NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2014, 5 (3), P. 427–434

VOLUME PROPERTIES OF WATER SOLUTIONS AND REFRACTION AT 25 °C WATER-SOLUBLE TRIS-MALONATE OF LIGHT FULLERENE – $C_{60}[=C(COOH)_2]_3$

K. N. Semenov[1], N. A. Charykov[2,3], A. S. Kritchenkov[1], I. A. Cherepkova[2], O. S. Manyakina[2], D. P. Tyurin[2], A. A. Shestopalova[2], V. A. Keskinov[2], K. V. Ivanova[2], N. M. Ivanova[1], D. G. Letenko[4], V. A. Nikitin[5], E. L. Fokina[1], O. V. Rakhimova[3]

[1]St. Petersburg State University, Saint-Petersburg, Russia
[2]St. Petersburg State Technological Institute (Technical University), Saint-Petersburg, Russia
[3]St. Petersburg State Electro-Technical University (LETI), Saint-Petersburg, Russia
[4]St. Petersburg State University Architecture Academy, Saint-Petersburg, Russia
[5]St. Petersburg State Technical University, Saint-Petersburg, Russia

keskinov@mail.ru

PACS 61.48.+c

The volume Properties of water soluble tris-malonate of light fullerene — $C_{60}[=C(COOH)_2]_3$ were investigated with the help of quartz pycnometers at 25 °C, including the concentration dependence of density, average molar volume of the solutions and partial molar volumes of $C_{60}[=C(COOH)_2]_3$ and H_2O. Concentration dependence of the refraction index in water solutions of $C_{60}[=C(COOH)_2]_3$ was also determined with the help of refractometer, specific and molar refraction of the components were calculated with the help of the rules of the additive refraction of solution components.

Keywords: tris-malonate of light fullerene, volume properties, refraction.

Received: 19 February 2014
Revised: 14 March 2014

1. Introduction

This article further develops the investigations, which were initiated by the article [1], devoted to the description of the synthesis and identification of tris-malonate $C_{60}[=C(COOH)_2]_3$ (the original synthesis of this water soluble derivative was described earlier in [2]).

2. Concentration dependence of density of water solutions of tris-malonate of light fullerene — $C_{60}[=C(COOH)_2]_3$

The concentration dependence for the density of aqueous solutions of the tris-malonate $C_{60}[=C(COOH)_2]_3$ at 25 °C was investigated by the method of pycnometry with the help of quartz pycnometers (Volume nearly $V \approx 2.5$ cm^3), accuracy of thermostat was $\Delta T = \pm 0.05$ grad. Data, concerning the densities of the solutions are represented lower in the Table 1 and in Fig. 1.

Aqueous solutions of the tris-malonate $C_{60}[=C(COOH)_2]_3$ were prepared by the following method; first, a basic solution (Ctris-malonate = 336 g/dm^3) was prepared by the direct dissolution of previously-synthesized $C_{60}[=C(COOH)_2]_3$ in the distilled water, double filtration of the solution through a ‘blue’ paper filter; the concentration of the solution was determined

