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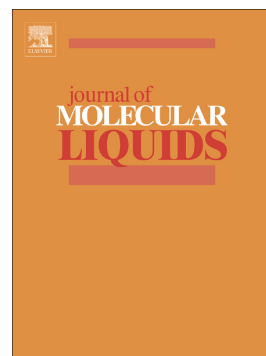
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Physico-chemical properties of $C_{60}(OH)_{22-24}$ water solutions: density, viscosity, refraction index, isobaric heat capacity and antioxidant activity

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ABSTRACT: This paper investigates the physico-chemical properties of several polyhydroxylated fullerene (fullerenol, $C_{60}(OH)_{22-24}$) water solutions. The values of densities (ρ), refraction indexes (n_D), isobaric heat capacities (C_p) and viscosities (η) were experimentally determined in the temperature range 278.15–323.15 K and at fullerenol concentrations up to 40 g·dm⁻³. For the highest fullerenol concentration (40 g·dm⁻³), density, viscosity and isobaric heat capacity modifications reach 4.5%, 56%, and 3%, respectively. Either temperature, T , and concentration, x , dependences of these physical properties were described by polynomial fittings or well-known expressions as the Vogel-Fulcher-Tamman equation, while T - x behaviors were described with the use of a second order polynomial function of both temperature and concentration (the standard deviations do not exceed 0.04). The dynamic and structural characteristics of (fullerene-water) and (fullerenol-water) binary systems were determined by using DFT and MD methods. Finally, the study was completed with the characterization of antioxidant activity of the fullerenol.

Keywords: fullerenol, aqueous solutions, density, viscosity, refraction index, isobaric heat capacity, molecular dynamics simulation, antioxidant activity

Introduction

Nowadays polyhydroxylated fullerenes (fullerenols or fullerols) are eligible to be the most studied and class of fullerene derivatives which are water-soluble [1–4]. This fact is related to the low toxicity and the simple structure of fullerenols, which allows additional modifications to conveniently adapt these structures in order to multiple practical applications. Thus, earlier studies have proposed the utilization of polyhydroxylated fullerenes as modifiers of polyelectrolytes [5,6], polymers [3,7], polymeric membranes for separation of gaseous and liquid mixtures [8,9], paints [10], concretes [11], lubricants [12], etc.

It is necessary to point out the following considerations: (i) not only individual light fullerenes (C_{60} and C_{70}) – $C_{60(70)}(OH)_x$ are usually considered as polyhydroxylated fullerenes, but also adducts of heavy fullerenes $C_n(OH)_x$ ($n = 60, 70, 76, 78, 84, 90$) are classified like that; (ii) in addition to hydroxyl groups, fullerenols can incorporate different oxygen-containing groups ($=O$, $-O-$) as well as salt-type groups ($[C_n(OH)_xO_y](ONa)_z$); (iii) mixtures of individual polyhydroxylated fullerenes of various compositions obtained from industrial fullerene mixtures as well as individual polyhydroxylated fullerenes of low purity (less than 95 %) can also be referred to as fullerenols.

In recent decades, the biological properties of water-soluble polyhydroxylated fullerenes have been intensively studied. Due to their structure with a hollow of spherical shape, hydrophilic properties and possibilities of modification followed by immobilization of various biologically active molecules, fullerenols are perspective nanoscaled carriers of drugs [3,13,14]. Additionally polyhydroxylated fullerenes reveal a powerful antioxidant ability (in *in vitro* and *in vivo* experiments), protective activity against radiation (UV and ionizing), antimutagenic, antitumor, and antimetastatic effects [15–19], effectiveness to reduce cardiotoxicity of some drugs and potential ability to inhibit the propagation of HIV and hepatitis C viruses [15]. Panova et al. [20] determined the influence of polyhydroxyfullerene (PHF) on improving of crop yield and quality of barley. Authors performed vegetation experiments in favorable and stressful

conditions and determined that fulleranol action is caused by antioxidant activity. At the same time, the plant growth and development impact mechanism still has not been studied [20]. To the extent of our knowledge, the following theoretical and experimental results have been obtained for polyhydroxylated fullerene derivatives: (i) Adnadjevic et al. [21,22] studied the isothermal kinetics of fulleranol $C_{60}(OH)_{24}$ formation in the alkaline medium using tetrabutylammonium hydroxide (TBAH) [21] and in heterogeneous process of C_{60} oxidation by H_2O_2 with the use of cetyltrimethyl ammonium bromide (CTAB) [22]; (ii) Different authors studied the physico-chemical properties of fulleranol aqueous solutions [23–28]. Thus, Sardenberg et al. [23] investigated electrochemical impedance for the $C_{60}(OH)_{22-26}$ and $C_{60}(OH)_{18-22}(OK)_4$ derivatives, Najaf [24] analyzed the dispersion, stability, and agglomeration for $C_{60}(OH)_x$, $x = 24-28$, Vranes et al. [25] measured densities, electrical conductivities as well as dynamic viscosities in the temperature interval 293.15–315.15 K for aqueous solutions of fulleranol obtained by hydrolysis of $C_{60}Br_{24}$. Previously in our scientific group we carried out investigation of the T - x solubility in binary systems $C_{60}(OH)_{22-24}-H_2O$ and $C_{70}(OH)_{12}-H_2O$, concentration dependences of density, pH, molar conductivity, dissociation constant, activity coefficient, associates size distribution in aqueous solutions at 298.15 K for $C_{60}(OH)_{22-24}$ and $C_{70}(OH)_{12}$ [26,27], as well as solubility in ternary systems $C_{60}(OH)_{22-24}-H_2O-NaCl$, $C_{60}(OH)_{22-24}-H_2O-Pr(NO_3)_3$, $C_{60}(OH)_{22-24}-H_2O-YCl_3$, $C_{60}(OH)_{22-24}-H_2O-UO_2SO_4$ and $C_{60}(OH)_{22-24}-H_2O-CuCl_2$ at 298.15 K [28]; (iii) Theoretical studies devoted to investigation of fulleranol molecules by density functional theory (DFT) and molecular dynamics (MD) methods are also reported in literature [29–33]. In particular, it was shown that the most stable fullerenols contain the hydroxyl groups in equatorial region of the fullerene core [30,31]. Dawid et al. [30] analyzed how the fullerene functionalization by hydroxyl groups significantly changes its electronic structure and leads to the formation of regions with increased and decreased electrostatic potential. The latest fact causes the association of the fulleranol and water molecules and

significantly increases the complicity of transport processes in comparison with individual fullerene–water binary system [31–33].

This paper presents the physico-chemical investigation of $C_{60}(OH)_{22-24}$ aqueous solutions at fullerenol concentrations in the range $0.25\text{--}40\text{ g}\cdot\text{dm}^{-3}$, which correspond to $3.96\cdot 10^{-6}\text{--}6.39\cdot 10^{-4}$ molar fractions, respectively. Densities, viscosities, refractive indexes and isobaric heat capacities in the temperature interval $278.15\text{--}323.15\text{ K}$ were experimentally obtained for the $C_{60}(OH)_{22-24}$ –water system, in order to analyze the temperature and concentration dependences of these properties. The structural behavior of systems containing fullerene and fullerenol were determined using DFT and molecular dynamics methods. Additionally, the antioxidant activity of $C_{60}(OH)_{22-24}$ was also analyzed in order to demonstrate potential of biomedical application of this compound.

2. Experimental section

2.1. Identification of fullerenol

The polyhydroxylated fullerene derivative $C_{60}(OH)_{24}$ with mass fraction purity 0.998 produced from Ltd ZAO “ILIP” (St. Petersburg) was used for thermodynamic investigation, more information about the used reagents is provided in Table 1. A group of physico-chemical methods was used in order to identify the fullerenol: IR spectroscopy (Shimadzu FTIR-8400S spectrometer, Japan), elemental analysis (EuroVector Euro EA3028-HT, Italy), mass-spectrometry (Shimadzu MALDI-TOF mass-spectrometer Axima–Resonance, Japan), UV–spectroscopy (Shimadzu UV-1800 spectrophotometer, Japan), ^{13}C NMR spectroscopy (NMR-spectrometer Bruker Avance III 400 WB, USA). FTIR: 3420 cm^{-1} (assigned to $\nu\text{O-H}$), 1608 cm^{-1} ($\nu\text{C=C}$), 1450 cm^{-1} ($\delta\text{C-O-H}$) and 1086 cm^{-1} ($\nu\text{C-O}$). Experimental elemental analysis data: (C: 63.72%; H: 2.22%), calc.: (C: 63.83%; H: 2.13%). The negative ion MALDI-TOF mass spectrum of fullerenol reveals ion fragmentation, at the same time detection of a molecular ions at m/z equal to 1094–1128 indicate that fullerenol consists of 22–24 hydroxyl groups. The visible and near UV electron spectrum of the fullerenol aqueous solution does not contain the absorption

peak near 335 nm which is typical for individual C₆₀ fullerene [26]. Although fullerenol UV-V spectra are not really helpful, they can be utilized for composition determination (for example, in the wavelengths range 300–500 nm, where measured absorption is not too high). Figure 1 shows the ¹³C NMR spectrum obtained using the CP/MAS method at a contact time of 2000 μs. An analysis of the obtained spectrum allows to characterize the fullerenol C₆₀(OH)₂₄ sample: (i) the peak in the region of 176.8 ppm can be attributed to the carbon atoms in the fullerene molecule bonded through the inbuilt oxygen atom (Fig. 1, identified with the letter *a*); (ii) the peak at 142.5 ppm corresponds to the structurally "pure" state of the carbon nuclei in the stoichiometric fullerene molecule (Fig.1, *b*), (iii) the intense peak with a chemical shift of 76.3 ppm is due to hydroxylated carbon atoms (Fig. 1, *c*); (iv) the chemical shift of 56.3 ppm can be identified as carbon atoms in the epoxy group (Fig. 1, *d*). Obtained experimental data are in good agreement with other literature results [34,35], taking into account the characteristic aspects of the solid-state NMR.

Fig. 2 shows the NMR spectra of the investigated substance obtained by exciting a signal with different pulse sequences. It can be seen that the above-mentioned spectral lines can be distinguished in both presented spectra. At the same time, on the spectrum obtained by the method of direct excitation, the lines in the region of 60 ppm and 175 ppm have low intensity, which indicates that the studied modified fullerene has practically no improperly modified elements.

Fig. 3 presents the results of the NMR spectra calculation by the DFT method based on plane waves with the PBE and RPBE functionals. It is shown that fullerenols with uniform and Saturn-like distribution of the hydroxyl groups differ significantly from one another in the effect on carbon atoms in the calculated NMR spectra. We can conclude that there is good agreement with the experimental and calculated NMR data.

Obtained experimental data on fullerenol identification also agree with those previously published [26,33,35–39]. According to the elemental analysis results, a relative molar weight of

1128 g·mol⁻¹, corresponding to the fulleranol molecule of C₆₀(OH)₂₄, was considered in all further calculations.

2.2. Density measurement

Using an Anton Paar DMA 5000 M vibrating-tube densimeter (Anton Paar GmbH, Graz, Austria), the densities, ρ , of fulleranol water solutions were determined in the temperature interval 278.15–323.15 K and C₆₀(OH)₂₂₋₂₄ concentrations up to 40 g·dm⁻³. Before each series of measurements we performed the calibration of apparatus at atmospheric pressure and in the same temperature range in which samples were studied, with the use of ambient air and deionized water. The accuracy of density determination with this device is 7·10⁻⁶ g·cm⁻³ (reproducibility 5·10⁻⁶ g·cm⁻³) while temperature is controlled with an accuracy of 0.01 K. Values reported in this work are the average of at least three independent replicates (repeatability of measurements was equal to 1·10⁻⁶ g·cm⁻³).

2.3. Viscosity measurement

The concentration dependence of the fulleranol aqueous solution viscosities, η , in the temperature interval 278.15–313.15 K and C₆₀(OH)₂₂₋₂₄ concentrations up to 40 g·dm⁻³ was measured using a Physica MCR 101 rotational rheometer (Anton Paar GmbH, Graz, Austria) equipped with a cone-plate geometry CP50-1 (50 mm diameter, 1° cone angle and 102 µm cone truncation). Sample temperature was regulated with an accuracy of 0.02 K by means of a Peltier P-PTD 200 system and a H-PTD 200 hood (Anton Paar GmbH, Graz, Austria), providing a stabilization period of at least 100 s before performing measurements. Three separate tests were carried out for each studied condition. The accuracy of viscosity determination with this device did not exceed 3%.

