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THERMODYNAMIC PARAMETERS OF THE SOLUBILITY OF 3-(1,5-DIPHENYLPYRROL-2-YL)PROPANOIC ACID IN ORGANIC SOLVENTS

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For the first time, the temperature dependence of the solubility of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid was experimentally determined in eight organic solvents (methyl acetate, ethyl acetate, acetone, acetonitrile, n-propanol, isopropanol, n-butanol, and isobutanol) within the temperature range of 275.5–322.0 K at atmospheric pressure. Based on the solubility data, the enthalpies and entropies of solvation were calculated. Using differential thermal analysis, the enthalpy of fusion at the melting point (T_{fus}=442.4±1.5K) was determined. The equations for recalculating the enthalpies and entropies of fusion to 298 K are presented. The thermodynamic parameters of the mixing process of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid with the solvents were also calculated. A compensation effect in the thermodynamic parameters of mixing was established, and the nature of the interactions between the solvent and the dissolved substance was analyzed.

Keywords: solubility, enthalpy of solvation, enthalpy of fusion, enthalpy of mixing, 3-(1,5-diphenylpyrrol-2-yl)propanoic acid.

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Introduction

Polysubstituted pyrrole derivatives are widespread in nature and can be found in alkaloids, hemoglobin, vitamin B_{12}, and chlorophyll [1–3]. This class of substances is mainly used in industry for the production of conductive materials for batteries, coatings for semiconductors, solar cells, dyes, and catalysts [4,5]. Furthermore, pyrrole derivatives are valuable components for the pharmaceutical industry due to their biological activity [6–8], and thus are used in the production of drugs with antioxidant, antibacterial and anti-inflammatory effects [9–11]. This variety of properties encourages scientists to synthesize new substances with a pyrrole fragment.

The availability of information on the thermodynamic parameters of solvation is one of the important factors in the selection of a solvent, since the vast majority of synthesis, purification and processing processes take place in a solvent environment.

To some extent, this work is a continuation of our series of studies on determining the thermodynamic properties of the solubility of substances with an arylfuran fragment in a number of organic solvents [12,13].

The purpose of this work is to determine the temperature dependence of the solubility of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid in a number of organic solvents and to calculate the thermodynamic parameters of the interaction between the solvent and the dissolved substance.

Experimental

The synthesis of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid was carried out according to the reaction scheme shown in Fig. 1.

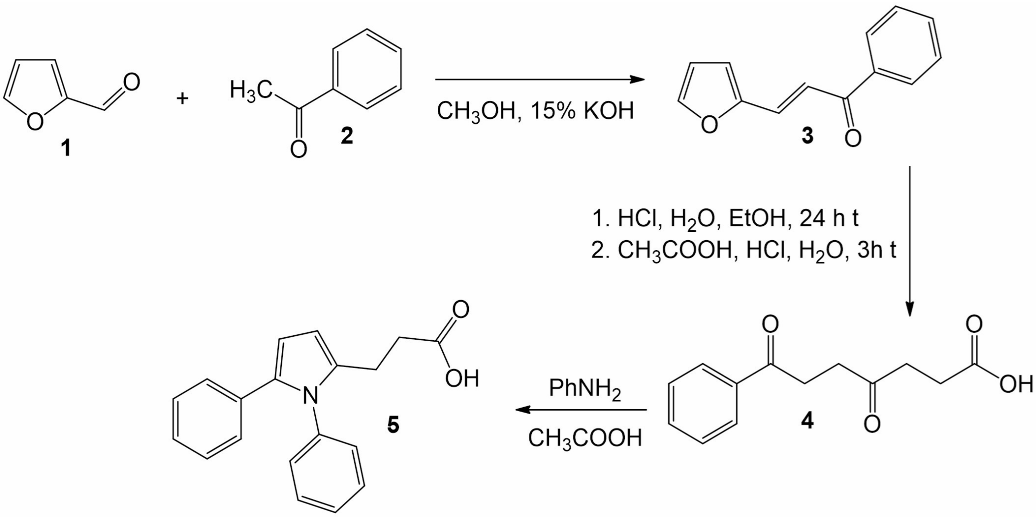

Fig. 1. Synthesis of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid

Furfurylidene acetophenone (3)

Under intense stirring, 0.05 mol of KOH (15% solution) was added to the reaction mixture of 80 g furfural (**1**), 100 g of acetophenone (**2**) and 200 mL of methanol. The temperature of the reaction mixture was maintained in the range of 293–298 K. After stirring for 3 hours, the reaction mixture was neutralized with acetic acid, diluted in 400 mL of water, extracted with dichloromethane, and washed with water. Then the organic layer was separated and dried with sodium sulfate. After removing the solvent, the residue was distilled in vacuum and furfurylidene acetophenone (**3**) was obtained. B.p. 150^{0}C/2 mm Hg.

