

Fullerol ionic fluids

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We report for the first time an ionic fluid based on hydroxylated fullerenes (fullerols). The ionic fluid was synthesized by neutralizing the fully protonated fullerol with an amine terminated polyethylene/polypropylene oxide oligomer (Jeffamine). The ionic fluid was compared to a control synthesized by mixing the partially protonated (sodium form) of the fullerols with the same
10 oligomeric amine in the same ratio as in the ionic fluids (20 wt% fullerol). In the fullerol fluid the ionic bonding significantly perturbs the thermal transitions and melting/crystallization behavior of the amine. In contrast, both the normalized heat of fusion and crystallization of the amine in the control are similar to that of the neat amine consistent with a physical mixture of the fullerols/amine with minimal interactions. In addition to differences in thermal behavior, the fullerol ionic fluid exhibits a complex viscoelastic behavior intermediate between the neat Jeffamine (liquid-like) and the control (solid-like).

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Introduction

Fullerenes are versatile molecules with fascinating chemical, electrochemical, physical and biological properties [1-3]. These properties have made them one of the most studied
20 chemical compounds during the last 20 years. Due to their versatility fullerenes have been used to synthesize supramolecular assemblies^[4], ordered arrays on various substrates^[5] or functional nanocomposites.^[6,7]

In this work, we exploit the functionality and reactivity of
25 hydroxylated fullerenes (fullerols) to synthesize for the first time ionic fluids based on fullerenes. Due to the intrinsic high thermal conductivity of carbon nanomaterials^[8] the new fluids may find application as thermal fluids or lubricants.

Recent work has shown that a new platform of hybrid
30 nanoparticles called nanoparticle ionic materials (NIMs) can be synthesized by attaching a charged molecular corona to a nanoparticle core and balancing the charge with certain counter ions. The concept is similar to molten salts or ionic liquids except that at least one of the building blocks has
35 nanoscale dimensions. Note that NIMs differ from nanoparticles dispersed in ionic liquids in that the presence of ionic interactions between the charged nanoparticles and the counterions result in a homogeneous, one-phase melt rather than previously reported two-phase dispersions of
40 nanoparticles suspended in the ionic liquid^[9]. Nanoparticle fluids based on metals, metal oxides, chalcogenides and carbon nanotubes have been already demonstrated^[10,11].

The first generation of NIMs was based on surface
45 modification of oxide nanoparticles with a quaternary ammonium silane followed by an ion-exchange of the Cl⁻ with a relatively bulky anion. Subsequently we demonstrated a second generation NIMs with reversed charges on the nanoparticle cores and counter ions. In that system propyl sulfonate functionalized nanoparticles (acid) are neutralized
50 with an oligomeric amine (base) to form a salt^[12]. In this paper we report the first solventless fullerene-based fluid with tunable viscoelastic properties. In contrast to previous NIMs, the fullerols do not require a charged molecular corona

attached to the nanoparticle core simplifying the required
55 chemistry. The covalently attached hydroxyl groups of the fullerols react directly with the amine molecules in an acid/base reaction. In addition, we demonstrate that the reaction of the hydroxyl groups on the fullerols with the amine is key to the formation of the ionic fluids, since a
60 physical mixture of the partially protonated (sodium form) of fullerol and amine in the same ratio leads to a material with entirely different thermal, flow and viscoelastic properties.

Experimental part

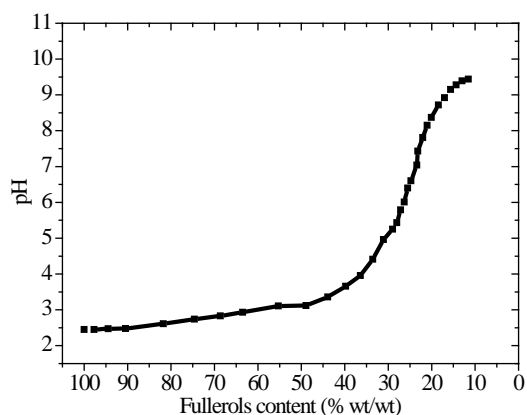
65 **Materials.** Hydroxylated fullerenes (fullerols) with a general formula C₆₀(OH)_x(ONa)_y with y=6-8 and x+y = 24 were purchased from Alfa Aesar. Polyetheramine (monoamine Jeffamine[®] M2070, molecular weight ~ 2000, PDI = 1.06) based on a propylene oxide/ethylene oxide (PO/PE)
70 copolymer backbone was obtained from Huntsmann. The (PO/EO) mol ratio is 10/31. All chemicals were used as received.

