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Mass transport properties of water soluble light fullerene tris-malonate – $C_{60}[=C(COOH)_2]_3$ in aqueous solutions

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The investigation of concentration dependence of mass transport properties (diffusion coefficients and viscosity) of the water soluble light fullerene tris-malonate – $C_{60}[=C(COOH)_2]_3$ in aqueous solutions was provided. Activation energies for the diffusion and viscous current were calculated.

Keywords: tris-malonate of light fullerene, mass transport properties.

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1. Introduction

This article furthers the investigations which were initiated previously [1–5], devoted to describing the synthesis and identification of the $C_{60}[=C(COOH)_2]_3$ tris-malonate [1] (the original synthesis of this water soluble derivative was described earlier in [5]), the investigation of volume and refraction properties of its aqueous solutions at 25 °C [2], poly-thermal solubility and complex thermal analysis [3], the concentration dependence of electric conductivity and pH for aqueous solutions [4], and concentration dependence of the last-mentioned properties for $C_{60}[=C(COOH)_2]_3$ aggregates [5].

This article is devoted to investigating the concentration dependence of mass transport properties (diffusion coefficients and viscosity) of water soluble light fullerene tris-malonate – $C_{60}[=C(COOH)_2]_3$ in aqueous solutions and calculation of activation energies for the diffusion and viscous current over a wide range of concentrations – up to 40 g/dm^3.

2. Diffusion of $C_{60}[=C(COOH)_2]_3$ in water solutions at 20 and 50 °C

The diffusion of $C_{60}[=C(COOH)_2]_3$ in the $C_{60}[=C(COOH)_2]_3$ – H_2O system was investigated with the help of an original diffusometer, which allowed the determination of the $C_{60}[=C(COOH)_2]_3$ concentration $C_{C60-tris-malonate}$ – mg/dm^3 (and the gradient of concentration – $\mathrm{grad}\ C_{\text{C60-tris-malonate}} = \partial C_{\text{C60-tris-malonate}}/\partial x$, where x is coordinate of the direction of uni-dimensional diffusion) by light absorption in the near UV spectral range – at $\lambda = 330$ nm [1], according to the first diffusion Fick's law (see, for example [6]):

$$dm_{\mathrm{C60-tris-malonate}}/dt = D \cdot S \cdot \partial \mathrm{C}_{\mathrm{C60-tris-malonate}}/\partial x, \qquad (1)$$

where: m is mass of C_{60}-tris-malonate, which crosses through the surface S per time t under concentration gradient $\partial \mathrm{C}_{\text{C60-tris-malonate}}/\partial x$.

Data were provided over a wide concentration range (5 g/dm^3 $\leq \mathrm{C}_{\text{C60-tris-malonate}} \leq$ 40 g/dm^3) for comparatively concentrated solutions at two temperatures 20 °C and 50 °C (293 K and 323 K).

The results of the determination are represented in Table 1 and in Fig. 1.

TABLE 1. Diffusion coefficient of C_{60}-tris-malonate of in water – D and diffusion activation energy – E_D

Number of solution No.	Concentration of C_{60} tris-malonate in water – C (mass.%)	Diffusion coefficient of C_{60} tris-malonate in water at 293 K – D_{293} 10^8 (cm^2/s)	Diffusion coefficient of C_{60} tris-malonate in water at 323 K – D_{323} 10^8 (cm^2/s)	Energy of the diffusion activation according to the Arrhenius equation – E_D (kJ/mole)
1*	0	5.5	11.0	18.2
2	0.5	4.6	9.1	17.6
3	1.0	4.1	7.9	17.2
4	2.0	3.8	7.5	17.8
5	4.0	3.7	7.5	18.5

* – Extrapolation to infinite diluted solution $C \to 0$ g/dm^3.

$E_D = 17.9 \pm 0.4$ kJ/mole, $\gamma_D = 1.31 \pm 0.05$ rel. un.

Temperature dependence of diffusion coefficient of C_{60}-tris-malonate in water was described with the help of both methods:

Arrhenius equation:

$$D_T = D_0 \exp(-E_D/RT), \qquad (2)$$

where: D_T is the diffusion coefficient at temperature $T(K)$, D_0 is the diffusion pre-exponent, E_D is the diffusion activation energy,

and Vant-Hoff rule multiplication:

$$\gamma_D = D_{T+10}/D_T. \qquad (3)$$

One can see from the data following:

1. It seems the diffusion coefficients (D) of C_{60}-tris-malonate in water solutions have much lower values (D on the order of 10^{-8} cm^2/s). Than those for their analogs – non-modified light fullerenes – C_{60} and C_{70} in organic (mainly aromatic) solvents [7] (D on the order of 10^{-7} – 10^{-6} cm^2/s).

