UDC 544.32

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DISSOLUTION OF 4,7-DIOXO-7-PHENYLHEPTANOIC ACID IN ORGANIC SOLVENTS

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The temperature dependences of the solubility of 4,7-dioxo-7-phenylheptanoic acid in organic solvents, in particular methyl acetate, ethyl acetate, acetonitrile, acetone, n-propanol, isopropanol, n-butanol and isobutanol, in the temperature range of 272–295 K were experimentally investigated. Based on the results obtained, the enthalpy ($\Delta_{sol}H$) and entropy ($\Delta_{sol}S$) of dissolution were determined. The enthalpy and entropy of melting of this acid were calculated using the method of differential thermal analysis. The thermodynamic parameters were reduced to the standard temperature of 298.15 K, and the enthalpies and entropies of mixing of the components at this temperature were also calculated. Based on the thermodynamic parameters of mixing, a compensation effect was revealed, and the nature of the interaction between the solvent and the solute was investigated.

Keywords: solubility, enthalpy of dissolution, enthalpy of mixing, enthalpy of melting, 4,7-dioxo-7-phenylheptanoic acid.

DOI: 10.32434/0321-4095-2026-164-1-42-49

Introduction

Levulinic acid (4-oxopentanoic acid) is one of the most important organic compounds that attracts considerable attention of researchers due to its unique physicochemical properties, wide range of biological activities and prospects for application in various fields of science and industry. This carboxylic acid is derived primarily from biomass [1], making it an environmentally friendly and renewable resource for chemical synthesis.

Levulinic acid derivatives, such as γ-valerolactone, methyllevulinate and levulinamides, and phenacyllevulinic acids, have a wide range of applications, including in medicine, pharmaceuticals, agrochemicals, polymers and fuels. For example, γ-valerolactone is used as a solvent and ingredient in pharmaceuticals, methyllevulinate is a promising candidate for biofuels, and levulinamides are used in the development of anti-inflammatory drugs [2–4]. They demonstrate antioxidant, anti-inflammatory and antimicrobial properties, which makes them promising for the development of new cosmetic products, such as acne and skin repair products, creams and serums for skin care [5–7]. In addition, levulinic acid derivatives are actively used in the production of biodegradable materials, in particular in the creation of bioplastics, as well as environmentally friendly alternatives to traditional chemical compounds in agriculture, for example, as components of biopesticides and plant growth stimulants.

Most synthesis processes take place in a reaction medium. Organic solvents are commonly used as reaction media. However, in most cases, this choice is made without taking into account the interactions of the solvent with the reacting substances and reaction products at the energy level, since such data are not available for most systems. Knowledge of the enthalpies and entropies of dissolution and mixing is also necessary to calculate heat balances of the synthesis and purification processes.

Recently, the number of works that experimentally investigate the energy interactions between solvents and dissolved substances has been increasing [8–10], but their number is hundreds of times lower than the number of works describing the synthesis of new substances.

Thus, the study of levulinic acid and its derivatives is a relevant area of modern science, which opens up new opportunities for the creation of sustainable technologies and materials capable of ensuring environmental safety and efficiency in various fields of human activity. In this article, we will consider the methods of preparation and thermodynamic properties of solutions of phenacyllevulinic acids, namely 4,7-dioxo-7-phenylheptanoic acid in organic solvents of different polarity.

The present study is a continuation of our work on determining the thermodynamic parameters of solutions, which has been carried out for a decade [8,11,12].

Experimental

The synthesis of 4,7-dioxo-7-phenylheptanoic acid was carried out according to the reaction scheme shown in Fig. 1.

Furfurylidene acetophenone (1)

To a mixture of acetophenone (48 g, 0.4 mol) and furfural (38.4 g, 0.4 mol) in 100 mL of methanol with intense stirring was added 0.024 mol of KOH as a 15% solution. The temperature was maintained at 20–25^{0}C. The reaction mixture was stirred for 3 h, neutralized with acetic acid, diluted with 200 ml of water, extracted with methylene chloride, washed with water, the organic layer was separated and dried with sodium sulfate. The solvent was removed and the residue was distilled in vacuo. Yield 53.8 g (68%), b.p. 148–150^{0}C/2 mm Hg.

