Supplementary Materials

Solubility diagrams of quasi-simple systems containing several water-soluble C_{60} fullerene derivatives

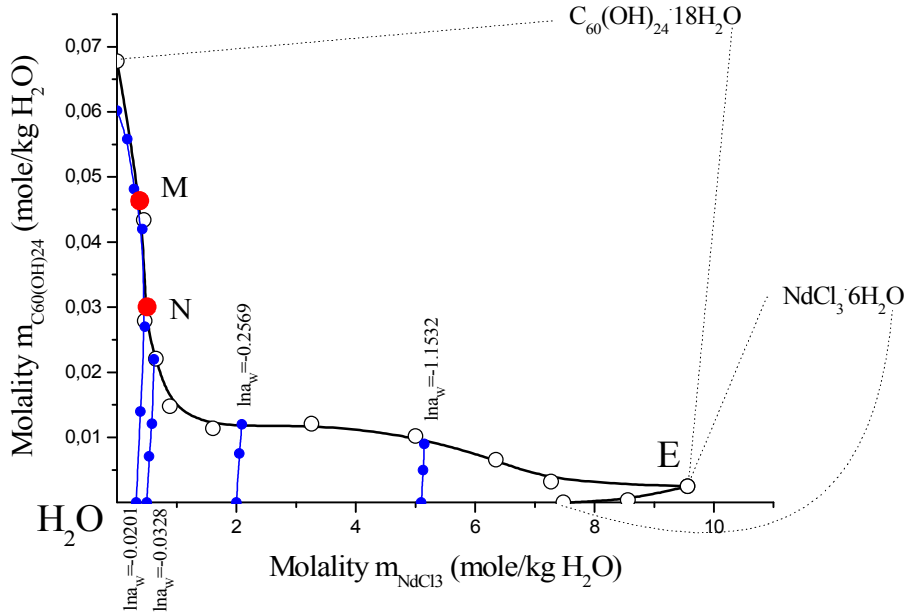


Fig. S1. Solubility diagram for the $C_{60}(OH)_{24}$–$NdCl_3$–H_2O ternary system at 25°C: open circles represent the authors' experimental data; E is the eutonic nonvariant point; blue circles and lines represent water iso-activity lines (values of the logarithm of water activity are indicated by numbers). Points M and N mark the boundaries of the diffusional stability of the solutions and lie on the spinodal.

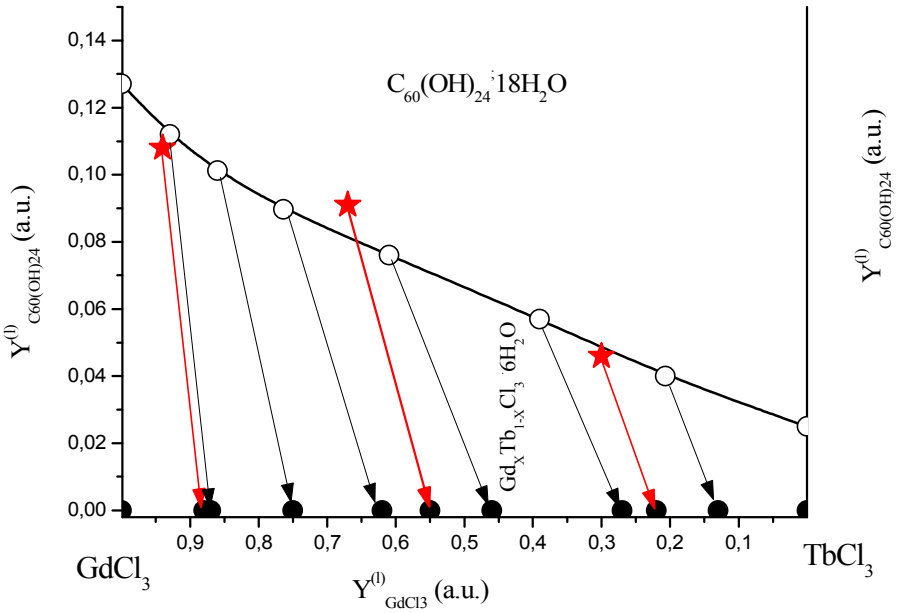


Fig. S2. Solubility diagram of the quaternary system $C_{60}(OH)_{24}$–$GdCl_3$–$TbCl_3$–H_2O at 25°C: open circles and lines represent the B-spline routine (ORIGIN); red stars indicate experimental data on saturated solution compositions; arrows mark calculated (black) and experimental (red)

liquid solution–solid solution nodes ($Y^{(l)}_{GdCl_3} = \frac{m_{GdCl_3}}{m_{GdCl_3}+m_{TbCl_3}+C_{60}(OH)_{24}}$; $Y^{(s)}_{GdCl_3} = X\ in\ \mathrm{Gd_xTb_{1-x}Cl_3 \cdot 6H_2O}$; $Y^{(l)}_{C_{60}(OH)_{24}} = \frac{m_{C_{60}(OH)_{24}}}{m_{GdCl_3}+m_{TbCl_3}+C_{60}(OH)_{24}}$).

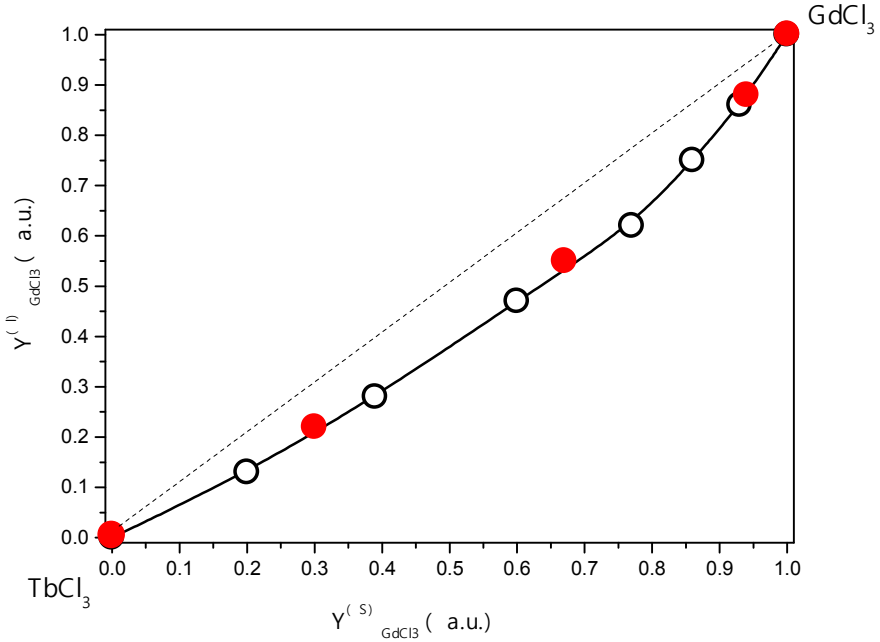


Fig. S3. Component distribution diagrams for the quaternary system $C_{60}(OH)_{24}$–$GdCl_3$–$TbCl_3$–H_2O at 25°C: (open circles and lines – B-spline subroutine (ORIGIN); red circles – experimental data; dashed straight line – diagonal of the Jänecke square).

