C60 Fullerene: Surface Energy and Interfacial Interactions in Aqueous Systems

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Abstract

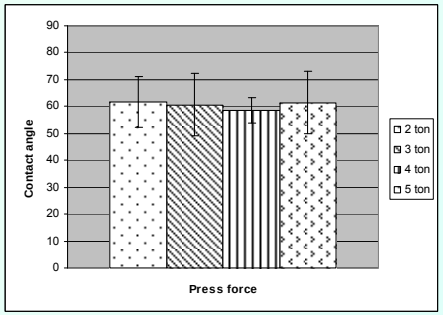
The underlying mechanisms of fullerene-fullerene, fullerene-water, and fullerene-soil surface interactions in aqueous systems are not well understood. To advance our understanding of these interfacial interactions, the surface properties of C_{60} and quartz surfaces were investigated. From application of the van Oss-Chaudhury-Good model and the Young-Dupre equation, the Lifshitz-van der Waals, acid-base, and the total surface energies of C_{60} powder and quartz surfaces were calculated from contact angle measurements using the sessile drop technique. C_{60} powder measurements indicate low to medium energy surfaces of 41.7 mJ/m^2 with a dominant Lifshitz-van der Waals component. In aqueous systems, hydrophobic attraction due to the high cohesion of water is the driving force for C_{60} aggregation. The high free energy of hydration (ΔGpwTotal = –90.5 mJ/m^2) indicates the high affinity of C_{60} particles for water. Hamaker constants of 4.02 x10^{-21} J (A_{pwp}) and 2.59x10^{-21} J (A_{pws}) were derived for C_{60}-C_{60} and C_{60}-quartz interactions in aqueous systems. The results of this study indicate that surface energy is an important physical parameter that should be considered as a basic characterization property of fullerene nanomaterials.

Experimental

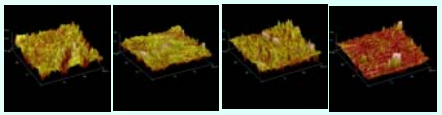
- 10 mg of ground C_{60} powder was pressed into a 4 mm diameter pellet.
- Contact angles measurements were performed using a contact angle goniometer.
- Six probe liquids were used in contact angle measurements: double deionized H_2O (DDI) resistivity > 18 MΩ/cm), glycerin, 1-bromonaphthalene (97%), formamide (deionized, 99.5%), diiodomethane (99%) and 1,1,2,2-tetrabromoethane (Laboratory grade).
- The pendant drop was dispensed just above the pellet surface and touch-off drops.
- The high speed with imaging period of 0.02 seconds accurately captured the contact of liquid with the pellet surfaces .

Figure 1. The pellet preparation using a 5-ton hydralic press

(a)



(b)



R_{rms} = 52.2 ± 30 nm R_{rms} = 43.6 ± 5.6 nm R_{rms} = 48.2 ± 22 nm R_{rms} = 41.5 ± 17.9 nm

Figure 2. The effect of pellet compactness on contact angle measurement. (a) Water contact angles on C_{60} pellets made under different press force. (b) Representative AFM images of pellet roughness (root mean square roughness, R_{rms}) under different press force.

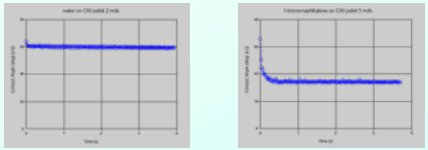


Figure 3. Examples of contact angle-time profiles. a). Constant contact angle profile; b). Decreasing contact angle profile.

(a)

	Test liquid		Dispersive	Polar	Acid	Base	Contact Angle (θ)	
		γ^{TOT}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}	C_{60}	quartz
1	water[a]	72.8	21.8	51.0	25.5	25.5	60.6 ± 2.6	8.8 ± 2.4
2	diiodomethane[a]	50.8	50.8	0.0	0.0	0.0	29.6 ± 2.9	39.4 ± 2.0
3	formamide[a]	58.0	39.0	19.0	2.3	39.6	45.0 ± 2.1	31.4 ± 9.3
4	glycerol[a]	64.0	34.0	30.0	3.9	57.4	79.2 ±3.7	54.3 ± 3.0
5	1-bromonaphthalene[a]	44.4	44.4	0.0	0.0	0.0	32.3 ±2.1	21.1 ±2.8
6	1,1,2,2-tetrabromoethane[b]	49.7	49.7	0.0	3.1	0.0	37.8 ± 3.1	41.1 ± 1.3

(b)

