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Physico-chemical properties of the fullerenol-70 water solutions

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ABSTRACT

The paper presents some data on physico-chemical study of the fullerenol-70 water solutions. The data on temperature dependence of solubility in water, concentration dependence of density, concentration dependence of the hydrogen ion concentration, specific conductivity, molar conductivity, dissociation constant, and dynamic light scattering are presented and characterized; composition of equilibrium solid phase in the fullerenol-70 + water binary system is determined.

1. Introduction

It is known that fullerenes (C_{60}, C_{70}) have different ways of application. However, their widespread use is limited by incompatibility with water and water solutions [1,2].

The present paper is devoted to the investigation of the physico-chemical properties of water-soluble fullerenol-70–$C_{70}(OH)_{12}$. It should be pointed that usually the term "fullerenol" includes hydroxyl- derivatives of all individual fullerenes $C_n(OH)_X$ (n = 60, 70, 76, 78, 84, 90) and mixtures of individual fullerenols of different compositions or individual fullerenols of low purity (for example, less than 95 wt.%); besides the hydroxyl groups, fullerenols can also include some other non-hydroxylic groups, such as oxygen groups (=O, –O–) $C_n(OH)_XO_Y$ and salt type groups, such as $[C_n(OH)_XO_Y](ONa)_Z$, etc. [3].

Fullerenols are one of the most important and promising fullerene derivatives that can be easily synthesized with tunable properties by varying the number of hydroxyl groups introduced. Analysis of literature demonstrates a wide spectrum of the fullerenol's application possibilities in various fields of science and technology, namely in: (i) biology and medicine (in chemotherapy, treatment of neurodegenerative diseases, radiobiology etc.) due to antioxidant, free radical acceptor, extent antiproliferative, antitumor and neuroprotective properties [4,5]; (ii)catalysis (in particular for the synthesis of cyclic carbonates from CO_2 and epoxides) [6]; (iii) development of photovoltaic devices [7]; (iv) as nanomodifiers of polyelectrolytes, paints, polymers [8–10].

The literature data devoted to the investigation of polyhydroxylated C_{70} fullerene are few in number (in comparison with fullerenol obtained from the C_{60} individual fullerene). Moreover the main part of investigations is devoted to the development of the fullerenol-70 synthesis. Chen et al. described the method of hydrolysis of the polycyclosulphated intermediate $C_{70}(SO_4)_x$ leading to polyhydroxylated fullerene the C_{70} molecule to form fullerenol $C_{70}(OH)_{14,16,18,20}$ [11]. Wang et al. used the PM3 semi-empirical method for identification of the $C_{70}(OH)_{14,16,18,20}$ possible geometric isomers obtained in ref. 11. The authors have estimated the stability of isomers, calculated their thermodynamic characteristics, and proposed the mechanism of the fullerenol-70 synthesis by hydrolysis of the polycyclosulphated intermediate $C_{70}(SO_4)_x$ [12]. Wang et al. determined that the most stable isomers are hydroxy-isomers, in which the hydroxyl groups are located in the "equatorial region" of fullerene, because the C–C bond length in this region is greater than in other regions of the molecule. Consequently, in this case the hydroxyl groups have

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less mutual repulsion, which causes additional stability. Thus, the relative stability of fullerenols increases with increasing of hydroxyl groups number in the equatorial region of the C_{70} molecule [12]. Xia et al. studied nanocomposites obtained by incorporation of molecules of fullerenol $C_{60}(OH)_n$ and $C_{70}(OH)_n$ in gels of SiO_2, SiO_2–TiO_2, GPTMS-SiO_2, and GPTMS-ATPS, by sol–gel method [13]. Chiang et al. synthesized the thermally stable solid materials containing soluble fullerenols, and found the possibility of the obtained nanocomposites application as optical limiters [14]. Meier et al. have developed a method of synthesis of fullerene diols 2–$C_{70}(OH)_2$ and 5,6–$C_{70}(OH)_2$ and characterized these species by IR, NMR, electron microscopy, and high performance liquid chromatography [15].

The present paper is devoted to the investigation of the physicochemical properties of the fullerenol-70 water solutions in particular solubility, density, conductivity as well as to investigation of the fullerenol-70 water solutions by the dynamic light scattering method.

2. Experimental

2.1. Materials

Fullerene C_{70} of mass fraction purity 99.9%, with the main detectable impurity C_{60} ($\omega = 0.001$) was used. The reagent was produced at ZAO "ILIP" (St. Petersburg) by Kretschmer method. The other reagents used were reagent grade benzene, methanol, 40% aqueous solution of tetrabutylammonium hydroxide, sodium hydroxide (purchased from Vecton Ltd, St.-Petersburg), and distilled water. The synthesis was carried out according to ref. 16 by the method of direct homogeneous catalytic oxidation of individual fullerene C_{70}. A saturated solution of C_{70} (1 g) in benzene (500 ml) was prepared by isothermal saturation at 20 °C for 8–10 h. The obtained solution was filtered using "Green Ribbon" filters to remove the undissolved C_{70}, whereupon 20 ml of 50% aqueous sodium hydroxide solution was added to the filtrate. The phase transfer catalyst (40% solution of tetrabutylammonium hydroxide in water) was added to the reaction mixture dropwise while stirring up to bleaching of the solution. Benzene was removed from the reaction mixture in a vacuum (0.1 mm Hg) at 40 °C. The remaining precipitate and alkaline solution were stirred for 10 h. Then an additional portion of water (200 ml) was added for completion of reaction. The resulting red-brown solution was separated from the undissolved residue using "Green Ribbon" filter. The filtrate was concentrated on a rotary evaporator (0.1 mm Hg) at 40 °C to 50 ml, whereupon 150 ml of methanol was added to the residue to precipitate the fullerenol-70. Reprecipitation procedure was repeated three times. The obtained substance was additionally washed by HCl (conc.) water solution and by methanol using Soxhlet apparatus. The fullerenol-70 was dried in a vacuum at 40 °C (0.1 mm Hg) for 4 h to remove the traces of methanol and benzene. The yield of the mixed product was 225 mg (from 1000 mg of C_{70}). The identification of the synthesized derivative ($C_{70}(OH)_{12}$) was carried out using the complex of the physico-chemical methods such as IR, UV–spectroscopy, mass-spectrometry, and elemental analysis. The obtained data on the fullerenol-70 identification are well agreed with the literature [16].

