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Cryometry and excess functions of fullerenols and trismalonates of light fullerenes – $C_{60}(OH)_{24\pm2}$ and $C_{70}[=C(COOH)_2]_3$ aqueous solutions

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Cryometry investigations of the $C_{60}(OH)_{24\pm2}$ – H_2O and $C_{70}[=C(COOH)_2]_3$ – H_2O binary systems were conducted over the 0.1 – 10 g concentration range of fullerenols per 1 dm^3 of solutions. The decreases of the temperatures at the onset of H_2O – ice crystallization were determined. Excess functions of aqueous solutions – water and fullerenols (trismalonates) activities and activity coefficients and excess Gibbs energy of the solutions were calculated. All solutions demonstrated huge deviations from those of ideal solutions. The last fact, to our opinion, is caused by a very specific – hierarchical type of association of fullerenols (trismalonates) solution components, which was proved by the results of visible light scattering analysis.

Keywords: Cryometry, activities, activity coefficients, fullerenols, trismalonates, water solution.

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1. Introduction

This article is the continuation of a series of articles devoted to the synthesis, identification and physico-chemical properties investigation of nanoclusters, which represented the moderately water soluble derivatives of light fullerenes C_{60} and C_{70} [1–14] – poly-hydroxyl fullerenols (fullerenol-d $C_{60}(OH)_{24\pm2}$ and malonic ester – trismalonate $C_{70}[=C(COOH)_2]_3$). In previous articles' authors have reported on the volume, refraction, electrical, transport properties of these water soluble nanoclusters and their aqueous solutions, also investigations of solubility in water in poly-thermal conditions and in some ternary water-salt systems and complex thermal analysis of nanocluster crystal-hydrates were performed.

2. Reasons for direct excess functions in fullerenols (trismalonates) – H_2O solutions determination

We are not aware of any direct experimental data concerning the determination of excess thermodynamic data (primarily activity coefficients) in binary (or more component) solutions of fullerenes or their derivatives in any solutions. This fact may, to our opinion, be explained by the very low solubility of such nanoclusters in the main part of the solvents (see, for example [15–17]). The synthesis of well water soluble nanoclusters (such as: poly-hydroxyl fullerenols $C_{60}(OH)_n$, $C_{70}(OH)_n$; some ethers – for example: trismalonic esters – trismalonate $C_{60}[=C(COOH)_2]_3$, $C_{70}[=C(COOH)_2]_3$, some adducts with amino-acids (for example arginine $C_{60}(C_6H_{12}NaN_4O_2)_8H_8$ or alanine [18]), the solubility of which in water depends on the type of nanocluster and temperature, may be from tens to hundreds of grams of nanocluster per dm^3 of water. This fact makes it possible to determine excess functions of the solution by standard methods, for example, cryometry (described in this article) or by the determination of water activity by isopiestic method. Such determination is, to our opinion, may be very interesting because of the following reasons.

Visible light scattering analysis in light fullerenols (trismalonates) – H_2O solutions at room temperature was provided repeatedly (see [1,5,14]). In all cases, one can see the following:

- No monomer molecular nanoclusters (with linear dimension diameter $d_0 \approx 1.5 - 2.0$ nm) were seen in all investigated solutions, even in the dilute solution ($C = 0.1$ g/dm^3).
- The diameters of the first type aggregates (first order clusters of percolation) have similar sizes – some tens of nm $d_1 \approx 20 - 80$ nm over the whole concentration range.
- The diameters of the second type aggregates (second order clusters of percolation) also have similar sizes – hundreds nm $d_2 \approx 100 - 400$ nm.
- The third type aggregates (third order clusters of percolation) have not been seen at any concentrations except in the most concentrated solution at $C > 1$ g/dm^3, where clusters with extremely huge linear dimension (some microns) are formed: $d_3 > 1000$ nm – the solution 'becomes very heterogeneous' but stable as a colloid system.
- So, to describe these facts in the aggregation process, a stepwise model of particle growth was invoked, in other words, a hierarchical type of association of fullerenols (trismalonates) components in water solution is observed. We consider that monomer spherical molecules form the first type spherical aggregates. Next, the initial spherical associates form the second type spherical associates. Next, the second type spherical associates form the third type spherical associates (the last ones correspond to the colloidal heterogeneous system).

3. The possibility of determining excess functions in fullerenol (trismalonates) – water solutions

In order to check the possibility of determining the excess function of $C_{60}(OH)_{24\pm2}$ – H_2O and $C_{70}[=C(COOH)_2]_3$ – H_2O in the selected concentration range by cryometry method, the following conditions must be met:

- The solubility in the $C_{60}(OH)_{24\pm2}$ – H_2O and $C_{70}[=C(COOH)_2]_3$ – H_2O binary systems at ~273.15 K is great enough so that the solution is formally homogeneous, i.e. does not consist of solid crystal hydrates of $C_{60}(OH)_{24\pm2}$ or $C_{70}[=C(COOH)_2]_3$. Preliminary experiments show that in both cases, the solubilities of both nanoclusters at 273.15 ± 1 K is ≈ 360 g/dm^3 for $C_{70}[=C(COOH)_2]_3$ and ≈ 210 g/dm^3 for $C_{60}(OH)_{24\pm2}$. So, if we choose the concentration range not more than tens g/dm^3 we can be sure that no solid crystal hydrates can co-crystallize with water ice during crystallization of the respective solutions.
- Additionally one must be sure that solutions of the nanoclusters are really homogeneous – do not delaminate and are not colloidal in nature. In this case, only more or less dilute solutions may satisfy these requirements (see lower points 10, 11 in Table 1 were not taken into account).
- The last requirement is that the temperature decrease ΔT should be more or less significant – hundredth, or even better, tenth of a K. This requirement is easily satisfied.

