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# Changes of Molar Volume from Solid to Liquid and Solution: The Particular Case of $C_{60}$

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**Abstract:** Partial molar volumes of solid $C_{60}$ at infinite dilution have been determined from high precision density measurements in 12 organic solvents characterized by different physicochemical properties and solubilizing capacity. Results appear unusual with respect to almost all organic solid substances in that not only are the values far smaller than the estimated molar volume of liquid $C_{60}$ but they even remain lower than the molar volume of the pure solid $C_{60}$. The results which range from 350 to 440 $cm^3\ mol^{-1}$ reveal the non-uniform behavior of this remarkable rigid molecule in solution. Although no readily obvious relationship between the partial molar volumes of $C_{60}$ in a particular solvent and properties of the solvent has been found, the observed rough dependence on the molar volume of the solvent might be interpreted in terms of the arrangement of the molecules differing in size and shape, and how they fit together in solution.

## Introduction

In a recent paper,[1] Adams et al. asked the following question about the size of fullerenes "How big are these molecules?" To deal with this problem, they calculated the van der Waals (vdW) surface areas and volumes of carbon fullerene molecules ranging from $C_{20}$ to $C_{240}$. Using coordinates derived from quantum-molecular-dynamics relaxation calculations of the equilibrium geometry, they determined two limit values of the van der Waals volume, i.e., 450 and 548 Å$^3$ for $C_{60}$ in particular. These extremes were obtained from the consideration of two different arrangements of the molecules in the solid state giving rise to a minimum (1.47 Å) and a maximum (1.76 Å) of the vdW radius of the individual carbon atoms. In fact, as far as solid $C_{60}$ is concerned, three types of volume can be calculated from its X-ray or electron-diffraction crystal structure determination.[2−11] First of all, assuming that the $C_{60}$ molecules are behaving approximately as spheres, a volume of 187 Å$^3$ is obtained from the mean atom-to-atom diameter (7.1 Å) of the $C_{60}$ molecule. This volume corresponds to the internal volume of the hollow sphere. Secondly, considering that, at room temperature, the $C_{60}$ molecules rotate freely and independently of each other (orientational disorder), a second volume amounting to 526 Å$^3$ is calculated from the mean center-to center distance (10.02 Å) between two adjacent $C_{60}$ units. This nearest-neighbor distance can also be observed from surface-area measurements[12−14] of Langmuir films of $C_{60}$, and corresponds to the van der Waals diameter of one $C_{60}$ molecule. The calculated volume therefore represents the van der Waals molecular volume, $V_{vdw}$, of $C_{60}$. Because this calculation considers the molecule as a sphere rather than a truncated icosahedron, the $V_{vdw}$ volume is somewhat greater than the value of 486 Å$^3$ obtained as the sum of 60 van der Waals volume increments of sp$^2$-hybridized carbon atoms (8.1 Å$^3$). Nevertheless, the two latter values fall within the theoretical limits reported by Adams et al. The difference between the van der Waals volume and the carbon cage itself represents the effective volume set by the $\pi$ electron clouds extending outward from each atom of carbon. Finally, from the density ($\rho = 1.678$ g cm$^{-3}$) taken from the X-ray lattice parameters of $C_{60}$ fcc crystal structure and from its molecular weight (720.66 g mol$^{-1}$), the molecular volume, $V$, of $C_{60}$ is calculated to be 712 Å$^3$. A slightly larger value would be obtained from the experimental density[11] ($\rho = 1.65$ g cm$^{-3}$) of solid $C_{60}$ determined by suspending crystal samples in aqueous $GaCl_3$ solutions of known densities. The excess of the molecular volume over the van der Waals volume ($V/V_{vdw} = 1.35$) represents the empty volume, and conforms to the pattern of closed-packed spheres shown by the crystal face-centered-cubic arrangement of the $C_{60}$ molecules. Remember that the van der Waals molecular volume defines the hard volume of the molecule, i.e., the volume from which others but the reference molecule are excluded in thermal collisions, while the molecular volume more efficiently represents the space occupied by one molecule of substance in its solid, liquid, or gas phase. As a

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**Table 1.** Van der Waals, $V_{vdw}$, and Molar, *V*, Volumes of Solids and Liquids

| compound | $V_{vdw}$,[a] $cm^3\ mol^{-1}$ | V,[b] $cm^3\ mol^{-1}$ | $V/V_{vdw}$ | $100(V - V_{vdw})/V$, % |
|---|---|---|---|---|
| solid | | | | |
| methane | 17.11 | 32.34[c] | 1.89 | 47.1 |
| naphthalene | 74.32 | 111.67 | 1.50 | 33.4 |
| *trans*-stilbene | 107.09 | 154.79 | 1.45 | 30.8 |
| camphor | 96.97 | 152.38 | 1.57 | 36.4 |
| benzoic acid | 64.99 | 96.43 | 1.48 | 32.6 |
| cholesterol | 256.64 | 361.98 | 1.41 | 29.1 |
| propionamide | 46.20 | 69.99 | 1.51 | 34.0 |
| urea | 32.89 | 44.93 | 1.37 | 26.8 |
| adipic acid | 80.47 | 107.09 | 1.33 | 24.9 |
| succinimide | 51.32 | 69.93 | 1.36 | 26.6 |
| glycine | 34.93 | 46.92 | 1.34 | 25.5 |
| *m*-aminobenzoic acid | 66.73 | 90.83 | 1.36 | 26.5 |
| glucose | 88.36 | 115.52 | 1.31 | 23.5 |
| fructose | 164.31 | 215.62 | 1.31 | 23.8 |
| liquid | | | | |
| oxygen (-183 °C) | 13.61 | 28.01 | 2.06 | 51.4 |
| nitrogen (-196 °C) | 13.25 | 34.69 | 2.62 | 61.8 |
| carbon disulfide | 31.20 | 60.29 | 1.93 | 48.3 |
| ethane (-100 °C) | 27.34 | 53.36 | 1.95 | 48.8 |
| *n*-pentane | 58.06 | 115.64 | 1.99 | 49.8 |
| *n*-dodecane | 129.74 | 221.65 | 1.71 | 41.5 |
| cyclohexane | 61.43 | 108.05 | 1.76 | 43.1 |
| benzene | 48.42 | 89.50 | 1.85 | 45.9 |
| ammonia (-79 °C) | 13.73 | 20.78 | 1.51 | 33.9 |
| water | 12.41 | 18.01 | 1.45 | 31.1 |
| water (100 °C) | 12.41 | 18.79 | 1.51 | 34.0 |
| methanol | 21.74 | 40.35 | 1.86 | 46.1 |
| *n*-pentanol | 62.70 | 108.17 | 1.73 | 42.0 |
| ethylene glycol | 36.26 | 55.65 | 1.53 | 34.8 |
| glycerol | 53.30 | 73.06 | 1.37 | 27.0 |

