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CONCENTRATION DEPENDENCE OF ELECTRIC CONDUCTIVITY AND pH FOR AQUEOUS SOLUTIONS OF WATER-SOLUBLE LIGHT FULLERENE – $C_{60}[=C(COOH)_2]_3$ TRIS-MALONATE

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Studies of the concentration dependence of electric conductivity and pH for aqueous solutions of the light fullerene – $C_{60}[=C(COOH)_2]_3$ tris-malonate were performed at 25 °C. From both data (from the equivalent electric conductivity and pH), the apparent degree of dissociation and concentration dissociation constants of $C_{60}[=C(COOH)_2]_3$ in aqueous solutions were calculated. Thermodynamic dissociation constants of $C_{60}[=C(COOH)_2]_3$ in aqueous solutions, calculated for infinitely dilute solutions by the both methods, were reasonably similar.

Keywords: tris-malonate of light fullerene, electric conductivity.

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1. Introduction

This article continues the investigations, which were initiated in articles [1–3], devoted to the synthetic description and identification of tris-malonate $C_{60}[=C(COOH)_2]_3$ [1] (the original synthesis of this water soluble derivative was described earlier in [4]). The investigation of volume and refraction properties of its aqueous solutions at 25 °C were discussed in [2], while poly-thermal solubility and complex thermal analysis were discussed in [3]. This article is devoted to the investigation of some transport properties – *e.g.* concentration dependence of electric conductivity and pH for light fullerene - $C_{60}[=C(COOH)_2]_3$ tris-malonate aqueous solutions. From both data, the apparent degree of dissociation, concentration and thermodynamic dissociation constants of $C_{60}[=C(COOH)_2]_3$ in aqueous solutions were calculated. These investigations will be used to determine the state of the $C_{60}[=C(COOH)_2]_3$ species in aqueous solutions.

2. Electric conductivity of water solutions of $C_{60}[=C(COOH)_2]_3$

The concentration dependence of specific electric conductivity of aqueous $C_{60}[=C(COOH)_2]_3$ solutions at 25 °C – $\varkappa$ ($S\cdot cm^{-1}$) was investigated by the measurement of the specific resistance of the solutions ρ ($\Omega\cdot cm$):

$$\varkappa = 1/\rho, \tag{1}$$

so, specific electric conductivity corresponds to the unit volume of the solution, put between two parallel planar electrodes with surfaces of 1 cm^2 and at a distance of 1 cm. The device, a HAMEG HM8118 LCR bridge (Rohde & Schwarz), temperatures $T = 25 \pm 0.1$ °C, Pt – electrodes were used. One can see that the dependence $\varkappa(W)$ (where W is mole fraction of $C_{60}[=C(COOH)_2]_3$) is non-monotonic and crosses through the maximum at $W = 0.005$ rel. un. The last fact is traditionally connected with electrophoresis and relaxation effects, which are characteristic to moderate electrolytes.

Equivalent electric conductivity (λ – S·cm^2/eq), i.e. conductivity for such electrolyte volume, which contains 1 equivalent of electrolyte was calculated:

$$\lambda = 1000\varkappa/C_N, \tag{2}$$

where: C_N is equivalent concentration (eq/l). Experimental data are represented in Table 1 and in Fig. 1. One can see natural monotonic growth of λ values when the concentration of the solutions' C_N decreases.

