

THERMODYNAMIC PROPERTIES
OF 2-CYANO-3-[5-(PHENYL)-2-FURYL]-2-PROPENAMIDE
AND 2-CYANO-3-[5-(4-METHYLPHENYL)-2-FURYL]-
2-PROPENAMIDE SOLUTIONS
IN ORGANIC SOLVENTS

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Abstract. The fusion temperature of 2-cyano-3-[5-(phenyl)-2-furyl]-2-propenamide and 2-cyano-3-[5-(4-methylphenyl)-2-furyl]-2-propenamide and their temperature dependence of dissolution in acetonitrile, benzene, dimethylketone, ethyl acetate and 2-propanol have been determined. According to the temperature dependence the differential enthalpies and entropies of the solution were calculated. Taking into account the entropies of fusion the entropies and enthalpies of mixing were calculated at 298 K. The effect of intermolecular interaction in the investigated solutions on their solubility and enthalpies of mixing has been analyzed.

Keywords: enthalpy of solution, entropy of solution, enthalpy of mixing, entropy of fusion, differential thermal analysis.

1. Introduction

A great number of modern drugs are created on the basis of five-term heterocyclic compounds with one or two heteroatoms. Their application has become possible due to a biological activity of natural heterocyclic compounds [1-2]. Thorough investigation of their synthetic analogues provides the synthesis of drugs of new generation. Alkylfuran derivatives belong to the compounds, which have diverse biological activity and may be used for the creation of new drugs with different pharmaceutical

properties, namely antimicrobial activity, as well as for treatment of neurodegenerative and cancer diseases [3-4].

2-Cyano-3-[5-(phenyl)-2-furyl]-2-propenamide and 2-cyano-3-[5-(4-methylphenyl)-2-furyl]-2-propenamide are the derivatives of alkylfuranes. They contain electron-donor and electron-acceptor functional groups which may be reactive centers at new drugs synthesis. The synthesis is usually conducted in the solvent medium, using especially purified reactants. The compounds purity is provided by a multistep purification including distillation, sublimation and recrystallization. The latter process is realized with widely used solvents. Therefore the investigation of solubility and thermodynamic parameters which accompany the solvent interaction with a solute is an actual problem to optimize extraction and purification processes of the organic compounds.

2. Experimental

The scheme of 2-cyano-3-[5-(phenyl)-2-furyl]-2-propenamide (**I**) and 2-cyano-3-[5-(4-methylphenyl)-2-furyl]-2-propenamide (**II**) synthesis is presented in Fig. 1.

The compounds **I** and **II** were obtained *via* interaction of equimolar quantities of corresponding aldehyde and cyanacetic acid amide. The reaction proceeds in the ethanol medium at heating in the presence of piperidine. The resulting precipitate was filtered, washed by ethanol and fourfold recrystallized from ethanol-dimethylformamide mixture.

The samples were identified by NMR spectroscopy. The spectra were recorded using Varian 600 instrument (600 MHz). DMSO-d₆ was used as a solvent. The chemical shifts (*d*, ppm) relative to DMSO signal (2.5 ppm) are represented in Table 1. Compounds purity was determined using Agilent 1100 HPLC equipped with diode matrix and mass selective detector on the column Zorbax SB-C18, 4.6x15 mm, An acetonitrile-water with 0.1 % TEA (95:5) was an eluent.

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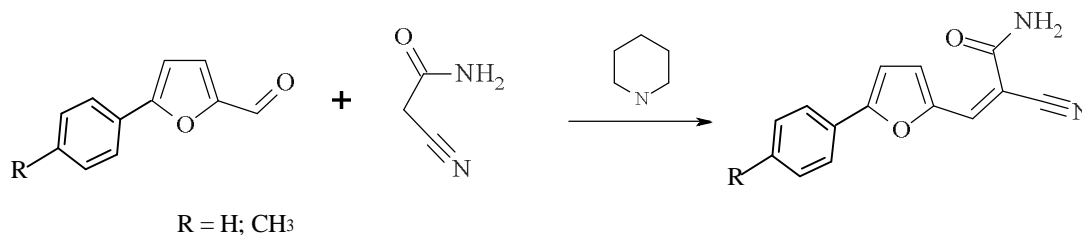