2.4. Refraction indexes measurement

Refraction indexes, n_D , were determined in the temperature interval 278.15–323.15 K and at fulleranol concentrations up to 30 g·dm⁻³ using an Anton Paar Abbemat Multi-Wavelength WR-MW Refractometer (Anton Paar GmbH, Graz, Austria) working at a wavelength of 589.3

nm (the sodium D line). The apparatus calibration was carried out at atmospheric pressure with dry air and deionized water. The accuracies of temperature control and refraction indexes determined with this device are equal to 0.002 K and $4 \cdot 10^{-5}$, respectively. Measurements were repeated three times for each sample and the repeatability of results did not exceed 0.1 %.

2.5. Isobaric heat capacities measurement

Isobaric heat capacities, C_p , were measured in the temperature interval 288.15–313.15 K for water, solid fullerenol and fullerenol-water mixtures by means of a heat-flux Differential Scanning Calorimeter Q2000 (TA Instruments, New Castle, USA) using a refrigerated cooling system RSC90. Experiments were conducted with the use of a quasi-isothermal Temperature Modulated Differential Scanning Calorimetry (TMDSC) method in which temperature was sinusoidally modulated with an amplitude of 0.5 K and a period of 80 s around target temperature. All tests were performed in a nitrogen atmosphere (mole fraction purity ≥ 0.99999). The relative expanded uncertainty C_p of measured values was equal to 3% (at the confidence level of 0.95) [40,41].

2.6. Computational method

The electronic structures of the fullerenol $C_{60}(OH)_{24}$ and the fullerene C_{60} were calculated by DFT method using Dmol³ module from the Materials Studio software package. Optimization of the geometry was performed using PW91 [42] functional with the dnp (version 4.4) basis set, and all electrons were included in the calculation. Used dnp basis sets are similar to 6-31G** sets and include polarization functions. On the basis of calculated charges and the universal force field (UFF), the dynamic and structural characteristics of fullerenol and fullerene in aqueous solutions were determined at $T = 293.15$ K (using Nose thermostat) in accordance with the classical molecular dynamics method using the Forcite module. Each binary system was modeled with a single fullerenol or fullerene molecule and 1500 water molecules in cubic boxes with periodic boundary conditions. The $C_{60}(OH)_{24}$ -water and C_{60} -water binary systems were

investigated using canonical NVT (number of particles, volume and temperature are constant) ensemble. The MD simulation time was 500 ps.

2.7. Antioxidant activity measuring method

The antioxidant activity of the fullerenol was carried out by using the interaction reaction of $C_{60}(OH)_{22-24}$ with the stable DPPH radical (2,2-diphenyl-1-picrylhydrazyl) using the BioRad xMark spectrofluorimeter (Hercules, CA, USA). The reaction mixture was pipetted into a 96-well plate and the absorbance was recorded on a spectrofluorimeter in order to obtain the kinetic dependence of the DPPH reduction by the test substance. The experiment was conducted in the darkness at the wavelength of 515 nm and $T = 298.15$ K. The absorbance of the reaction mixture was recorded every minute during 7 min of an experiment, then every 10 min for a further 170 min and the final value was obtained after six days. Stirring of the reaction mixture was carried out using an orbital shaker.

3. Results and discussions

3.1. Densities and derived volumetric properties of $C_{60}(OH)_{22-24}$ water solutions

Experimental density results of $C_{60}(OH)_{22-24}$ aqueous solutions at fullerenol concentrations up to $40 \text{ g} \cdot \text{dm}^{-3}$ and in the temperature interval 278.15–323.15 K are shown in Table 2 and Fig. 4. Density values increase with the concentration of $C_{60}(OH)_{22-24}$, with enhancements of up to 4.5%. Average molar volumes ($\bar{V}$) of solutions (see Fig. 5) were calculated using the experimental data on densities on the basis of Eq. 1:

$$\bar{V} = \frac{V}{n_{H_2O} + n_{C_{60}(OH)_{22-24}}} \quad (1),$$

where: V is a volume of the $C_{60}(OH)_{22-24}$ aqueous solution; n_{H_2O} and $n_{C_{60}(OH)_{22-24}}$ are the mole number of water and $C_{60}(OH)_{22-24}$ in 1 dm^3 of solution. By using Eqs. (2, 3) we calculated the partial molar volumes of the components present in the solution (V_{H_2O} and $V_{C_{60}(OH)_{22-24}}$) [43]:

$$V_{H_2O} = \left(\frac{\partial V}{\partial n_{H_2O}} \right)_{T,P,n_{C_{60}(OH)_{22-24}}} \quad V_{C_{60}(OH)_{22-24}} = \left(\frac{\partial V}{\partial n_{C_{60}(OH)_{22-24}}} \right)_{T,P,n_{H_2O}} \quad (2),$$

$$V_{H_2O} = \bar{V} - x_{C_{60}(OH)_{22-24}} \left(\frac{\partial \bar{V}}{\partial x_{C_{60}(OH)_{22-24}}} \right)_{T,P} \quad V_{C_{60}(OH)_{22-24}} = \bar{V} - x_{H_2O} \left(\frac{\partial \bar{V}}{\partial x_{H_2O}} \right)_{T,P} \quad (3),$$

where: $x_{C_{60}(OH)_{22-24}}$ and x_{H_2O} molar fraction of fulleranol and water, correspondingly.

Figs. 6 and 7 present the concentration dependences of water and $C_{60}(OH)_{22-24}$ partial molar volumes (V_{H_2O} and $V_{C_{60}(OH)_{22-24}}$) in the temperature interval 278.15–323.15 K. Concentration dependences of the $C_{60}(OH)_{22-24}$ partial molar volumes ($V_{C_{60}(OH)_{22-24}}$) have complex behavior: in the region of low concentrations the fulleranol partial molar volumes are negative and the absolute values are extremely high (Fig. 7). It means that even the addition of a limited quantity of $C_{60}(OH)_{22-24}$ leads to significant compacting and structuring of aqueous solutions. The $C_{60}(OH)_{22-24}$ molecules are embedded into the structure of water solutions and occupy the volume corresponding to the electronic structure. Similar structuring effects of nanocluster solutions were previously detected in binary systems containing carboxylated fullerenes ($C_{60}[C(COOH)_2]_3$, $C_{70}[C(COOH)_2]_3$) [44,45], and light fullerene derivatives with L-amino acids such as arginine ($C_{60}(C_6H_{13}N_4O_2)_8H_8$) [46], threonine ($C_{60}(C_4H_9NO_3)_2$) [47], lysine ($C_{60}(C_6H_{14}N_2O_2)_2$) [48] and hydroxyproline ($C_{60}(C_5H_9NO_3)_2$) [49].

It is well known that higher-order derivatives of Gibbs potential (in our case second derivatives), corresponding to the first derivatives of volume or entropy, are significantly more sensitive to the solution structure or even superstructure than lower-order partial derivatives. Second order mixed derivatives of Gibbs potential were determined from experimental densities of fulleranol aqueous solutions according to Maxwell relations:

$$\frac{\partial^2 \bar{G}}{\partial P \partial T} = \frac{\partial^2 \bar{G}}{\partial T \partial P} = \left(\frac{\partial \bar{V}}{\partial T} \right)_P = - \left(\frac{\partial \bar{S}}{\partial P} \right)_T \quad (4)$$

where $\bar{G}, \bar{V}, \bar{S}$ are the average molar Gibbs potential, volume and entropy, respectively.

One can see that the $(\partial \bar{V} / \partial T)_P (x_{C_{60}(OH)_{22-24}})$ –function passes through a minimum at the characteristic concentration $x_{C_{60}(OH)_{22-24}} \approx 4 \cdot 10^{-5}$ at all investigated temperatures (see Fig. 8).

This concentration corresponds to beginning of the $C_{60}(OH)_{22-24}$ aqueous solution phase separation (losing of diffusion stability). This fact is associated with a complex and hierarchical type of the fulleranol derivatives association in aqueous solution, namely with the formation of the second type associates with linear dimensions of thousands of nm [26].

Similar results were obtained by using another mixed derivative of Gibbs potential:

$$\frac{\partial^2 \bar{G}}{\partial P \partial x} = \frac{\partial^2 \bar{G}}{\partial x \partial P} = \left(\frac{\partial \bar{V}}{\partial x} \right)_{T,P} = \left(\frac{\partial \mu_{C_{60}(OH)_{22-24}}}{\partial P} \right)_T - \left(\frac{\partial \mu_{H_2O}}{\partial P} \right)_T = V_{C_{60}(OH)_{22-24}} - V_{H_2O} \quad (5)$$

where: μ_i , V_i are the chemical potential and partial molar volume of i -th component.

One can see as the $(\partial \bar{V} / \partial x)_{P,T}(x_{C_{60}(OH)_{22-24}})$ dependence also passes through a minimum at the characteristic concentration $x_{C_{60}(OH)_{22-24}} \approx 4 \cdot 10^{-5}$ (Fig. 9).

In addition, we calculated the concentration and temperature dependences of isobaric thermal expansivities (α_p) of the $C_{60}(OH)_{22-24}$ aqueous solutions (see Fig. 10). The results of α_p were obtained from second-order polynomial fittings of $\rho(T)$ using the thermodynamic definition of this property:

$$\alpha_p = - \left(\frac{1}{\rho} \right) \left(\frac{\partial \rho}{\partial T} \right)_p \quad (6),$$

where ρ is the density of the fulleranol aqueous solution and T is the absolute temperature.

In the temperature interval 283.15–318.15 K, isobaric thermal expansivities follow the same concentration dependence as $(\partial \bar{V} / \partial T)_p$ and $(\partial \bar{V} / \partial x)_{P,T}$ derivatives and also pass through minima at $x_{C_{60}(OH)_{22-24}} \approx 4 \cdot 10^{-5}$.

3.2. Temperature dependence of viscosity of $C_{60}(OH)_{22-24}$ aqueous solutions

After preliminary tests to confirm the Newtonian behavior of the highest fulleranol concentration ($40 \text{ g} \cdot \text{dm}^{-3}$) at shear rates ranging from 50 to 1000 s^{-1} and temperatures 278.15–323.15 K, dynamic viscosities were obtained at shear rates of 100 s^{-1} for all the reported conditions. The concentration dependences of this property, $\eta(C)$, for the $C_{60}(OH)_{22-24}$ aqueous

solutions are presented in Table 3 and Fig. 11. One can see as dynamic viscosities rise with increasing of $C_{60}(OH)_{22-24}$ concentration. A maximum increase of 56% is observed at 283.15 K in the case of $40 \text{ g}\cdot\text{dm}^{-3}$ fullerene concentration.

We applied the Eyring theory [50] of transition state to calculate the thermodynamic characteristics of viscous flow for the fullerenol aqueous solutions. According to this theory [50], the equation for viscosity is given by Eq. 7:

$$\eta = \frac{hN_A}{V} \exp\left(\frac{\Delta G}{RT}\right) \quad (7),$$

where η – dynamic viscosity, h – Planck constant, N_A – Avogadro number, V – molar volume.

Eq. 8 allows calculating the activation Gibbs energy of viscous flow (ΔG):

$$\Delta G = RT \ln \frac{\eta V}{hN_A} \quad (8).$$

Activation entropies (ΔS) and enthalpies (ΔH) of viscous flow were calculated according to Eqs. 9, 10 (see Table 4):

$$\Delta H = -RT^2 \frac{\partial}{\partial T} \left(\ln \frac{\eta V}{hN_A} \right) \quad (9),$$

$$\Delta S = -\frac{\Delta G - \Delta H}{T} \quad (10).$$

ΔH and ΔS provide structural information about solute species and solute–solvent interactions. An analysis of Table 4 shows the stability of enthalpy (ΔH) and entropy (ΔS) values of viscous flow within the studied concentration range ($0\text{-}40 \text{ g}\cdot\text{dm}^{-3}$) taking into account the accuracy of numerical differentiation. The positive values of ΔH indicate the presence of specific interactions between constituent molecules, the negative values of (ΔS) evidence that the formation of activated complex introduces molecular order probably due to interactions between the solution components.