[a] Calculated from atomic volume increments of ref 16. [b] Calculated from densities (at 20 °C for solids and 20−25 °C for liquids unless otherwise noted) given in *Handbook of Chemistry and Physics*; Chemical Rubber Co.: Cleveland, 1960, except for methane. [c] Calculated from density at 77 K.

matter of fact, the molecular (molar) volume may be considered to be made up of the sum of the van der Waals volume of one molecule (Avogadro's number *N* of touching molecules) plus a varying amount of empty space which is called the "free volume" or "empty volume". The proportion of free volume in a crystal or in a liquid depends on the shape of the molecules, and how well they fit together or, in the case of a solid, on how the molecules are packed in the crystal. The goodness of fit is generally evaluated by the Kitaigorodski packing coefficient, the values of which lie in the range of 0.65−0.77 for the great majority of organic crystals;[15] a higher value of the coefficient reflects a more efficient occupation of space by the molecules. The closest possible packing of spheres gives a packing density of 0.74, thus meaning that, at 0 K, a crystal made up of closed-packed spheres has only 74% of its total volume occupied by the spheres, and 26% occupied by empty volume so that $V/V_{vdw} = 1.35$. The packing of organic substances in their solid or liquid state is expected to vary from compound to compound as their stability is achieved from the balance between the tendency of the molecules to stay as close as possible and the need to avoid interpenetration. It is obvious that the proportion of empty volume is reduced as the molecules become less spherical and as they become more able of hydrogen bonding which brings the molecules closer to each other. Hence, no simple relation between *V* and $V_{vdw}$ is to be expected. Some examples of the ratio $V/V_{vdw}$ and of the proportion of free volume for solids and liquids are given in Table 1. Reported on a molar scale, the van der Waals and molar volumes of solid $C_{60}$ at room temperature amount respectively to 317 and 429 $cm^3\ mol^{-1}$.

While the solid phase behavior of $C_{60}$ has been extensively studied at both high and low temperatures, there are, to our knowledge, no experimental data either on its melting properties or on its liquid phase behavior. It has even been suggested[17] that $C_{60}$ would have no stable liquid phase. Since, to date, no data are available on the molar volume of liquid $C_{60}$, and since no measure, except those reported in our preliminary work,[18] on the solution partial molar volume of this remarkable molecule has appeared in the literature, we present results of density measurements of dilute solutions of $C_{60}$ dissolved in 12 organic solvents differing in both their physicochemical properties and solubilizing capacity (Table 2), i.e. *n*-hexadecane, *cis*-decaline, benzene, toluene, *o*-xylene, 1,2,4-trimethylbenzene, 1-methylnaphthalene, chlorobenzene, *o*-dichlorobenzene, 1,2,4-trichlorobenzene, 1-chloronaphthalene, and carbon disulfide. It is from now on important to point out that almost all solutions showed similar magenta-purple coloration indicating the absence of any particular specific interaction between $C_{60}$ and a given solvent, except for solutions in naphthalenes exhibiting rather brownish-yellow color. For these particular solvents, the observation of a different coloration would be consistent with the possible formation of charge-transfer complexes between the fullerene and the polycyclic aromatic solvents.[30] Densitometric measurements were analyzed according to the method described by Liron and Cohen[31−32] to yield the limiting partial molar volumes of $C_{60}$ at infinite dilution. Because in highly dilute solutions the solute molecules are essentially isolated from each other, the limiting partial molar volumes encode information not only on the intrinsic molar volume of $C_{60}$ but also on how this molecule with its rigid, well-defined cage structure behaves in solution once surrounded by solvent molecules. These values are of importance in numerous thermodynamic processess, and their knowledge is therefore particularly helpful for rationalizing the extraction, the chromatographic separation, the solubility, and the reactivity of fullerene in different solvent media.

## Experimental Section

**Chemicals.** Buckminsterfullerene $C_{60}$ (99.98 mol·% purity from Strem Chemicals), adamantane (Fluka, mp 269−270 °C; purum,

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**Table 2.** Physicochemical Properties of Pure Solvents and Solubility of $C_{60}$

| solvent | $d^{4}_{20}$, [a] g cm$^{-3}$ | $V$, cm$^3$/mol | $\eta^{20}_{D}$ [a] | PI,[19] eV | $\epsilon^{20-23}$ | $\delta$,[23-24] MPa$^{1/2}$ | $S$,[23,25-27] mg/mL |
|---|---|---|---|---|---|---|---|
| *n*-hexadecane | 0.773 | 292.9 | 1.433 | | 2.06 | 16.4 | 0.15 [b] |
| *cis*-decahydronaphthalene | 0.896 | 154.3 | 1.481 | 9.26 | 2.20 | 18.8 | 2.2 |
| benzene | 0.879 | 88.9 | 1.501 | 9.25 | 2.27 | 18.6 | 1.4−1.9[c] |
| toluene | 0.866 | 106.4 | 1.497 | 8.82 | 2.38 | 18.2 | 2.1 - 3.2[c] |
| *o*-xylene | 0.881 | 120.5 | 1.505 | 8.56 | 2.57 | 18.0 | 5.2−8.7 |
| 1,2,4-trimethylbenzene | 0.876 | 137.2 | 1.505 | 8.27 | 2.38 | 18.3 | 17.9 |
| 1-methylnaphthalene | 1.020 | 139.4 | 1.614 | 7.85 | 2.91 | 21.2 | 33.0−33.2 |
| chlorobenzene | 1.106 | 101.8 | 1.525 | 9.06 | 5.62 | 19.6 | 5.7−7.0 |
| *o*-dichlorobenzene | 1.305 | 112.6 | 1.552 | 9.08 | 9.93 | 20.5 | 24.6 - 27.0 |
| 1,2,4-trichlorobenzene | 1.455 | 124.7 | 1.571 | 9.04 | 3.95 | 19.0 | 8.5−21.3 |
| 1-chloronaphthalene | 1.192 | 136.4 | 1.633 | 8.13 | 5.04 | 20.0 | 51.0 |
| carbon disulfide | 1.263 | 60.3 | 1.627 | 10.07 | 2.64 | 20.5 | 7.9−11.8 |

[a] Given by the supplier. [b] Estimated from ref 28. [c] Letcher et al.[29] report solubility values of 0.89 and 0.54 mg/mL for $C_{60}$ in benzene and toluene at 298.1 K.