2.2. Apparatus and procedures

The measurements of the concentration dependence of density of the fullerenol-70 aqueous solutions were performed by the pycnometer method. We used quartz pycnometer, volume calibration was performed with distilled water, the accuracy of temperature control during the density measurement was $\Delta T = \pm 0.1 \div 0.2°$, the accuracy of densities determination is equal to $\Delta\rho = \pm 0.001\ g \cdot cm^{-3}$.

The temperature dependence of the $C_{70}(OH)_{12}$ solubility in water in the temperature range 293.15–353.15 K was carried out by the method of isothermal saturation in ampoules. The saturation time was equal to 8 h; temperature was maintained with accuracy equal to ±0.05. For the fullerenol-70 water solutions saturation the thermostatic shaker (LAUDA ET 20) was used at a shaking frequency $\omega \approx 80c^{-1}$, quantitative determination of fullerenol-70 in water was performed using the gravimetric method (by evaporation at 50 °C (p = 0.1 mm Hg) of the fullerenol-70 aqueous solution up to dryness). The relative uncertainty of the solubility determination was equal to ±3%. Relative air humidity was 40–50%.

For the thermogravimetric investigation of the fullerenol-70 crystallohydrate we have used NETZSCH STA 449F3STA449F3A-0483-M apparatus, the temperature range was 293–873 K at the air, the heating rate was 5 K/min.

For determination of the $C_{70}(OH)_{12}$ water solutions specific conductivities the Cyber Scan PC-300 measuring device was used. The relative uncertainty of the specific conductivity determination was equal to ±1%. The solutions used were saturated by atmospheric air.

Concentration dependence of hydrogen ion concentration of the fullerenol-70 water solutions was measured using pH-meter–Mill Volt-meter pH-121 and glass electrode with hydrogen function EVL 1 M3. Verification of the electrode was performed with the help of water basic buffer solutions NH_4OH–NH_4Cl. Accuracy of measurements was the following: ΔpH = ±0.1.

The fullerenol-70 nanoparticle size distribution measurements in aqueous solutions of different concentrations were carried out by the dynamic light scattering with the help of Malvern Zetasizer 3000 (Great Britain) device.

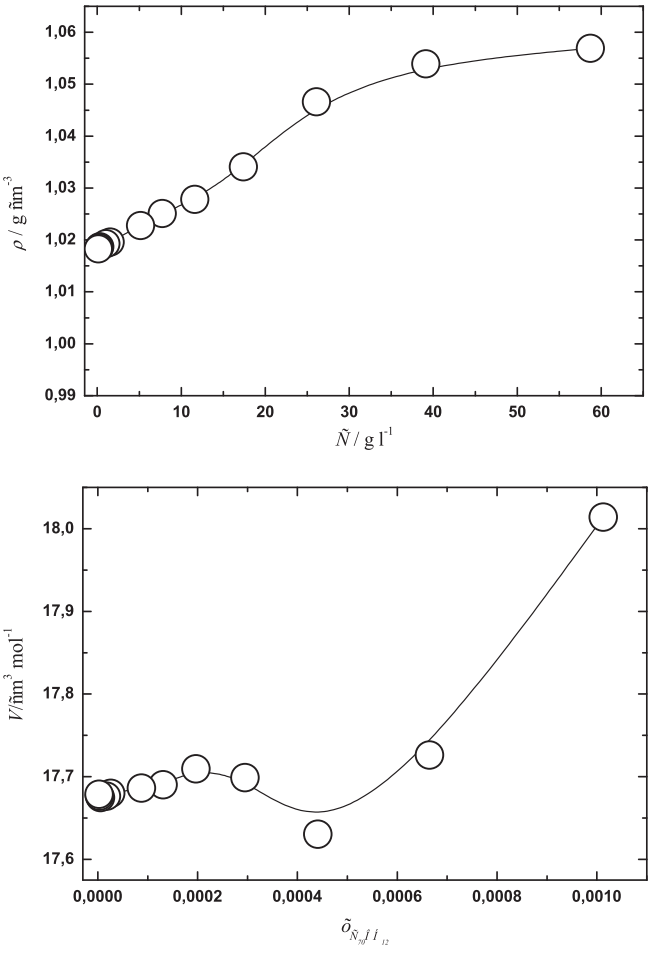

Fig. 1. Concentration dependence of density (1.1) and average molar volume of the fullerenol-70 water solutions (1.2) at 298.15 K.