TABLE 1. Cryometry data and excess function in the binary solutions fullerenol-60-d – H_2O (marked by *) and trismalonate-C_{70} – H_2O (marked by **) at 273.15 K

Number	*Molar fraction of fullerenol-60-d in solution $x_{\text{fullerenol-60-d}}$ (rel.un.)	*Temperature of water crystallization decrease ΔT (K)	**Molar fraction of trismalonate-C_{70} in solution $x_{\text{fullerenol-70-d}}$ (rel. un.)	**Temperature of water crystallization decrease ΔT (K)
1	0.000	0.000	0.000	0.000
2	$1.607 \cdot 10^{-6}$	0.047	$1.736 \cdot 10^{-6}$	0.045
3	$3.981 \cdot 10^{-6}$	0.070	$4.430 \cdot 10^{-6}$	0.064
4	$7.933 \cdot 10^{-6}$	0.099	$8.616 \cdot 10^{-6}$	0.089
5	$1.586 \cdot 10^{-5}$	0.149	$1.714 \cdot 10^{-5}$	0.126
6	$3.952 \cdot 10^{-5}$	0.234	$4.275 \cdot 10^{-5}$	0.183
7	$7.905 \cdot 10^{-5}$	0.350	$8.506 \cdot 10^{-5}$	0.271
8	$1.185 \cdot 10^{-4}$	0.469	$1.281 \cdot 10^{-4}$	0.343
9	$1.579 \cdot 10^{-4}$	0.565	$1.710 \cdot 10^{-4}$	0.410
10			$5.130 \cdot 10^{-4}$	0.785***
11			$8.510 \cdot 10^{-4}$	1.095***

Number	*$\ln a_{\text{H2O}}$ (water activity) (rel. un.)	**$\ln a_{\text{H2O}}$ (water activity) (rel. un.)	*a_{H2O} (water activity) (rel. un.)	**a_{H2O} (water activity) (rel. un.)
1	0.000	0.000	1.00000	1.00000
2	$-4.236 \cdot 10^{-4}$	$-4.056 \cdot 10^{-4}$	0.99958	0.99959
3	$-6.309 \cdot 10^{-4}$	$-5.775 \cdot 10^{-4}$	0.99937	0.99942
4	$-8.922 \cdot 10^{-4}$	$-8.027 \cdot 10^{-4}$	0.99911	0.9992
5	-0.00134	-0.00113	0.99866	0.99887
6	-0.00211	-0.00165	0.99789	0.99835
7	-0.00315	-0.00244	0.99685	0.99756
8	-0.00422	-0.00309	0.99579	0.99692
9	-0.00508	-0.00369	0.99493	0.99632

Number	*$\ln \gamma_{\text{H2O}}$ (water activity coefficient) (rel. un.)	**$\ln \gamma_{\text{H2O}}$ (water activity coefficient) (rel. un.)	*derivative $\frac{d \ln \gamma_{\text{H2O}}}{d x_{\text{fullerenol-d}}}$ (rel. un.)	**derivative $\frac{d \ln \gamma_{\text{H2O}}}{d x_{\text{trismalonate-C70}}}$ (rel. un.)
1	0.00000	0.00000	-262.6	-230.3
2	$-4.22 \cdot 10^{-4}$	$-4.03 \cdot 10^{-4}$	-174.4	-147.0
3	$-6.26 \cdot 10^{-4}$	$-5.73 \cdot 10^{-4}$	-75.71	-57.99
4	$-8.84 \cdot 10^{-4}$	$-7.94 \cdot 10^{-4}$	-60.303	-45.28
5	-0.00132	-0.00112	-43.51	-28.68
6	-0.00207	-0.00161	-28.42	-18.436
7	-0.00307	-0.00236	-25.71	-15.83
8	-0.0041	-0.00296	-23.47	-13.49
9	-0.00492	-0.00352	-20.82	-13.05

Number	*derivative $\frac{d\ln\gamma_{\text{fullerenol-d}}}{dx_{\text{fullerenol-d}}}$ (rel. un.)	**derivative $\frac{d\ln\gamma_{\text{trismalonate-C70}}}{dx_{\text{trismalonate-C70}}}$ (rel. un.)	$^{*}\ln\gamma_{\text{fullerenol-60-d}}$ (rel. un.)	$^{**}\ln\gamma_{\text{trismalonate-C70}}$ (rel. un.)
1	–	–	–	–
2	$1.08\cdot10^{8}$	$8.38\cdot10^{7}$	2628	2737
3	$1.901\cdot10^{7}$	$1.31\cdot10^{7}$	2737	2829
4	$7.60\cdot10^{6}$	$5.24\cdot10^{7}$	2780	2860
5	$2.74\cdot10^{6}$	$1.67\cdot10^{6}$	2807	2878
6	719101	431233	2835	2896
7	325211	186088	2862	2914
8	198035	105294	2885	2931
9	131834	76302	2906	2947