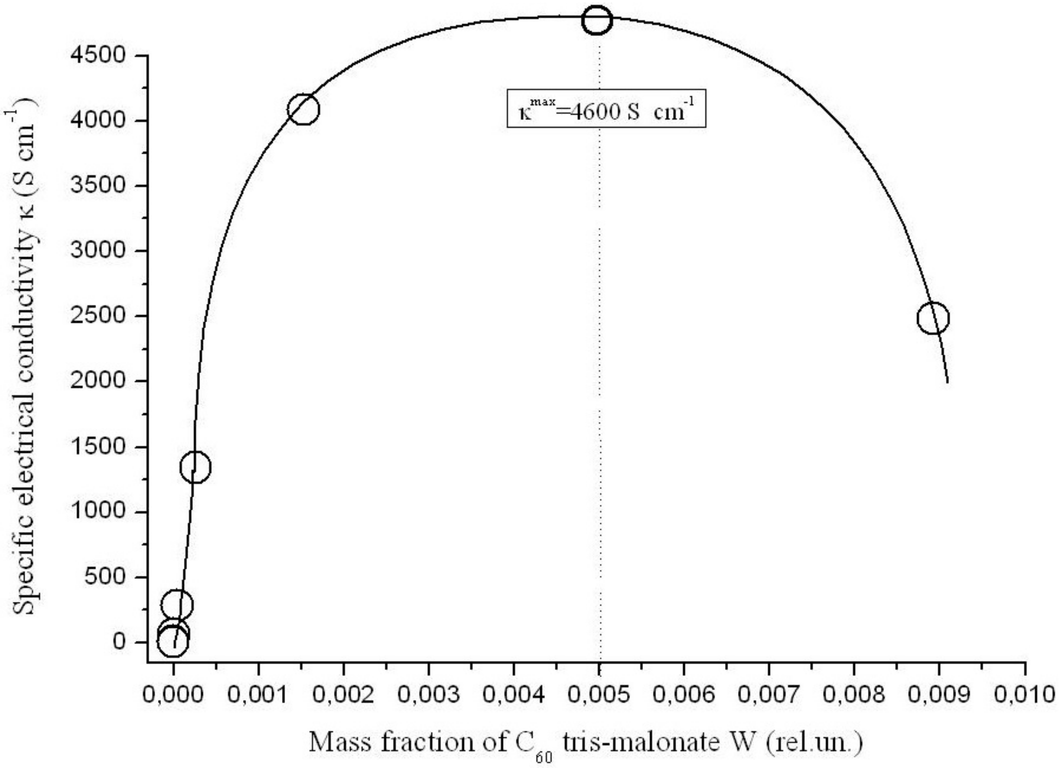

FIG. 1. Concentration dependence of specific electric conductivity of $C_{60}[=C(COOH)_2]_3$ aqueous solutions

In order to determine the equivalent electric conductivity value in infinitely dilute solutions – λ_0, we have extrapolated the dependence $\lambda(C_N^{1/2})$ into the value $C_N^{1/2} = 0$, according to well-known Onsager equation [6]:

$$\lambda = \lambda_0 - AC_N^{1/2}, \tag{3}$$

where A in the conditions of the experiment is constant (see Fig. 3).

TABLE 1. Experimental data, concerning electric conductivity of water solutions of $C_{60}[=C(COOH)_2]_3$

Solution number No.	Volume concentration C (g/l)	Mass fraction W (rel.un.)	Equivalent concentration C_N (eq/l)	Specific electric conductivity $\varkappa$ (S·cm^{-1})	Equivalent electric conductivity λ (S·cm^2/eq)
1	0.0	0.0	0.0	—	$1.33 \cdot 10^{10}$ (extrapolation)
2	0.0002	0.000000206	0.000000315	3.30	$1.05 \cdot 10^{10}$
3	0.0012	0.00000123	0.00000190	14.5	$7.61 \cdot 10^{9}$
4	0.0071	0.00000727	0.0000112	63.1	$5.60 \cdot 10^{9}$
5	0.0428	0.0000437	0.0000681	285	$4.18 \cdot 10^{9}$
6	0.256	0.000260	0.000409	1340	$3.27 \cdot 10^{9}$
7	1.534	0.00154	0.00249	4090	$1.64 \cdot 10^{9}$
8	9.201	0.00892	0.0154	2490	$1.61 \cdot 10^{8}$

Solution number No.	Apparent dissociation degree α (rel.un.)	– lg (concentration dissociation constant) pK_D (rel.un.)
1	1.0 (extrapolation)	6.15 (extrapolation)
2	0.74	—
3	0.54	5.92
4	0.40	5.53
5	0.30	5.07
6	0.23	4.54
7	0.11	4.41
8	0.011	5.69