The partially protonated fullerol, C₆₀(OH)_x(ONa)_y, is converted first to the fully protonated form using a proton exchange resin.
75 Fluids were prepared by adding dropwise a 5 wt % solution of Jeffamine M-2070 in 18MΩ-cm deionized water to the fullerol solution while closely monitoring the pH. Once the equivalent point of the reaction is established, a series of materials can be synthesized with different fullerol/amine ratios. In this work the
80 pH was brought to 7.8 (slightly above the equivalent point) to ensure full reaction of the hydroxyl groups with the amine. After the reaction the water is removed slowly under vacuum at 60°C for several days to yield a dark-coloured fluid. For comparison a control sample was prepared by mixing the partially protonated
85 C₆₀(OH)_x(ONa)_y directly with Jeffamine 2070 in the same fullerol/amine ratio as in the ionic fluid.

Dynamic light scattering and zeta potential measurements were made at 25 °C using a Malver Zetasizer Nano-ZS. TGA measurements were obtained on a TA Instruments model
90 Q500. UV-Visible spectrum was recorded on a Shimadzu 2100 spectrometer. Rheological measurements were performed at 20°C on a Paar Physica Modular Compact

Rheometer 501 (MCR 501) using a cone and plate geometry with a 25mm diameter plate and 1° cone angle. Differential Scanning Calorimetry (DSC) scans were obtained using a TA Instruments Q1000 equipped with a liquid nitrogen cooling system. All samples were first heated to 100°C at a rate of 10°C/min, then cooled to -90°C and heated back up to 100°C at the same rate.

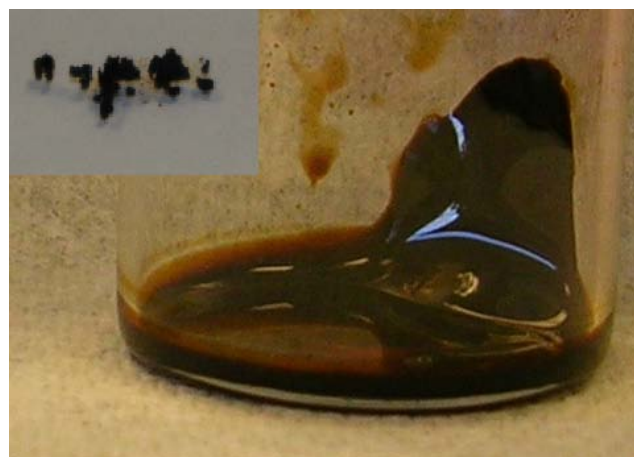
Results and Discussion



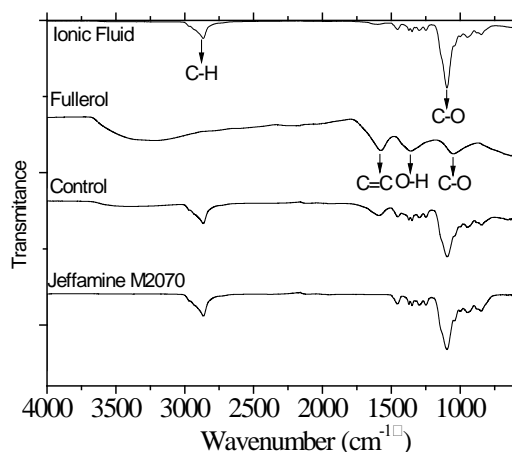
10 **Figure 1.** Titration curve between the oligomeric amine (Jeffamine) and the fully protonated fullerols

The covalently attached hydroxyl groups of the fullerols react with the amine molecules in an acid/base reaction to form the corresponding salt. Due to the electron withdrawing ability of the fullerene cage the hydroxylated fullerols are acidic with a pH of 2.7. A typical titration curve is shown in Figure 1. The pH of the unreacted fullerols starts at 2.7, becomes 7 at the equivalent point and reaches almost 10 when all the fullerol molecules have reacted and excess amine is present. For the purpose of our work the pH was brought slightly above the equivalent point to pH = 7.8 in order to ensure that all the hydroxyl groups have reacted. Thermogravimetric analysis confirms the concentration of the fullerol in the fluid is about 20 wt %. Figure 2 shows that the resulting material is a dark coloured homogeneous fluid. In contrast to the fullerol ionic fluid the control made by mixing the partially protonated form of the fullerol with the amine in the same ratio (20 wt %) appears grainy and solid-like (inset in Figure 2). The high pH of the partially protonated form, $C_{60}(OH)_x(ONa)_y$, prevents any reaction with the amine molecules leading to a physical mixture of fullerols in the amine matrix.

