

Molecular Weight of C₆₀ in Solution by Vapor Pressure Osmometry

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The interpretation of solution-phase voltammetric,^{1,2} ¹³C NMR,^{1,3-5} electronic,²⁻⁶ optical limiting,⁷ and nonlinear optical¹⁸ data on buckminsterfullerene and the implementation of C₆₀'s chemical reactions^{1,9-11} depend in part on a knowledge of its effective molecular weight, i.e., its monomeric, dimeric, etc., nature in solution. Aggregates of C₆₀ in benzene have been observed, as evidenced by a leveling off of the concentration dependence of the square of the third-order nonlinear optical susceptibility.⁸ The effective molecular weight in solution is related also to the report that C₆₀ aggregates may form upon transfer of a 1:1 mol: mol Langmuir-Blodgett film of C₆₀:1-octadecanol.¹² Yet to date no measure of the solution molecular weight of this remarkable molecule has appeared. We now present vapor pressure osmometry data which has been collected in two aromatic solvents and analyzed to yield the molecular weight of C₆₀ in liquid solution.

Buckminsterfullerene was obtained from SES Research, Houston, TX. It was purified by dissolution in toluene, filtration through a fritted glass funnel, evaporation of the solvent, and drying overnight at 150 °C under dynamic vacuum. The purity of the resulting material was verified by mass spectrometry, which revealed neither residual solvent nor contamination by C₇₀. The buckminsterfullerene solid was stored under a nitrogen atmosphere using standard Schlenk flasks¹³ or a Vacuum Atmospheres Corp. glovebox. Benzil (C₆H₅COCOC₆H₅, MW 210.23) was obtained from Wescan Instruments, Inc., Santa Clara, CA, and spectrophotometric grade chlorobenzene and toluene were obtained from Aldrich Chemical Co. Weighing and osmometry were done in air. Vapor pressure osmometry was performed on a Wescan 232A instrument.

A chlorobenzene stock solution containing 1.7 g of C₆₀ per kilogram of solution was prepared gravimetrically. Similarly, the toluene stock solution contained 1.1 g of C₆₀ per kilogram of solution. Expressed in milligrams per milliliter, the concentrations are 1.9 mg mL⁻¹ in chlorobenzene, calculated using the density

of a 0.62 mg mL⁻¹ solution in chlorobenzene,¹⁴ (1.11 g mL⁻¹ at ambient temperature, equal to the solvent density¹⁵), and 0.96 mg mL⁻¹ in toluene, calculated using the density of toluene,¹⁵ assumed to be equal to the solution density. The stock solutions were made as concentrated as conveniently possible, and interestingly enough the concentration in toluene used here (0.96 mg mL⁻¹) is less than half the reported value for a saturated solution (2.15 mg mL⁻¹).^{16,17} The source of the difference has not been determined, but time may be a factor. Solutions in one study¹⁶ were mixed for 5 h, and those here were mixed for a lower period of time. Dilutions of the stock solutions were made gravimetrically.

Vapor pressure osmometry¹⁸ is an application of Raoult's law, one corollary of which is that the vapor pressure lowering is proportional to the mole fraction of the nonvolatile solute. In practical vapor pressure osmometry, vapor pressures are not measured. Instead, the temperature difference caused by balancing the vapor pressures of the solution and pure solvent in a solvent-saturated atmosphere is determined. This temperature difference is directly proportional to the voltage difference ΔV . The number-average molecular weight¹⁹ M_n is determined by extrapolation of a plot of $K/(\Delta V/C)$ to zero concentration, where K is an experimentally determined instrument constant and C is the concentration of solute in grams of solute per kilogram of solution.

In order to provide enough solvent vapor for conveniently fast measurement of a ΔV large enough to be detected in vapor pressure osmometry, solvent vapor pressures between 50 and 400 Torr must be maintained.¹⁸ To achieve this in our systems it was necessary to use temperatures above 25 °C. The operating temperatures were 70 °C in chlorobenzene and 47 °C in toluene.

The purified solid C₆₀ gave the following elemental analysis.²⁰ Anal. (C₆₀N_{0.134}O_{0.020}) C, H, N: calcd, 99.70, 0.00, 0.26; found, 99.68, 0.19, 0.26. This indicates that essentially all of the sample consists of carbon, that very little hydrocarbon material is present (no C-H stretching modes were observed in the FTIR), and that, as expected,²¹ some of the interstitial sites are occupied by N₂ and O₂. No attempt was made to shield the solid from air during the elemental analysis.

