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# SOLUBILITY OF 4,7-DIOXO-7-(4-METHYLPHENYL)HEPTANOIC ACID IN SOME ORGANIC SOLVENTS

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The temperature dependences of the solubility of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid in organic solvents, namely methyl acetate, ethyl acetate, acetonitrile, acetone, n-propanol, iso-propanol, n-butanol and iso-butanol, were studied and the thermodynamic parameters of solubility were calculated. The enthalpy and entropy of melting of the acid under study were determined by differential thermal analysis. The thermodynamic parameters were recalculated to the generally accepted temperature of 298.15 K. The enthalpies and entropies of mixing of the components at 298.15 K were calculated.

*Keywords:* solubility, enthalpy of dissolution, enthalpy of mixing, enthalpy of melting, 4,7-dioxo-7-(4-methylphenyl)heptanoic acid.

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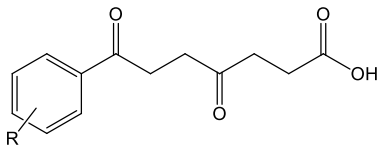
## 1. Introduction

The synthesis of new organic substances is a key area in organic chemistry and the pharmaceutical industry [1]. Thanks to the continuous development of synthetic chemistry, chemical technologies and synthesis methods, it has become possible to create molecules with desirable properties that have applications in medicine, agriculture, materials science and other fields.

Promising substances for the above industries are phenacyllevulinic acid derivatives, which combine two functional groups: the phenyl group (phenacyl) [2-4] and levulinic acid (γ-ketovaleric acid) [5-7], which has ketone and carboxyl groups.



These compounds are an intermediate in the formation of various bioactive substances, and can also be involved in alkylation and acylation reactions to form new furan heterocycles with potential activity as antibacterial or antitumour agents [8–12], as a basis for the development of insecticides, fungicides and herbicides that help protect crops from pests and diseases [13,14] to create new materials with unique properties or catalysts for various chemical reactions [15,16].

However most processes involving the transformation of one substance into another are accompanied by the release or absorption of heat. Therefore information about the values of thermal effect parameters and the thermal nature of the processes is one of the main data required for the optimisation of synthesis or control of production processes.

At present thermodynamic parameters have been experimentally established for most simple (monofunctional) organic compounds but such studies continue to be performed for more complex polyfunctional compounds [17–21], but such studies are conducted less than is required for new technological production processes.

Despite the simple process of synthesis of this class of substances their thermochemical properties of individual substances and solutions remain unclear.

The purpose of this work is to study and analyse the thermodynamic characteristics of the solubility of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid in various organic solvents.

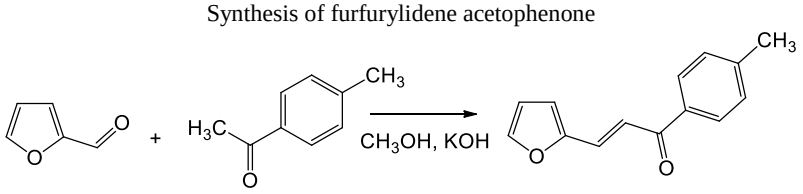
**2. Materials and methods of research**

To study the thermodynamic parameters of the solubility of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid. the following solvents were chosen: methyl and ethyl acetate, acetonitrile, dimethyl ketone and a number of alcohols: propanol, iso-propanol, n-butanol, and iso-butanol.

The synthesis of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid was carried out in the following sequence. The first step was the synthesis of furfurylidene acetophenone:

*Scheme 1*

Synthesis of furfurylidene acetophenone

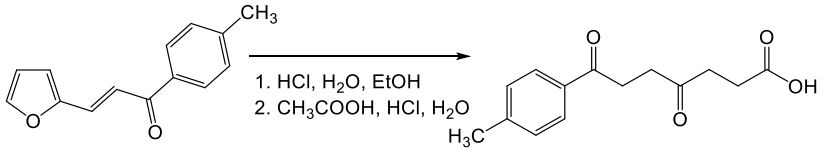



To a mixture of 100 g of acetophenone. 80 g of furfural in 200 ml of methanol with intense stirring add 0.05 mol of KOH in the form of a 15 % solution. The temperature is maintained in the range of 293–298 K (water bath). The reaction mixture is stirred for 3 hours neutralised with acetic acid diluted with 400 ml of water extracted with methylene chloride washed with water and separated on a separatory funnel dried with sodium sulfate. The solvent is removed and the residue is distilled in vacuum at 423 K and 267 Pa.

At the second stage the test substance 4,7-dioxo-7-(4-methylphenyl)heptanoic acid is obtained.

