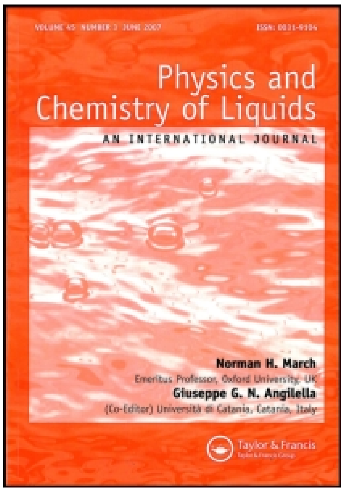

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Amovilli, C. and March, N. H.(2007) 'Interaction energy between fullerene molecules when immersed in nondipolar solvents', Physics and Chemistry of Liquids, 45: 1, 1 — 6
To link to this Article: DOI: 10.1080/00319100600995595
URL: http://dx.doi.org/10.1080/00319100600995595

Physics and Chemistry of Liquids
Vol. 45, No. 1, February 2007, 1–6

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Interaction energy between fullerene molecules when immersed in nondipolar solvents

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(*Received 6 September 2006*)

Recently we have calculated the interaction energy between fullerenes in free space. It has subsequently come to our attention that many experiments involving fullerene solutions have been realized. Here, we generalize earlier work of Robinson and March, on the reduction of the magnitude of the dispersion interaction between argon atoms in free space when part of dense liquid argon, to apply to an assembly of fullerene molecules in nondipolar solvents such as CCl_4, CS_2, and CSe_2. The refractive index of such solvents is shown to play a major role in reducing the long-range interaction below its free-space value.

Keywords: Fullerenes in solution; Clausius–Mossotti equation; Solvent effect

In a recent study, we have calculated the interaction energy of a pair of C_{60} molecules in free space as a function of their separation [1]. It has subsequently come to our attention that a variety of experiments have been carried out on fullerene in different types of solvents [2–6].

This has prompted us to enquire how the above free-space interaction energy is to be modified when the forces between the C_{60} molecules occur through the intermediary of a dielectric solution of nondipolar solvents. To make a start on this problem, we have gone back to the calculation of Robinson and March [7] (see also Renne and Nijboer [8]) on the modification of the long-range dispersion interaction

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Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online © 2007 Taylor & Francis
DOI: 10.1080/00331910060099559

between a pair of argon atoms, but now in liquid argon itself. Their result may be written in the form

$$C_6^{\text{medium}} = C_6^{\text{vacuo}}\left(1 - \frac{2\pi}{3}n\alpha + \cdots\right) \tag{1}$$

where n denotes the fluid number density while α is the polarizability of a single argon atom. The calculation of Robinson and March, based on equation (1), is that the presence of the dielectric medium weakens the dispersion energy $-C_6^{\text{vacuo}}/R^6$, with R the (assumed large enough) distance between Ar atoms, reducing it to about 0.94 of its free-space value.

We address below, how we expect equation (1) to be modified when we consider the above-mentioned problem of the interaction between a pair of C_{60} molecules immersed in a nondipolar liquid solvent. Again, the natural starting point is the free-space interaction between a pair of fullerene molecules. Then, as in our previous work [1], we write the interaction energy as

$$E_{\text{int}} = A\sum_{i,j=1}^{60}\frac{1}{R_{ij}^{12}} - B\sum_{i,j=1}^{60}\sum_{k,l=1}^{60}\frac{\nu_{ik}\nu_{jl}}{R_{ij}R_{kl}} \tag{2}$$

where i and k indicate C sites on one molecule and j and l on the other molecule, R_{ij} are distances between sites of different molecules and, finally, ν_{ik} is the connectivity matrix

$$\nu_{ik} = 3 \quad (i = k) = -1 \quad (i - k \text{ connected}) = 0 \quad (\text{otherwise}). \tag{3}$$

A and B are universal parameters for graphitic structures and have been found to be $A = 33{,}000\,\text{eV}\,\text{Å}^{12}$ and $B = 4.15\,\text{eV}\,\text{Å}^{2}$. Such values of A and B reproduce the correct equilibrium distance and binding energy of the dimer of fullerene in free-space.