>99%), congressane (Aldrich, mp 244−245 °C; 98%), *n*-hexane (Fluka, bp 68−70 °C; puriss. p.a. ACS; >99.5%), *n*-dodecane (Fluka, bp 214−216 °C; puriss. p.a.; >99.8%), *n*-hexadecane (Merck, >99%), *cis*-decahydronaphthalene (Fluka, bp 192−194 °C; purum; >98%), benzene (Fluka, bp 80 °C; puriss. p.a. ACS; >99.5%), toluene (Fluka, bp 110 °C; for UV spectr. ACS; >99.5%), *o*-xylene (Fluka, bp 143−145 °C; puriss. p.a.; >99.5%), 1,2,4-trimethylbenzene (Fluka, bp 167−169 °C; puriss.; ∼99%), 1-methylnaphthalene (Fluka, bp 241−245 °C; pract.; ∼97%, <3% 2-methylnaphthalene), chlorobenzene (Fluka, bp 131−133 °C; puriss. p.a. ACS; >99.5%) *o*-dichlorobenzene (Fluka, bp 179−180 °C; puriss. p.a.; >99%), 1,2,4-trichlorobenzene (Fluka, bp 212−214 °C; puriss.; >99%, <1% 1,2,3-trichlorobenzene), 1-chloronaphthalene (Fluka, bp 117−120 °C; pract.; ∼90%, ∼10% 2-chloronaphthalene), carbon tetrachloride (Fluka, bp 75−78 °C; puriss. p.a. ACS; >99.5%), and carbon disulfide (Fluka, bp 46 °C; puriss. p.a. ACS; >99.5%) were used as received without any further purification.

**Apparatus and Procedure**. For most solvents tested, at least 5−10 solution samples of decreasing mass fraction were prepared by successive addition of a known amount of a stock solution to a known quantity of solvent. The addition is carried out by weighing with a precision of $\pm 10^{-5}$ g. The stock solution of $C_{60}$ in a particular solvent is prepared, in a stoppered glass vessel, by adding a known mass of solvent to a weighed amount of pure solute such that the concentration of the resulting solution remains lower than the reported solubility of $C_{60}$ in the given solvent. Prior to proceeding to the higher dilutions, the stock solution is sonicated for 15 min to ensure complete dissolution and stirred overnight in the dark by means of a Teflon-coated magnetic stirring bar in a water bath thermostated at 25.0 ± 0.5 °C to achieve equilibration. The results are the same whether the solution of $C_{60}$ was stirred for 24 or 48 h. Due to the high volatility of carbon disulfide, each graded sample is prepared in this case by direct weighing of varying amounts of solvent and $C_{60}$.

The partial molar volumes of $C_{60}$ at infinite dilution, $\overline{V^{\infty}_{C_{60}}}$, are determined from high-precision density measurements carried out at 25.00 ± 0.01 °C on a DMA-58 vibrating tube density meter (Anton Paar, A-8054 Graz, Austria), capable of a precision reproducible to within $\pm 1\ 10^{-5}$ g cm$^{-3}$. Before each series of measurements, the apparatus is calibrated at atmospheric pressure with distilled water and dry air whose densities were taken from the literature.[33,34]

The specific volume, $V_S$, the reciprocal of density, of a series of diluted solutions containing the same solvent, is plotted against the $C_{60}$ mass fraction, $m_{C_{60}}$, in the respective solutions. As, for all samples studied, the solute mass fraction is smaller than 0.01, the obtained curves are essentially linear. This results from the fact that, in dilute solution, the partial specific volume of the solvent equals the specific volume of the pure solvent, and that the partial specific volume of the solute does not change noticeably over the concentration range considered. The corresponding plots can thus all be described by a linear equation:

$$V_S = a + bm_{C_{60}} \qquad (1)$$

The intercept represents the partial specific volume of the solvent, $\overline{V^{\infty}_{SSolv}}$, at infinite dilution, whereas the partial specific volume of $C_{60}$, $\overline{V^{\infty}_{SC_{60}}}$, is obtained from the sum of both the intercept and the slope of the curve. Curve fitting was performed by linear least-squares regression analysis using the SPSS program. Finally, the product of the specific volume of $C_{60}$ by its molecular weight ($MW_{C_{60}} = 720.66$ D) gives the desired partial molar volume according to eq 2.

$$\overline{V^{\infty}_{C_{60}}} = \overline{V^{\infty}_{SC_{60}}} MW_{C_{60}} \qquad (2)$$

For each solvent, the whole process is repeated at least three times (except for *n*-hexadecane in which the solubility of $C_{60}$ is extremely small; accordingly, the corresponding results must be considered with great caution).

## Results and Discussion

The limiting partial molar volume, $\overline{V^{\infty}_{C_{60}}}$, of $C_{60}$ obtained by linear extrapolation of the experimental specific volumes to a solute mass fraction of 1 (95% confidence interval) together with the determination coefficient, $r^2$, of the linear regression and the number of observations, $n$, used in the regression are gathered in Table 3. The table also reports the initial amounts of fullerene weighed to prepare the stock solutions as well as the corrsponding $C_{60}$ concentration. Typical examples of the

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**Table 3.** Partial Molar Volumes, $\overline{V_{C_{60}}^{\infty}}$, of $C_{60}$ at Infinite Dilution at 25 °C