*Scheme 2*

Synthesis of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid




A mixture of 0.2 mol of the corresponding furfurylidene acetophenone, 300 ml of ethyl alcohol 90 ml of conc. HCl and 15 ml of water were refluxed for 24 hours. The alcohol was distilled off under reduced pressure 200 ml of conc. was added to the obtained black viscous mass HCl 200 ml of glacial acetic acid, 400 ml of water and heated under reflux for 3 hours. After cooling the formed light yellow crystalline precipitate was decanted from the resin residue filtered washed three times with cold water and recrystallized from aqueous alcohol. Yield 65 %, m.p. 391–392 K.

For solubility studies the substance obtained after 4-fold recrystallisation was used. The purity of the acid is indirectly confirmed by the unchanged value of the melting point and the value of the enthalpy of melting within the experimental error.

To study the solubility of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid a number of widely used organic solvents with boiling points close to 371 K and different polarities produced by Merck, were chosen namely acetonitrile CAS 75-05-8, w/w ≥99.9 %; methyl acetate CAS 79-20-9, w/w ≥99.0 %; ethyl acetate CAS 71-43-2, w/w ≥99.8 %; n-propanol CAS 71-23-8, w/w ≥99.5 %; iso-propanol CAS 67-63-0, mass fraction of the main substance ≥99.8 % w/w; n-butanol CAS 71-36-3, mass fraction of the main substance ≥99.9 % w/w; iso-butanol CAS 78-92-2, mass fraction of the main substance ≥99.8 % w/w; acetone CAS 67-64-1, mass fraction of the main substance ≥99.5 % w/w.

The dissolution process of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid was carried out in a sealed vessel with a thermometer stirrer and a sampling hole. The dissolution vessels were placed in a thermostat that maintained a temperature accuracy of ±0.1 K. Stirring was performed at 30 rpm. and the dissolution process lasted 120 min with constant stirring. Samples for analysis were taken after the solution had completely settled. The study was carried out both at increasing and decreasing temperatures. Samples of solutions weighing 1.0–2.0 g were taken and placed in pre-prepared and weighed bureks. which were hermetically sealed and weighed to determine the mass of the saturated solution. After that. the bureaux were opened and the solvent was evaporated in a drying oven at a temperature of 323–373 K until a constant weight was reached. The mass of the dry residue was determined by weighing the bullion after drying. Weighing at all stages was carried out on a balance VLR-200 with an accuracy of ±0.0002 g.

The determination of the enthalpy of fusion ($_{\Delta fus}H$) of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid was carried out using differential thermal analysis (DTA) data. The samples were analyzed on a Paulik-Paulik-Erdey Q-1500 D derivatograph in a dynamic mode with a heating rate of 5 K/min in an air atmosphere.

To calculate $_{\Delta fus}H$ we used the thermochemical equation (1), which takes into account the correction for the possible mass loss of the sample during the melting process:

$$K \cdot S = q_{fus} + q_{vap} = m_o \cdot \Delta_{fus}H + \Delta m_{vap} \cdot \Delta_{vap}H, \quad (1)$$

where $q_{fus}$ and $q_{var}$ are the amount of heat (J) absorbed during the melting and evaporation of the sample, respectively; $m_o$ is the mass of the sample (g) corresponding to

the temperature of its melting onset $T_{fus}$; $\Delta m_{vap}$ is the mass loss of the sample (vapor mass, g) during the period taken into account to determine the peak area S (K·s) under the DTA curve; K is the heat transfer coefficient (J/K·s) for the used installation equal to $K = 8.202 \cdot 10^{-5}$; $\Delta_{fus}H$ and $\Delta_{vap}H$ are the specific enthalpies of melting and vaporization of the substance (J/g). $\Delta_{vap}H$ was calculated from the thermogravimetric analysis according to the method described in detail in [22].

### 3. Research results and discussion

Table 1 shows the primary results of the dissolution process of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid where the masses of solvent $m_1$ and solute $m_2$, g are indicated; solubility expressed in mole fractions ($x_2$); temperature $T$, K at which the solubility was determined. The experimental data were processed by the least squares method and presented in the linear form of the Schröder equation (2) [23], which is also presented in Table 1.

$$\ln x_2 = -\Delta_{sol}H/RT + \Delta_{sol}S/R, \quad (2)$$

where $\Delta_{sol}H$ and $\Delta_{sol}S$ are the differential changes in enthalpy and solubility entropy. Hereinafter the errors of all values are given for a significance level of 0.95.

