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Colloidal Interaction in Ionic Liquids: Effects of Ionic Structures and Surface Chemistry on Rheology of Silica Colloidal Dispersions

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To understand the important factors that dominate colloidal stability in ionic liquids (ILs), rheology of the dispersions of hydrophilic and hydrophobic silica nanoparticles were investigated in ILs with different ionic structures. The dispersion of hydrophilic silica nanoparticles in [BF$_4$] anion-based ILs and in an IL containing a hydroxyl group, 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethane sulfonyl)amide ([C$_2$OHmim][NTf$_2$]), showed an intriguing shear thickening response. Nonflocculation of the hydrophilic silica nanoparticles in the [BF$_4$] anion-based ILs and in [C$_2$OHmim][NTf$_2$], where the interparticle electrostatic repulsion appears to be depressed, suggests that an IL-based steric hindrance or solvation force provides an effective repulsive barrier for the colloidal aggregation. On the other hand, the other dispersions presented shear thinning behavior with an increase in shear rates and gelled at relatively low particle concentrations. The elastic modulus (*G*′) of the gels formed by the hydrophilic silica was correlated with the polarity scale, λ_{Cu}, of the ILs, indicating that the silica–IL interactions, especially the silica–anion interactions, appear to affect the rheological behavior, even in flocculated systems. All the ILs used in this study can be solidified by the addition of hydrophobic silica particles. The rheological behavior of the silica colloidal dispersions was strongly affected by the ionic structure of the ILs and the surface structure of the silica particles.

Introduction

Because of various interesting phenomena, including reinforcement, shear thinning, shear thickening, gel formation, and shear-induced sol–gel phase transition, colloidal dispersions play important roles as major components in a wide variety of well-established applications. These distinguished rheological behaviors strongly depend on the internal microstructures of colloidal dispersions (stable dispersions or aggregates) and solid concentrations under equilibrium or shear flow. Indeed, the colloidal stability is influenced by many factors, such as the nature of the dispersion medium and the colloidal surface chemistry of the dispersions.[1] Therefore, it is important to elucidate the dependence of the rheological behaviors of colloidal dispersions on such parameters. There have been many efforts to understand the rheology of colloidal dispersions in various molecular solvents and polymer melts. Khan et al. investigated the rheological properties of dispersions of fumed silica with different surface groups in various polar and nonpolar organic media and low-molecular-weight oligoethers with different end-capping groups.[2] In their systematic studies, they found that the resulting rheological behavior reflected the dispersion state, namely, the colloidal stability and the flocculated structure. Furthermore, they found that hydrogen bonding interaction between surface silanol groups and a dispersion medium leads to a specific enhancement of the colloidal stability. Thus, an investigation of rheological properties offers deep insight into colloidal interactions in dispersions, in addition to their importance in many practical applications.

We are interested in ionic liquids (ILs) as the dispersion media of colloidal particles. ILs are composed entirely of ions and are fluid at ambient conditions. ILs are receiving considerable interest in many fields of chemistry and in the chemical industry because of their unique physicochemical properties, including negligible vapor pressure, nonflammability, and distinguished thermal and chemical stabilities.[3] To understand the nature of ILs as a new class of solvent, the influence of the ionic structure of ILs on various fundamental properties has been intensively studied.[4] Since ILs possess high ionic conductivity and a wide electrochemical potential window, the use of ILs as electrolytes is also an attractive area of research for future electrochemical devices.[5] From the viewpoint of dispersion media for colloidal nanomaterials, a number of studies have reported the use of ILs, including studies on producing functional nanomaterials in ILs,[6] the enhancement of colloidal stability,[7] phase transfer to ILs from other dispersed media,[8] catalytic reaction using metal clusters in ILs,[9] and magnetorheological fluids based on dispersions of magnetic particles in ILs.[10] Additionally, the solidification of ILs using colloidal particles is of great interest in terms of their application as solid electrolytes in IL-based electrochemical

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devices, such as fuel cells, lithium batteries, and dye-sensitized solar cells (DSSCs). For instance, Grätzel et al. reported high-performance DSSCs using a solidified IL electrolyte based on the gelation of an inorganic colloidal dispersion in an IL.[11]

In contrast to these successful applications of ILs combined with nanomaterials, only a few studies have considered the fundamental colloid science in ILs.[12] Despite the highly concentrated ionic character of ILs, where electrostatic repulsion to stabilize colloidal particles normally needs to be suppressed, certain colloidal particles can be dispersed even in the absence of any stabilizers such as surfactants and polymers.[6c,d,13] Such a striking stabilization using ILs have been reported for not only inorganic colloids but also protein solutions.[14] Nevertheless, the details of the colloidal interaction leading to dispersion or aggregation in ILs remain obscure. So far, we have studied colloidal dispersions in ILs by using silica nanoparticles as model colloidal systems, because colloidal silica is the most common nanomaterial with a well-established surface chemistry, and its dispersions have been well explored in various media. On the basis of the Derjaguin−Landau−Verwey−Overbeek (DLVO) theory, which readily explains the qualitative feature of colloidal stability in terms of the interplay of London−van der Waals attraction and electrostatic repulsion, colloidal stability was investigated in various ILs by employing monodispersed silica nanoparticles.[15] From the DLVO estimation, together with practical experiments, it was found that electrostatic charge stabilization was likely to be inefficient due to the extensively high ionic strength of the ILs and the resulting surface-charge screening. Moreover, we also explored rheology, ionic transport, and the microstructure of nanocomposite gels formed by the flocculation of silica nanoparticles in a widely used hydrophobic IL, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)-amide ([C$_2$mim][NTf$_2$]), to present a facile methodology affording highly conductive solid electrolytes and functionalized soft materials.[16] For colloidal interactions, a moderate interparticle repulsion was detected by means of rheology and light scattering measurement, even in the finally flocculated system; a reaction-limited cluster aggregation (RLCA) model was proposed for silica nanoparticles in [C$_2$mim][NTf$_2$].

