

# Rheology of Silica Dispersions in Organic Liquids: New Evidence for Solvation Forces Dictated by Hydrogen Bonding

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Dispersions of hydrophilic fumed silica are investigated in a range of polar organic media. The silica forms stable, low-viscosity sols exhibiting shear thickening behavior in a host of liquids, including ethylene glycol and its oligomers and short-chain alcohols, such as *n*-propanol. In contrast, the silica flocculates into colloidal gels in other liquids, such as glycols with methyl end-caps and longer-chain alcohols. We suggest that there is a causal relationship between the hydrogen-bonding ability of the liquid and the colloidal microstructure observed. In strongly hydrogen-bonding liquids, a solvation layer is envisioned to form on the silica surface through hydrogen bonding between liquid molecules and surface silanol groups (Si–OH). This gives rise to short-range, non-DLVO repulsions (“solvation forces”) which stabilize the silica particles. In contrast, in the case of liquids with limited hydrogen-bonding ability, silanols on adjacent silica particles are envisioned to interact directly by hydrogen bonding. This leads to particle flocculation and ultimately to gelation. Our study further fuels the debate regarding the existence of solvation forces in dispersions.

## A. Introduction

Colloidal dispersions form the backbone of materials ranging from the commonplace (food, cosmetics) to the exotic (nanocomposites, fiber-optic cable gels). Among the various kinds of colloidal particulate matter, silica (SiO<sub>2</sub>), in its various forms, is perhaps the most widespread. Accordingly, dispersions of silica have been investigated in great detail, both in academia and in industry.<sup>1,2</sup> One particular form of silica of interest to us is *fumed silica*,<sup>3,4</sup> which we have employed as a gelling agent in polyether liquids to yield *composite polymer electrolytes* for use in rechargeable lithium batteries.<sup>5</sup> To optimize and predict the behavior of such complex dispersed systems, it is important to first elucidate the colloidal interactions in model silica dispersions and then understand how these interactions influence the rheological character of the system.

We therefore undertake a fundamental study on fumed silica dispersions in polar organic media. We focus exclusively on a single type of fumed silica: the native, hydrophilic variety which has silanol (Si–OH) groups on its surface.<sup>3</sup> This silica is dispersed in a variety of organic liquids, specifically a range of low molecular weight

oligoethers, including poly(ethylene glycols) (PEGs) and poly(propylene glycols) (PPGs). We use rheological techniques (steady and dynamic) to probe the microstructure in these dispersions. Our emphasis is on elucidating the colloidal interactions that dictate the microstructure of these systems. Issues dealing with silica having hydrophobic surface chemistry are elaborated on in a separate publication.<sup>6</sup>

Fundamental studies on silica dispersions date as far back as the 1920s (see refs in Iler<sup>1</sup>) and have mostly focused on aqueous media.<sup>7–12</sup> It is now well-known that the DLVO theory of charge stabilization cannot account for all the behavior observed with aqueous silica sols. For example, Allen and Matjevic<sup>8</sup> reported that aqueous sols of colloidal silica showed exceptional stability toward flocculation by electrolytes at low pH close to the point of zero charge. This finding was corroborated by Harding<sup>9</sup> for fumed silica sols as well, provided the size of the fumed silica primary particles was small (<30 nm).

The behavior of silica in organic media has also been investigated for several decades, although fewer studies exist than in the case of aqueous systems.<sup>13–20</sup> More than

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25 years ago, Benitez et al.<sup>13</sup> pointed out that hydrophilic (as well as partially methylated) fumed silica forms stable dispersions in methanol, ethanol, acetone, and dioxane. Similar findings have been made for Stober silica particles as well.<sup>18–20</sup> Quite remarkably, these dispersions are observed to be stable despite a minimal surface charge and in the absence of dissolved polymeric species.

The unusual stability of silica sols can be correlated with a monotonic short-range repulsion between silica surfaces that has been detected through surface force measurements.<sup>21–24</sup> This repulsion force has primarily been studied in aqueous media,<sup>21–23</sup> although it has also recently been reported for some polar organic liquids.<sup>24</sup> The origin of this short-range repulsion, however, is still a topic of controversy. It was originally believed that an immobilized surface layer of liquid (solvation or hydration layer<sup>25</sup>) was formed on the silica particles by hydrogen bonding (H-bonding) between liquid molecules and surface silanol groups, and that these layers contributed to the observed repulsive forces.<sup>21,22</sup>

Recent studies, on the other hand, have alternately attributed the repulsions to a layer of “silica gel” (~1 nm thick) that is formed on the silica surface upon prolonged interaction with liquids such as water.<sup>23</sup> This layer (consisting of protruding silanol and silicic acid groups) can then contribute a monotonic short-range repulsion that is understood purely on the basis of steric grounds. The various hypotheses seem to agree, however, that it is the physicochemical nature of the silica surface that dictates the interactions occurring at the silica–liquid interface.

Silica (especially fumed silica) is also known for its ability to enhance the viscosity of organic media.<sup>3,4,17</sup> This can be understood as the opposite of stabilization (i.e., it results from the formation of interparticle linkages which arise due to a net attractive force between particles). When such linkages are formed extensively and span the sample volume, the result is a colloidal gel (i.e., a three-dimensional network of particles).<sup>26</sup> During the process of gelation, the initial viscous liquid is converted into a self-supporting material which exhibits elastic character. Since many of the applications of fumed silica revolve around its thickening properties, an understanding of the parameters which control thickening and gelation is just as important as an understanding of stabilization.

In the case of hydrophilic fumed silica, gel formation has been demonstrated in nonpolar liquids such as mineral oil, cyclohexane, and other hydrocarbons.<sup>3,17</sup> The main driving force for silica gelation is expected to be the formation of hydrogen bonds between silanol (Si–OH) groups on adjacent silica units.<sup>3,4</sup> It has been surmised that silica can effectively thicken only those liquids whose molecules do not contain highly polar groups or groups with hydrogen-bonding ability.<sup>4</sup> If polar groups are present, a preferential interaction between these groups

and the surface silanols is expected, and as a result only a low level of thickening would occur. However, such rules-of-thumb are useful only as a starting point; they cannot be generally relied upon for predictive capabilities, as we shall see from our results.

To probe the microstructures and hence the colloidal interactions present in our dispersions, we resort to rheology under steady and dynamic shear.<sup>27</sup> In steady-shear rheology, the response of the sample is measured under flow conditions, and the (apparent) viscosity is determined as a function of shear rate. In dynamic rheology, a low-amplitude oscillatory shear is applied on the sample, and the response of the material is monitored in terms of two parameters: the elastic modulus ( $G'$ ) and the viscous modulus ( $G''$ ). The frequency spectrum for a given system (i.e., the variation of  $G'$  and  $G''$  with oscillation frequency) provides a signature of the microstructure existing in the system.<sup>26</sup> The utility of dynamic rheology lies in the fact that materials can be probed in their at-rest state without causing disruption of their underlying structures.<sup>27</sup> Thus, dynamic rheology offers a more direct correlation with microstructure than steady rheology.

In this study, we carefully probe the nature of silica dispersions in various polar organic media using a combination of steady and dynamic rheology. We can thus clearly elucidate the microstructure in each system and thereby construct a suitable basis for comparing different systems. As we shall demonstrate, our range of dispersions typically fall into two extreme classes: (a) stable (non-flocculated) sols and (b) colloidal gels. We then attempt to unearth the fundamental mechanisms responsible for the diverse behavior of these colloidal systems.

## B. Experimental Section

The colloidal particulate matter used in this study is fumed silica, which is an amorphous form of silicon dioxide (SiO<sub>2</sub>) prepared by a flame hydrolysis process.<sup>3,4</sup> Its primary structure consists of branched aggregates (~0.1 μm long) formed by the fusion of nonporous spherical particles (~10 nm diameter). This aggregated structure is responsible for the unique properties of fumed silica. Note that the aggregates cannot be disrupted further by shear. Fumed silica is also referred to as “pyrogenic silica” or by its trade names Aerosil and Cabosil. The silica used in this study was kindly supplied by Degussa Corporation, Akron, OH, and is denoted by the manufacturer as Aerosil 200, abbreviated here as A200. This is the native, unmodified fumed silica with a surface covered with silanol (Si–OH) groups to the tune of 2.5 [SiOH] groups/nm<sup>2</sup> or equivalently about 0.84 mmol/g.<sup>3</sup> The silanol groups render the silica hydrophilic, and the silica can consequently be wetted by water. The primary particles of the A200 silica are 12 nm in diameter, and the BET surface area is ~200 m<sup>2</sup>/g. Prior to use in dispersions, the silica was dried for 24 h in a vacuum oven at 120 °C.