The apparent dissociation degree α (rel.un.) was calculated, according to the equation (neglecting transmission coefficients of the ions):

$$\alpha = \lambda / \lambda_0, \tag{4}$$

and is represented in Table 1 and Fig. 4. ($\lambda_0 \approx 1.40 \cdot 10^{10}$ S·cm^2/eq). One can see that at more or less significant concentrations $C_N > 0.01$ eq/l $C_{60}[=C(COOH)_2]_3$, it is weakly electrolytic and at lower concentrations, $C_N = 10^{-7} - 10^{-2}$ eq/l, it is moderately and even strongly electrolytic.

The concentration dependence of the concentration dissociation constant – K_D was calculated according to the 'Ostwald law of the dilution' (neglecting activity coefficients of the ions and non-dissociated molecule – $\gamma_i = \gamma_\pm = 1$):

$$K_D = C_N \alpha^2 / (1 - \alpha), \tag{5}$$

and is also represented in Table 1 and Fig. 5. Thermodynamic dissociation constant – K_D^{therm} was calculated by the extrapolation of $K_D(C_N)$ values for an infinitely dilute solution:

$$K_D^{therm} = \lim_{C_N \to 0}(K_D), \quad pK_D = -\lg K_D. \tag{6}$$

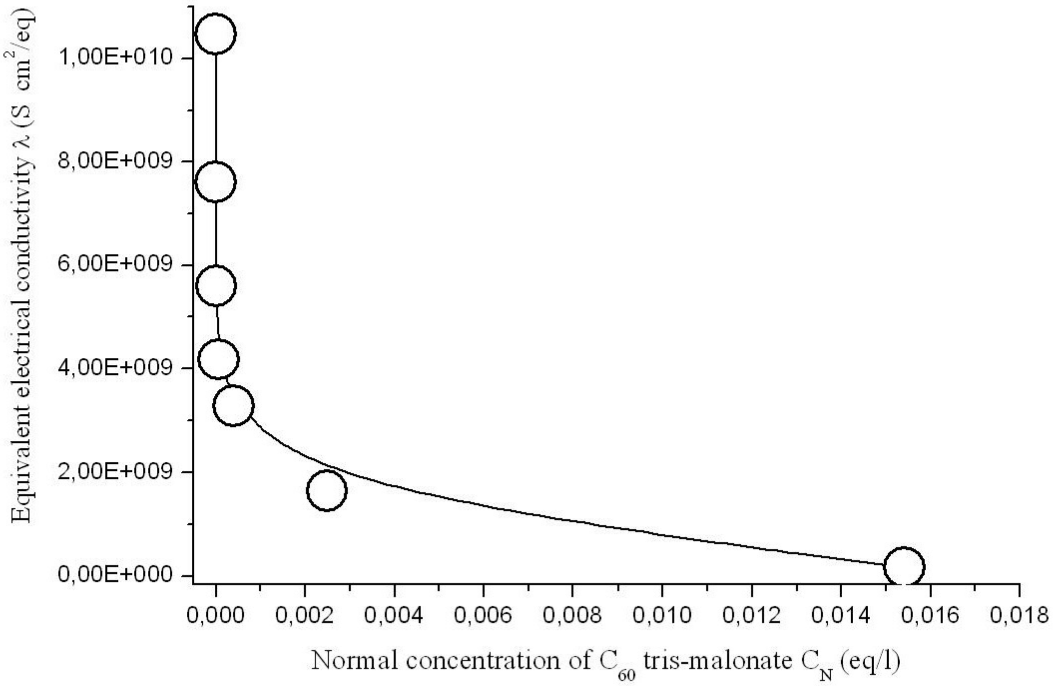

FIG. 2. Concentration dependence of equivalent electric conductivity for $C_{60}[=C(COOH)_2]_3$ aqueous solutions

According to our calculation, one obtains the value $pK_D^{therm} = 6.15 \pm 0.25$ rel.un.