2. Additionally, the authors of [7] tried to crudely estimate the radius of the particles in the diffusion processes (r_D) according to the Smolukhovskiy – Stokes – Einstein law (spherical approximation):

$$D = \frac{kT}{6\pi\eta r_D}, \qquad (4)$$

where: D – diffusion coefficient, T – temperature (K), k – Boltzmann constant, η – dynamic viscosity of the solvent, r_D – radius of spherical particle.

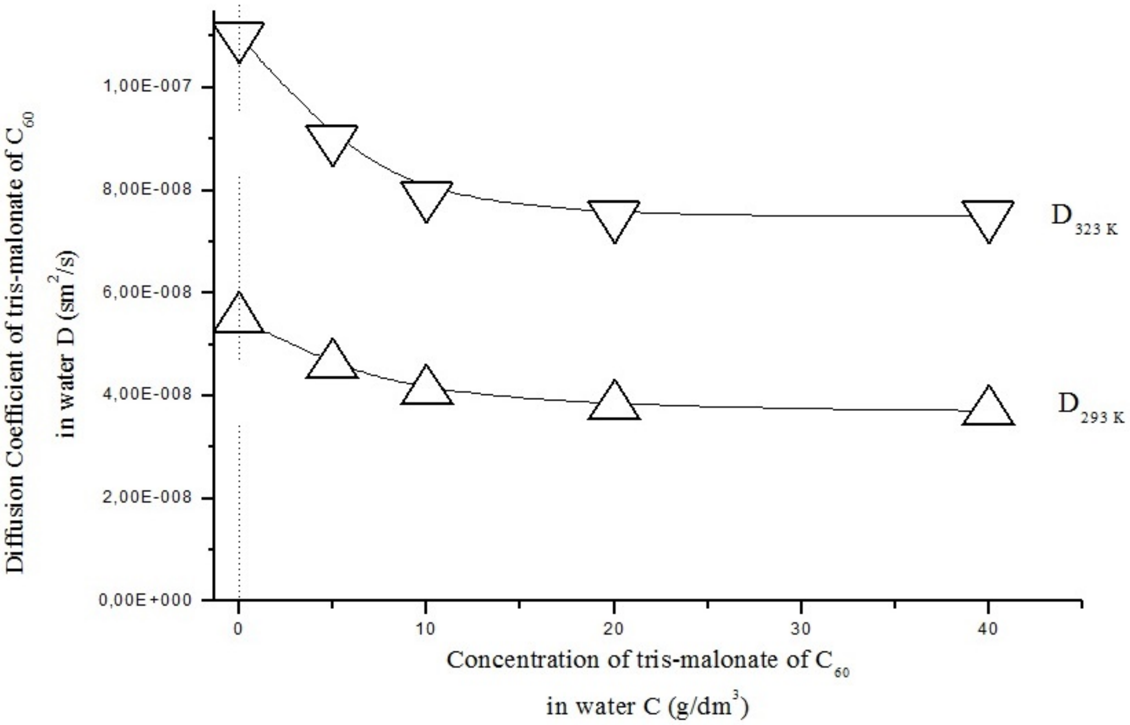

FIG. 1. Diffusion coefficient of C_{60}-tris-malonate in water

In different solvents they obtained values for r_D ranging from 0.4 – 3 nm; the considerable growth of r_D when comparing non-associated and non-solvated light fullerenes ($r_D \approx 0.35$ nm [8]) may be the result of light fullerene association in clusters and perhaps simultaneous intensive interaction of fullerenes with solvent molecules.

In the case of our water soluble light fullerene derivatives, one can expect a higher degree of association and hydration, which was proven earlier by light scattering experiments [5]. In that work, the formation of three types of aggregates was observed with the following characteristic radii: $r_D \approx 20 - 40$ nm (for type 1 aggregates), $r_D \approx 150 - 250$ nm (for type 2 aggregates), $r_D \approx 2000 - 3000$ nm (for type 3 aggregates). Simultaneously, non-aggregated forms were not found at all [5]. Such a stepwise hierarchical association model was proven earlier in analog binary $C_{60}(OH)_n$ fullerenol – H_2O – systems see, for example [9, 10].

