Table I

compd	scan rate, mV/s	ODCB[a] (V)[d]			THF (V)[d]			CH_2Cl_2 (V)[d]			PhCN (V)[d]		
		E_1	E_2	E_3	E_1	E_2	E_3	E_1	E_2	E_3	E_1	E_2	E_3
C_{60}	100 (Ag/AgCl)	–0.40	–0.76	–1.25	–0.21	–0.81	–1.39	–0.33	–0.73	–1.22	–0.33	–0.76	–1.25
	1000 (Ag/AgCl)	–0.41	–0.81	–1.27	–0.18	–0.81	–1.40	–0.39	–0.78	–1.25	–0.33	–0.78	
C_{70}	100 (Ag/AgCl)	–0.41	–0.78		–0.18	–0.74	–1.28	–0.38	–0.76	–1.17	–0.33[b]	–0.74[b]	
	1000 (Ag/AgCl)	–0.32[b]	–0.77[b]	–1.23[b]	–0.19	–0.78	–1.29	–0.35	–0.74	–1.17			
Fc[c]	100 (Ag/AgCl)		+0.67			+0.67			+0.59			+0.58	

[a] ODCB = o-dichlorobenzene. [b] Scan rate = 25 mV/s. [c] Fc = ferrocene. [d] E_1, E_2, and E_3 are half-cell potentials; e.g., $E_1 = {}^1/_2(E^p{}_{1red} + E^p{}_{1ox})$.

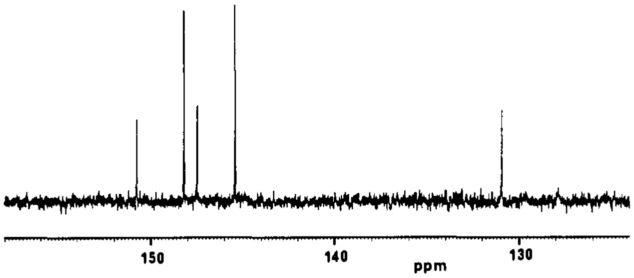


Figure 1. ^{13}C NMR spectrum of a solution of C_{70} in 1,1,2,2-tetrachloroethane-d_2 (6800 scans).

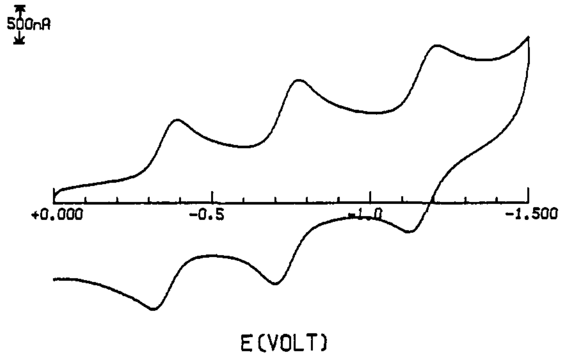
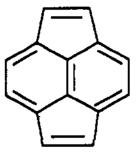


Figure 2. Cyclic voltammogram of fullerene C_{70} in CH_2Cl_2 with 0.1 M $Bu_4N^+BF_4^-$ at ambient temperature. Working and counter electrodes were Pt, the reference electrode was Ag/AgCl, and the scan rate was 1000 mV/s (entry 4 in Table I).

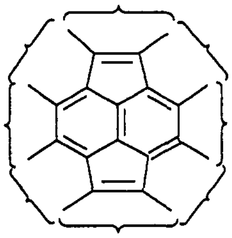
potential could be ascribed to two factors:[8]

a. Negatively charged carbon atoms resulting from electron capture would have more sp^3 character and would have longer bond lengths to their neighbors and hence decrease the strain energy of the cluster; conversely, positively charged members of the cage resulting from electron loss would have more sp^2 character and would have shorter bond lengths to their neighbors and hence increase the strain energy of the cage.

b. If one could consider C_{60} a spherical "superbenzopyracylene", the cage would be expected to be electronegative because pyracylene has a relatively high electron affinity and its LUMO is a NBMO.[9]



Pyracylene



"C_{60}"

On the other hand, C_{70} is more strained than C_{60}[10] and it has fewer pyracylene bonds.[11,12] For reason a, above, the larger strain relief would tend to increase C_{70}'s electron affinity relative to C_{60} but the fewer pyracylene bonds would have the opposite effect. It is possible that both effects operate and cancel each other to produce the observed results.