This study presents the first systematic study on colloidal interaction in ILs. It deals with the dependence of the ionic species of ILs on the rheological behavior of colloidal dispersions, which is relevant to the colloidal stability arising from particle−particle and particle−medium interactions in ILs. Two different silica nanoparticles, with hydrophilic and hydrophobic surfaces, were used as dispersed colloids, and the effects of the surface affinity for various ILs on the rheological response of their dispersions were highlighted. To account for the effects of the solvent nature of ILs, we used solvent polarity parameters and discuss the silica−IL interaction, which dictates the resulting rheological behavior.

Experimental Section

Materials. The two different silica nanoparticles used in this study, Aerosil 200 and Aerosil R104, were kindly supplied by Nippon Aerosil Co., Ltd. Aerosil 200 is a hydrophilic fumed silica with surface silanol (Si−OH) groups, while Aerosil R104 is a hydrophobic fumed silica having methyl (Si−CH$_3$) groups on the surface. The primary particles of both materials are 12 nm in diameter. Each type of silica particle was dried for 24 h in a vacuum oven at 120 °C before use. 1-Ethyl-3-methylimidazolium ethylsulfate ([C$_2$mim]-[EtSO$_4$]) was a gift from Solvent Innovation, GmbH. *N*,*N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate ([DE-ME][BF$_4$]) was generously supplied by Nisshinbo Industries, Inc. 1-Butyl-3-methylimidazolium thiocyanate ([C$_4$mim][SCN]),[17] 1-bu-tyl-3-methylimidazolium dicyanoamide ([C$_4$mim][N(CN)$_2$]),[18] and 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethane sul-fonyl)amide ([C$_2$OHmim][NTf$_2$])[19] were prepared following the procedure reported in the literature, with a slight modification. The synthetic procedures for the other ILs were described in our previous work.[20] The ILs were dried for 24 h at 70 °C under a vacuum condition and stored in a glovebox. The water content of the ILs was determined by Karl Fischer titration using a Mitsubishi Chemical CA-07 moisture meter. The nominal halide content in [C$_2$mim][EtSO$_4$], specified by Solvent Innovation, GmbH, was below 500 ppm, and that in [C$_4$mim][SCN] and [C$_4$mim][N(CN)$_2$] was determined, using ion chromatography, to be below 280 ppm and 50 ppm, respectively. The ion chromatography was carried out at 40 °C on an LC-20ADsp liquid chromatography system (Shimadzu) equipped with a column (Shodex IC NI-424, Showa Denko) and a conductivity detector (CDD-10Avp, Shimadzu). The halide content in the other water-miscible ILs was maintained below the solubility limit of AgCl in water (1.4 mg L^{-1}), which was checked by adding AgNO$_3$ solution. For the water-immiscible ILs, the [NTf$_2$] anion-based ILs and [C$_4$mim][PF$_6$] halides in the aqueous phases in contact with the ILs could not be detected by using the AgNO$_3$ solution. Reichardt's betaine dye was purchased from Aldrich and used as received. [Cu(acac)(tmen)][BPh$_4$] (acac = acetylacetone, tmen = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) was synthesized following a reported procedure.[21]

Preparation of Silica Dispersions in the ILs. The silica nanoparticles (Aerosil 200 and R104) were mixed in 11 different ILs in an argon-filled glovebox. All of the silica particle dispersions in the ILs were prepared by mechanical mixing with a conditioning mixer (AR-250, THINKY, Tokyo) for 10 min to ensure homogeneous mixing, followed by 3 min of degassing to remove air bubbles in the samples. The obtained samples were again dried for 24 h under vacuum with heating at 70 °C prior to use for each rheological measurement.

Measurements. The rheological measurements were performed with a rheometer (Physica MCR301, Anton Paar) under dry air conditions at 25 °C. Two types of cone-and-plate geometries were employed for the measurement: one had a diameter of 25 mm and a cone angle of 2°, and the other had a diameter of 50 mm and a cone angle of 1°. To erase any previous shear histories and allow the samples to establish their equilibrium structures, a steady preshear was applied at a shear rate of 1 s^{-1} for 60 s followed by a 120 s rest period before each dynamic rheological measurement. To determine the linear viscoelastic limit, a dynamic measurement as a function of strain amplitude was conducted before each dynamic frequency sweep measurement. The frequency sweep was performed at constant strain amplitude (typically, 0.1−0.5% strain). For the solvatochromic measurements, UV−vis spectra were recorded with a USB2000 spectrometer (Ocean Optics, Inc.) equipped with a light source (DT-mini, Ocean Optics, Inc.). $E_T(30)$ values were calculated using the