Number	$^{*}\ln a_{\text{fullerenol-60-d}}$ (rel. un.)	$^{**}\ln a_{\text{trismalonate-C70}}$ (rel. un.)	$^{*}\varphi_{\text{fullerenol-60-d}}$ (rel. un.)	$^{**}\varphi_{\text{trismalonate-C70}}$ (rel. un.)
1	–	–	–	–
2	2614	2724	−195	−205
3	2724	2816	−219	−228
4	2768	2848	−235	−244
5	2795	2867	−252	−261
6	2824	2886	−278	−286
7	2852	2905	−302	−309
8	2875	2922	−318	−326
9	2897	2938	−330	−338

Number	$^{*}G^{\text{ex}}/RT$ (rel. un.)	$^{**}G^{\text{ex}}/RT$ (rel. un.)	$^{*}G^{\text{mix}}/RT$ (rel. un.)	$^{**}G^{\text{mix}}/RT$ (rel. un.)
1	0.00000	0.00000	0.00000	0.00000
2	−0.00186	−0.00178	−0.00186	−0.00178
3	−0.00275	−0.00254	−0.00275	−0.00254
4	−0.00388	−0.00353	−0.00388	−0.00353
5	$1.903\cdot10^{-5}$	$2.123\cdot10^{-5}$	$1.894\cdot10^{-5}$	$2.114\cdot10^{-5}$
6	$4.844\cdot10^{-5}$	$5.381\cdot10^{-5}$	$4.825\cdot10^{-5}$	$5.360\cdot10^{-5}$
7	$9.831\cdot10^{-5}$	$1.081\cdot10^{-4}$	$9.795\cdot10^{-5}$	$1.077\cdot10^{-4}$
8	$1.488\cdot10^{-4}$	$1.640\cdot10^{-4}$	$1.482\cdot10^{-4}$	$1.634\cdot10^{-4}$
9	$1.999\cdot10^{-4}$	$2.203\cdot10^{-4}$	$1.993\cdot10^{-4}$	$2.196\cdot10^{-4}$

*** – unstable, heterogeneous solution.

4. Cryometry investigation in the $C_{60}(OH)_{24\pm2}$ - H_2O and $C_{70}[=C(COOH)_2]_3$ – H_2O binary systems. Main thermodynamic equations

Let us introduce designation:

$$\Delta F = F^S - F^L, \quad \Delta T = T_0^f - T, \tag{1}$$

where T_0^f – is the melting point for pure solvent, for water $T_0^f = 273.15$ K, T – current temperature (K), ΔF – molar change of thermodynamic function F, F^S – molar function F for the solid phase, F^L – molar function F for the liquid phase.

Condition of chemical phase equilibrium liquid (l) – solid (s) for pure solvent – water (w):

$$\mu w_0^S = \mu w_0^L + RT \ln a_w, \tag{2}$$

where: μw_0^S, μw_0^L – standard chemical potential of the solvent – water, in the solid and liquid phases, correspondingly, a_w – water activity in the scale of molar fractions in symmetrical normalization scale. Thus:

$$-\Delta H_w^f + \Delta C_P \left(T - T_0^f\right) + T\left[\Delta S_w^f - \Delta C_P \ln\left(T/T_0^f\right)\right] = RT \ln a_w, \tag{3}$$

$$\ln\left(T/T_0^f\right) = \ln\left(T_0^f - \Delta T/T_0^f\right) = \ln\left(1 - \Delta T/T_0^f\right) \approx -\Delta T/T_0^f, \tag{4}$$

where: ΔH_w^f, ΔS_w^f, ΔC_P – molar enthalpy, entropy and change of isobaric heat capacity of water at the temperature T_0^f. So:

$$-\Delta H_w^f \left[1 - T/T_0^f\right] + \Delta C_P \left[T - T_0^f - T \ln\left(T/T_0^f\right)\right] = RT \ln a_w, \tag{5.1}$$

$$-\Delta H_w^f \Delta T/T_0^f + \Delta C_P \Delta T \left(-1 + T/T_0^f\right) = RT \ln a_w, \tag{5.2}$$

$$\frac{-\Delta H_w^f \Delta T - \Delta C_P \Delta T^2}{R\left(T_0^f - \Delta T\right) T_0^f} = \ln a_w. \tag{5.3}$$

Later, we shall use formula (5.3) as a base one for the calculation of the solution's excess functions. In all calculations, we will use symmetrical normalization of the excess functions, as if nanoclusters are very weak electrolytes – practically non-electrolytes (see, for example [4, 6, 12]). So, we assume that:

$$a_{\mathrm{H2O}}\left(\mathrm{x_{H2O}} = 1\right) = \gamma_{\mathrm{H2O}}\left(\mathrm{x_{H2O}} = 1\right) = 1, \tag{6.1}$$

$$a_{\mathrm{nanocluster}}\left(\mathrm{x_{nanocluster}} = 1\right) = \gamma_{\mathrm{nanocluster}}\left(\mathrm{x_{nanocluster}} = 1\right) = 1, \tag{6.2}$$

where: a_i, γ_i – activity and activity coefficients of i-th solution component.

Experimental data were obtained with the help of metastatic Beckman thermometer. Data are represented in the Fig. 1 and Table 1. The arrow in the Fig. 1 shows the temperature decrease in the case of an ideal non-electrolyte solution. So, one can see how huge temperature decrease is observed in our cases for water soluble nanocluster solutions.