| solvent | assay | stock solution[a] | | sample mass fraction range ($10^4$) | $n$ | $\overline{V_{C_{60}}^{\infty}}$ cm$^3$ mol$^{-1}$ | $r^2$ |
|---|---|---|---|---|---|---|---|
| | | $w(C_{60})$, mg | cc($C_{60}$), mg/mL | | | | |
| n-hexadecane | 1 | 8.70 | 0.13 | 1.71−0.45 | 4 | 438.4 ± 67.3 | 0.98937 |
| | 2 | 1.53 | 0.13 | 1.72−0.52 | 3 | 436.8 ± 477.7 | 0.99436 |
| *cis*-decahydronapthalene | 1 | 14.93 | 1.52 | 14.44−4.23 | 6 | 404.1 ± 7.8 | 0.99981 |
| | 2 | 13.95 | 1.20 | 13.40−3.50 | 8 | 400.9 ± 12.9 | 0.99900 |
| | 3 | 14.22 | 1.28 | 14.36−3.21 | 7 | 399.7 ± 10.5 | 0.99950 |
| benzene | 1 | 11.63 | 1.02 | 11.63−1.63 | 11 | 355.9 ± 6.5 | 0.99966 |
| | 2 | 10.68 | 0.78 | 8.94−0.92 | 9 | 356.1 ± 9.7 | 0.99946 |
| | 3 | 12.71 | 1.13 | 12.90−1.94 | 8 | 362.5 ± 16.9 | 0.99867 |
| toluene | 1 | 13.76 | 1.97 | 22.72−4.64 | 7 | 361.2 ± 8.3 | 0.99977 |
| | 2 | 14.02 | 1.51 | 17.45−2.63 | 8 | 370.0 ± 6.3 | 0.99982 |
| | 3 | 11.36 | 0.89 | 9.27−2.79 | 6 | 363.8 ± 12.0 | 0.99966 |
| | 4 | 11.52 | 0.90 | 10.43−1.43 | 7 | 358.3 ± 9.2 | 0.99972 |
| | 5 | 10.33 | 0.87 | 10.09−2.72 | 6 | 364.4 ± 19.4 | 0.99912 |
| *o*-xylene | 1 | 14.51 | 2.32 | 26.57−3.08 | 8 | 377.9 ± 4.7 | 0.99989 |
| | 2 | 15.46 | 2.77 | 31.68−4.04 | 8 | 372.5 ± 3.9 | 0.99993 |
| | 3 | 23.07 | 2.36 | 26.86−3.68 | 8 | 384.2 ± 16.1 | 0.99866 |
| | 4 | 20.29 | 2.05 | 23.48−4.66 | 8 | 381.2 ± 6.3 | 0.99979 |
| 1,2,4-trimethylbenzene | 1 | 16.10 | 2.89 | 33.05−3.12 | 9 | 365.7 ± 8.3 | 0.99959 |
| | 2 | 15.27 | 2.50 | 28.63−2.67 | 9 | 373.8 ± 3.3 | 0.99993 |
| | 3 | 23.18 | 2.67 | 30.61−3.78 | 9 | 373.1 ± 5.2 | 0.99983 |
| 1-methylnaphthalene | 1 | 51.52 | 10.62 | 10.38−9.10 | 6 | 388.9 ± 12.7 | 0.99918 |
| | 2 | 22.59 | 2.28 | 22.29−3.76 | 7 | 387.7 ± 7.3 | 0.99961 |
| | 3 | 23.77 | 2.26 | 22.19−3.37 | 8 | 391.7 ± 4.6 | 0.99979 |
| chlorobenzene | 1 | 15.44 | 3.15 | 28.53−6.01 | 5 | 370.7 ± 16.1 | 0.99906 |
| | 2 | 14.63 | 2.46 | 22.37−3.00 | 7 | 380.8 ± 4.0 | 0.99984 |
| | 3 | 14.37 | 2.33 | 21.50−3.40 | 6 | 375.7 ± 3.8 | 0.99990 |
| 1,2-dichlorobenzene | 1 | 14.71 | 3.03 | 23.30−5.70 | 5 | 387.3 ± 5.8 | 0.99964 |
| | 2 | 14.94 | 3.02 | 23.17−7.81 | 5 | 388.9 ± 2.5 | 0.99993 |
| | 3 | 31.40 | 5.94 | 45.46−14.14 | 7 | 386.6 ± 1.4 | 0.99995 |
| | 4 | 5.37 | 1.09 | 8.37−2.38 | 6 | 391.6 ± 8.9 | 0.99843 |
| | 5 | 15.30 | 2.74 | 21.08−3.55 | 7 | 391.8 ± 2.9 | 0.99975 |
| 1,2,4-trichlorobenzene | 1 | 16.09 | 3.32 | 22.93−5.77 | 5 | 392.8 ± 8.9 | 0.99788 |
| | 2 | 14.38 | 2.54 | 17.52−1.69 | 8 | 398.4 ± 1.1 | 0.99987 |
| | 3 | 16.35 | 2.83 | 19.53−2.69 | 7 | 396.2 ± 3.6 | 0.99906 |
| | 4 | 23.21 | 2.37 | 16.34−2.57 | 10 | 394.6 ± 2.8 | 0.99884 |
| 1-chloronaphthalene | 1 | 15.02 | 3.13 | 26.05−2.79 | 5 | 395.0 ± 3.1 | 0.99994 |
| | 2 | 25.44 | 2.56 | 21.55−12.06 | 5 | 401.8 ± 10.2 | 0.99927 |
| | 3 | 30.06 | 3.05 | 25.70−2.20 | 9 | 413.2 ± 4.5 | 0.99933 |
| | 4 | 31.06 | 3.16 | 26.51−3.94 | 9 | 396.5 ± 2.5 | 0.99982 |
| | 5 | 26.89 | 2.74 | 22.98−4.53 | 9 | 395.4 ± 1.9 | 0.99990 |
| carbon disulfide | 1 | | | 38.13−8.59 | 7 | 350.6 ± 5.9 | 0.99947 |
| | 2 | | | 37.88−7.01 | 8 | 352.2 ± 5.4 | 0.99940 |

[a] Amount of $C_{60}$ weighed for preparing the stock solution, $w(C_{60})$, and concentration of the stock solution, cc($C_{60}$).

linear dependence of the experimental specific volume on the mass fraction of $C_{60}$ in solution are plotted on Figure 1. The observed linearity of the curves indicates that the microenvironment of $C_{60}$ in a particular solvent remains constant as the solution is diluted.

Before proceeding to the analysis of the results, it was important to assess our experimental method, in particular regarding its applicability in a domain of low but finite mass fraction concentration. For that purpose, we determined some limiting partial molar volumes for two additional globular molecules, i.e. adamantane ($C_{10}H_{16}$) and congressane (diamantane, $C_{14}H_{20}$) from density measurements of a series of solutions of decreasing concentration in a domain (1) comparable to and (2) one order of magnitude greater than those used with $C_{60}$. For each solute−solvent pair reported in Table 4, a good agreement is obtained between apparent molar volumes determined over both solution mass fraction concentration ranges, allowing hence some confidence to the values relative to the $C_{60}$ partial molar volume determinations.