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Table 1. Water Content, Determined by Karl–Fisher Titration, and Viscosity at 25 °C for the ILs Used in This Study

ionic liquid	water content (ppm)	viscosity (mPa s)
[C_2mim][EtSO$_4$]	303	90.2
[C_4mim][CF$_3$SO$_3$]	23	84.4[a]
[C_4mim][CF$_3$CO$_2$]	467	79.6[a]
[C_4mim][N(CN)$_2$]	56	27.8
[C_4mim][SCN]	789	49.5
[C_2mim][BF$_4$]	1240	33.0
[C_4mim][BF$_4$]	119	99.6[a]
[DEME][BF$_4$]	39	218.2
[C_4mim][PF$_6$]	60	249.6[a]
[C_2mim][NTf$_2$]	29	32.6[a]
[C_2OHmim][NTf$_2$]	17	85.5

[a] obtained from our previous study in ref 4b.

equation $E_T(30) = 28591/\lambda_{betaine}$, where $\lambda_{betaine}$ is the maximum absorbance wavelength of Reichardt's betaine dye. The λ_{Cu} values in the ILs were determined from the maximum absorbance wavelength of [Cu(acac)(tmen)][BPh$_4$].

Results and Discussion

Effects of the Ionic Structure of the ILs. All of the ILs used in this study were Newtonian fluids (see Supporting Information (SI), Figure S1). Their viscosities at 25 °C are listed in Table 1, along with their water content, as determined by Karl Fischer titration. It is known that ionic interactions (i.e., electrostatic, van der Waals, and hydrogen-bonding) dominate the macroscopic viscosities of ILs. Further, it has been reported that the temperature dependency of the viscosity of an IL is well described by the Vogel–Fulcher–Tamman equation over a broad range of temperatures.[20,22] Thus, the viscosities of ILs are drastically changed by variations in their ionic structures and temperatures. We performed rheological measurements of the silica colloidal dispersions in different ILs under a constant temperature of 25 °C.

The effects of the ionic species on the rheological behavior of the hydrophilic silica dispersions (Aerosil 200) were studied in different ILs. In both static and dynamic rheology, two distinct characteristic rheological responses were observed. Figure 1 presents the frequency dependence of the dynamic viscoelastic properties of the dispersion in [C_2mim][NTf$_2$] (Figure 1a) and in [C_4mim][BF$_4$] (Figure 1b). As clearly shown in Figure 1a, the dispersion containing 5 wt % of the hydrophilic silica in [C_2mim][NTf$_2$] exhibits a frequency-independent elastic modulus (G') that is higher than its viscous modulus (G'') by 1 order of magnitude; the system behaves as a soft solid (gel). This indicates that the silica particles are colloidally unstable and flocculate into a three-dimensional particulate network in [C_2mim][NTf$_2$]. In contrast, a frequency-dependent viscous response is observed in the dispersion in [C_4mim][BF$_4$] (Figure 1b). The G'' is higher than G' over the entire frequency range with a strong frequency-dependency; the system is characterized as a nonflocculated sol. Such a viscous response in [C_4mim][BF$_4$] suggests that particle aggregation does not occur even in concentrated dispersions containing 15 wt % of the silica nanoparticles. The shear-rate responses of viscosity for the silica dispersions are shown in Figure 2. The apparent viscosity for the dispersion in [C_2mim][NTf$_2$] at low shear rates exhibits extensively high values, which is relevant to the particulate network structure, and decreases with an increase in the shear rate (Figure 2a). Such a shear thinning behavior is derived from the disruption of the interparticle physical bonds of the flocculated silica networks by

shear application. This shear thinning has also been observed in a dispersion of hematite in [C_2mim][EtSO$_4$][23] and in a dispersion of single-walled carbon nanotubes (SWCNTs) in [C_4mim][BF$_4$].[24] Figure 2b shows the steady shear response of the dispersions in [C_4mim][BF$_4$] with different silica concentrations. In contrast to the dispersion of hydrophilic silica in [C_2mim][NTf$_2$] (Figure 2a) and the dispersion of SWCNTs in [C_4mim][BF$_4$],[24] the viscosities of the hydrophilic silica dispersions in [C_4mim][BF$_4$] are relatively insensitive to shear rates, maintaining low values at low shear rates. This suggests the absence of the silica network structure. However, at higher shear rates, a drastic increase in the viscosity is detected with increasing shear rate (shear thickening). The apparent viscosity is enhanced at higher silica concentrations; the viscosity of the 15 wt % dispersion rises by 1 order of magnitude. A similar result has been found for hydrophilic silica dispersed in low molecular weight poly(propylene glycol) (PPG).[25] To investigate the ionic structure in more detail in relation to this distinct difference in the viscoelastic response, rheological measurements of dispersions in ILs with different ionic structures were conducted under steady and oscillatory shear. As shown in Figure 3, we find a similar shear thickening response in the [BF$_4$] anion-based ILs and in [C_2OHmim][NTf$_2$], whereas all of the other dispersions exhibit shear thinning responses (see SI, Figure S2). For shear thickening behavior, an important parameter characterizing the phenomena is the critical shear rate corresponding to the onset of shear thickening. The enhancement of viscosity occurred at the critical shear rate between 10^0 and 10^1 s^{-1} for all of our samples showing shear thickening response (Figures 2b and 3). Moreover, the critical shear rate slightly decreased with an increase in silica content (Figure 2b). These results are fairly consistent with the reported data for hydrophilic silica dispersion in PPG.[25] The agreements suggest that similar phenomena occur in our IL system and the reported PPG system despite completely different solvent natures, i.e., whether ionic or molecular solvent. However, we have not understood well why the viscosity is peaked at a specific shear rate. Oscillatory shear measurements also showed that the systems were characterized as nonflocculated sols in the [BF$_4$] anion-based ILs and in [C_2OHmim][NTf$_2$] (see SI, Figure S4). Thus, both the cationic and anionic structures of ILs have the potential to alter the characteristic rheological properties. We also checked the effects of the water content of the dispersions on the rheological response. In the same colloidal dispersions in ILs, the existence of water may affect the rheology because hygroscopic ILs easily adsorb water. However, it was found that water did not affect the characteristic rheological response (shear thinning or shear thickening) in our systems; the hydrophilic silica dispersion in [C_4mim][BF$_4$] containing water showed a shear thickening response, whereas the dispersion of the considerably hydrated [C_2mim][EtSO$_4$] presented shear thinning behavior and gelation (see SI, Figure S5).