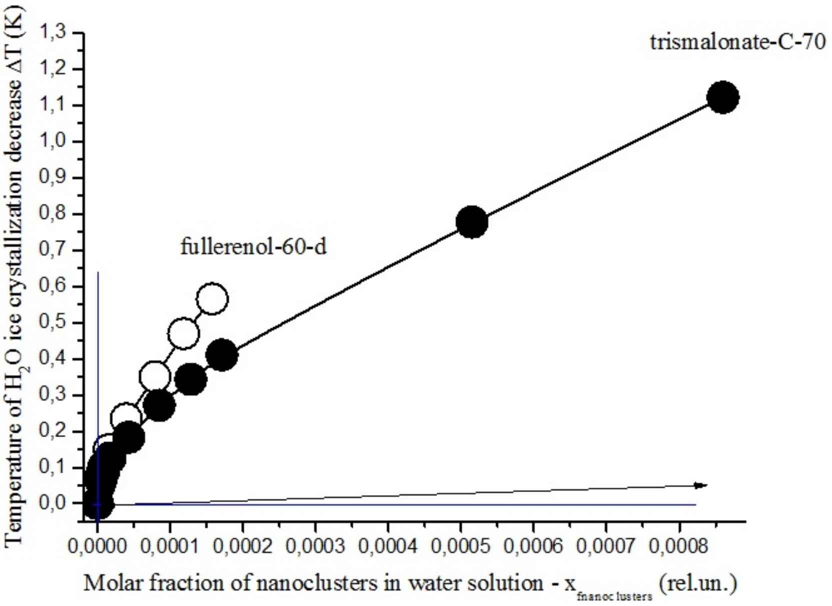

FIG. 1. The decrease of the temperatures of the beginning of the H_2O – ice crystallization in fullerenols (trismalonates) – H_2O solutions ($\Delta T = 273.15 - T$)

5. Partial excess functions of water and fullerenols (trismalonates) components in the $C_{60}(OH)_{24\pm2}$ – H_2O and $C_{70}[=C(COOH)_2]_3$ – H_2O binary systems

The graphics for the dependence ln of water activity ($\ln a_{\mathrm{H2O}}$), ln of water activity coefficient ($\ln \gamma_{\mathrm{H2O}}$), against molar fraction of fullerenols (trismalonates) in aqueous solutions are represented in Fig. 2, 3 in Table 1. The dependence of the derivative of ln of water (nanocluster) activity coefficients ($d \ln \gamma_{\mathrm{H2O}}/d\mathrm{x}_{\text{fullerenol-d(trismalonates-C-70)}}$) and ($d \ln \gamma_{\text{fullerenol-d(trismalonate-C-70)}}/d\mathrm{x}_{\text{fullerenol-d(trismalonate-C-70)}}$) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions are also represented in Fig. 4, 5 (curves – approximation, points – experimental data). The approximation is also represented in the Fig. 4, 5. For calculation we used the Gibbs-Duheim equation:

$$\left(\frac{\partial \ln a_{\text{nanocluster}}}{\partial \ln \mathrm{x}_{\text{nanocluster}}}\right)_T = -\frac{\mathrm{x}_{\mathrm{H2O}}}{\mathrm{x}_{\text{nanocluster}}}\left(\frac{\partial \ln a_{\mathrm{H2O}}}{\partial \ln \mathrm{x}_{\mathrm{H2O}}}\right)_T. \tag{7}$$

The dependence of ln of fullerenols (trismalonates) activity coefficients ($\ln \gamma_{\text{fullerenol-d(trismalonate-C-70)}}$) and the ln of fullerenols (trismalonates) activity ($\ln a_{\text{fullerenol-d(trismalonate-C-70)}}$) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions are represented in Fig. 6, 7 and Table 1.

6. Excess and Mixing Gibbs energy in the binary systems: $C_{60}(OH)_{24\pm2}$ – H_2O and $C_{70}[=C(COOH)_2]_3$ – H_2O. Miscibility gap and micro-heterogeneous behavior of the solutions

We have also calculated the dependence of the excess Gibbs energy of the solutions (G^{ex}) in fullerenols (trismalonates) – H_2O solutions against the molar fraction of fullerenols (trismalonates) in aqueous solutions (Fig. 8) and the dependence of the Gibbs energy of solution mixing (G^{mix}) and the miscibility gap in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) (Fig. 9) and also Table 1:

$$G^{\mathrm{ex}} = RT\left[\ln \gamma_{\text{nanocluster}} + \mathrm{x}_{\mathrm{H2O}} \ln \gamma_{\mathrm{H2O}}\right], \tag{8}$$

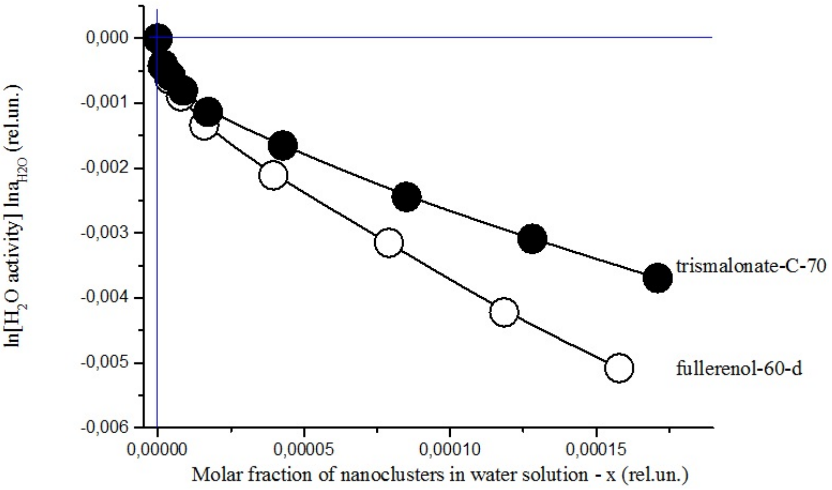

FIG. 2. The dependence of ln of water activity ($\ln a_{\mathrm{H2O}}$) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions.

