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A chemometrics approach to predict the dispersibility of graphene in various liquid phases using theoretical descriptors and solvent empirical parameters

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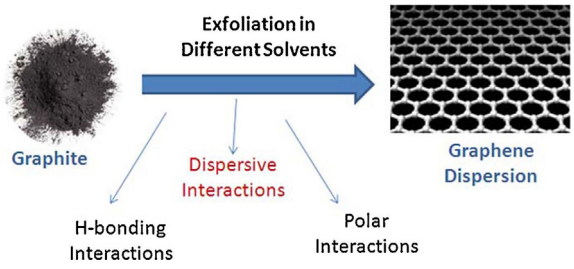
HIGHLIGHTS

- Two linear models were constructed to predict the dispersibility of graphene in liquid phases.
- Involved solute–solvent interactions were discussed in these colloidal systems.
- Dispersive interactions, in comparison with H-bonding and polar interactions, might be more significant.
- Some new solvents were proposed for graphene synthesis.

GRAPHICAL ABSTRACT



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ABSTRACT

This work focuses on the dispersibility of graphene in different solvent phases. A chemometrics study was performed on the dispersibility of graphene in liquid phases. Two multilinear regression models were constructed using theoretical and empirical parameters of the solvents. The model based on solvent empirical parameters resulted in better statistical qualities as well as better description ability. This model which was constructed by empirical parameters covered 85% and 90% of the variance in the train and test sets respectively. Based on the molecular descriptors and empirical parameters appeared in the models, it was suggested that some weak van der Waals interaction would help in the dispersibility of graphene. Among these interactions, dispersive interactions, in comparison with H-bonding and polar interactions, might have a more significant role in increasing the graphene dispersibility.

1. Introduction

The research on graphene has been one of the most outstanding recent achievements. Despite to the short history of graphene [1], it has became one of the most exciting nanomaterials and offered a unique combination of electrical, optical, thermal, and mechanical properties [1,2].

A graphene sheet has a hexagonal two dimensional (2D) lattice of carbon atoms with sp^2 hybridization. Consequently, individual graphene sheets form a 3D crystal. Ideal graphene consists only of six-member rings, but structural defects in graphene lead to the formation of five and seven-member rings and leading to bending of the flat surface [3].

Graphene is most commonly prepared as individual flakes by micromechanical cleavage of graphite and has applied in a lot of fields such as spectroscopic [4–6], nanoscale electrical and mechanical applications or characterizations [1,2,7–10]. It should be noted that the yield and throughput associated with micromechanical cleavage synthesis is extremely low and so this technique is not

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Table 1
Solvent names and related D_G and log D_G values.