*Table 1*

Temperature dependence of the solubility of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid in organic solvents

| $T$, K | $m_1$, г | $m_2$, г | $X_2 \cdot 10$ | $T$, K | $m_1$, г | $m_2$, г | $X_2 \cdot 10$ | $T$, K | $m_1$, г | $m_2$, г | $X_2 \cdot 10$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| **Methyl acetate** | | | | | | | | | | | |
| 275.95 | 1.5322 | 0.1469 | 2.78 | 281.65 | 1.6308 | 0.2046 | 3.61 | 284.65 | 1.4508 | 0.2041 | 4.03 |
| 275.95 | 1.5664 | 0.1502 | 2.78 | 281.65 | 1.3379 | 0.1676 | 3.60 | 287.65 | 0.9008 | 0.1438 | 4.55 |
| 275.95 | 1.7827 | 0.1708 | 2.78 | 283.95 | 1.1443 | 0.1527 | 3.83 | 287.65 | 1.0746 | 0.1702 | 4.51 |
| 278.75 | 1.2483 | 0.1357 | 3.14 | 283.95 | 1.3022 | 0.1743 | 3.84 | 287.65 | 1.4382 | 0.2289 | 4.53 |
| 278.75 | 1.3804 | 0.1478 | 3.10 | 283.95 | 1.1258 | 0.1524 | 3.88 | 288.85 | 1.2430 | 0.2141 | 4.89 |
| 278.75 | 1.3545 | 0.1450 | 3.10 | 284.65 | 1.1197 | 0.1557 | 3.98 | 288.85 | 1.3764 | 0.2407 | 4.96 |
| 281.65 | 1.3968 | 0.1750 | 3.60 | 284.65 | 1.1528 | 0.1618 | 4.02 | 288.85 | 1.2076 | 0.2096 | 4.92 |
| **$\ln x_2 = (8.86 \pm 0.44) - (3433 \pm 124) \cdot 1/T$** | | | | | | | | | | | |
| **Ethyl acetate** | | | | | | | | | | | |
| 280.65 | 1.1645 | 0.0276 | 0.84 | 284.55 | 1.4310 | 0.0384 | 0.94 | 294.15 | 1.2836 | 0.0558 | 1.52 |
| 280.65 | 1.4504 | 0.0345 | 0.84 | 284.55 | 1.5916 | 0.0426 | 0.94 | 295.95 | 1.5180 | 0.0688 | 1.58 |
| 280.65 | 1.6498 | 0.0391 | 0.83 | 288.05 | 1.5453 | 0.0493 | 1.12 | 295.95 | 1.8710 | 0.0845 | 1.58 |
| 281.85 | 1.2229 | 0.0301 | 0.87 | 288.05 | 1.6390 | 0.0523 | 1.12 | 295.95 | 1.4994 | 0.0682 | 1.59 |
| 281.85 | 1.5805 | 0.0390 | 0.87 | 288.05 | 1.6058 | 0.0514 | 1.12 | 299.65 | 0.9918 | 0.0528 | 1.86 |
| 281.85 | 1.6867 | 0.0416 | 0.87 | 290.65 | 1.6619 | 0.0597 | 1.26 | 299.65 | 1.5643 | 0.0832 | 1.85 |
| 284.15 | 1.0604 | 0.0282 | 0.93 | 290.65 | 1.7017 | 0.0611 | 1.26 | 299.65 | 1.9720 | 0.1039 | 1.84 |
| 284.15 | 1.7288 | 0.0459 | 0.93 | 290.65 | 1.5772 | 0.0566 | 1.26 | 302.45 | 1.3449 | 0.0780 | 2.02 |
| 284.15 | 1.7719 | 0.0471 | 0.93 | 294.15 | 1.5865 | 0.0687 | 1.51 | 302.45 | 1.5073 | 0.0867 | 2.00 |
| 284.55 | 0.9891 | 0.0265 | 0.94 | 294.15 | 1.8345 | 0.0790 | 1.51 | 302.45 | 2.1500 | 0.1227 | 1.99 |
| **$\ln x_2 = (7.93 \pm 0.32) - (3574 \pm 88) \cdot 1/T$** | | | | | | | | | | | |
| **Acetonitrile** | | | | | | | | | | | |
| 277.75 | 1.2697 | 0.0634 | 0.82 | 281.05 | 1.3849 | 0.0776 | 0.92 | 288.25 | 1.2742 | 0.0911 | 1.17 |
| 277.75 | 1.4531 | 0.0722 | 0.81 | 281.75 | 0.9367 | 0.0537 | 0.94 | 288.25 | 1.3978 | 0.1003 | 1.17 |
| 277.75 | 1.2517 | 0.0618 | 0.81 | 281.75 | 1.3437 | 0.0775 | 0.95 | 290.95 | 1.3363 | 0.1078 | 1.32 |
| 278.85 | 1.3640 | 0.0710 | 0.85 | 281.75 | 1.2272 | 0.0707 | 0.94 | 290.95 | 1.3666 | 0.1115 | 1.33 |
| 278.85 | 1.4600 | 0.0750 | 0.85 | 286.15 | 1.2387 | 0.0818 | 1.08 | 290.95 | 1.0476 | 0.0854 | 1.33 |
| 278.85 | 1.5275 | 0.0792 | 0.85 | 286.15 | 1.1222 | 0.0738 | 1.08 | 293.25 | 1.2286 | 0.1052 | 1.40 |
| 281.05 | 1.2590 | 0.0704 | 0.92 | 286.15 | 1.4823 | 0.0969 | 1.07 | 293.25 | 1.4874 | 0.1274 | 1.40 |
| 281.05 | 1.6945 | 0.0949 | 0.92 | 288.25 | 0.9822 | 0.0704 | 1.17 | 293.25 | 1.2779 | 0.1097 | 1.40 |
| **$\ln x_2 = (5.48 \pm 0.28) - (2858 \pm 81) \cdot 1/T$** | | | | | | | | | | | |