Table S1. Comprehensive thermal analysis of the crystalline hydrates $C_{60}(C_6H_{13}N_2O_2)_2 \cdot 5H_2O$, $C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$, $C_{60}(C_5H_9NO_3)_2 \cdot 2H_2O$ in the temperature range 20÷000°C (heating in an open vessel in air at 3 K/min).

N	T_{st}-T_{extr}-T_{fin} (C)	$(\Delta m_{eff}/m_0)^{exp}$· 100%	$(\Delta m_{eff}/m_0)^{th}$· 100%	Thermo-oxidation process
		$C_{60}(C_6H_{14}N_2O_2)_2 \cdot 5H_2O$		
1.	30-70-160	8.2	8.2	$C_{60}(C_6H_{14}N_2O_2)_2 \cdot 5H_2O \rightarrow C_{60}(C_6H_{14}N_2O_2)_2 + 5H_2O$
2.	170-210-305	11.6	11.1	$C_{60}(C_6H_{14}N_2O_2)_2 + O_2 \rightarrow C_{60}(NH(CH_2)_4CH_3)_2 + 2CO_2 + N_2 + 2H_2O$
3.	320-400-520	11.2	10.6	$C_{60}(NH(CH_2)_4CH_3)_2 + 14\ O_2 \rightarrow C_{60}(NHCH{=}O)_2 + 8CO_2 + 10H_2O$
4.	560-590-630	2.4	2.5	$C_{60}(NHCH{=}O)_2 \rightarrow C_{60}NH_2(NHCH{=}O) + CO$
5.	630-690-760	2.9	2.5	$C_{60}NH_2(NHCH{=}O) \rightarrow C_{60}(NH_2)_2 + CO$
6.	780-800-820	2.8	2.8	$C_{60}(NH_2)_2 + O_2 \rightarrow C_{60} + 2H_2O + N_2$
7.	820-930-1050…	More than 14	More than 14	Partial oxidation of C_{60} fullerene core
		$C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$		
1.	30-70-170	10.7	10.2	$C_{60}[\text{-NH-CH(CH(OH)CH}_3\text{)-COOH}]_2 \cdot 6H_2O \rightarrow C_{60}[\text{-NH-CH(CH(OH)CH}_3\text{)-COOH}]_2 + +6H_2O$
2.	200-20-400	12.2	11.7	$C_{60}[\text{-NH-CH(CH(OH)CH}_3\text{)-COOH}]_2 \rightarrow C_{60}[\text{-NH-CH=CH-CH}_3]_2 + 2CO_2 + 2H_2O$
3.	400-580-720	4.6+6.7=11.1	10.5	$C_{60}[\text{-NH-CH=CH-CH}_3] + 9\ O_2 \rightarrow C_{60} + 6CO_2 + 6H_2O + 2N_2$
4.	750-850-1000…	More than 19	More than 19	Partial oxidation of C_{60} fullerene core
		$C_{60}(C_5H_9NO_3)_2 \cdot 2H_2O$		
1.	30-155-200	3.5	3.7	$C_{60}(C_5H_9NO_2)_2 \cdot 2H_2O \rightarrow C_{60}(C_5H_9NO_2)_2 + 2H_2O$
2.	220-350-460	8.4	8.8	$C_{60}(C_5H_9NO_2)_2 \rightarrow C_{60}(NC_4H_9)_2 + 2CO_2$
3.	500-620-830	5.7+8.5=14.2	14.4	$C_{60}(NC_4H_9)_2 + 12.5O_2 \rightarrow C_{60} + N_2\ 8CO_2 + 9H_2O$
4.	850-900-980…	More than 60	More than	Oxidation of C_{60} fullerene core

T_{st}-T_{extr}-T_{fin} - DTG effect temperatures: onset–peak–end, $(\Delta m_{eff}/m_0)^{exp}$, $(\Delta m_{eff}/m_0)^{th}$ – relative mass loss observed during the process, determined experimentally and calculated based on the thermo-oxidative process; m0 is the initial mass of the crystall hydrate.

Table S2. Solubility diagrams for the systems $C_{60}(C_6H_{13}N_2O_2)_2$ -$C_{60}(C_4H_8NO_3)_2 – H_2O$ (Fig.3.1), $C_{60}(C_4H_8NO_3)_2 – C_{60}(C_5H_9NO_2)_2 – H_2O$ (Fig.3, b), $C_{60}(C_6H_{13}N_2O_2)_2$ - $C_{60}(C_5H_9NO_2)_2 – H_2O$ (Fig.3.3) at 25°C: lna_W is the logarithm of water activity; $lna(i)$ and $X^{(0)}(i)$ are the activity and mole fraction of the i-th component in the binary system i-H_2O at a given value of lna_W; and X(i) and Z(i) are the mole fraction and Jänecke index of the i-th component in the ternary system at a given value of lna_W.

$C_{60}(C_6H_{13}N_2O_2)_2$ -$C_{60}(C_4H_8NO_3)_2 – H_2O$ System

$C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$ Crystallization curve

lna_W (a.u.)	$lna\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$X^{(0)}\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$Z\ C_{60}(C_4H_8NO_3)_2$ (a.u.)
-0,00357	-3,73717	0,00093	1,0000
-0,00375	-3,55181	0,00102	0,84731
-0,00400	-3,32291	0,00117	0,67497
-0,00425	-3,12174	0,00132	0,5528
-0,00450	-2,94354	0,00149	0,46326
-0,00475	-2,78459	0,00166	0,39577
-0,00500	-2,64193	0,00185	0,34367
-0,00525	-2,51318	0,00204	0,30261

$C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$ Crystallization curve

$X^{(0)}\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$Z\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$X\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)
0,00023	0,00000	0,00093	0,00000
0,00026	0,15269	0,00087	0,000039
0,00029	0,32503	0,00079	0,000096
0,00033	0,44720	0,00073	0,00015
Experiment		0,00076	0,00019
0,00037	0,53674	0,00093	0,00000
0,00042	0,60423	0,00087	0,000039
0,00046	0,65633	0,00079	0,000096
0,00051	0,69739	0,00073	0,00015
0,00056	0,73034	0,00076	0,00019
0,00057	0,72787	0,00093	0,00000
Experiment		0,00063	0,00044

$C_{60}(C_6H_{13}N_2O_2)_2 \cdot 5H_2O$ Crystallization curve

lna_W (a.u.)	$lna\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X^{(0)}\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$Z\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)
-0,00537	-9,76383	0,00054	1,00000
-0,00540	-9,70839	0,00054	0,94685
-0,00550	-9,52803	0,00056	0,79099
-0.00551	-9.55456	0,00056	0.78111
$X^{(0)}\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$Z\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$X\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X\ C_{60}(C_4H_8NO_3)_2$ (a.u.)
0,00214	0,00000	0,00054	0,00000
0,00216	0,05315	0,00051	0,00011
0,00225	0,20901	0,00045	0,00047
0,00225	0,21889	0,00042	0,000605
Experiment		0,00044	0,00063

