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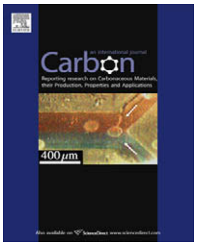

Redox potentials and binding enhancement of fullerene and fullerene–cyclodextrin systems in water and dimethylsulfoxide

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ABSTRACT

The formal redox potentials of electron transfer reactions of fullerene, methanofullerene, fullerene–cyclodextrin complex and methanofullerene conjugates with cyclodextrins in aqueous and dimethylsulfoxide solutions are reported. These new compounds are surface active and retain the redox activity of C_{60} even in aqueous medium. Compounds have been characterized by an electrochemical admittance technique, which offers an advantage of separating faradaic and capacitive properties. Observed difference of formal redox potentials of the free fullerene forms and their cyclodextrin-containing compounds were used to determine the binding enhancement. Results are interpreted in terms of inter-molecular host–guest interactions of C_{60}-cyclodextrin conjugates.

1. Introduction

Redox potential is an important parameter in characterization of new electroactive materials. This communication reports the determination of the formal redox potentials of a series of the fullerene-containing compounds designed for applications in protic media. We use the advantage of electrochemical impedance techniques, which allow the separation of redox and adsorptive phenomena in the surface-active systems on the basis of different phase relations.

Fullerene C_{60} (**1**) is a highly hydrophobic compound with a cage-like structure [1]. The lowest unoccupied molecular orbital of C_{60} is threefold degenerate, which enables up to six electron transfers [2–5]. Rich redox chemistry is a subject of an intensive research [6]. Highly reactive reduced forms of fullerene attract interest for application as redox mediators [7,8], in photovoltaic cells [9,10] and possibly also in the field of pharmaceutical products [11–13]. These applications are often impeded by insolubility of C_{60} in aqueous medium [14]. Different approaches for making aqueous solutions of fullerene have been reported. A high-power sonication [15] of a two-phase mixture of C_{60} solution in benzene and water produces an aqueous emulsion containing C_{60}. A more efficient method is based on the complexation of C_{60} with cyclodextrins

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[16,17], dextran and saccharose [18] or other supramolecular ligands [19–21], which yield water soluble fullerene complexes. The redox chemistry of fullerenes in water using cast films of fullerene embedded in artificial lipids [22] was also explored. The complexation with γ-cyclodextrin (γCD) seems to be the most viable method. The formation of a complex **3** [C_{60}(γCD)$_2$] with stoichiometry 1:2 was confirmed [23]. The preparation of the complex **3** was described by several authors [7,17,23]. The reported stability constant of **3** in water is $K = 2.6 \times 10^7\ \mathrm{dm^3\,mol^{-1}}$ [23].

The effect of electrolytes on the redox behavior of methanofullerenes was reported by Zhang et al. [24]. The competing complexation of cyclodextrins with other solution components can lead to expulsion of C_{60} from the cyclodextrin cavity and has to be taken into consideration. It was suggested that a covalent attachment of cyclodextrins to fullerene could promote the formation of an intra-molecular complex. Four new conjugates **4**–**7** of fullerene and cyclodextrin were recently synthesized for this purpose (Fig. 1) [25–27]. Compounds **2** and **3** are included in the present study for comparison with compounds **4**–**7**, where the formation of a complex is an issue. Derivatives **4** and **5** have a covalent link attached to the primary CD rim. This modification achieved the highest solubility of fullerene-containing compounds in water. It was shown that **4** and **5** have a strong tendency to form aggregates in aqueous solutions and the internal complexation of fullerene by cyclodextrin moiety was not proven [28]. Compounds **6** and **7** contain cyclodextrin ligands attached to the secondary CD rim. These two derivatives were not yet scrutinized with respect to their complexation properties.