3. So, also according to the Smolukhovskiy – Stokes – Einstein law (using the temperature dependence of the dynamic viscosity of the solvent – water – see Fig. 2), one can obtain the following radius values for the particles in the diffusion processes in the $C_{60}[=C(COOH)_2]_3$ – H_2O system: $r_D = 30 - 60$ nm. From these data, we can confirm that practically, only type 1 C_{60}-tris-malonate aggregates participate in mass transport diffusion processes. Other type aggregates are not realized in solution (monomers of C_{60}-tris-malonate [5]), or are not labile enough for effective mass transport (type 2 and -3 aggregates – [5]). The fact that diffusion coefficients decrease while the concentration of C_{60}-tris-malonate increases may be explained by the proposition that the relative mass fraction of main transport particles (type 1 aggregates of $C_{60}[=C(COOH)_2]_3$) decreases with concentration growth, while the concentration of larger, non-mobile particles increases.

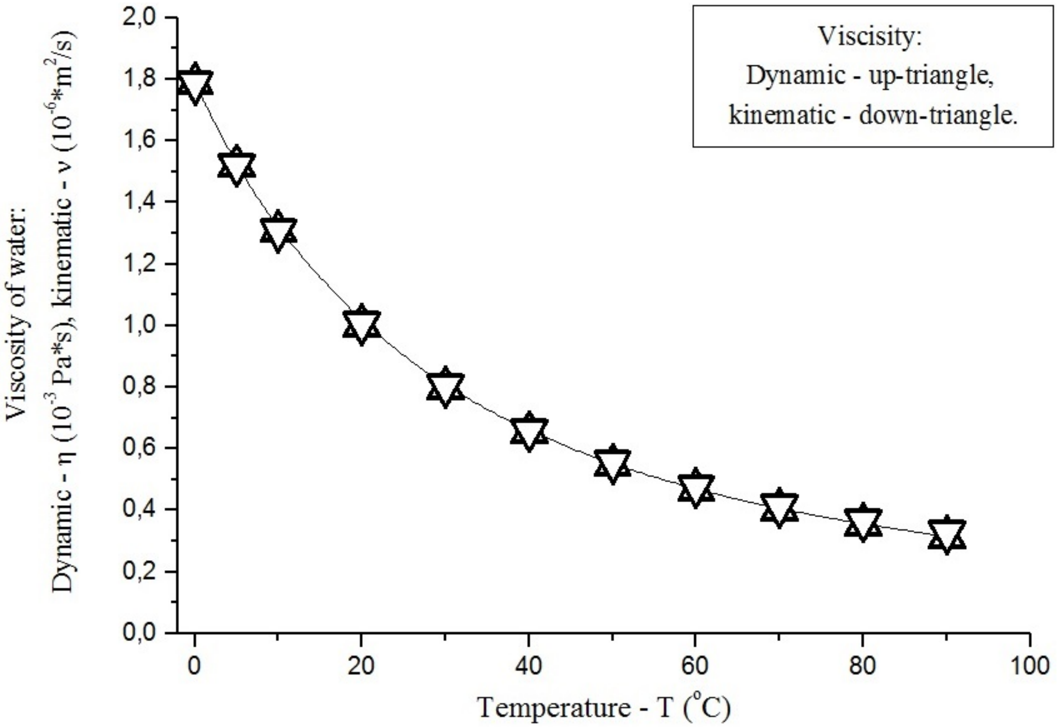

FIG. 2. Temperature dependence of the dynamic and kinematic viscosity of the water

3. Viscosity of $C_{60}[=C(COOH)_2]_3$ water solutions at 20 and 50 °C

The dynamic viscosity of C_{60}-tris-malonate in aqueous solutions was derived using the capillary viscosity-meter method by the determining the liquid flow times of the solutions through the vertical capillary (the glass viscosity-meter is of the type 'VNJ' (Ecochim. Rus. – Ukr.))

The determined kinetic viscosity of C_{60}-tris-malonate in aqueous solutions was additionally used to derive the densities at constant temperature with the help of quartz pycnometer [2].

Air thermostats were used, with an accuracy of temperature fixation of $\Delta T = \pm 0.5$ K.

According to Newton's law of viscosity (internal friction), the dynamic viscosity for 'Newtonian liquids' (η) is defined as:

$$F_{l-f} = \eta \Delta V S, \tag{5}$$

where: F_{l-f} – is the force of the internal friction, $\Delta V = \mathrm{grad}\, V = \partial V / \partial x$ (x – is the direction, perpendicular to the vector of the velocity of liquid layer – V), S – surface of contact layers.

Kinematic viscosity (ν) is defined as:

$$\nu = \eta / \rho, \tag{6}$$

where: ρ – is the density of liquid.