$C_{60}(C_4H_8NO_3)_2 – C_{60}(C_5H_9NO_2)_2 – H_2O$ System

$C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$ Crystallization curve

lna_W (a.u.)	$lna\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$X^{(0)}\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$Z\ C_{60}(C_4H_8NO_3)_2$ (a.u.)
-0.00359	3.715671	$9.33632 \cdot 10^{-4}$	1.00000
-0.0039	3.410881	0.001108	0.740286
-0.0042	3.160043	0.001291	0.57709
-0.0045	2.943579	0.001488	0.465603
-0.0048	2.754876	0.001699	0.386229
-0.0051	2.588913	0.001924	0.327756
-0.0054	2.441814	0.002162	0.283431
-0.0057	2.310535	0.002415	0.249009
-0.0059	2.230587	0.002591	0.230153

-0.0061	2.155988	0.002774	0.213865
-0.0063	2.086217	0.002962	0.199691
-0.0065	2.020821	0.003157	0.187275
-0.0067	1.959401	0.003358	0.17633
-0.0069	1,9016	0,00357	0,16663
$X^{(0)}$ $C_{60}(C_5H_9NO_2)_2$ (a.u.)	Z $C_{60}(C_5H_9NO_2)_2$ (a.u.)	X $C_{60}(C_4H_8NO_3)_2$ (a.u.)	X $C_{60}(C_5H_9NO_2)_2$ (a.u.)
0.001986	0.0000000	$9.35699\cdot 10^{-4}$	0.0000000
0.002345	0.259714	$8.20244\cdot 10^{-4}$	$6.08941\cdot 10^{-4}$
0.00272	0.42291	$7.44996\cdot 10^{-4}$	0.00115
0.003122	0.534397	$6.92752\cdot 10^{-4}$	0.001669
0.003553	0.613771	$6.56095\cdot 10^{-4}$	0.002181
0.004011	0.672244	$6.30452\cdot 10^{-4}$	0.002697
0.004498	0.716569	$6.12870\cdot 10^{-4}$	0.003223
0.005012	0.750991	$6.01373\cdot 10^{-4}$	0.003764
0.00537	0.769847	$5.96396\cdot 10^{-4}$	0.004134
0.00574	0.786135	$5.93209\cdot 10^{-4}$	0.004513
0.006123	0.800309	$5.91569\cdot 10^{-4}$	0.004900
0.006518	0.812725	$5.91278\cdot 10^{-4}$	0.005297
0,00735	0,83337	$5{,}9412\cdot 10^{-4}$	0,00612
эксперимент		0,00057	0.0059

$C_{60}(C_5H_9NO_2)_2 \cdot 2H_2O$ Crystallization curve

lna_W (a.u.)	lna $C_{60}(C_5H_9NO_2)_2$ (a.u.)	$X^{(0)}$ $C_{60}(C_5H_9NO_2)_2$ (a.u.)	Z $C_{60}(C_5H_9NO_2)_2$ (a.u.)
-0.0058	1.116984	0.005189	1.000000
-0.0059	1.09804	0.00537	0.980042
-0.0061	1.062015	0.00574	0.945743
-0.0063	1.02828	0.006123	0.914736
-0.0065	0.996622	0.006518	0.886585
-0.0067	0.966854	0.006926	0.860927
-0.0069	0,93881	0,00735	0,83746
$X^{(0)}$ $C_{60}(C_4H_8NO_3)_2$ (a.u.)	Z $C_{60}(C_4H_8NO_3)_2$ (a.u.)	X $C_{60}(C_5H_9NO_2)_2$ (a.u.)	X $C_{60}(C_4H_8NO_3)_2$ (a.u.)
0.002502	0.000000	0.005182	0.00000
0.002591	0.019958	0.005263	$5.17184\cdot 10^{-5}$
0.002774	0.054257	0.005429	$1.50496\cdot 10^{-4}$
0.002962	0.085264	0.005601	$2.52588\cdot 10^{-4}$
0.003157	0.113415	0.005779	$3.58083\cdot 10^{-4}$
0.003358	0.139073	0.005962	$4.67055\cdot 10^{-4}$
0,00357	0,16254	0,00612	$5{,}9412\cdot 10^{-4}$
Experiment		0.0059	0,00057

$C_{60}(C_6H_{13}N_2O_2)_2$ - $C_{60}(C_5H_9NO_2)_2$ – H_2O System

$C_{60}(C_6H_{13}N_2O_2)_2 \cdot 5H_2O$ Crystallization curve

lna_W (a.u.)	lna $C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X^{(0)}$ $C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	Z $C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)
-0.00537	9.766119	$5.37866\cdot 10^{-4}$	1.000000
-0.0057	9.188854	$6.0758\text{E}\cdot 10^{-4}$	0.564031
-0.0059	8.871066	$6.51897\cdot 10^{-4}$	0.410888
-0.0061	8.574525	$6.97773\cdot 10^{-4}$	0.305754
-0.0063	8.297172	$7.45208\text{E}\cdot 10^{-4}$	0.231928
-0.0065	8.0372	$7.94202\cdot 10^{-4}$	0.179012
-0.0067	7.793027	$8.44756\cdot 10^{-4}$	0.14037
$X^{(0)}$ $C_{60}(C_5H_9NO_2)_2$ (a.u.)	Z $C_{60}(C_5H_9NO_2)_2$ (a.u.)	X $C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	X $C_{60}(C_5H_9NO_2)_2$ (a.u.)
0.004448	0.0000	$5.39465\cdot 10^{-4}$	0.00000
0.005012	0.435969	$3.42694\cdot 10^{-4}$	0.002185
0.00537	0.589112	$2.67857\cdot 10^{-4}$	0.003163
0.00574	0.694246	$2.13347\cdot 10^{-4}$	0.003985
0.006123	0.768072	$1.72835\cdot 10^{-4}$	0.004703
0.006518	0.820988	$1.42172\cdot 10^{-4}$	0.005351

0.006926	0.85963	$1.18578\cdot 10^{-4}$	0.005954
Experiment		0,00014	0,0055

$C_{60}(C_5H_9NO_2)_2 \cdot 2H_2O$ Crystallization curve

lna_W (a.u.)	$lna\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$X^{(0)}\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$Z\ C_{60}(C_5H_9NO_2)_2$ (a.u.)
-0.0058	1.116984	0.005189	0.998585
-0.0059	1.09804	0.00537	0.980042
-0.0061	1.062015	0.00574	0.945743
-0.0063	1.02828	0.006123	0.914736
-0.0065	0.996622	0.006518	0.886585
-0.0067	0.966854	0.006926	0.860927

$X^{(0)}\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$Z\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$X\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)
$6.29544\cdot 10^{-4}$	0.000000	0.005182	0.000000
$6.51897\cdot 10^{-4}$	0.019958	0.005263	$1.30108\cdot 10^{-5}$
$6.97773\cdot 10^{-4}$	0.054257	0.005429	$3.78591\cdot 10^{-5}$
$7.45208\cdot 10^{-4}$	0.085264	0.005601	$6.3539\cdot 10^{-5}$
$7.94202\cdot 10^{-4}$	0.113415	0.005779	$9.00746\cdot 10^{-5}$
$8.44756\cdot 10^{-4}$	0.139073	0.005962	$1.17483\cdot 10^{-4}$
Experiment		0,0055	0,00014

Table S3. Solubility diagram for the системе $C_{60}(C_6H_{13}N_2O_2)_2$ -$C_{60}(C_4H_8NO_3)_2$ - $C_{60}(C_5H_9NO_2)$ - H_2O system at 25°C: lna_W is the logarithm of water activity; ln a(i) and $X^{(0)}(i)$ are the activity and mole fraction of the i-th component in the binary i–H_2O system at a given value of lna_W, $X(i)$, $Z(i)$ are the mole fraction and Janecke index of the i-th component in the quaternary system at a given value of lna_W, $Y(i)$ is the Janecke index of the i-th component in the quaternary system used for constructing the diagram.

