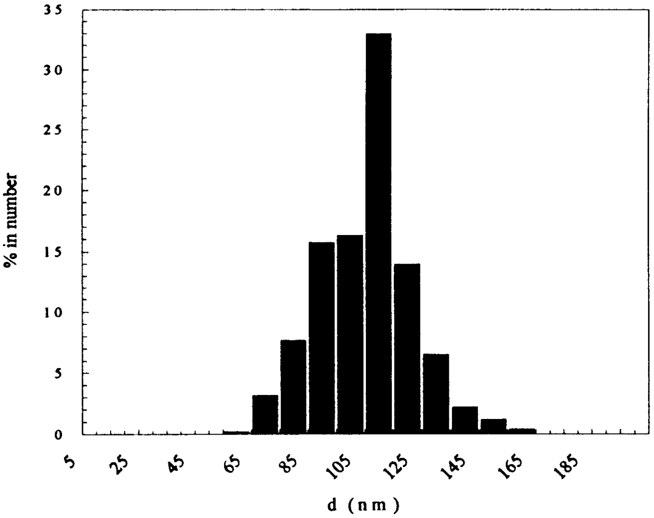


Fig. 2 Histogram of the population of DMAC–ST–ZL particles

Table 3 ^{29}Si relative area of NMR peaks for different silica particles. The approximate percentage of grafted Q^3 groups is calculated from the ratio alkyl peak/Q^3 before reaction

Silica peak	Q^3	Q^4	Alkyl peak	Approximate percentage of grafted Q^3 groups
DMAC–ST–ZL	115	100		
DMAC–HMDS	84	100	29	25%
DMAC–ST–HMDS	57	100	80	
DMAC–DMDS (default of DMDS)	106	100	9	8%
DMAC–DMDS (excess of DMDS)	70	100	39	34%
DMAC–DMDS + HMDS	60	100	49	43%

linking the silanes together and anchoring the net on the water film. Here we can imagine that the net is anchored to several particles, sticking them together. In the case of HMDS and DMDS, the formation of such a net does not occur since these molecules are monofunctional, and the bridging of two or more particles is thus impossible.

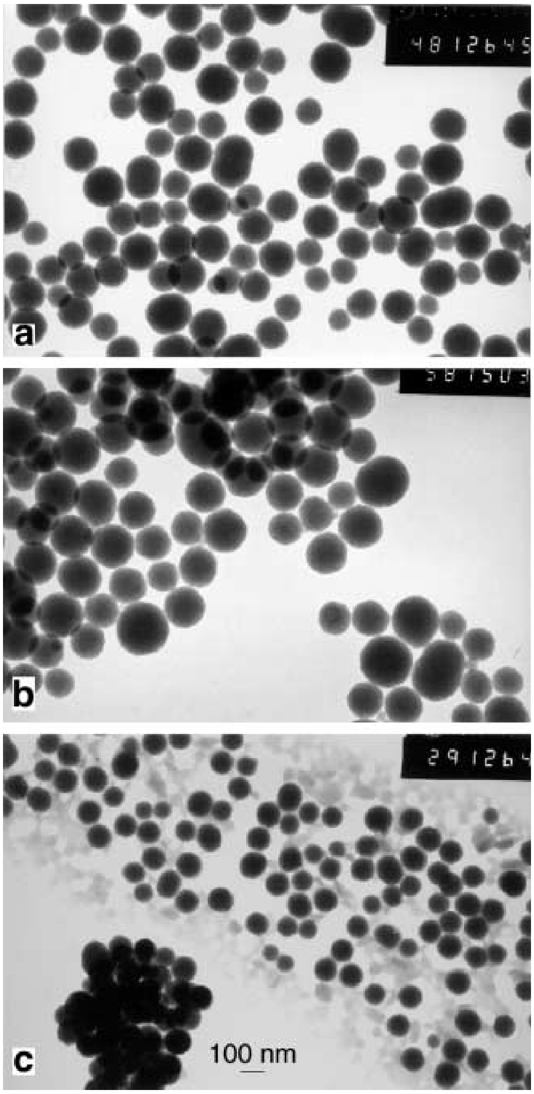


Fig. 3 Transmission electron microscopy pictures of **a** DMAC–HMDS silica particles, **b** DMAC–dimethyldodecylchlorosilane (*DMDS*) silica particles, and **c** DMAC–octadecyltrichlorosilane (*OTS*) silica particles