4,7-Dioxo-7-phenylheptanoic acid (2)

A mixture of furfurylidene acetophenone **1** (39.6 g, 0.2 mol), 300 mL ethyl alcohol, 90 mL conc. HCl and 15 mL water was boiled with reflux for 24 hours. The alcohol was distilled off and black viscous mass was obtained. Then 200 mL of conc. HCl, 200 mL of glacial acetic acid, 400 mL of water were added and heated under reflux for next 3 hours. After cooling, the resulting light-yellow crystalline precipitate of 4,7-dioxo-7-phenylheptanoic acid **2** was decanted from the residual resin, filtered, washed three times with water and recrystallized from ethanol. Yield 19.2 g (41%), m.p. 110–112^{0}C. IR (ATR, cm^{-1}): 2910; 2615; 1710; 1672; 1635; 1595; 1450; 1409; 1352; 1270; 1208; 1189; 1128; 1102; 1073; 1025; 976; 941; 901; 830; 767; 730; 693; 623; 566; 473. MS (m/z): 235 (M^++1). Calcd. for $C_{13}H_{14}O_4$: C 66.67; H 6.02; found: C 66.51; H 5.90.

Mass spectrometry analysis was performed using an Agilent 1100 LC/MSD with API-ES/APCI mode. The Shimadzu IRSpirit-T apparatus was used to obtain data on the infrared spectrum.

The solubility of 4,7-dioxo-7-phenylheptanoic acid was studied in organic solvents produced by Merck. The selected range of solvents includes representatives of esters, nitriles, ketones, higher and lower alcohols, 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

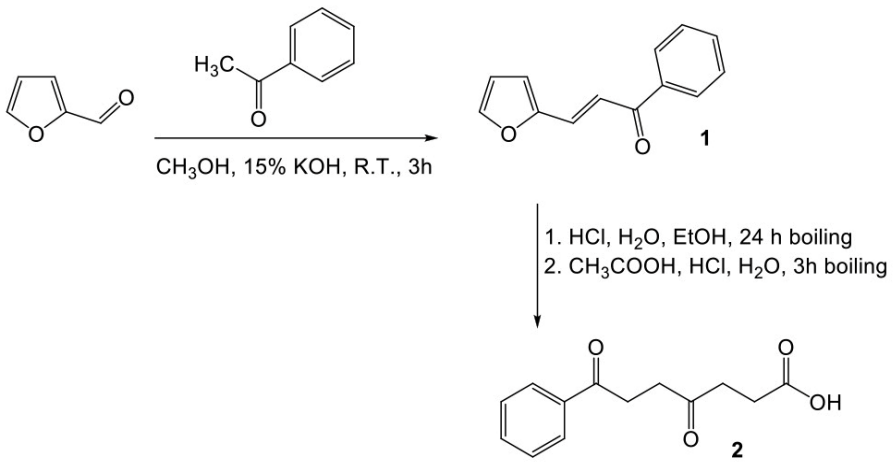

Fig. 1. 4,7-dioxo-7-phenylheptanoic acid reactions synthesis

of the main substance ≥99.8% w/w; n-butanol CAS 71-36-3, mass fraction of the main substance i99.9% 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 process of dissolving 4,7-dioxo-7-phenylheptanoic acid was carried out gravimetrically according to the method described elsewhere [8–10], using a sealed vessel with a thermometer, stirrer, and a sampling hole. The saturation of the solution was carried out in a thermostat whose temperature was maintained with an accuracy of ±0.1 K for 120 minutes with constant stirring at a speed of 30 rpm, followed by 60 minutes without stirring. During this time, the suspended particles of the solid phase were completely settled. Samples of solutions weighing 1.0–2.0 g were taken and placed in pre-prepared and weighed vessels, which were hermetically sealed and weighed to determine the mass of the saturated solution. After that, the vessels 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 study was carried out both at increasing and decreasing temperatures. The absence of a hysteresis loop in the temperature dependence of solubility indicates the establishment of a state close to equilibrium.