A total of 19 different liquids, comprising 15 different molecular structures, were examined as part of this study (Table 1). The liquids were all Newtonian media, and their viscosities at 25 °C are reported in the table. Dispersions of silica in each liquid were prepared by mixing the components intensely in a Silverson SL2 mixer (Silverson Machines, Chesham, U.K.) until homogeneity was reached. Extreme care was taken to ensure good mixing quality in all our samples, since this aspect is critical to the flocculation capabilities of fumed silica.<sup>3</sup> The resulting dispersions were exposed to vacuum (~1 kPa) at room temperature for several hours to remove entrained air bubbles. Dispersions in propylene carbonate (PC) and dimethyl carbonate (DMC) alone were prepared in an argon-filled glovebox, because these liquids are semivolatiles and hygroscopic. For studies on electrolyte effects, two lithium salts (lithium perchlorate and lithium imide) were

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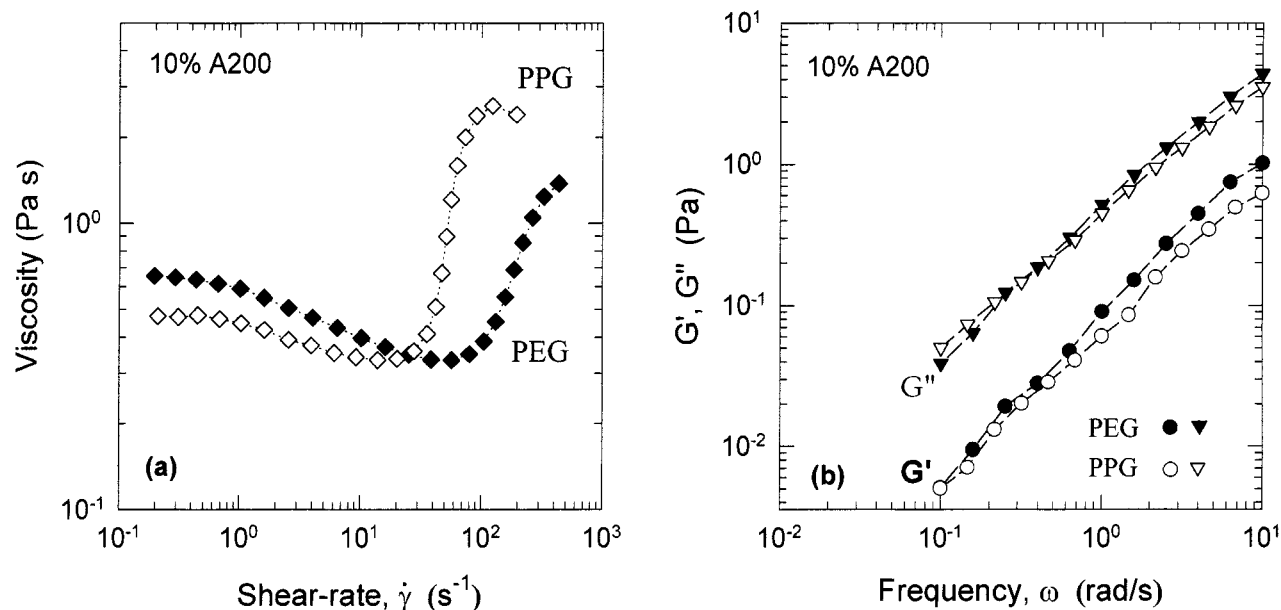
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**Figure 1.** Rheology of fumed silica (A200) dispersions in PEG 300 and PPG 425: (a) steady shear; (b) dynamic shear.

**Table 1.** Characteristics of Liquids Used in This Study

liquid (and MW if oligomeric)	molecular structure	viscosity at 25 °C (mPa s)
ethylene glycol (EG)	HO-CH <sub>2</sub> -CH <sub>2</sub> -OH	18
propylene glycol (PG)	HO-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH	47
ethylene glycol dimethyl ether (EG-dm)	CH <sub>3</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>3</sub>	0.5
propylene glycol dimethyl ether (PG-dm)	CH <sub>3</sub> -O-CH <sub>2</sub> -CH(CH <sub>3</sub> )-O-CH <sub>3</sub>	0.6
1-propanol	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -OH	2.0
1-heptanol	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>6</sub> -OH	5.5
propylene carbonate (PC)	CH <sub>2</sub> -CH(CH <sub>3</sub> )-CO <sub>3</sub> (cyclic)	2.5
dimethyl carbonate (DMC)	(CH <sub>3</sub> )-CO <sub>3</sub> -CH <sub>3</sub>	0.6
polyethylene glycol (PEG), 300 g/mol	HO-(CH <sub>2</sub> -CH <sub>2</sub> -O) <sub>n</sub> -H	69
PEG monomethyl ether (PEG-m), 350 g/mol	HO-(CH <sub>2</sub> -CH <sub>2</sub> -O) <sub>n</sub> -CH <sub>3</sub>	27
PEG monobutyl ether (PEG-b), 200 g/mol	HO-(CH <sub>2</sub> -CH <sub>2</sub> -O) <sub>n</sub> -C <sub>4</sub> H <sub>9</sub>	8.5
PEG dimethyl ether (PEG-dm) 250 g/mol	CH <sub>3</sub> -O-(CH <sub>2</sub> -CH <sub>2</sub> -O) <sub>n</sub> -CH <sub>3</sub>	7.0
500 g/mol		26
PEG methyl ether methacrylate (PEG-m-methac), 400 g/mol	CH <sub>3</sub> -O-(CH <sub>2</sub> CH <sub>2</sub> O) <sub>n</sub> -COO-C(CH <sub>3</sub> )=CH <sub>2</sub>	23
PEG diacrylate (PEG-diac), 400 g/mol	CH <sub>2</sub> =CH-COO-(CH <sub>2</sub> CH <sub>2</sub> O) <sub>n</sub> -COO-CH=CH <sub>2</sub>	58
polypropylene glycol (PPG) 425 g/mol	HO-[CH <sub>2</sub> -CH(CH <sub>3</sub> )-O] <sub>n</sub> -H	67
1000 g/mol		140
3000 g/mol		580
PPG diglycidyl ether (PPG-digly), 380 g/mol	CH(O)CH <sub>2</sub> -CH <sub>2</sub> -O-[CH <sub>2</sub> CH(CH <sub>3</sub> O)] <sub>n</sub> -CH <sub>2</sub> -CH(O)CH <sub>2</sub>	36

used, and the silica was dispersed in the salt solution. Silica concentrations in all our systems are reported as w/w of silica/liquid.

Rheological experiments were conducted using a Rheometrics dynamic stress rheometer (DSR-II). All experiments were run at ambient temperature (25 °C). Experiments were done using three different geometries: cone-and-plate, parallel plate, and couette (concentric cylinder). The cone-and-plate geometry was generally preferred for the dispersions, while liquid viscosities were determined using the couette apparatus. Two different cone-and-plate fixtures were used: the larger fixture having a diameter of 40 mm and a cone angle of 0.04 rad, and the smaller fixture having a diameter of 25 mm and a cone angle of 0.1 rad. Before each dynamic experiment, a steady preshear was applied at a shear rate of 1 s<sup>-1</sup> for 60 s followed by a 120 s rest period. This procedure was necessary to erase any previous shear histories on the sample and to ensure that the sample establishes its equilibrium structure.<sup>28</sup>