3. pH of aqueous solutions of $C_{60}[=C(COOH)_2]_3$

The concentration dependence of pH for aqueous $C_{60}[=C(COOH)_2]_3$ solutions was measured with the help of pH-meter – Mill Volt-meter pH-121 and glass electrode with hydrogen function EVL 1M3 (rus.). Calibration of the electrode was performed with the help of water basic buffer solutions NH_4OH – NH_4Cl. Accuracy of measurements was $\Delta pH = \pm 0.1$ rel.un. The results are represented in the Table 2 and Fig. 6.

The concentration dependence of the apparent dissociation degree α (rel.un.) was calculated according to trivial equation:

$$\alpha = \exp\left((14 - pH) \cdot \ln 10\right)/C_N. \tag{7}$$

The concentration dependence of the concentration dissociation constant – K_D was calculated according to the 'Ostwald's law of dilution' (see earlier eq. (5), also neglecting activity coefficients of the ions and non-dissociated molecule).

The results of the calculation of α and K_D concentration dependencies are also represented in the Table 2 and Fig. 7, 8.

The thermodynamic dissociation constant – K_D^{therm} was calculated by the extrapolation of $K_D(C_N)$ values for infinitely dilute solutions. According to our calculations, one obtains a value for the pK_D^{therm} of 6.01 ± 0.30 rel.un. So, this method proves that in comparatively concentrated solutions ($5.8 \cdot 10^{-4} \leq C_N \leq 5.8 \cdot 10^{-2}$ eq/l), $C_{60}[=C(COOH)_2]_3$ is a weak

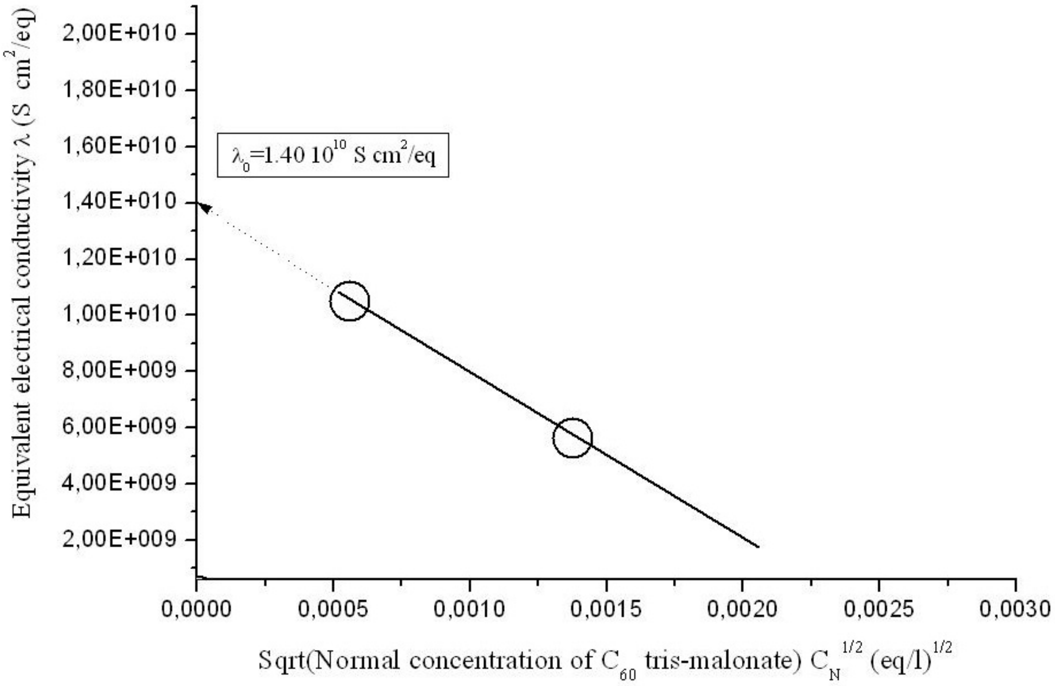

FIG. 3. Extrapolation of concentration dependence of equivalent electric conductivity for $C_{60}[=C(COOH)_2]_3$ aqueous solutions for an infinitely dilute solution in the variables $\lambda(C_N^{1/2})$