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

Results and discussion

Table 1 shows the primary data of the dissolution process of 4,7-dioxo-7-phenylheptanoic acid, where m_1 is the mass of solvent; m_2 is the mass of dissolved substance (g); x_2 is the solubility expressed in mole fractions; and T is the temperature (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 Schroeder equation (1), which is also presented in Table 1.

$$\ln x_2 = -\Delta_{sol}H^0/RT + \Delta_{sol}S^0/R, \quad (1)$$

where $\Delta_{sol}H^0$ is the enthalpy of solvation; $\Delta_{sol}S^0$ is the entropy of solvation.

Hereinafter, the errors of all values are given for a significance level of 0.95.

$$\ln x_2 = (17.26 \pm 0.62) - (6574 \pm 181) \cdot 1/T$$

Differential changes in the enthalpy ($\Delta_{sol}H^0$) and entropy ($\Delta_{sol}S^0$) of the dissolution of 4,7-dioxo-7-phenylheptanoic acid were calculated using the temperature dependence of solubility (Table 1) according to equations 2 and 3, and the results are presented in Table 2.

$$\Delta_{sol}H^0 = R \cdot B, \quad (2)$$

$$\Delta_{sol}S^0 = R \cdot A. \quad (3)$$

Since the calculated thermodynamic parameters of dissolution $_{sol}H^0$ and $\Delta_{sol}S^0$ include mixing processes ($\Delta_{mix}H^0$ and $\Delta_{mix}S^0$) and the phase transition of the crystalline substance into the liquid phase of the solution ($\Delta_{fus}H^0$ and $\Delta_{fus}S^0$), equations (4) and (5) are valid:

$$\Delta_{sol}H^0 = \Delta_{mix}H^0 + \Delta_{fus}H^0, \quad (4)$$

$$\Delta_{sol}S^0 = \Delta_{mix}S^0 + \Delta_{fus}S^0. \quad (5)$$

Equation (6) was used to calculate $\Delta_{fus}H^0$, which takes into account the correction for the mass loss of the sample during the melting process:

$$K \cdot S = q_{fus} + q_{vap} = m_o \cdot \Delta_{fus}H + \Delta m_{vap} \cdot \Delta_{vap}H, \quad (6)$$

where q_{fus} and q_{vap} 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 its melting point T_{fus}; Δm_{vap} is the mass loss of the sample (mass of vapour, g) over 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 unit equal to $K = T_{fus} \cdot 8.202 \cdot 10^{-5}$; $\Delta_{fus}H^0$ and $\Delta_{vap}H^0$ are the specific enthalpies of fusion and evaporation of the substance (J/g), respectively. The calculation results are shown in Table 3.

The value of $\Delta_{vap}H^0$ was calculated from the data of the thermogravimetric method of analysis according to the temperature dependence of the evaporation rate $V = \Delta m'/\Delta\tau$ in the temperature interval when the substance was in a liquid aggregate state, before the onset of thermal oxidation degradation processes. The temperature dependence of the evaporation rate of the substance was approximated by the linear form of the Arrhenius equation $\ln V = A - B/T$, where $B = E_{act}/R$.

Table 1

Temperature dependence of the solubility of 4,7-dioxo-7-phenylheptanoic acid in organic solvents