Curve of joint crystallization of $C_{60}(C_6H_{13}N_2O_2)_2 \cdot 5H_2O$ and $C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$				
lna_W (a.u.)	ln a $C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X^{(0)}$ $C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	Z $C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	X $C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)
-0,00554	9,45996	$5{,}71137 \cdot 10^{-4}$	0,75208	$4{,}29542 \cdot\cdot 10^{-4}$
-0,0057	9,18885	$6{,}0758 \cdot 10^{-4}$	0,56403	$3{,}42694 \cdot 10^{-4}$
-0,0059	8,87107	$6{,}51897 \cdot 10^{-4}$	0,41089	$2{,}67857 \cdot 10^{-4}$
Experiment				0.00025
-0,0061	8,57453	$6{,}97773 \cdot 10^{-4}$	0,30575	$2{,}13347 \cdot 10^{-4}$
-0,0063	8,29717	$7{,}45208 \cdot 10^{-4}$	0,23193	$1{,}72835 \cdot 10^{-4}$
-0,0065	8,0372	$7{,}94202 \cdot 10^{-4}$	0,17901	$1{,}42172 \cdot 10^{-4}$
-0,0067	7,79303	$8{,}44756 \cdot 10^{-4}$	0,14037	$1{,}18578 \cdot 10^{-4}$
-0,0069	7,56325	$8{,}96869 \cdot 10^{-4}$	0,11167	$1{,}00149 \cdot 10^{-4}$
-0,0071	7,34664	$9{,}50541 \cdot 10^{-4}$	0,09001	$8{,}55562 \cdot 10^{-4}$
-0,0073	7,14209	0,00101	0,07343	$7{,}38551 \cdot 10^{-4}$
lna_W (a.u.)	ln a $C_{60}(C_4H_8NO_3)_2$ (a.u.)	$X^{(0)}$ $C_{60}(C_4H_8NO_3)_2$ (a.u.)	Z $C_{60}(C_4H_8NO_3)_2$ (a.u.)	X $C_{60}(C_4H_8NO_3)_2$ (a.u.)
-0,00554	2,37874	0,00228	0,26500	$6{,}03815 \cdot 10^{-4}$
-0,0057	2,31053	0,00242	0,24777	$5{,}98373 \cdot 10^{-4}$
-0,0059	2,23059	0,00259	0,229	$5{,}93422 \cdot 10^{-4}$
Experiment				0.00061
-0,0061	2,15599	0,00277	0,2128	$5{,}90251 \cdot 10^{-4}$
-0,0063	2,08622	0,00296	0,1987	$5{,}88618 \cdot 10^{-4}$
-0,0065	2,02082	0,00316	0,18634	$5{,}88329 \cdot 10^{-4}$
-0,0067	1,9594	0,00336	0,17545	$5{,}89222 \cdot 10^{-4}$
-0,0069	1,9016	0,00357	0,1658	$5{,}91165 \cdot 10^{-4}$
-0,0071	1,84712	0,00378	0,15719	$5{,}94046 \cdot 10^{-4}$
-0,0073	1,79567	0,004	0,14949	$5{,}97773 \cdot 10^{-4}$
lna_W (a.u.)	$X^{(0)}$ $C_{60}(C_5H_9NO_2)_2$ (a.u.)	Z $C_{60}(C_5H_9NO_2)_2$ (a.u.)	X $C_{60}(C_5H_9NO_2)_2$ 2 (a.u.)	
-0,00554	0,00468	0,00000	0,000000	
-0,0057	0,00501	0,1882	$9{,}43184 \cdot 10^{-4}$	
-0,0059	0,00537	0,36011	0,00193	
Experiment			0,0024	
-0,0061	0,00574	0,48145	0,00276	
-0,0063	0,00612	0,56938	0,00349	
-0,0065	0,00652	0,63465	0,00414	
-0,0067	0,00693	0,68418	0,00474	
-0,0069	0,00735	0,72254	0,00531	
-0,0071	0,00778	0,7528	0,00586	
-0,0073	0,00822	0,77708	0,00639	
lna_W (a.u.)	$YC_{60}(C_4H_8NO_3)_2$ (a.u.)	$YC_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	Y $C_{60}(C_5H_9NO_2)_2$ (a.u.)	
-0,00554	0,58766	0,41234	0,00000	
-0,0057	0,31757	0,18187	0,50056	
-0,0059	0,21232	0,09584	0,69184	
Experi-ment	0.187	0.077	0.736	
-0,0061	0,16547	0,05981	0,77472	
-0,0063	0,13857	0,04069	0,82074	
-0,0065	0,12088	0,02921	0,84991	
-0,0067	0,10819	0,02177	0,87004	