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

A mixture of 0.2 mol of furfurylidene acetophenone (**3**), 300 mL of ethyl alcohol, 90 mL of concentrated HCl and 15 mL of water was boiled with reflux for 24 hours. The alcohol was distilled off and black viscous mass was obtained. Then 200 mL of concentrated HCl, 200 mL of glacial acetic acid, and 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 (**4**) was decanted from the residual resin, filtered, washed three times with water and recrystallised from ethanol. M.p. 186–187^{0}C.

3-(1,5-Diphenylpyrrol-2-yl)propanoic acid (5)

0.025 mol (5.85 g) of 4,7-dioxo-7-phenylheptanoic acid (**4**) was mixed with 0.025 mol of aniline and 50 mL of glacial acetic acid. This mixture was refluxed for 6 hours. After cooling, the reaction mixture was transferred to a flask with 100 mL of cold water and stirred. After 20 min, the resulting precipitate of acid (**5**) was filtered off, washed with water and recrystallized from an ethanol/dimethylformamide mixture. Yield 5.3 g (73%), m.p. 172–173^{0}C.

A sample after 3 times recrystallization from an ethanol/dimethylformamide mixture was used for the study.

The structure of compound **5** was confirmed by NMR and IR spectroscopy data. The NMR spectra were recorded on Varian 500 spectrometer in DMSO-d_6 using TMS as reference. The IR spectra was obtained on a Shimadzu IRSpirit-T instrument.

3-(1,5-Diphenylpyrrol-2-yl)propanoic acid. ^{1}H NMR (500 MHz), δ, ppm: 12.14 (br.s, 1H), 7.49–7.37 (m, 3H), 7.21 (d, J=7.3 Hz, 2H), 7.13 (t, J=7.5 Hz, 2H), 7.06 (t, J=7.3 Hz 1H), 7.00 (d, J=7.2 Hz, 2H), 6.33 (d, J=3.6 Hz, 1H), 6.07 (d, J=3.6 Hz, 1H), 2.60 (t, J=7.7 Hz, 2H), 2.43 (t, J=7.7 Hz, 2H). ^{13}C NMR (126 MHz), δ, ppm: 173.94, 138.94, 134.95, 133.82, 133.33, 129.62, 128.89, 128.39, 128.27, 127.54, 126.06, 109.08, 106.70, 32.99, and 22.50. FT-IR (ν, cm^{-1}): 2924, 1701.

The purity grade was indirectly confirmed by the constant value of the melting point and the enthalpy of fusion and vaporization.

The choice of organic solvents was made taking into account their availability, low boiling point and widespread use. Therefore, for our experimental studies of the temperature dependence of solubility, organic solvents produced by Merck were used, namely: methyl acetate (CAS 79-20-9, EC Number 201-185-2), ethyl acetate (CAS 141-78-6, EC Number 205-500-4), acetone (CAS 67-64-1, EC Number 200-662-2), acetonitrile (CAS 75-05-8, EC Number 200-835-2), n-propanol (CAS 71-23-8, EC Number 200-746-9), isopropanol (CAS 67-63-0, EC Number 200-661-7), n-butanol (CAS 71-36-3, EC Number 200-751-6) and isobutanol (CAS 78-83-1, EC Number 201-148-0).

Experimental studies aimed to determine the temperature dependence of the solubility of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid in selected organic solvents were performed according to the method disrobed elsewhere [14]. A saturated acid solution was prepared in a three-necked flask equipped with a stirrer, thermometer, and sampling hole. An organic solvent was added to the flask and the acid sample was dissolved in excess. The flask was immersed in a water thermostat at the set temperature with an accuracy of ±0.1 K. The rotational speed of the stirrer was 40–50 rpm, which allowed maintaining the solid phase in suspension. The duration of stirring was 120 minutes. After stirring, the solution was settled for 60 min. Solution was taken in series of three samples weighing 1.25–1.35 g and transferred to pre-weighed empty glass vials. The sample vials were hermetically sealed and weighed on a VLR-200 balance (with accuracy of ±0.0002 g). The sample vials were then placed in an oven and dried to a constant weight. Respectively, the mass of dissolved acid in the solution (m_2) was calculated as the difference between the masses of vials with dry residue and empty ones. The solvation was carried out in the mode of both increasing and decreasing temperature. The absence of a hysteresis loop in the temperature dependence of solubility served to confirm the establishment of a state close to equilibrium.