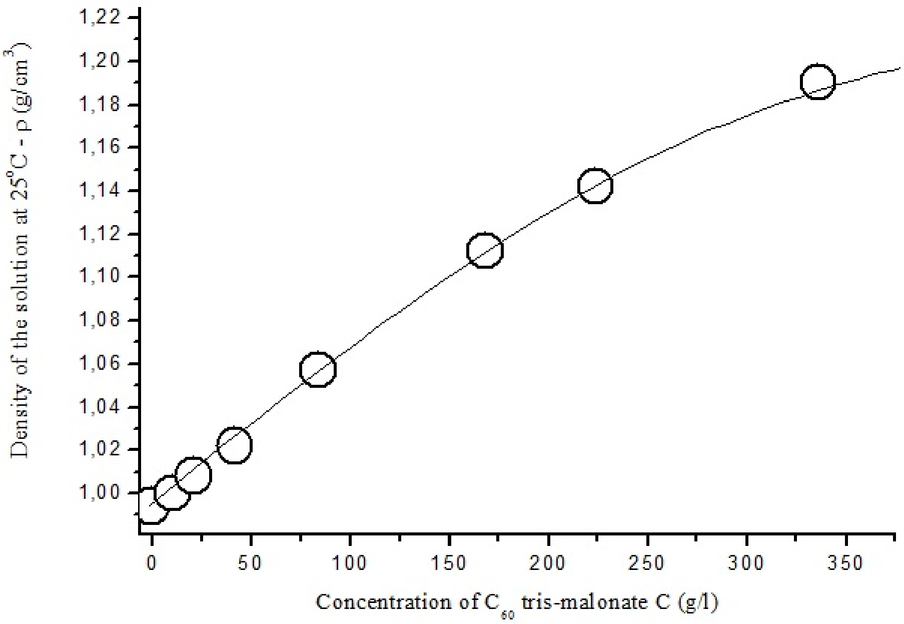

FIG. 1. Concentration dependence of density of water solutions of tris-malonate $C_{60}[=C(COOH)_2]_3$ at 25 °C

TABLE 1. Concentration dependence of Volume Properties of water solutions of tris-malonate $C_{60}[=C(COOH)_2]_3$

N of solution	Concentration C (g/dm^3)	Density ρ (g/cm^3)	Average molar volume of solution $\bar{V}$ (cm^3/mole)	Partial molar volume of H_2O V_{H_2O} (cm^3/mole)	Partial molar volume of tris-malonate $V_{tris-malonate}$ (cm^3/mole)
1	0	0.994	18.000	18.00	1021.00
2	10.5	1.000	18.187	18.00	1021.00
3	21.0	1.008	18.382	18.00	1021.00
4	42.0	1.022	18.792	18.00	1021.00
5	84.0	1.057	19.720	18.00	1021.00
6	168	1.112	22.045	18.00	1021.00
7	224	1.142	24.041	17.99	1020.99
8	336	1.190	29.643	17.99	1020.99

gravimetrically by soft drying in a vacuum dry box at 65 °C and residual pressure ≈ 0.1 mm Hg for 2 hours. More dilute solutions were prepared from the basic one by the direct dilution of the determined mass of the basic solution by water to the calculated volume at $T = 25 \pm 0.05$ °C.

3. Average and partial molar volumes

Average molar volume of solution can be calculated as [3,4]:

$$\bar{V} = V/(nH_2O + n_{tris-malonate}), \tag{1}$$

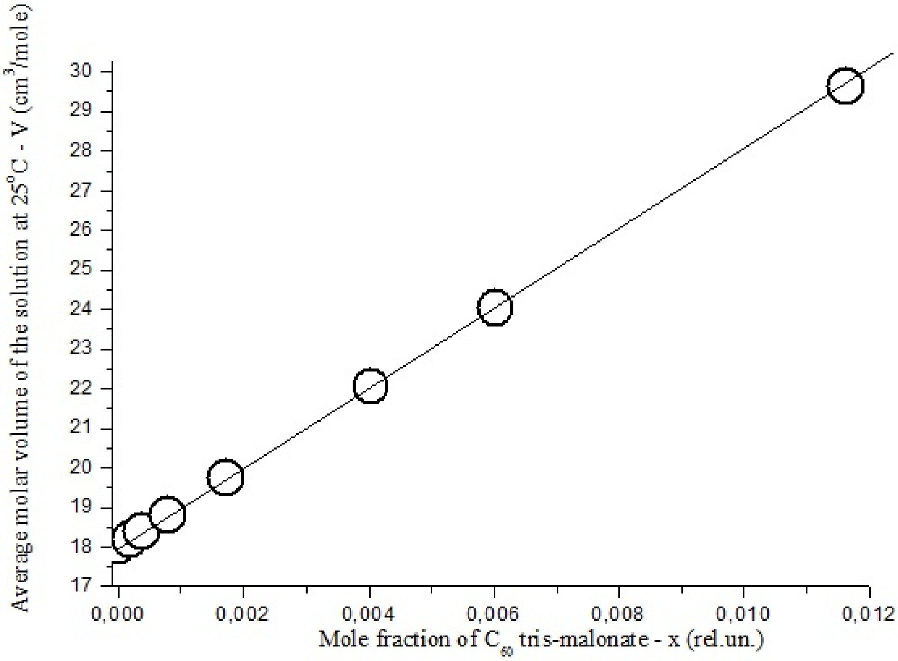

FIG. 2.1. Concentration dependence of the function $\bar{V}$

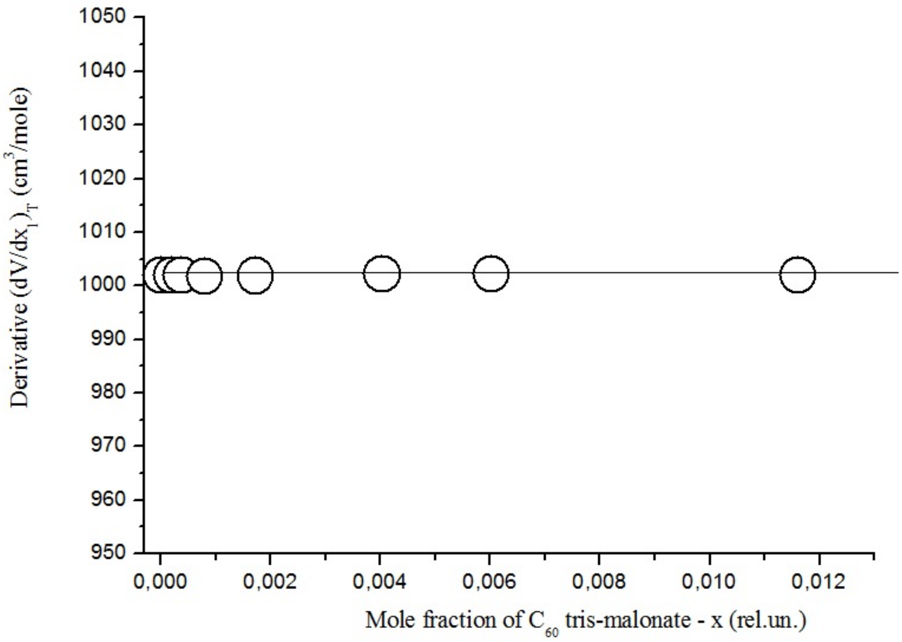

FIG. 2.2. Concentration dependence of the function $(\partial\bar{V}/\partial x_j)_{T,P}$

where: V — volume of 1 dm^3 of the solution, n_i — moles of i-th component in 1 dm^3 of the solution are also represented in the Table 1 and in Fig. 2.1.

Partial molar volume of the components of the solution: V_{H_2O} and $V_{tris-malonate}$ according to the connection between average molar and partial molar functions [3, 4]:

$$V_i = (\partial V/\partial n_i)_{T,P,n_j} = \bar{V} - x_j(\partial\bar{V}/\partial x_j)_{T,P}, \quad (2)$$

where: x_i — mole fraction of i-th component in the solution are also represented in the Table 1 (concentration dependence of the function $(\partial\bar{V}/\partial x_j)_{T,P}$ is represented in Fig. 2.2).

From the obtained volume data, one can see the following:

1. the dependence $\bar{V}(x_{tris-malonate})$ is practically linear,
2. so, the derivative is insignificant $(\partial\bar{V}/\partial x_{tris-malonate})_{T,P} \approx 0$,
3. so, partial molar volumes of both components are practically constant: $V_{HOH} \approx 18.0$, $V_{tris-malonate} \approx 1021$ cm^3/mole, i.e. both components are built in the structure of the solution without any visible complicating interactions. We will try to explain the reasons for such anomalous behavior below.