Using the logarithmic form of Frenckel-Andrade equation [47,48], we calculated the entropic factor and the activation energy of viscous flow (see Table 4):

$$\ln \eta = \ln A_s + \frac{E_a}{R} \frac{1}{T} \quad (11),$$

where A_s – pre-exponential entropic factor, R – ideal gas constant, E_a – activation energy of viscous flow, T – absolute temperature.

The activation temperatures were determined according to Eq.12 (see Table 4):

$$T_A = \frac{-E_a}{R \ln A_s} \quad (12).$$

In addition, the values for van't-Hoff's viscosity coefficient (γ_n) of $C_{60}(\text{OH})_{22-24}\text{-H}_2\text{O}$ binary system were calculated according to:

$$\gamma_n^{\frac{\Delta T}{T}} = \frac{\eta_{T-\Delta T}}{\eta_T} \quad (13),$$

which can be numerically expressed as:

$$\gamma_n = \frac{\eta_{T-10}}{\eta_T} = 1.26 \pm 0.05 \quad (14),$$

where γ_n is the van't-Hoff's viscosity coefficient. The high stability of van't-Hoff's viscosity coefficient for the $C_{60}(\text{OH})_{22-24}\text{-H}_2\text{O}$ binary system is comparatively shown in Fig. 12.

On the basis of the Vogel-Fulcher-Tamman equation – VFT, we described the temperature dependences of dynamic viscosities for the fulleranol $C_{60}(\text{OH})_{22-24}\text{-H}_2\text{O}$ binary system (see Fig. 13):

$$\log_{10} \eta(T) = \log_{10} \eta_0 + \frac{A}{T - B} \quad (15),$$

where η_0 , A and B are the fitting parameters. Absolute average deviations (AAD) and standard deviations (SD) between experimental values and those obtained from Eq. 13 were calculated according to Eqs. 16, 17:

$$AAD = \left[\sum_{i=1}^n \left(\frac{\eta_{\text{exp},i} - \eta_{\text{cal},i}}{\eta_{\text{exp},i}} \right) \right] \cdot \frac{100}{n} \quad (16),$$

$$SD = \left[\frac{\sum_{i=1}^n (\eta_{exp,i} - \eta_{cal,i})^2}{(n-p)} \right]^{\frac{1}{2}} \quad (17),$$

where $\eta_{exp,i}$ and $\eta_{cal,i}$ are the experimental and calculated dynamic viscosities of the $C_{60}(OH)_{22-24}$ aqueous solutions, respectively; n is the number of experimental points, and p is the number of adjusted parameters. Correlation parameters of the VFT-equation and obtained deviations are presented in Table 5.

3.3. Refraction of $C_{60}(OH)_{22-24}$ water solutions

Table 6 gathers the experimental refraction indexes (n_D) of $C_{60}(OH)_{22-24}$ aqueous solutions at fullereneol concentrations up to $30 \text{ g} \cdot \text{dm}^{-3}$ and temperatures ranging in the interval $283.15\text{--}323.15 \text{ K}$. Concentration dependences of specific and molar refractions of the fullereneol aqueous solutions were calculated by means of the Lorentz-Lorenz equations [48]:

$$r = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \frac{1}{\rho} \quad (18),$$

$$R = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \frac{\bar{M}}{\rho} \quad (19),$$

where r , R are specific and molar refractions, $\bar{M}$ is an average molecular weight of a solution, i.e. $\bar{M} = x_{H_2O} \cdot M_{H_2O} + x_{C_{60}(OH)_{22-24}} \cdot M_{C_{60}(OH)_{22-24}}$. Table 7 presents the obtained refractions (molar and specific) of the studied fullereneol aqueous solutions. Molar ($R_{C_{60}(OH)_{22-24}}$) and specific ($r_{C_{60}(OH)_{22-24}}$) refractions values (see Table 7) were calculated in accordance with the additivity rule of refractions (see Eqs. 20.1, 20.2):

$$r = (r_{H_2O} \cdot w_{H_2O} + r_{C_{60}(OH)_{22-24}} \cdot w_{C_{60}(OH)_{22-24}}) \cdot \frac{1}{100} \quad (20.1),$$

$$R = R_{H_2O} \cdot x_{H_2O} + R_{C_{60}(OH)_{22-24}} \cdot x_{C_{60}(OH)_{22-24}} \quad (20.2),$$

where r_i , R_i are specific and molar refractions of the i -th component; while w_i , x_i are mass and molar fractions of the i -th component.

As an example, the r and R values of $C_{60}(OH)_{22-24}$ in aqueous solutions calculated from experimental refraction indexes at 298.15 K are plotted in Fig. 14. The values of specific and molar refractions in the temperature interval 283.15–323.15 K are gathered in Table 1 of Supplementary materials.

Additionally, it is possible to estimate the fulleranol refraction using the Eisenlohr additivity rule [42] based on atomic refractions and chemical bonds increments:

$$R^{\text{add}} \approx 60R_c + 24R_H + 24R_{O(OH)} \approx 207 \div 214 \text{ cm}^3 \cdot \text{mol}^{-1} \quad (21).$$

The discrepancy in the determination of molar refraction is associated with the selection of the spectral lines ($H_\alpha[\lambda = 658.3 \text{ nm}]$ and $H_\gamma[\lambda = 436.1 \text{ nm}]$). The value of specific refraction of fulleranol can be calculated according to:

$$r^{\text{add}} = \frac{R^{\text{add}}}{M(C_{60}(OH)_{24})} \approx 0.183 \div 0.189 \text{ m}^3 \cdot \text{g}^{-1} \quad (22).$$

One can see (Fig. 14) as both specific and molar refraction values of fulleranol derivatives calculated using Eisenlohr additivity rule are in good agreement with the data obtained from the experimental refraction indexes of the fulleranol solutions.

3.4. Isobaric heat capacities of $C_{60}(OH)_{22-24}$ water solutions

Experimental isobaric heat capacities obtained for pure water, polyhydroxylated fullerene ($C_{60}(OH)_{22-24}$) and fulleranol aqueous solutions in the temperature interval 288.15–313.15 K are shown in Fig. 15. In the studied interval of temperatures polyhydroxylated fullerene exhibits C_p values in the range $1.075 - 1.157 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, which are close to the results reported in literature [46,48,51,52] for other fullerene derivatives. The isobaric heat capacities of pure water here measured are in agreement with literature data ($AAD = 0.2\%$) [53]. Heat capacities obtained for the $C_{60}(OH)_{22-24}$ -water binary system decrease slightly as increases the fulleranol content in the aqueous solution. Reductions in this property reach 3% for the highest analyzed $C_{60}(OH)_{22-24}$

content ($40 \text{ g}\cdot\text{dm}^{-3}$) and lower as temperature rises. In addition, we carried out a comparison between experimental results and heat capacities obtained by means of the following weighted average equation (Eq. 23), which is widely used for prediction of the heat capacity of different dispersions [40,53]:

$$C_{p,suspension} = w \cdot C_{p,C_{60}(OH)_{22-24}} + (1-w) \cdot C_{p,H_2O} \quad (23),$$

$$AAD = \left[\sum_{i=1}^n \left(\frac{C_{p,exp,i} - C_{p,cal,i}}{C_{p,exp,i}} \right) \right] \cdot \frac{100}{n} \quad (24),$$

where w is a mass fraction of the fullerene, $C_{p,exp}$ and $C_{p,cal}$ are the experimental and calculated values of the $C_{60}(OH)_{22-24}$ aqueous solutions isobaric heat capacities, respectively. Fig. 16 shows the good agreement between experimental and predicted C_p values ($AAD = 0.22 \%$). In addition, the following second-order polynomial function was used for the description of temperature dependences of water and fullerene heat capacities:

$$C_p = a_0 + a_1 T + a_2 T^2 \quad (25),$$

where a_i are the fit parameters. As a result, the following parameters of Eq. 25 were obtained for pure water: $a_0 = 4.1902 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, $a_1 = -0.0051 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-2}$, $a_2 = 0.0005 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-3}$ and for solid fullerene: $a_0 = 1.0601 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, $a_1 = 0.0148 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-2}$, $a_2 = 0.0002 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-3}$.

3.5. Correlation

Both temperature and concentration dependences of density, viscosity and refraction indexes were described by means of the following second-order polynomial function, $M(T, x)$:

$$M = A + \sqrt{x} \sum_{i=1}^3 b_i \cdot T^{i-1} + \sqrt{1-x} \sum_{i=4}^6 b_i \cdot T^{i-4} \quad (26),$$

where M represents the correlated property (density, viscosity or refraction index), x is a mole fraction of $C_{60}(OH)_{22-24}$, T is absolute temperature, while A , b_i ($i = 1-6$) are the corresponding fitting parameters which were calculated by a least-square method using MATLAB software.

In order to estimate the accordance between experimental and calculated values for the studied viscosity, density and refraction index of the $C_{60}(OH)_{22-24}$ -water solutions, we calculated the standard deviation (SD) and determination coefficient (R^2) using Eqs. 27–28 [55]:

$$SD = \left[\frac{\sum_{i=1}^n (x_{exp,i} - x_{cal,i})^2}{n} \right]^{1/2} \quad (27),$$

$$R^2 = \frac{\sum_{i=1}^n \left(x_{cal,i} - \frac{1}{n} \sum_{i=1}^n x_{exp,i} \right)^2}{\sum_{i=1}^n \left(x_{exp,i} - \frac{1}{n} \sum_{i=1}^n x_{exp,i} \right)^2} \quad (28),$$

where: $x_{cal,i}$ and $x_{exp,i}$ - the calculated and experimental values, while n - the number of measurements. Table 8 presents the obtained fitting parameters together with determined coefficients while standard deviations for predicted values are gathered in Table 9. The good agreement between experimental and calculated values, with a standard deviation less than 0.04, can be observed for the three properties in Fig. 16.

3.6. Molecular dynamics simulation

Despite several investigations, the question of possible fullerene isomers is still opened. In particular, He et al. [29] showed that the fullerene $C_{60}(OH)_{24}$ with the highest stability has the «Saturn-like» distribution of hydroxyl groups (Fig. 17 a). In addition, we performed the calculation for the fullerene with uniform distribution of hydroxyl groups (Fig. 17 b). The distribution of electronic density for individual fullerene is presented together with the two structural isomers of fullerene calculated by DFT method (see Fig. 17). The charge distributions in calculated molecules were determined according to Mulliken scheme (see Table 10). Analysis of Table 10 shows that arrangement of hydroxyl groups in equatorial area of the fullerene core («Saturn-like» fullerene) leads to increasing of ionicity of hydrogen and oxygen atoms and at the same time decrease the total energy of molecule.

The detailed description of interaction between water and fullerene or fullerene molecules was carried out by analyzing radial distribution functions (RDF) obtained from

molecular dynamics calculations. RDF between carbon atoms of the fullerene core and water molecules are presented in Fig. 18. Hydrophobic properties of C₆₀ fullerene are connected with the electronic density network around the molecule (Fig 18 a). The addition of hydroxyl groups to the fullerene core and hydrogen bonds' formation in aqueous solutions leads to inhomogeneity of the fullerenol's electronic density. It can be clearly observed as functionalization of C₆₀ by hydroxyl groups leads to the formation of the following peaks in RDF-profiles corresponding to location of water molecules around the hydroxyl groups: (i) single peak (around 2.40 Å, Fig. 18 b) in the case of fullerenol with uniform distribution of hydroxyl groups, (ii) double peak (around 2.28 and 2.45 Å, Fig. 18 c) in the case of distorted structure of «Saturn-like» fullerenol. This fact is caused by the inequivalence of hydroxyl groups in the fullerenol molecule.

3.7. Antioxidant activity of C₆₀(OH)₂₂₋₂₄

The kinetic dependence of the reaction mixture optical density is presented in the Table 1 of Supplementary materials. Fig. 19 schematically represents the proposed mechanism for the reaction between C₆₀(OH)₂₂₋₂₄ and DPPH. This process involves two stages: a hydrogen transfer to the DPPH radical (fast step), a nucleophilic attack of a C=C bond (rate-determining step).