Irrespective of the particular values of the partial molar volume taken by $C_{60}$ in the various solvents, the most surprising result is that almost all values are lower than the molar volume of pure solid $C_{60}$ at 25 °C, i.e., 429 cm$^3$ mol$^{-1}$. This is an unexpected discovery in comparison to the usually observed behavior of almost all organic nonelectrolyte substances, the volume of which always increases when passing from the solid to the liquid state. To ensure that these results are really unusual, comparison with other systems are presented to show (1) that the volume of a molecule is always greater in liquid than in solid state and (2) that the limiting partial molar volume of an organic substance in nonspecifically interacting solvents does not appreciably differ from the value of the pure substance in its pure liquid (hypothetical supercooled liquid) state. In the following, all comparisons will be made on the basis of molar volumes, because, in contrast to the van der Waals molar volumes, they more efficiently represent the space occupied by 1 mol of substance within the solid or liquid phase or in the solvent. A rule of thumb states that the amount of empty volume is increased during the melting process by about 10−15% allowing the molecules to rotate more freely and to twist into more conformations than in the crystal. Water is unusual in that it has a larger molar volume in the solid state (19.65 cm$^3$ mol$^{-1}$) than in the liquid state (18.02 cm$^3$ mol$^{-1}$) at the melting point. The molar volume further increases, although more slowly, with any temperature elevation due to increasing amplitude of thermal vibrations, so that at the boiling point about half of the volume of a liquid composed of small approximately spherical molecules corresponds to empty volume. A limited

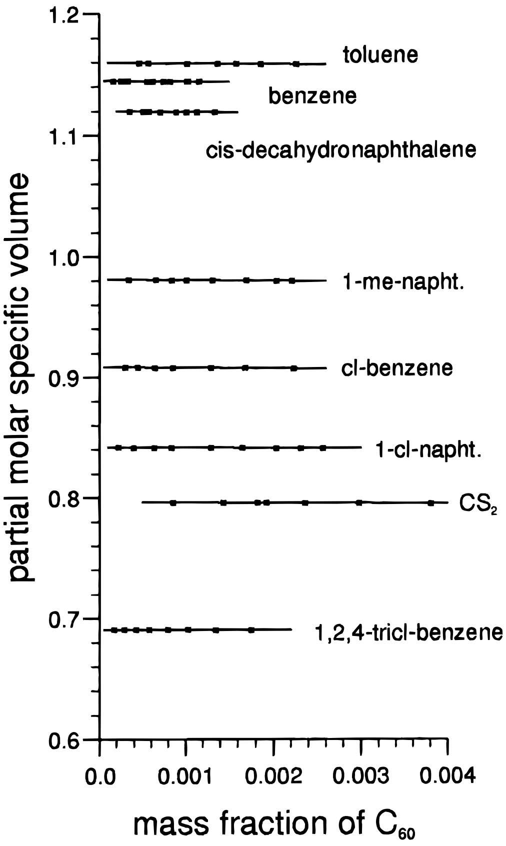

**Figure 1.** Apparent partial molar volume of $C_{60}$ in organic solvents versus the mass fraction of $C_{60}$ in solution at 25 °C.

**Table 4.** Partial Molar Volumes, $\overline{V}^{\infty}$, of Adamantane and Congressane at Infinite Dilution at 25 °C

| solute | solvent | sample mass fraction range ($10^4$) | $n$ | $\overline{V}^{\infty}$, $cm^3\ mol^{-1}$ | ref |
|---|---|---|---|---|---|
| adamantane | *n*-hexane | 87.20−2.5 | 9 | 137.8 ± 7.8 | this work |
| | | 140.63−22.97 | 10 | 136.9 ± 0.3 | 35 |
| | *n*-dodecane | 101.10−2.8 | 8 | 144.6 ± 1.2 | this work |
| | | 147.51−27.71 | 9 | 141.3 ± 0.3 | 36 |
| | $CCl_4$ | 27.10−2.4 | 8 | 137.6 ± 5.8 | this work |
| | | 147.51−27.71 | 9 | 140.1 ± 0.1 | 35 |
| congressane | *n*-hexane | 26.91−4.69 | 10 | 160.2 ± 5.0 | this work |
| | | 207.71−27.64 | 8 | 161.5 ± 3.4 | this work |
| | benzene | 26.48−5.43 | 8 | 177.4 ± 1.2 | this work |
| | | 193.7−28.39 | 9 | 177.8 ± 0.7 | this work |

**Table 5.** Volume Changes of Crystals on Melting[a]

| substance | $T_m$, °C | $V_x(T_m)$ | $V_l(T_m)$ | Δ*V*, % | ref |
|---|---|---|---|---|---|
| *n*-eicosane | 36.5 | 326.1 | 363.2 | 11.4 | 37 |
| *n*-heneicosane | 40.2 | 343.5 | 381.2 | 11.0 | 37 |
| *n*-docosane | 44.3 | 358.6 | 399.2 | 11.3 | 37 |
| *n*-tricosane | 47.5 | 375.0 | 417.0 | 11.2 | 37 |
| *n*-tetracosane | 51.0 | 391.0 | 434.9 | 11.2 | 37 |
| *n*-hexatriacontane | 75.5 | 582.3 | 649.8 | 11.6 | 38 |
| 2,3-dimethylnaphthalene | 101.4 | 160.7 | 175.5 | 9.2 | 39 |
| 2,6-dimethylnaphthalene | 111.8 | 169.4 | 200.7 | 18.5 | 39 |
| acenaphthene | 93.4 | 129.7 | 145.8 | 12.4 | 39 |
| anthracene | 215.4 | 153.2 | 178.9 | 16.8 | 39 |
| phenanthrene | 98.5 | 155.6 | 169.2 | 8.7 | 38 |
| chrysene | 250.0 | 186.8 | 209.9 | 12.4 | 39 |
| water | 0.0 | 19.65 | 18.02 | -8.3 | 40 |

[a] $V_x(T_m)$ = molar volume of solid at melting point. $V_l(T_m)$ = molar volume of liquid at melting point. $T_m$ = melting point. $\Delta V(\%) = 100[V_l(T_m) - V_x(T_m)]/V_x(T_m)$.

**Table 6.** Volume Change of Solids with Increasing Temperature[a]

| *n*-hexatriacontane[b] | | naphthalene[c] | | pyrene[d] | | $C_{60}$[e] | |
|---|---|---|---|---|---|---|---|
| *T*, K | *V*, $cm^3/mol$ | *T*, K | *V*, $cm^3/mol$ | *T*, K | *V*, $cm^3/mol$ | *T*, K | *V*, $cm^3/mol$ |
| 293 | 528.5 | 92 | 103.5 | 133 | 153.8 | 5 | 416.8 |
| 303 | 529.8 | 109 | 103.9 | 155 | 154.2 | 100 | 417.6 |
| 313 | 531.9 | 143 | 104.6 | 191 | 155.1 | 110 | 417.8 |
| 323 | 534.1 | 184 | 105.5 | 213 | 156.1 | 153 | 418.6 |
| 333 | 536.3 | 239 | 107.0 | 244 | 156.7 | 200 | 419.1 |
| 348 | 582.3 | 296 | 108.8 | 293 | 158.4 | 260 | 422.2 |
| 349 | 649.8 | 352 | 130.9 | 424 | 186.8 | 298 | 429.0 |