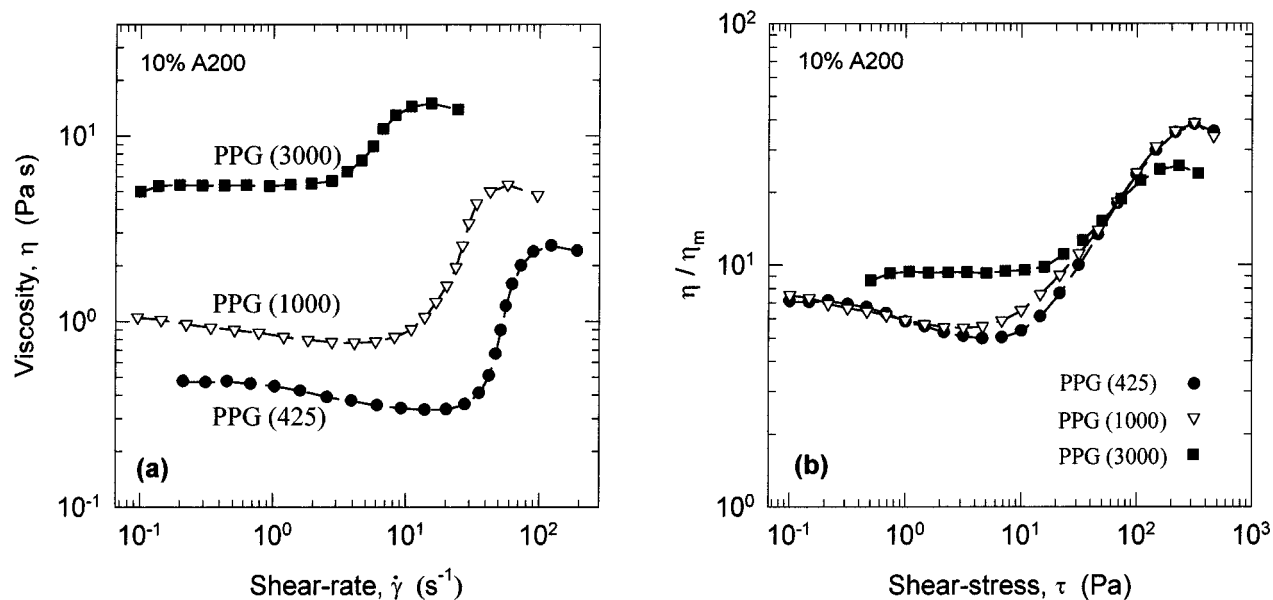
### C. Results

We begin by considering dispersions of hydrophilic (A200) fumed silica in two oligoether liquids: a poly(ethylene glycol) (PEG) of molecular weight 300 and a

poly(propylene glycol) (PPG) of molecular weight 425. In Figure 1 we describe the rheology (steady and dynamic) of 10% A200 silica dispersions in the two media. The steady-shear data (Figure 1a) show a Newtonian plateau at low shear rates, with a low value of the zero-shear viscosity (<1 Pa s). At higher shear rates, the viscosity increases rapidly with shear rate (shear thickening) over a narrow range of shear rates, and thereafter the viscosity begins to drop again. The increase in viscosity due to shear thickening is by as much as an order of magnitude. Under dynamic rheology (Figure 1b) we find that the viscous modulus  $G''$  exceeds the elastic modulus  $G'$  over the entire frequency range, with both moduli depending strongly on frequency. Such a dynamic rheological response is characteristic of a system showing purely viscous behavior—in the context of colloidal dispersions it implies that the dispersion is a structureless sol, consisting of distinct, nonfloculated units.<sup>24</sup> Thus, taken together, the rheological data reveal that dispersions of silica in PEG and PPG are essentially low-viscosity sols.

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**Figure 2.** Effect of liquid viscosity on the rheology of fumed silica dispersions. Data are shown for polypropylene glycols (PPGs) of molecular weights 425, 1000, and 3000 (viscosities of 67, 140, and 580 mPa s, respectively): (a) viscosity as a function of shear rate; (b) relative viscosity as a function of shear stress.

We found similar rheological behavior for all concentrations of A200 silica examined in the above PEG and PPG. Shear thickening was detected at concentrations as low as 2% silica. The magnitude of the shear-thickening effect progressively increased with silica concentration while at the same time the point of incipient shear thickening was shifted toward lower shear rates. These effects of particle concentration are entirely consistent with trends reported in the shear-thickening literature and are discussed in detail elsewhere.<sup>29</sup> Interestingly, the presence of shear thickening in our systems is itself an indication that flocculation effects are negligible, because this phenomenon is typically observed only in nonfloculated dispersions.<sup>30</sup>

We now examine the effect of liquid viscosity on silica dispersions. This study was performed in a range of PPGs of varying molecular weight. Figure 2a shows the steady-shear rheological behavior of 10% A200 silica dispersions in PPGs of molecular weight 425, 1000, and 3000 (with viscosities of 67, 140, and 580 mPa s, respectively). All the dispersions show shear thickening at high shear rates. In all cases, the viscosity in the Newtonian limit (i.e., the zero-shear viscosity  $\eta_0$ ) is quite low ( $<10$  Pa s). As the PPG molecular weight (and hence liquid viscosity) increases, the shear thickening begins at a lower shear rate, but the rise in viscosity is smaller. An alternate way to represent these data is by plotting the relative viscosity (i.e., viscosity of the dispersion  $\eta$  scaled by the viscosity of the continuous medium  $\eta_m$ ) versus shear stress  $\tau$ . As shown in Figure 2b, the data overlap reasonably well, with the shear thickening initiated at approximately the same shear stress in all cases. Such scaling behavior is in accord with current theories on shear thickening,<sup>30</sup> and we will not discuss these aspects further in this paper. The important point here is that the rheology and hence the microstructure are qualitatively unchanged, even as the liquid viscosity is varied over an order of magnitude. All these dispersions are stable, nonfloculated sols.

One aspect to note here is that the zero-shear viscosity  $\eta_0$  of the fumed silica sols in Figure 2 assumes somewhat

high values—thus, the relative viscosity  $\eta_0/\eta_m \approx 10$ , which is higher than would be predicted by simple theoretical considerations for nonfloculated suspensions of spherical particles (e.g., the Einstein or Batchelor equations<sup>26</sup>). The reason for this discrepancy lies in the complex geometry of fumed silica aggregates, as these aggregates are known to be fractal structures.<sup>31</sup> (The aggregates are the primary units of fumed silica and cannot be disrupted by shear.) The open nature of these fractal aggregates allows them to occlude considerable amounts of liquid, thereby contributing to a much larger effective solids volume fraction and to greater stress dissipation.<sup>29</sup> The elongated shape of these aggregates may also be a contributing factor toward the high viscosity, compared to spherical particles. Thus, the higher values of relative viscosity do not imply that our dispersions are flocculated.

We now analyze the effect of varying the end-group on the oligomeric chain. The oligoethers typically possess hydroxyl (OH) end-groups, but these can be replaced by a variety of other functionalities. We will initially focus on the effect of methyl end-caps on the rheology. For this we examine three different liquids: PEG, which has two OH end-groups; PEG monomethyl ether (PEG-m), which has one OH end-group and one methyl ( $\text{CH}_3$ ) end-group; and PEG dimethyl ether (PEG-dm), which has two  $\text{CH}_3$  end-groups. The molecular weights of the three liquids are comparable (300, 350, and 250, respectively).

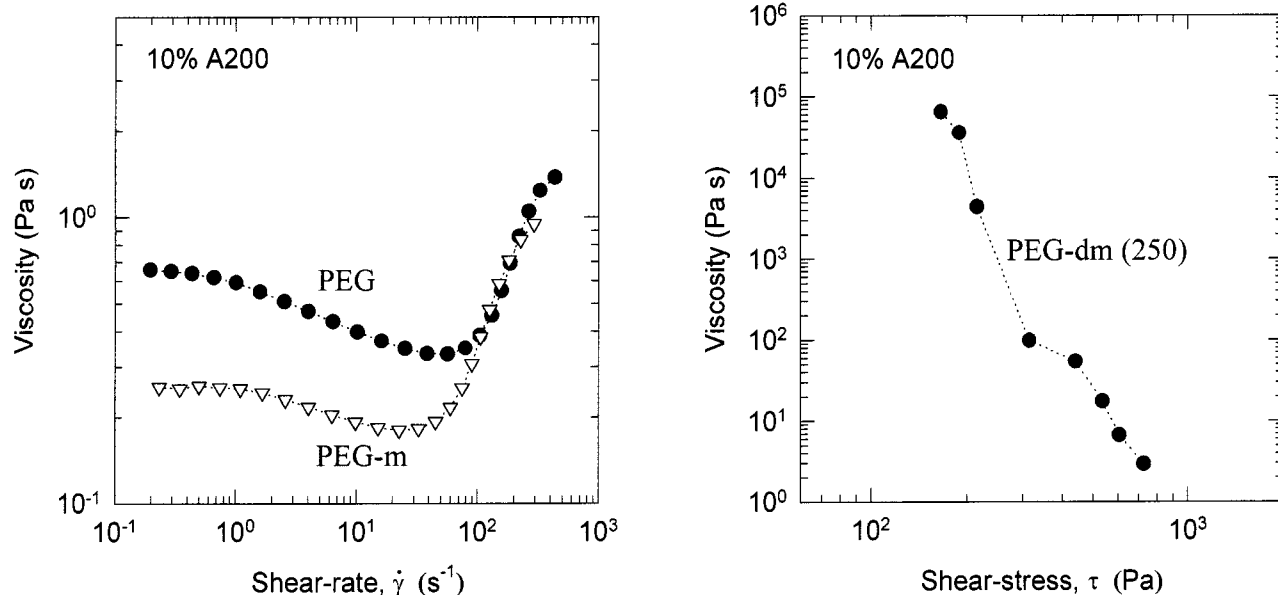
Steady-shear rheologies for 10% A200 silica dispersions in these three liquids are presented in Figure 3. Figure 3a reveals that dispersions in PEG and PEG-m are both low-viscosity sols that exhibit shear thickening. The higher value of the zero-shear viscosity in PEG reflects the higher viscosity of the PEG continuous phase over that of PEG-m. (Note that PEG shows considerable H-bonding in its liquid state owing to its two OH end-groups; hence, its melting and boiling points, as well as viscosity, are higher than those of PEG-m and PEG-dm at an equivalent molecular weight.<sup>32</sup>) The silica dispersion in PEG-dm shows very different results, however (Figure 3b). In this