In conclusion, we discovered that pure C_{60} and pure C_{70} exhibit the same first reduction wave potentials in four different solvents of disparate solvent properties. A reversible reduction potential of only –0.21 V vs Ag/AgCl was found in THF, indicating that the radical anion salts of these fullerenes should be preparable in that solvent. Our results are in agreement with theoretical calculations for C_{60} but not for C_{70}. According to theoretical calculations,[11] the latter would be expected to have a value of $E_1{}^{1/2}$ closer to 0 relative to Ag/AgCl. We interpret our observations in terms of relief of strain[13] and pyracylene-type electronic character of the fullerenes.

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(8) Haddon, R. C. (see ref 5, above), has stated that C_{60} fullerene is an aromatic compound, but no reference is made to the Hückel rule. The C_{60} would be a "4*n*" system, and addition of two electrons would make this a $(4n + 2)\pi$ aromatic dianion.

(9) Trost, B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *J. Am. Chem. Soc.* **1971**, *93*, 737.

(10) From mass spectrometric measurements, it was determined that C_{70} is 8 kcal/mol less stable than C_{60}: Sharma, D. K., et al., in preparation.

(11) Haddon et al. (Haddon, R. C.; Brus, L. E.; Raghavacharty, K. *Chem. Phys. Lett.* **1986**, *131*, 165) reported that C_{70} has a LUMO of $\sim 0 \times \beta$.

(12) If the Hückel rule would apply (see ref 8, above), then C_{70} would be a $(4n + 2)\pi$ aromatic molecule.

(13) Dr. R. C. Haddon has pointed out that what we have termed strain may be the same as his interpretation of bonding in the fullerenes in terms of *rehybridization* (Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243). The higher s character of the bonding system ($s^{0.093}p$) makes it more electronegative.

Formation of Reversed Vesicles

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There is a symmetry among most amphiphilic self-organizing structures in regard to the distribution of polar and nonpolar components. Normal and reversed micelles and normal and reversed hexagonal liquid crystals, as well as normal and reversed O/W and W/O macro- and microemulsions and bicontinuous phases, are documented examples of this symmetrical pattern. One notable exception is vesicles. Normal vesicles or liposomes possessing closed hydrocarbon shells separating well-defined aqueous interior and exterior phases were first described in 1964.[1,2] These first vesicles were prepared by dispersing phospholipid lamellar liquid crystals in water. Since then many other amphiphiles with

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(1) Bangham, A. D.; Horne, R. W. *J. Mol. Biol.* **1964**, *8*, 660.

(2) Bangham, A. D. *Prog. Biophys. Mol. Biol.* **1968**, *18*, 29.