As expected materials prepared at pH below the equivalent point (i.e. systems containing more than 20 wt% fullerol) behave increasingly like gels and solids. Similar behavior was observed when a diamine (Jeffamine XTJ 504, MW~500) was used. In the latter the presence of two bridging amines leads to a material composed of a 3D network of fullerols, which exhibits a solid-like behavior even below the equivalent point.



45 **Figure 2.** Fullerol ionic fluid obtained after neutralizing the fully protonated fullerol with jeffamine and drying the sample at 60 °C for several days in order to completely remove the water. The resulting fullerene ionic fluid is a homogeneous, viscous liquid. Inset: Control sample made by mixing the partially protonated fullerol with the Jeffamine in the same ratio as in the ionic fluid



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Figure 3. FT-IR spectrum of the fullerol ionic fluid, jeffamine, fullerols and control sample

In the following we focus on the fullerol ionic fluid containing 20 wt % fullerol. The FT-IR spectrum of the fullerol ionic fluid contains peaks characteristic of both the fullerol and the oligomeric amine (Figure 3). Note that the broad peak associated with OH groups ($\sim 3400\text{ cm}^{-1}$) is completely absent from the spectrum of the fullerol fluid suggesting complete reaction of OH groups with the amine molecules. The band at $\sim 2920\text{ cm}^{-1}$ is due to the C-H vibrations from the Jeffamine. The relatively small number of terminal ammonium groups present due to the high molecular weight of the Jeffamine makes it difficult to observe them in the FT-IR spectra. Note that the FT-IR spectrum of the control shows a weak absorption due to the hydroxyls, since the high pH of the sample prevents any reaction with the amine

molecules.

Thermogravimetric analysis of the fullerol ionic fluid shows virtually no weight loss up to 150 °C indicating the complete absence of water. Thus, the fluid character is an intrinsic property of the material rather than due to the presence of water or other solvents in the system. TGA also suggests that the material is thermally stable up to about 300 °C.

Light scattering measurements of the fullerol ionic liquid in water show an average particle size of about 5 nm. If we use 1 nm for the size of the fullerol cores and 2.4 nm as the average size of the Jeffamine (radius of gyration of the end-to-end distance of a freely jointed chain) we estimate the size for the undissociated units around 5.8 in excellent agreement with the measured particle size. The light scattering shows that some larger particles with a size around 10 nm are also present suggesting that a limited number of fullerols form small clusters possibly via hydrogen bonding^[12, 13] (Scheme 1) The zeta potential of the fullerol fluid in water is -20 mV. This value is consistent with the presence of negatively charged fullerols and suggests that some dissociation takes place in water.

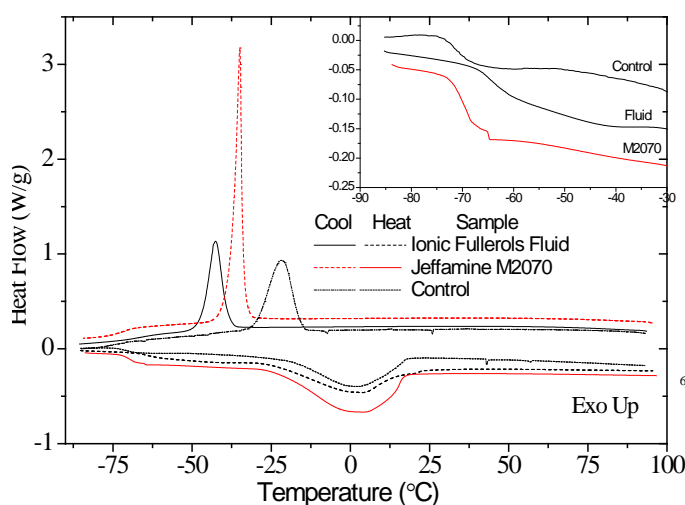


Figure 4. DSC of fullerol ionic liquid, Jeffamine and control. The inset shows the T_g region of the heating curves.

Figure 4 compares the DSC traces of the fullerol fluid, Jeffamine and the control. To eliminate effects from thermal history the second heating cycle is shown. The DSC heating trace for neat Jeffamine shows a T_g at -71 °C and a broad melting transition at 3 °C. The corresponding transitions for the fullerol fluid and control are T_g = -55°C and T_m = 3°C and T_g = -72°C and T_m = 2°C, respectively. The heat of fusion for the fullerol fluid is 41 J/g compared to 64 and 49 J/g for the neat Jeffamine and control, respectively. The T_g of the control is very similar to that of Jeffamine. In contrast the T_g of the fullerol fluid broadens significantly and shifts to -55°C. The crystallization temperature of the fullerol fluid decreases from -35 for the neat Jeffamine to -43°C. The crystallization temperature for the control is -25 °C.