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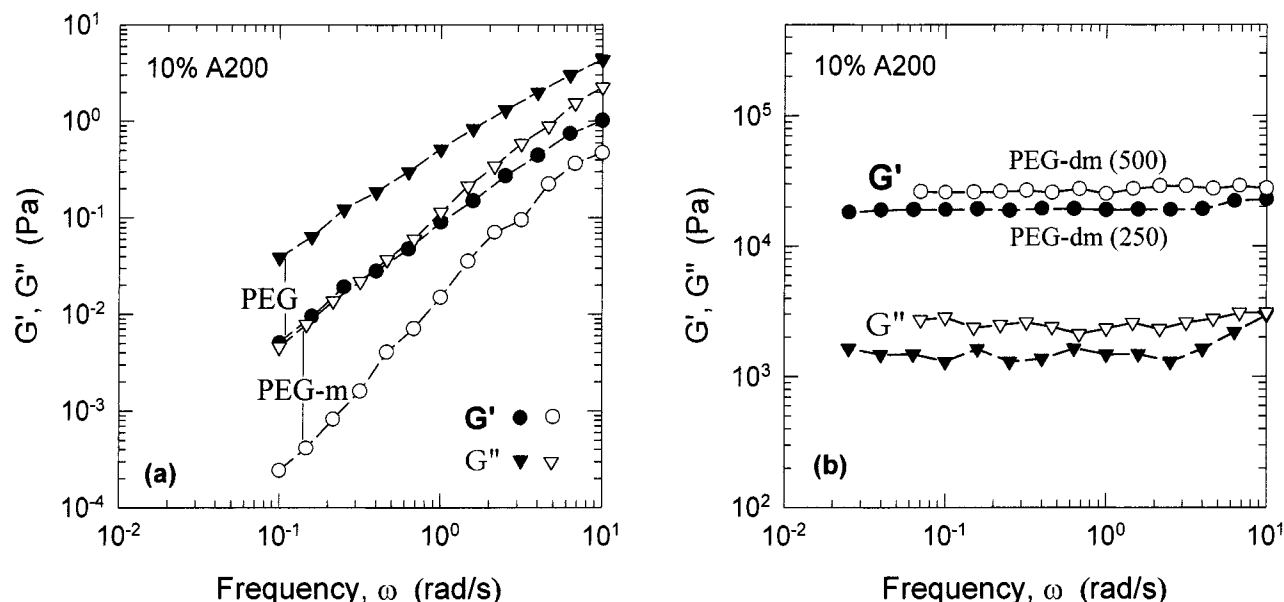
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**Figure 3.** Effect of end-capping on the steady-shear rheology of fumed silica dispersions in glycols. Data are shown for the following polyethylene glycols: (a) PEG (two OH end-groups) and PEG-m (one OH and one CH<sub>3</sub> end-group); (b) PEG-dm (two CH<sub>3</sub> end-groups).



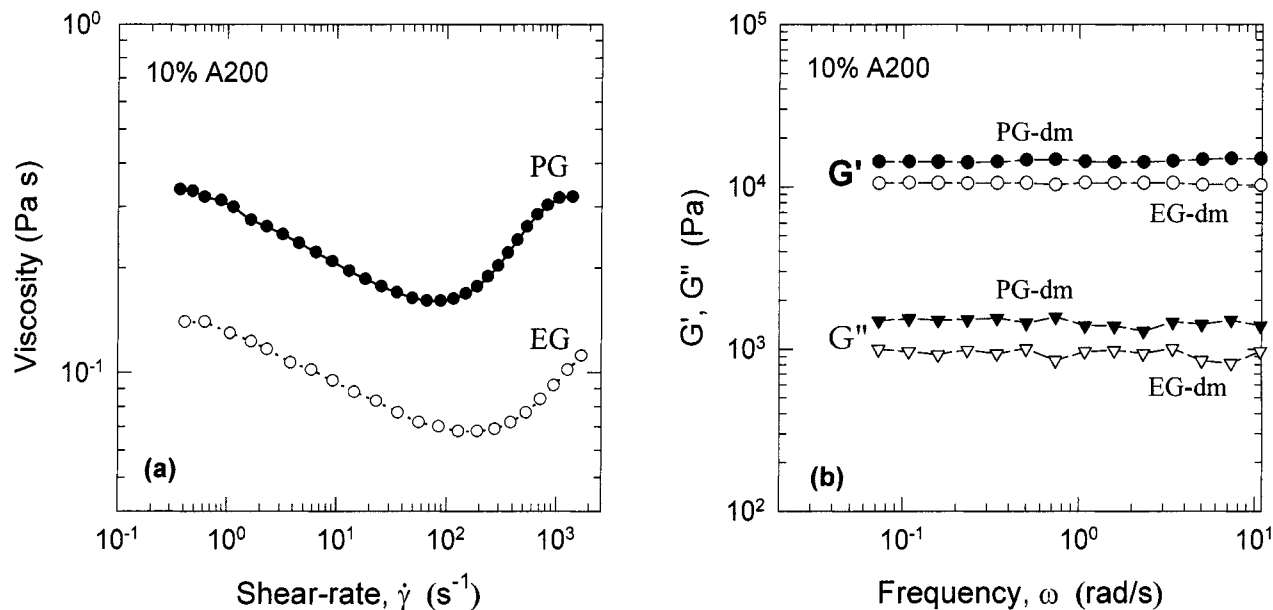
**Figure 4.** Effect of end-capping on the dynamic rheology of fumed silica dispersions in glycols. Data are shown for the following polyethylene glycols: (a) PEG (two OH end-groups) and PEG-m (one OH and one CH<sub>3</sub> end-group); (b) PEG-dm (two CH<sub>3</sub> end-groups) of two molecular weights (250 and 500).

case, the viscosity is plotted as a function of shear stress. We find that the viscosity is essentially infinite ( $>10^5$  Pa s) at shear stresses below  $\sim 200$  Pa, at which point the material yields abruptly. The presence of such a *yield stress* points to the existence of a network structure in this system.

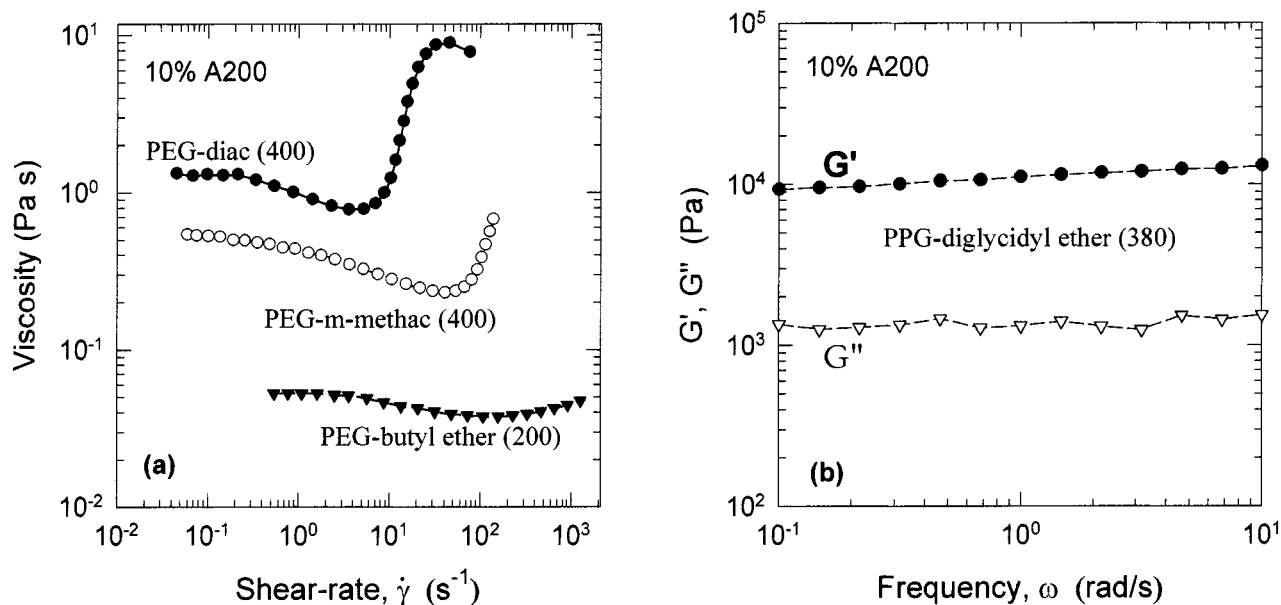
The distinction between these systems is better illustrated by their dynamic rheological response. As shown in Figure 4a, the PEG and PEG-m systems exhibit a viscous response (frequency-dependent moduli,  $G' < G''$ ). In contrast, silica dispersions in PEG-dm show a highly elastic response (Figure 4b). That is, in the latter case, the moduli are *frequency-independent*, and the elastic modulus  $G'$  significantly exceeds the viscous modulus  $G''$ . The elastic behavior of the PEG-dm sample signifies that a three-dimensional network structure is present (i.e., the system is a gel).<sup>26</sup> This intriguing result was verified with a PEG-dm of higher molecular weight—thus, a gellike