Values for η, as a rule, are measured in (Pa·s) or in (P (Poise – lat.) = Пз (Пуаз – rus.) = Pa·s/10), values ν – in (m^2/s, cm^2/s) or in non-systematic units (°E – Engler degree):

$$\nu = 0.073\,^{\circ}\mathrm{E} - 0.063\,^{\circ}\mathrm{E}. \tag{7}$$

Temperature dependence of the dynamic viscosity of C_{60}-tris-malonate in aqueous solutions was described with both methods.

The analog of Arrhenius equation for the viscous current (also named as equation of Frencel – Andrade [12]):

$$\eta_T = \eta_0 \exp(+E_\eta/RT), \tag{8}$$

where: η_T is dynamic viscosity at temperature $T(K)$, η_0 is dynamic viscosity pre-exponent, E_η is energy of activation of the viscous current, and analog of Vant-Hoff rule multiplication for the viscous current – γ_η:

$$\gamma_\eta = \eta_{T-10}/\eta_T. \tag{9}$$

Viscosity data are represented in the Table 2 and Fig. 3.

TABLE 2. Concentration dependence of the dynamic and kinematic of C_{60}-tris-malonate in aqueous solutions at 298 and 323 K

Number of solution No.	Concentration of C_{60} tris-malonate C (mass.%)	Dynamic viscosity η_{298} $(\mathrm{Pa \cdot s \cdot 10^{-3}})$	Kinematic viscosity ν_{298} $(\mathrm{m^2/s \cdot 10^{-6}})$	Dynamic viscosity η_{323} $(\mathrm{Pa \cdot s \cdot 10^{-3}})$	Viscosity activation energy according to the Arrhenius equation – E_η (kJ/mole)
1	0.0	0.894	0.893	0.548	15.7
2	0.00001	0.886	0.885	0.544	15.6
3	0.0001	0.872	0.872	0.536	15.6
4	0.001	0.849	0.849	0.523	15.5
5	0.01	0.777	0.777	0.480	15.4
6	0.1	0.641	0.641	0.398	15.2
7	0.5	0.643	0.642	0.401	15.1
8	1.0	0.645	0.643	0.404	14.9

$$E_\eta = 15.3 \pm 0.3 \text{ kJ/mole}, \quad \gamma_\eta = 1.21 \pm 0.05 \text{ rel. un.}$$

From the data in Fig. 3 and Table 2 one can see the following:

1. Values for $\eta(C)$ decrease while the concentration increases in dilute solutions and becomes nearly constant in more concentrated ($C > 0.1$ mass.% of C_{60}-tris-malonate in water) at both temperatures.

2. To describe the dependence of the dynamic viscosity on the concentration of C_{60}-tris-malonate in aqueous solutions (C) at a constant temperature – $\eta(C)$ (in the initial region of the function ($C \to 0$)), one can use the empirical Bachinskiy equation:

$$\eta = \frac{c_B}{V_m - b_B}, \tag{10}$$

where: V_m is average molar volume of water solution of C_{60}-tris-malonate (can be determined from the density measurements – [2]); c_B and b_B are constants of the Bachinsckiy equation and may be dependent on temperature and the type of the system only. So, using Taylor decomposition of the function $\eta(C)$ in the region $C > 0$, one can easily obtain the following equations for the calculation of the constants of Bachinsckiy equation:

$$b_B = \frac{V_m^0(\eta^0 - \eta^x) - \eta^x(\partial V_m/\partial x)^0 x}{\eta^0 - \eta^x}, \tag{11}$$