T, K	m_1, g	m_2, g	$x_2 \cdot 10^2$	T, K	m_1, g	m_2, g	$x_2 \cdot 10^2$	T, K	m_1, g	m_2, g	$x_2 \cdot 10^2$
methyl acetate											
276.8	1.6843	0.0692	1.28	279.1	1.3765	0.0651	1.47	285.6	2.1118	0.1451	2.13
276.8	1.4443	0.0598	1.29	280.0	1.2285	0.0620	1.57	285.6	1.6679	0.1152	2.14
276.8	1.1115	0.0463	1.30	280.0	1.4152	0.0716	1.57	286.9	1.5361	0.1177	2.37
278.5	1.6816	0.0800	1.48	280.0	1.2991	0.0655	1.57	286.9	1.7176	0.1317	2.37
278.5	1.4991	0.0708	1.47	282.0	1.5734	0.0877	1.73	286.9	1.4866	0.1143	2.37
278.5	1.5118	0.0713	1.47	282.0	1.7697	0.0982	1.72	291.0	1.5284	0.1471	2.95
278.5	1.2448	0.0579	1.45	282.0	1.6824	0.0935	1.73	291.0	1.6609	0.1570	2.90
278.5	1.7869	0.0845	1.47	284.5	1.2215	0.0812	2.06	291.0	1.5284	0.1471	2.95
278.5	1.1936	0.0561	1.46	284.5	1.6056	0.1070	2.06	294.4	1.0891	0.1254	3.51
279.1	1.5354	0.0738	1.50	284.5	1.2321	0.0820	2.06	294.4	1.3756	0.1591	3.53
279.1	1.2686	0.0606	1.49	285.6	1.1794	0.0809	2.12	294.4	1.4560	0.1686	3.53
$\ln x_2=(12.23\pm0.29)-(4588\pm82)\cdot1/T$											
ethyl acetate											
277.3	1.1080	0.0133	0.45	283.3	1.7423	0.0298	0.64	285.5	1.3225	0.0259	0.73
277.3	1.7068	0.0204	0.45	283.3	1.4095	0.0241	0.64	287.9	1.4484	0.0338	0.87
277.3	1.5830	0.0190	0.45	284.1	1.1237	0.0204	0.68	287.9	1.5487	0.0362	0.87
278.5	1.2875	0.0159	0.46	284.1	1.6680	0.0303	0.68	287.9	1.4773	0.0338	0.85
278.5	1.5543	0.0195	0.47	284.1	1.6093	0.0293	0.68	290.4	1.6295	0.0439	1.00
278.5	1.6618	0.0209	0.47	284.5	1.3166	0.0239	0.68	290.4	1.3922	0.0369	0.99
279.0	1.4120	0.0184	0.49	284.5	1.6550	0.0298	0.67	290.4	1.5165	0.0408	1.00
279.0	1.6376	0.0214	0.49	284.5	1.3088	0.0236	0.67	290.6	1.5584	0.0417	1.00
279.0	1.2836	0.0168	0.49	285.5	1.3053	0.0260	0.74	290.6	1.3920	0.0368	0.98
283.3	1.4709	0.0252	0.64	285.5	1.7752	0.0350	0.74	290.6	1.3968	0.0370	0.99
$\ln x_2=(12.53\pm0.36)-(4981\pm102)\cdot1/T$											
acetonitrile											
272.35	1.2957	0.0237	0.32	279.45	1.3557	0.0320	0.41	290.95	1.4929	0.0603	0.70
272.35	1.3122	0.0237	0.32	281.15	1.4539	0.0372	0.45	290.95	1.2045	0.0487	0.70
272.35	1.3213	0.0241	0.32	281.15	1.1634	0.0298	0.45	292.15	1.0411	0.0442	0.74
274.45	1.3065	0.0250	0.33	281.15	1.3385	0.0343	0.45	292.15	1.2483	0.0529	0.74
274.45	1.1854	0.0225	0.33	283.85	1.2600	0.0352	0.49	292.15	0.7968	0.0340	0.74
274.45	1.4063	0.0270	0.34	283.85	1.5409	0.0427	0.48	294.95	1.2817	0.0599	0.81
277.25	1.2394	0.0266	0.38	283.85	1.1105	0.0312	0.49	294.95	1.4634	0.0689	0.82
277.25	1.2834	0.0278	0.38	287.65	1.1754	0.0407	0.60	294.95	0.8866	0.0414	0.81
277.25	1.3801	0.0298	0.38	287.65	1.4234	0.0495	0.61	296.75	1.3447	0.0670	0.87
279.45	1.1075	0.0262	0.41	287.65	1.1486	0.0397	0.60	296.75	1.4399	0.0713	0.86
279.45	1.4245	0.0339	0.42	290.95	1.1384	0.0461	0.70	296.75	1.3088	0.0650	0.86
$\ln x_2=(6.99\pm0.31)-(3481\pm87)\cdot1/T$											
acetone											
272.1	1.3300	0.0537	0.99	278.7	1.2993	0.0616	1.16	284.0	1.2465	0.0661	1.30
272.1	1.4525	0.0586	0.99	278.7	1.1325	0.0541	1.17	285.8	1.2368	0.0684	1.35
272.1	1.4808	0.0598	0.99	279.3	1.1650	0.0545	1.15	285.8	1.3843	0.0771	1.36
275.5	1.1903	0.0510	1.05	279.3	1.5074	0.0713	1.16	285.8	1.5206	0.0847	1.36
275.5	1.5189	0.0656	1.06	279.3	1.3652	0.0643	1.16	294.2	1.2245	0.0810	1.61
275.5	1.3018	0.0555	1.05	283.5	1.1953	0.063	1.29	294.2	1.4192	0.0938	1.61
276.1	0.9683	0.0433	1.10	283.5	1.3102	0.069	1.29	294.2	1.2403	0.0821	1.62
276.1	1.4711	0.0650	1.08	283.5	1.3179	0.0695	1.29	295.5	1.0761	0.0723	1.64
276.1	1.6052	0.0717	1.10	284.0	1.2279	0.0642	1.28	295.5	1.3323	0.0895	1.64
278.7	1.0765	0.0514	1.17	284.0	1.3918	0.0734	1.29	295.5	1.3063	0.0888	1.66
$\ln x_2=(1.90\pm0.15)-(1773\pm41)\cdot1/T$											