[a] Calculated from the volume and the number of molecules in the unit cell. [b] Reference 38. [c] Reference 41 and 42. [d] Reference 42 and 43. [e] Reference 4 and 6−9.

number of examples of volume changes on melting or with temperature increase are presented in Tables 5 and 6. A similar analysis performed on a great number of both apolar and polar compounds shows that the molar volume of a substance in its liquid (or hypothetical supercooled liquid state) appears to be 10 to 20% greater than their solid counterparts, irrespective of the type of system in which the substance crystallizes. Particular examples of such increases are observed in the 13% expansion of the liquid molar volume (97.1, 108.8, 144 $cm^3\ mol^{-1}$) over their solid counterparts (86.1, 96.1, 127.3 $cm^3\ mol^{-1}$) for the carbon tetrachloride, cyclohexane, and adamantane pseudo-spherical molecules which, like $C_{60}$, crystallize in the cubic system.[44−46] Accordingly, one would expect the molar volume of pure liquid $C_{60}$ to lie between 470 and 490 $cm^3\ mol^{-1}$. However, as $C_{60}$ comes much closer to being spherical than any other molecule cited, its liquid molar volume could be lower than the values calculated on the 10−15% volume expansion upon melting.

The volume of a solution obtained by dissolving a solid or liquid solute in a solvent is usually greater than the original volume of the solvent. The increase is however not necessarily equal to the volume of the added solute, because the empty volume associated with each molecule of solute varies when going from its old to its new environment: the distribution of the solute molecules throughout the solvent produces an adjustment of spacing, and it might be expected that when molecules differing in size, shape, and weight are mixed, they will arrange themselves so that the new volume is not exactly the sum of the volumes added. Furthermore, the change cannot be entirely ascribed to the dissolved substance; the solvent also must be affected, but then, the true volume of the dissolved compound cannot be determined since the proportional changes of the constituents are unknown. For highly dilute solutions, it is however reasonable to attribute the overall change of volume to the solute only. It is an experimental fact that the volume occupied by a substance in solution, i.e., its apparent molar volume, at any given temperature varies from one solvent to another, and also with the concentration of the solution. The limiting partial molar volume, $\overline{V}^{\infty}$, of the solute at zero concentration is then obtained by extrapolation to infinite dilution of the apparent molar volume measured at different concentrations.

The formation of dilute solutions of a given nonelectrolyte is accompanied either by an increase or a decrease in volume with respect to the molar volume of the pure substance in its liquid or supercooled liquid state (Table 7). Practically, the partial molar volume at infinite dilution never decreases below the molar volume of the solid substance. Furthermore, when arranged according to the decreasing partial molar volume of the dissolved substance, the order of the solvents differs from one solute to another. The difference observed in sequence can be accounted for by assuming that either the expansion or contraction effects are due to the action of forces depending on the nature of both the solute and the solvent or they are influenced by the respective shapes of the constituent molecules.

**Table 7.** Solvent Effect on the Limiting Partial Molar Volume (cm$^3$ mol$^{-1}$), $\overline{V^\infty}$, of Solutes

| solvent | $\overline{V^\infty}$ | solvent | $\overline{V^\infty}$ |
|---|---|---|---|
| *n*-Hexane (25 °C)[47−49] [pure liquid: 131.6 cm$^3$ mol$^{-1}$; pure solid (158 K): 97.0 cm$^3$ mol$^{-1}$][50] | | | |
| cyclohexane | 133.6 | ethanol | 133.9 |
| benzene | 133.8 | *n*-octanol | 129.5 |
| $CCl_4$ | 132.3 | | |
| *n*-Heptane (25 °C)[47−49,51,52] [pure liquid: 147.5 cm$^3$ mol$^{-1}$; pure solid (100 K): 112.6 cm$^3$ mol$^{-1}$][53] | | | |
| $CS_2$ | 154.4 | cyclohexane | 150.0 |
| methanol | 152.3 | $CCl_4$ | 149.3 |
| benzene | 150.3 | *n*-octanol | 146.3 |
| ethanol | 150.1 | | |
| Cyclohexane (25 °C)[36,48,49,52] [pure liquid: 108.8 cm$^3$ mol$^{-1}$; pure solid (195 K): 96.1 cm$^3$ mol$^{-1}$][44] | | | |
| acetone | 114.2 | *n*-dodecane | 110.3 |
| methanol | 113.9 | $CCl_4$ | 110.5 |
| $CS_2$ | 112.1 | *n*-octanol | 109.9 |
| ethanol | 111.7 | *n*-hexane | 108.6 |
| benzene | 111.1 | | |
| Adamantane (25 °C)[36,48] [pure liquid: 144.6 cm$^3$ mol$^{-1}$; pure solid (298 K): 127.3 cm$^3$ mol$^{-1}$][45] | | | |
| methanol | 144.5 | *n*-dodecane | 141.3 |
| acetone | 144.5 | $CCl_4$ | 140.1 |
| benzene | 142.7 | cyclohexane | 138.7 |
| ethanol | 142.4 | *n*-hexane | 136.9 |
| Naphthalene (18 °C)[54] [pure liquid: 123.5 cm$^3$ mol$^{-1}$; pure solid (296 K): 108.9 cm$^3$ mol$^{-1}$][41] | | | |
| ethylene bromide | 125.50 | $CCl_4$ | 122.75 |
| nitrobenzene | 124.85 | *n*-heptane | 122.75 |
| $CS_2$ | 124.85 | methyl acetate | 122.50 |
| chlorobenzene | 124.30 | ethyl acetate | 121.15 |
| pyridine | 123.80 | methanol | 120.00 |
| toluene | 123.30 | ethanol | 119.15 |
| ethyl iodide | 123.15 | diethyl ether | 112.90 |