-0,0069	0,09855	0,01670	0,88476	
-0,0071	0,09091	0,01309	0,89600	
-0,0073	0,08466	0,01046	0,90488	
Curve of joint crystallization of $C_{60}(C_6H_{13}N_2O_2)_2 \cdot 5H_2O$ and $C_{60}(C_5H_9NO_2)_2 \cdot 2H_2O$				
lna_W (a.u.)	$lna\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$X^{(0)}\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$Z\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$X\ C_{60}(C_5H_9NO_2)_2$ (a.u.)
-0,0067	7,79303	8,44756E-4	0,14037	$1{,}18578 \cdot 10^{-4}$
-0,0069	7,56325	8,96869E-4	0,11167	$1{,}00149 \cdot 10^{-4}$
-0,0071	7,34664	9,50541E-4	0,09001	$8{,}55562 \cdot 10^{-5}$
-0,0073	7,14209	0,00101	0,07343	$7{,}38551 \cdot 10^{-5}$
lna_W (a.u.)	$lna\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X^{(0)}\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$Z\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)
-0,0067	0,96685	0,00693	0,86093	0,00596
-0,0069	0,93881	0,00735	0,83746	0,00615
-0,0071	0,91235	0,00778	0,81591	0,00635
-0,0073	0,88734	0,00822	0,79608	0,00655
lna_W (a.u.)	$X^{(0)}\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$Z\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$X\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	
-0,0067	0,00336	0,00000	0,00000	
-0,0069	0,00357	0,05088	$1{,}8139 \cdot 10^{-4}$	
-0,0071	0,00378	0,09408	$3{,}55488 \cdot 10^{-4}$	
-0,0073	0,004	0,13049	$5{,}21735 \cdot 10^{-4}$	
lna_W (a.u.)	$YC_{60}(C_4H_8NO_3)_2$ (a.u.)	$Y\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$Y\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	
-0,0067	0,00000	0,0195	0,9812	
-0,0069	0,0282	0,01557	0,95624	
-0,0071	0,05238	0,01261	0,93502	
-0,0073	0,07306	0,01034	0,9166	
Curve of joint crystallization of $C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$ and $C_{60}(C_5H_9NO_2)_2 \cdot 2H_2O$				
lna_W (a.u.)	$lna\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$X^{(0)}\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$Z\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	$X\ C_{60}(C_5H_9NO_2)_2$ (a.u.)
-0,0067	0,96685	0,00693	0,86093	0,00596
-0,0069	0,93881	0,00735	0,83746	0,00615
-0,0071	0,91235	0,00778	0,81591	0,00635
-0,0073	0,88734	0,00822	0,79608	0,00655
lna_W (a.u.)	$lna\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$X^{(0)}\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$Z\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$X\ C_{60}(C_4H_8NO_3)_2$ (a.u.)
-0,0067	1,95952	0,00336	0,17547	$5{,}89291 \cdot 10^{-4}$
-0,0069	1,90171	0,00357	0,16581	$5{,}91230 \cdot 10^{-4}$
-0,0071	1,84722	0,00378	0,15721	$5{,}94107 \cdot 10^{-4}$
-0,0073	1,79577	0,004	0,1495	$5{,}97831 \cdot 10^{-4}$
lna_W (a.u.)	$X^{(0)}C_{60}(C_6H_{13}N_2O_2)_2$ ((a.u.)	$Z\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$X\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	
-0,0067	$8{,}44958 \cdot 10^{-4}$	0,13907	$1{,}17511 \cdot 10^{-4}$	
-0,0069	$8{,}97083 \cdot 10^{-4}$	0,11166	$1{,}00172 \cdot 10^{-4}$	
-0,0071	$9{,}50768 \cdot 10^{-4}$	0,09001	$8{,}55746 \cdot 10^{-4}$	
-0,0073	0,00101	0,07343	$7{,}38713 \cdot 10^{-5}$	
lna_W (a.u.)	$Y\ C_{60}(C_4H_8NO_3)_2$ (a.u.)	$Y\ C_{60}(C_6H_{13}N_2O_2)_2$ (a.u.)	$Y\ C_{60}(C_5H_9NO_2)_2$ (a.u.)	
-0,0067	0,08839	0,01763	0,89398	
-0,0069	0,08642	0,01464	0,89894	
-0,0071	0,08451	0,01217	0,90331	
-0,0073	0,08278	0,01023	0,90699	

Table S4.
Results of C-H-N-O elemental analysis of bis-adducts of fullerene C_{60} and essential amino acids.

N	Amino-acid	Bis-adduct crystal hydrate formula	Theoretical content (mass.%)				Experimental content (mass.%)			
			N	C	H	O	N	C	H	O
1.	Lysine	$C_{60}(C_6H_{13}N_2O_2)_2*5H_2O$	5.0	78	3.8	13	5.1	78	3.5	13
2.	Threonine	$C_{60}(C_4H_8NO_3)_2*6H_2O$	2.6	77	2.6	18	2.4	76	2.7	19
3.	Hydroxyproline	$C_{60}(C_5H_9NO_2)_2*2H_2O$	2.8	85	2.2	10	3.0	84	2.3	11

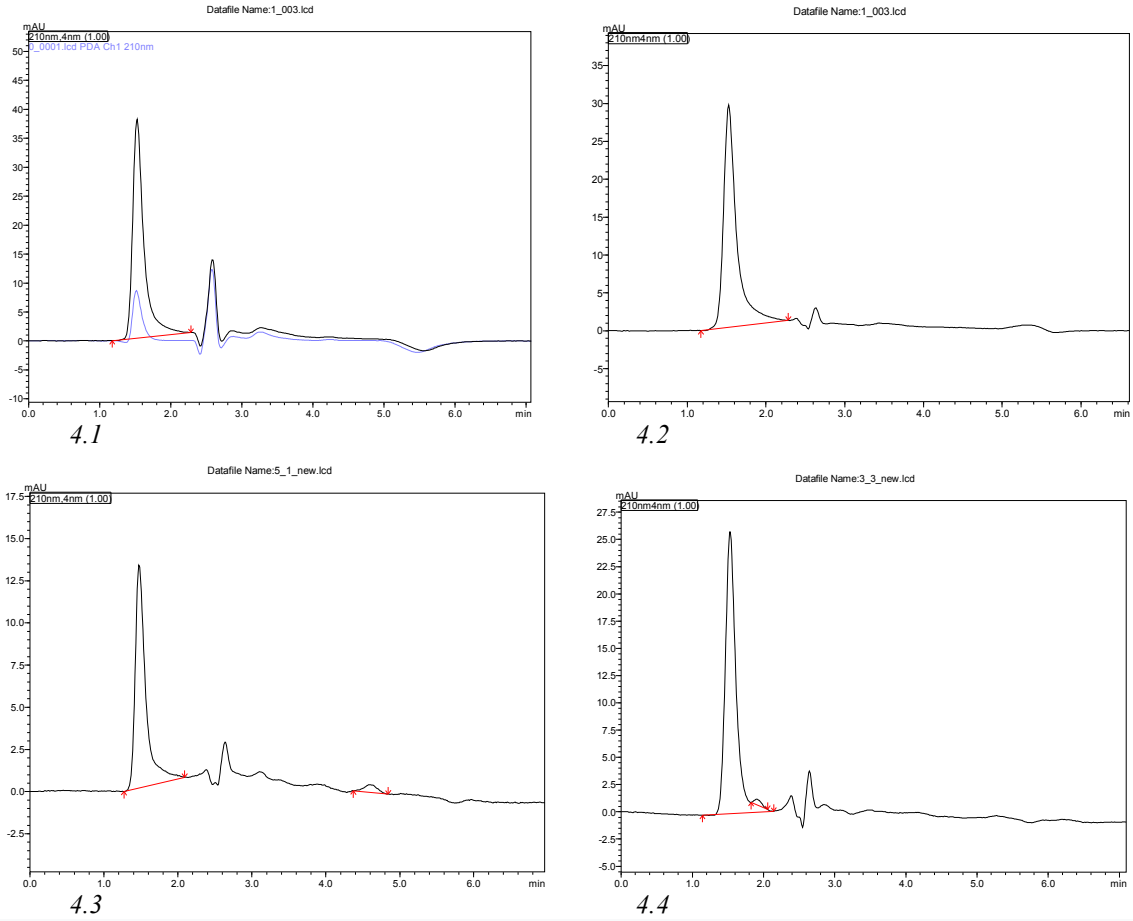


Fig. 4. Background-subtracted HPLC traces of C_{60}-essential amino acid bis-adducts: $C_{60}(C_6H_{13}N_2O_2)_2$ (Fig. 4.2), $C_{60}(C_4H_8NO_3)_2$ (Fig. 4.3), and $C_{60}(C_5H_9NO_2)_2$ (Fig. 4.4). Fig. 4.1 shows an example of a raw HPLC trace for the lysine bis-adduct (top) and the water background (bottom).