As in equation (1), we focus on the change in the dispersion interaction entering equation (2) brought about by the medium. In equation (2), the dispersion contribution corresponds to the second term in the right-hand side. The first term, being related to Pauli repulsion, is not influenced by the solvent because it represents a kind of interaction due to the contact between the interacting systems. As we have shown in our previous work [1], dispersion energy in (2): (i) results from an integration over an imaginary frequency and involving generalized frequency dependent polarizabilities of fullerene molecules, (ii) gives the correct asymptotic behavior, and (iii) subsumes the site–site interactions of the type $-C_{6,ij}/R_{ij}^6$ of other commonly used C_{60} pair potentials (see, for example, [9]). Thus, equation (1) with the considerations above lead us to propose the following expression for the dispersion energy between two C_{60} molecules immersed in a nondipolar solvent

$$E_{\text{disp,sol}} = E_{\text{disp,vac}}\left[1 - \frac{2\pi}{3}n^*\alpha + \cdots\right] \tag{4}$$

in which α is the dipolar polarizability of a molecule of the solvent and n^* the local number density of the solvent itself. Equation (4) must be viewed as some low order expression of a more complicated series expansion. In the expression above, we explicitly indicate the solvent local number density because the medium effect on the solute pair dispersion energy is played by the solvent molecules surrounding the pair and then, the accessible volume to these solvent molecules is smaller than in the pure liquid. At least, for dilute solution, we can write

$$n^* = \Phi n \tag{5}$$

where Φ is the volume fraction of the solvent and n the number density of the pure solvent. This equation (5) allows us to make use of the Clausius–Mossotti equation (see, for example, [10]) to replace $n\alpha$ in equation (4). For dispersion interactions, the dielectric response is characterized by the high-frequency dielectric constant of the medium which is commonly determined by η^2, the square of the refractive index (see, for example, [11]). Thus, by taking,

$$\frac{n\alpha}{3\epsilon_0} = \frac{\eta^2 - 1}{\eta^2 + 2}, \tag{6}$$

where ϵ_0 is the vacuum dielectric permittivity, $1/4\pi$ in the units of equations (1) and (4) becomes

$$E_{\mathrm{disp,sol}} = E_{\mathrm{disp,vac}}\left[1 - \frac{\Phi}{2}\frac{(\eta^2 - 1)}{(\eta^2 + 2)} + \cdots\right] \tag{7}$$

in which we make use also of equation (5). In terms of Padé approximant [0/1], one can also write

$$E^{[0/1]}_{\mathrm{disp,sol}} = \frac{E_{\mathrm{disp,vac}}}{1 + (\Phi(\eta^2 - 1)/2(\eta^2 + 2))} \tag{8}$$

which is an interesting relation for practical application of more general use.

Turning to the present problem of the fullerene pair potential in solution, we have chosen three nondipolar solvents, CCl_4, CS_2, and CSe_2. The physico-chemical properties of the selected solvents which are relevant to the present study are displayed in table 1.

With the data of table 1 we have calculated the interaction energy for a fullerene pair immersed in a solvent using equation (2) and scaling the dispersion contribution according to equation (7). In figure 1 we plot the results for the limiting cases of the free space and of the solution at infinite dilution where the effect of the solvent is maximum ($\Phi = 1$). We remark that, looking at solubilities of table 1, the volume fraction of the solvent should be, in any case, > 0.99. Reduction of dispersion energy due to the dielectric medium is shown to be 0.86 for CCl_4, 0.82 for CS_2, and 0.78 for CSe_2. Finally, in table 2 we report equilibrium distances and binding energies of a fullerene pair in free space and in solution resulting from our calculations.

Table 1. Molar volume (V), refractive index (η) relative to air at 589 nm and C_{60} solubility (S) for the solvents considered in this work. V and η are at 293 K while S is at 298 K [2].