response is seen in Figure 4b for the case of PEG-dm 500 as well, with the gel modulus  $G'$  being slightly higher than that in PEG-dm 250.

We thus find that end-capping of oligoether molecules by nonpolar methyl groups causes the silica to flocculate into a gel. We were interested to see whether similar behavior is also observed in the monomeric analogues of the above oligomers. Therefore, we studied silica dispersions in ethylene glycol (EG) and propylene glycol (PG), as well as their methyl end-capped counterparts, viz. ethylene glycol dimethyl ether (EG-dm) and propylene glycol dimethyl ether (PG-dm) (more correctly termed 1,2-dimethoxyethane and 1,2-dimethoxypropane, respectively). Steady-shear rheological data for 10% A200 dispersions in EG and PG are shown in Figure 5a. We have shown the steady-shear data for these systems because they clearly indicate that the dispersions are nonfloculated sols (low value of viscosity, shear thicken-



**Figure 5.** Rheology of fumed silica dispersions in glycols and their end-capped analogues: (a) steady-shear rheology of dispersions in ethylene glycol (EG) and propylene glycol (PG) (the data show that these are nonfloculated systems); (b) dynamic rheology of dispersions in ethylene glycol dimethyl ether (EG-dm) and propylene glycol dimethyl ether (PG-dm) (the data show these to be colloidal gels).



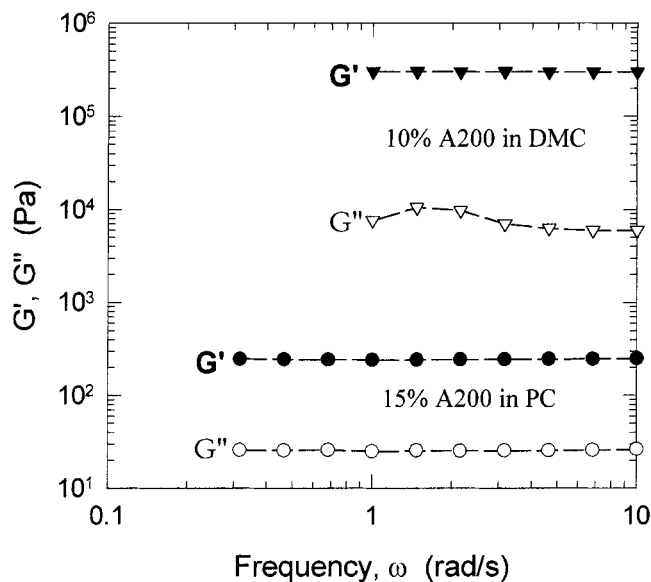
**Figure 6.** Rheology of fumed silica dispersions in oligoethers with different end-functionalities: (a) steady-shear rheology in PEG-diacrylate 400, PEG-monomethyl ether monomethacrylate 400, and PEG-monobutyl ether 200—all these dispersions are nonfloculated sols; (b) dynamic rheology in PPG-diglycidyl ether 380—this is shown to be a colloidal gel.

ing). In contrast, the dispersions in EG-dm and PG-dm are both observed to be gels (Figure 5b). For these systems, we have shown the dynamic rheological data because they clearly highlight their gel-like character ( $G' > G''$ , frequency-independent moduli).

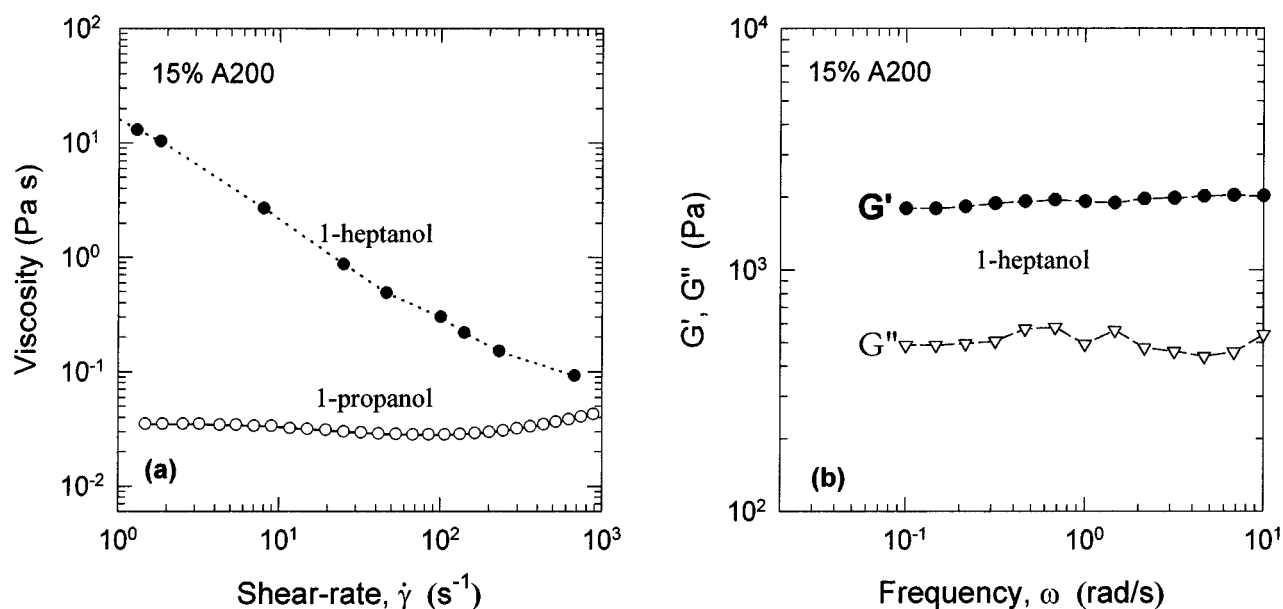
We have also examined a range of oligoethers with other end-functionalities. One class of PEGs of specific interest to us are those with acrylate or methacrylate end-groups, which are often used as components in gel electrolytes due to their ability to be chemically cross-linked into rigid solids. Note that acrylates and methacrylates comprise the carboxylate ester (COO) functionality. Steady-shear rheological data for dispersions of 10% A200 fumed silica in two such liquids, viz. PEG monomethyl ether monomethacrylate (400 g/mol) and PEG diacrylate (400 g/mol), are shown in Figure 6a. In the same figure we have also

plotted the data for 10% A200 in PEG monobutyl ether (200 g/mol). We observe that the rheology of each of the above systems is characteristic of a nonfloculated sol, with a low viscosity at low shear rates and shear thickening at high shear rates. This is to be contrasted with the dynamic rheological data for a 10% A200 dispersion in PPG diglycidyl ether (380 g/mol) (Figure 6b). In this case, the oligomer possesses a glycidyl (three-member epoxy ring) functionality at either end. The response of this system is seen to be characteristic of a colloidal gel.

We have also studied silica dispersions in two other classes of liquids: carbonates and alcohols. Among the carbonates, we considered propylene carbonate (PC) and dimethyl carbonate (DMC)—two liquids which are often used in electrolyte applications for lithium-ion batteries. These are relatively volatile liquids, thus complicating



**Figure 7.** Dynamic rheology of fumed silica dispersions in carbonates. Data are shown for a 10% A200 silica dispersion in dimethyl carbonate (DMC) and a 15% A200 silica dispersion in propylene carbonate (PC).