The thermodynamic parameters of the melting process of the studied acid were determined on a derivatograph Q-1500 D Paulik-Paulik-Erdey system in a dynamic mode with a heating rate of 5 K/min in an air atmosphere [15].

The calculation of the enthalpy of fusion ($\Delta_{fus}H^0$) was performed according to the following equation, taking into account the loss of part of the heat due to the vaporization of the sample:

$$K \cdot S = Q_{fus} + Q_{vap} = m_0\Delta_{fus}H^0 + m_{vap}\Delta_{vap}H^0, \quad (1)$$

where Q_{fus} and Q_{vap} are the amount of heat absorbed during sample fusion and vaporization, respectively, J; $\Delta_{fus}H^0$ and $\Delta_{vap}H^0$ are specific enthalpies of fusion and vaporization of the sample, respectively, J/g; m_0 is the mass of the sample corresponding to the temperature of its fusion beginning T_{fus}, g; Δm_{vap} is a loss of sample mass (vapor mass) over the period taken into account when determining the peak area S (K·s) on the differential thermal analysis curve, g; and K is the heat transfer coefficient of the derivatograph, J/(K·s).

The value of $\Delta_{vap}H^0$ was calculated from the temperature dependence of the vaporization rate of the sample in the temperature range where the acid sample was in a liquid phase before the degradation process began. To determine the vaporization rate, the integral curve of the sample mass loss was differentiated every 30 seconds. The temperature dependence of the vaporization rate of a substance was approximated by the linear form of the Arrhenius equation ($\ln v = A - B/T$, where $B = E_{act}/R$). At the same time, the values of the enthalpy of vaporization and the activation energy (E_{act}) were considered equal, since vapor condensation in the presence of the liquid phase is practically an activation-free process:

$$\Delta_{vap}H^0 = E_{act} + RT_{fus}. \quad (2)$$

Results and discussion

The primary results of the experimental study of the temperature dependence of the solubility of extremely dilute solutions of the acid under study in organic solvents (Table 1) were processed by the least squares method and presented in the form of the following linear equation:

$$\ln x_2 = -\frac{\Delta_{sol}H^0}{RT} + \frac{\Delta_{sol}S^0}{R}, \quad (3)$$

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

Hereinafter, all the results of the experimental data processing are calculated taking into account the Student's coefficient for a significance level of 0.95.

The determined thermodynamic solubility parameters $\Delta_{sol}H^0$ and $\Delta_{sol}S^0$ characterize not only the process of solution formation (mixing of components), but also the phase transition of the acid under study into the liquid phase of the solution. Therefore, to calculate the change in the enthalpy ($\Delta_{mix}H^0$) and entropy ($\Delta_{mix}S^0$) of mixing (dissolution) of components, which characterize their interaction in solution, it is necessary to take into account the values of the enthalpy ($\Delta_{fus}H^0$) and entropy ($\Delta_{fus}S^0$) of fusion:

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

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

The calculated values of $\Delta_{fus}H^0$, $\Delta_{vap}H^0$, and the component values of equations (1) and (2) are given in Table 2, as well as the temperature interval (T_1–T_2) within which $\Delta_{vap}H^0$ was calculated and the total mass loss of the sample in the given temperature interval ($\Sigma\Delta m$).

The value of $\Delta_{fus}S^0$ was calculated according to the following known equation $\Delta_{fus}S^0 = \Delta_{fus}H^0/T_{fus}$.