*End of table 1*

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Acetone** | | | | | | | | | | | |
| 277.15 | 1.1420 | 0.1133 | 2.27 | 279.65 | 1.0362 | 0.1154 | 2.54 | 285.25 | 1.1177 | 0.1456 | 2.96 |
| 277.15 | 1.1112 | 0.1113 | 2.29 | 279.65 | 1.2697 | 0.1411 | 2.53 | 285.25 | 1.3126 | 0.1722 | 2.98 |
| 277.15 | 1.1398 | 0.1146 | 2.30 | 279.65 | 1.4028 | 0.1563 | 2.54 | 285.25 | 1.5095 | 0.1989 | 2.99 |
| 277.65 | 0.9383 | 0.0973 | 2.37 | 283.45 | 1.4049 | 0.1702 | 2.76 | 286.95 | 1.3711 | 0.1898 | 3.14 |
| 277.65 | 1.2593 | 0.1288 | 2.34 | 283.45 | 1.0435 | 0.1265 | 2.76 | 286.95 | 1.2727 | 0.1758 | 3.13 |
| 277.65 | 1.1395 | 0.1166 | 2.34 | 283.45 | 1.1060 | 0.1330 | 2.74 | 286.95 | 1.2140 | 0.1678 | 3.13 |
| 278.65 | 1.0428 | 0.1107 | 2.42 | 283.75 | 1.0078 | 0.1237 | 2.79 | 288.05 | 0.8907 | 0.1283 | 3.26 |
| 278.65 | 0.9246 | 0.0984 | 2.43 | 283.75 | 1.1171 | 0.1370 | 2.79 | 288.05 | 1.2510 | 0.1818 | 3.29 |
| 278.65 | 1.0844 | 0.1155 | 2.43 | 283.75 | 1.2228 | 0.1502 | 2.79 | 288.05 | 1.0745 | 0.1551 | 3.27 |
| **ln $x_2$=(5.17±0.36)–(2476±103)·1/T** | | | | | | | | | | | |
| ***n*-Propanol** | | | | | | | | | | | |
| 285.65 | 0.9291 | 0.0157 | 0.41 | 291.65 | 0.9239 | 0.0234 | 0.61 | 294.35 | 1.0971 | 0.0327 | 0.72 |
| 285.65 | 1.2874 | 0.0221 | 0.41 | 291.65 | 1.5816 | 0.0397 | 0.60 | 294.35 | 1.3164 | 0.0394 | 0.72 |
| 285.65 | 1.3523 | 0.0232 | 0.41 | 291.65 | 1.2781 | 0.0321 | 0.61 | 294.35 | 1.5000 | 0.0448 | 0.72 |
| 288.65 | 1.5176 | 0.0312 | 0.50 | 291.65 | 0.9239 | 0.0234 | 0.61 | 296.05 | 0.9040 | 0.0308 | 0.82 |
| 288.65 | 1.4057 | 0.0288 | 0.49 | 291.65 | 1.5816 | 0.0397 | 0.60 | 296.05 | 1.9915 | 0.0676 | 0.82 |
| 288.65 | 1.3387 | 0.0274 | 0.49 | 291.65 | 1.2781 | 0.0321 | 0.61 | 296.05 | 1.4897 | 0.0510 | 0.82 |
| 289.15 | 1.2151 | 0.0251 | 0.50 | 292.65 | 1.2043 | 0.0327 | 0.65 | 297.45 | 1.0284 | 0.0396 | 0.92 |
| 289.15 | 1.5621 | 0.0321 | 0.49 | 292.65 | 1.2598 | 0.0342 | 0.65 | 297.45 | 1.7694 | 0.0685 | 0.93 |
| 289.15 | 1.6144 | 0.0336 | 0.50 | 292.65 | 1.3091 | 0.0355 | 0.65 | 297.45 | 1.3909 | 0.0538 | 0.93 |
| **ln $x_2$=(14.98±0.78)–(5857±227)·1/T** | | | | | | | | | | | |
| **Iso-propanol** | | | | | | | | | | | |
| 284.35 | 1.1941 | 0.0191 | 0.39 | 288.65 | 1.2202 | 0.0252 | 0.50 | 294.05 | 1.4334 | 0.0456 | 0.77 |
| 284.35 | 1.0830 | 0.0171 | 0.38 | 290.55 | 1.4874 | 0.0346 | 0.56 | 294.05 | 1.4181 | 0.0452 | 0.77 |
| 284.35 | 1.0625 | 0.0168 | 0.38 | 290.55 | 1.2550 | 0.0291 | 0.56 | 296.15 | 1.3294 | 0.0490 | 0.89 |
| 286.55 | 0.9892 | 0.0172 | 0.42 | 290.55 | 1.2375 | 0.0288 | 0.56 | 296.15 | 1.4001 | 0.0518 | 0.89 |
| 286.55 | 1.3155 | 0.0229 | 0.42 | 291.45 | 1.2134 | 0.0306 | 0.61 | 296.15 | 1.4098 | 0.0520 | 0.88 |