**Figure 8.** Rheology of fumed silica dispersions in alcohols of different chain lengths, viz. 1-propanol and 1-heptanol: (a) steady rheology; (b) dynamic rheology.

both the sample preparation and the rheological experimentation. As indicated earlier, dispersions of silica in PC and DMC were mixed in an argon-filled glovebox. Moreover, the rheological experiments were conducted in a short period of time to minimize solvent loss due to evaporation. Dynamic rheological data for the samples in DMC (10% A200) and PC (15% A200) are shown in Figure 7. Both systems show a characteristic gel-like response, which can be recognized despite the abbreviated nature of the frequency sweeps (data points at lower frequencies, corresponding to longer times, were not collected). Despite a higher silica concentration, the PC sample shows a much lower gel modulus  $G'$ , indicating that it is a comparatively weak gel.

The rheology of fumed silica dispersions in alcohols has been studied earlier by others,<sup>14,15</sup> thus providing a basis for comparison with our work. We investigated dispersions of 15% A200 silica in alcohols of different alkyl chain lengths, viz. 1-propanol and 1-heptanol. The steady-shear rheology of these dispersions is shown in Figure 8a. The

1-propanol dispersion exhibits a very low viscosity and mild shear thickening, indicating it to be a nonfloculated sol. The 1-heptanol dispersion shows a much higher viscosity and a marked degree of shear thinning. Dynamic rheology confirms (Figure 8b) that the dispersion in 1-heptanol is indeed a colloidal gel. Our viscosity data match very well with that reported by Makarov and Gamera<sup>14</sup> for the same systems.

To summarize our results, we can distinguish between two classes of fumed silica dispersions. In some liquids, fumed silica forms nonfloculated sols that show a low viscosity under steady shear and a viscous response under dynamic shear. Visual examination reveals that these nonfloculated dispersions behave like homogeneous liquids and are easily pourable. Most samples are transparent or slightly translucent and show no visual evidence of phase separation, precipitation, or increases in turbidity over long periods of time. Thus, on the basis of a combination of rheology and visual observations, we can categorize these systems as *stable silica sols*.



**Table 2. Summary of Findings on Microstructure in Silica Dispersions**

sol systems	gel systems
1-propanol	1-heptanol
EG	EG-dm
PG	PG-dm
	PC
	DMC
PEG 300	PEG-dm 250
PEG-m 350	PEG-dm 500
PEG-b 200	
PEG-m-methac 400	
PEG-diac 400	
PPG 425	PPG-digly 380
PPG 1000	
PPG 3000	

**Table 3. Bulk Parameters for Various Media**

component	dielectric constant, <sup>a</sup> $\epsilon$	refractive index, <sup>b</sup> $n$	Hamaker constant, <sup>c</sup> $A$ ( $10^{-20}$ J)
silica	3.8	1.460	6.42
EG	37.0	1.431	5.72
PG	32.0	1.432	5.74
EG-dm	7.2	1.379	4.51
PG-dm	6.0	1.384	4.68
1-propanol	20.3	1.384	4.69
1-heptanol	12.1	1.424	5.51
PC	64.4	1.421	5.51
DMC	3.1	1.368	4.20
PEG 300	15.6	1.463	6.40
PEG-m 350	10.9	1.455	6.19
PEG-b 200	10.0	1.440	5.85
PEG-dm 250	7.9	1.441	5.85
PEG-dm 500	5.8	1.441	5.85
PEG-m-meth 400	8.0	1.461	6.30
PEG-diac 400	6.0	1.467	6.41
PPG 425	10.1	1.447	6.01
PPG 1000	8.1	1.449	6.03
PPG 3000	5.7	1.451	6.04
PPG-digly 380	6.0	1.464	6.34

<sup>a</sup> Obtained from or estimated on the basis of data in Brandrup and Immergut,<sup>32</sup> Lange,<sup>33</sup> or Van der Hoeven and Lyklema.<sup>34</sup> <sup>b</sup> Reported by the respective manufacturers. <sup>c</sup> Calculated using eq 2 and using the  $\epsilon$  and  $n$  values from this table. All values pertain to 298 K.

In contrast, there are several liquids in which the fumed silica organizes into a three-dimensional particulate network. Consequently, these materials exhibit an extremely high viscosity and/or a yield stress under steady shear and show frequency-independent moduli, with  $G' > G''$ , under dynamic shear. Visual examination indicates that these gels are soft, free-standing solids that can bear their own weight in a sample container. This class of materials can therefore be categorized as *colloidal silica gels*. A summary of our results for silica dispersions in various liquids, organized into two classes (sols and gels), is shown in Table 2. A few relevant parameters for our liquids are listed in Table 3, and these will be useful for the discussions to follow.

One further point needs to be added with regard to the silica gels. Because gels are volume-filling networks, gel formation always requires a minimum concentration of particles.<sup>26</sup> For some fumed silica gels, the gelation concentration is so low (<2 wt %) that it is difficult to detect accurately using rheology (which is why this parameter has not been reported). On the other hand, in other liquids (notably PC and 1-heptanol), a fairly large silica concentration is required for gel formation. However, in the latter systems, we begin to observe flocculation effects even at low concentrations, well below that required for gelation. Flocculation is reflected in steady shear as a high viscosity at low shear rates coupled with shear-

thinning behavior (thereby, an absence of shear thickening), while, in dynamic shear, the elastic modulus  $G'$  becomes comparable to the viscous modulus  $G''$  over a part of the frequency range (viscoelasticity). We generally observe that systems which show flocculation effects at low silica concentration will eventually form gels at high concentration, and vice versa. In contrast, stable silica sols continue to show purely viscous behavior *over the entire concentration range*.

## D. Discussion

We now delve into the possible mechanisms responsible for stability and flocculation in our systems. We consider three factors (electrostatic interactions, van der Waals forces, and solvation phenomenon) in interpreting our results and examine which of these factors are consistent with our experiments.

**Electrostatic Interactions.** Our liquids are typically polar media, in which inorganic salts are soluble, at least to some extent. Hence the first possibility we consider is of electrostatic effects. In line with the DLVO theory, the addition of salts is expected to screen out electrostatic interactions due to double layers and thereby destabilize a stable suspension.<sup>25,26</sup> We therefore studied the effect of salt addition to several of our stable silica sols. These studies were done up to very high salt concentrations (>2 M). In all cases, systems with added salt showed the same remarkable stability as that observed in the absence of salt. No perceptible changes could be visually observed over several months in these systems.

The addition of salts does have a small effect on the rheology of silica dispersions, due mainly to the fact that salt addition increases the liquid viscosity. This is illustrated in Figure 9 for the case of two liquids: PEG 300 and propylene glycol (PG). The rheology of 10% A200 silica dispersions in these liquids in the presence of 1 M lithium salt is shown alongside the data for the base liquid at the same silica concentration (i.e., weight fraction, based on liquid). We find that the rheology in the presence of salt is qualitatively similar to that without salt (i.e., we still observe a low zero-shear viscosity as well as shear thickening). The higher viscosity values for the systems with salt can be attributed to the increased viscosity of the continuous phases. For example, the addition of 1 M LiClO<sub>4</sub> increases the viscosity of PG from 47 to 138 mPa s. Thus, we can conclude that, on the basis of visual observation and rheology, salts have a negligible effect on the colloidal behavior of our systems.