The values of $\Delta_{fus}H^0$ and $\Delta_{fus}S^0$ of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid were

Table 1

Solubility temperature dependence of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid *

T, K	m_1, g	m_2, g	$x_2 \cdot 10^3$	T, K	m_1, g	m_2, g	$x_2 \cdot 10^3$	T, K	m_1, g	m_2, g	$x_2 \cdot 10^3$
methyl acetate											
294.0	1.3235	0.0298	5.69	299.5	1.4409	0.0423	7.42	305.5	1.4877	0.0530	8.98
294.0	1.6039	0.0361	5.70	299.5	1.4688	0.0430	7.40	310.0	1.6808	0.0712	10.66
294.0	1.6684	0.0376	5.70	301.0	1.4695	0.0448	7.69	310.0	1.5509	0.0657	10.66
294.2	1.4062	0.0318	5.72	301.0	1.4892	0.0449	7.62	310.0	1.5145	0.0650	10.79
294.2	1.5463	0.0352	5.75	301.0	1.5388	0.0464	7.61	312.0	1.5804	0.0702	11.17
294.2	1.4431	0.0330	5.78	302.9	1.2849	0.0429	8.43	312.0	1.3896	0.0611	11.06
298.0	1.5717	0.0418	6.72	302.9	1.5445	0.0518	8.46	312.0	1.5079	0.0662	11.04
298.0	1.4750	0.0391	6.69	302.9	1.4879	0.0497	8.43	315.5	1.3059	0.0669	12.87
298.0	1.5150	0.0402	6.70	305.5	1.2949	0.0467	9.09	315.5	1.6692	0.0849	12.77
299.5	1.5587	0.0453	7.33	305.5	1.5901	0.0564	8.95	315.5	1.3589	0.0688	12.71
$\ln x_2$=(6.52±0.292)–(3430±87)·1/T											
ethyl acetate											
294.5	1.4124	0.0241	5.14	302.5	1.4782	0.0353	7.17	309.5	1.4989	0.0457	9.15
294.5	1.5252	0.0264	5.21	302.5	1.5314	0.0365	7.16	309.6	1.3610	0.0422	9.29
294.5	1.5196	0.0260	5.16	305.5	1.4773	0.0383	7.79	309.6	1.4743	0.0455	9.25
298.0	1.3391	0.0269	6.04	305.5	1.4705	0.0387	7.90	309.6	1.4989	0.0457	9.15
298.0	1.5273	0.0310	6.11	305.5	1.4997	0.0398	7.96	312.2	1.3121	0.0469	10.71
298.0	1.5019	0.0302	6.04	307.9	1.3613	0.0394	8.68	312.2	1.5048	0.0536	10.66
301.9	1.3335	0.0307	6.91	307.9	1.5362	0.0447	8.73	312.2	1.4829	0.0525	10.60
301.9	1.4790	0.0339	6.88	307.9	1.4529	0.0419	8.66	317.0	1.2920	0.0542	12.54
301.9	1.5253	0.0350	6.90	309.5	1.3610	0.0422	9.29	317.0	1.4862	0.0615	12.36
302.5	1.4883	0.0352	7.10	309.5	1.4743	0.0455	9.25	317.0	1.4632	0.0606	12.37
$\ln x_2$=(7.05±0.32)–(3629±99)·1/T											
acetone											
275.5	1.2233	0.0363	5.88	284.4	1.3255	0.0514	7.68	297.5	1.3475	0.0793	11.59
275.5	1.3547	0.0404	5.91	287.1	1.3134	0.0553	8.32	297.5	1.2987	0.0763	11.58
275.5	1.3624	0.0406	5.91	287.1	1.3914	0.0576	8.19	300.5	1.2700	0.0814	12.62
276.5	1.2014	0.0364	6.00	287.1	1.2802	0.0545	8.42	300.5	1.3164	0.0843	12.61
276.5	1.3711	0.0414	5.99	288.9	1.1629	0.0519	8.82	300.5	1.2527	0.0802	12.60
276.5	1.3738	0.0415	5.99	288.9	1.3679	0.0603	8.71	303.2	1.2149	0.0827	13.40
280.0	1.2646	0.0437	6.85	288.9	1.3292	0.0587	8.73	303.2	1.3168	0.0894	13.35
280.0	1.3782	0.0469	6.75	293.0	1.2401	0.0625	9.96	303.2	1.3017	0.0884	13.37
280.0	1.3284	0.0456	6.80	293.0	1.3469	0.0679	9.95	306.0	1.4181	0.1089	15.08
284.4	1.2199	0.0480	7.78	293.0	1.3308	0.0672	9.97	306.0	1.0881	0.0830	14.99
284.4	1.3320	0.0513	7.63	297.5	1.1619	0.0680	11,52	306.0	0.8271	0.0633	15.03
$\ln x_2$=(4.17±0.15)–(2567±44)·1/T											
acetonitrile											
295.5	1.2594	0.0103	1.16	299.5	1.3712	0.0147	1.51	307.0	1.2929	0.0186	2.03
295.5	1.3637	0.0118	1.22	299.5	1.3023	0.0143	1.55	313.1	1.1703	0.0220	2.64
295.5	1.3007	0.0113	1.23	303.0	1.1846	0.0139	1.65	313.1	1.3410	0.0250	2.62
298.3	1.1924	0.0114	1.35	303.0	1.3506	0.0158	1.65	313.1	1.2590	0.0237	2.65
298.3	1.3286	0.0128	1.36	303.0	1.3063	0.0153	1.65	316.5	1.1167	0.0252	3.18
298.3	1.3384	0.0129	1.36	303.2	1.2040	0.0144	1.69	316.5	1.3379	0.0303	3.18
298.5	1.2071	0.0124	1.45	303.2	1.2915	0.0157	1.71	316.5	1.2681	0.0289	3.20
298.5	1.3456	0.0139	1.45	303.2	1.3294	0.0162	1.71	321.5	1.2108	0.0352	4.09
298.5	1.3002	0.0135	1.46	307.0	1.0847	0.0154	2.00	321.5	1.2864	0.0364	3.98
299.5	1.4712	0.0158	1.51	307.0	1.3316	0.0190	2.01	321.5	1.2670	0.0356	3.95
$\ln x_2$=(7.82±0.45)–(4299±139)·1/T											