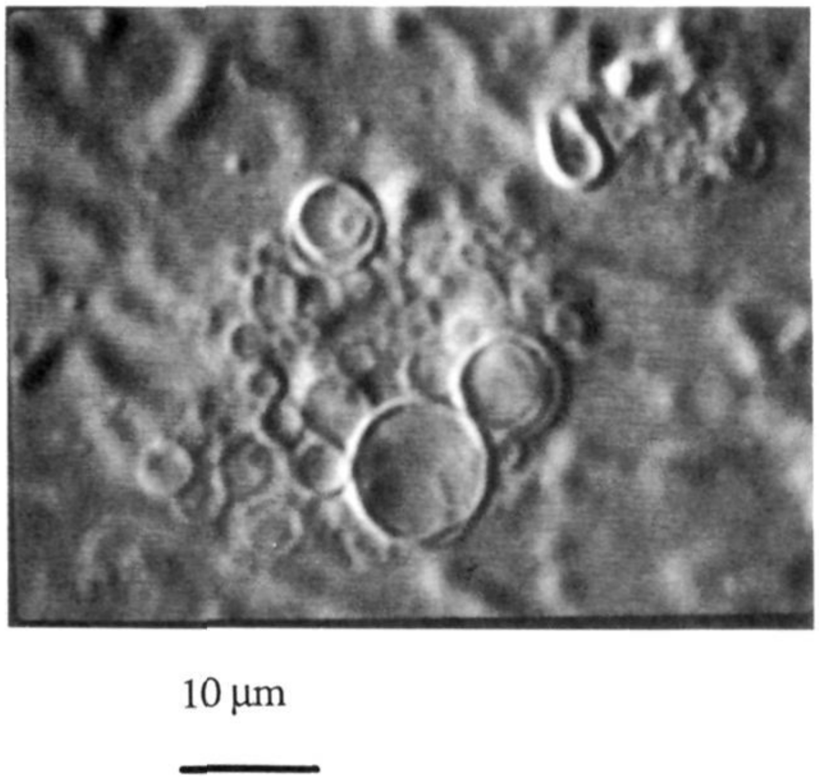

Figure 1. Reversed vesicles in hydrocarbon by VEM at room temperature (25 °C). The composition is 1 wt % water and 99 wt % dodecane solution containing 2.5 wt % $R_{12}EO_4$.

phase behavior similar to that of lecithin have been prepared in the vesicular state. Vesicles play an important role in many physiologic processes such as endocytosis, exocytosis, and pinocytosis, serve as the basic model for biological membranes, and are employed in industrial processes.[3,4] The literature on normal vesicles and liposomes is now vast, but the question of whether reversed vesicles form remains unanswered. In this paper, we present the first evidence establishing the existence of reversed or inverted vesicles.

The nonionic surfactant tetraethyleneglycol dodecyl ether ($R_{12}EO_4$) dissolves in dodecane to form isotropic solutions; no liquid crystal structures are observed in this binary system. However, upon addition of a small amount of water, these isotropic solutions split into a lamellar liquid crystalline phase, as demonstrated by polarized light microscopy, which is in equilibrium with an excess oil phase.[5,6] Unlike most lamellar liquid crystals, the $R_{12}EO_4$ system solubilizes large amounts of hydrocarbon within the single-phase region. For example, even a mixture of 7 wt % $R_{12}EO_4$, 89 wt % dodecane, and 9 wt % water gives a single-phase system. Small-angle X-ray scattering measurements establish that addition of oil increases the interlayer spacing between adjacent water–EO bilayer regions.[7,8] This reversed bilayer system parallels normal bilayer systems in which addition of water increases the spacing between the hydrocarbon bilayers.

Reversed vesicles and liposomes are readily formed by handshaking a two-phase system containing liquid crystals and excess oil. Like normal vesicles, the inverted vesicles coalesce and revert back to a lamellar liquid crystalline phase over a period of hours to days. Figure 1 shows a video enhanced microscope (VEM) image of the vesicles formed from a system of 1 wt % water and 99 wt% dodecane solution containing 2.5 wt % $R_{12}EO_4$. Vesicular size distribution is large; diameters range from submicron to 10–20 μm. Real time VEM images show intense fluctuations of the aqueous vesicular walls, which are very thin in comparison with the vesicular volumes. However, judging from the thickness of vesicular walls in Figure 1, the reversed vesicles are a multilayer type as indicated in Figure 2. By assuming that all the surfactant in excess of its monomer solubility in dodecane, i.e., 1.7 wt %, is incorporated into the vesicles, we estimate that there are 2.5 water molecules/EO unit in the vesicular wall.