| 286.55 | 1.2323 | 0.0211 | 0.41 | 291.45 | 1.5501 | 0.0390 | 0.61 | 297.65 | 0.9278 | 0.0387 | 1.00 |
| 288.65 | 1.2201 | 0.0252 | 0.50 | 291.45 | 1.5375 | 0.0387 | 0.61 | 297.65 | 1.8651 | 0.0785 | 1.01 |
| 288.65 | 1.3033 | 0.0268 | 0.50 | 294.05 | 1.1562 | 0.0370 | 0.77 | 297.65 | 1.6469 | 0.0690 | 1.00 |
| **ln $x_2$=(16.68±0.92)–(6341±267) ·1/T** | | | | | | | | | | | |
| ***n*-Butanol** | | | | | | | | | | | |
| 283.65 | 0.9030 | 0.0162 | 0.53 | 289.65 | 1.1910 | 0.0266 | 0.66 | 294.65 | 1.2165 | 0.0323 | 0.79 |
| 283.65 | 1.1341 | 0.0206 | 0.54 | 290.15 | 1.3325 | 0.0302 | 0.67 | 294.65 | 1.3659 | 0.0362 | 0.79 |
| 283.65 | 1.0821 | 0.0194 | 0.53 | 290.15 | 1.2823 | 0.0292 | 0.68 | 295.15 | 0.9630 | 0.0263 | 0.81 |
| 286.85 | 0.8893 | 0.0178 | 0.59 | 290.15 | 1.4227 | 0.0323 | 0.67 | 295.15 | 1.4069 | 0.0384 | 0.81 |
| 286.85 | 1.3240 | 0.0268 | 0.60 | 292.15 | 1.1643 | 0.0283 | 0.72 | 295.15 | 1.4008 | 0.0382 | 0.81 |
| 286.85 | 1.3040 | 0.0260 | 0.59 | 292.15 | 1.0111 | 0.0246 | 0.72 | 295.65 | 1.0117 | 0.0281 | 0.82 |
| 289.15 | 1.0746 | 0.0236 | 0.65 | 292.15 | 1.2324 | 0.0303 | 0.73 | 295.65 | 1.1299 | 0.0311 | 0.82 |
| 289.15 | 1.1127 | 0.0243 | 0.65 | 294.15 | 1.1715 | 0.0306 | 0.77 | 295.65 | 1.3805 | 0.0384 | 0.82 |
| 289.15 | 1.2120 | 0.0266 | 0.65 | 294.15 | 1.3186 | 0.0347 | 0.78 | 297.65 | 1.0989 | 0.0326 | 0.88 |
| 289.65 | 0.9480 | 0.0212 | 0.66 | 294.15 | 1.0949 | 0.0289 | 0.78 | 297.65 | 1.0390 | 0.0305 | 0.87 |
| 289.65 | 1.2538 | 0.0282 | 0.67 | 294.65 | 0.9631 | 0.0255 | 0.78 | 297.65 | 1.3262 | 0.0393 | 0.88 |
| **ln $x_2$=(5.34±0.14)–(2999±42) ·1/T** | | | | | | | | | | | |
| **Iso-butanol** | | | | | | | | | | | |
| 277.95 | 1.0265 | 0.0407 | 1.17 | 285.65 | 0.9849 | 0.0536 | 1.60 | 293.95 | 0.7505 | 0.0590 | 2.29 |
| 277.95 | 1.3412 | 0.0533 | 1.17 | 285.65 | 1.1407 | 0.0623 | 1.60 | 293.95 | 1.0804 | 0.0840 | 2.27 |
| 277.95 | 1.2197 | 0.0488 | 1.18 | 285.65 | 1.2060 | 0.0656 | 1.60 | 293.95 | 0.9760 | 0.0765 | 2.29 |
| 280.95 | 1.1968 | 0.0519 | 1.28 | 288.65 | 0.9737 | 0.0606 | 1.82 | 297.65 | 1.2112 | 0.1084 | 2.60 |
| 280.95 | 1.4464 | 0.0643 | 1.31 | 288.65 | 1.2160 | 0.0750 | 1.81 | 297.65 | 1.4552 | 0.1309 | 2.62 |
| 280.95 | 1.2278 | 0.0532 | 1.28 | 288.65 | 1.0850 | 0.0659 | 1.78 | 297.65 | 1.3110 | 0.1180 | 2.62 |
| 284.45 | 1.0191 | 0.0510 | 1.47 | 291.65 | 1.2288 | 0.0881 | 2.10 | 303.65 | 1.3693 | 0.1542 | 3.25 |
| 284.45 | 1.3739 | 0.0686 | 1.47 | 291.65 | 1.4382 | 0.1021 | 2.08 | 303.65 | 1.2474 | 0.1395 | 3.23 |
| 284.45 | 1.2749 | 0.0620 | 1.43 | 291.65 | 1.3659 | 0.0976 | 2.09 | 303.65 | 1.4354 | 0.1622 | 3.26 |
| **ln $x_2$=(7.97±0.31)–(3458±90) ·1/T** | | | | | | | | | | | |