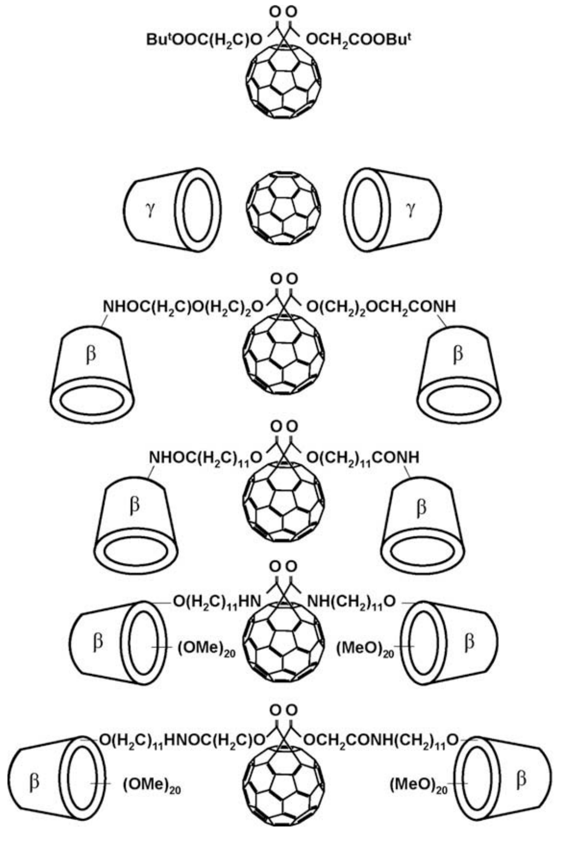

Fig. 1 – Chemical structures of fullerene derivatives. Truncated cones with a Greek symbol represent the corresponding cyclodextrin moiety.

In the first part of this study we address the problem to which extent the redox properties of fullerene are retained in compounds **4**–**7**. We expect that the change of the reversible redox potentials of fullerene derivatives complexed with a covalently bound cyclodextrin could confirm the internal complexation and eventually yield an estimate of the stability constants. The estimation of stability constants from the difference of reversible half-wave potentials $E_{1/2}$ is an established method in coordination chemistry [29]. However, it is much less frequently used in complexation of non-metallic compounds. The reduction of the oxidized form, "Ox", in a form of its complex Ox $\mathrm{L_p}$ with number (p) of ligands (L) proceeds according to a scheme, in which either a complete dissociation precedes the reduction to the reduced form, "Red", or the electron transfer is coupled with a change of the number of ligands

$$\mathrm{Ox\,L}_p + n\mathrm{e}^- \leftrightharpoons \mathrm{Red\,L}_{(p-q)} + q\mathrm{L} \tag{1}$$

The observed difference of reversible redox potentials of the complex and the free form $\Delta E_{1/2}$ is related to the consecutive stability constant K_i

$$\Delta E_{1/2} = \frac{RT}{nF} \ln\ K_\mathrm{i}[\mathrm{L}]^q \tag{2}$$

neglecting the difference of diffusion coefficients of both forms involved. A similar approach was adapted to supramolecular complexes using a simple square scheme, which includes host–guest equilibrium and the redox change. The square scheme applicable to our system involves a redox active guests (C_{60} and C_{60}^{-}) and the cyclodextrin ligand L. Consecutive stability constants K_i in this formulation are replaced by the stability constant of the oxidized form K_Ox and of the reduced form K_Red

$$\begin{array}{ccccc} \mathrm{L} & + & \mathrm{Ox} & \leftrightharpoons & \mathrm{Ox\,L} \\ & & n\,\mathrm{e}^- \downarrow\uparrow & & \downarrow\uparrow n\,\mathrm{e}^- \\ \mathrm{L} & + & \mathrm{Red} & \leftrightharpoons & \mathrm{Red\,L} \end{array} \tag{3}$$

Often the reduced form is more strongly bound to the host molecule than in the initial oxidized form. In such a case the system is characterized by the ratio of complex stability or association constants $r = K_\mathrm{Red}/K_\mathrm{Ox}$, which is defined as the binding enhancement [30]. The value of the binding enhancement may be estimated by the difference in formal potentials for the free E_F^0 and complexed E_C^0 guest

$$r = \frac{K_\mathrm{Red}}{K_\mathrm{Ox}} = \exp\left[-\frac{nF(E_\mathrm{F}^0 - E_\mathrm{C}^0)}{RT}\right] = \exp\left[-\frac{nF\Delta E_{1/2}}{RT}\right] \tag{4}$$

The application of Eqs. (2) or (4) to complexation of fullerene and cyclodextrin requires the knowledge of the reversible potential E_F^0 of the uncomplexed form of C_{60} in a given solvent. The redox potential of fullerene in water is not known. The reason is the insolubility of C_{60}. Hence the estimation of the redox potentials of C_{60} in solvents, where the complexation with cyclodextrin is expected, is the first issue to be addressed in this communication.