Unexpected Size of [60]Fullerene in Solution

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[60]Fullerene has a smaller apparent size in solution than in the solid phase.

The only experimental knowledge we have today about the size of C_{60} in the condensed phase comes from its X-ray and neutron diffraction crystal structure determination.[1–5] Given the experimental face-centred cubic structure of solid C_{60} at room temperature, one calculates a van der Waals molar volume of 317 cm^3 mol^{-1} from the mean centre-to-centre distance between two adjacent C_{60} units, and a molar volume of 429 cm^3 mol^{-1} from the dimensions and the number of molecules in the crystallographic unit cell. The excess of the molar volume over that of van der Waals represents the empty volume which conforms with the general pattern of closed-packed spheres displayed by the fcc arrangement of the C_{60} molecules.

The proportion of free volume in a solid or in a liquid depends on the shape of the molecules and how well they fit together. A rule of thumb states that the proportion of empty volume is increased during the melting process by 10–15%, and is further increased with any temperature elevation. Examples of such increases are seen in the 13% expansion of the liquid molar volume (97.1, 108.8, 123.5, 144 cm^3 mol^{-1}) over their solid counterparts (86.1, 96.1, 108.8, 127.3 cm^3 mol^{-1}) for the pseudo-spherical molecules CCl_4, cyclohexane, naphthalene and adamantane, respectively. It is interesting to note that, like C_{60}, CCl_4, cyclohexane and adamantane adopt face-centred cubic crystal structures.[6–8] Accordingly, one could predict the molar volume of liquid C_{60} to be *ca.* 480 cm^3 mol^{-1}.

Regarding the molar volume of liquid C_{60} either in pure phase or in solution, no experimental data are available to date in the literature. We thus propose to fill the gap by reporting its limiting partial molar volumes in two solvents differing in both their physico-chemical nature and their solubilizing capacity,[9] *i.e. cis*-decalin and 1,2-dichlorobenzene.

In these solvents, the partial molar volumes of C_{60} at infinite dilution, obtained from high-precision density measurements of solutions of decreasing concentration, are respectively, 401 and 389 cm^3 mol^{-1}. For each solvent tested, at least 5–8 solution samples of decreasing mass fraction ranging from 3.0×10^{-3} to 3.0×10^{-4} were prepared by successive addition of a known quantity of a stock solution to a known quantity of solvent. The addition was carried by mass.

High-precision densitometric measurements were carried out at 25.0 ± 0.01 °C on a DMA-58 vibrating tube density meter capable of precision to within $\pm 1\ 10^{-5}$ g cm^{-3}. Full details concerning the materials and the experimental procedure will be discussed elsewhere.

The results (average of triplicate measurements) clearly show that C_{60} behaves differently from one solvent to another. However, beyond the particular values of the partial molar volume, the most surprising result lies in the fact that these values not only are far smaller than the estimated molar volume of liquid C_{60}, but even remain *ca.* 10% lower than the molar volume of the pure solid C_{60}. This constitutes a surprising result with respect to the above mentioned behaviour of almost all organic substances whose molar volume normally increases by *ca.* 10% when passing from pure solid to the liquid state.

Furthermore, the observed values appear to be unusual if one considers that in solvents in which there is little or no complex formation or ionization of the solute, mixing is generally attended by a small contraction or expansion of the liquid solute. For instance, the molar solution volumes of the globular cyclohexane and adamantane molecules at infinite dilution in n-hexane (108.6, 136.9 cm^3 mol^{-1}), in n-dodecane (110.3, 141.3 cm^3 mol^{-1}), and in CCl_4 (110.5, 140.1 cm^3 mol^{-1}) solutions[10] at 25 °C are almost identical with their volumes as pure liquids.[11]

The question is thus: why does C_{60} present a behaviour different than that of most organic crystals, and in particular of solids of pseudo-spherical shape? What could be the reason for the lowering of the molar volume of C_{60} accompanying the formation of dilute solutions?

In the absence of clear evidence for strong charge-transfer complex formation (the solutions are magenta with both solvents used), the explanation should probably be sought from the arrangement of the C_{60} molecules in the solid state itself. In the solid state, both the high symmetry of the buckyball C_{60} molecule surrounded by a spherical shell of π-electrons and the symetrical arrangement of the molecules within the crystal (each molecule has twelve crystallographically equivalent nearest neighbours in a cubooctahedral environment) prevent the molecules from coming close together. The repulsion between the π-electron clouds in all directions of the space constrains the molecules to remain apart from each other at relatively long fixed equilibrium distances.

In contrast, a solution consists of a collection of molecules which are in constant motion. In liquid phase, the molecules do not have to arrange themselves in order to reduce the repulsive interactions simultaneously in the three dimensions. Moreover, in highly dilute solutions, the solute molecules are isolated from each other leaving as principal interactions the solute–solvent and solvent–solvent contacts. Depending on the solvent nature, the $C_{60}\cdots$solvent contact distances may then be smaller than the non-bonded distances in pure solid C_{60} thus leading to smaller molar volumes of C_{60} in solution. On the other hand, the $C_{60}\cdots$solvent distances differing from one solvent to another give rise to different values of its partial molar volume. However, a detailed discussion of the solvent dependence of the partial molar volume of C_{60} appears to be premature until more data are available.

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