Differential changes in the enthalpy ($\Delta_{sol}H^o$) and entropy ($\Delta_{sol}S^o$) of acid dissolution were calculated using the temperature dependence of solubility (Table 1) according to Equations 3–4 and are presented in Table 2:

$$\Delta_{sol}H^o = R \cdot B, \quad (3)$$

$$\Delta_{sol}S^o = R \cdot A. \quad (4)$$

*Table 2*

Thermodynamic parameters of solubility of 4.7-dioxo-7-(4-methylphenyl)heptanoic acid in organic solvents at 298.15 K

| No. | Solvent | $x_2$ | $\Delta_{sol}H^o$ kJ/mol | $\Delta_{sol}S^o$ J/mol | $\Delta_{mix}H^o$ kJ/mol | $\Delta_{mix}S^o$ J/mol |
|---|---|---|---|---|---|---|
| 1 | methyl acetate | 0.0702 | 28.5±1.0 | 73.7±3.7 | –2.6±3.0 | –3.4±7.8 |
| 2 | ethyl acetate | 0.0172 | 29.71±0.73 | 65.9±2.7 | –1.4±2.9 | –1.2±7.7 |
| 3 | acetonitrile | 0.0164 | 23.76±0.67 | 45.6±2.3 | –7.3±2.9 | –31.5±7.6 |
| 4 | acetone | 0.0435 | 20.59±0.86 | 43.0±3.0 | –10.5±2.9 | –34.1±7.8 |
| 5 | n-propanol | 0.0094 | 48.7±1.9 | 124.5±6.5 | 17.6±3.4 | 47.4±9.7 |
| 6 | iso-propanol | 0.0102 | 52.7±2.2 | 138.8±7.6 | 21.6±3.6 | 62.0±10.0 |
| 7 | n-butanol | 0.0089 | 24.93±0.35 | 44.4±1.2 | –6.2±2.8 | –32.7±7.3 |
| 8 | iso-butanol | 0.0266 | 28.75±0.75 | 66.3±2.5 | –2.4±2.9 | –10.8±7.6 |

It is known from [24] that the calculated thermodynamic parameters of dissolution $\Delta_{sol}H^o$ and $\Delta_{sol}S^o$ include mixing processes ($\Delta_{mix}H^o$; $\Delta_{mix}S^o$) and the phase transition of a crystalline substance into the liquid phase of the solution ($\Delta_{fus}H^o$; $\Delta_{fus}S^o$) described by equations 5, 6:

$$\Delta_{sol}H^o = \Delta_{mix}H^o + \Delta_{fus}H^o , \quad (5)$$

$$\Delta_{sol}S^o = \Delta_{mix}S^o + \Delta_{fus}S^o . \quad (6)$$

The results of determining the enthalpy and entropy of acid melting are presented in the Table 3.