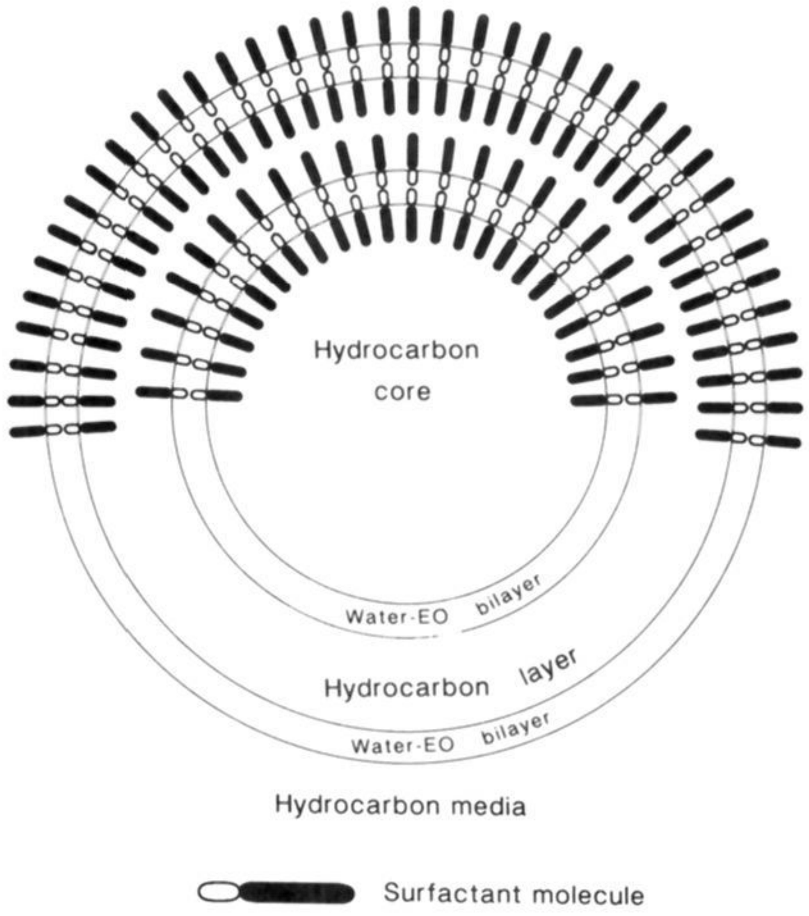

Figure 2. Schematic structure of reversed vesicle. The hydrocarbon tails of surfactant are represented by black rods, and the hydrophilic groups are indicated by open ellipses attached to the tails.

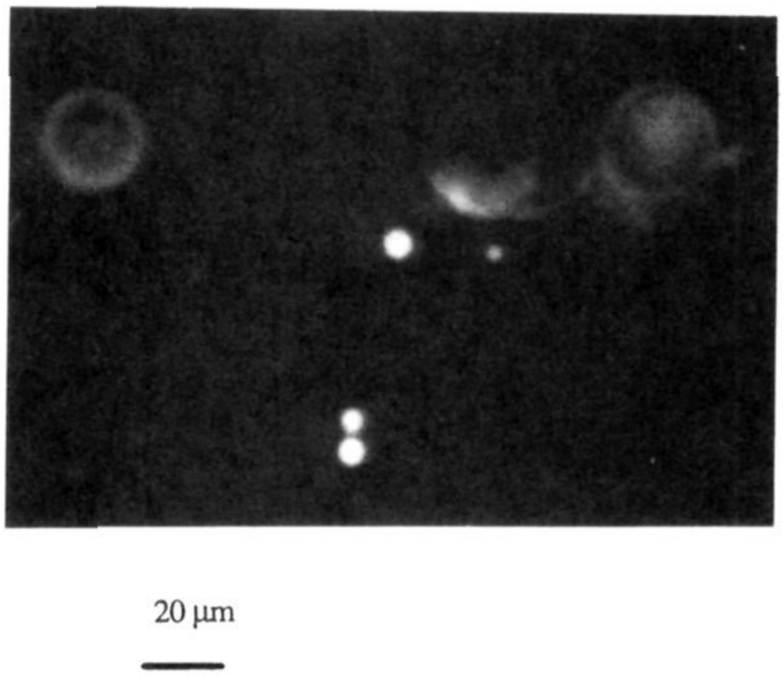

Figure 3. Fluorescence photograph for reversed vesicles at room temperature (25 °C). The composition is identical with that given in Figure 1, except that the aqueous phase also contains 2 mM 5-carboxyfluorescein.

Figure 3 shows a fluorescence image obtained by adding a water-soluble fluorescent agent, 5-carboxyfluorescein (2 mM), to the vesicular system. Only the vesicular walls are visible. Addition of the fluorescent agent changes the phase equilibrium slightly and causes water droplets, the small bright spots in Figure 2, to separate out.

Fluorescent and VEM images establish the existence of inverted vesicules in which closed intershells separate well-defined hydrocarbon interior and exterior phases. Symmetry along amphiphilic self-organizing structure appears to be a general phenomenon in nature.

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(7) Lichterfeld, F.; Schmeling, T.; Strey, R. *J. Phys. Chem.* **1986**, *90*, 5762.

(8) Kunieda, H., et al., unpublished data.