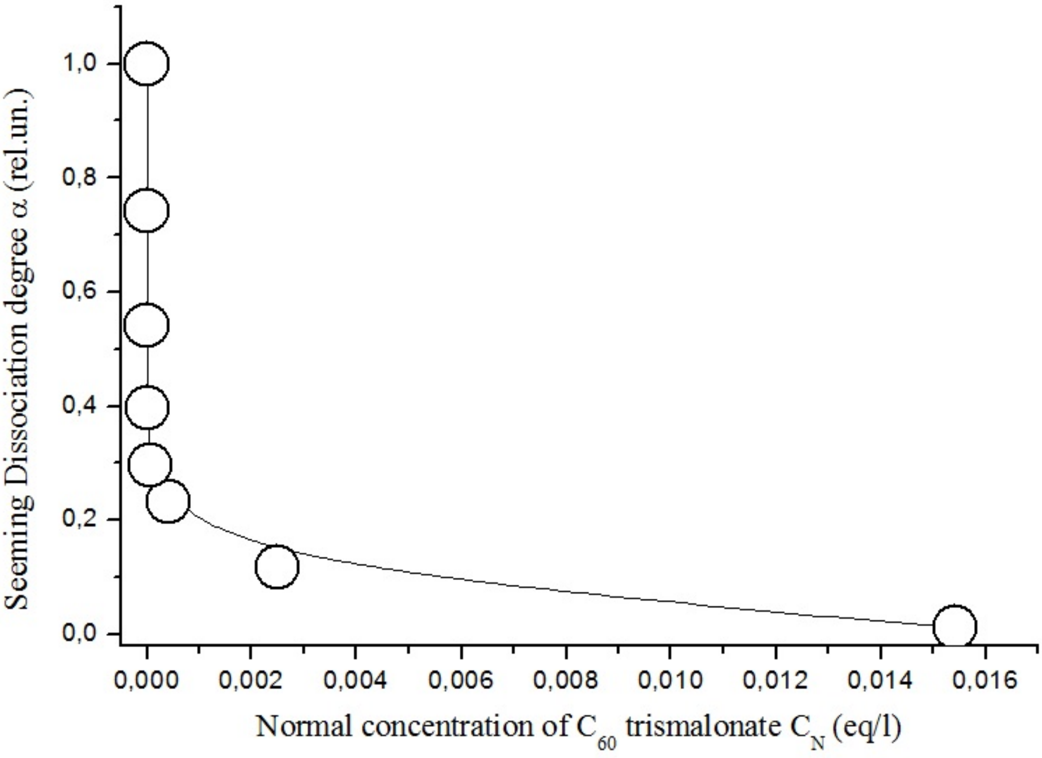

FIG. 4. Concentration dependence of apparent dissociation degree α

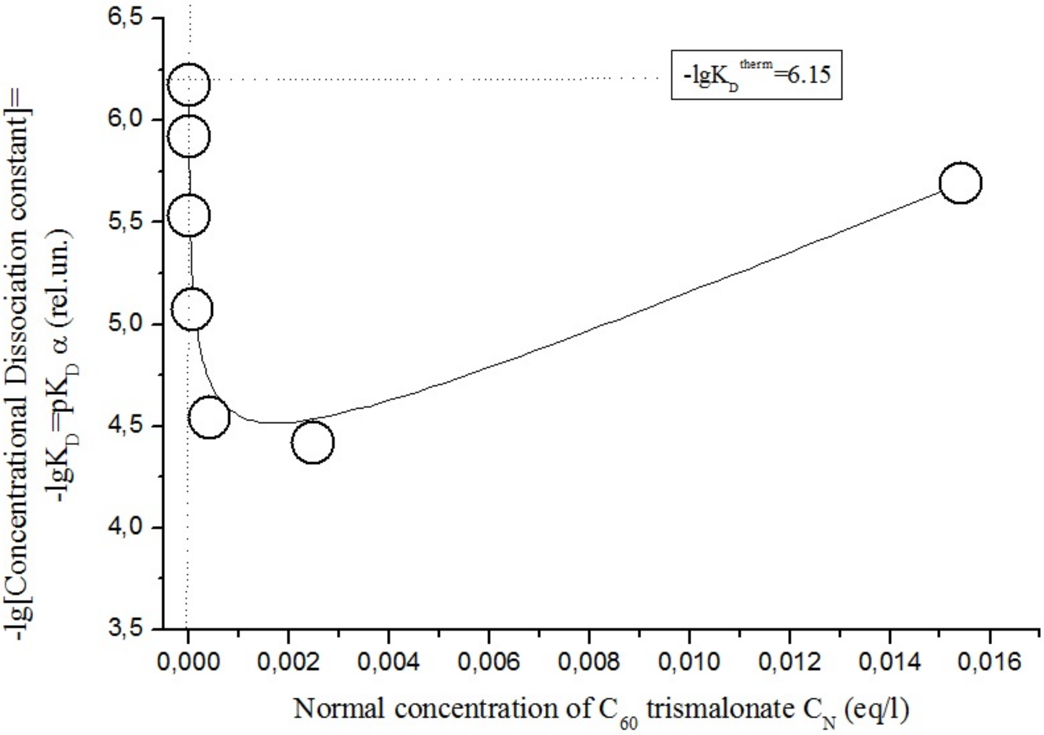

FIG. 5. Concentration dependence of the logarithm of concentration dissociation constant: $pK_D = -\lg K_D$

TABLE 2. Experimental data, concerning pH of $C_{60}[=C(COOH)_2]_3$ aqueous solutions

Solution number No.	Volume concentration C (g/l)	Equivalent concentration C_N (eq/l)	Hydrogen indicator (rel.un.)	Seeming dissociation degree α (rel.un.)	lg (concentration dissociation constant) pK_D (rel.un.)
9	0.0	0.0	—	1.00 (extrapolation)	6.01 (extrapolation)
10	0.1	0.000585	9.00	0.0171	6.76
11	1.0	0.00585	9.41	0.00439	6.92
12	2.5	0.0146	9.62	0.00272	6.97
13	5.0	0.0292	9.69	0.00171	7.07
14	10.0	0.0585	9.80	0.00108	7.17

electrolyte. Obviously in more dilute solutions the tris-malonate will be moderately electrolytic and in very dilute solutions, will be formally strong.

If one compares the thermodynamic dissociation constant – K_D^{therm}, obtained by both methods — i.e. from electric conductivity and pH, they will note fairly good agreement, $pK_D^{therm} = 6.07 \pm 0.40$ rel.un. However, if one compares the concentration dissociation constant – pK_D, they will see sufficient deviation in the concentration functions $pK_D(C_N)$. From the electric conductivity, the pK_D changes during dilution of the solution in the range ($pK_D = 5.69 > 6.15$), crossing through the minimum), and from pH, it changes in the range