The kinetic equation for the pseudo-first order reaction was used in order to quantify the velocities of both reaction steps describing the interaction of C₆₀(OH)₂₂₋₂₄ and DPPH [56]:

$$\ln \frac{(A_{\infty} - A_t)}{(A_{\infty} - A_0)} = -kt \quad (29),$$

where A_{∞} , A_t , A_0 are the optical densities of the solution after «infinity» (after six days of the experiment), at time t and at the beginning of the reaction, respectively. Kinetic data on the interaction of DPPH with C₆₀(OH)₂₂₋₂₄ are presented in Fig. 20.

Using the Eq. (29), the following rate constants were obtained for both stages of the reaction of DPPH with C₆₀(OH)₂₂₋₂₄: $k_1 = 0.0058 \text{ min}^{-1}$ (fast step) and $k_2 = 0.0009 \text{ min}^{-1}$ (rate-determining step). An analysis of the literature [57] has showed that in the case of individual fullerene C₆₀ (concentration 100 μM) the rate constant k_2 is equal to 0.0007 min^{-1} , for C₆₀(OH)₃₀

$k_1 = 0.0063 \text{ min}^{-1}$ and $k_2 = 0.0014 \text{ min}^{-1}$. The values of the rate constants for $\text{C}_{60}(\text{OH})_{22-24}$ are expected to be lower than for $\text{C}_{60}(\text{OH})_{30}$, since, in accordance with the proposed mechanism, a decrease in the degree of hydroxylation of the fullerene surface should lead to a decrease in the DPPH reduction rate.

3.8. Conclusions

This paper presents a comprehensive physico-chemical characterization of $\text{C}_{60}(\text{OH})_{22-24}$ solutions in water, including densities, viscosities, refraction indexes, isobaric heat capacities and antioxidant activity. The concentration behavior of partial molar volumes obtained from experimental densities shows that significant compacting and structuring aqueous solutions can be obtained even with low fullerenol concentrations. Activation enthalpies and entropies of viscous flow calculated from viscosity measurements of the solutions indicate the existence of interactions between constituent molecules. Additionally, T - x -experimental densities, viscosities and refractive indexes were correlated using the second order polynomial functions with SD values less than 0.04. The structural behavior in binary systems containing individual C_{60} -fullerene as well as fullerenols with different types of hydroxyl groups distribution (“Saturn-like” and uniform) were determined using DFT and molecular dynamics methods. The investigation of physico-chemical properties of water-soluble polyhydroxylated fullerenes underlies the application in materials science and nanobiomedicine.

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Table 1. Provenance and mass fraction purity of the reagents.

№	Name	CAS №	Supplier	Mass fraction purity
1	Fullerenol C ₆₀ (OH) ₂₄	–	Ltd ZAO “ILIP”, Russia	≥ 0.998
2	2,2-Diphenyl-1-picrylhydrazyl (DPPH)	1707-75-1	Merck, Germany	≥ 0.970
3	Human Serum Albumin (HAS)	70024-90-7	Biolot, Russia	≥ 0.950

Table 2. Experimental temperature and concentration dependences of density (ρ) of the $C_{60}(OH)_{22-24}$ aqueous solutions. C – $C_{60}(OH)_{22-24}$ concentration in the water solution.

$C / \text{g}\cdot\text{dm}^{-3}$	$\rho / \text{g}\cdot\text{cm}^{-3}$									
	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0	1.000021	0.999763	0.999167	0.998273	0.997113	0.995720	0.994105	0.992283	0.990272	0.988093
0.3	1.000699	1.000438	0.999839	0.998942	0.997780	0.996382	0.994764	0.992943	0.990941	0.988773
0.5	1.004053	1.003770	1.003183	1.002290	1.001127	0.999726	0.998105	0.996282	0.994272	0.992087
1	1.005664	1.005394	1.004788	1.003888	1.002724	1.001322	0.999699	0.997877	0.995862	0.993683
2.5	1.013684	1.013403	1.012789	1.011879	1.010711	1.009303	1.007675	1.005847	1.003832	1.001647
5.0	1.018789	1.018487	1.017853	1.016930	1.015743	1.014320	1.012676	1.010833	1.008800	1.006593
7.5	1.021384	1.021057	1.020403	1.019459	1.018250	1.016808	1.015145	1.013281	1.011220	1.008964
10	1.024150	1.023799	1.023128	1.022170	1.020951	1.019496	1.017825	1.015949	1.013878	1.011625
15	1.028479	1.028081	1.027364	1.026361	1.025057	1.023555	1.021828	1.019925	1.017900	1.015686
20	1.032405	1.031971	1.031228	1.030204	1.028928	1.027424	1.025707	1.023792	1.021690	1.019424
30	1.039375	1.038882	1.038087	1.037022	1.035705	1.034161	1.032409	1.030452	1.028302	1.025962
40	1.045437	1.044906	1.044068	1.042953	1.041586	1.039993	1.038195	1.036190	1.033973	1.031482

Table 3. Experimental temperature (T) and concentration dependences of viscosity (η) of the $C_{60}(OH)_{22-24}$ aqueous solutions obtained at shear rates of 100 s^{-1} . C – concentration of $C_{60}(OH)_{22-24}$ in aqueous solution.

$C / \text{g} \cdot \text{dm}^{-3}$	$\eta / \text{mPa} \cdot \text{s}$							
	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0	1.52	1.31	1.14	1.00	0.890	0.797	0.719	0.653
0.25	1.52	1.31	1.14	1.00	0.890	0.797	0.719	0.654
0.5	1.53	1.31	1.14	1.00	0.890	0.797	0.720	0.657
1	1.54	1.31	1.14	1.01	0.891	0.798	0.721	0.658
2.5	1.55	1.32	1.15	1.02	0.892	0.807	0.722	0.660
5	1.58	1.35	1.16	1.03	0.903	0.815	0.728	0.670
7.5	1.63	1.38	1.18	1.04	0.915	0.826	0.735	0.675
10	1.67	1.43	1.20	1.06	0.929	0.840	0.749	0.682
15	1.77	1.51	1.25	1.10	0.967	0.874	0.768	0.704
20	1.88	1.62	1.32	1.16	1.02	0.925	0.810	0.746
30	2.10	1.84	1.49	1.31	1.15	1.01	0.902	0.832
40	2.33	2.04	1.70	1.50	1.31	1.13	0.993	0.921

Table 4. Concentration dependences of entropic factor ($\ln(A_s)$), activation energy of viscous flow (E_a), Arrhenius temperature (T_A), activation enthalpy (ΔH) and entropy (ΔS). C – concentration of $C_{60}(OH)_{22-24}$ in aqueous solution.

$C / \text{g}\cdot\text{dm}^{-3}$	$E_a / \text{J}\cdot\text{mol}^{-1}$	$\ln(A_s) / \text{mPa}\cdot\text{s}$	T_A / K	$\Delta H / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta S / \text{J}\cdot\text{mol}^{-1}$
0	17453.96	-7.1473	293.72	17.25	-87.81
0.25	17460.30	-7.1496	293.74	17.26	-87.79
0.5	17467.53	-7.1505	293.82	17.27	-87.76
1	17530.93	-7.1747	293.89	17.33	-87.55
2.5	17591.33	-7.1938	294.12	17.39	-87.34
5	17782.88	-7.2575	294.72	17.58	-86.80
7.5	18194.94	-7.4097	295.35	17.99	-85.54
10	18529.58	-7.5271	296.09	18.32	-84.58
15	19155.22	-7.7405	297.65	18.94	-82.84
20	19304.04	-7.7433	299.85	19.08	-82.83
30	19697.79	-7.7899	304.14	19.47	-82.50
40	19803.56	-7.7195	308.56	19.79	-82.41

Table 5. Correlation parameters for the Vogel–Fulcher–Tammann equation (Eq. 15). C – volume concentration of $C_{60}(OH)_{22-24}$ in aqueous solution; s – standard deviation; AAD – absolute average deviation.

	$C_{C_{60}(OH)_{22-24}} / g \cdot dm^{-3}$											
	0	0.25	0.5	1	2.5	5	7.5	10	15	20	30	40
A / K	332.54	332.54	332.54	332.65	332.73	332.99	333.49	333.87	334.55	334.71	335.09	335.18
B / K	116.50	116.50	116.50	116.93	117.20	118.17	120.06	121.56	124.22	124.89	126.43	126.69
$\eta_0 / mPa \cdot s$	0.0132	0.0132	0.0132	0.0131	0.0131	0.0129	0.0124	0.0121	0.0117	0.0121	0.0130	0.0144
$SD / mPa \cdot s$	0.003	0.003	0.004	0.004	0.004	0.006	0.006	0.008	0.010	0.011	0.011	0.008
$AAD / \%$	0.42	0.46	0.60	0.72	0.66	0.81	0.98	1.25	1.58	1.80	1.58	1.37

Table 6. Concentration dependences of the $C_{60}(OH)_{22-24}$ water solutions refraction indexes (n_D) in the temperature interval 283.15–323.15 K.

$C/g \cdot dm^{-3}$	n_D								
	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0.001	1.33386	1.33357	1.33317	1.33268	1.33211	1.33148	1.33078	1.33001	1.32919
0.03	1.33398	1.33370	1.33330	1.33282	1.33223	1.33160	1.33090	1.33013	1.32930
0.06	1.33402	1.33374	1.33334	1.33286	1.33227	1.33164	1.33095	1.33018	1.32934
0.125	1.33406	1.33377	1.33337	1.33289	1.33230	1.33166	1.33097	1.33020	1.32936
0.25	1.33409	1.33381	1.33341	1.33292	1.33234	1.33171	1.33101	1.33024	1.32940
0.5	1.33415	1.33386	1.33347	1.33298	1.33240	1.33177	1.33108	1.33030	1.32947
1	1.33428	1.33398	1.33360	1.33309	1.33253	1.33191	1.33120	1.33044	1.32960
2.5	1.33470	1.33434	1.33394	1.33347	1.33291	1.33227	1.33158	1.33083	1.33003
5	1.33526	1.33500	1.33454	1.33409	1.33356	1.33300	1.33225	1.33152	1.33072
10	1.33663	1.33631	1.33592	1.33540	1.33495	1.33436	1.33363	1.33288	1.33212
15	1.33799	1.33761	1.33722	1.33672	1.33629	1.33568	1.33496	1.33423	1.33351
20	1.33921	1.33889	1.33852	1.33806	1.33759	1.33701	1.33638	1.33566	1.33491
30	1.34186	1.34160	1.34112	1.34067	1.34023	1.33967	1.33906	1.33836	1.33767

Table 7. Refraction properties of the $C_{60}(OH)_{22-24}$ solutions in water at 298.15 K. C —concentration in volume, n_D - refraction index, r , R - specific and molar refractions of $C_{60}(OH)_{22-24}$ aqueous solutions, $r_{C_{60}(OH)_{22-24}}$ and $R_{C_{60}(OH)_{22-24}}$ - specific and molar refractions of $C_{60}(OH)_{22-24}$ derivative.

$C / g \cdot dm^{-3}$	n_D	$r / cm^3 \cdot g^{-1}$	$R / cm^3 \cdot mol^{-1}$	$r_{C_{60}(OH)_{22-24}} / cm^3 \cdot g^{-1}$	$R_{C_{60}(OH)_{22-24}} / cm^3 \cdot mol^{-1}$
0.03	1.33248	0.20602	3.70853	0.174	210
0.06	1.33271	0.20602	3.70863	0.174	210
0.125	1.33307	0.20602	3.70886	0.175	211
0.25	1.33276	0.20602	3.70927	0.175	211
0.5	1.33397	0.20601	3.71011	0.175	212
1	1.33453	0.20599	3.71180	0.176	212
2.5	1.33740	0.20595	3.71672	0.178	213
5	1.33914	0.20589	3.72508	0.179	214
10	1.34085	0.20577	3.74177	0.180	215
15	1.34220	0.20568	3.75881	0.183	216
20	1.34347	0.20560	3.77577	0.184	217
30	1.34569	0.20544	3.80978	0.186	216

Table 8. Fitting parameters A , a_i ($i = 1-6$) for description of temperature and concentration dependences of densities (ρ), dynamic viscosities (η) and refraction indexes (n_D) of aqueous solutions of $C_{60}(OH)_{22-24}$ according to Eq. 26. R^2 – determination parameter (see Eq. 28).