Continued Table 1

T, K	m_1, g	m_2, g	$x_2 \cdot 10^2$	T, K	m_1, g	m_2, g	$x_2 \cdot 10^2$	T, K	m_1, g	m_2, g	$x_2 \cdot 10^2$
n-propanol											
275.0	1.2413	0.0078	0.16	284.4	1.3905	0.0147	0.27	292.5	1.3393	0.0211	0.40
275.0	1.1496	0.0073	0.16	284.4	1.2095	0.0127	0.27	294.0	1.0690	0.0179	0.43
275.0	1.3634	0.0086	0.16	286.7	1.0662	0.0123	0.30	294.0	1.3029	0.0220	0.43
276.5	1.1366	0.0078	0.18	286.7	1.3309	0.0153	0.29	294.0	1.3833	0.0232	0.43
276.5	1.3360	0.0092	0.18	286.7	1.6164	0.0188	0.30	295.8	1.1609	0.0205	0.45
276.5	1.4227	0.0097	0.17	291.0	1.0983	0.0158	0.37	295.8	1.2803	0.0226	0.45
278.2	1.3156	0.0099	0.19	291.0	1.7779	0.0252	0.36	295.8	1.4092	0.0252	0.46
278.2	1.2831	0.0097	0.19	291.0	1.3322	0.0190	0.36	301.9	1.2840	0.0306	0.61
278.2	1.2660	0.0095	0.19	292.5	1.0813	0.0171	0.41	301.9	1.2856	0.0304	0.60
284.4	1.1007	0.0116	0.27	292.5	1.5135	0.0243	0.41	301.9	1.4216	0.0342	0.61
$\ln x_2=(8.42\pm0.18)-(4082\pm52)\cdot1/T$											
isopropanol											
280.9	1.2246	0.0110	0.23	285.6	1.3377	0.0174	0.33	289.0	1.5315	0.0258	0.43
280.9	1.3449	0.0121	0.23	286.8	1.4193	0.0202	0.36	289.0	1.2099	0.0205	0.43
280.9	1.1734	0.0103	0.23	286.8	1.1710	0.0168	0.37	291.2	1.0276	0.0199	0.50
281.7	1.3889	0.0135	0.25	286.8	1.6179	0.0233	0.37	291.2	1.3840	0.0270	0.50
281.7	1.2007	0.0117	0.25	288.0	1.2048	0.0187	0.40	291.2	1.2894	0.0249	0.49
281.7	1.2431	0.0119	0.25	288.0	1.3414	0.0208	0.40	292.9	0.9697	0.0209	0.55
285.1	0.942	0.0118	0.32	288.0	1.2417	0.0194	0.40	292.9	1.3069	0.0285	0.56
285.1	1.1570	0.0144	0.32	288.5	1.2815	0.0203	0.41	292.9	1.2556	0.0270	0.55
285.1	1.2403	0.0154	0.32	288.5	1.3500	0.0216	0.41	294.5	0.9537	0.0245	0.66
285.6	1.2665	0.0165	0.33	288.5	1.3049	0.0209	0.41	294.5	1.2561	0.0317	0.64
285.6	1.4238	0.0184	0.33	289.0	1.1013	0.0184	0.43	294.5	1.4543	0.0371	0.65
$\ln x_2=(15.80\pm0.36)-(6142\pm105)\cdot1/T$											
n-butanol											
275.5	0.9298	0.0081	0.27	284.0	1.1808	0.0149	0.40	286.9	1.1973	0.0167	0.44
275.5	1.0789	0.0093	0.27	284.0	1.0558	0.0133	0.40	286.9	1.2906	0.0186	0.46
275.5	0.9106	0.0078	0.27	284.0	1.0186	0.0129	0.40	286.9	1.2207	0.0171	0.44
282.4	0.9956	0.0116	0.37	286.0	1.0196	0.0138	0.43	291.6	1.1428	0.0189	0.52
282.4	1.2040	0.0140	0.37	286.0	1.2013	0.0162	0.43	291.6	1.1806	0.0196	0.52
282.4	1.1428	0.0133	0.37	286.0	0.9176	0.0124	0.43	291.6	1.0773	0.0177	0.52
282.5	1.3523	0.0162	0.38	287.3	0.9260	0.0131	0.45	292.5	1.2169	0.0206	0.53
282.5	1.0941	0.0131	0.38	287.3	1.2549	0.0178	0.45	292.5	1.1142	0.0191	0.54
282.5	1.0410	0.0125	0.38	287.3	1.3527	0.0192	0.45	292.5	1.2484	0.0212	0.53
$\ln x_2=(5.71\pm0.36)-(3196\pm103)\cdot1/T$											
isobutanol											
282.6	0.9477	0.0077	0.26	290.0	1.0661	0.0150	0.44	293.0	0.8430	0.0151	0.56
282.6	0.9927	0.0079	0.25	290.0	1.1056	0.0161	0.46	293.0	1.1636	0.0207	0.56
282.6	1.3264	0.0105	0.25	290.0	1.4447	0.0212	0.46	293.0	1.0307	0.0186	0.57
284.5	1.0420	0.0095	0.29	291.3	1.2614	0.0195	0.49	293.1	1.3075	0.0234	0.56
284.5	1.2399	0.0111	0.28	291.3	1.3938	0.0218	0.49	293.1	1.2095	0.0218	0.57
284.5	1.3191	0.0120	0.29	291.3	1.4828	0.0228	0.49	293.1	1.1401	0.0204	0.56
288.1	0.8851	0.0104	0.37	292.5	1.0318	0.0180	0.55	293.5	1.1211	0.0213	0.60
288.1	1.0437	0.0122	0.37	292.5	1.2263	0.0214	0.55	293.5	0.9986	0.0189	0.60
288.1	1.4123	0.0167	0.37	292.5	1.2387	0.0218	0.56	293.5	1.2347	0.0235	0.60
$\ln x_2=(17.26\pm0.62)-(6574\pm181)\cdot1/T$											

