CONCENTRATION DEPENDENCE OF ELECTRIC CONDUCTIVITY AND pH FOR AQUEOUS SOLUTIONS OF WATER-SOLUBLE LIGHT FULLERENE — $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ TRIS-MALONATE

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Studies of the concentration dependence of electric conductivity and pH for aqueous solutions of the light fullerene — $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ 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 $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ in aqueous solutions were calculated. Thermodynamic dissociation constants of $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ 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 $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ [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 - $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ tris-malonate aqueous solutions. From both data, the apparent degree of dissociation, concentration and thermodynamic dissociation constants of $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ in aqueous solutions were calculated. These investigations will be used to determine the state of the $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ species in aqueous solutions.

2. Electric conductivity of water solutions of $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$

The concentration dependence of specific electric conductivity of aqueous $C_{60}[^{\text{=}}C(\text{COOH})_{2}]_{3}$ solutions at 25 °C — $\kappa$ (S·cm$^{-1}$) was investigated by the measurement of the specific resistance of the solutions $\rho$ (Ω·cm):
\[ \kappa = 1/\rho, \quad (1) \]

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 \( \kappa(W) \) (where \( W \) is mole fraction of \( \text{C}_{60}[=\text{C}(_2\text{COOH})_3]_3 \)) 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 (\( \lambda = \text{S}\cdot\text{cm}^2/\text{eq} \)), i.e. conductivity for such electrolyte volume, which contains 1 equivalent of electrolyte was calculated:

\[ \lambda = 1000\kappa/C_N, \quad (2) \]

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 \( \lambda \) values when the concentration of the solutions’ \( C_N \) decreases.

![Graph](image.png)

**Fig. 1.** Concentration dependence of specific electric conductivity of \( \text{C}_{60}[=\text{C}(_2\text{COOH})_3]_3 \) aqueous solutions

In order to determine the equivalent electric conductivity value in infinitely dilute solutions – \( \lambda_0 \), 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]:

\[ \lambda = \lambda_0 - AC_N^{1/2}, \quad (3) \]

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

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

<table>
<thead>
<tr>
<th>Solution number No.</th>
<th>Apparent dissociation degree $\alpha$ (rel.un.)</th>
<th>$-\lg$ (concentration dissociation constant) $pK_D$ (rel.un.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0 (extrapolation)</td>
<td>6.15 (extrapolation)</td>
</tr>
<tr>
<td>2</td>
<td>0.74</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>0.54</td>
<td>5.92</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>5.53</td>
</tr>
<tr>
<td>5</td>
<td>0.30</td>
<td>5.07</td>
</tr>
<tr>
<td>6</td>
<td>0.23</td>
<td>4.54</td>
</tr>
<tr>
<td>7</td>
<td>0.11</td>
<td>4.41</td>
</tr>
<tr>
<td>8</td>
<td>0.011</td>
<td>5.69</td>
</tr>
</tbody>
</table>

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

$$\alpha = \frac{\lambda}{\lambda_0}, \quad (4)$$

and is represented in Table 1 and Fig. 4. ($\lambda_0 \approx 1.40\cdot10^{10}$ 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 – $\gamma_i = \gamma_{\pm} = 1$):

$$K_D = C_N\alpha^2/(1 - \alpha), \quad (5)$$

and is also represented in Table 1 and Fig. 5. Thermodynamic dissociation constant – $K_D^{\text{therm}}$ was calculated by the extrapolation of $K_D(C_N)$ values for an infinitely dilute solution:
According to our calculation, one obtains the value $pK_D^{\text{therm}} = 6.15 \pm 0.25$ rel.un.

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

The concentration dependence of pH for aqueous $\text{C}_{60}[=\text{C}(\text{COOH})_2]_3$ 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 $\text{NH}_4\text{OH} – \text{NH}_4\text{Cl}$. Accuracy of measurements was $\Delta \text{pH} = \pm 0.1$ rel.un. The results are represented in the Table 2 and Fig. 6.

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

$$\alpha = \exp\left(\left(14 - pH\right) \cdot \ln 10\right) / C_N.$$  \hspace{1cm} (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 $\alpha$ and $K_D$ concentration dependencies are also represented in the Table 2 and Fig. 7, 8.

The thermodynamic dissociation constant – $K_D^{\text{therm}}$ 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 $pK_D^{\text{therm}}$ of $6.01 \pm 0.30$ 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), $\text{C}_{60}[=\text{C}(\text{COOH})_2]_3$ is a weak
Concentration dependence of electric conductivity and hydrogen indicator...

**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 $\alpha$. 

$\lambda_0 = \text{1.40} \times 10^{9} \text{ S cm}^2\text{eq}^{-1}$. 

$\text{Sqrt(Normal concentration of C}_{60} \text{tris-malonate C}_{N}^{1/2}\text{(eq/l)}^{1/2}}$
FIG. 5. Concentration dependence of the logarithm of concentration dissociation constant: $pK_D = -\log K_D$

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

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

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 $-K_D^{\text{therm}}$, obtained by both methods — i.e. from electric conductivity and pH, they will note fairly good agreement, $pK_D^{\text{therm}} = 6.07 \pm 0.40$ 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
Concentration dependence of electric conductivity and hydrogen indicator . . .

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

**FIG. 7.** Concentration dependence of apparent dissociation degree $\alpha$ for $C_{60}[\text{=C(COOH)}_2]_3$ 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: 
$(3.1 \cdot 10^{-7} \leq C_N \leq 1.5 \cdot 10^{-2} \text{ eq/l})$ and 
$(5.8 \cdot 10^{-4} \leq C_N \leq 5.8 \cdot 10^{-2} \text{ eq/l})$, 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.

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References