Quasielastic light scattering

The bare silica particles, DMAC–ST–ZL, (measurements performed in water) have a hydrodynamic radius of 61 ± 1 nm, independent of the scattering angle. This confirms that the size of the particles is rather well defined, as shown before by TEM experiments. The silica particles grafted by HMDS give similar results in alcohol ($R_{\mathrm{H}} = 63 \pm 2$ nm), which shows that the grafting process does not affect much the size of the particles and does not aggregate them, which is perfectly consistent with the TEM results. On the other hand (Table 1), when the dispersion medium is dodecane, HMDS-grafted particles are highly aggregated, probably because the particles are not hydrophobic enough owing to low and/or short grafting. Conversely, when the silylating agent is DMDS, we observe strong aggregation in alcohols (Table 1), but also a dependence of the apparent hydrodynamic radius on scattering angles (70 nm at 90° against 100 nm at 30°, Table 4), which is seen as a slight aggregation on a microscopic scale. In fact, a more careful examination of the TEM micrographs shows that most of the particles are perfectly dispersed, but a few are aggregated.

In the same way, QELS experiments (Table 4) confirm the high level of aggregation of DMAC–OTS particles already observed by TEM, although they appear fairly dispersed in nonpolar solvents on a macroscopic scale according to the results of Table 1.

Rheological behaviour

The rheology of hard spheres has been studied for a while, from a theoretical point of view as well as from an experimental point of view. When the suspensions are diluted (volume fraction, Φ, smaller than 0.05) and Newtonian, Einstein [22] and Batchelor [23] found the expression

$$\eta = \eta_{\mathrm{F}}(1 + 2.5\Phi + k\Phi^2 + \cdots) \ , \tag{2}$$

where η_{F} is the viscosity of the solvent.

Table 4 Evolution of R_{Happ} with the angle for different types of silica

	Solvent (QELS)	$R_{\mathrm{H\ QELS\ app}}$ 90°	$R_{\mathrm{H\ QELS\ app}}$ 30°	R_{TEM}
DMAC–ST–ZL	Water	61.5 nm	62.5 nm	50 nm
DMAC–HMDS	Ethanol	62 nm	65 nm	50 nm
DMAC–DMDS	Dodecane	70 nm	102 nm	Unchanged, with a few aggregates
DMAC–OTS	Toluene	300–400 nm	$\gg$500 nm	Aggregated

When the suspensions are more concentrated, the equations are increasingly complex and therefore phenomenological laws have been developed [24, 25], for example,

$$\eta = \left(1 - \frac{\Phi}{\Phi_\mathrm{p}}\right)^{-2} . \tag{3}$$

In these equations, η_r is the relative viscosity, η/η_F, and Φ_p is the maximum packing volume fraction.

In fact, increasing the concentration can also lead to non-Newtonian behaviour when hydrodynamic forces and Brownian motion coexist. The Peclet number, $Pe = 8\pi\frac{\eta_\mathrm{F}a^3\dot{\gamma}}{kT}$, measures the ratio between the characteristic time of the rotation of the particles due to diffusion and the characteristic time due to hydrodynamics. In this expression, a is the radius of the spheres and $\dot{\gamma}$ is the shear rate. When $Pe \gg 1$, hydrodynamics effects are predominant, whereas when $Pe \ll 1$, Brownian motion predominates. Hard-spheres suspensions are shear-thinning when Φ is high and the plots $\eta = f(\dot{\gamma})$ display two Newtonian plateau (one at low-shear, η_0, and the other one at infinite shear, η_∞, with $\eta_\infty < \eta_0$). Such suspensions can be fitted by semiempirical equations [3, 26, 27], for example,

$$\eta_\mathrm{r} = \eta_{\mathrm{r}\infty} + \frac{\eta_{\mathrm{r}0} - \eta_{\mathrm{r}\infty}}{1 + \sigma_\mathrm{m}} , \tag{4}$$

where $\sigma_\mathrm{m} = \alpha\frac{\eta_\mathrm{F}\dot{\gamma}a^3}{kT}$, with α depending on the shape of the particles.