*Table 3*

Melting enthalpies of 4.7-dioxo-7-(4-methylphenyl)heptanoic acid samples

| $m_0$, g | $\Delta m_{vap}\cdot 10^3$, g | $S$, K·s | $q_{vap}$, J | $\Delta_{fus}H_{Tfus}$, kJ/mol | $\Delta_{fus}H_{298}$, kJ/mol | $\Delta_{fus}S_{Tfus}$, kJ/mol | $\Delta_{fus}S_{298}$, kJ/mol |
|---|---|---|---|---|---|---|---|
| $T_{fus}$ = 391.45±1.50 K; K = 0.03211 J/K·s | | | | | | | |
| 0.1000 | 0.436 | 479.7 | 0.1265 | 37.9 | 31.2 | 96.9 | 77.3 |
| 0.1008 | 0.475 | 468.6 | 0.1377 | 36.7 | 30.2 | 93.8 | 74.9 |
| 0.1056 | 0.497 | 571.8 | 0.1441 | 38.8 | 32.0 | 99.2 | 79.1 |
| Average value: | | | | 37.8 ± 2.6 | 31.1 ± 2.8 | 96.6 ± 6.7 | 77.1 ± 7.2 |

The change in entropy at the melting point ($\Delta_{fus}S_{Tfus}$), the values of which are given in Table 3, was calculated by equation (7):

$$\Delta_{fus}S_{T_{fus}} = \Delta_{fus}H_{T_{fus}} \Big/ T_{fus} , \quad (7)$$

The thermodynamic parameters determined during the experimental studies belong to different temperatures, for example, $_{\Delta sol}H^o$ and $_{\Delta sol}S^o$ were calculated in the temperature range given in Table 1, and the value of $\Delta_{fus}H^o$ was determined at the melting point of the substance. To summarise the results and calculate the thermodynamic parameters ($\Delta_{mix}H^o$; $\Delta_{mix}S^o$) at the generally accepted temperature of 298.15 K, it became necessary to recalculate the values of $\Delta_{fus}H^o$; $\Delta_{fus}S^o$ to 298.15 K. For this purpose, equations 8 and 9 were used [18]. The results of the recalculation are shown in Table 3.

$$\Delta_{fus}H^o{}_{298.15} = \Delta_{fus}H^o{}_{T_{fus}} - \Delta_{fus}Cp^o \cdot \left(T_{fus} - 298.15\right) = \Delta_{fus}H^o{}_{T_{fus}} \cdot \frac{0.35 \cdot T_{fus} + 298.15}{1.35 \cdot T_{fus}} \quad (8)$$

$$\Delta_{fus}S^o{}_{298.15} = \Delta_{fus}S^o{}_{T_{fus}} - \Delta_{fus}Cp^o \cdot ln\frac{T_{fus}}{298.15} = \Delta_{fus}S^o{}_{T_{fus}} \cdot \frac{1.35 - ln\frac{T_{fus}}{298.15}}{1.35} \quad (9)$$

The sign and value of the thermodynamic mixing parameters $\Delta_{mix}H^o$; $\Delta_{mix}S^o$ depend on the change in the energy of intermolecular bonds that are destroyed in the starting substances and formed by the interaction between the solvent and solute molecules. Thus, the negative values of $\Delta_{mix}H^o$ and $\Delta_{mix}S^o$ of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid with acetone, acetonitrile, methyl- and ethyl acetate are due to the fact that intermolecular interactions in pure solvents are provided by dipole-dipole and dispersion interactions, the destruction of which requires less energy than is released during the formation of new bonds. As for the interaction of the substance under study with alcohols, in solutions of lower alcohols, the thermodynamic parameters of the mixing process are positive, while with higher alcohols they are negative. This difference is due to the fact that higher alcohols form a slightly weaker hydrogen bond due to steric hindrance. It is known [25] that the energy of hydrogen bonding in alcohols can vary from 2 to 23 kJ/mol. It is also worth noting that the interaction between the solvent and the dissolved substance occurs between the functional groups of the solvent and 4,7-dioxo-7-(4-methylphenyl)heptanoic acid, as evidenced by the presence of a compensatory effect of the mixing process (Fig. 1, equation 10) (correlation coefficient 0.979).

$$\Delta_{mix}H_{298.15} = 0.317 \cdot \Delta_{mix}S_{298.15} + 1.68, \quad (10)$$

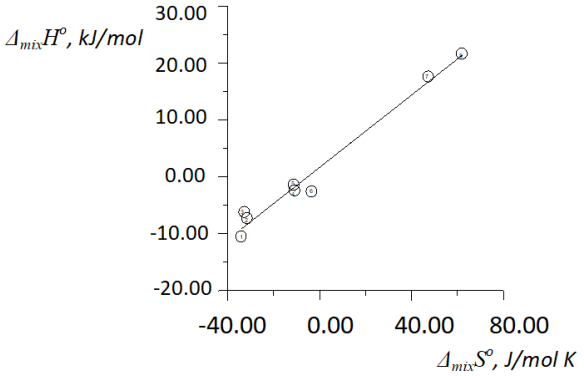



Fig. 1. Relationship between enthalpy and entropy of mixing of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid in organic solvents. Points: *1* – acid solution in acetone; *2* – acid solution in acetonitrile; *3* – acid solution in *n*-butanol; *4* – acid solution in iso-butanol; *5* – acid solution in ethyl acetate; *6* – acid solution in methyl acetate; *7* – acid solution in *n*-propanol; *8* – acid solution in iso-propanol