		Dispersive	Polar	Acid	Base
	γ^{TOT}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
1, 2, 3	46.2	44.4	1.8	0.0	19.2
1, 2, 4	49.0	49.0	0.0	0.0	0.7
1, 3, 5	41.0	38.9	2.1	3.1	0.4
1, 3, 6	41.1	38.9	2.1	3.1	0.4
1, 4, 5	40.0	40.0	0.0	0.0	4.6
1, 4, 6	32.6	32.6	0.0	0.0	10.4
average	**41.7± 5.9**	**40.6 ± 5.8**	**1.0 ± 1.2**	**1.0 ± 1.7**	**5.9 ± 8.0**

(c)

		Dispersive	Polar	Acid	Base
	γ^{TOT}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
1, 2, 3	45.0	39.9	5.1	0.1	66.9
1, 2, 4	48.8	48.8	0.0	0.0	51.5
1, 3, 5	45.2	45.2	0.0	0.0	77.6
1, 3, 6	57.1	17.5	39.6	6.2	63.8
1, 4, 5	50.5	50.5	0.0	0.0	54.2
1, 4, 6	38.7	14.3	24.4	1.6	91.3
average	**47.6**	**36.0**	**11.5**	**1.3**	**67.5**
Clean glass [a]	51.7	33.7	18.0	1.3	62.2
SiO2 (Fisher Scientific) [a]	50.7	39.2	11.5	0.8	41.4
Quartz plate [b]	57.2	36.1	21.12	9.4	11.86

Table. (a) Surface Tension Components and Parameters of Test Liquids Used in Contact Angle Measurement (in mJ/m^2) and Contract Angles with 95% Confidence Limit (in deg) measured on C_{60} pellets and quartz; (b) Surface Tension Components and Parameters of C_{60} (in mJ/m^2) with 95% Confidence Limit, Derived from (a); (c) Surface Tension Components and Parameters of Quartz (in mJ/m2), Derived from (a).

$$A_{pp} = 24\pi\gamma_p^{LW} l_o^2$$

$$A_{pwp} = \left(\sqrt{A_{pp}} - \sqrt{A_{ww}}\right)^2 \qquad A_{C60-w-C60} = 4.02\times10^{-21} J$$

$$A_{pwp} = \left(\sqrt{A_{pp}} - \sqrt{A_{ww}}\right)^2 \qquad A_{C60-w-quartz} = 2.59\times10^{-21} J$$

Figure 4. Hamarker constants of C_{60}-C_{60} interactions in water and C_{60} interactions with quartz surfaces in water.

$$\gamma_{pw} = \left(\sqrt{\gamma_p^{LW}} - \sqrt{\gamma_w^{LW}}\right)^2 + 2\left(\sqrt{\gamma_p^+\gamma_p^-} + \sqrt{\gamma_w^+\gamma_w^-} - \sqrt{\gamma_p^+\gamma_w^-} - \sqrt{\gamma_p^-\gamma_w^+}\right)$$

$$\Delta G_{pwp} = -2\gamma_{pw} \qquad \Delta G_{C60-w-C60} = -48.0 mJ/m^2$$

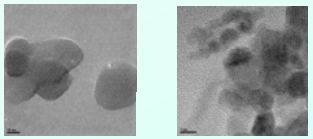


Figure 5. C_{60}-C_{60} agregation in water.

$$\gamma_{pw} = \left(\sqrt{\gamma_p^{LW}} - \sqrt{\gamma_w^{LW}}\right)^2 + 2\left(\sqrt{\gamma_p^+\gamma_p^-} + \sqrt{\gamma_w^+\gamma_w^-} - \sqrt{\gamma_p^+\gamma_w^-} - \sqrt{\gamma_p^-\gamma_w^+}\right)$$

$$\Delta G_{pw} = \gamma_{pw} - \gamma_p - \gamma_w \qquad \Delta G_{C60-w} = -90.5 mJ/m^2$$

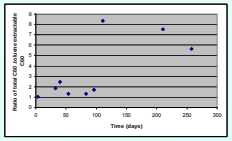


Figure 6. Hydration of C_{60}.

Conclusions

- This study demonstrates that contact angle measurements by the sessile drop technique can be used to derive important surface properties of nanoparticle powders.
- Using this technique, C_{60} powder surfaces are shown to have low-medium surface energy (41.7 mJ/m^2) and the electromagnetic Lifshitz-van der Waals component is the major component of the surface energy of C_{60}.
- Total surface energy derived by VOCG model is close to the critical surface tension.
- The Hamaker constants of C_{60} –C_{60} interaction and C_{60}-quartz interaction in water were also derived.
- The strong cohesion of water induced the hydrophobic attraction, which is the driving force for C_{60} aggregation.
- Interaction energies indicate that C_{60} powder will not bind to monopolar quartz surfaces in water.