In Fig. 4 we present the rheological behaviour of DMAC–HMDS suspensions in 2-propanol when the volume fraction is varied from 0.20 to 0.55 and in Fig. 5 the curves obtained in dodecane. At such concentrations, the suspensions in the two solvents look totally different: the suspensions in alcohol tend to become opalescent at high volume fractions, whereas in dodecane they remain white and QELS measurements proved that the particles aggregate in this apolar solvent, even in dilute medium.

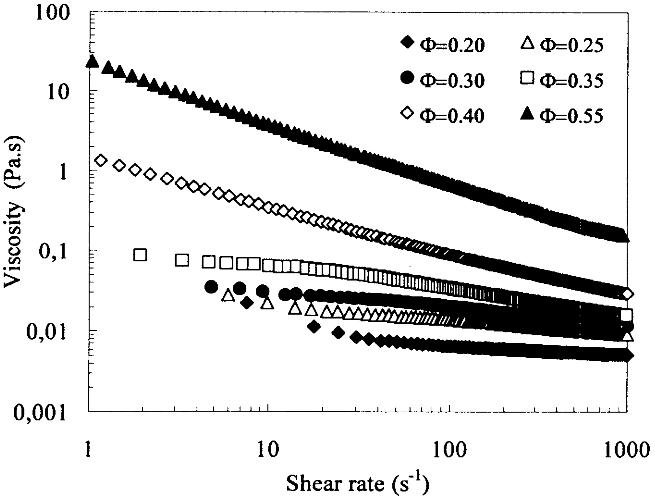


Fig. 4 Evolution of the viscosity of DMAC–HMDS suspensions in 2-propanol

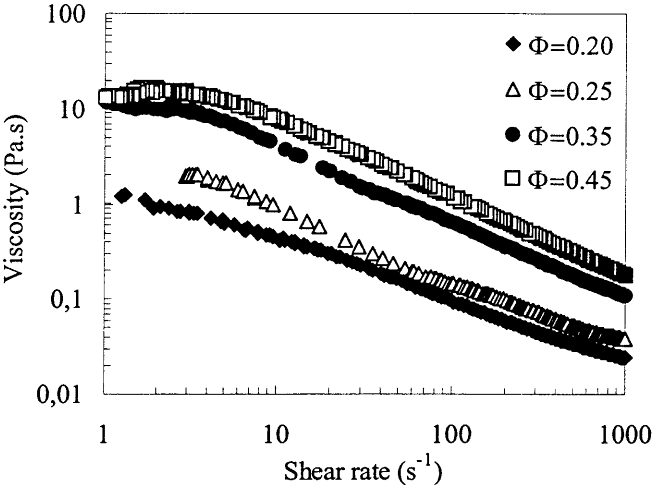


Fig. 5 Evolution of the viscosity of DMAC–HMDS suspensions in dodecane

In both cases, the viscosity increases with the volume fraction [24, 25, 28] and when $\Phi > 0.25$ the suspensions display more and more shear-thinning behaviour, as already observed [3, 27]. Note that for a given volume fraction, the relative viscosity of the suspensions in alcohol is lower than the viscosity in dodecane, and this reflects again an aggregation of the particles in dodecane.

