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Effect of packing on the cluster nature of C nanotubes: An information entropy analysis

Francisco Torrens[a,*], Gloria Castellano[b,c]

[a]*Institut Universitari de Ciència Molecular, Universitat de València, Edifici d'Instituts de Paterna, P. O. Box 22085, E–46071 València, Spain*
[b]*Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, E-46022 València, Spain*
[c]*Departamento de Ciencias Experimentales, Facultad de Ciencias Experimentales, Universidad Católica de Valencia San Vicente Mártir, Guillem de Castro–94, E–46003 València, Spain*

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Abstract

The possibility of the existence of single−wall carbon nanotubes (SWNTs) in organic solvents in the form of clusters is discussed. A theory is developed based on a *bundlet* model for clusters, which enables describing the distribution function of clusters by size. Comparison of the calculated values of solubility with experiments would permit obtaining energetic parameters characterizing the interaction of an SWNT with its surrounding, in a solid or solution. Fullerenes and SWNTs are unique objects, whose behaviour in many physical situations is characterized by remarkable peculiarities. Peculiarities in solutions show up first in that fullerenes and SWNTs represent the only soluble forms of carbon, what is related to the originality in the molecular structure of fullerenes and SWNTs. The fullerene molecule is a virtually uniform closed spherical or spheroidal surface, and an SWNT is a smooth cylindrical unit. Both structures give rise to the relatively weak interaction between the neighbouring molecules in a crystal and promote interaction of the molecules with those of a solvent. Another peculiarity in solutions is related to their trend to form clusters, consisting of a number of fullerene molecules or SWNTs. The energy of interaction of a fullerene molecule or SWNT with solvent molecules is proportional to the surface of the former molecule and roughly independent of the orientation of solvent molecules. All these phenomena have a unified explanation in the framework of the bundlet model of a cluster, in accordance with which the free energy of an SWNT involved in a cluster is combined from two components, viz. a volume one proportional to the number of molecules n in a cluster, and a surface one proportional to $n^{1/2}$. Algorithms for classification are proposed based on the criteria *information entropy* and its production. Many classification algorithms are based on information entropy. When applying these procedures to sets of moderate size, an excessive number of results appear compatible with data, and this number suffers a combinatorial explosion. However, after the *equipartition conjecture*, one has a selection criterion between different variants resulting from classification between hierarchical trees. According to this conjecture, for a given charge or duty, the best configuration of a flowsheet is the one in which the entropy production is most uniformly distributed. Information entropy, cluster and principal component analyses agree.

Keywords: Solubity of carbon nanotubes; *Bundlet* model for clusters; Droplet model for clusters; Nanotube; Fullerene; Nanohorn

1. Introduction

Clusters constitute a bridge between molecular systems and solids, as well as exhibit challenging features. Extraordinary physical and chemical peculiarities in the behaviour of fullerenes in solutions are related to their exotic structure and to the possibility of cluster formation, and this make fullerene solutions interesting objects, possessing unusual thermodynamic, kinetic, optical and other properties. Among these unusual properties should be mentioned the nonmonotonic temperature dependence of solubility of fullerenes in some solvents [1], as well as the nonlinear concentration dependence of the third–order nonlinear optical susceptibility [2]. Of considerable scientific interest is the solvatochromic effect [3,4], which is exhibited in a sharp alteration in the spectrum of the optical absorption of C_{70} dissolved in a mixture of organic solvents, because

*Corresponding author. Tel.: +3496 3544431; fax: 3496 3543274.
E-mail address: Francisco.Torrens@uv.es (F. Torrens).