In previous work,[15] we reported that colloidal stabilization based on electrostatic repulsion hardly occurs in ILs, where the composed ions are self-dissociated to a considerable extent. The presence of nonflocculated dispersions in the [BF$_4$] anion-based ILs and in [C_2OHmim][NTf$_2$] implies that other repulsive interactions, such as a steric hindrance and a solvation force[26] derived from the IL itself, play an important role in the inhibition of the particle aggregation leading to the network structure formation in the ILs. Khan et al. reported the shear thickening

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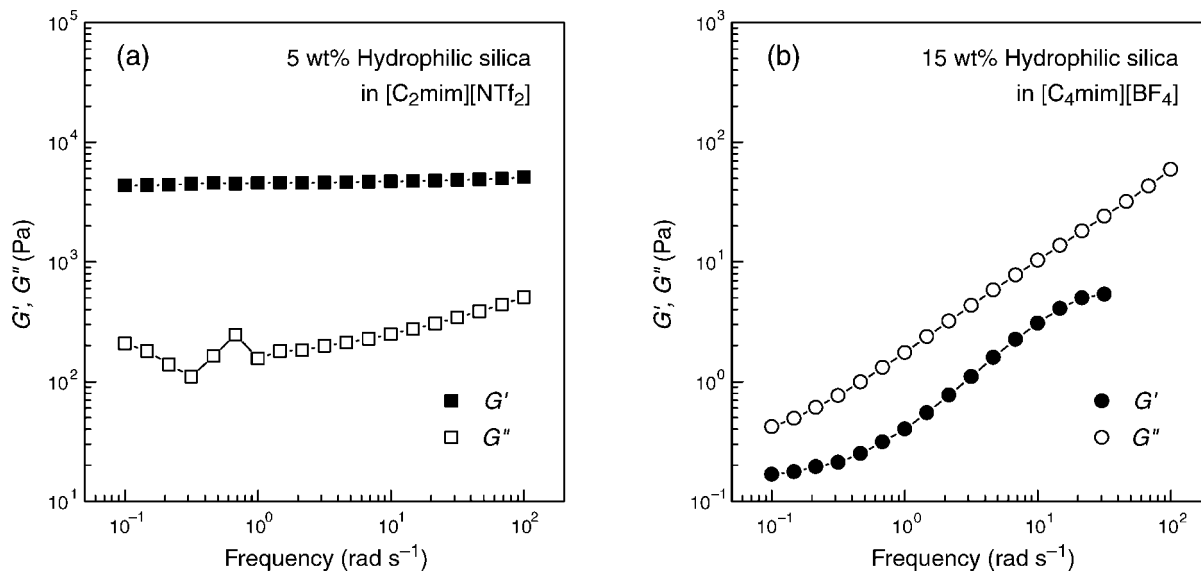
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Figure 1. Dynamic elastic (G') and viscous (G'') moduli as a function of frequency for (a) the dispersion of 5 wt % hydrophilic silica (Aerosil 200) in [C_2mim][NTf$_2$] and (b) the dispersion of 15 wt % hydrophilic silica (Aerosil 200) in [C_4mim][BF$_4$].
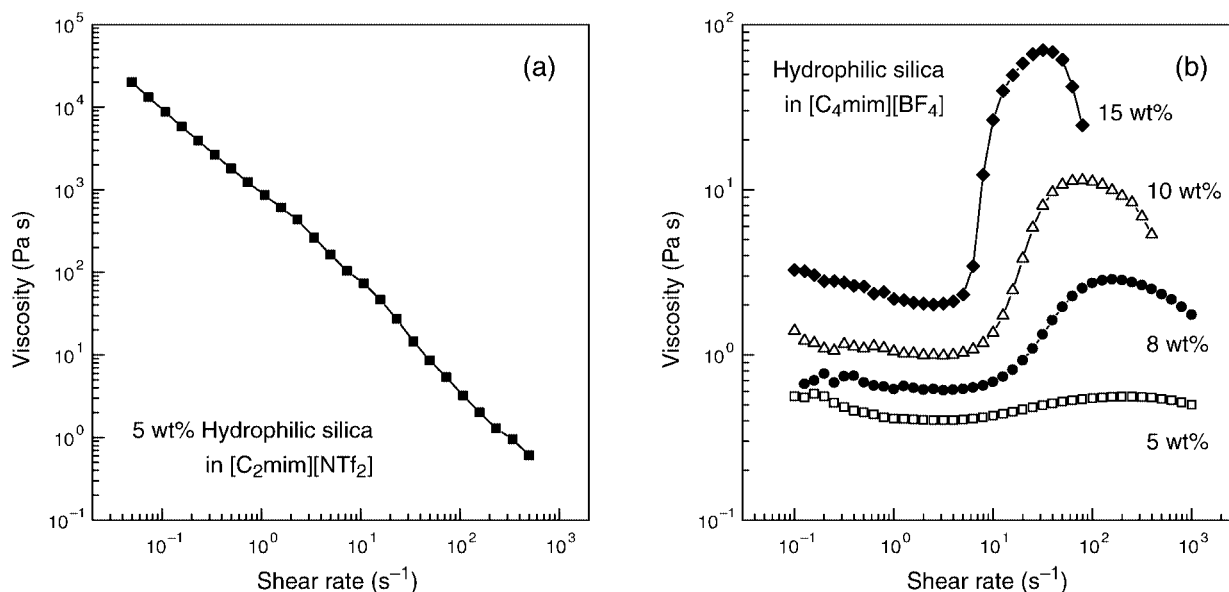