Plots²² of $M_n = K/(\Delta V/C)$ vs C are given in Figure 1 for C₆₀ and benzil standard in the two solvents. Least-squares extrapolation to $C = 0$ as indicated gives the number-average molecular weight of C₆₀ as 930 ± 5 g mol⁻¹ in chlorobenzene and 700 ± 10 g mol⁻¹ in toluene. The errors represent the probable error of the intercept,²³ and it should be noted that the concentrations used are at the low end of the recommended values. Precision is an important issue, especially with regard to the chlorobenzene value. Two standard runs were done in chlorobenzene, two standard runs in toluene, four C₆₀ runs in chlorobenzene, and two C₆₀ runs in toluene. The best standard run and the best C₆₀ run in each solvent was chosen, and the standard used with each C₆₀ was done close in time to the C₆₀. No great variation in the standard runs within a given solvent was observed, and all four C₆₀/

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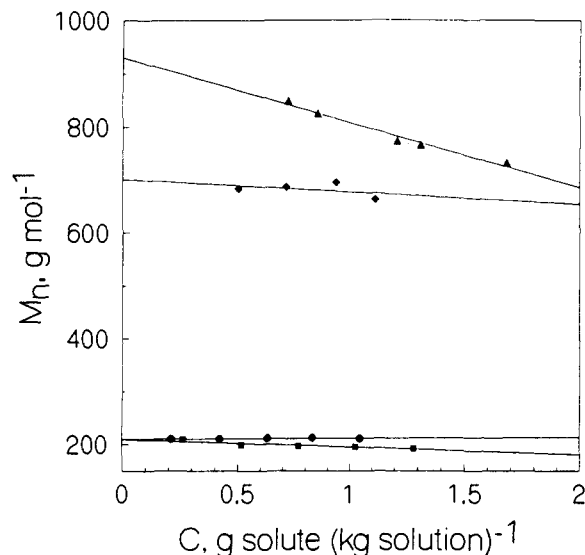


Figure 1. $M_n = K/(\Delta V/C)_0$ vs concentration of solute from vapor pressure osmometry: \blacktriangle , C_{60} in chlorobenzene; \blacklozenge , C_{60} in toluene; \bullet , benzil in chlorobenzene; \blacksquare , benzil in toluene. The lines are least-squares fits. Benzil is a vapor pressure osmometry standard with a molecular weight of 210.23 g mol^{-1} .

chlorobenzene runs gave significantly elevated M_n values. There was one good C_{60} /toluene run, and the other was discounted due to instrumental problems. The least-squares fit for benzil in chlorobenzene is

$$M_n = 1.355C + 210.2$$

and for benzil in toluene is

$$M_n = -14.67C + 209.9$$

It is obvious from Figure 1 that buckminsterfullerene behaves differently in chlorobenzene and toluene, while the standard is virtually identical in both solvents. The difference is not due to a batch problem since the same C_{60} batch was used for all runs.

The addition of two chlorobenzene molecules to C_{60} gives a complex with a molecular weight close to the observed value of 930. Such a complex would not, however, be detectable by vapor pressure osmometry. The buckminsterfullerene was weighed dry, before exposure to solvent, and C in the above expression is derived from this weight. The ΔV value would also be unaffected, since vapor pressure lowering is a colligative²⁴ property and the number of solute particles (molecules or complexes) would not change.

The number of noncomplexed solvent molecules in the case of addition of two chlorobenzene molecules would be essentially constant due to the dilute nature of the solutions. Thus the difference in molecular weight is not due to complex formation with chlorobenzene.

Since the vapor pressure osmometer used here is a calorimetric device, the appearance of extraneous heat will affect the experimental molecular weights. Examination of the above expression for M_n reveals that for monomeric C_{60} ($M_n = 720 \text{ g mol}^{-1}$) to appear to have a molecular weight of 930, an endothermic reaction must occur, i.e., ΔV must be lower. The $^1\text{H NMR}$ of the system was examined in order to investigate this possibility. Spectra at 294–5 K were collected in chlorobenzene with external deuteriochloroform lock and external tetramethylsilane on a Bruker AC 250 instrument. Spectra of chlorobenzene, a concentrated C_{60} solution in chlorobenzene at 0.9 h, and the same C_{60} sample at 23.5 h are all essentially identical. Reaction of C_{60} with a protio species or catalysis by C_{60} of a reaction of chlorobenzene would be expected to produce compounds visible in the $^1\text{H NMR}$. For example, catalysis of a reaction producing biphenyl would produce resonances in the δ 7.3–7.7 region.²⁵ No extraneous peaks were in evidence.

It is tempting, therefore, to attribute the difference between chlorobenzene and toluene to a small amount of dimerization in chlorobenzene. An M_n value of 930 would correspond to a sample containing, on average, 0.71 mol of monomers for every 0.29 mol of dimers. This finding is surprising, however, even in the light of previous observations,^{8,12} and must necessarily be viewed with caution. We have observed chlorobenzene to be a better room temperature solvent for C_{60} than toluene,^{16,17} and more solvating power is associated with decreasing, not increasing, formation of solute dimers, and yet the better solvent has the higher M_n . It is possible that the elevated value may be due to the temperature dependence of the solubility¹⁷ of C_{60} .

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