Table 2

Thermodynamic parameters of solubility of 4,7-dioxo-7-phenylheptanoic acid in organic solvents at 298 K

No.	Solvent	$x_2 \cdot 10^3$	$\Delta_{sol}H^0$, kJ/mol	$\Delta_{mix}H^0$, kJ/mol	$\Delta_{sol}S^0$, J/mol·K	$\Delta_{mix}S^0$, J/mol·K
1	methyl acetate	42.2	38.14±0.68	3.2±2.0	101.4±2.4	12.6±3.8
2	ethyl acetate	15.2	41.41±0.85	6.5±2.1	103.9±3.0	15.1±4.2
3	acetone	9.18	28.94±0.74	–6.0±2.0	58.1±2.6	–15.6±4.0
4	acetonitrile	17.4	14.74±0.34	–20.2±1.9	15.8±1.2	–73.0±3.2
5	n-propanol	5.1	33.94±0.43	–1.0±1.9	70.0±1.5	–18.8±3.4
6	isopropanol	8.14	51.06±0.86	16.2±2.1	131.4±2.9	42.6±4.2
7	n-butanol	6.64	26.57±0.86	–8.3±2.1	47.5±3.0	–41.3±4.2
8	isobutanol	6.09	54.7±1.5	19.8±2.4	143.5±5.2	54.7±6.0

