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POLY-THERMAL SOLUBILITY AND COMPLEX THERMAL ANALYSIS OF WATER-SOLUBLE TRIS-MALONATE OF LIGHT FULLERENE – $C_{60}[=C(COOH)_2]_3$

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The poly-thermal solubility of the tris-malonate $C_{60}[=C(COOH)_2]_3$ – H_2O binary system was investigated from 20 – 80 °C with the help of the method of isotherm saturation in ampoules. Concentration of tris-malonate $C_{60}[=C(COOH)_2]_3$ in solutions was determined by light absorption at 330 nm. A diagram of the solubility is non-monotonic, consisting of 2 branches, which correspond to 2 different crystal-hydrates of $C_{60}[=C(COOH)_2]_3$ and one non-variant point, corresponding to the saturation both crystal-hydrates. Complex thermal analysis of $C_{60}[=C(COOH)_2]_3$ crystal hydrates, in equilibrium with a saturated aqueous solution at room temperature, was performed from 20 – 600 °C. Consecutive effects of the losses of C=O and C=O + H_2O were determined.

Keywords: tris-malonate of light fullerene, solubility, density, complex thermal analysis.

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1. Introduction

This article continues investigations which were initiated in previous studies [1, 2], which were devoted to the description of the synthesis and identification of tris-malonate $C_{60}[=C(COOH)_2]_3$ [1] (the original synthesis of this water soluble derivative was described earlier in [3]) and the investigation of volume and refraction properties of its aqueous solutions at 25 °C [2]. This article is devoted to the investigation of poly-thermal solubility in binary system: tris-malonate $C_{60}[=C(COOH)_2]_3$ – H_2O. It is well-known that fullerenes themselves are practically insoluble in water and aqueous solutions. For example, the real solubility of C_{60} in water at 25 °C is $1.3 \cdot 10^{-11}$ g/dm^3 and C_{70} is $1.1 \cdot 10^{-13}$ g/dm^3 [4–10]. This fact sufficiently limits the application of fullerenes in medicine, pharmacology, food industry etc., because fullerenes are incompatible with water and water based 'physiological liquids' such as blood, lymph, gastric juice etc. So, the synthesis and studying of the main properties, first of all solubility in water-based systems is very important. Such water soluble derivatives of light fullerenes as fullerenols, different malonates, complex esters of amino-acids etc have been investigated widely (see, for example [4, 11–13]).

TABLE 1. Solubility in binary system: tris-malonate C_{60}[=C(COOH)$_2$]$_3$ – H_2O from 20 – 80 °C

No.	Temperature (°C)	Solubility C (g/dm^3)	Density of saturated solutions ρ (g/sm^3)	Solid phase
1	20	254	1.112	C_{60}[=C(COOH)$_2$]$_3$·3H_2O
2	30	315	1.128	— ″ —
3	40	342	1.131	— ″ —
4	50	399	1.133	— ″ —
5	60	437	1.136	C_{60}[=C(COOH)$_2$]$_3$·3H_2O^+ C_{60}[=C(COOH)$_2$]$_3$
6	70	389	1.111	C_{60}[=C(COOH)$_2$]$_3$
7	80	357	0.948	— ″ —

2. Poly-thermal solubility of tris-malonate C_{60}[=C(COOH)$_2$]$_3$ in water

Poly-thermal solubility in binary system: tris-malonate C_{60}[=C(COOH)$_2$]$_3$ – H_2O from 20 – 80 °C is investigated with the help of the isotherm saturation method in ampoules (frequency $\nu \approx 2$ sec^{-1}, temperature accuracy $\Delta T \approx 0.05$ deg., time of saturation $t \approx 6$ h). Concentration of tris-malonate C_{60}[=C(COOH)$_2$]$_3$ in saturated solutions was determined by light absorption at 330 nm (after the dilution and cooling of saturated solutions) see [1]:

$$C_{tris-malonate}(\mathrm{mg/dm^3}) \approx 146 D_{330} \quad (l = 1 \text{ cm}), \tag{1}$$

where D_{330} – is optical density of the solution at λ =330 nm and ditch width $l = 1$ cm.