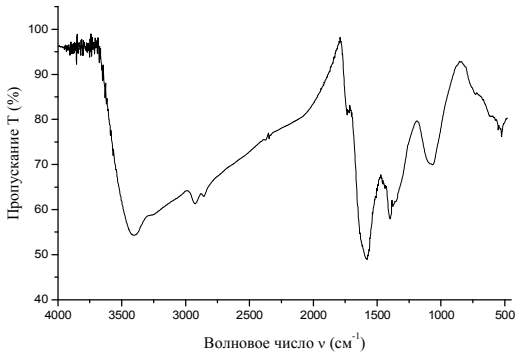


Fig.5.1.

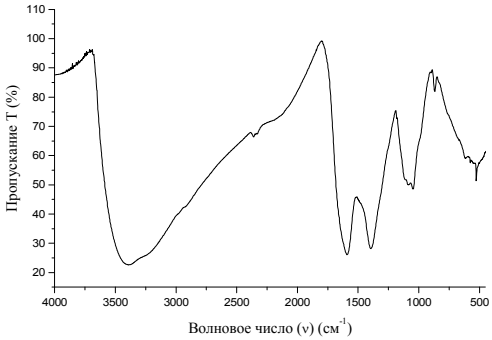


Fig.5.2.

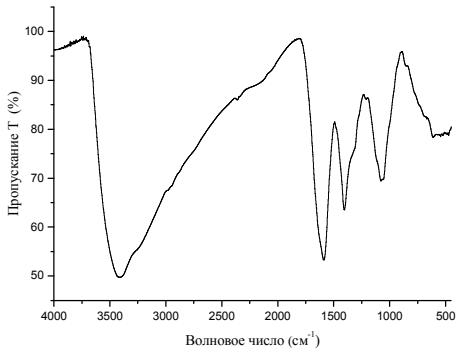


Fig.5.3.

Fig. 5. Infrared spectra of crystalline hydrates of C60 fullerene bis-adducts with essential amino acids: $C_{60}(C_6H_{13}N_2O_2)_2{\cdot}5H_2O$ (Fig.5.1.), $C_{60}(C_4H_8NO_3)_2{\cdot}6H_2O$ (Fig.5.2.), $C_{60}(C_5H_9NO_2)_2{\cdot}2H_2O$ (Fig.5.3.).

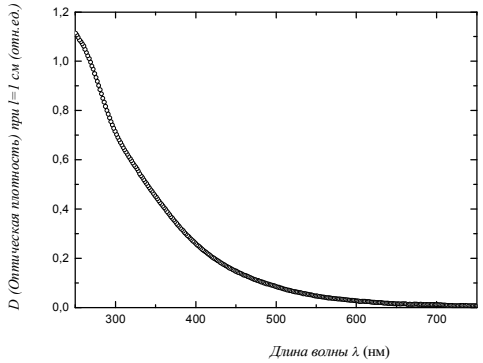


Fig.6.1.

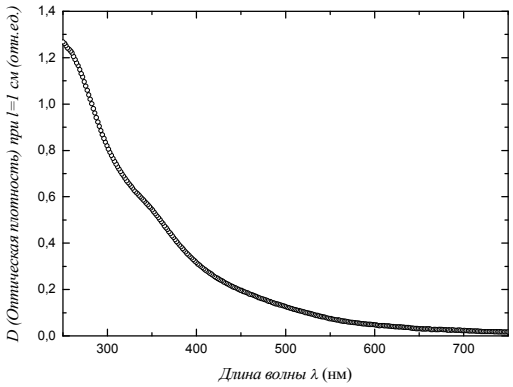


Fig.6.2.

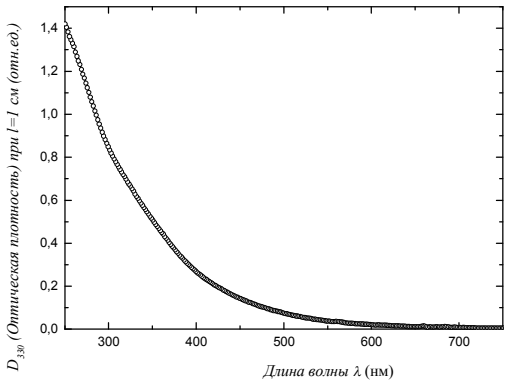


Fig.6.3.

Fig. 6. Electronic spectra of crystalline hydrates of C60 fullerene bis-adducts with essential amino acids: $C_{60}(C_6H_{13}N_2O_2)_2 \cdot 5H_2O$ (Fig.6.1.), $C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$ (Fig.6.2.), $C_{60}(C_5H_9NO_2)_2 \cdot 2H_2O$ (Fig.6.3).

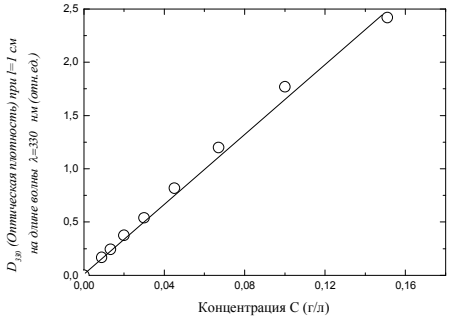


Fig.7.1.

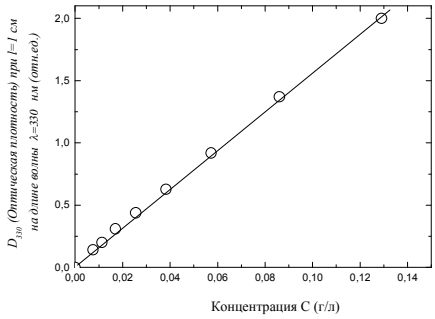


Fig.7.2.

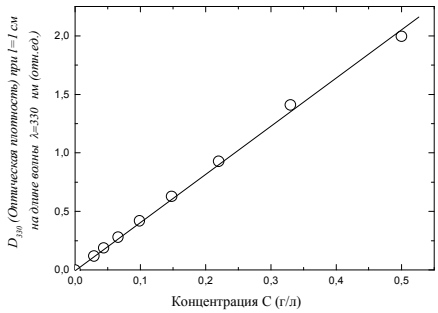


Fig.7.3.

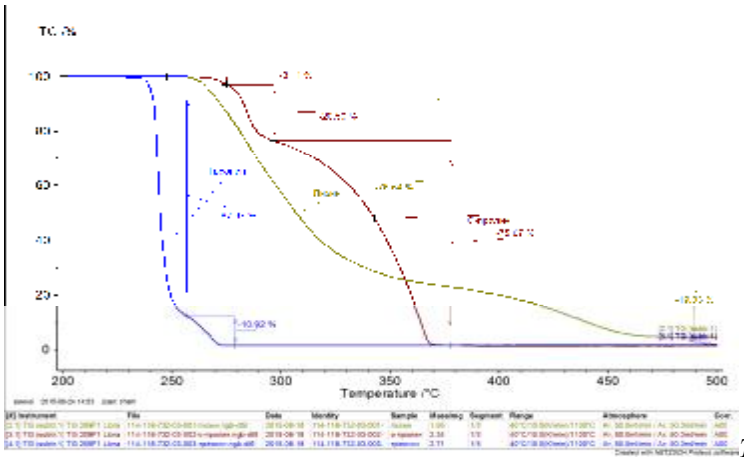
Fig. 7. Applicability of the Bouguer-Lambert-Beer law to aqueous solutions of C60 fullerene bis-adducts with essential amino acids: $C_{60}(C_6H_{13}N_2O_2)_2$ (Fig. 7.1), $C_{60}(C_4H_8NO_3)_2$ (Fig. 7.2), and $C_{60}(C_5H_9NO_2)_2$ (Fig. 7.3) at a wavelength of $\lambda = 330$ nm.