Figure 2. Shear rate dependencies of viscosity for (a) the dispersion of 5 wt % hydrophilic silica (Aerosil 200) in [C_2mim][NTf$_2$] and (b) the dispersions of hydrophilic silica (Aerosil 200) in [C_4mim][BF$_4$] with different silica particle concentrations.

response of nonflocculated hydrophilic-fumed-silica suspensions in poly(ethylene glycol) (PEG) and PPG having OH end-groups and short-chain alcohols, along with a shear thinning response and gelation in PEG with methyl end-groups.[2b] They concluded that hydrogen bonding between the liquid molecules and the surface silanol groups resulted in the formation of a solvation layer on the silica surface, and that this layer gave rise to a repulsive solvation force, which stabilized the silica particles. An atomic force microscopy study,[27] spectroscopy,[28] and dynamic light scattering measurements[29] have also indicated that alcohols can form solvation layers on the silica surface, creating a barrier for particle aggregations. In our case, [C_2OHmim] cations containing OH end-groups may have a strong interaction with

the surface silanol groups through hydrogen bonding. As described later, [C_2OHmim][NTf$_2$] evidently showed a higher hydrogen bond donor ability (i.e., higher $E_T(30)$ value in Table 2) than the other ILs. [BF$_4$] anions may also interact with the hydrophilic silica particles through hydrogen bonding between the F atoms of [BF$_4$] anions and the surface silanol groups. Although we could not detect a hydrogen bonding interaction between [BF$_4$] anions and the silanol groups by spectroscopic measurements, such as Fourier transform infrared (FT-IR) and NMR, such hydrogen bonding interaction was found by the use of FT-IR measurements in a previous report.[30] In agreement with the reported cases of alcohols and oligoethers with OH end-groups,[2b] we believe that solvation layers are formed and that the repulsive solvation force derived from the IL molecules can enhance the colloidal stability of silica particles in the [BF$_4$] anion-based ILs and in [C_2OHmim][NTf$_2$]. Recently, surface solvation in ILs has

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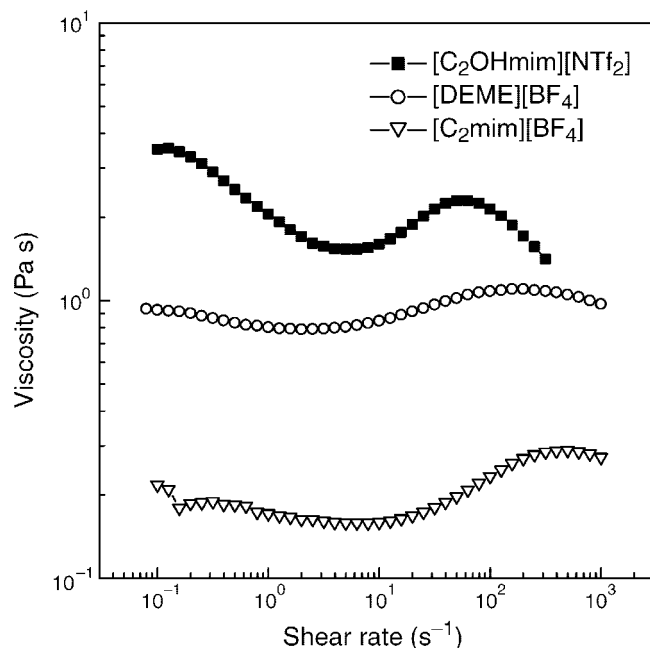
Figure 3. Shear rate dependencies of viscosity for the dispersions of 5 wt % hydrophilic silica (Aerosil 200) in the [BF$_4$] anion-based ILs and in [C$_2$OHmim][NTf$_2$].