Experimental solubility data are represented in the Table 1 and Fig. 1. One can see the following:

1. The solubility tris-malonate C_{60}[=C(COOH)$_2$]$_3$ is very high thousands g/dm^3, these values correspond to the solubility of such well-soluble phases as fullerenol-d [11–13] or, for example halite – NaCl.
2. Solubility against temperature changes non-monotonically, crossing through the maximum at 60 °C.
3. Diagram consists of 2 branches, which correspond to 2 different compounds: a trihydrate – C_{60}[=C(COOH)$_2$]$_3$·3H_2O and an anhydrous form – C_{60}[=C(COOH)$_2$]$_3$ and one non-variant point (O in Fig. 1), corresponding to the saturation both compounds. Such parity at room temperature (one molecule of crystal-hydrate water per two carboxyl groups of malonate is typical for malonates – for example for sodium malonate – Na–COO–CH_2–COO–Na·H_2O [14].

3. Poly-thermal densities of saturated tris-malonate C_{60}[=C(COOH)$_2$]$_3$ aqueous solutions

To calculate the volume concentration of saturated tris-malonate C_{60}[=C(COOH)$_2$]$_3$ aqueous solutions and also in order to have the possibility of recalculating the solubility diagram into the other concentration scales (for example mass % or mole fraction), one needs to investigate the concentration poly-thermal density. These data were obtained by the method of