Solution property	A	a_1	a_2	a_3	a_4	a_5	a_6	R^2
$\rho / \text{g}\cdot\text{cm}^{-3}$	-34.548	3.4023	-0.0059925	$7.1501\cdot 10^{-6}$	35.195	0.0025765	$-4.7236\cdot 10^{-6}$	0.9932
$\eta / \text{mPa}\cdot\text{s}$	2274.1	1579.54	-10.134	0.016065	-2229.1	-0.27642	$4.3109\cdot 10^{-4}$	0.9942
n_D	33.368	1.2448	-0.0086497	$1.5194\cdot 10^{-5}$	-32.139	$7.9779\cdot 10^{-4}$	$-1.5121\cdot 10^{-6}$	0.9992

Table 9. Standard deviation (SD) for predicted values of density (ρ), dynamic viscosity (η) and refraction index (n_D) for $C_{60}(OH)_{22-24}$ -water binary system (according to Eqs. 26-27).

x	SD		
	$\rho / \text{g}\cdot\text{cm}^{-3}$	$\eta / \text{mPa}\cdot\text{s}$	n_D
0	0.0015	0.029	0.00022
0.000000016	-	-	0.00006
0.000000478	-	-	0.00005
0.000000951	-	-	0.00008
0.00000203	-	-	0.00008
0.00000398	0.0019	0.014	0.00008
0.00000796	0.0005	0.012	0.00007
0.0000159	0.0013	0.012	0.000034
0.0000394	0.0017	0.016	0.000030
0.0000788	0.0015	0.022	0.00006
0.000118	0.0004	0.022	-
0.000158	0.00007	0.023	0.00004
0.000236	0.0007	0.023	0.00004
0.000315	0.0008	0.021	0.000024
0.000475	0.00035	0.022	0.00004
0.000634	0.0006	0.04	-

Table 10. Average charges of oxygen (O) and hydrogen (H) atoms determined according to Mulliken scheme and total energies of fullerenols with uniform and «Saturn-like» distribution of hydroxyl groups.

Type of hydroxyl group distribution in fulleranol	O (e)	H (e)	Total energy (Ha)
Uniform distribution	-0.523	0.311	-4106.3
«Saturn-like»	-0.537	0.336	-4106.5

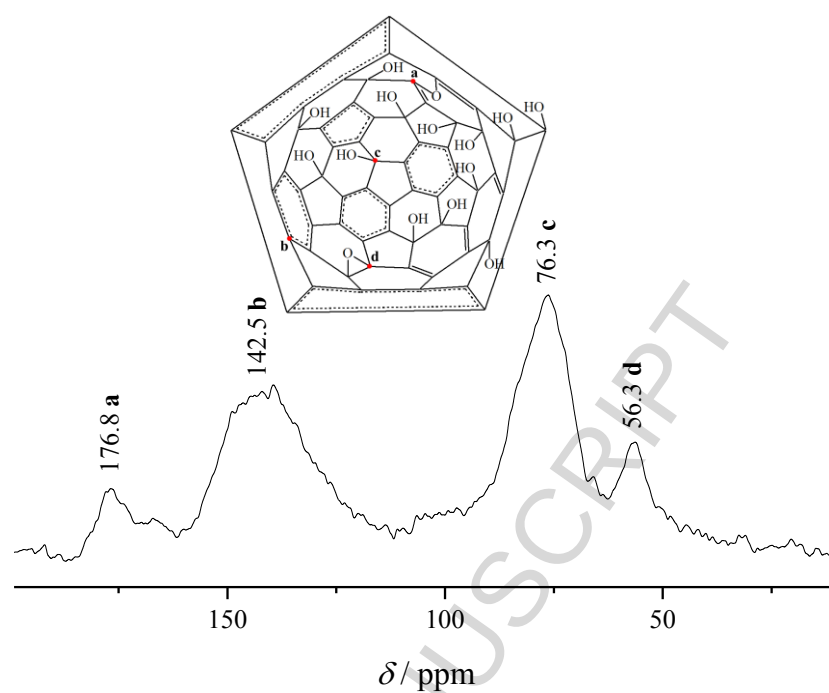


Fig. 1. ^{13}C NMR spectrum obtained using CP/MAS method at contact times of 2000 μs .

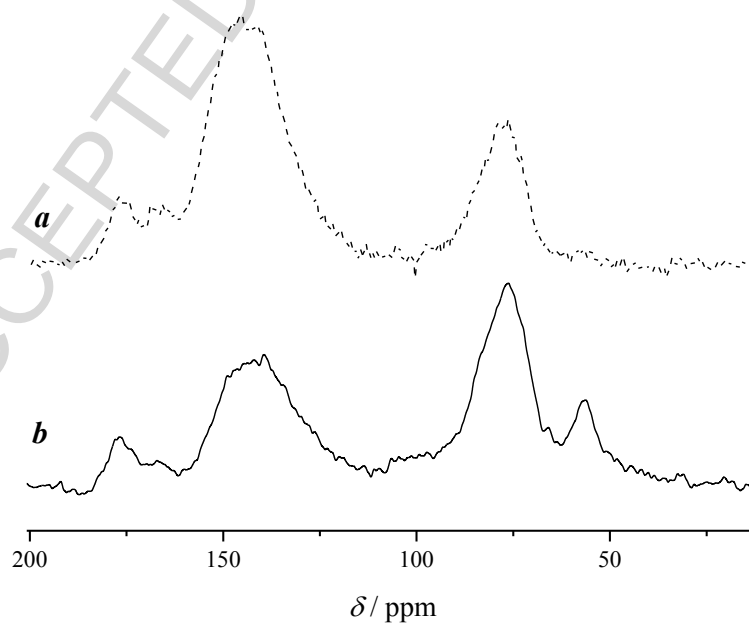


Fig. 2. ^{13}C NMR spectra of fullerene-3,6,9,12-tetraol obtained using DE (*a*) and CP/MAS (contact time - 2 ms) (*b*).

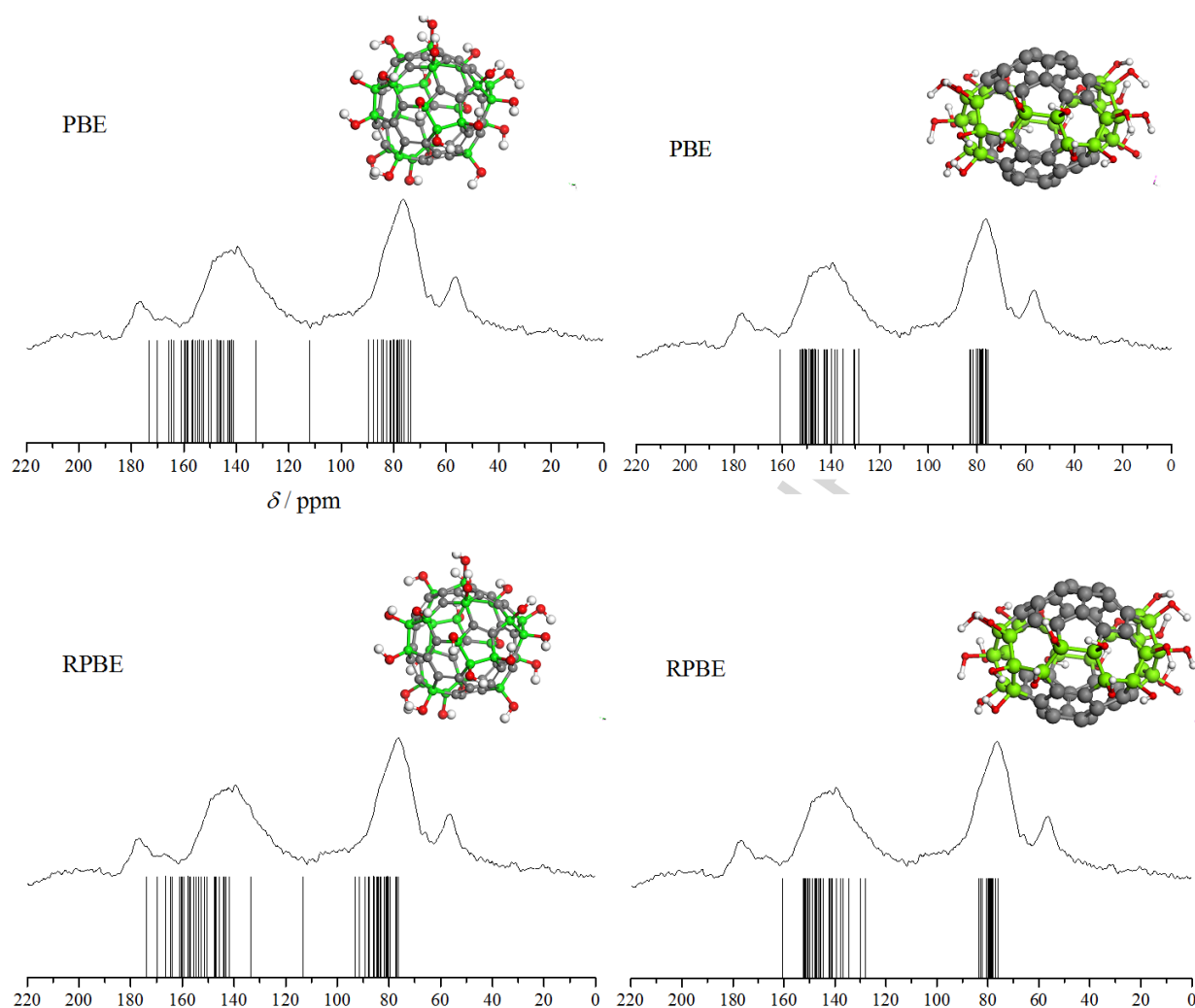


Fig. 3. Comparison between DFT-calculated NMR spectra for two types of fullereneol molecule in comparison with experimental ^{13}C NMR spectrum, obtained using CP/MAS method.

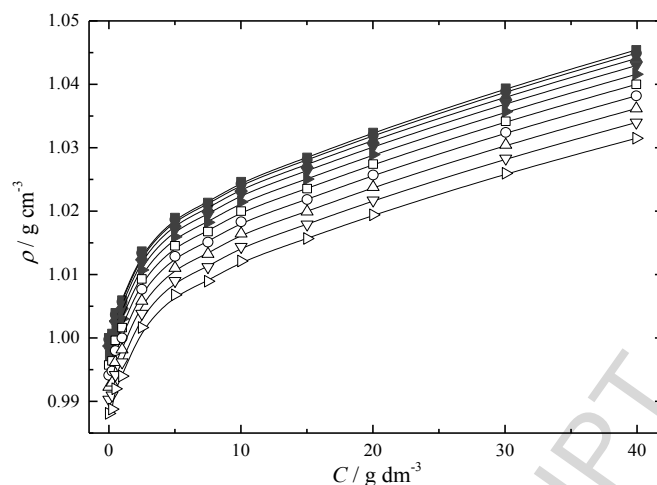


Fig. 4. Fullerenol concentration (C) dependences of the $C_{60}(OH)_{22-24}$ water solution densities (ρ) at (■) 278.15 K, (●) 283.15 K, (▲) 288.15 K, (▼) 293.15 K, (►) 298.15 K, (□) 303.15 K, (○) 308.15 K, (△) 313.15 K, (▽) 318.15 K and (▷) 323.15 K. Solid lines are included to guide the eye.