Table 2. Solvent Polarity Parameters, E_T(30) and λ_{Cu}, of the ILs

ionic liquid	E_T(30) (kcal mol^{-1})	λ_{Cu} (nm)
[C$_2$mim][EtSO$_4$]	55.6	606
[C$_4$mim][CF$_3$SO$_3$]	51.7[a]	579[a]
[C$_4$mim][CF$_3$CO$_2$]	50.9[a]	638[a]
[C$_4$mim][N(CN)$_2$]	53.9	641
[C$_4$mim][SCN]	55.0	690
[C$_4$mim][BF$_4$]	52.2[a]	540[a]
[DEME][BF$_4$]	49.4	537
[C$_4$mim][PF$_6$]	52.4[a]	517[a]
[C$_2$mim][NTf$_2$]	52.2[a]	547[a]
[C$_2$OHmim][NTf$_2$]	60.8[b]	556

[a] Obtained from our previous study in ref 4b. [b] Obtained from ref 19.

also been reported; repulsive solvation force for protic ILs-silica system has been detected by surface force measurement.[31] Such surface solvation layers of an IL has also been directly confirmed by atomic force microscopy.[32]

Furthermore, we found that the ionic structure of the ILs also affects the properties of flocculated particulate network systems. The resulting solidified samples (nanocomposite gels) showed different frequency-independent elastic moduli (G') when the ionic structure of the ILs was changed, as shown in SI, Figure S3. This frequency-independent G' is the most important meaningful parameter because the plateau G' is a static parameter that is relevant to colloidal interactions in the flocculated systems. Indeed, the G' of the colloidal gels was strongly correlated with the colloidal interaction between particles.[33] Such pair interaction potential was also dependent on the mutual balance between particle−particle and particle−medium interactions. We consider here the particle−medium interaction of the nanocomposite gels by using the polarity parameter of the ILs. The solvent polarities of certain ILs have been estimated from the UV−vis spectra of
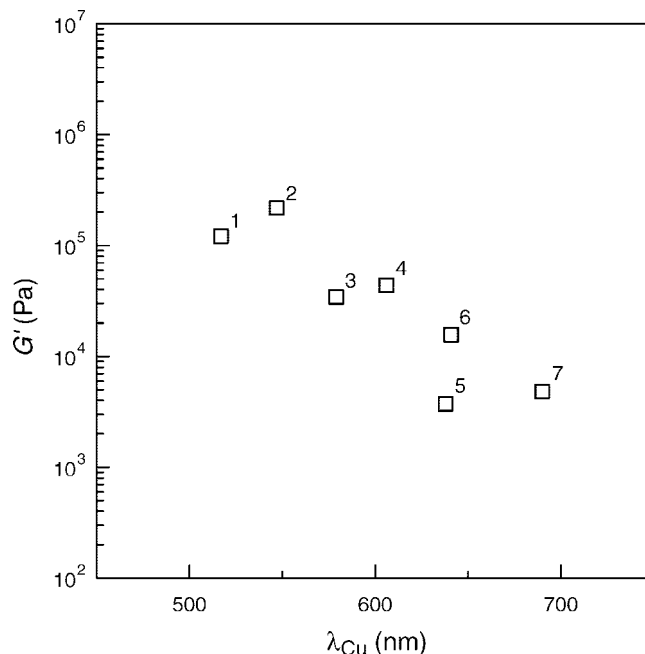

Figure 4. Elastic moduli (G') of the gelled 10 wt % hydrophilic silica (Aerosil 200) dispersions in the ILs as a function of λ_{Cu} for the ILs. The values for G' were obtained at 1 rad s^{-1}. (1) [C$_4$mim][PF$_6$], (2) [C$_2$mim][NTf$_2$], (3) [C$_4$mim][CF$_3$SO$_3$], (4) [C$_2$mim][EtSO$_4$], (5) [C$_4$mim][N(CN)$_2$], (6) [C$_4$mim][CF$_3$CO$_2$], (7) [C$_4$mim][SCN].

solvatochromic probe dyes.[4b,34] Table 2 summarizes the polarity parameters, E_T(30) and λ_{Cu}, of the ILs used in this study. Here, the E_T(30) polarity parameter of the ILs can be correlated with the hydrogen bond donating acidity or Lewis acidity and is commonly sensitive to the cationic structure of an IL, while the λ_{Cu} values of the ILs are linked to the hydrogen bond accepting basicity or Lewis basicity and mainly depend on the anionic structure of an IL. Furthermore, the surface polarity of hydrophilic silica has also been well characterized; hydrophilic silica tends to act as a solid acid (hydrogen bond donor).[35] Interestingly, we find a good correlation between G' and λ_{Cu} in the nanocomposite gels; G' decreases with an increase in the λ_{Cu} value of the ILs (Figure 4), whereas G' is independent of the E_T(30) values of the ILs. In the ILs exhibiting higher λ_{Cu} values (higher Lewis basicity), the silica−silica interaction appears to be more attenuated as a result of the high silica−IL interaction. Consequently, the weaker physical bonds between the silica particles lead to a lower G'. Thus, the G' of the nanocomposite gels can be controlled by altering the interaction between the silica surface and the ILs.