We also tried to fit the curves with Eq. (4), by taking η_0, η_∞, and α as parameters, which is possible when the volume fraction is lower than 0.35 (Fig. 6) but not for higher fractions since there is a lack of measurements for low shear rates (η_0 is then not accessible). When the solvent used is 2-propanol, the values of $\eta_{\mathrm{r}0}$ and $\eta_{\mathrm{r}\infty}$ derived are consistent with theory and experiments [29], and α corresponds to spheres. In the case of dodecane, the values of the parameter α are too large compared to those of Ref. [29], and if we try to fit the curves with a fixed value of $\alpha = 5.70$ [29], the value commonly taken for spheres, the derived values of $\eta_{\mathrm{r}0}$ and $\eta_{\mathrm{r}\infty}$ are unrealistic. This reflects once more the aggregated state of the particles.

$(\eta/\eta_\mathrm{F})^{-0.5}$ is plotted versus Φ for different solvents (2-propanol, 1-butanol, dodecane) in Fig. 7. The viscosities were measured at a shear rate of 1,000 s^{-1}, which corresponds to η_∞ for a volume fraction up to roughly 0.4. The maximum volume fraction, Φ_p, obtained from Eq. (3) by extrapolating the plot when $\eta_\infty/\eta_\mathrm{F} = 0$, is close to 0.60 in all cases, but whereas suspensions in alcohols follow exactly the behaviour predicted by

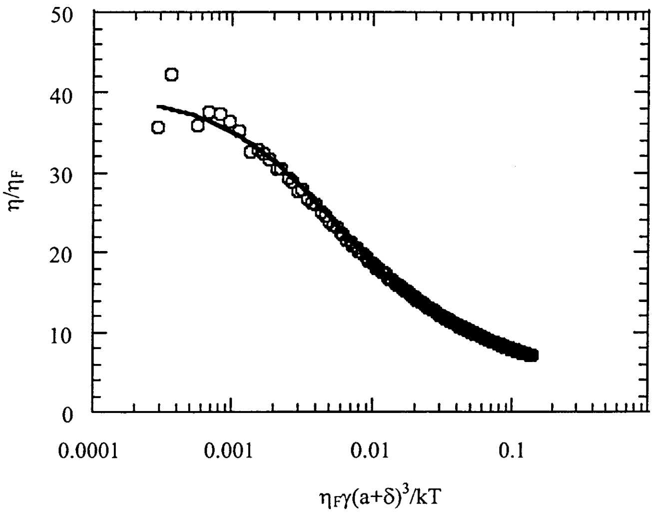


Fig. 6 Variation of the relative viscosity versus the Peclet number (DMAC–HMDS in 2-propanol, $\Phi = 0.35$). The radius of the particles, *a*, is replaced here by the effective radius ($a + \delta$), δ being the range of repulsive interactions between spheres. The *line* is the curve fit obtained with Eq. (6)

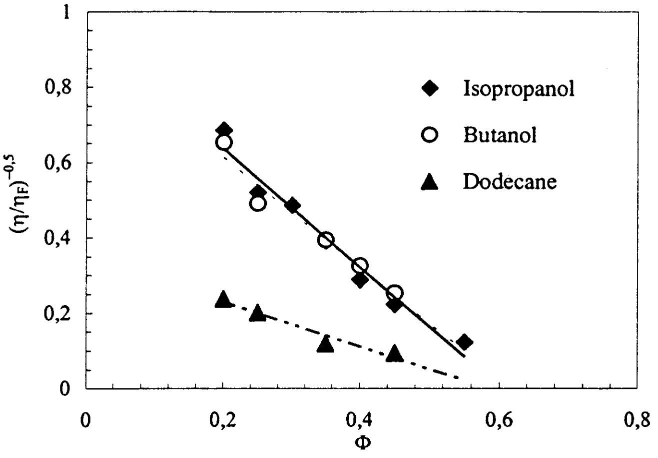


Fig. 7 Plots of $(\eta/\eta_F)^{-0.5}$ versus Φ of DMAC–HMDS suspensions in 2-propanol, butanol, and dodecane

Eq. (3), in the case of dodecane, the slope of the straight line in Fig. 7 is smaller than expected. From the examination of all the results, we can consider that DMAC–HMDS displays hard-sphere behaviour in 2-propanol and 1-butanol. In dodecane, the trapping of solvent in the aggregates leads to deviations from this behaviour.