Fig. 1. Scheme of 2-cyano-3-[5-(phenyl)-2-furyl]-2-propenamide and 2-cyano-3-[5-(4-methylphenyl)-2-furyl]-2-propenamide synthesis

Table 1

NMR ¹H spectra and purity of investigated compounds

Compound	Chemical shifts, δ , ppm	Purity, %
I	¹ H NMR (600 MHz, DMSO) δ 7.35 (d, J = 3.7 Hz, 1H, Fur), 7.41 – 7.47 (m, 2H), 7.50–7.54 (m, 2H), 7.70 (br.s, 1H, NH ₂), 7.80 (br.s, 1H, NH ₂), 7.91 (d, J = 7.6 Hz, 2H, C ₆ H ₅), 7.99 (s, 1H, CH)	100.0
II	¹ H NMR (600 MHz, DMSO) δ 2.35 (s, 2,5H, CH ₃), 2.36 (s, 0,5H, CH ₃), 7.28 (d, J = 3.7 Hz, 1H, Fur) 7.33 (d, J = 7.9 Hz, 2H, C ₆ H ₄), 7.41 (d, J = 3.8 Hz, 1H, Fur), 7.67 (br.s, 0.85H, NH ₂ , E-isomer), 7.71 (br.s, 0.15H, NH ₂ , Z-isomer), 7.75 (br.s, 0.3 H, NH ₂ , Z- isomer), 7.77 (br.s, 0.7 H, NH ₂ , E- isomer), 7.80 (d, J = 8.1 Hz, 2H, C ₆ H ₄), 7.96 (s,0.85 H, =CH, E-isomer), 7.97 (s,0.15 H, =CH, Z-isomer)	16.0/74.0 Z/E isomer

Table 2

Physico-chemical properties of the solvents

Solvents	M, g/mol	n_D^{20}		T_{boil} K		Content of the main component, wt %
		lit.	determ.	lit.	determ.	
Acetonitrile	41.053	1.3442 [5]	1.3444	81.6 [5]	81.4	99.9
Benzene	78.112	1.5017[5]	1.5019	80.1[5]	79.0	99.9
Dimethylketone	58.080	1.3591 [5]	1.3590	56.2 [5]	56.0	99.8
Ethylacetate	88.106	1.3724 [5]	1.3722	77.1 [5]	76.8	99.9
2-Propanol	60.096	1.3776 [5]	1.3776	82.2 [5]	81.9	99.9

A series of widely used low-boiling solvents differed by polarity was chosen for investigations. Before usage the solvents were purified *via* fractional distillation followed by their identification relative to a refractive index (n_D^{20}) and boiling temperature (T_{boil}). The content of the main component was determined using a gas-liquid chromatography. Table 2 represents physico-chemical properties of the investigated solvents and data from the literature for comparison.

The solvents were saturated in a hermetic glass vessel equipped with a Teflon stirrer, thermometer and nipple for sampling. Before the experiments the substance was kept in the solvent at room temperature for two days. Then it was stirred at the experiment temperature for 90 min. The water temperature in a thermostat was kept with an accuracy of ± 0.1 K. Stirrer rotation speed was 30–40 rev/min. To confirm the achieved equilibrium the studies were carried out at higher and lower temperatures. The absence of hysteresis loop on the temperature dependence curve confirms the state close to an equilibrium one.

The sampling was carried out by a series of 2-3 samples which were transferred in previously weighed bottles. After the bottles were hermetically closed and weighed they were opened and dried till the constant weight in the oven at 343 K. The dry sample was weighed and its mole fraction in the saturated solution was calculated. The analytical balance VLR-200 was used for weighting with the accuracy of ± 0.0002 g.