Effects of Silica Surface. To study the effect of silica surface structures on the interaction with the ILs, we performed rheological measurements of the dispersions of methyl-terminated, hydrophobic silica nanoparticles and compared the results with those of the hydrophilic silica dispersions. In addition, the gelation of ILs is essential for the development of IL-based solid electrolytes that exhibit high ionic conductivity and favorable processability. Although certain ILs could not be solidified with hydrophilic silica, gelation successfully occurred in all of the examined ILs by the addition of hydrophobic silica nanoparticles.

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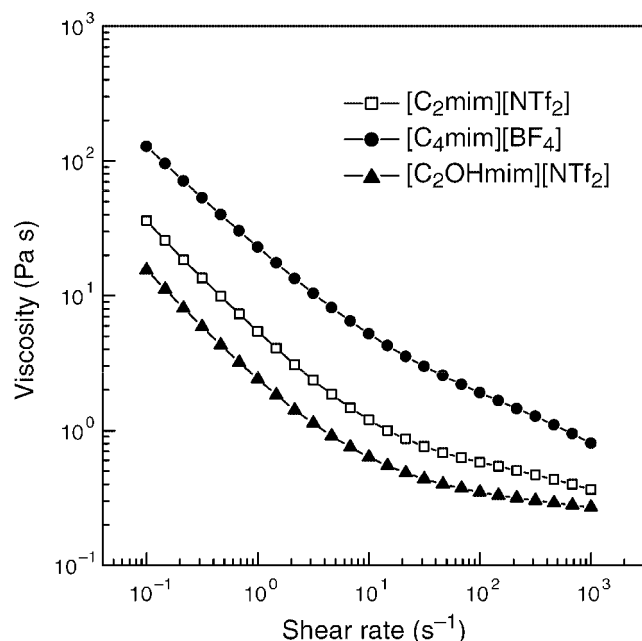
Figure 5. Shear rate dependencies of viscosity for 5 wt % hydrophobic silica (Aerosil R104) dispersions in the ILs.

Figure 5 shows typical results for the shear rate dependency of the apparent viscosity of the hydrophobic silica dispersion in the ILs. In contrast to the results for hydrophilic silica nanoparticles, as shown in Figures 2b and 3, we find that the dispersions exhibit shear thinning responses even in [C$_4$mim][BF$_4$] and [C$_2$OHmim][NTf$_2$], indicating the flocculation of the particles. All of the dispersions in the other examined ILs also exhibited shear thinning behavior (see SI, Figure S6). Although surface modification frequently improves the colloidal stability by steric hindrance,[15] these results suggest that the methyl-substituted surface of the hydrophobic silica has poor affinity for the examined ILs, and that the repulsive interaction is absent between the particles. Moreover, it is also found that the hydrogen bonding between the [BF$_4$] anion and [C$_2$OHmim] cation and the silica surface is attenuated by the surface modification from silanol groups to methyl groups. Dynamic oscillatory shear measurements also clearly show that the dispersions in the ILs behave as soft-solids (gels) formed by the space-spanning silica aggregates, as G' is higher than G'' without a considerable dependence on frequency. Figure 6 shows the typical results for dispersions in [C$_4$mim][BF$_4$] and [C$_2$OHmim][NTf$_2$] containing 5 wt % of the hydrophobic silica nanoparticles. The dynamic responses for the other ILs are shown in SI, Figure S7.

Furthermore, the surface structure of the silica nanoparticles affected the properties of the resulting gels. Figure 7 illustrates the dependence of the frequency-independent gel modulus G' on the particle volume fraction (ϕ) for the nanocomposite gels based on [C$_2$mim][NTf$_2$] and silica nanoparticles with different surface structures. For each surface structure, a power-law scaling relationship is observed ($G' \propto \phi^n$). We find that the exponent of n for the hydrophilic silica ($n = 4.65$)[16] is higher than that for the hydrophobic silica ($n = 3.96$). Moreover, the G' value of the hydrophilic silica is greater than that of the hydrophobic silica dispersions over the entire range of ϕ. These results are indicative of the difference in the strength of the interparticle interaction between the hydrophilic and hydrophobic silica nanoparticles in the IL. For the hydrophilic silica, interparticle hydrogen bonding arising from the surface silanol groups enhances the attractive interaction, whereas only the van der Waals attraction (London's
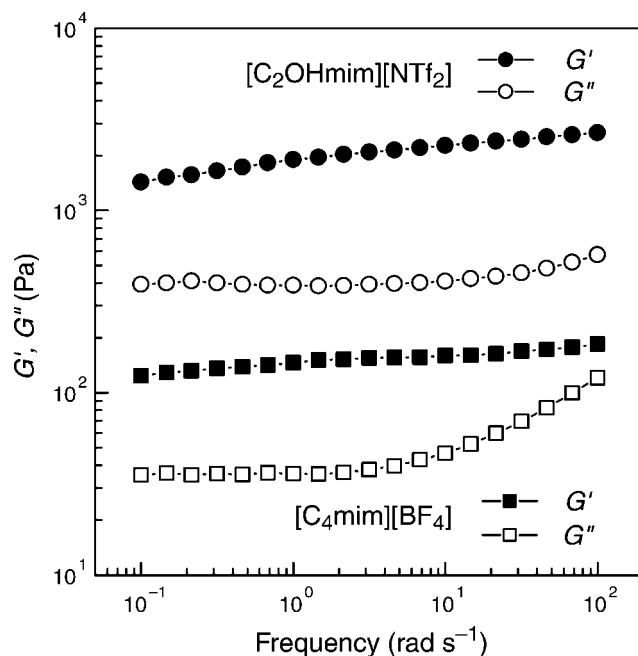