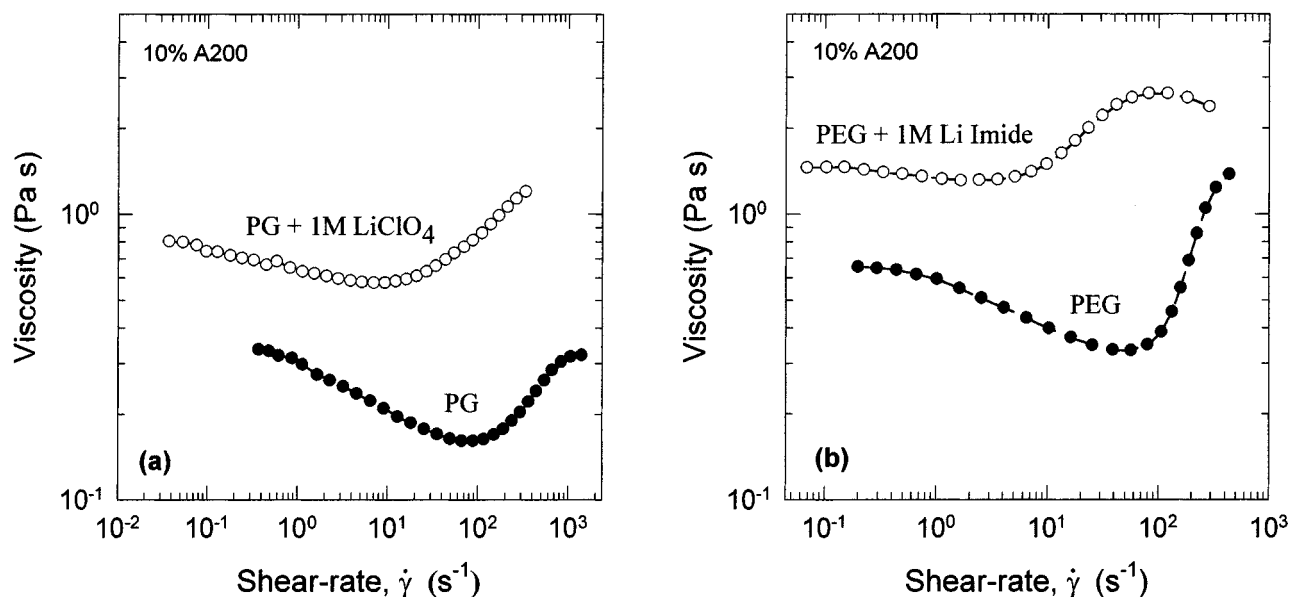
The issue of electrostatic stabilization in nonaqueous media has been addressed at length in recent reviews.<sup>34,35</sup> According to Van der Hoeven and Lyklema,<sup>34</sup> the crucial factor is the dielectric constant  $\epsilon$  of the liquid, and they distinguish between highly polar ( $\epsilon > 11$ ) and semipolar media ( $5 < \epsilon < 11$ ). Electrostatic stabilization can readily occur in highly polar media, whereas it only occurs under certain circumstances in semipolar media. As shown in Table 3, the liquids used in our studies span a wide range of dielectric constants, varying from highly polar (EG, PG, PC) to semipolar (DMC, PG-dm). Comparing Tables 2 and 3, we observe no correlation between stability and dielectric constant—for instance, we observe gel formation in PC, which has the highest dielectric constant ( $\epsilon = 64.4$ ). At the same time, stable dispersions are observed in low

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**Figure 9.** Rheology of fumed silica dispersions in the presence of salts. The silica concentration in either case is 10 wt % by weight of liquid: (a) data in propylene glycol (PG) with and without 1 M lithium perchlorate salt; (b) data in polyethylene glycol (PEG) with and without 1 M lithium imide salt.

$\epsilon$  liquids (e.g., PEG, PPGs) as well as highly polar liquids (e.g., EG, PG), and we have every reason to believe that the same mechanism is responsible for stability in all these systems. Moreover, in none of our dispersions did we find any apparent changes in stability due to electrolyte addition.

Charging of particle surfaces in nonaqueous media is well-documented in the literature.<sup>18,36</sup> For example, Spange et al.<sup>36</sup> report electrokinetic ( $\zeta$ ) potentials of  $\sim -37$  mV for colloidal silica dispersions in ethanol. (The  $\zeta$ -potential and the surface potential  $\psi$  can be assumed to be identical in low  $\epsilon$  media, for all practical purposes.) Nonetheless, as pointed out by Van der Hoeven and Lyklema,<sup>34</sup> it is not enough to have a high  $\zeta$ -potential to effect electrostatic repulsion in nonaqueous media. The repulsion between charged particles arises when the electrical double layers around those particles begin to interpenetrate. The repulsive force is equal to the gradient of the overlap potential. Now, since the ionic strength in these media is typically very low, the electric double layer is considerably extended, so that the surface potential  $\psi$  varies slowly with distance from the particle surface. Consequently, the overlap potential will also vary slowly with distance, which means that the repulsive force between particles will be low. Morrison<sup>35</sup> also seems to agree with these arguments and states that electrostatic stabilization is not possible in nonaqueous systems at *high particle concentrations*. Since our sols are observed to be stable up to very high concentrations, this again points to nonelectrostatic effects. Our analysis therefore suggests that electrostatic interactions play a negligible role in the systems considered here.

**Van der Waals Interactions.** A second possibility is that our results simply reflect the van der Waals (vdW) forces between silica particles in various media (i.e., a sol is formed when the vdW forces between bare silica particles are low), whereas high vdW forces lead to gel formation. The vdW force between two spherical particles of radius  $R$  and Hamaker constant  $A_p$  in a medium of Hamaker constant  $A_m$  is given by<sup>25,26</sup>

$$V_{\text{vdW}} = -\frac{R}{12d}[(\sqrt{A_m} - \sqrt{A_p})^2] \quad (1)$$

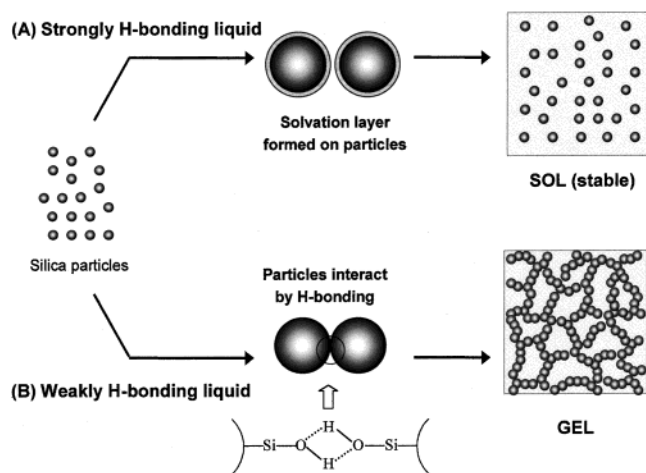
Here  $d$  is the distance of separation between the particle surfaces. This equation is derived by assuming that the net Hamaker constant is the geometric mean of the Hamaker constants for the individual phases.<sup>25</sup> Thus, the vdW forces are high if there is significant disparity between the Hamaker constant  $A_m$  of the liquid and the Hamaker constant  $A_p$  of the particles. In Table 3 we have tabulated the relevant Hamaker constants for the various media. These were calculated for each material using its dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ) (both of which are also tabulated alongside) and using the following equation:<sup>25</sup>

$$A = \frac{3}{4}kT \frac{(\epsilon - 1)^2}{(\epsilon + 1)^2} + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n^2 - 1)^2}{(n^2 + 1)^{3/2}} \quad (2)$$

In the equation,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $h$  is Planck's constant, and  $\nu_e$  is the main electronic absorption frequency for the dielectric permittivity (taken to be  $3 \times 10^{15} \text{ s}^{-1}$  for all our media).<sup>25</sup> This equation corresponds to the nonretarded Hamaker constant of the media in a vacuum.

For our systems, we generally find that, the dispersive contribution to the Hamaker constants (second term in eq 2, due to the refractive indices) generally dominates over the static contribution (first term in eq 2, due to the dielectric constants). This implies that, for  $A_m \approx A_p$  (and hence  $V_{\text{vdW}} \approx 0$ ), the refractive indices of the silica particles and the liquid medium should be matched (i.e.,  $n_m \approx n_p$ ). Indeed, this condition is nearly met for a number of our systems (Table 3), and the corresponding samples show optical clarity as a result. However, an equal number of these optically clear ( $V_{\text{vdW}} \approx 0$ ) systems are found to be both sols and gels (e.g., sol in PEG 300 but gel in PPG-diglyceride 380 (PPG-digly)). Thus, comparing Tables 2 and 3, we observe no obvious correlation per se between vdW forces and dispersion microstructure. Moreover, the fact that gels are formed in systems where the vdW interactions are relatively low (PPG-digly 380, PEG-dm

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**Figure 10.** Schematic representation of two possible scenarios that can occur in the case of silica particles dispersed in a liquid: (A) strongly H-bonding liquid (a solvation layer is formed on the particles by H-bonding, resulting in a stable sol); (B) weakly H-bonding liquid (the particles interact directly by H-bonding to form a gel).

250) suggests that a different mechanism is responsible for gel formation.

**Solvation Phenomena Due to H-Bonding Interactions.** Closer inspection of our results in Table 2 suggests that the key aspect distinguishing the sol from the gel systems is the hydrogen-bonding capability of the liquid suspending media. According to this hypothesis, fumed silica forms stable sols in liquids which possess sufficient capacity to form H-bonds, and conversely, fumed silica forms gels in liquids which have a perceptibly lower H-bonding capability. This aspect forms the basis for our arguments, and we will amplify and substantiate this hypothesis using findings from a variety of earlier studies.