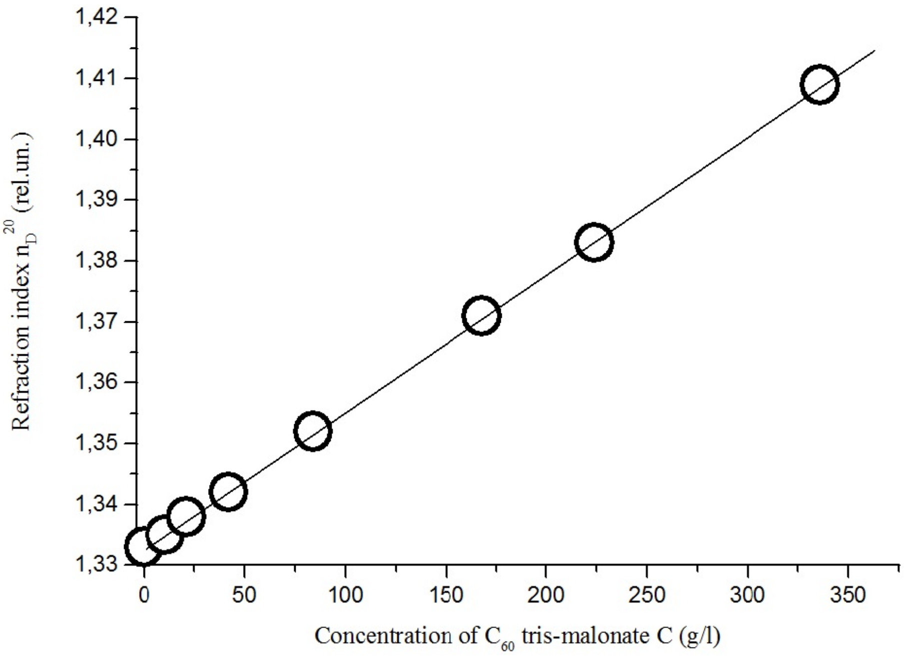

FIG. 3.1. Refraction indexes of queous tris-malonate $C_{60}[=C(COOH)_2]_3$ solutions at 25 °C

4. Refraction of the solution

Concentration dependence of the refraction index (n_D) in aqueous solutions of $C_{60}[=C(COOH)_2]_3$ was also determined with the help of a Mettler Toledo refractometer. Data is presented in Table 2 and Fig. 3.1. The specific refraction of aqueous solutions of $C_{60}[=C(COOH)_2]_3$ was calculated according to the well-known formula:

$$r = \left(n_D^2 - 1/n_D^2 + 2\right)(1/\rho), \tag{3}$$

and is represented in Fig. 3.2.

According to the specific refraction additivity rule:

$$r = r_{tris-malonate} \cdot w_{tris-malonate} + r_{HOH}(1 - w_{tris-malonate}), \tag{4}$$

where r_i, w_i — specific refraction of i-th component of the solution, we also calculated specific refraction of components — tris-malonate and H_2O (see Table 2 and Fig.3.3).

We also calculated molar refraction of $C_{60}[=C(COOH)_2]_3$ aqueous solutions according to the formula:

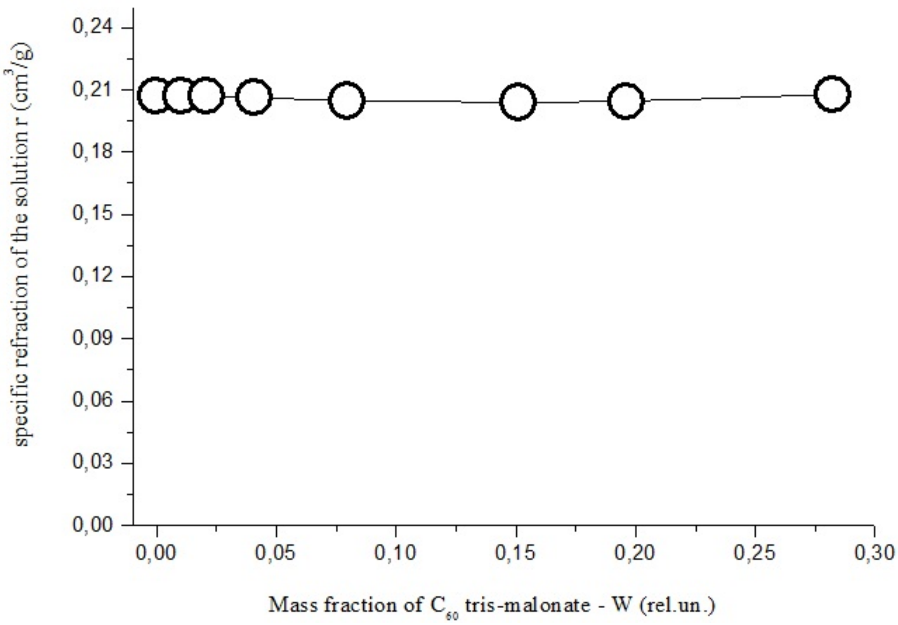

FIG. 3.2. Specific refraction of queous tris-malonate $C_{60}[=C(COOH)_2]_3$ solutions at 25 °C

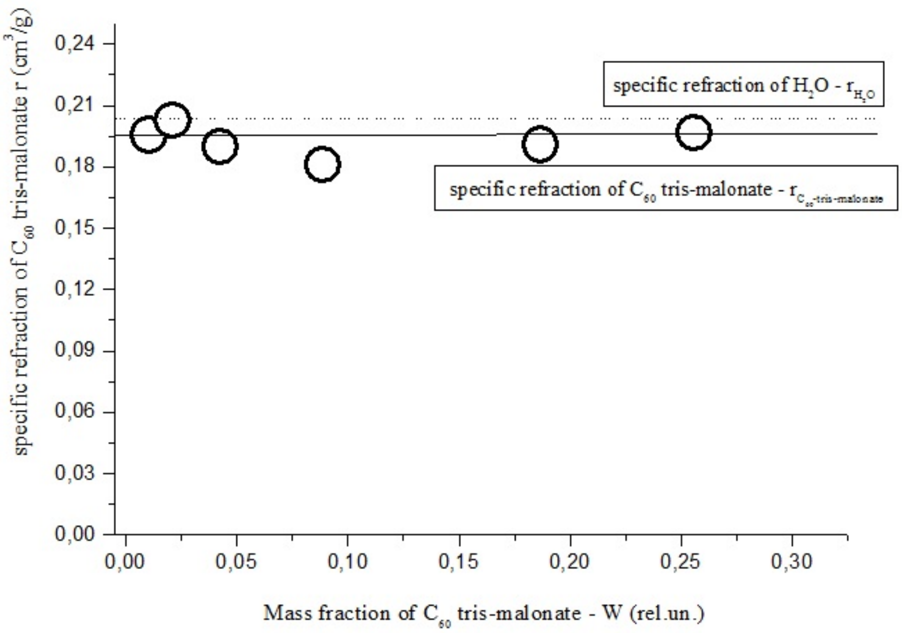

FIG. 3.3. Specific refraction of tris-malonate $C_{60}[=C(COOH)_2]_3$ and water (for the comparison) in aqueous solutions at 25 °C

$$R = ({}^{n_D^2 - 1}/_{n_D^2 + 2})(\bar{M}/\rho), \tag{5}$$

where $\bar{M}$ — average molar mass of the components of the solution ($\dot{M} = M_{tris-malonate} \cdot x_{tris-malonate} + M_{\mathrm{H_2O}}(1 - x_{tris-malonate})$, M_i — mass of tris-malonate C_{60} (1026 a.un.) and H_2O (18 a.u.), x_i — molar fraction of i-th component. Data are represented in the Fig. 4.1 and Table 2.

TABLE 2. Concentration dependence of refraction indexes of aqueous tris-malonate $C_{60}[=C(COOH)_2]_3$ solutions and specific and molar refraction of the components at 25 °C

N of solution	Refraction index n_D^{20} (rel. un.)	Specific refraction of the solution r (cm^3/g)	Specific refraction of tris-malonate $r_{tris-malonate}$ (cm^3/g)	Molar refraction of the solution R (cm^3/mole)	Molar refraction of tris-malonate $R_{tris-malonate}$ (cm^3/mole)
1	1.333	0.2069	–	3.7260	–
2	1.335	0.2068	0.1954	3.7625	200.50
3	1.338	0.2068	0.2022	3.8004	207.59
4	1.342	0.2062	0.1887	3.8803	194.47
5	1.352	0.2046	0.1777	4.0611	185.52
6	1.371	0.2039	0.1868	4.5141	195.61
7	1.383	0.2043	0.1932	4.9027	201.57
8	1.409	0.2077	0.2098	5.9939	214.42