At infinite shear rates, the maximum volume fraction is expected to be 0.71 [3]. The effective volume fraction, Φ_e, can be expressed by

$$\Phi_e = \Phi\left(1 + \frac{\delta}{R_H}\right)^3 , \qquad (5)$$

where δ is the range of the repulsive interactions. From these results we can evaluate $\delta = 3.5$ nm. If we consider that there can be an electrical double layer around the particles in alcohols, the Debye length is $\kappa^{-1} \propto \frac{\varepsilon}{\sqrt{I}}$, where I is the ionic strength of the solution and ε is the dielectric permittivity of the solvent, and δ could be of this order of magnitude.

With the smaller particles (DMAC–ST–HMDS, diameter 20 nm), as soon as $\Phi > 0.15$, the suspensions look like transparent gels. The maximum volume fraction is found at 0.21, which corresponds with $\delta \sim 5$ nm. For the two types of particles, δ is of the same order of magnitude. Finally, in Fig. 8 we plotted the relative viscosity of suspensions of DMAC–HMDS and DMAC–ST–HMDS in 2-isopropanol versus the Peclet number, $\eta_F\dot{\gamma}(a + \delta)^3/kT$. The two plots are practically superposable, which is again in good agreement with the hard-sphere model.

Silica particles grafted with C_{12} alkyl chains (DMAC–DMDS) give rise to more viscous suspensions than DMAC–HMDS when dispersed in dodecane at the same concentration. With the same representation as previously, a value of Φ_p of 0.5 was found, with again a much lower slope for $(\eta_r)^{-0.5} = f(\Phi)$ than predicted from Eq. (3).

Conclusion

We have synthesised model hydrophobised silica particles. HMDS and DMDS are “good” silylating agents, insofar as they cannot self-polymerise, as OTS molecules do. The challenge of this synthesis was to prevent any kind of aggregation of the particles during the reaction

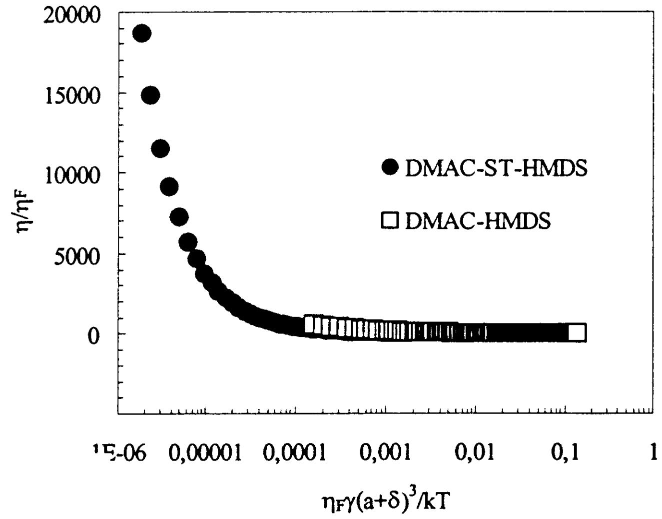


Fig. 8 Relative viscosity of DMAC–HMDS and DMAC–ST–HMDS suspensions in 2-propanol versus the Peclet number ($\Phi_e = 0.47$)

and/or the purification steps. TEM and QELS showed that this was achieved, at least when HMDS and DMDS are used. Silica particles grafted with HMDS display hard-sphere behaviour in alcohols such as 2-propanol and 1-butanol, but not in dodecane in which they appear to be slightly aggregated.

We now have a system in which the hydrophobicity can be varied by changing the length of the grafted alkyl chains. These silica particles are used to test the efficiency of hydrophobically modified poly(sodium acrylates) as dispersing agents for hydrophobic particles in water [30].

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