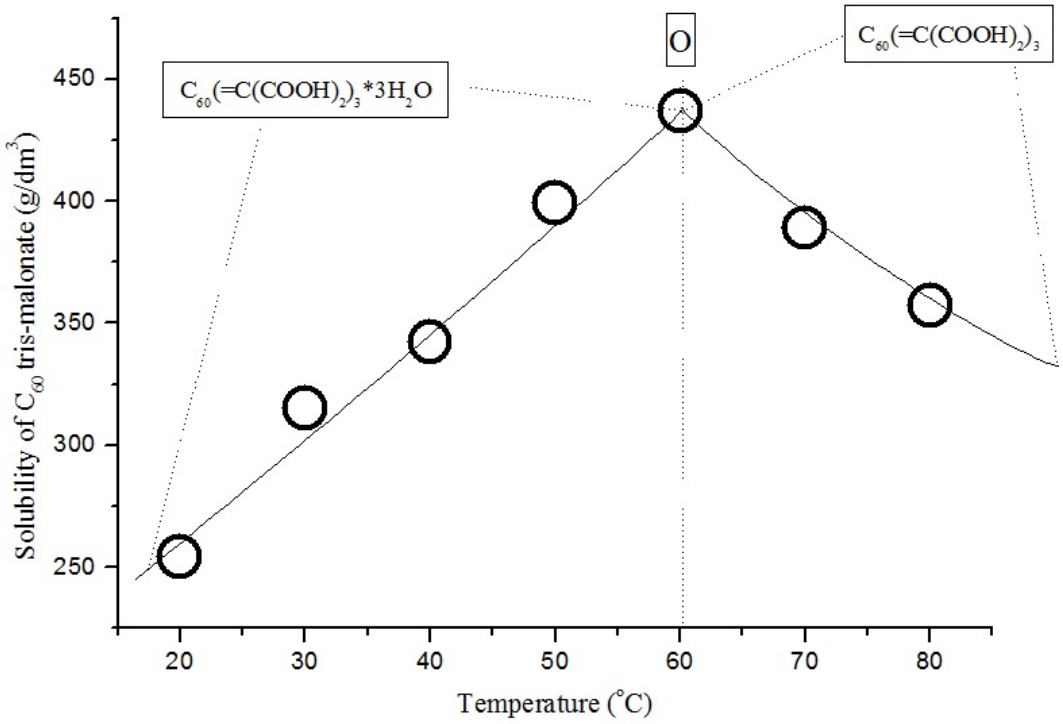

FIG. 1. Solubility in binary system: tris-malonate $C_{60}[=C(COOH)_2]_3 - H_2O$

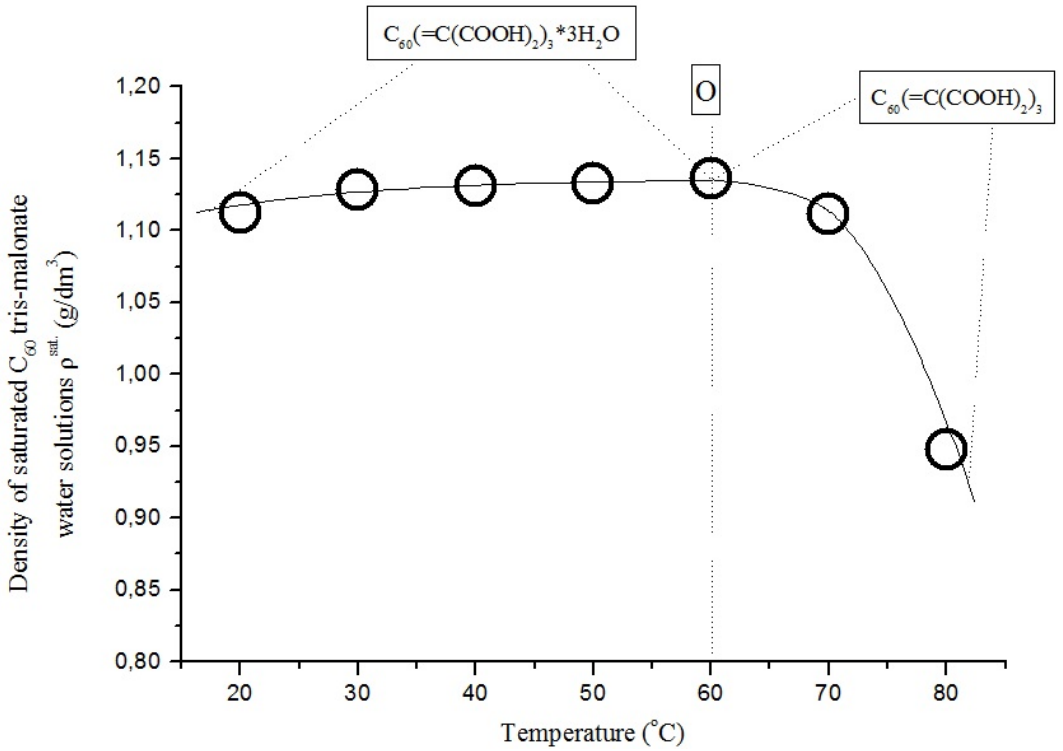

FIG. 2. Poly-thermal densities of saturated tris-malonate $C_{60}[=C(COOH)_2]_3$ aqueous solutions

pycnometry with the help of quartz pycnometers [2]. Data are also represented in the Table 1 and Fig. 2.

TABLE 2. The results of complex thermal analysis of crystal-hydrates of C_{60}[=C(COOH)$_2$]$_3$

No. of thermal effect (i)	T^m $(T_b \div T_e)$ (°C)	$\Delta m_i/\Delta m_0$ calculation (%)	$\Delta m_i/\Delta m_0$ experiment (%)	Process	Product of decomposition
0	—	0.0	0.0	—	$C_{60}(=C(COOH)_2)_3 \cdot 3H_2O$
1	97 $(60 \div 130)$	5.2	5.0	–3HOH	$C_{60}(=C(COOH)_2)_3$
2	150 $(140 \div 180)$	2.6	2.5	–C=O	$C_{60}(=C(COOH)_2)_2COH(COOH)$
3	208 $(195 \div 240)$	2.6	2.8	–C=O	$C_{60}=C(COOH)_2(COH(COOH))_2$
4	271 $(255 \div 295)$	2.6	2.7	–C=O	$C_{60}(COH(COOH))_3$
5	337 $(320 \div 385)$	4.3	4.1	–C=O–HOH	$C_{60}=CO(COH(COOH)_2$
6	420 $(400 \div 440)$	4.3	4.3	–C=O–HOH	$C_{60}(=CO)_2COHCOOH$
7	488 $(480 \div 520)$	4.3	4.2	–C=O–HOH	$C_{60}(=CO)_3$
Sum effect	25 – 560	25.9	25.6	–3HOH– –6C=O– –3HOH	$C_{60}(=CO)_3$

where: T^m — temperature maximum of thermal effect, T_b and T_e — temperatures of the beginning and end of the effect, $\Delta m_i/\Delta m_0$ — the mass loss, m_0 — initial mass.