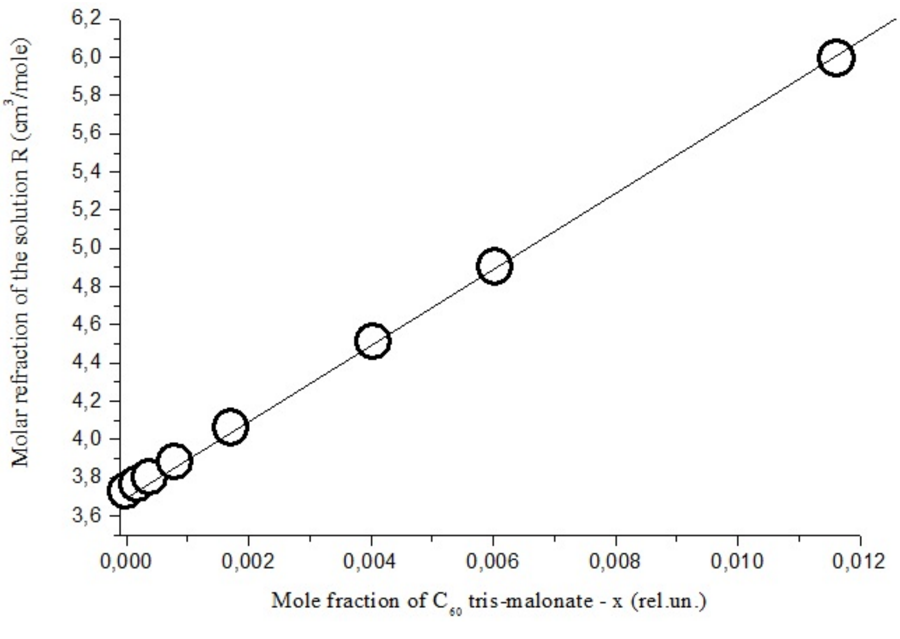

FIG. 4.1. Molar refraction of queous tris-malonate $C_{60}[=C(COOH)_2]_3$ solutions at 25 °C

According to the obvious parity, connecting specific and molar (R_i) refractions of the components:

$$R_i = r_i \cdot M_i, \qquad (6)$$

we also calculated last ones (see Table 2 and Fig. 4.2).

From obtained refractione data one can see the following:

1. The dependence $n_D(C)$ is nearly linear;

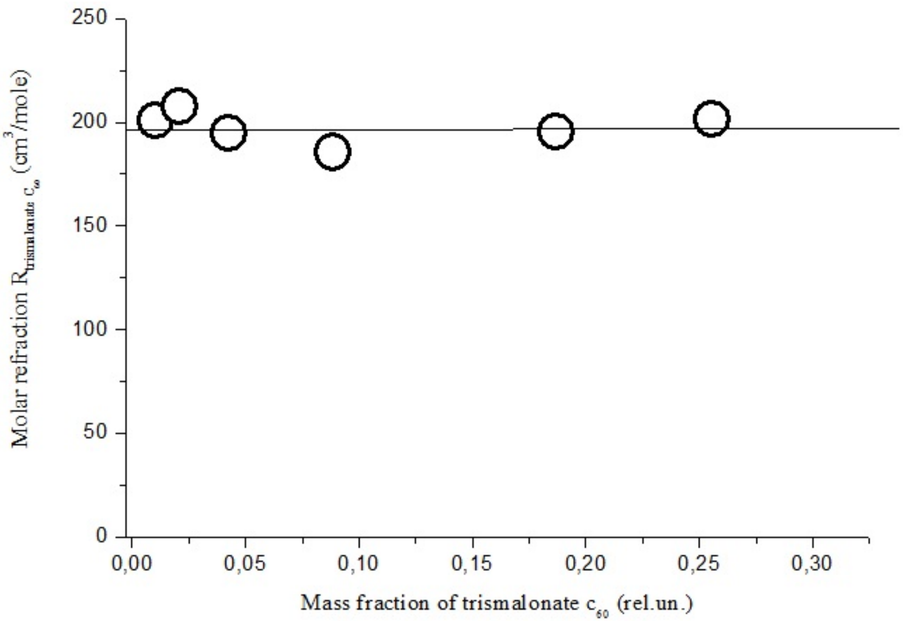

FIG. 4.2. Molar refraction of tris-malonate in aqueous solutions at 25 °C

2. Specific refraction of the solution practically is independent of the concentration ($r \approx 0.205 \pm 0.002$ cm^3/g);
3. Specific refractions for both components of the solution are also practically independent of the concentration and absolutely unexpectedly are very similar:

$$r_{tris-malonate} \approx 0.195 \pm 0.1 \approx r_{H_2O} \approx 0.206 \pm 0.1 \quad \mathrm{cm}^3/\mathrm{g}; \tag{7}$$

4. The concentration dependence of molar refraction of water solutions of tris-malonate at 25 °C $R(x_{tris-malonate})$ is also nearly linear;
5. Molar refraction of tris-malonate $R_{tris-malonate}$ is practically independent of the concentration:

$$R_{tris-malonate} \approx 201 \pm 7 \quad \mathrm{cm}^3/\mathrm{mole}; \tag{8}$$

6. That in essence the casual fact for the specific refractions'similarity of both components (at a huge difference of the molecular dimensions) determines such simple concentration behavior for the refraction characteristics. Specific refraction is accepted to be associated with the volume of electronic orbits falling on the mass unit of the phase, and in the case of our solutions, the casual equality of these components'characteristics allows to them form the mixed solution in such a way that the intermolecular forces are compensatory.
7. We also check ourselves, by calculating molar refraction of tris-malonate C_{60} by the additivity rule (R^{add}):

$$R^{\mathrm{add}} \approx 69R_c + 6\mathrm{R}_{\mathrm{O(-OH)}} + 6R_{O(=C=O)} + 6R_H \approx 195.3 - 200.3 \quad \mathrm{cm}^3/\mathrm{mole}, \tag{9}$$

where: $R_{i(j)}$ — atomic refraction of i-th atom in j-th functional group. Some discrepancy in the calculation connected with the choice of the different spectral lines: for the line $H_\alpha[\lambda = 658.3(nm)]$ - $R^{\mathrm{add}} \approx 195.3$ cm^3/mole; and for the line $H_\gamma[\lambda = 436.1(nm)]$ - $R^{\mathrm{add}} \approx 200.3$ cm^3/mole (data, according to Eizenlor).

Alternative calculation (according to Fogel [5]) gives the following result:

$$R^{\mathrm{add}} \approx 63R_c + 6\mathrm{R}_{-\mathrm{COOH}} \approx 205.2 \quad \mathrm{cm}^3/\mathrm{mole}, \tag{10}$$

where $\mathrm{R}_{-\mathrm{COOH}}$ is the refraction of carboxylic group. In the both cases, the result of the calculation is considered more or less successful and confirms the experimental data.

5. Conclusion

Thus, the partial and average molar volume and refractive properties of aqueous solutions of the water soluble light fullerene derivative- $C_{60}[=C(COOH)_2]_3$, at 25 °C were investigated.

Acknowledgement

Research was performed with using the equipment of the Resource Center 'GeoModel' of Saint-Petersburg State University.

This work has been accomplished as the part of the Ministry of Education and Science of the placecountry-regionRussian Federation research assignment 'Realization of scientific research (fundamental studies, applied research and advanced developments)'. Project code: 2548.

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] 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).

[3] A.V.Storonkin. *Thermodynamics of Heterogeneous Systems*. Rus. Leningrad: LGU, Book 1, Part 1, 2. 467 pp. (1967).

[4] A.Muenster. *Chemical thermodynamics*. Rus. Transl. from Engl. Moscow: Mir (1971).

[5] *Atomic refractions according to Fogel.* Directory of Chemist/ red. B.P. Nikol'skiy. Rus. Leningrad: Chemistry, 1, 395 pp. (1982).