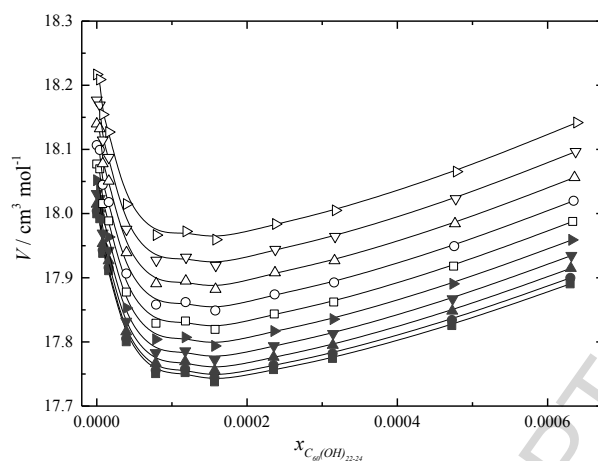


Fig. 5. Concentration dependences of average molar volume ($\bar{V}$) of the $C_{60}(OH)_{22-24}$ water solution at (■) 278.15 K, (●) 283.15 K, (▲) 288.15 K, (▼) 293.15 K, (►) 298.15 K, (□) 303.15 K, (○) 308.15 K, (△) 313.15 K, (▽) 318.15 K and (▷) 323.15 K. x – molar fraction of fullereneol. Solid lines are included to guide the eye.

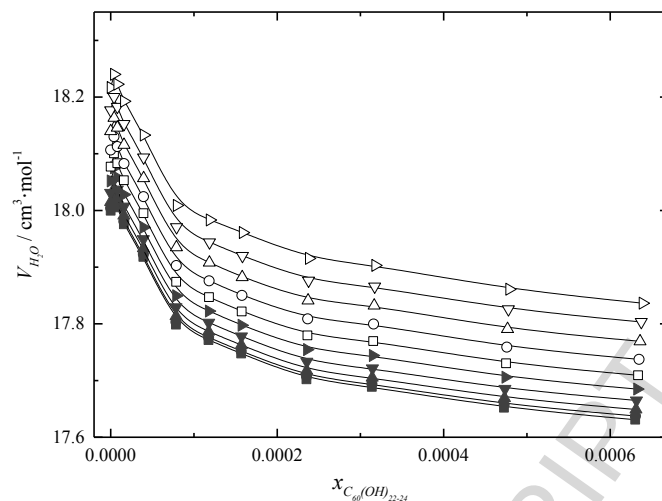


Fig. 6. Fullerol mole fraction, x , dependences of water partial volumes (V_{H_2O}) at different temperatures: (■) 278.15 K, (●) 283.15 K, (▲) 288.15 K, (▼) 293.15 K, (►) 298.15 K, (□) 303.15 K, (○) 308.15 K, (△) 313.15 K, (▽) 318.15 K and (▷) 323.15 K. x — molar fraction of fullerenol. Solid lines are included to guide the eye.

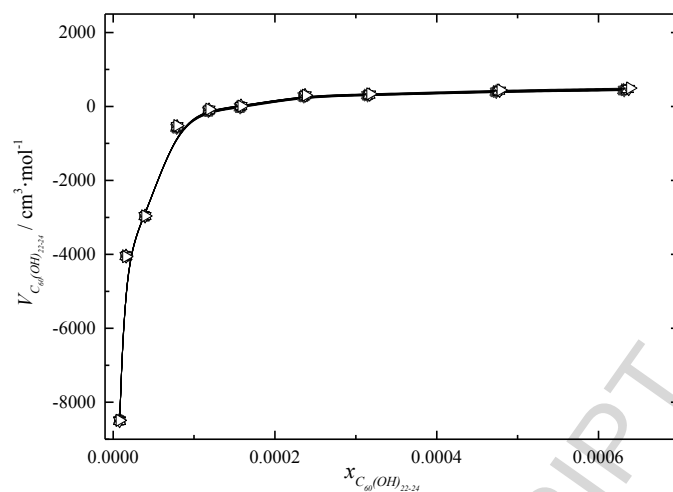


Fig. 7. Mole fraction dependence of the partial volumes of fullereneol ($V_{C_{60}(OH)_{22-24}}$) in the temperature range 278.15–323.15 K, (■) 278.15 K, (●) 283.15 K, (▲) 288.15 K, (▼) 293.15 K, (►) 298.15 K, (□) 303.15 K, (○) 308.15 K, (△) 313.15 K, (▽) 318.15 K and (▷) 323.15 K. x – molar fraction of fullereneol. Solid lines are included to guide the eye.

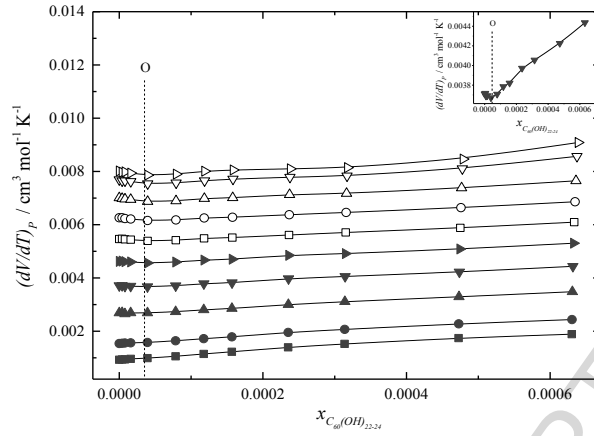


Fig. 8. Concentration dependences of the $\left(\frac{\partial V}{\partial T}\right)_p$ – derivatives in the temperature range 278.15–323.15 K: (■) $\left(\frac{\partial V_{27815}}{\partial T}\right)_p$, (●) $\left(\frac{\partial V_{28315}}{\partial T}\right)_p$, (▲) $\left(\frac{\partial V_{28815}}{\partial T}\right)_{T,P}$, (▼) $\left(\frac{\partial V_{29315}}{\partial T}\right)_p$, (►) $\left(\frac{\partial V_{29815}}{\partial T}\right)_p$, (□) $\left(\frac{\partial V_{30315}}{\partial T}\right)_{T,P}$, (○) $\left(\frac{\partial V_{30865}}{\partial T}\right)_p$, (△) $\left(\frac{\partial V_{31315}}{\partial T}\right)_p$, (▽) $\left(\frac{\partial V_{31815}}{\partial T}\right)_p$ and (▷) $\left(\frac{\partial V_{32315}}{\partial T}\right)_{T,P}$. O – is an extreme point $\left(\frac{\partial^2 V}{\partial x \partial T}\right)_p = 0$, $x = 4 \cdot 10^{-5}$. Solid lines are included to guide the eye.

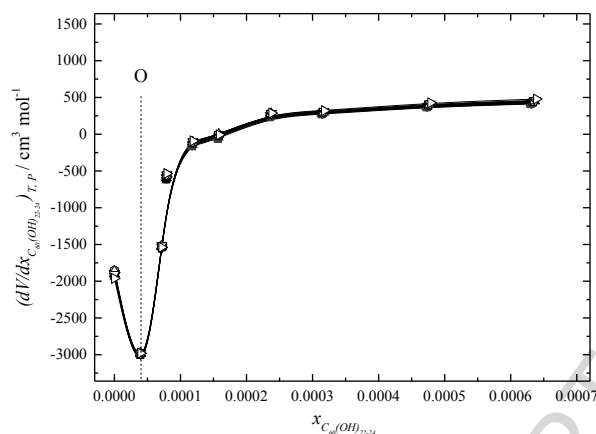


Fig. 9. Concentration dependences of the $\left(\frac{\partial V}{\partial x_{C_{60}(OH)_{22-24}}}\right)_{T,P}$ – derivatives in the temperature range 278.15 – 323.15 K. (■) 278.15 K, (●) 283.15 K, (▲) 288.15 K, (▼) 293.15 K, (►) 298.15 K, (□) 303.15 K, (○) 308.15 K, (△) 313.15 K, (▽) 318.15 K and (▷) 323.15 K. O– is an extremum point $\left(\frac{\partial^2 V}{\partial x^2}\right)_{T,P} = 0$, $x = 4 \cdot 10^{-5}$). Solid lines are included to guide the eye.

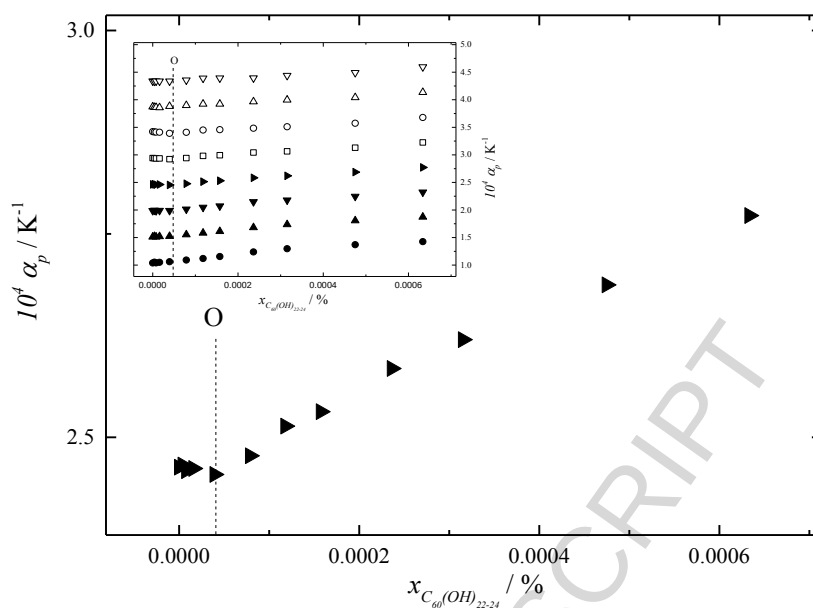


Fig. 10. Concentration dependence of isobaric thermal expansivity (α_p) for the $C_{60}(OH)_{22-24}$ - H_2O binary system. (●) 283.15 K, (▲) 288.15 K, (▼) 293.15 K, (►) 298.15 K, (□) 303.15 K, (○) 308.15 K, (△) 313.15 K and (▽) 318.15 K. x – molar fraction of fullerenol.

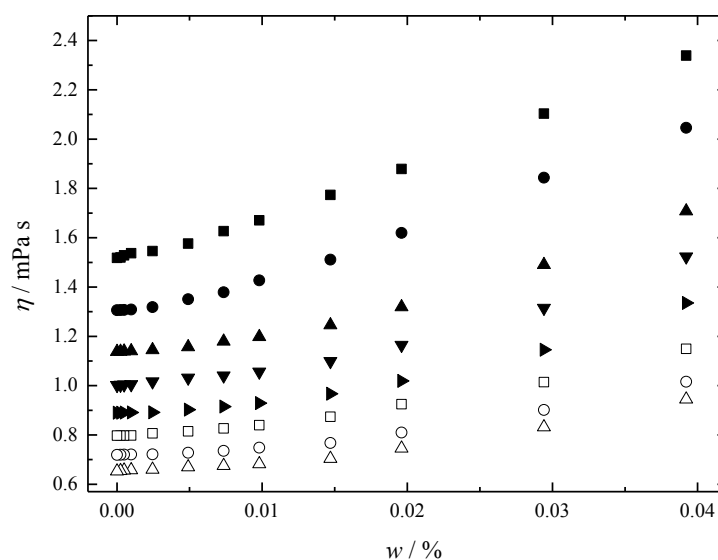


Fig. 11. Concentration dependences of dynamic viscosity (η) at shear rates of 100 s^{-1} for the $C_{60}(OH)_{22-24}$ - H_2O binary system at (■) 278.15 K, (●) 283.15 K, (▲) 288.15 K, (▼) 293.15 K, (►) 298.15 K, (□) 303.15 K, (○) 308.15 K and (△) 313.15 K. w - mass fraction of fullerenol.