The heat of crystallization for the fluid is 29 J/g compared to 56 and 41 J/g for the neat Jeffamine and control, respectively. Finally the crystallization peak of the neat Jeffamine and the fullerol fluid are much sharper compared to the control suggesting that the former are much more homogeneous compared to the latter. If we account for the lower amount of Jeffamine in the control the normalized heat of fusion and crystallization of the control are similar to the neat Jeffamine. In contrast, the corresponding values for the ionic fluid are much smaller. The results from the thermal analysis are consistent with a physical, two-phase mixture with limited interactions between the fullerol and the amine in the control. In contrast in the fullerol fluid, the presence of ionic bonding perturbs significantly the crystallization behavior of the amine molecules.



Scheme 1. Proposed aggregation of fullerol cores via hydrogen bonding leading to larger particles in the fluid

Dynamic rheological measurements of all samples were performed at 20°C. Figure 5 shows the results of oscillatory shear tests. For the pure Jeffamine only the loss modulus, G'' was observed. At 20°C $G'' \sim \omega$ and the complex viscosity is constant with a value of $|\eta^*| = 0.44 \text{ Pa}\cdot\text{s}$, both of which indicate that the Jeffamine behaves as a simple Newtonian liquid. In contrast, the fullerol fluid shows a very different behavior. First, both the loss, G'' and storage modulus, G' are about two orders of magnitude larger than those for the Jeffamine (Fig.5). Second, $G' \sim \omega^{1.02}$ and $G'' \sim \omega^{0.82}$ are roughly parallel to each other. In addition, the complex viscosity for the fullerol fluid shows some shear thinning. All of these observations are consistent with a change in rheological behavior from a simple liquid for the Jeffamine to a more complex viscoelastic fluid for the fullerol ionic fluid.^[14] The control as expected exhibits a totally different behavior. Both the storage and loss moduli are almost three orders of magnitude higher than those corresponding to the ionic fluid. In addition the storage modulus is higher than the loss modulus. The latter as well as the nearly frequency independent behavior of the moduli suggest a solid-like behavior consistent with the grainy

appearance of the control samples.^[11a]

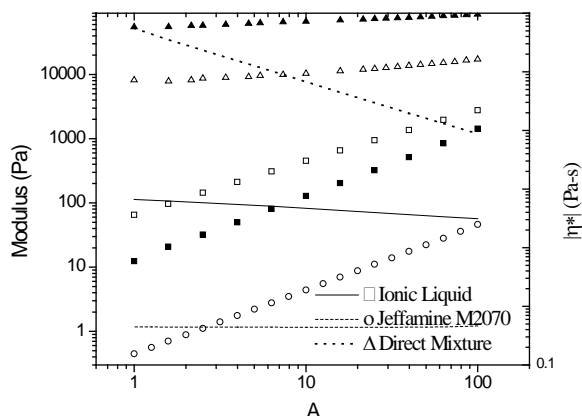


Figure 5. Oscillatory shear data as a function of frequency for the fullerol ionic fluid, Jeffamine, and control. Plot of G' (closed symbols) and G'' (open symbols) for both the fullerol liquid (squares) and Jeffamine M2070 (circles). Also plotted are the values of the complex viscosity for the fullerol liquid (line) and Jeffamine M2070 (dashed line).

In summary, reaction of the fully protonated fullerols with an amine terminated polyethylene/polypropylene oxide oligomer leads to a fullerol ionic fluid. In contrast to previously published nanoparticle ionic fluids, the new system does not require a charged molecular corona attached to the inorganic cores simplifying the required chemistry. The results reported here demonstrate that the reaction of the hydroxyl groups in the fullerols with the oligomeric amine is key to the formation of the fluids, since a control sample of the partially protonated, sodium form of the fullerol and the same amine at a similar fullerol/amine ratio leads to a material with different thermal, flow and viscoelastic properties. First a significant shift and broadening of the T_g of the fullerol fluid compared to the neat amine and control are observed. Also both the normalized heat of fusion and crystallization of the control sample are similar to the neat amine while the corresponding values for the fluid are much smaller. The results from the thermal analysis are consistent with a physical, two-phase mixture with limited interactions between the fullerol and the amine in the control. In contrast, the presence of ionic bonding in the fullerol ionic fluid perturbs significantly the crystallization behavior of the amine. Dynamic rheological measurements for the fullerol ionic fluid reveal a complex viscoelastic behavior intermediate between the neat jeffamine (liquid-like) and the control (gel or solid-like).

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Notes and references

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