Solvent	V (cm^3 mol^{-1})	η	S (g/L)
CCl_4	96.5	1.4601	0.32
CS_2	60.3	1.6319	7.9
CSe_2	63.4	1.8454	Not available

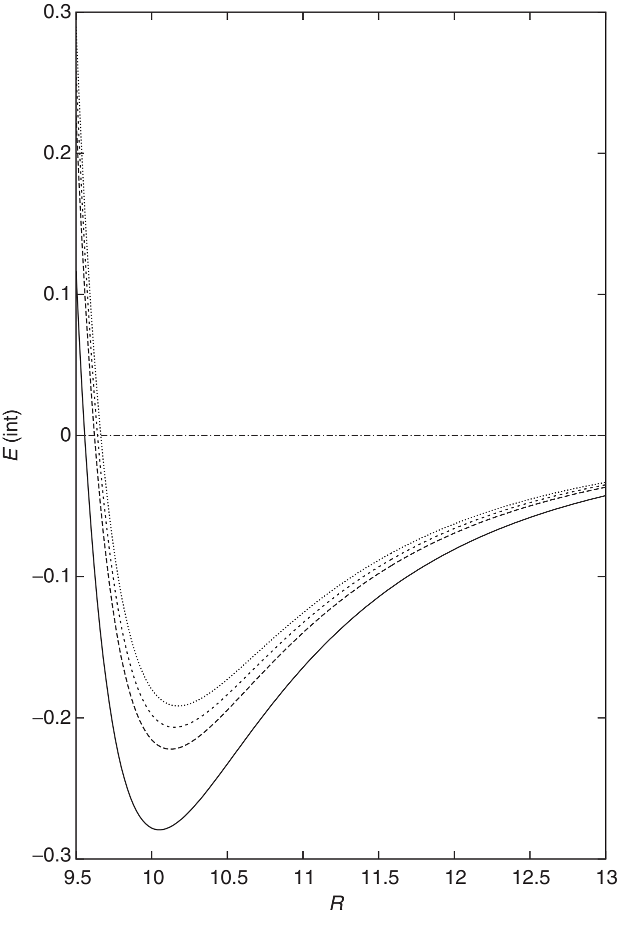

Figure 1. Interaction energy (eV) between two C_{60} molecules against the separation R (Å) in free space (lower curve) and, in the order from the lower to the upper, in CCl_4, CS_2, and CSe_2 at infinite dilution (Φ, the solvent volume fraction, equal to 1).

Table 2. Calculated equilibrium distances (R_{eq}) and binding energies (E_b) for a fullerene pair *in vacuo* and at infinite dilution in some selected nondipolar solvents.

Solvent	(R_{eq}) (Å)	(E_b) (eV)
CCl_4	10.12	0.222
CS_2	10.15	0.207
CSe_2	10.18	0.192
in vacuo	10.05	0.279

It is interesting to notice from table 2, that solvents affect only slightly the equilibrium distance, but can reduce significantly the binding energy, more precisely by 20% in CCl_4, 26% in CS_2, and 31% in CSe_2. We believe that this reduction plays an important role in the formation of solvates, special solute–solvent solid binary mixtures obtained by crystallization from solutions [12]. The stoichiometry and the phase behavior of different C_{60}–$n$$CCl_4$ solvates have been object of experimental investigations in the past [13].

Solute–solute interactions are also important in determining deviation from ideality of solute activity at infinite dilution. In McMillan–Mayer theory [14], the osmotic pressure of a solution is expanded in power series of the solute concentration exactly as in the virial expansion for the pressure of a real gas. In this theory, the second virial coefficient is written in the same way as for the real gas but with the solute–solute potential of mean forces (PMF) instead of the intermolecular potential. Such PMF can be obtained by classical simulations and depends on solute–solute, solute–solvent, and solvent–solvent interactions. Our modified C_{60}–C_{60} potential, in our opinion, is well adapted to provide a suitable solute–solute potential for such simulations. For C_{60} in CS_2 as solvent, Henderson [15] has measured the second virial coefficient by neutron scattering. This measured value at ambient conditions is positive in contrast with the pure C_{60} second virial coefficient which is found negative up to much higher temperatures [9]. This fact suggests that the C_{60}–C_{60} PMF in CS_2 is dominated by repulsive interactions. Although the PMF is not the pair potential, our finding goes in the same direction of this experimental result.

In summary, the main achievement of this short communication is to modify the treatment of Robinson and March [7], leading to equation (1) above, to deal with a pair of fullerene C_{60} molecules interacting in a liquid dielectric medium representing a nondipolar solvent such as those considered here, namely CCl_4, CS_2, and CSe_2.

Acknowledgements

N.H.M. completed his contribution to this study during a visit to Pisa in 2006. He wishes to thank Professor M. P. Tosi for generous hospitality and for the most stimulating atmosphere at the Scuola Normale Superiore.

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