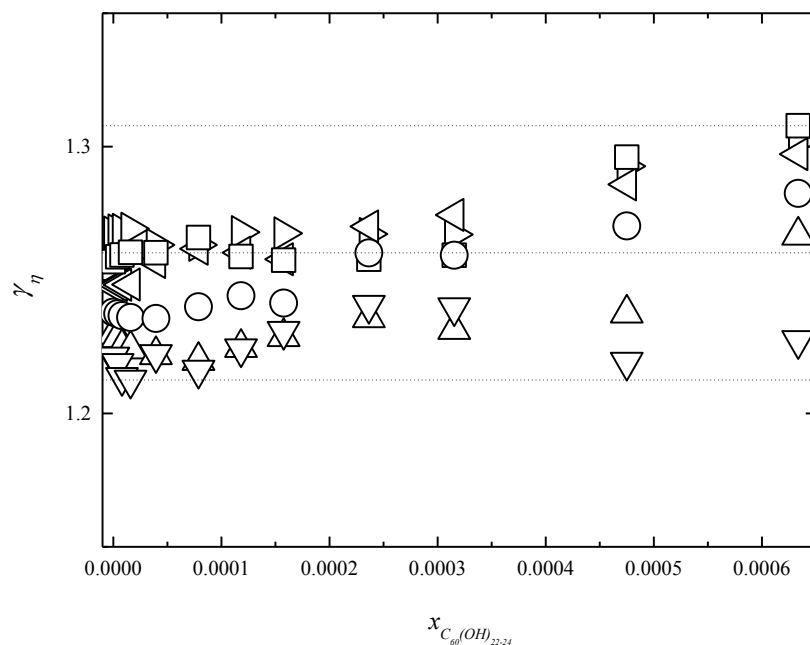


Fig. 12. Concentration dependence of van't-Hoff's viscosity coefficient ($\gamma_n = 1.26 \pm 0.05$) for

the $C_{60}(OH)_{22-24}$ - H_2O binary system. ($\square$) $(\frac{\eta_{29815}}{\eta_{31315}})^{\frac{10}{\Delta T}}$, ($\circ$) $(\frac{\eta_{29315}}{\eta_{30815}})^{\frac{10}{\Delta T}}$, ($\triangle$) $(\frac{\eta_{28815}}{\eta_{30315}})^{\frac{10}{\Delta T}}$, (∇)

$(\frac{\eta_{30315}}{\eta_{31315}})^{\frac{10}{\Delta T}}$, ($\triangleleft$) $(\frac{\eta_{29815}}{\eta_{30815}})^{\frac{10}{\Delta T}}$ and ($\triangleright$) $(\frac{\eta_{29315}}{\eta_{30315}})^{\frac{10}{\Delta T}}$. x — mole fraction of fulleranol.

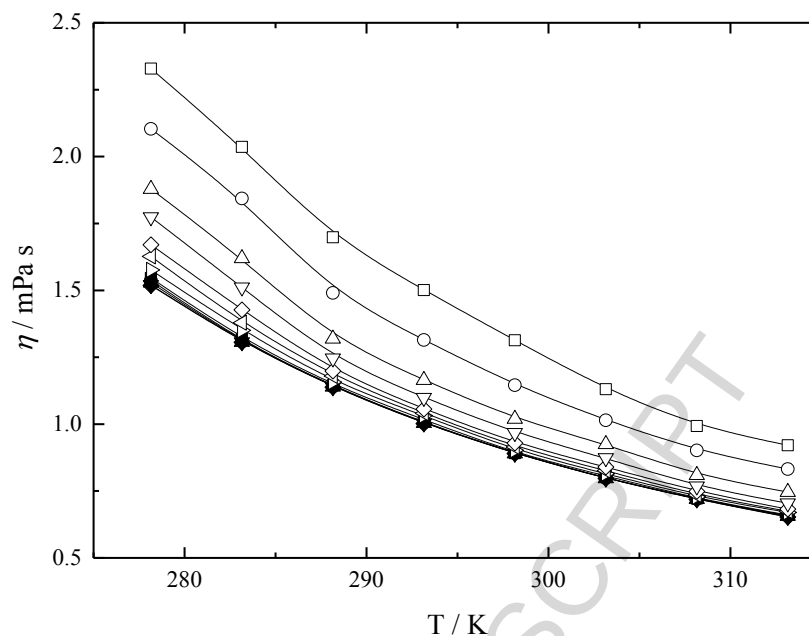


Fig. 13. Temperature (T) dependences of dynamic viscosity (η) at shear rates of 100 s^{-1} for the $\text{C}_{60}(\text{OH})_{22-24}\text{-H}_2\text{O}$ binary system. Points— experimental data, solid lines— results provided by Vogel-Fulcher-Tamman (VFT) equation, see Eq. 15, at different $\text{C}_{60}(\text{OH})_{22-24}$ concentrations: ($\square$) $40 \text{ g}\cdot\text{dm}^{-3}$, ($\circ$) $30 \text{ g}\cdot\text{dm}^{-3}$, ($\triangle$) $20 \text{ g}\cdot\text{dm}^{-3}$, (∇) $15 \text{ g}\cdot\text{dm}^{-3}$, ($\diamond$) $10 \text{ g}\cdot\text{dm}^{-3}$, ($\triangleleft$) $7.5 \text{ g}\cdot\text{dm}^{-3}$, ($\triangleright$) $5 \text{ g}\cdot\text{dm}^{-3}$, ($\blacksquare$) $2.5 \text{ g}\cdot\text{dm}^{-3}$, ($\bullet$) $1 \text{ g}\cdot\text{dm}^{-3}$, ($\blacktriangle$) $0.5 \text{ g}\cdot\text{dm}^{-3}$, ($\blacktriangledown$) $0.25 \text{ g}\cdot\text{dm}^{-3}$ and ($\blacklozenge$) water: $0\cdot\text{dm}^{-3}$.

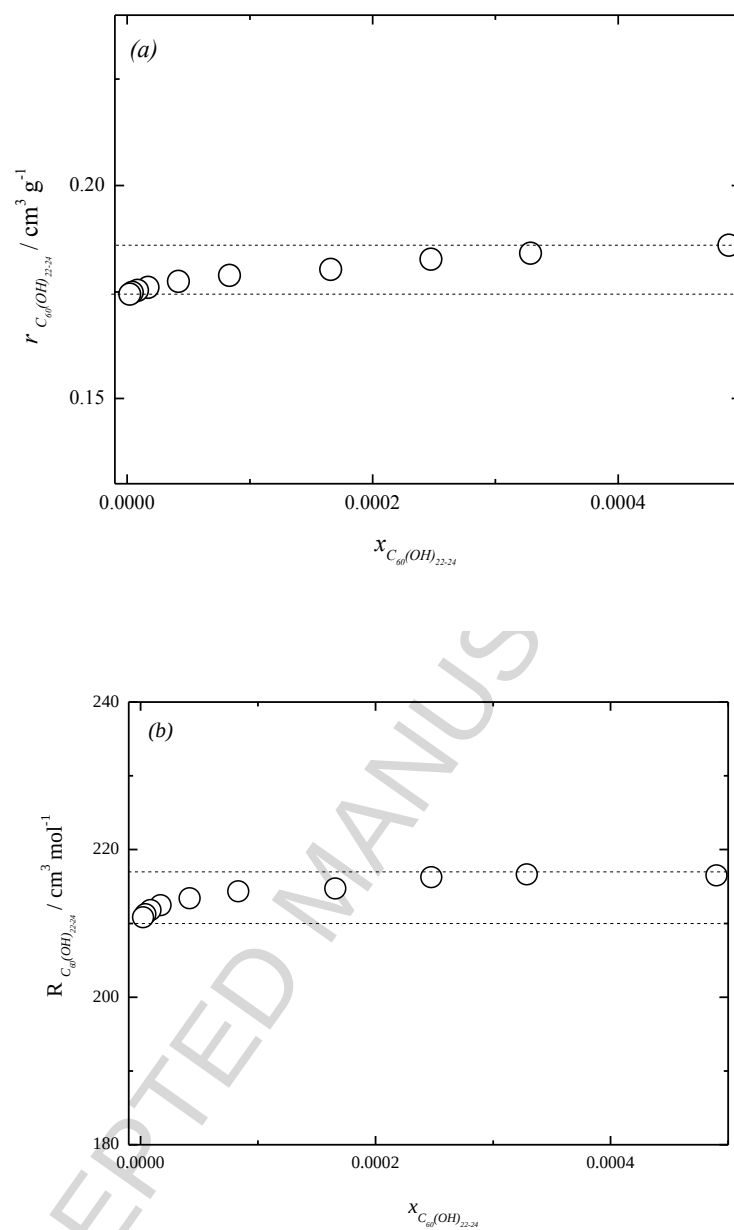


Fig. 14. Concentration dependence of specific (a) and molar (b) refraction of $C_{60}(OH)_{22-24}$ in aqueous solutions at 298.15 K, $x_{C_{60}(OH)_{22-24}}$ – molar fraction of fullerenol.

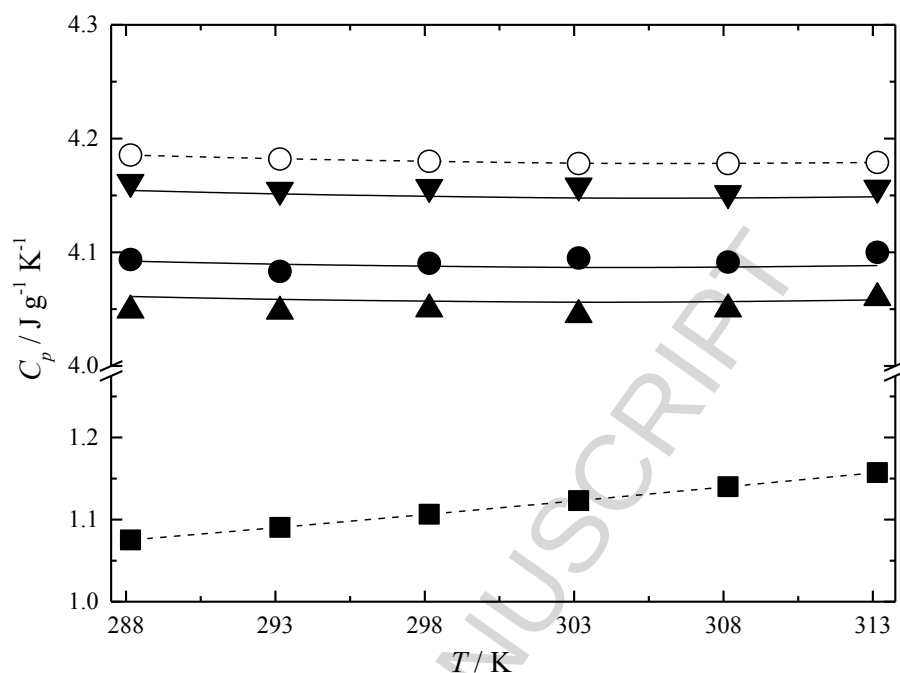
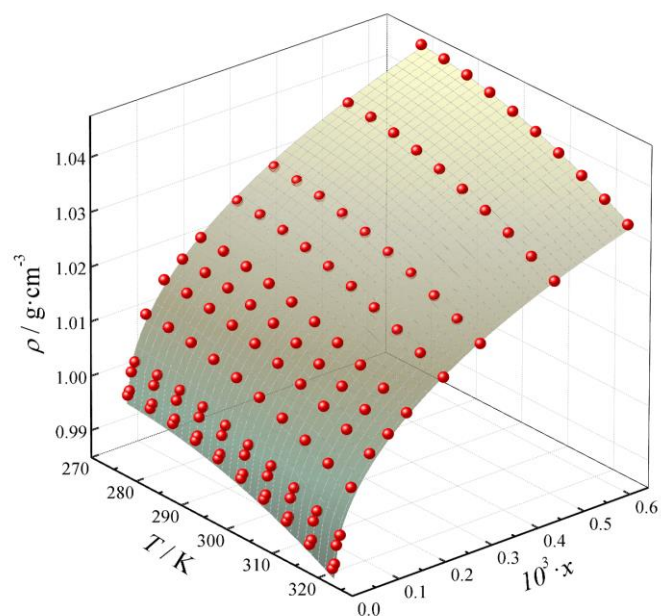
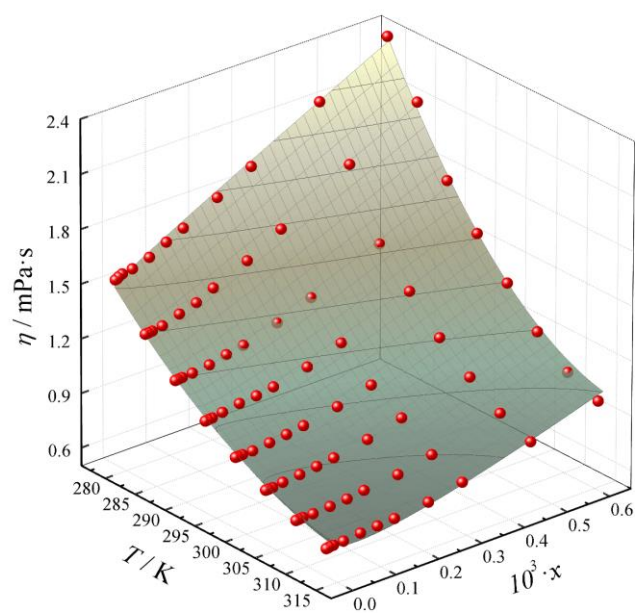