One can see the following:

1. Diagram has one singular point (O in Fig. 2), where the type of crystal-hydrates and course of the curve are changing $\rho^{sat}(T)$.
2. Before point O ($T = 20 \to 60^oC$), the density is practically constant, and after point O ($T = 60 \to 80$°C), the density starts to decrease comparatively quickly. The last fact is connected with two reasons: the solubility of 'more heavy component' – tris-malonate decreases (see Fig. 1), and the density of the solvent decreases while temperature is also increasing.

4. Complex thermal analysis of crystal-hydrates of C_{60}[=C(COOH)$_2$]$_3$

Complex thermal analysis of C_{60}[=C(COOH)$_2$]$_3$ hydrates, in equilibrium with saturated aqueous solution at room temperature, was performed from 20 – 600 °C. A NETZSCH STA 449F3 thermo-gravimeter was used (velocity of the analysis $v \approx 5$ K/min, atmosphere – air, sample mass $m \approx 27.3$ mg). Results are represented in the Table 2 and Fig. 3.

One can see the following:

1. The first effect of losing 3 molecules of H_2O from the trihydrate proves the solubility data (the start of the effect $T_b \approx 60$ °C corresponds to the singular points in the Fig. 1, 2).
2. The subsequent three effects correspond to 'decarbonylation' (C=O removal) from the three different malonate groups, thus each removal stabilizes residual groups. 'Rigid