Продовження Table 1

T, K	m_1, g	m_2, g	$x_2\cdot10^3$	T, K	m_1, g	m_2, g	$x_2\cdot10^3$	T, K	m_1, g	m_2, g	$x_2\cdot10^3$
n-propanol											
293.6	1.3154	0.0092	1.44	303.4	1.3329	0.0177	2.73	309.1	1.3736	0.0247	3.70
293.6	1.3915	0.0097	1.44	305.6	1.2281	0.0172	2.89	309.1	1.3016	0.0232	3.66
293.6	1.3042	0.0089	1.41	305.6	1.3682	0.0193	2.91	312.1	1.1963	0.0241	4.15
298.5	1.2996	0.0128	2.04	305.6	1.2964	0.0183	2.91	312.1	1.3788	0.0278	4.14
298.5	1.3540	0.0133	2.02	308.5	1.2066	0.0204	3.48	312.1	1.3107	0.0265	4.15
298.5	1.3227	0.0131	2.05	308.5	1.3735	0.0228	3.41	317.2	1.1688	0.0320	5.62
303.4	1.1710	0.0150	2.64	308.5	1.3017	0.0216	3.41	317.2	1.3419	0.0367	5.61
303.4	1.3488	0.0174	2.65	309.1	1.1941	0.0214	3.69	317.2	1.3042	0.0346	5.44
$\ln x_2=(11.42\pm0.29)–(5269\pm87)\cdot1/T$											
isopropanol											
290.5	1.2519	0.0078	1.28	301.1	1.3236	0.0151	2.35	308.6	1.3829	0.0231	3.43
290.5	1.3865	0.0084	1.25	303.5	1.2324	0.0157	2.62	308.6	1.2999	0.0215	3.40
290.5	1.3629	0.0084	1.27	303.5	1.4114	0.0180	2.62	312.0	1.2793	0.0260	4.18
298.5	1.2160	0.0119	2.02	303.5	1.3118	0.0168	2.64	312.0	1.3280	0.0270	4.18
298.5	1.4050	0.0141	2.07	305.4	1.1789	0.0170	2.97	312.0	1.3357	0.0278	4.28
298.5	1.3513	0.0132	2.01	305.4	1.3569	0.0193	2.93	317.1	1.2230	0.0336	5.64
301.1	1.2382	0.0140	2.33	305.4	1.3302	0.0193	2.98	317.1	1.3234	0.0362	5.61
301.1	1.3552	0.0154	2.34	308.6	1.2148	0.0203	3.44	317.1	1.2992	0.0357	5.64
$\ln x_2=(10.93\pm0.30)–(5116\pm90)\cdot1/T$											
n-butanol											
297.5	1.2979	0.0112	2.19	303.4	1.3164	0.0148	2.85	313.2	1.3341	0.0214	4.06
297.5	1.3978	0.0121	2.20	305.6	1.2584	0.0154	3.10	313.2	1.3345	0.0214	4.06
297.5	1.3160	0.0112	2.16	305.6	1.3358	0.0162	3.08	314.9	1.1696	0.0208	4.50
298.5	1.1520	0.0108	2.38	305.6	1.3388	0.0162	3.07	314.9	1.2811	0.0229	4.53
298.5	1.4246	0.0128	2.28	307.5	1.2795	0.0173	3.43	314.9	1.3464	0.0238	4.48
298.5	1.3240	0.0122	2.34	307.5	1.3551	0.0190	3.55	317.0	1.1660	0.0222	4.82
301.1	1.2118	0.0123	2.58	307.5	1.3458	0.0181	3.41	317.0	1.3949	0.0269	4.88
301.1	1.3725	0.0141	2.61	309.0	1.2155	0.0170	3.55	317.0	1.2978	0.0234	4.57
301.1	1.3250	0.0137	2.62	309.0	1.3583	0.0194	3.62	322.2	1.1947	0.0276	5.84
303.4	1.3371	0.0147	2.79	309.0	1.3310	0.0190	3.62	322.2	1.3554	0.0313	5.84