**Table 8.** Limiting Partial Molar Volume (cm$^3$ mol$^{-1}$), $\overline{V^\infty_{I_2}}$, of Iodine[a] at 25 °C[55−57]

| solvent | $\overline{V^\infty_{I_2}}$ | solvent | $\overline{V^\infty_{I_2}}$ |
|---|---|---|---|
| Violet Solutions | | | |
| $C_7F_{16}$ | 100.0 | isooctane | 66.7 |
| *c*-$C_4F_6Cl_2$ | 81.2 | *c*-$(CH_3)_8Si_4O_4$ | 66.6 |
| 2,2,3-$C_4Cl_3F_7$ | 78.6 | *n*-heptane | 66.3 |
| cyclohexane | 68.2 | $CHCl_3$ | 65.6 |
| $CCl_2F$-$CF_2Cl$ | 67.7 | $CS_2$ | 62.3 |
| $SiCl_4$ | 67.1 | $CHBr_3$ | 60.8 |
| $CCl_4$ | 66.7 | | |
| Non-Violet Solutions | | | |
| dioxane | 67.8 | *n*-propanol | 60.6 |
| 1,2-dichloroethane | 67.1 | $(C_2H_5O)_4Si$ | 60.5 |
| $(CH_2OH)_2$ | 66.6 | ethanol | 60.0 |
| fluorobenzene | 65.0 | pyridine | 59.1 |
| chlorobenzene | 64.9 | ethyl bromide | 57.8 |
| bromobenzene | 63.6 | butyl ether | 56.0 |
| mesitylene | 62.7 | ethyl iodide | 54.8 |
| *p*-xylene | 62.5 | 1,4-dimethylnaphthalene | 53.5 |
| benzene | 62.4 | 1-methylnaphthalene | 52.2 |
| toluene | 61.6 | isopropyl ether | 50.8 |
| *n*-butanol | 61.0 | diethyl ether | 49.6 |

[a] Molar volume of iodine:[54] pure supercooled liquid, 59.4 cm$^3$ mol$^{-1}$; pure solid, 51.5 cm$^3$ mol$^{-1}$.

The volume change on mixing therefore cannot be quantitatively predicted by a simple theory. As a general rule, solute−solvent attractive interactions (hydrogen bond or donor-acceptor complex formation) lead to a reduction of the partial molar volume of the solute due to shortening of the equilibrium intermolecular distance, while repulsive interactions are accompanied by opposite changes. A good illustrative example is brought about by iodine (Table 8). In this case, the solvents have been divided into two classes: the non-complexing solvents which cause a violet color, and the complexing solvents in which the iodine molecules are more or less chemically bound to solvent molecules. These latter solutions show a red-brown-yellow color. In the first group, there is little or no complex formation and the limiting partial molar volume of iodine remains for all solutions greater than the extrapolated molar volume of pure liquid iodine at 25 °C, i.e., 59 cm$^3$ mol$^{-1}$. Moreover, the limiting partial molar volume increases almost roughly proportionally with decreasing the solubility parameter of the solvent, i.e., the partial molar volume of the solute increases substantially when the solvents change from good to poor.[55−58] In contrast, the solute volume contraction is strong in solutions containing respectively ethyl iodide, methylnaphthalenes, alcohols, or ethers. These solvents have all been found to form charge-transfer complexes[59,60] in which iodine acts as an electron acceptor and the solvent as the donor. Although the partial molar volumes in aromatic solvents (benzene, toluene, xylene, mesitylene) are lower than in comparable noncomplexing solvents, such as cyclohexane, they are larger than in the ethers. Solvation in the aromatics has therefore been interpreted in terms of "collision complexes" according to Orgel and Mulliken[61] rather than as definite stoichiometric complexes. That the solvent and iodine molecules form weak solvent−solute complexes is shown by the sensitivity of the color of many solutions to temperature, the color becoming more violet or less brown with the rise of temperature, and vice versa. Similar tests performed on non-purple solutions of $C_{60}$ in both naphthalene solvents did not show any change of color on raising the temperature up to 150 °C.

From the foregoing, the limiting partial molar volumes of $C_{60}$ appear completely unexpected in that the observed values are not only far smaller than the expected molar volume of liquid $C_{60}$ but even remain lower than the molar volume of the pure solid $C_{60}$ (except in *n*-hexadecane). This unusual behavior could be issued from the need of minimizing the repulsive interactions within the solid state itself. In the solid state, both the high symmetry of the pseudosphere molecule surrounded by a spherical envelop of 60 $\pi$-electrons and the arrangement of the molecules within the crystal (each molecule has 12 crystallographically equivalent nearest neigbhors in a cuboctahedral environment) prevent the molecules from coming close together. The repulsion between the $\pi$-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, in liquid, the $C_{60}$ molecules which are in perpetual motion do not have to organize 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 distance may then be smaller than the nonbonded distances in pure solid or liquid $C_{60}$, thus leading to

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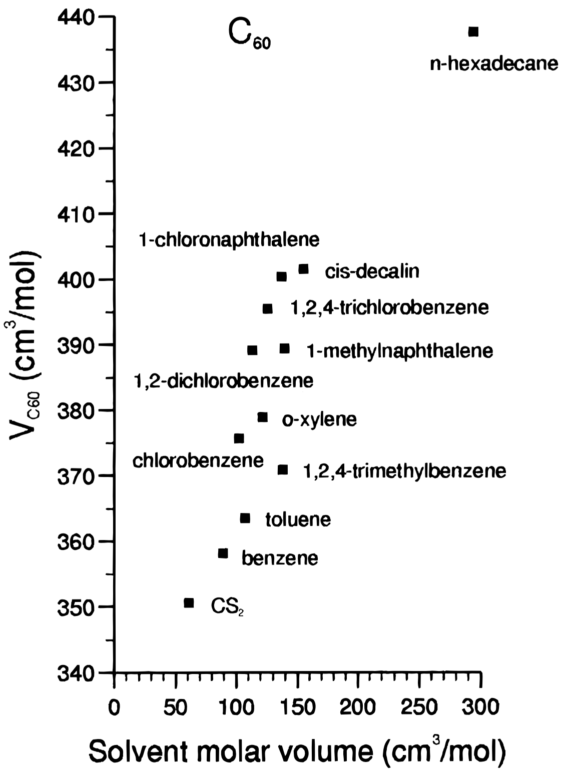

**Figure 2.** Solvent dependence of the limiting partial molar volumes of $C_{60}$ (average values) at infinite dilution in organic solvents at 25 °C.

smaller partial molar volume in solution. On the other hand, the $C_{60}\cdots$solvent intermolecular distances differing from one solvent to another give rise to different values of its limiting partial molar volume. Inspection of the results given in Table 3 clearly confirms that $C_{60}$ in solution behaves differently in different solvents, and therefore, the partial molar volumes are really informative not only on the size of the solute but also on the extent to which it may interact with the solvent molecules. A volume change upon mixing can however stem from different origins, as mentioned by Handa and Benson in their review article:[62] (1) differences in sizes and shapes of the component molecules; (2) structural changes; (3) differences in the intermolecular interaction energy between like and unlike molecules; and (4) formation of new chemical species. Although volume changes normally occur because of a combination of these various factors, much effort has been made to understand the origin of the $C_{60}$ partial molar volume dependence on the solvent. An examination of the possible correlations between the average limiting partial molar volume in a particular solvent and the solvent properties including molar volume, *V*, refraction index, $\eta_D^{20}$, dielectric constant, $\epsilon$, Hildebrand solubility parameter, $\delta$, ionization potential, PI, and solubilizing capacity, *S*, did not show any simple relation. The major finding from the foregoing analysis is that the molar volume parameter is important in determining the apparent molar volume of $C_{60}$ at infinite dilution. As a measure of the solvent size, the correlation observed (Figure 2) would indicate that factor 1 of Handa might be regarded as the prime cause of the variation of the $C_{60}$ size in solution. Similar solvent dependence of the limiting partial molar volumes is also observed for iodine in noncomplexing solvents (Table 8) and for two macrocycle ligands, i.e. 18-crown-6-ether[63] and cryptand-222[64] (Figures 3 and 4). $C_{60}$ and solvent molecules have to organize themselve in order to maximize the contacts while avoiding interpenetration. With its undeformable large sphere-like cage structure, $C_{60}$ accommodates more easily in small size solvent molecules,