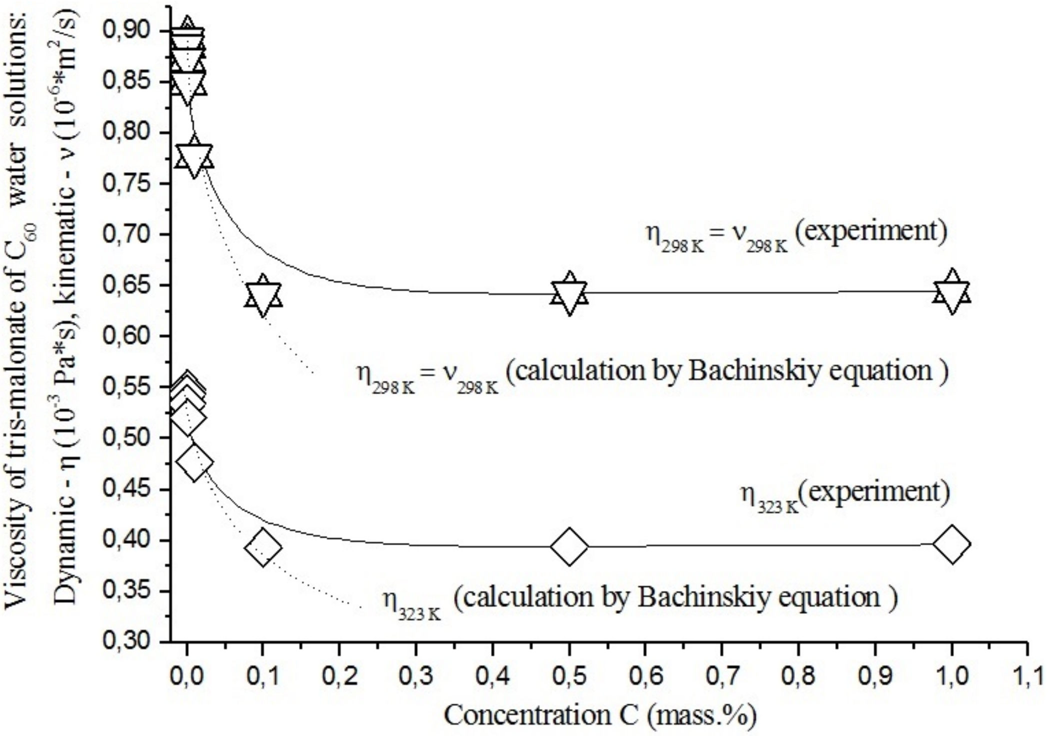

FIG. 3. Dynamic and kinematic viscosity of C_{60}-tris-malonate in aqueous solutions at 298 K and 323 K

$$c_B = \frac{\eta^0 \eta^x (\partial V_m/\partial x)^0 x}{\eta^0 - \eta^x}, \tag{12}$$

where: V_m^0 – average molar volume of pure solvent – water, η^0 – the dynamic viscosity of the solvent, C – concentration in mass.% and x – molar fraction of C_{60}-tris-malonate in aqueous solutions:

$$x = \frac{C}{1026[C/1026 + (100 - C)/18]}, \tag{13}$$

η^x – the dynamic viscosity of solution with molar fraction x, $(\partial V_m/\partial x)^0 = \lim\limits_{x \to 0}(\partial V_m/\partial x) \approx$ const ≈ 1002 cm^3/mole [2].

Calculation of the dependence $\eta_(C)$ using equations (10) – (12) is represented in Fig. 3. One can see more or less good agreement between the experimental and calculated data in comparatively dilute aqueous C_{60}-tris-malonate solutions – quick drop of η while C is increasing from $C \approx 0 \to C \approx 0.1$ mass.%. Such decrease of the function $\eta(C)$, even in dilute solutions is atypical enough for the solutions with high molecular weight compounds. In more concentrated solutions, $C \approx 0.1 \to C \approx 1.0$ mass.%, the results between the experimental and the calculated differed considerably, and according to our point of view, naturally increases (see Fig. 3) – the function $\eta(C)$ continues to decrease and becomes nearly constant. These facts may be explained by the following: there two influences, which cause the change of $\eta(C)$ in different directions. First – the destruction of hydrogen bonds structure between solvent molecules, can decrease η (this influence is stronger in dilute solutions), second – increasing the concentration of the main mass transport species (in the direction perpendicular to the velocity vector of the liquid layers), can only increase η (this influence becomes more pronounced at higher concentrations). In the $1.0 \geq C \geq 0.1$ mass.% concentration range these two factors have approximately equal weight, and as a result, $\eta(C)$ crosses through a 'soft minimum'.

3. Dependencies of dynamic and kinematic viscosity $\eta(C)$ and $\nu(C)$ are naturally approximately equal at 298 K, because densities of aqueous C_{60}-tris-malonate are very close to $\rho \approx 1$ g/cm^3.

4. Values for $\eta(C)$ decrease at higher temperatures over the entire concentration range ($0.0 < C < 1$ mass.%).

4. Conclusions

The investigation of concentration dependence of mass transport properties (diffusion coefficients and viscosity) of water soluble light fullerene tris-malonate – $C_{60}[=C(COOH)_2]_3$ in aqueous solutions in concentration range (0 – 1 mass.%) and at 298 and 323 K was performed and the results obtained were provided. The diffusion and viscous current activation energies were calculated. It was shown, that the type 1 aggregates of $C_{60}[=C(COOH)_2]_3$ with the linear dimensions on the order of tens of nm determine the mass transport properties in aqueous solutions over the entire concentration range tested.

Acknowledgement

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