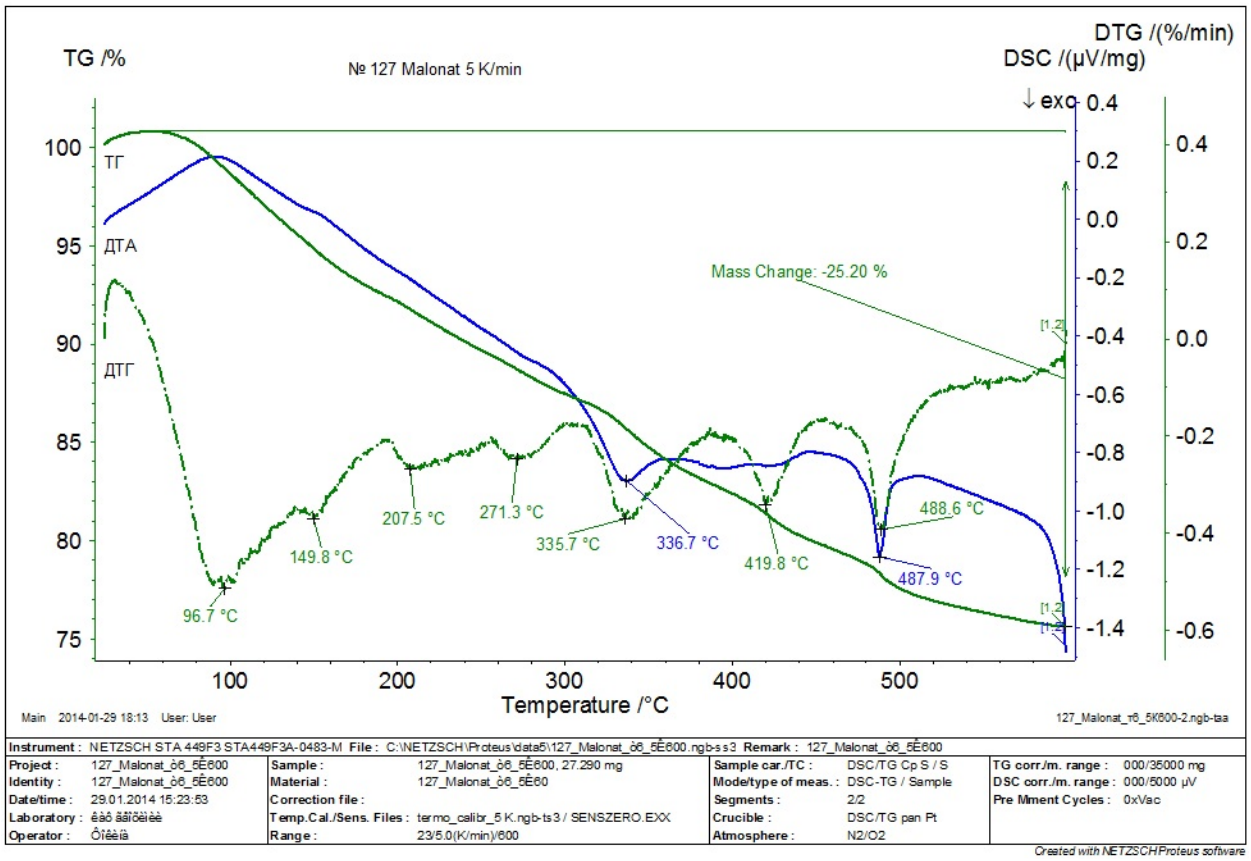

FIG. 3. The results of complex thermal analysis of crystal-hydrates of $C_{60}[=C(COOH)_2]_3$ (curves in the left axis Thermo-Gravimetry (TG) — top; Differential Thermo-Gravimetry (DTG) — bottom; Differential Thermal Analysis (DTA) — middle)

decarboxylation' (CO_2 removal) did not occur because of the tertiary nature of the carbon atom with geminally-substituted carboxyl groups.

3. The subsequent three effects also correspond to 'decarbonylation with dehydration' (C=O and H_2OH loss) from the three different malonate groups, thus against each allocation stabilizes residual groups. In these cases such process cannot occur without dehydrogenation because ketone hydrates (one carbon atom with two hydroxyl groups, $OH-(R_2)C(R_1)-OH$) are usually unstable.
4. One can see that (according to TG curve) mass effect of the first three allocations is nearly 60 relative % from the mass effect of second three allocations, which also proves the complex mechanism of malonate decomposition.

Thus, poly-thermal solubility of water soluble tris-malonate of light fullerene – $C_{60}[=C(COOH)_2]_3$ from 20 – 80 °C and complex thermal analysis of the last one in the temperature range 25 – 600 °C were investigated. One can see that diagram of solubility in the binary system consists of two branches, which correspond to the crystallization of the C_{60} – tris-malonate trihydrate and tris-malonate without water, correspondingly. Complex thermal analysis demonstrates six-stage soft and crude decarbonylation processes, with the formation of gaseous CO and CO + H_2O, correspondingly.

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References

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

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

[3] I.Lamparth, A.Hirsch. Water-soluble malonic acid derivatives of C_{60} with a defined three-dimensional structure. *J. Chem. Soc Chem. Commun.*, P. 1727–1728 (1994).

[4] L.B.Piotrovskiy, O.I.Kiselev. *Fullerenes in biology*. Rus. S-Petersburg, (2006) 334 pp.

[5] D.Heymann. Solubility of C_{60} in alcohols and alkanes. *Carbon*, **34** (5), P. 627–631 (1996).

[6] M.T.Beck, G.Mandi. Solubility of C_{60}. *Fullerene science and technology*, **5**, P. 291–310 (1997).

[7] M.V.Korobov, A.L.Smith. Solubility of Fullerenes. *Fullerenes: Chemistry, Physics and Technology*, John Wiley & Sons, New York, P. 53–59 (2000).

[8] K.N.Semenov, N.A.Charykov, V.A.Keskinov, et al. Solubility of light Fullerenes in Organic Solvents. *J. Chem. Eng. Data*, **55**, P. 13–36 (2010).

[9] D. Heymann. Solubility of fullerenes C_{60} and C_{70} in seven normal alcohols and their deduced solubility in water. *Fullerene Science and Technology*, **4** (3), P. 509–515 (1996).

[10] D. Heymann. Solubility of fullerenes C_{60} and C_{70} in water. *Lunar and Planetary Science*, **27**, P. 543–544 (1996).

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

[12] 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., P. 1–48 (2011).

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

[14] Rus. Technical Conditions (TU) 6-09-4921-80. CAS Number 141-95-7.