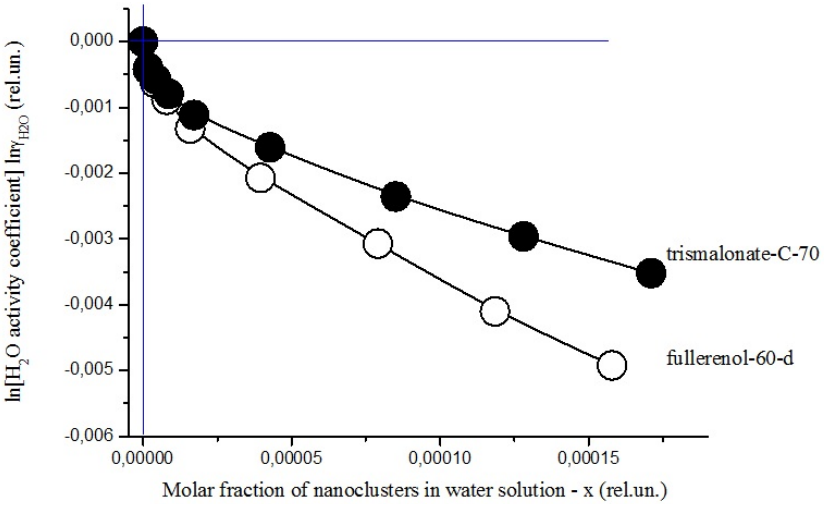

FIG. 3. The dependence of ln of water activity coefficients ($\ln \gamma_{\mathrm{H2O}}$) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions.

$$G^{\mathrm{mix}} = RT\left[\mathrm{x}_{\mathrm{nanocluster}} \ln a_{\mathrm{nanocluster}} + \mathrm{x}_{\mathrm{H2O}} \ln a_{\mathrm{H2O}}\right]. \tag{9}$$

One can see the inflection points in the Fig. 8, 9 where the second derivatives: $\left[\partial^2 G^{\mathrm{mix}}/\partial \mathrm{x}^2_{\mathrm{nanocluster}}\right]_{T,P}$ and $\left[\partial^2 G^{\mathrm{ex}}/\partial \mathrm{x}^2_{\mathrm{nanocluster}}\right]_{T,P}$ change signs or derivatives $\left[\partial G^{\mathrm{mix}}/\partial \mathrm{x}_{\mathrm{nanocluster}}\right]_{T,P}$ and $\left[\partial G^{\mathrm{ex}}/\partial \mathrm{x}_{\mathrm{nanocluster}}\right]_{T,P}$ cross through zero. Geometrically, this means that convexity in the graphics $G^{\mathrm{ex}}\left(\mathrm{x}_{\mathrm{nanocluster}}\right)$ and $G^{\mathrm{mix}}\left(\mathrm{x}_{\mathrm{nanocluster}}\right)$ is replaced by the concavity. Additionally, if the behavior of the first function is arbitrarily the sign of the derivative, then $\left[\partial^2 G^{\mathrm{mix}}/\partial \mathrm{x}^2_{\mathrm{nanocluster}}\right]_{T,P}$ in the concentration range of diffusion stability should be positive. So, we can consider that in the region $\mathrm{x}_{\mathrm{nanocluster}} > 2 \cdot 10^{-5}$ rel. un., the homogeneous solution exfoliates and becomes micro-heterogeneous. Experiments with light scattering show us that it is concentration region of the transition of the first type aggregates (first order clusters of percolation) with the linear dimensions $d_1 \approx 20 - 80$ nm to the second type aggregates (second

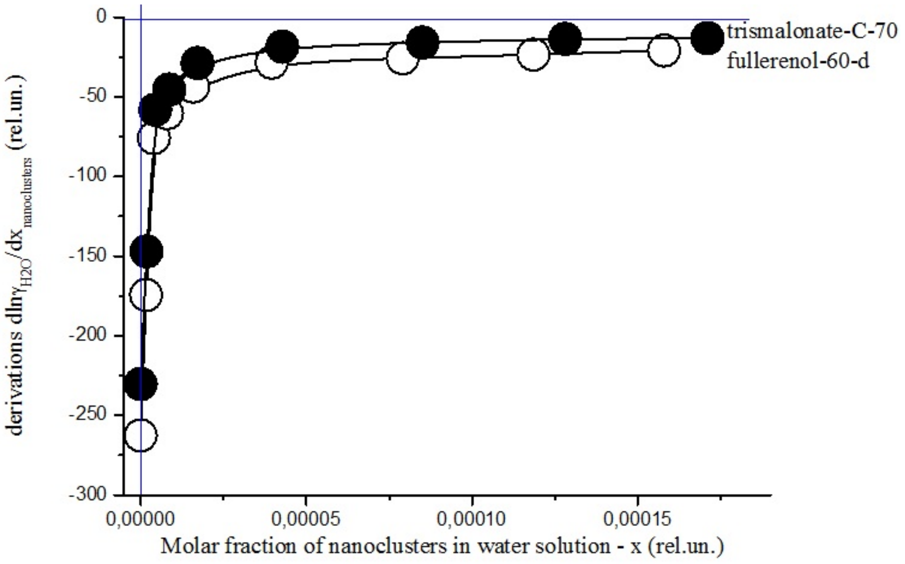

FIG. 4. The dependence of the derivative of ln of water activity coefficients ($d\ln\gamma_{\mathrm{H2O}}/dx_{\text{fullerenol-d(trismalonates-C-70)}}$) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions (curves – approximation, points – experimental data).