Table 3

Phase transition enthalpies of 4,7-dioxo-7-phenylheptanoic acid

m_0, g	$\Delta m_{vap} \cdot 10^3$, g	S, K·s	q_{vap}, J	$\Delta_{fus}H^0_{Tfus}$, kJ/mol	T_1–T_2, K	$\Sigma\Delta m' \cdot 10^3$, g	A	–B, K	$\Delta_{vap}H^0$, kJ/mol
T_{fus}=383.2±1.3 K; K=0.03143 J/K·s									
0.1009	0.139	579.3	0.0554	42.1	456.7–585.9	57.2	19.28	10395	89.6
0.1059	0.265	592.3	0.1054	40.9	480.7–593.6	68.0	19.40	10470	90.2
0.0981	0.120	565.3	0.0477	42.3	496.5–578.3	44.1	19.49	10560	90.5
Mean value:				41.8±1.7	Mean value:				90.1±1.2

When calculating $\Delta_{vap}H^0$, we also took into account the correction for the work of expansion in the gaseous state, equation (7):

$$E_{act} + RT_{fus} = \Delta_{vap}H^0. \quad (7)$$

The temperature interval at which $\Delta_{vap}H^0$ was calculated; the total mass loss of the sample in the specified temperature interval, $\Sigma\Delta m'$; the coefficients of the linear equation and the value $\Delta_{vap}H^0$ calculated by equation (7) are summarized in Table 3.

The change in entropy at the melting point ($\Delta_{fus}S_{Tfus}$), which is 109.1±2.6 J/mol·K, was calculated using the following equation:

$$\Delta_{fus}S^0 = \Delta_{fus}H^0/T_{fus}.$$

The thermodynamic parameters $\Delta_{sol}H^0$ and $\Delta_{sol}S^0$ determined during experimental studies are close to or belong to the temperature of 298 K. Therefore, in order to calculate $\Delta_{mix}H^0$ and $\Delta_{mix}S^0$ at this temperature, we recalculated $\Delta_{fus}H^0$ and $\Delta_{fus}S^0$ to 298 K using equations (8) and (9):

$$\Delta_{fus}H^0_{298} = \Delta_{fus}H^0_{Tfus} \cdot \frac{0.35 \cdot T_{fus} + 298}{1.35 \cdot T_{fus}}, \quad (8)$$

$$\Delta_{fus}S^0_{298} = \Delta_{fus}S^0_{Tfus} \cdot \frac{1.35 - \ln\frac{T_{fus}}{298}}{1.35}. \quad (9)$$

The recalculated values of $\Delta_{fus}H^0$ and $\Delta_{fus}S^0$ are 34.9±1.9 kJ/mol and 88.8±2.6 J/mol·K, respectively. The results of the calculations of $\Delta_{mix}H^0$ and $\Delta_{mix}S^0$ are given in Table 2.

The sign and magnitude of the thermodynamic mixing parameters $\Delta_{mix}H^0$ and $\Delta_{mix}S^0$ are determined by changes in the energy of intermolecular bonds that are destroyed in the initial components and bonds formed by the interaction between solvent and solute molecules. Negative values of the thermodynamic mixing parameters are observed in solutions formed by solvents with a less branched structure, in which there is practically no steric factor to overcome which requires additional energy expenditure.

The presence of a compensating effect in the process of mixing 4,7-dioxo-7-phenylheptanoic acid with solvents indicates the similarity of interactions between the functional groups of solvents and acid (Fig. 2). This effect is confirmed by a sufficiently high correlation coefficient of 0.973 of linear equation (10).

$$\Delta_{mix}H_{298.15} = 0.3035 \cdot \Delta_{mix}S_{298.15} + 2.174. \quad (10)$$