	Chemical name	D_G (μg/ml)	Log D_G
S1	Cyclopentanone (CPO)	8.5 (±1.2)	0.93 (±0.06)
S2	Cyclohexanone	7.3 (±1.3)	0.86 (±0.08)
S3	N-formyl piperidine (NFP)	7.2 (±1.0)	0.86 (±0.06)
S4	Vinyl pyrrolidone (NVP)	5.5 (±1.5)	0.74 (±0.12)
S5	1,3-Dimethyl-2-imidazolidinone (DMEU)	5.4 (±1.3)	0.73(±0.10)
S6	Bromobenzene	5.1 (±ND[a])	0.71 (±ND)
S7	Benzonitrile	4.8 (±0.6)	0.68 (±0.05)
S8	N-methyl-pyrrolidone (NMP)	4.7 (±1.9)	0.67 (±0.18)
S9	Benzyl Benzoate	4.7 (±1.9)	0.67 (±0.18)
S10	N,N′-Dimethylpropylene urea (DMPU)	4.6 (±1.3)	0.66 (±0.12)
S11	γ-Butyrlactone (GBL)	4.1 (±1.1)	0.61 (±0.12)
S12	Dimethylformamide (DMF)	4.1 (±1.4)	0.61 (±0.15)
S13	N-ethyl-pyrrolidone (NEP)	4.0 (±0.7)	0.60 (±0.08)
S14	Dimethylacetamide (DMA)	3.9 (±1.5)	0.59 (±0.17)
S15	Cyclohexylpyrrolidone (CHP)	3.7 (±1.0)	0.57 (±0.12)
S16	DMSO	3.7 (±1.5)	0.57 (±0.18)
S17	Dibenzyl ether	3.5 (±0.6)	0.54 (±0.07)
S18	Chloroform	3.4 (±0.7)	0.53 (±0.09)
S19	Isopropylalcohol (IPA)	3.1 (±1.0)	0.49 (±0.14)
S20	Chlorobenzene	2.9 (±0,5)	0.46 (±0.07)
S21	1-Octyl-2-pyrrolidone (N8P)	2.8 (±1.0)	0.45 (±0.16)
S22	1-3-Dioxolane	2.8 (±1.4)	0.45 (±0.22)
S23	Ethyl acetate	2.6 (±1.2)	0.41 (±0.20)
S24	Quinoline	2.6 (±0.6)	0.41 (±0.10)
S25	Benzaldehyde	2.5 (±1.5)	0.40 (±0.26)
S26	Ethanolamine	2.5 (±0.4)	0.40 (±0.07)
S27	Diethyl phthalate	2.2 (±1.9)	0.34 (±0.37)
S28	N-Dodecyl-2-pyrrolidone (N12P)	2.1 (±1.1)	0.32 (±0.23)
S29	Pyridine	2.0 (±1.7)	0.30 (±0.37)
S30	Dimethyl phthalate	1.8 (±0.4)	0.26 (±0.10)
S31	Formamide	1.7 (±ND)	0.23 (±ND)
S32	Ethanol	1.6 (±0.7)	0.20 (±0.19)
S33	Vinyl acetate	1.5 (±0.7)	0.18 (±0.20)
S34	Acetone	1.2 (±0.4)	0.08 (±0.14)
S35	Water	1.1 (±0.4)	0.04 (±0.16)
S36	Ethylene glycol	1.0 (±0.8)	0.00 (±0.35)
S37	Toluene	0.8 (±0.4)	−0.10 (±0.22)
S38	Heptane	0.3 (±0.4)	−0.52 (±0.58)
S39	Hexane	0.2 (±0.1)	−0.70 (±0.22)
S40	Pentane	0.16 (±0.05)	−0.80 (±0.14)

[a] Not determined.

suitable for any large scale applications or graphene thin-film formation [11–13]. Exfoliating the graphite in the liquid phase is a way to increase the yield or preparing the graphene for some specific applications [14].

A method to achieve this goal was preparing graphene oxide dispersion and then reduces the obtaining oxide solution [15–17]. However, this technique could result in a dramatic change in the electronic properties of graphene. Another possible procedure in the literature for production of graphene, is the exfoliation of graphite in certain solvents or in aqueous surfactant solutions [18–20]. In spite of interesting effect of solvents in graphene synthesis, very little is known about the details of the interactions between solvent and graphene [14]. Theoretical works that provide an insight to the type of involved interactions in graphene–solvent system are rare. Hernandez et al. tried to find a relationship between Hildebrand solubility parameters, Hansen solubility parameters, surface tension and the dispersibility of graphene [14]. Also, Shih et al. developed a theoretical framework based on molecular dynamic simulations and the kinetic theory of colloid aggregation to elucidate the mechanism of stabilization of the liquid-phase-exfoliated graphene sheets in some polar solvents [21]. Therefore, there is a demand for further theoretical works on the role of solvents in the dispersibility of graphene.

In this work we used the quantitative structure–property relationship (QSPR) approach to find a relation between dispersibility of graphene and structural or physical/chemical parameters of the solvents. According to the best of our knowledge, this is the first report on the application of QSPR analysis for the liquid-phase-exfoliated graphene, as a highly important subject. It might not needed to state that the well known quantitative structure–property/activity relationship (QSPR/QSAR) methods provide scientific tools for data exploring and data understanding and for the prediction of the property/activity of new untested chemicals, drugs or biomolecules [22–26]. These methods make it possible to predict the activity/property of a given compound using its molecular structure; so the need of trial-and-error experiments could be significantly decreased.

2. Materials and methods

2.1. Data set

The dispersibility of graphene (D_G) in 40 solvents was obtained from the study of Hernandez et al. [14]. The values of D_G in each solvent and the experimental standard deviation related to each value (in parenthesis) are listed in Table 1. More details about the data set and experimental procedure for calculation of D_G are noted in [14].

In order to obtain the relationship between the graphene solubility as dependent variable and solvent structures as independent variables, logarithm of the dispersibility of graphene (log D_G) were used.