Derivatographic investigations were carried out using Q-1500 D Paulik-Paulik-Erdey derivatograph. The samples were analyzed under dynamic mode with the heating rate of 3 K/min in the air medium.

3. Results and Discussion

The investigation results are given in Table 3: experimental temperature (T); weight (m_2) and mole fraction (x_2) of dissolved compounds. The results of the temperature dependence are approximated by the equation $\ln x_2 = A - B/T$ (Table 3). Here and hereinafter the errors of all values are given for the significance level of 0.95.

Table 3

**Temperature dependence of investigated compounds solubility
in the organic solvents**

<i>T</i> , K	$m_2 \cdot 10^3$, g	$x_2 \cdot 10^3$	<i>T</i> , K	$m_2 \cdot 10^3$, g	$x_2 \cdot 10^3$	<i>T</i> , K	$m_2 \cdot 10^3$, g	$x_2 \cdot 10^3$	<i>T</i> , K	$m_2 \cdot 10^3$, g	$x_2 \cdot 10^3$
1	2	3	4	5	6	7	8	9	10	11	12
Compound I											
Acetonitrile											
296.8	2.90	0.48	309.6	5.85	0.92	323.0	11.70	1.43	339.5	18.95	2.81
296.8	3.00	0.47	309.6	5.95	0.89	325.6	10.70	1.59	339.5	195.5	2.79
296.8	3.30	0.49	314.5	6.75	1.10	325.6	15.40	1.68	339.5	20.70	2.82
299.4	3.20	0.53	314.5	7.95	1.03	332.0	13.50	2.09	343.4	21.80	3.10
299.4	3.70	0.58	314.5	8.85	1.00	332.0	15.85	2.10	343.4	23.00	3.14
299.4	3.80	0.57	320.1	10.45	1.37	332.0	25.40	2.11	343.4	23.95	3.10
303.3	4.00	0.67	320.1	13.80	1.35	336.0	17.20	2.42	346.5	17.65	3.69
303.3	4.30	0.67	323.0	8.60	1.39	336.0	144.50	2.41	346.5	18.30	3.67
303.3	4.50	0.67	323.0	9.50	1.43	336.0	179.50	2.45	346.5	21.60	3.61
$\ln x_2 = (6.13 \pm 0.21) - (4081 \pm 67) \cdot 1/T$											
Benzene											
298.4	0.80	0.20	314.0	1.80	0.43	323.2	4.00	0.63	331.5	4.20	0.82
298.4	0.90	0.19	314.0	2.35	0.43	327.9	3.00	0.70	331.5	5.10	0.86
298.4	1.00	0.20	314.0	2.60	0.46	327.9	3.00	0.72	333.5	5.45	0.97