Table S5. Comprehensive thermal analysis of the crystalline hydrates $C_{60}(C_6H_{13}N_2O_2)_2 \cdot 5H_2O$, $C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$, $C_{60}(C_5H_9NO_3)_2 \cdot 2H_2O$ in the temperature range 20÷000°C (heating in an open vessel in air at 3 K/min).

N	T_{st}-T_{extr}-T_{fin} (C)	$(\Delta m_{eff}/m_0)^{exp} \cdot 100\%$	$(\Delta m_{eff}/m_0)^{th} \cdot 100\%$	Thermo-oxidation process
		$C_{60}(C_6H_{14}N_2O_2)_2 \cdot 5H_2O$		
1.	30-70-160	8.2	8.2	$C_{60}(C_6H_{14}N_2O_2)_2 \cdot 5H_2O \rightarrow C_{60}(C_6H_{14}N_2O_2)_2 + 5H_2O$
2.	170-210-305	11.6	11.1	$C_{60}(C_6H_{14}N_2O_2)_2 + O_2 \rightarrow C_{60}(NH(CH_2)_4CH_3)_2 + 2CO_2 + N_2 + 2H_2O$
3.	320-400-520	11.2	10.6	$C_{60}(NH(CH_2)_4CH_3)_2 + 14\ O_2 \rightarrow C_{60}(NHCH=O)_2 + 8CO_2 + 10H_2O$
4.	560-590-630	2.4	2.5	$C_{60}(NHCH=O)_2 \rightarrow C_{60}NH_2(NHCH=O) + CO$
5.	630-690-760	2.9	2.5	$C_{60}NH_2(NHCH=O) \rightarrow C_{60}(NH_2)_2 + CO$
6.	780-800-820	2.8	2.8	$C_{60}(NH_2)_2 + O_2 \rightarrow C_{60} + 2H_2O + N_2$
7.	820-930-1050…	More than 14	More than 14	Partial oxidation of C_{60} fullerene core
		$C_{60}(C_4H_8NO_3)_2 \cdot 6H_2O$		
1.	30-70-170	10.7	10.2	$C_{60}[\text{-NH-CH(CH(OH)CH}_3\text{)-COOH}]_2 \cdot 6H_2O \rightarrow C_{60}[\text{-NH-CH(CH(OH)CH}_3\text{)-COOH}]_2 + 6H_2O$
2.	200-20-400	12.2	11.7	$C_{60}[\text{-NH-CH(CH(OH)CH}_3\text{)-COOH}]_2 \rightarrow C_{60}[\text{-NH-CH=CH-CH}_3]_2 + 2CO_2 + 2H_2O$
3.	400-580-720	4.6+6.7=11.1	10.5	$C_{60}[\text{-NH-CH=CH-CH}_3] + 9\ O_2 \rightarrow C_{60} + 6CO_2 + 6H_2O + 2N_2$
4.	750-850-1000…	More than 19	More than 19	Partial oxidation of C_{60} fullerene core
		$C_{60}(C_5H_9NO_3)_2 \cdot 2H_2O$		
1.	30-155-200	3.5	3.7	$C_{60}(C_5H_9NO_2)_2 \cdot 2H_2O \rightarrow C_{60}(C_5H_9NO_2)_2 + 2H_2O$
2.	220-350-460	8.4	8.8	$C_{60}(C_5H_9NO_2)_2 \rightarrow C_{60}(NC_4H_9)_2 + 2CO_2$
3.	500-620-830	5.7+8.5=14.2	14.4	$C_{60}(NC_4H_9)_2 + 12.5O_2 \rightarrow C_{60} + N_2\ 8CO_2 + 9H_2O$
4.	850-900-980…	More than 60	More than	Oxidation of C_{60} fullerene core

T_{st}-T_{extr}-T_{fin} - DTG effect temperatures: onset–peak–end, $(\Delta m_{eff}/m_0)^{exp}$, $(\Delta m_{eff}/m_0)^{th}$ – relative mass loss observed during the process, determined experimentally and calculated based on the thermo-oxidative process; m0 is the initial mass of the crystall hydrate.

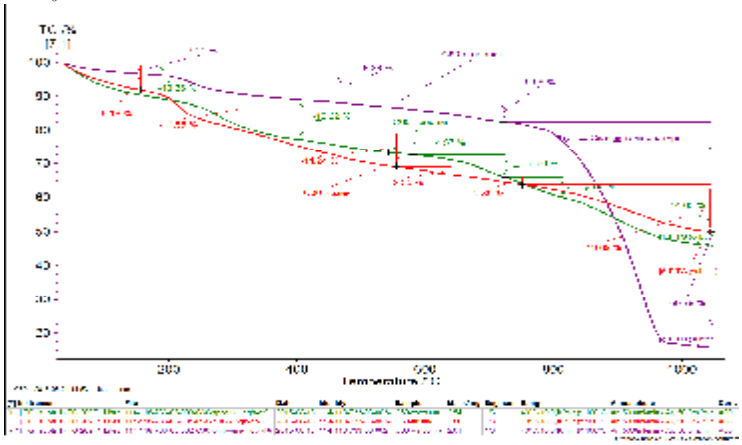
$m/m_0 \cdot 100\%$



T(°C)

Fig. 8.1.

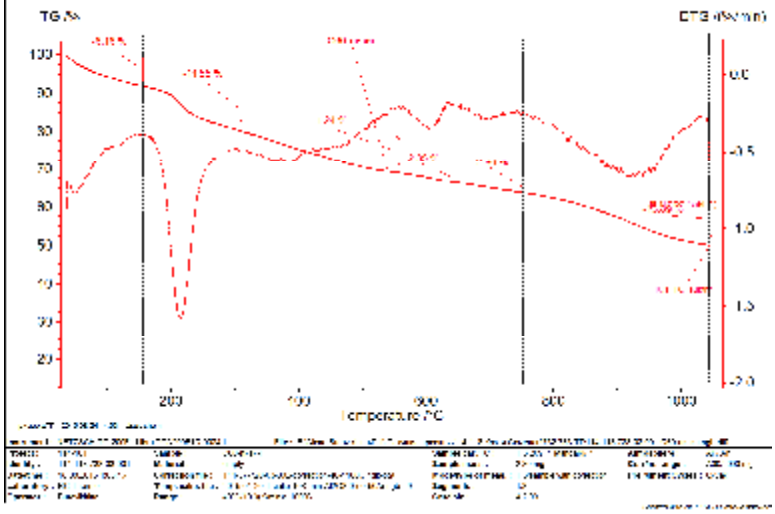
m/m_0·100%



T (°C)

Fig. 8.2.

d[m/m_0·100%]/dT(1/K)-DTG



T (°C)

Fig. 8.3.