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of a slight change in the solvent content. These and some other peculiarities in the behaviour of fullerenes in solutions are attributable to the phenomenon of the formation of clusters in a solution [5,6]. A thermodynamic approach to the description of this phenomenon based on a droplet model of a cluster enables describing uniquely numerous peculiarities in the behaviour of fullerenes in solutions and predicting new effects, e.g., the concentration and temperature dependences of the diffusion and thermal diffusion coefficients of fullerenes in solutions, as well as the concentration dependence of the heat of solution of fullerenes. Decrease in pyridine-soluble material observed after soaking coals in solvents, which is due to an increase in cross-linking associated with the formation of ionic domains or clusters, similar to those observed in ionomers [7] was examined. Stable aqueous dispersions of fullerenes, $C_{60–70}$, were prepared by simply injecting into water a saturated solution of $C_{60–70}$ in tetrahydrofuran (THF), followed by THF removal by purging gaseous nitrogen $N_{2(g)}$. It is not possible to extract $C_{60–70}$ from a solution in toluene to water and from a dispersion in water to toluene. Similar results were reported for other $C_{60–70}$ aqueous dispersion systems [8]. Upon contact with water, C_{60} spontaneously forms a stable aggregate $(C_{60})_n$ with nanoscale dimensions [9]. The colour, hydrophobicity and reactivity of individual C_{60} are substantially altered in $(C_{60})_n$. In solution, $(C_{60})_n$ is crystalline in order and remains as underivatized C_{60} throughout the formation/stabilization process that can later be chemically reversed. Particle size can be affected by formation parameters. Once formed, $(C_{60})_n$ remains stable in solution at or below ionic strengths of $0.05\,\mathrm{mol\,L^{-1}}$ for months. Water itself might form a donor–acceptor complex with C_{60} leading to a weakly charged colloid [10–12]. In contrast, C_{60}, dissolved in water via complexation with *cyclo*dextrin$_8$, was extracted to toluene [13,14]. In the case of C_{60} incorporated into artificial lipid membranes, C_{60} was not extracted to toluene, but the extraction became possible once the vesicle was destructed by adding KCl [15]. Addition of KCl was also required to extract poly(vinylpyrrolidone)-solubilized $C_{60–70}$ to toluene [16]. When NaCl was added to a $C_{60–70}$ aqueous dispersion, $C_{60–70}$ were extracted into toluene and the toluene phase exhibited faint magenta or orange, characteristic colours for a solution of C_{60} or C_{70} in toluene, respectively. $C_{60–70}$ are dispersed as monodisperse clusters $(C_{60–70})_n$ in water. High-resolution transmission electron microscopy revealed the polycrystalline nature of $(C_{60–70})_n$. Preparation of the dispersion is easy, and the dispersions thus obtained are of excellent colloidal stability. The surface of $(C_{60–70})_n$ is negatively charged, and the electrostatic repulsion between the negatively charged $(C_{60–70})_n$ surfaces is important for the stability of the dispersions.

An assembly of randomly packed spheres can represent certain features of the geometry of simple liquids [17]. The density of random close (RC) packing, 0.637 ± 0.005, corresponded closely to the densities of the rare-gas liquids at their triple points. The radial distribution of RC packing agreed well with the radial distributions of the rare-gas liquids determined by X-ray and neutron diffraction. The lower limit of the packing density measured was 0.601 ± 0.005. Although random *loose* (RL) packing may not be as basic a geometrical arrangement as RC packing, it might correspond to a simple liquid at a temperature somewhat above its triple point. Models of randomly packed hard spheres exhibited some features of the properties of simple liquids [18]. The value of the maximum packing density of spheres can be determined from models, if care is taken to ensure random packing at the boundary surfaces, and if correction is made for volume errors at the boundaries. Experiments for both the RL- and RC-packed densities were reported. A computer analysis of the results permitted a one-step, two-parameter extrapolation to infinite volume. The figure so obtained for the RC-packed density was 0.6366 ± 0.0005. The virial expansion for the pressure of hard discs and hard spheres was a monotonically increasing function of the number density ρ and diverged at the density of closest packing with the critical exponent $\gamma = 1$ [19]. The virial series described a metastable fluid phase for $\rho_0 < \rho < \rho_c$, where ρ_0 is the density of the fluid–solid transition. For hard discs, the known values of the virial coefficients B_n were well represented by $B_n = (C - Dn^{-1})\rho_c^{-(n-1)}$ for $n \geqslant 4$, with C and D being positive constants. Adopting this approximation for $n \geqslant 7$ led to a simple, closed-form equation of state for the fluid phase, which yielded values of the pressure throughout the regime $0 < \rho < \rho_0$ that were only slightly larger than the series acceleration estimates. The algorithm of packing noncongruent spheres was generalized for the case of packing arbitrary convex three-dimensional (3D) objects, suggesting an algorithm building close packing of arbitrary set of 3D special figures (*sphere-polyhedrons*) [20]. The model can be applied: (1) for investigation of properties of compact packings of complex-form convex objects, (2) for creating starting configurations while structure–imitation modelling agglomeration and forming powders based on the particles method.

Calculations on solvents and co–solvents of single-wall carbon nanotubes (SWNTs) were reviewed with *cyclo*pyranoses, as well as partition of solvents and co–solvents of SWNTs with *cyclo*pyranoses and proteins. In earlier publications, periodic tables of SWNTs were discussed [21,22]. A program based on the AQUAFAC model was applied to calculate the aqueous coefficients of SWNTs [23]. A molecular modelling comparative study of SWNT solvents and co–solvents provided a classification in *best*, *good* and *bad* solvents [24–28]. The *bundlet* model for clusters of SWNTs was presented [29–31]. The aim of the present report is to perform a comparative study on the properties of fullerenes (droplet model) and SWNTs (bundlet model). In the present report, a wide class of phenomena accompanying the behaviour of SWNTs in solutions is analysed from a unique point of view, taking into account the trend of SWNTs to cluster formation in