304.9	1.20	0.28	317.5	2.00	0.50	327.9	4.10	0.73	333.5	5.50	0.99
304.9	2.20	0.29	317.5	2.05	0.51	329.0	3.00	0.81	333.5	6.00	0.97
304.9	2.30	0.28	317.5	3.20	0.51	329.0	3.30	0.77	337.4	4.05	1.18
309.1	1.20	0.34	320.7	2.00	0.59	329.0	4.60	0.75	337.4	4.30	1.20
309.1	1.40	0.33	320.7	2.05	0.56	330.3	1.60	0.87	337.4	4.80	1.20
311.8	3.00	0.37	320.7	3.80	0.58	330.3	2.20	0.88	343.6	3.80	1.44
311.8	3.65	0.40	323.2	2.00	0.64	330.3	2.20	0.91	343.6	6.00	1.40
311.8	4.30	0.38	323.2	3.30	0.62	331.5	3.80	0.88	343.6	8.00	1.40
$\ln x_2 = (6.44 \pm 0.31) - (4436 \pm 100) \cdot 1/T$											
Dimethylketone											
297.0	8.45	2.11	302.9	7.90	2.56	306.5	14.40	2.82	315.0	13.90	3.65
297.0	9.85	2.16	302.9	9.95	2.48	308.0	12.40	2.90	315.0	14.70	3.68
297.0	9.95	2.13	303.3	11.55	2.64	308.0	12.75	2.92	315.0	15.90	3.64
297.5	7.95	2.19	303.3	12.55	2.62	308.0	16.30	2.87	317.5	10.05	3.86
297.5	8.10	2.18	303.3	12.65	2.65	310.9	10.45	3.10	317.5	10.90	3.82
297.5	9.15	2.22	303.5	9.65	2.51	310.9	11.05	3.13	317.5	13.40	3.85
301.0	8.50	2.47	303.5	10.70	2.49	310.9	13.60	3.14	321.6	9.70	4.31
301.0	10.60	2.36	303.5	11.10	2.49	312.4	10.25	3.34	321.6	17.55	4.24
301.0	10.90	2.45	306.5	9.35	2.86	312.4	17.70	2.29	321.6	17.80	4.25
302.9	7.60	2.45	306.5	9.95	2.84	312.4	21.20	3.30			
$\ln x_2 = (2.90 \pm 0.28) - (2688 \pm 85) \cdot 1/T$											
Ethylacetate											
296.1	4.20	1.25	309.1	6.75	1.88	323.7	8.00	2.75	332.0	27.50	3.39
296.1	4.90	1.27	314.0	8.25	2.16	325.6	9.55	3.02	333.5	14.60	3.73
296.1	5.20	1.22	314.0	10.95	2.10	325.6	10.25	2.84	333.5	14.75	3.66
299.7	4.10	1.37	314.2	6.95	2.14	325.6	11.15	2.96	333.5	18.45	3.62
299.7	4.20	1.40	314.2	8.55	2.07	327.0	9.15	3.10	337.4	9.05	4.02
299.7	4.30	1.39	314.2	9.00	2.15	327.0	11.30	2.91	337.4	12.65	4.08
303.9	6.00	1.67	320.7	7.35	2.46	329.0	8.65	3.24	337.4	16.20	4.08

