Formation of Giant Solvation Shells around Fulleride Anions in Liquid Ammonia

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One of the greatest challenges of fullerene science is the low solubility of these molecules in most common solvents and their tendency to form fractal aggregates in solution.[1−3] This limits our ability to manipulate fullerenes and their derivatives and restricts their characterization by solution techniques. A detailed understanding of fullerene solvation is required in order to separate the different fullerenes from each other and from their precursors. Indeed, a major breakthrough for experimental fullerene science was the discovery by Krätschmer et al.[4] that C_{60} is soluble in benzene, to ∼1.5 mg/mL.[1] This allowed workable quantities of C_{60} (fullerite) crystal to be precipitated from solution.

An important alternative route to fulleride dissolution involves metal−ammonia solutions.[5] These liquids contain solvated electrons, which allow us to exploit the singular redox chemistry of fullerene in solution via the sequential reduction of C_{60} fullerite crystals to soluble C_{60}^{n-} anions ($n = 2-5$).[6,7] In addition to providing a unique arena in which fulleride anions can be studied, concentrated fulleride−metal−ammonia solutions are showing great promise for purification, charge storage, and thin film deposition. Here, we measure the structure of these solutions using advanced neutron scattering techniques. We show intense ordering of the solvent molecules around the C_{60}^{5-} anions, in two well-defined solvation shells. Our results elucidate the intriguing network of hydrogen bonds in the solvent, which permits the attainment of high concentrations of monodisperse solvent separated fulleride anions.

Our experiment uses neutron diffraction in conjunction with second-order isotopic substitution[8,9] of deuterium (D) and hydrogen (H) to study the detailed structure of the solution of composition $C_{60}K_5(NH_3)_{250}$. In brief, this technique allows us to separate the various contributions to the overall structure of these complex fluids; see Figure 1.[10−14]

The solution was prepared in situ by condensing anhydrous ammonia gas onto preweighed potassium metal and C_{60} fullerite powder under vacuum conditions at 230 K. The dissolution process takes ∼2 h and results in a color change from blue (solvated electrons) to brick red (solvated fulleride). The raw experimental data were corrected using standard techniques to produce three partial structure factors, $S_{HH}(k)$, $S_{XH}(k)$, and $S_{XX}(k)$, where H refers to hydrogen and X to any other atom (N, C, or K). These functions are shown in Figure 2a. Direct Fourier transform of these partial structure factors yields the composite partial radial distribution functions, $g_{HH}(r)$, $g_{XH}(r)$, and $g_{XX}(r)$, shown in Figure 2b. These average relative density distributions show clearly the intramolecular correlations in ammonia and fulleride, located below 2 Å. However, unambiguous interpretation of intermolecular structure in $g_{XH}(r)$ and $g_{XX}(r)$ is complicated by the mixture of correlations over the relevant length scales.

To interpret our data, we have therefore chosen to use empirical potential structural refinement (EPSR).[10−14] This technique starts with an ensemble of the system (sides >40 Å; containing 8 × C_{60}^{5-}
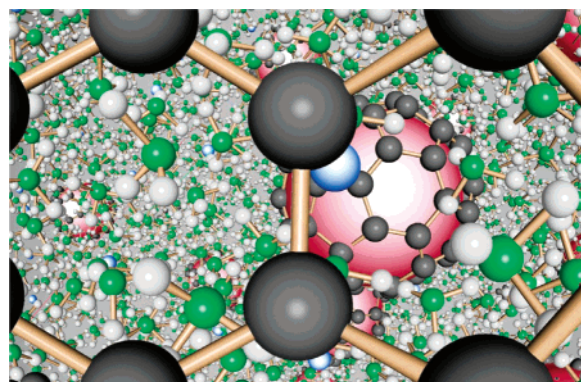

Figure 1. An equilibrium configuration of the solution of composition $C_{60}K_5(NH_3)_{250}$, from EPSR analysis, viewed from "inside" a fulleride. Readers should note that the fulleride anions are solvated and dispersed and that neutron scattering with isotope labeling allows us to separate out the individual contributions to the overall structure of these complex solutions. Key: C_{60}^{5-}, red; K^+, blue; H, light gray; N, green.
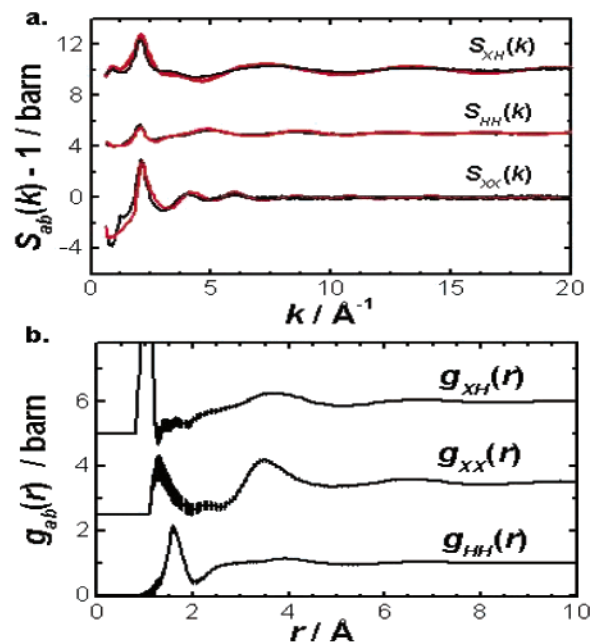
Figure 2. (a) Measured composite partial structure factors, $S_{ab}(k)$, obtained from the second-order difference method in conjunction with hydrogen−deuterium isotopic labeling (black). EPSR ensemble fits are shown in red. (b) Composite partial radial distribution functions, $g_{ab}(r)$, obtained by Fourier inversion of the partial structure factors. Note that intramolecular correlations occur below 2 Å.