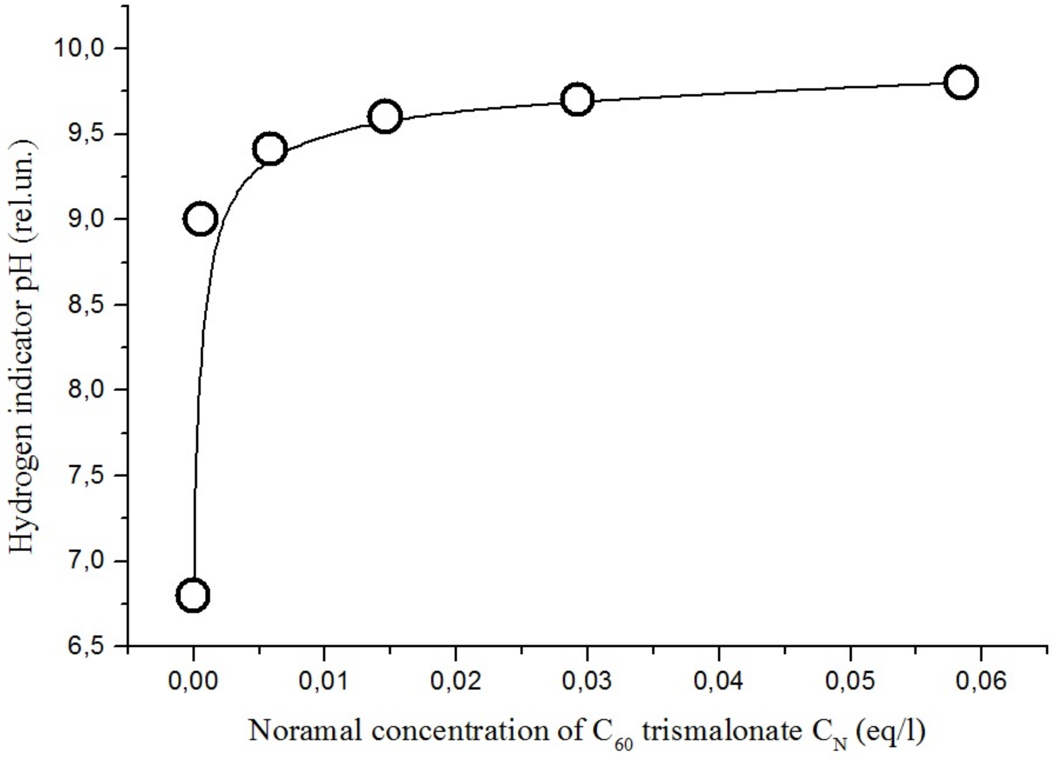

FIG. 6. Concentration dependence of pH for $C_{60}[=C(COOH)_2]_3$ aqueous solutions

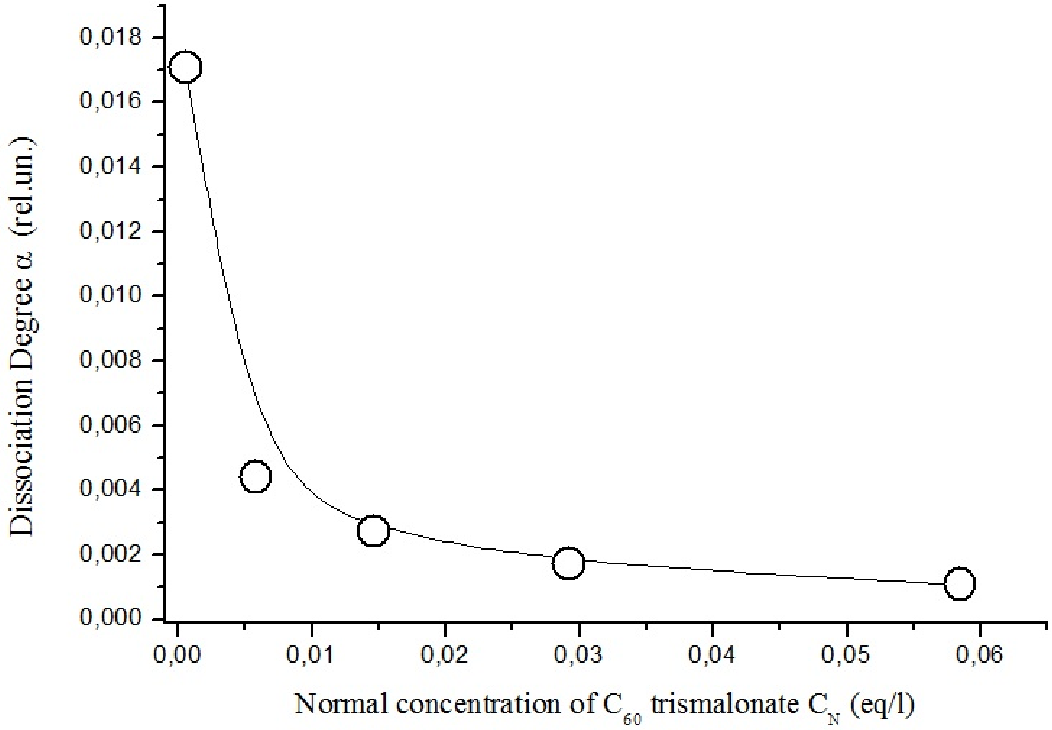

FIG. 7. Concentration dependence of apparent dissociation degree α for $C_{60}[=C(COOH)_2]_3$ aqueous solutions