303.4	1.2831	0.0142	2.81	313.2	1.2173	0.0200	4.16	322.2	1.3251	0.0305	5.82
$\ln x_2=(6.52\pm0.29)–(3758\pm88)\cdot1/T$											
isobutanol											
294.9	1.2909	0.0081	1.59	302.9	1.3696	0.0123	2.28	312.5	1.3105	0.0183	3.54
294.9	1.3531	0.0084	1.58	302.9	1.3175	0.0120	2.31	313.2	1.3361	0.0184	3.49
294.9	1.3385	0.0084	1.59	305.5	1.2057	0.0119	2.50	313.2	0.9663	0.0130	3.41
298.1	1.2127	0.0084	1.76	305.5	1.3698	0.0134	2.48	313.2	0.9775	0.0143	3.71
298.1	1.3784	0.0098	1.81	305.5	1.3022	0.0130	2.53	317.6	1.0374	0.0180	4.39
298.1	1.3405	0.0094	1.78	307.4	1.2329	0.0144	2.96	317.6	1.3449	0.0220	4.14
301.0	1.2219	0.0100	2.08	307.4	1.3114	0.0153	2.96	317.6	1.3234	0.0216	4.14
301.0	1.3610	0.0109	2.03	307.4	1.3420	0.0159	3.01	322.5	1.2305	0.0275	5.65
301.0	1.3291	0.0107	2.04	312.5	1.2109	0.0173	3.62	322.5	1.2979	0.0284	5.54
302.9	1.1964	0.0107	2.27	312.5	1.3456	0.0187	3.52	322.5	1.3089	0.0286	5.53
$\ln x_2=(8.25\pm0.40)–(4343\pm123)\cdot1/T$											

Note: * – T is the temperature at which solubility was determined, K; m_1 is the mass of solvent, g; m_2 is the mass of dissolved acid, g; and x_2 is the mole fraction of dissolved acid in the solution.

determined at T_{fus} ; the values of $\Delta_{sol}H^0$ and $\Delta_{sol}S^0$ were determined in the temperature intervals within which the generally accepted temperature of 298 K is present. Therefore, in order to generalize the results of the experimental studies, it was decided to recalculate $\Delta_{fus}H^0$ and $\Delta_{fus}S^0$ to 298 K using equations (6) and (7):

$$\Delta_{fus}H^0_{298} = \Delta_{fus}H^0_{T_{fus}}\left[1+\frac{298-T_{fus}}{1.35\cdot T_{fus}}\right], \tag{6}$$

$$\Delta_{fus}S^0_{298} = \Delta_{fus}S^0_{T_{fus}}\left[1+0.74\cdot\ln\frac{298}{T_{fus}}\right]. \qquad (7)$$

The recalculated values of the thermodynamic parameters of the melting process ($\Delta_{fus}H^0_{298} = 33.1 \pm 1.3$ kJ/mol; $\Delta_{fus}S^0_{298} = 69.7 \pm 2.0$ J/(mol·K)) were used to determine $\Delta_{mix}H^0_{298}$ and $\Delta_{mix}S^0_{298}$ according to equations (4) and (5) (Table 3). Table 3 also shows the mole fractions of the dissolved substance at 298 K in a number of solvents used and the standard values of their enthalpy $\Delta_{sol}H^0_{298}$ and entropy $\Delta_{sol}S^0_{298}$ of solvation.

