Electrochemistry of pyrimidine containing azahomo- and aziridino[1,2][60]fullerenes

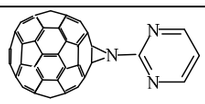
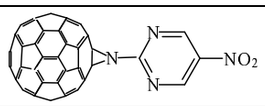
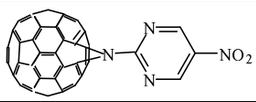
I. P. Romanova, D. G. Yakhvarov,

V. V. Kalinin, O. G. Sinyashin

A.E.Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Centre of Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation,
Fax: +7(843 2) 75 2253. E-mail:romanova@iopc.knc.ru

It is known that anion-radical salts of fullerenes with organic donors show unique superconductive and ferromagnetic properties. However it is necessary to solve the problem of fullerene solubility in organic solvents and increase their electron affinity for the successful syntheses of anion-radical salts. One of possible solutions of these problems is the addition of electron-withdrawing fragments to the fullerene sphere. For this purpose the pyrimidine and nitropyrimidine heterocycles were added to C_{60} by the reaction of [60]fullerene with corresponding azides. As a result the aziridino[1,2][60]fullerenes (6.6-closed adducts) (**I, II**) and azahomofullerene (**III**) (5.6-opened adduct) were obtained. The electrochemical behaviour of obtained derivatives of fullerene was studied using the method of the cyclic voltammetry measurements. It is known that in solutions C_{60} shows up to six successive, full reversible, one-electron reductions. In studied conditions (solvent: mixture of o-DCB:MeCN=3:1, supporting electrolyte: 0.1M Bu_4NBF_4, working electrode: carbon glass (S_{work}=3.14 mm2), reference electrode: $Ag/AgNO_3$, 0.01M in MeCN, temperature 20°C) C_{60} shows only four waves of reductions. The electrochemical reduction of fullerene derivatives **I-III** was successive also and passed in the range of potentials from - 0.70 to - 2,5 V. The pyrimidine fragments were reduced in this range also. As a result cyclic voltammograms of **I-III** exhibited six reduction waves, four of them being reversible and corresponding to the transfer of electrons onto the fullerene. It is of importance that all of the reduction potentials of all derivatives **I-III** are less negative than the corresponding potentials of [60]fullerene. The most pronounced effect was observed for nitropyrimidine containing 6.6-adduct **II**, the least pronounced – for pyrimidine containing 6.6-adduct **I** (the first potentials of the peaks of cathodic and anodic waves of C_{60} and derivatives **I-III** are showed in table).

The unique electrochemical behaviour of derivatives **I-III** is stipulated by the combination of several factors: a) by the electron-accepting properties of nitrogen atoms in imino-bridge of azahomofellerene **III** and in aziridine cycle of aziridini[1,2][60]fullerenes **I-II**, b) by electron-accepting properties of pyrimidine cycle and nitro-group, c) by the structure of homofullerene sphere in azahomofellerene **III** and d) by the “periconjugation” of fullerene and pyrimidine fragments and nitropyrimidine fragments in **I** and **II**.

Compound		K_1		A_1	
		-E, V	*I, μA*	*-E, V*	*I, μA*
	C_{60}	0.83	4.2	0.76	3.0
I		0.78	2.5	0.72	1.6
II		0.73	3.0	0.65	1.3
III		0.75	3.5	0.69	1.2

K_1 – first cathode wave
A_1 – anodic component of the first cathode wave