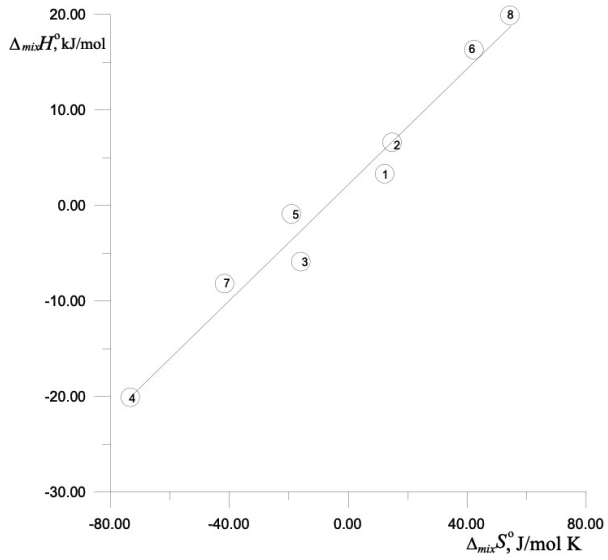

Fig. 2. Relationship between enthalpy and entropy of mixing of 4,7,-dioxo-7-phenylheptanoic acid in organic solvents. Points: 1 – acid solution in methyl acetate; 2 – acid solution in ethyl acetate; 3 – acid solution in acetonitrile; 4 – acid solution in acetone; 5 – acid solution in n-propanol; 6 –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

Conclusions

The thermodynamic parameters determined during experimental studies play a key role in the study of the dissolution of phenacyllevulinic acids, in particular 4,7-dioxo-7-phenylheptanoic acid, in organic solvents of different polarities. The analysis of such parameters as heat and entropy of mixing provides a deeper understanding of the nature of the interaction between acid and solvent molecules, which will have a positive impact on the efficiency of acid use in the synthesis of new compounds with biological activity. In addition, understanding the dissolution process allows us to determine the optimal crystallization conditions, which contributes to the production of high-quality pure drug components.

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Received 08.05.2025
Revised 09.10.2025
Accepted 30.12.2025
Published 25.02.2026

РОЗЧИНЕННЯ 4,7-ДІОКСО-7-ФЕНІЛГЕПТАНОВОЇ КИСЛОТИ В ОРГАНІЧНИХ РОЗЧИННИКАХ

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Експериментально досліджено температурні залежності розчинності 4,7-діоксо-7-фенілгептанової кислоти в органічних розчинниках, зокрема метилацетаті, етилацетаті, ацетонітрилі, ацетоні, н-пропанолі, ізопропанолі, н-бутанолі та ізобутанові, в температурному інтервалі 272–295 K. На основі отриманих результатів визначено ентальпії ($\Delta_{sol}H$) та ентропії ($\Delta_{sol}S$) розчинення. Ентальпія та ентропія плавлення сполуки були оцінені методом диференціального термічного аналізу. Усі термодинамічні параметри було перераховано на стандартну температуру 298,15 K, а також виконано обчислення ентальпій і ентропій змішування компонентів за цієї температури. На основі термодинамічних параметрів змішування виявлено компенсаційний ефект і досліджено характер взаємодії між розчинником і розчиненою речовиною.

Ключові слова: розчинність; ентальпія розчинення; ентропія розчинення; ентальпія змішування; ентальпія плавлення; 4,7-діоксо-7-фенілгептанова кислота.

DISSOLUTION OF 4,7-DIOXO-7-PHENYLHEPTANOIC ACID IN ORGANIC SOLVENTS

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The temperature dependences of the solubility of 4,7-dioxo-7-phenylheptanoic acid in organic solvents, in particular methyl acetate, ethyl acetate, acetonitrile, acetone, n-propanol, isopropanol, n-butanol and isobutanol, in the temperature range of 272–295 K were experimentally investigated. Based on the results obtained, the enthalpy ($\Delta_{sol}H$) and entropy ($\Delta_{sol}S$) of dissolution were determined. The enthalpy and entropy of melting of this acid were calculated using the method of differential thermal analysis. The thermodynamic parameters were reduced to the standard temperature of 298.15 K, and the enthalpies and entropies of mixing of the components at this temperature were also calculated. Based on the thermodynamic parameters of mixing, a compensation effect was revealed, and the nature of the interaction between the solvent and the solute was investigated.

Keywords: solubility; enthalpy of dissolution; enthalpy of mixing; enthalpy of melting; 4,7-dioxo-7-phenylheptanoic acid.

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