The value and sign of the heat of mixing of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid in the solvents used is determined as the difference in energy consumed in the destruction of intermolecular bonds in the initial components and released when new bonds are formed between the solvent and the dissolved substance. Thus, the values of the enthalpies of mixing in methyl acetate and ethyl acetate are slightly less than zero, which indicates the energy equivalence of bonds between homogeneous and heterogeneous molecules in solution. However, the value of $\Delta_{mix}H^0_{298}$ of the studied acid with acetone indicates the formation of much stronger new bonds than in the original molecules due to the relative «compactness» of the acetone molecule and similar polarity with methyl and ethyl acetate.

At the same time, the highest values of the enthalpy of mixing are observed when dissolved in propanol isomers, which are lower alcohols, due to the energy expenditure during the breaking of hydrogen bonds between alcohol molecules. The values of these energies are much higher than the energy of intermolecular interactions between different molecules in the resulting solution. The values of $\Delta_{mix}H^0_{298}$ of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid in butanols are insignificant and close to zero, which is due to the nature of higher alcohols, since an increase in the length of the hydrocarbon radical causes a decrease in polarity, which directly affects the value of $\Delta_{mix}H^0_{298}$.

The value of $\Delta_{mix}H^0_{298}$ of the studied acid with acetonitrile is also close to zero, since in the acetonitrile molecule the energy of intermolecular interactions is provided only by dipole-dipole interactions.

It is also worth noting the so-called compensation effect (Fig. 2), which indicates the same type of interactions between the carboxyl group of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid and the corresponding functional groups of the selected range of solvents.

Conclusions

The thermodynamic properties of the solubility of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid were determined for the first time in methyl acetate, ethyl acetate, acetone, acetonitrile, n-propanol, isopropanol, n-butanol, and isobutanol. The results of the experimental studies can be used to predict the reaction

Table 2

Determined enthalpies of fusion and vaporization of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid

Sample number	T_1–T_2, K	$\Sigma\Delta m\cdot10^3$, g	A	–B, K	$\Delta_{vap}H$, kJ/mol	m_0, g	Δm_{vap}, g	S, K·s	q_{vap}, J	$\Delta_{fus}H$, kJ/mol
T_{fus}=442.4±1.5 K; K=0.03628 J/K·s										
1	522.6–600.8	35.7	24.08	12445	107.10	0.1009	0.0013	436.9	0.4813	44.4
2	511.2–593.8	11.2	23.10	12414	106.90	0.1096	0.0013	456.9	0.4621	42.8
Mean value:					107.00±0.14	Mean value:				43.6±1.2

Table 3

Thermodynamic parameters of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid solutions at 298 K

Solvent	$x_2\cdot10^3$	$\Delta_{sol}H^0_{298}$, kJ/mol	$\Delta_{sol}S^0_{298}$, J/mol·K	$\Delta_{mix}H^0_{298}$, kJ/mol	$\Delta_{mix}S^0_{298}$, J/mol·K
methyl acetate	6.74	28.52±0.72	54.1±2.4	–4.6±1.5	–15.6±3.1
ethyl acetate	5.94	30.17±0.82	58.6±2.7	–2.9±1.5	–11.1±3.4
acetone	11.70	21.34±0.37	34.6±1.3	–11.8±1.3	–35.7±2.4
acetonitrile	1.35	35.70±1.20	65.0±3.7	2.6±1.8	–4.7±4.2
n-propanol	1.92	43.81±0.73	94.8±2.4	10.7±1.5	25.1±3.1
isopropanol	1.90	42.53±0.75	90.6±2.4	9.4±1.5	20.9±3.1
n-butanol	2.26	31.24±0.73	54.0±2.4	–1.9±1.5	–15.7±3.1
isobutanol	1.78	36.10±1.00	68.5±3.3	3.0±1.6	–1.2±3.9