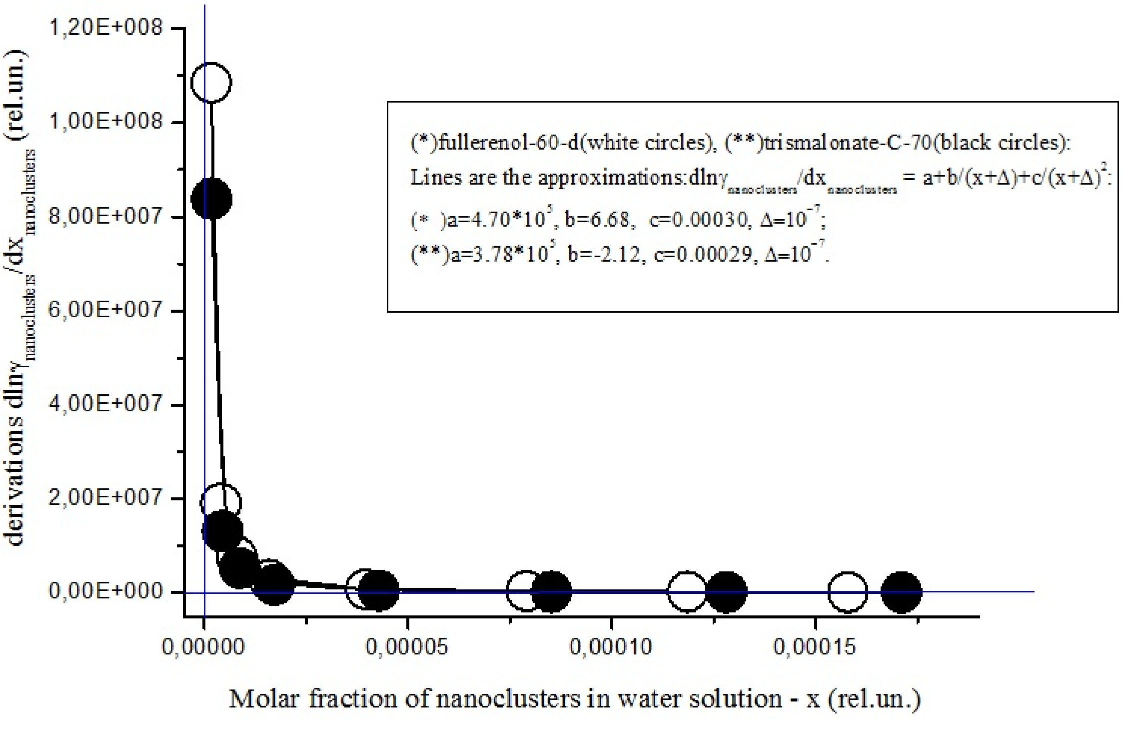

FIG. 5. The dependence of the derivative of ln of fullerenols (trismalonates) activity coefficients ($d\ln\gamma_{\text{fullerenol-d(trismalonate-C-70)}}/dx_{\text{fullerenol-d(trismalonate-C-70)}}$) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions.

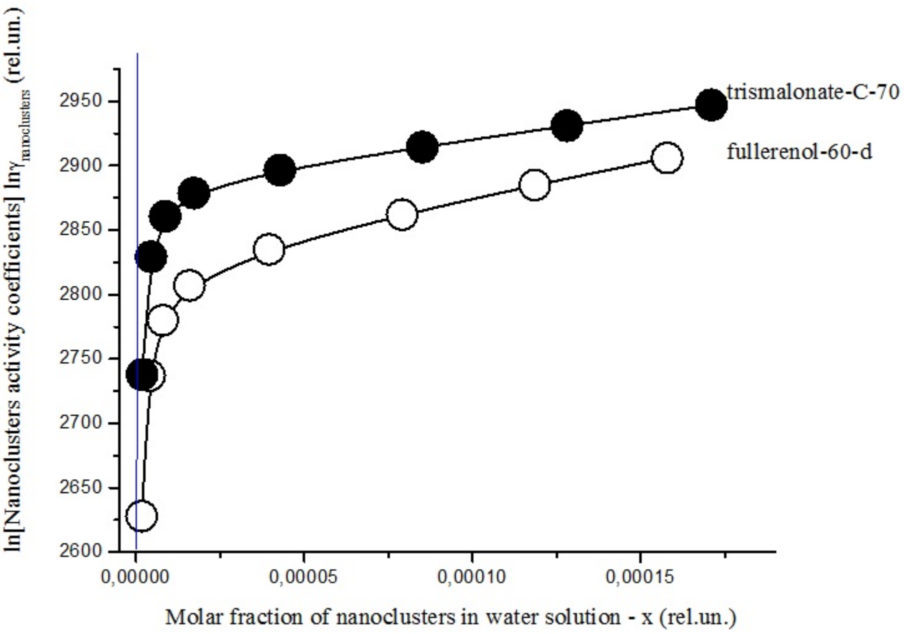

FIG. 6. The dependence of ln of fullerenols (trismalonates) activity coefficients ($\ln\gamma_{\text{fullerenol-d(trismalonate-C-70)}}$) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions.