Figure 6. Elastic (G') and viscous (G'') moduli as a function of frequency for the dispersions in [C$_4$mim][BF$_4$] and [C$_2$OHmim][NTf$_2$] containing 5 wt % of the hydrophobic silica (Aerosil R104).
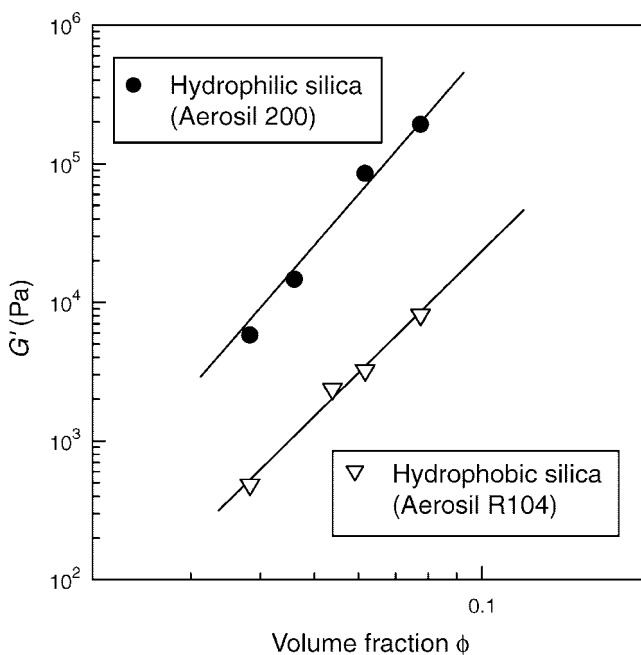

Figure 7. Elastic moduli (G') as a function of the volume fraction (ϕ) of the two different silica particles in [C$_2$mim][NTf$_2$]. The values for G' were obtained at 1 rad s^{-1}.

dispersive force) of the methyl-substituted hydrophobic silica contributes to the interparticle bonds for the formation of the network structures. Thus, the surface structure of the silica also plays a crucial role in determining the resulting rheological responses of the dispersions in the ILs.

Conclusion

The rheological behaviors of hydrophilic and hydrophobic silica colloidal dispersions in various ILs were systematically studied under stationary and oscillatory shear. We demonstrated that characteristic rheological behaviors (e.g., shear thinning,

shear thickening, and gelation), which are commonly presented in typical dispersion systems, could also be observed in the silica colloidal dispersions in the ILs. In particular, for the first time we found shear thickening responses in the nonflocculated dispersions of the hydrophilic silica in the [BF$_4$] anion-based ILs and in [C$_2$OHmim][NTf$_2$]. Moreover, the elastic moduli (G') of the gels caused by the formation of hydrophilic silica networks showed a good correlation with the λ_{Cu} values of the ILs. The rheological behavior of the dispersions was strongly dependent on the ionic structure of the ILs.

The methyl-substituted hydrophobic silica particles successfully solidified all of the examined ILs. This procedure may provide a facile route to the fabrication of highly conductive, IL-based solid electrolytes. The elastic moduli (G') of the gels formed by the hydrophobic silica were lower than those of the gels based on the hydrophilic silica, indicating a difference in the interparticle attraction between the surface silanol and the surface methyl groups in the ILs. Consequently, the surface chemistry of the silica also dominated the rheological behavior in the ILs.

The experimental evidence for the nonflocculated systems observed in the certain ILs raises an interesting possibility that steric hindrance and/or solvation force derived from the IL itself plays an important role in stabilizing colloidal particles in the ILs. The IL-based steric force may be reasonable because the ions of typical IL are usually bulky enough to separate each colloidal surface in the presence of strong binding interaction between the ILs and the colloidal surface. The formation of a protective multilayer composed of supramolecular IL aggregates surrounding metal nanoparticles has been found by Dupont et al.[12a] Such a multilayered IL structure at the colloidal surface may sterically inhibit colloidal aggregation. In our case, two specific ions, [BF$_4$] anion and [C$_2$OHmim] cation, may interact with silica surface through H-bonding. Such a strong binding of the ions to silica surface may give rise to steric hindrance derived from the ions themselves. Another speculated repulsive force, the solvation force, is often observed in aqueous dispersions of

biomolecules and colloids, in which water molecules form the structured hydration layer at the surfaces due to their unusual structure-forming ability through hydrogen bonding.[26] Likewise, ILs are known to be a structure-forming liquid by hydrogen bonding,[36] cation-π,[37] and van der Waals[38] interactions between the ions. It is interesting to note that repulsive solvation force based on ILs has been found on well-defined substrates such as mica, silica, and graphite.[31] We believe that the IL-based solvation force is also effective in stabilizing the colloidal particles in the ILs.

Supporting Information Available: The experimental data from the static and dynamic rheology measurements for the hydrophilic and hydrophobic silica dispersions in the ILs. This material is available free of charge via the Internet at http://pubs.acs.org.

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