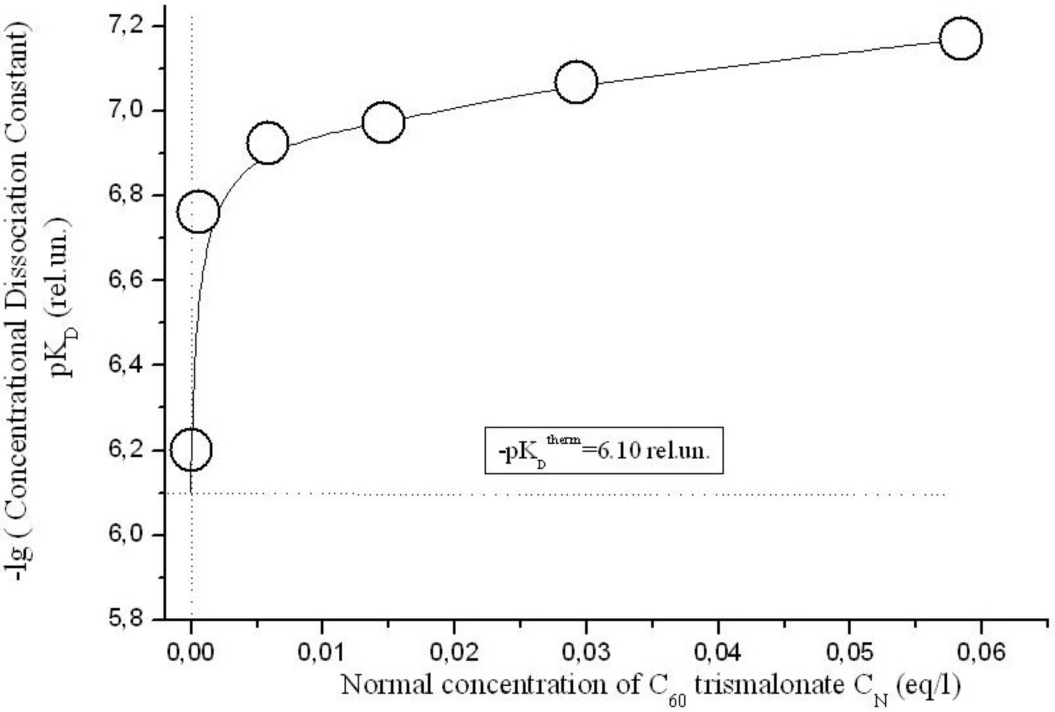

FIG. 8. Concentration dependence of lg (concentration dissociation constant) pK_D of $C_{60}[=C(COOH)_2]_3$ aqueous solutions

($pK_D = 7.17 > 6.01$), changing monotonicity. We can explain this fact, first, the concentration ranges in the investigations were different: ($3.1 \cdot 10^{-7} \leq C_N \leq 1.5 \cdot 10^{-2}$ eq/l) and ($5.8 \cdot 10^{-4} \leq C_N \leq 5.8 \cdot 10^{-2}$ eq/l), correspondingly. The second reason, in our opinion, is that we have neglected the transmission coefficients of the ions and activity coefficients of ions and non-dissociated forms, correspondingly, but the concentration dependence of these functions is sufficiently different for both types of the experiment.

Thus, the concentration dependence of electric conductivity and pH for aqueous solutions of the water soluble light fullerene – $C_{60}[=C(COOH)_2]_3$ tris-malonate were investigated. The dissociation degree and constants of the tris-malonate were calculated. The values for the thermodynamic dissociation constants, calculated using the solutions' electrical conductivity and pH data, are reasonably similar.

Acknowledgement

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