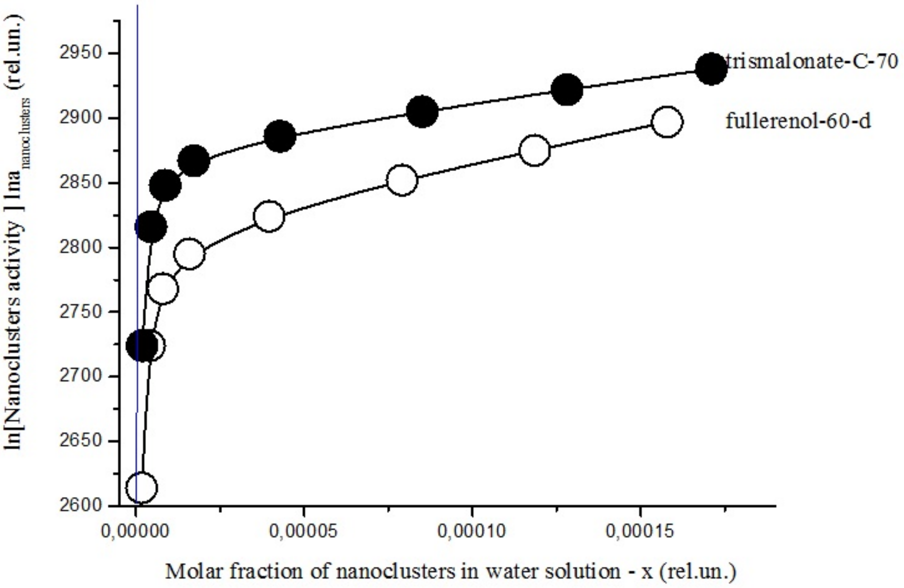

FIG. 7. The dependence of ln of fullerenols (trismalonates) activity ($\ln a_{\text{fullerenol-d(trismalonate-C-70)}}$) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions.

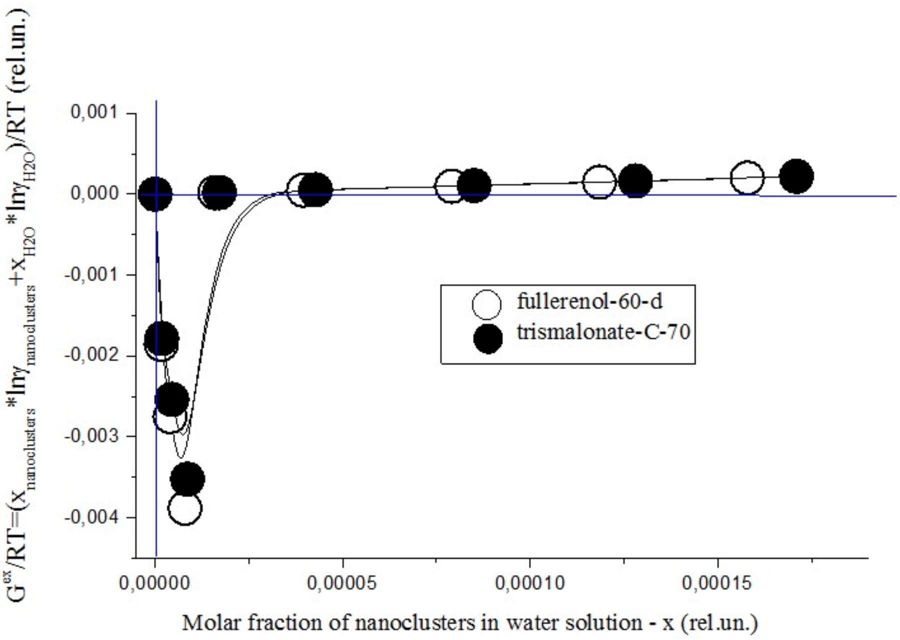

FIG. 8. The dependence of the excess Gibbs energy of the solutions (G^{ex}) in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions

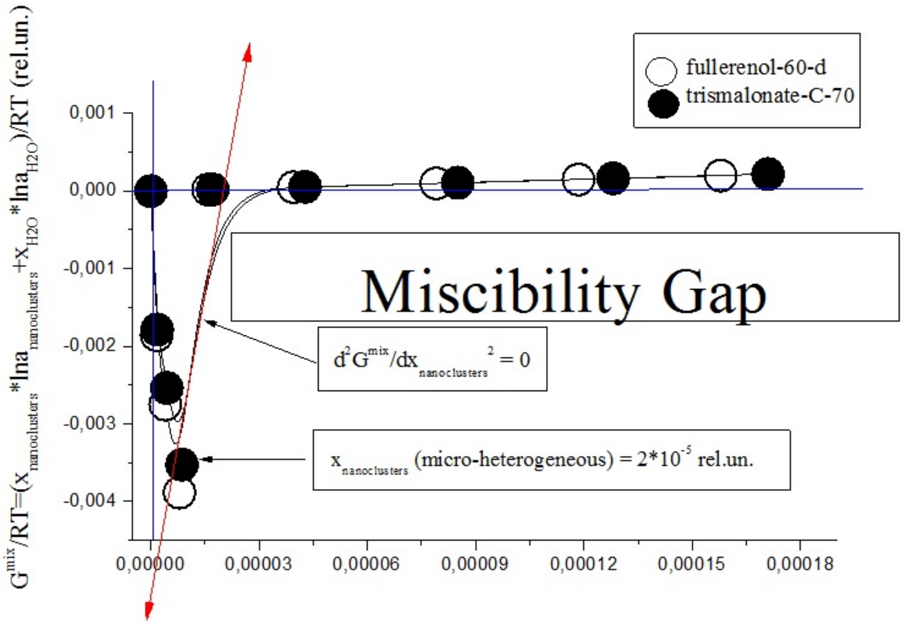

FIG. 9. The dependence of the Gibbs energy mixing of the solutions (G^{mix}) and the miscibility gap in fullerenols (trismalonates) – H_2O solutions against molar fraction of fullerenols (trismalonates) in aqueous solutions

order clusters of percolation) with the linear dimensions $d_2 \approx 100 - 400$ nm. In other words, this is the concentration range where a transition occurs from a nano-heterogeneous system to a micro-heterogeneous one.