anions, 20 K^+ and 2000 NH_3s) which is equilibrated by classical Monte Carlo under pairwise (Lennard-Jones and Coulomb) seed potentials.[15,16] Then, an iterative procedure is used to refine the
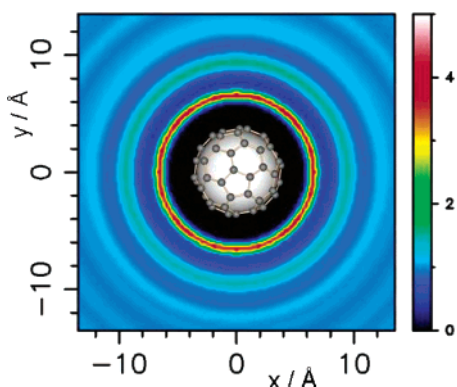
Figure 3. Two-dimensional projection of the solvation of C_{60}^{5-} anions by ammonia. This figure shows the ensemble average relative density of ammonia molecules around a reference fulleride. The C_{60}^{5-} anion is located in the white sphere at the origin. These "giant" solvation shells double the effective radius of the fulleride in solution.

interatomic forces of the ensemble, until the average structure reproduces the diffraction data. From this ensemble, in addition to being able to extract two- and three-dimensional information from our experiments, EPSR enables us to use the known geometry of the C_{60}^{5-} as a probe of the local environment around it. In Figure 3, we show the two-dimensional projection of the average spatial density of ammonia molecules around a reference fulleride anion. These data immediately reveal a dense spherical first solvation shell of ammonia at a distance of 5.5−7.5 Å from the center of the C_{60}^{5-} anion (cage diameter 3.54 Å). Beyond this, there exists a second solvation shell at a distance of 8.5−10.5 Å.

The average coordination numbers within the first and second solvation shells are approximately 45 and 80 ammonias, respectively. The question is then the following: how are these solvent molecules oriented; for example, do they form hydrogen bonds to the fulleride anion?

Analysis of the EPSR ensemble enables us to extract all the individual site−site radial distribution functions for the atomic pair correlations in our system, including the center of mass of the C_{60}. We find an average of one hydrogen atom per ammonia molecule is directed toward the center of the C_{60}^{5-} in the first solvation shell. At first sight, this number may seem surprisingly small, since the anion is highly charged. However, by adopting this orientation, the ammonia molecules are then able to complete hydrogen bonds within and across the solvation shells, to form clathrate-like configurations. The average nearest-neighbor C···H and C60···H (center of mass) distances are 2.60 and 5.80 Å, respectively. When we recall that the fulleride cage radius is 3.54 Å, we conclude that the ammonia molecules are typically located over the pentagonal and hexagonal rings to form an N−H···π hydrogen bond. These unusually short C···H distances are consistent with those observed in solid $(ND_3)_8Na_2C_{60}$ and $(ND_3)_xNaRb_2C_{60}$, where the ammonia molecules are shared between fulleride and metal ions.[17,18]

By analyzing the N−H radial distribution function in our solutions, we calculate that on average approximately 1.6 N−H···N hydrogen bonds are formed from each nitrogen atom. However, when we include hydrogen bonds to π-orbitals and discount ammonia molecules solvated to potassium ions, we find 2.0 hydrogen bonds per molecule. This figure is identical to that found

in bulk ammonia.[19] We conclude that the fulleride anions are accommodated within an ammonia matrix whose hydrogen bonding is relatively unperturbed from that in the bulk.

Our EPSR analysis also yields the radial distribution functions centered on the potassium ions. We find that the cations are solvated by approximately six ammonia molecules, at an average distance of around 2.87 Å. This is consistent with the solvation observed in bulk metal−ammonia solutions and therefore gives us confidence in our analysis.[20] However, we caution here that the weighting of the K−N and K−D correlations is very small in our data.

To summarize, we show that ammonia strongly solvates C_{60}^{5-} via the formation of two distinct "giant" solvation shells. The formation of these shells doubles the effective radius of the fulleride and therefore provides a unique opportunity to disperse, manipulate, and process these molecules and their derivatives in solution. Our results also demonstrate how wide-angle neutron diffraction techniques can be used to measure solvent ordering around a large ion in a polar solvent.

Supporting Information Available: More information on the techniques of EPSR and isotopic substitution and a table showing neutron weighting coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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