We consider first how stable sols are formed in strongly H-bonding liquids. In these systems, we believe that the liquid molecules organize at the silica interface by forming H-bonds with silanol (Si-OH) groups present on the silica surface. This would lead to a *solvation layer* that coats each silica unit. The strong binding of the liquid molecules within the solvation layer is then expected to contribute a short-range repulsive force preventing particle contact (Figure 10A). Thus, we can envision that the solvated particles are stabilized against coagulation by an additional repulsive force ("solvation force") that does not fall within the framework of the DLVO theory.

In the alternate scenario, when the liquid has a low H-bonding capability, a colloidal silica gel is formed. In such cases, the formation of a solvation layer around each particle is precluded due to the low affinity between liquid molecules and the silica surface. Instead, the silica particles are envisioned to directly interact with each other through H-bonding interactions between the surface silanol (Si-OH) groups. The preponderance of such interparticle bonds throughout the sample volume will then result in a colloidal gel (Figure 10B). Thus, we believe that H-bonding and not vdW interactions is responsible for gel formation.

To generalize, when fumed silica is added to a given liquid, we envision a competition for H-bonding to surface silanols on each silica particle from two sources: (1) liquid molecules and (2) silanols on other particles. The relative strength of the interactions between silica and liquid compared to those of the silica-silica and liquid-liquid interactions will determine whether a solvation layer is formed and, hence, whether we obtain a sol or a gel. To

test our hypothesis, we need to quantify the H-bonding abilities of the various media examined here. Unfortunately, H-bonding is still not very well understood and cannot be captured in terms of bulk parameters. Nevertheless, the distinction between our sol and gel systems can be tied more conclusively to H-bonding using various findings in the literature.

Korn et al.<sup>37</sup> conducted a series of adsorption studies of various organic species onto fumed silica from carbon tetrachloride ( $\text{CCl}_4$ ). Molecules of *n*-alkanols were shown to act as H-bond donors to the silica, and as a result they adsorbed strongly onto the silica surface. Furthermore, the adsorption tendency decreased as the *n*-alkanol chain length increased. These results are consistent with our findings in *n*-propanol and *n*-heptanol (Figure 8, Table 2). The weak interaction of *n*-heptanol molecules with the silica explains why we see gels at high concentrations. We would thus expect that, in *n*-alkanols of longer chain lengths, gels should be formed at even lower concentrations.

Korn et al.<sup>37</sup> also found strong adsorption in the case of glycols, which they again explained as being due to the H-bond donor effect of the OH groups on the glycols. Other species such as esters and ethers were also found to adsorb; however, in these cases, the adsorption enthalpies were lower, since these molecules are H-bond acceptors. The lower H-bonding abilities of ether and ester groups are also consistent with the cohesive energy data provided by Brandrup and Immergut<sup>32</sup> for various functional groups. These data show that the relative cohesive energies of alcohol, ester, and ether groups roughly fall in the ratio 20:5:2. Consequently, H-bonding should be appreciably stronger between silanol (Si-OH) and hydroxyl (OH) groups in comparison to that between Si-OH and ether oxygens (C-O-C).

End-group effects have also been reported in studies on polymer adsorption to various particles, including silica. Killmann and Melchior<sup>38</sup> studied the adsorption of PEGs with OH and methyl end-groups (molecular weight  $\sim 600$ ) onto fumed silica. The PEG with two methyl end-caps showed significantly lower adsorption. Similarly, Patel et al.<sup>39</sup> studied the adsorption of different end-functionalized poly(dimethyl siloxanes) (PDMS) on fumed silica and again found that OH-terminated PDMS adsorbed to a much greater extent than the methyl-terminated polymer. In general, end-groups are known to impact several key interfacial properties of polymer chains, including their surface tension.<sup>39,40</sup> These effects are typically significant only for low-molecular-weight oligomers, because the contribution of the end-groups decreases with polymer molecular weight.<sup>40</sup>

The above findings are quite consistent with our own observations of stability in OH-terminated oligomers (EG, PEG, PEG-m) and gelation in methyl-terminated oligomers (EG-dm, PG-dm, PEG-dm) (cf. Figures 3–5). Thus, H-bonding of oligoether molecules with the fumed silica surface will take place mainly through the OH end-groups. Oligoethers with at least one OH end-group will be able to form a solvation layer on silica through H-bonding (scenario A in Figure 10), thereby leading to a sol. On the other hand, methyl end-capped oligoethers, in which the

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(40) Jalbert, C.; Koberstein, J. T.; Hariharan, A.; Kumar, S. K. *Macromolecules* **1997**, *30*, 4481.

ether oxygens (C–O–C) are the only polar entities, will not be able to form solvation layers, and so the silica–silica interaction will be dominant (scenario B in Figure 10), thus leading to a gel.

Our study suggests that solvation layers are formed on the surface of silica particles when dispersed in strongly H-bonding liquids. The idea of solvation layers and the attendant repulsive forces is not a new one. Hydration forces were postulated for silica sols in water more than 30 years ago.<sup>1,7–9</sup> In the case of silica in nonaqueous liquids, only a few studies have critically examined the solvation issue. Kiraly et al.<sup>19</sup> indirectly provided some evidence for a solvation layer on Stober silica dispersed in ethanol/cyclohexane mixtures. The solvation layer, inferred through adsorption experiments, consisted of pure ethanol (a strong H-bonding medium). By extension, one would expect the same solvation phenomena to occur in pure ethanol. Ketelson et al.<sup>20</sup> postulated the existence of short-range repulsive forces for the case of Stober silica in acetone. The authors, however, attributed these forces to a silicic acid gel layer on the particles, in accordance with the findings of Israelachvili and co-workers.<sup>23,41</sup>

A causal relationship between H-bonding and solvation forces has also been invoked by various researchers. For the case of fumed silica, Barthel<sup>4</sup> states that, in a highly polar liquid with a strong tendency to form H-bonds, adsorption of the liquid onto the particle surface would occur due to which surface silanols would be shielded from mutual interaction, thus suppressing the thickening effect. Thus, the relative affinity of Si–OH sites for adsorption of liquid molecules versus their affinity for other Si–OH sites is stated as the key factor. Modern theories to explain hydration/solvation forces invariably center around the H-bonding interactions in the system. For example, Besseling<sup>42</sup> attributes the hydration repulsion to frustrations in H-bonding caused by mismatches in the numbers of donors and acceptors within the hydration layer.

Our study clearly provides experimental evidence for the correlation between H-bonding and solvation forces and hence with silica dispersion microstructure. The hypothesis of solvation forces seems to be the most plausible explanation for the stability of such a large range of systems (Table 2). None of the competing hypotheses, such as the formation of a “silica gel layer” or the existence of density fluctuations, seem consistent with all of our results. Our findings are also in accord with the results of Forsman et al.,<sup>43</sup> who argue that repulsive solvation forces could be observed in nonaqueous solvents, provided the solvent–surface interaction is strong relative to the surface–surface interaction. Similarly, our interpretation

of gelation in low H-bonding liquids due to interparticle H-bonds seems a highly plausible explanation for which there is also support in the literature.<sup>4,17,45</sup>

Our current inability to relate H-bonding to bulk (molecular) parameters makes it difficult to formulate criteria for predicting silica stability/thickening in different liquids. As such, it also emphasizes the inadequacy of existing rules of thumb for this purpose. Thus, criteria based on polarity (dielectric constant) can fail, since fumed silica gels are formed even in highly polar liquids (e.g., PC). Likewise, the mere presence of strongly H-bonding groups on the liquid molecules is not sufficient to prevent gelation if the molecule is otherwise nonpolar (e.g., 1-heptanol). Moreover, subtle changes in molecular structure (e.g., change in end-groups of oligoethers) are enough to tilt the balance between stability and gelation. Thus, an improved ability to quantify H-bonding interactions is necessary to facilitate a priori predictions of silica microstructure in a given liquid.

## E. Conclusions

Hydrophilic fumed silica forms both stable sols and rigid gels in polar organic liquids. We have identified a causal relationship between the hydrogen-bonding ability of the liquid and colloidal behavior. Two cases are found:

**Strongly Hydrogen-Bonding Liquids.** These liquids are able to H-bond with the silanols on the silica surface, resulting in the formation of a solvation layer around each particle. This leads to repulsive solvation forces which stabilize the silica particles so that the samples behave as stable sols. Examples of such liquids include the lower *n*-alkanols and oligomeric glycols.

**Weakly Hydrogen-Bonding Liquids.** These liquids interact weakly with the silica surface, thus enabling adjacent particles to adhere through H-bonds between the surface silanols groups. Such particle–particle bonds lead to gel formation. Examples of these liquids include end-capped oligoethers, higher *n*-alkanols, and cyclic carbonates.

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