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References

[1] K.N. Semenov, N.A. Charykov, I.V. Murin, Yu.V. Pukharenko. Physico-Chemical Properties of C_{60}-tris-malonic-derivative Water Solutions. *J. of Molecular Liquids*, 2015, **202**, P. 50–58.

[2] K.N. Semenov, N.A. Charykov, I.V. Murin, Yu.V. Pukharenko. Physico-chemical properties of the fullerenol-70 water solutions. *J. of Molecular Liquids*, 2015, **202**, P. 1–8.

[3] D.P. Tyurin, K.N. Semenov, et al. Dissociation of Fullerenol-d water solutions and their electric conductivity. *Rus. J. of Phys. Chem.*, 2015, **89** (5), P. 764–768.

[4] I.A. Pestov, V.A. Keskinov, et al. Solubility of $[C_{60}(=C(COOH)_2)_3$ in ternary system $[C_{60}(=C(COOH)_2)_3]$–$SmCl_3$–H_2 at 25 °C. *Rus. J. of Phys. Chem.*, 2015, **89** (6), P. 990–992.

[5] K.N. Semenov, N.A. Charykov, et al. Dependence of the dimension of the associates of water-soluble tris-malonate of light fullerene – $C_{60}[= C(COOH)_2]_3$ in water solutions at 25 °C. *Nanosystems: Physics, Chemistry, Mathematics*, 2015, **6** (2), P. 294–298.

[6] D.P. Tyurin, K.N. Semenov, et al. Dissociation of Fullerenol-70-d in Aqueous Solutionsand Their Electric Conductivity. *Russian Journal of Physical Chemistry A*, 2015, **89** (5), P. 771–775.

[7] K.N. Semenov, I.G. Kanterman, et al. Solid–Liquid Phase Equilibria in the Fullerenol-d–$CuCl_2$–H_2O System at 25 °C. *Russian Journal of Physical Chemistry*, 2014, **88** (6), P. 1073–1076.

[8] K.N. Semenov, N.A. Charykov, et al. Synthesis and identification water-soluble tris-malonate of light fullerene – $C_{60}[(=C(COOH)_2]_3$. *Nanosystems: physics, chemistry, mathematics*, 2014, **5** (2), P. 315–319.

[9] K.N. Semenov, N.A. Charykov, et al. Volume properties of water solution and refraction at 25 °C water-soluble tris-malonate of light fullerene – $C_{60}[= C(COOH)_2]_3$. *Nanosystems: physics, chemistry, mathematics*, 2014, **5** (3), P. 427–434.

[10] K.N. Semenov, N.A. Charykov, et al. Poly-thermal solubility and complex thermal analysis of water-soluble tris-malonate of light fullerene – $C_{60}[= C(COOH)_2]_3$. *Nanosystems: physics, chemistry, mathematics*, 2014, **5** (3), P. 435–440.

[11] K.N. Semenov, I.G. Kanterman, et al. Solubility in the Ternary System Fullerenol-d–Uranyl Sulfate–Water at 25 °C. *Radiokhimiya*, 2014, **56** (5), P. 493–495.

[12] K.N. Semenov, N.A. Charykov, et al. Concentration dependence of electric conductivity and pH for aqueous solutions of water soluble light fullerene $C_{60}[= C(COOH)_2]_3$ trismalonate. *Nanosystems: physics, chemistry, mathematics*, 2014, **5** (5), P. 709–717.

[13] K.N. Semenov, N.A. Charykov, et al. Fullerenol-d Solubility in Fullerenol-d – Inorganic Salt-Water Ternary Systems at 25 °C. *Industrial & Engineering Chemistry Research*, 2013, **52**, P. 16095–16100.

[14] K.N. Semenov, N.A. Charykov, V.A. Keskinov. Fullerenol Synthesis and Identification. Properties of the Fullerenol Water Solutions. *J. Chem. Eng. Data*, 2011, **56**, P. 230–239.

[15] K.N. Semenov, N.A Charykov. Solubility of light fullerenes and fullerenol in biocompatible with human beings solvents. Chapter in Handbook: *Grapes: Cultivation, Varieties and Nutritional Uses*. Nova Sciences Publishers, Inc., Editor R.P.Murphy et al., 2011, P. 1–48.

[16] K.N. Semenov, N.A. Charykov. Phase Equilibria in the FullereneContaining Systems. Handbook on Fullerene: Synthesis, Properties and Applications, Editor R.F.Verner, C.Benvegny, 2012, P. 1–91.

[17] K.N. Semenov, N.A. Charykov. *Solubility of light fullerenes and it's derivatives*. Germany: LAMBERT Academic Publishing, 2011, 237 p.

[18] L.B. Gan, C.P. Luo, et al. Water-soluble fullerene derivatives, synthesis and characterization of β-alanine C_{60} adducts. *Chinese Chemical letters*, 1994, **5** (4), P. 275–278.