Fig. 8. Thermogravimetric analysis of essential amino acids (TG curves): $C_6H_{14}N_2O_2$ – lysine (middle curve at 300°C), $C_4H_9NO_3$ – threonine (bottom curve), $C_5H_{10}NO_2$ – hydroxyproline (top curve) (Fig. 8.1); crystal hydrates $C_{60}(C_6H_{13}N_2O_2)_2{\cdot}5H_2O$ (bottom curve at 600°C), $C_{60}(C_4H_8NO_3)_2{\cdot}6H_2O$ (middle curve), $C_{60}(C_5H_9NO_3)_2{\cdot}2H_2O$ (top curve) (Fig. 8.2); and an example of a DTG curve for $C_{60}(C_6H_{13}N_2O_2)_2{\cdot}5H_2O$ (Fig. 8.3).

Table S6. Cryometric data and thermodynamic functions in the systems $(C_4H_8NO_3)_2$ - H_2O, $C_{60}(C_6H_{13}N_2O_2)_2$ – H_2O; $C_{60}(C_4H_8NO_3)_2$ - H_2O; $C_{60}(C_6H_{13}N_2O_2)_2$ - H_2O; $C_{60}(OH)_{24\pm2}$ - H_2O at 272.58–273.15 K.

System $C_{60}(C_5H_9NO_3)_2$ - H_2O				
Molar fraction of $C_{60}(C_5H_9NO_3)_2$ in solution $X_{C60(C5H9NO3)2}$ (a.u.)	Decrease of Temperature crystallization start ΔT (K)	lna_{H2O} ln(water activity) (a.u.)	$ln\gamma_{H2O}$ ln(water activity coefficinent) (a.u.)	$ln\gamma^{as}{}_{C60(C5H9NO3)2}$ ln(activity coefficient of $C_{60}(C_5H_9NO_3)_2$) (a.u.)
0,000	0,000	0,000	0,000	0,000
$3{,}68*10^{-6}$	0.010	$-9{,}64*10^{-5}$	$-9.006*10^{-5}$	6.90
$8{,}35*10^{-6}$	0.020	$-1{,}93*10^{-4}$	$-1.801*10^{-4}$	13.9
$2{,}37*10^{-5}$	0.040	$-4{,}00*10^{-4}$	$-3.601*10^{-4}$	28.4
$7{,}88*10^{-5}$	0.075	$-7{,}24*10^{-4}$	$-6.718*10^{-4}$	61.2
$2{,}80*10^{-4}$	0.14	-0,00135	-0.00125	158
System $C_{60}(C_4H_8NO_3)_2$ - H_2O				
Molar fraction of $C_{60}(C_4H_8NO_3)_2$ in solution $X_{C60(C4H8NO3)2}$ (a.u.)	Decrease of Temperature crystallization start ΔT (K)	lna_{H2O} ln(water activity) (a.u.)	$ln\gamma_{H2O}$ ln(water activity coefficinent) (a.u.)	$ln\gamma^{as}{}_{C60(C4H8NO3)2}$ ln(activity coefficient of $C_{60}(C_4H_8NO_3)_2$) (a.u.)
0,0000	0,000	0,000	0,000	0,000
$5.903*10^{-6}$	0.020	$-1.931*10^{-4}$	$-1.872*10^{-4}$	5.58
$1.177*10^{-5}$	0.035	$-3.380*10^{-4}$	$-3.262*10^{-4}$	10.7
$2.355*10^{-5}$	0.060	$-5.794*10^{-4}$	$-5.558*10^{-4}$	19.7
$4.711*10^{-5}$	0.10	$-9.654*10^{-4}$	$-9.183*10^{-4}$	33.3
$9.420*10^{-5}$	0.135	-0.001303	-0.001209	46.7
$1.884*10^{-4}$	0.17	-0.001641	-0.001457	49.4
System $C_{60}(C_6H_{13}N_2O_2)_2$ - H_2O				
Molar fraction of $C_{60}(C_6H_{13}N_2O_2)$ in solution $X_{C60(C6H13N2O2)2}$ (a.u.)	Decrease of Temperature crystallization start ΔT (K)	lna_{H2O}	$ln\gamma_{H2O}$	$ln\gamma^{ass}{}_{C60(C6H13N2O2)2}$ ln(activity coefficient of $C_{60}(C_6H_{13}N_2O_2)_2$) (a.u.)
0,000	0,000	0,000	0,000	0,000
$5{,}39*10^{-6}$	0,030	$-2{,}897*10^{-4}$	$-2{,}843*10^{-4}$	6,96
$1{,}08*10^{-5}$	0,050	$-4{,}828*10^{-4}$	$-4{,}721*10^{-4}$	13,5
$2{,}15*10^{-5}$	0,085	$-7{,}724*10^{-4}$	$-7{,}509*10^{-4}$	25,3
$4{,}32*10^{-5}$	0,15	-0,00145	-0,00141	44,4
$8{,}66*10^{-5}$	0,23	-0,00222	-0,00213	63,0
$1{,}74*10^{-4}$	0,35	-0,00337	-0,00320	21,2
$3{,}50*10^{-4}$	0,44	-0,00424	-0,00389	-384

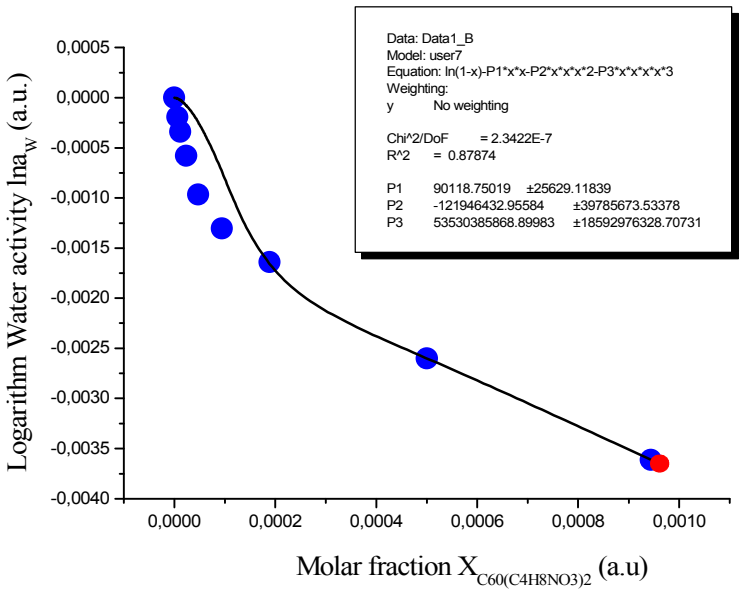


Fig. 9. Dependence of $lna_w(X_{nano})$ for the binary system $C_{60}(C_4H_8NO_3)_2$–H_2O: lines — VD-AS calculation; blue dots — cryometric experimental data at temperatures of 272.5÷273.15 K; red dot — data from the authors' isopiestic experiment at 298 K.