**4. Conclusion**

In the course of experimental studies, the solubility of 4,7-dioxo-7-(4-methylphenyl)heptanoic acid in a number of organic solvents was determined for the first time, namely: methyl acetate > acetone > iso-butanol > ethyl acetate > acetonitrile > iso-propanol > propanol > butanol. Based on the temperature dependence, the thermodynamic parameters of the dissolution process were calculated, which, taking into account the heat of fusion, made it possible to understand the nature of the interaction between acid and solvent molecules. Such an assessment is necessary to optimize the synthesis of new compounds with pharmacophore properties using 4,7-dioxo-7-(4-methylphenyl)heptanoic acid.

**5. Подяка**

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## РОЗЧИНЕННЯ 4,7-ДІОКСО-7-(4-МЕТИЛФЕНІЛ)ГЕПТАНОВОЇ КИСЛОТИ У ДЕЯКИХ ОРГАНІЧНИХ РОЗЧИННИКАХ

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Синтез нових органічних речовин є головним напрямом у хімічній та фармацевтичній індустрії. Інформація про значення теплових ефектів, які супроводжують процеси синтезу, очистки чи переробки речовин, є однією з передумов, яка потрібна для практичного застосування. Тому дослідження теплових ефектів, які відбуваються під час взаємодії фенациллевулінових кислот з речовинами, що слугують реакційним середовищем чи які використовують для очищення цільових продуктів, є актуальною.

Експериментальне дослідження температурної залежності розчинності 4,7-діоксо-7-(4-метилфеніл)гептанової кислоти з органічними розчинниками різних класів дало змогу розрахувати ентальпії ($\Delta_{sol}H$) та ентропії ($\Delta_{sol}S$) розчинення: у метилацетаті ($\Delta_{sol}H$) = 28,5±1,0 кДж/моль, ($\Delta_{sol}S$) = 73,7±3,7 Дж/моль·К; етилацетаті ($\Delta_{sol}H$) = 29,71±0,73 кДж/моль, ($\Delta_{sol}S$) = 65,9±2,7 Дж/моль·К; ацетонітрилі ($\Delta_{sol}H$) = 23,76±0,67 кДж/моль, ($\Delta_{sol}S$) = 45,6±2,3 Дж/моль·К; ацетоні ($\Delta_{sol}H$) = 20,59±0,86 кДж/моль, ($\Delta_{sol}S$) = 43,0±3,0 Дж/моль·К; *н*-пропанолі ($\Delta_{sol}H$) = 48,7±1,9 кДж/моль, ($\Delta_{sol}S$) = 124,5±6,5 Дж/моль·К; ізопропанолі ($\Delta_{sol}H$) = 52,7±2,2 кДж/моль, ($\Delta_{sol}S$) = 138,8±7,6 Дж/моль·К; *н*-бутанолі ($\Delta_{sol}H$) = 24,93±0,35 кДж/моль, ($\Delta_{sol}S$) = 44,4±1,2 Дж/моль·К та ізобутанолі ($\Delta_{sol}H$) = 28,75±0,75 кДж/моль, ($\Delta_{sol}S$) = 66,3±2,5 Дж/моль·К.

Визначені значення термодинамічних параметрів процесу розчинення містять термодинамічні параметри змішування компонентів та фазововий перехід кристалічної речовини в рідку фазу розчину: $\Delta_{sol}H^o = \Delta_{mix}H^o + \Delta_{fus}H^o$ та $\Delta_{sol}S^o = \Delta_{mix}S^o + \Delta_{fus}S^o$. За даними

диференційно-термічного аналізу визначено ентальпію та ($\Delta_{fus}H_{391,45}$ = 37,8±2,6 кДж/моль) та розраховано ентропію ($\Delta_{fus}S_{391,45}$= 96.6±6.7 Дж/моль К) плавлення досліджуваної сполуки. З метою узагальнення отриманих результатів термодинамічні параметри процесу плавлення перераховано до загальноприйнятої температури 298,15 К, за якими розраховано ентальпії та ентропії змішування компонентів при 298,15 К.

Такі термодинамічні дослідження розчинності допомагають удосконалити виробничі процеси, зменшити витрати на енергію, підвищити вихід кінцевих продуктів і знизити негативний вплив на навколишнє середовище.

*Ключові слова:* розчинність, ентальпія розчинення, ентальпія змішування. ентальпія плавлення, 4,7-діоксо-7-(4-метилфеніл)гептанова кислота.

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