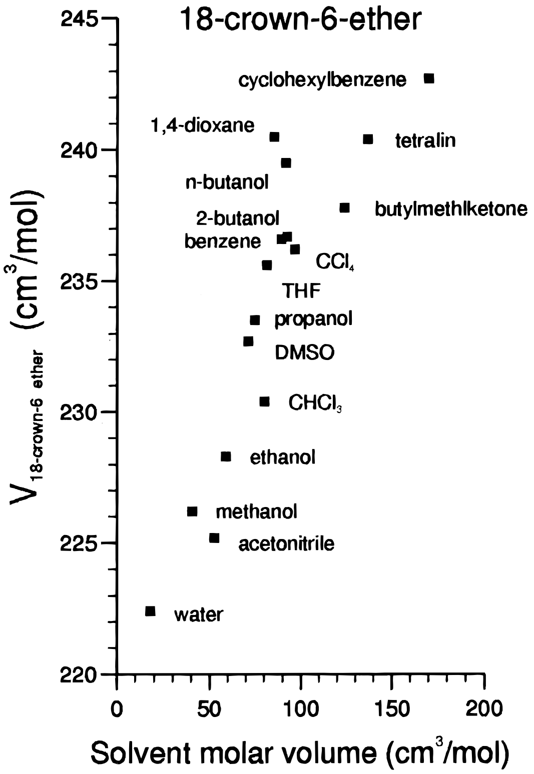

**Figure 3.** Solvent dependence of the limiting partial molar volume of 18-crown-6-ether at infinite dilution in organic solvents at 25 °C. Estimated liquid molar volume from group contribution: 243.6 $cm^3$ $mol^{-1}$. Solid molar volume from X-ray structure: 214.5 $cm^3$ $mol^{-1}$.[65]

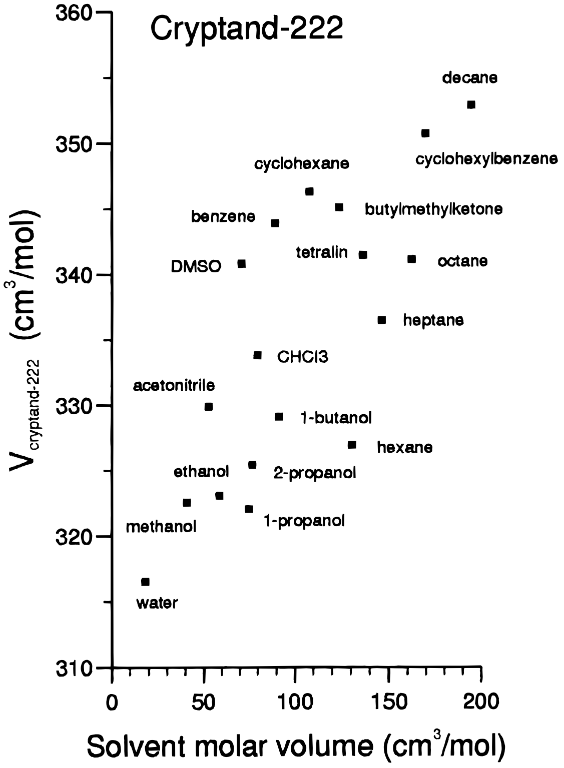

**Figure 4.** Solvent dependence of the limiting partial molar volumes of cryptand-222 at infinite dilution in organic solvents at 25 °C. Estimated liquid molar volume from group contribution: 345.6 $cm^3$ $mol^{-1}$. Solid molar volume from X-ray structure: 317.9 $cm^3$ $mol^{-1}$.[66]

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like $CS_2$, than in bigger ones, like *n*-hexadecane. In other words, if the $C_{60}$ molecules are separated by solvent molecules that are much smaller, then the space surrounding each $C_{60}$ is filled much more efficiently leading to smaller effective volumes in solutions involving smaller size solvents. Obviously, this conclusion does not preclude that, in solution, $C_{60}$ interacts with the surrounding solvent molecules in a nonspecific way, and may even form donor−acceptor molecular complexes in which it acts as electron acceptor like iodine in aromatic solvents.

## Conclusion

The main conclusions drawn from the present analysis can be summarized as follows:

1. The molar volume of an organic substance in the pure phase or in solution always exceeds its van der Waals or intrinsic volume by a varying amount of empty volume related to the packing of the molecules either between each other or with the solvent molecules.

2. The melting process increases the molar volume of a pure substance in a proportion of about 10−15% (water constitutes an exception with a decrease of about 10% of its molar volume).

3. Any temperature increase always leads to an expansion of the free and molar volume of a substance.

4. The limiting partial molar volume of a dissolved substance reflects not only the volume of the pure liquid solute but also the extent to which it interacts with the solvent. Complexation generally results in decreasing the partial molar volume due to the shortening of the equilibrium distance between solute and solvent molecules.

5. In most cases the volume change upon mixing in noninteracting solvents is relatively small, and the volume assumed in solution by a solid, liquid, or gas is never far away from the volume that the substance would occupy if liquid at the same temperature.

6. From points 2 to 5, it may be concluded that the molar volume of a substance is about 10 to 20% greater in its liquid phase or in solution than in its solid phase.

On the basis of the foregoing conclusions, the partial molar volume of $C_{60}$ at infinite dilution in the solvents considered in this work appears unusual, remaining substantially lower than the solid molar volume determined from its X-ray crystal structure determination. The reason for this must presumably be sought in the arrangement of the molecules themselves within the solid phase. Although, for the time being, it appears difficult to reach any conclusion concerning the changes of the limiting partial molar volumes of $C_{60}$ from one solvent to another, the observed dependence on only the molar volume of the solvents might be interpreted in terms of the “steric” effect of the way the molecules organize themselves in solution and how they fit together.

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