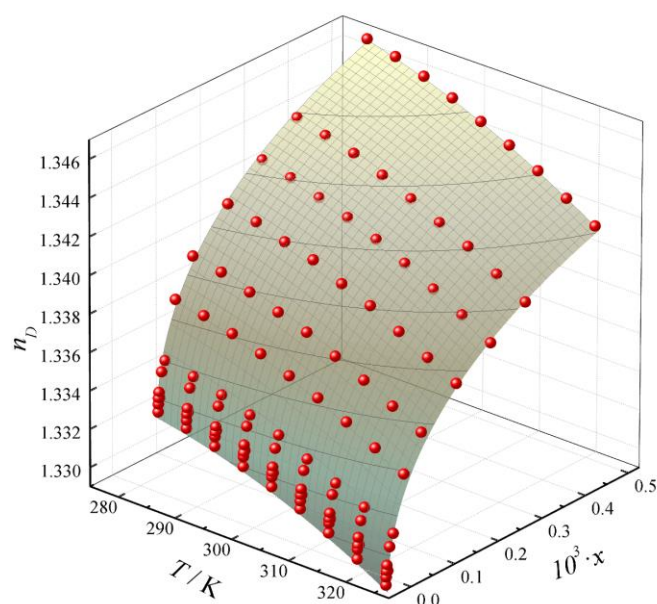
Fig. 15. Temperature (T) dependences of isobaric heat capacities (C_p) for fulleranol- $C_{60}(OH)_{22-24}$ (■), water (○) and $C_{60}(OH)_{22-24}$ aqueous solutions at different fulleranol concentrations: 10 g·dm⁻³ (▼), 30 g·dm⁻³ (●) and 40 g·dm⁻³ (▲). Dashed lines correspond to temperature descriptions of heat capacities by polynomial fittings (Eq. 25). Solid lines correspond to the heat capacities predicted for the fulleranol aqueous solutions using Eq. 23.



(a)



(b)



(c)

Fig. 16. Temperature and concentration dependence of density (a), viscosity (b) and refraction indexes (c) of $C_{60}(OH)_{22-24}$ aqueous solutions, where: ρ – density of solution, η – dynamic viscosity, n_D – refraction index, T – absolute temperature, x – mole fraction of $C_{60}(OH)_{22-24}$. Experimental data are presented as red spheres, curved surfaces represent data calculated using Eq. (26).

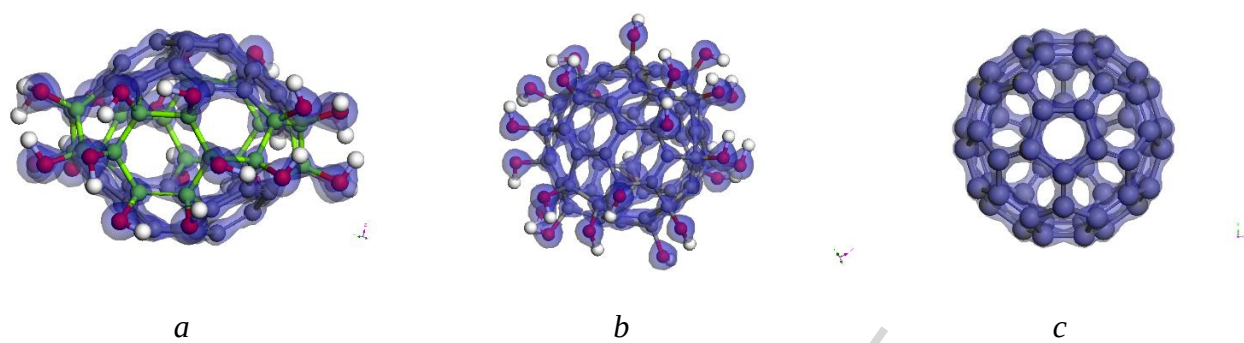


Fig. 17. Distributions of electronic density for Saturn-like fullerene $C_{60}(OH)_{24}$ (*a*), fullerene $C_{60}(OH)_{24}$ with uniform distribution of hydroxyl groups (*b*) and individual fullerene C_{60} (*c*).

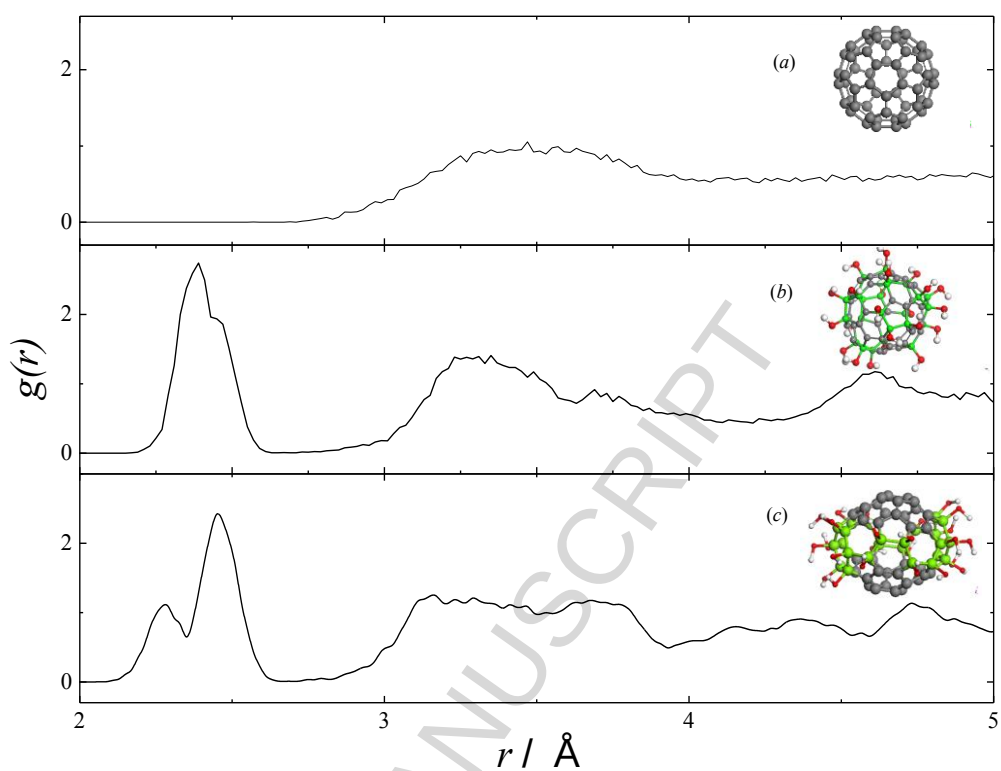


Fig. 18. Radial distribution function between carbon atoms of the fullerene core and water molecules: fullerene C_{60} (a), fullerenol with uniform distribution of hydroxyl groups $\text{C}_{60}(\text{OH})_{24}$ (b), and Saturn-like fullerenol $\text{C}_{60}(\text{OH})_{24}$ (c).

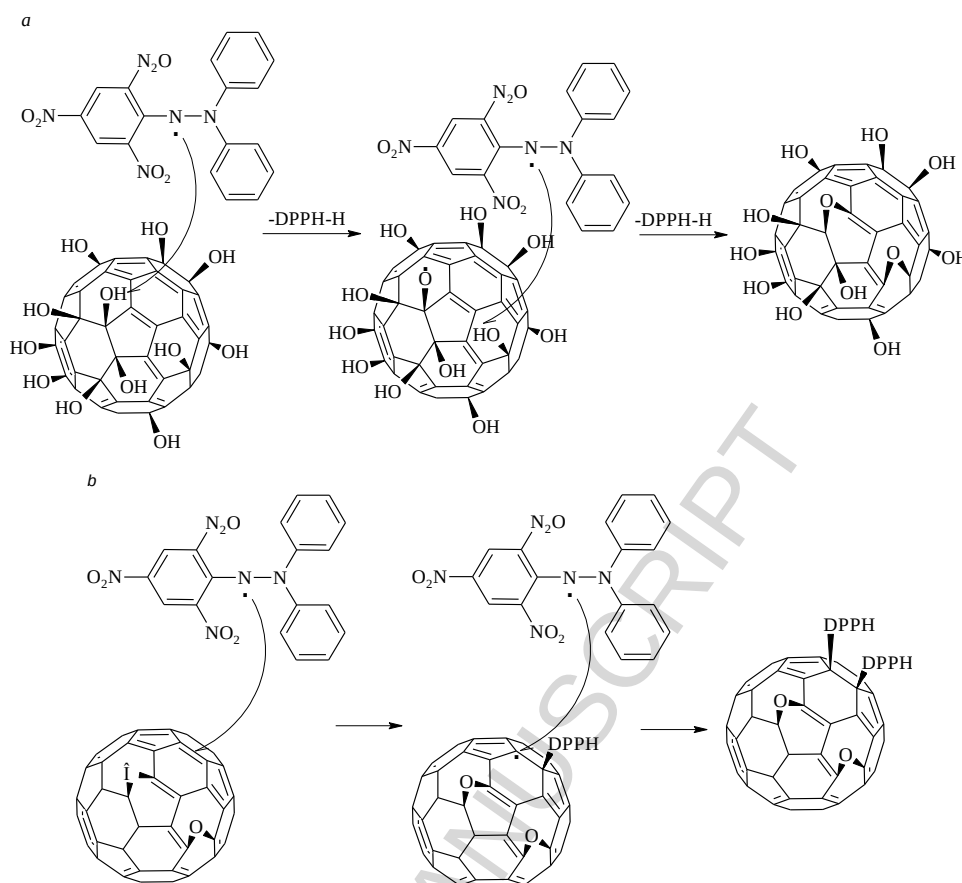


Fig. 19. The proposed reaction mechanism of DPPH with $C_{60}(OH)_{22-24}$: *a* – fast step (a hydrogen transfer to the DPPH radical), *b* – rate-determining step (a nucleophilic attack of the C=C bond).

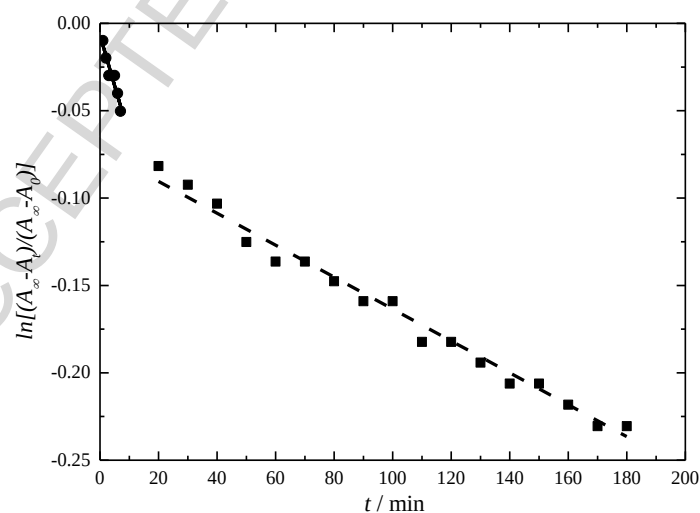


Fig. 20. The kinetic dependence of the DPPH radical reduction reaction by $C_{60}(OH)_{22-24}$ fulleranol. The solid line is the fastest step (hydrogen transfer to the DPPH radical), the dashed line corresponds to the rate-determining step (nucleophilic attack of the C=C bond).

Highlights

- physico-chemical properties of the fulleranol aqueous solutions were investigated;
- T - x -experimental densities, viscosities and refractive indexes were correlated;
- dynamic and structural characteristics of fulleranol solutions were determined.

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