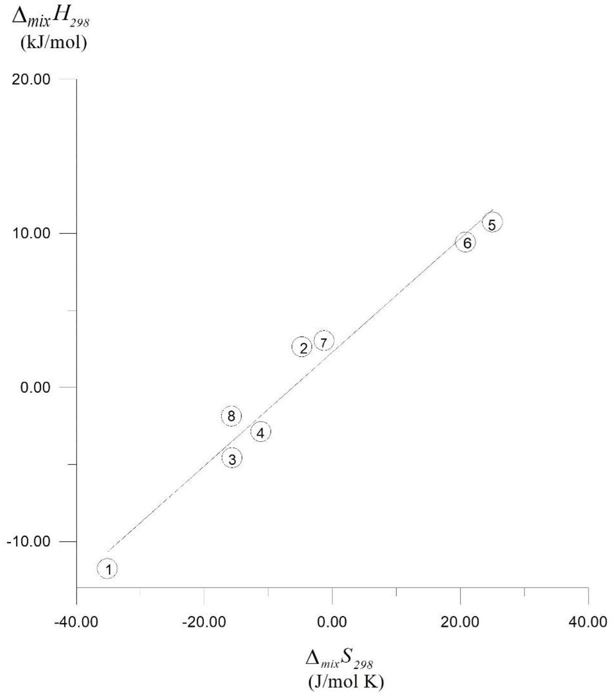

Fig. 2. Dependence of the enthalpy of mixing on the entropy of mixing in different solvents: (1) acetone; (2) acetonitrile; (3) methyl acetate; (4) ethyl acetate; (5) n-propanol; (6) isopropanol; (7) n-butanol; and (8) isobutanol. $\Delta_{mix}H=0.369\Delta_{mix}S+2.287$; R=0.967

behavior of the substance under study in solution, as well as to optimize purification and separation processes.

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ТЕРМОДИНАМІЧНІ ПАРАМЕТРИ РОЗЧИННОСТІ 3-(1,5-ДИФЕНІЛПІРОЛ-2-ІЛ)ПРОПАНОВОЇ КИСЛОТИ В ОРГАНІЧНИХ РОЗЧИННИКАХ

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Вперше експериментально встановлено температурну залежність розчинності 3-(1,5-дифенілпірол-2-іл)пропанової кислоти у восьми органічних розчинниках (метилацетат, етилацетат, ацетон, ацетонітрил, н-пропанол, ізопропанол, н-бутанол, ізобутанол) в інтервалі температур 275,5–322,0 К при атмосферному тиску. За температурними залежностями розчинності розраховано ентальпії та ентропії розчинення. На основі даних диференційно-термічного аналізу визначено ентальпію плавлення при температурі плавлення (T_{fus}=442,41,5 K). Наведено рівняння, за якими здійснювали перерахунок ентальпій та ентропій плавлення синтезу до 298 К. Розраховано термодинамічні параметри процесу змішування 3-(1,5-дифенілпірол-2-іл)пропанової кислоти з розчинниками. За термодинамічними параметрами змішування встановлено ефект компенсації та проаналізовано природу взаємодії між розчинником і розчиненою речовиною.

Ключові слова: розчинність, ентальпія розчинення, ентальпія плавлення, ентальпія змішування, 3-(1,5-дифенілпірол-2-іл)пропанова кислота.

THERMODYNAMIC PARAMETERS OF THE SOLUBILITY OF 3-(1,5-DIPHENYLPYRROL-2-YL)PROPANOIC ACID IN ORGANIC SOLVENTS

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For the first time, the temperature dependence of the solubility of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid was experimentally determined in eight organic solvents (methyl acetate, ethyl acetate, acetone, acetonitrile, n-propanol, isopropanol, n-butanol, and isobutanol) within the temperature range of 275.5–322.0 K at atmospheric pressure. Based on the solubility data, the enthalpies and entropies of solvation were calculated. Using differential thermal analysis, the enthalpy of fusion at the melting point (T_{fus}=442.4±1.5K) was determined. The equations for recalculating the enthalpies and entropies of fusion to 298 K are presented. The thermodynamic parameters of the mixing process of 3-(1,5-diphenylpyrrol-2-yl)propanoic acid with the solvents were also calculated. A compensation effect in the thermodynamic parameters of mixing was established, and the nature of the interactions between the solvent and the dissolved substance was analyzed.

Keywords: solubility; enthalpy of solvation; enthalpy of fusion; enthalpy of mixing; 3-(1,5-diphenylpyrrol-2-yl)propanoic acid.

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