Table 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
303.9	6.90	1.66	320.7	8.00	2.55	329.0	13.20	3.17	338.0	21.65	4.01
303.9	7.00	1.63	320.7	8.25	2.66	329.0	13.85	3.17	338.0	21.75	4.01
308.5	6.25	1.78	321.0	8.30	2.61	330.1	6.70	3.38	338.0	28.85	3.93
308.5	6.65	1.83	321.0	9.05	2.56	330.1	8.60	3.32	343.6	17.90	4.83
308.5	9.30	1.84	321.0	11.30	2.63	330.1	10.85	3.33	343.6	19.90	4.80
309.1	5.90	1.92	323.7	6.05	2.77	332.0	19.15	3.40	343.6	21.20	4.75
309.1	6.40	1.97	323.7	6.45	2.73	332.0	21.95	3.40			
$\ln x_2 = (2.80 \pm 0.16) - (2808 \pm 51) \cdot 1/T$											
2-Propanol											
297.3	1.15	0.19	306.5	1.15	0.30	315.0	1.95	0.46	321.6	2.55	0.64
297.3	1.20	0.19	306.5	1.50	0.30	315.0	2.10	0.47	321.6	3.45	0.66
297.3	1.20	0.20	306.5	1.65	0.30	315.0	2.40	0.45	321.6	3.95	0.67
299.2	1.65	0.19	308.0	1.40	0.34	316.0	1.70	0.51	323.0	2.80	0.69
299.2	1.80	0.20	308.0	1.60	0.35	316.0	2.45	0.50	323.0	2.85	0.73
299.2	1.80	0.20	308.0	2.20	0.34	316.0	3.10	0.51	323.0	3.00	0.72
302.8	0.90	0.24	310.1	1.80	0.36	317.5	1.85	0.53	326.9	4.55	0.82
302.8	1.30	0.20	310.1	1.85	0.35	317.5	2.35	0.54	326.9	4.80	0.82
302.8	1.60	0.24	310.1	1.90	0.36	317.5	2.85	0.54	326.9	7.65	0.84
303.5	0.90	0.27	311.9	1.35	0.39	320.5	2.65	0.64	328.1	4.20	0.91
303.5	0.95	0.26	311.9	2.00	0.41	320.5	3.30	0.63	328.1	4.50	0.92
303.5	1.25	0.27	311.9	2.25	0.40	320.5	4.80	0.61	328.1	5.40	0.94
$\ln x_2 = (8.45 \pm 0.31) - (5072 \pm 97) \cdot 1/T$											
Compound II											
Acetonitrile											
293.5	8.50	1.30	303.4	11.00	1.76	308.8	14.50	2.24	312.7	10.35	2.51
293.5	10.10	1.31	303.4	11.00	1.83	310.0	13.30	2.38	312.7	12.70	2.43
293.5	10.75	1.29	303.6	9.40	1.91	310.0	13.45	2.24	312.7	16.45	2.50
297.6	10.00	1.53	303.6	12.20	1.90	310.0	13.60	2.35	316.9	19.00	2.79
297.6	10.85	1.53	303.6	12.30	1.85	312.5	12.60	2.53	316.9	20.30	2.79
297.6	12.40	1.48	305.6	11.35	1.91	312.5	13.40	2.53	316.9	22.00	2.82
298.0	8.90	1.54	305.6	12.35	1.93	312.5	22.35	2.45	320.5	18.55	3.16
298.0	10.00	1.51	305.6	16.15	1.88	312.6	15.30	2.48	320.5	23.25	3.19
298.0	12.00	1.52	308.8	12.40	2.13	312.6	17.10	2.42	320.5	26.50	3.18
303.4	9.30	1.80	308.8	14.50	2.15	312.6	22.15	2.44			
$\ln x_2 = (3.89 \pm 0.28) - (3094 \pm 86) \cdot 1/T$											
Benzene											
297.4	2.25	0.58	312.3	10.0	1.11	323.3	8.85	1.64	333.3	8.00	2.49
297.4	2.45	0.58	318.0	4.60	1.39	323.3	11.55	1.68	333.3	13.05	2.46
297.4	3.60	0.54	318.0	7.80	1.43	325.0	7.35	1.88	333.3	8.20	2.55
303.1	3.00	0.74	318.0	8.70	1.43	325.0	7.85	1.91	338.0	12.70	3.06
303.1	3.10	0.74	321.9	6.85	1.67	325.0	12.85	1.87	338.0	15.55	2.99
303.1	3.70	0.73	321.9	8.50	1.67	327.0	9.95	2.02	338.0	18.80	3.14
307.8	3.10	0.92	321.9	7.55	1.70	327.0	11.95	1.93	340.5	10.90	3.39
307.8	3.60	0.93	322.1	5.45	1.69	327.0	10.15	1.95	340.5	16.70	3.39
307.8	5.80	0.92	322.1	5.85	1.63	330.0	8.35	2.21	340.5	14.30	3.39
312.3	4.70	1.14	322.1	6.00	1.64	330.0	8.35	2.24			
312.3	4.80	1.16	323.3	7.10	1.71	330.0	13.00	2.16			
$\ln x_2 = (6.41 \pm 0.20) - (4127 \pm 65) \cdot 1/T$											
Dimethylketone											
293.4	14.00	6.14	294.8	30.90	6.18	301.5	30.95	7.35	310.1	29.65	8.72

Table 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
293.4	15.15	6.02	297	24.85	6.57	303.9	22.50	7.77	310.1	35.60	8.72
293.4	19.25	5.99	297	26.90	6.61	303.9	26.50	7.78	312.5	31.15	9.40
293.4	23.00	5.99	297	28.45	6.57	303.9	54.70	7.85	312.5	38.55	9.47
293.4	27.85	6.05	297.8	20.30	6.64	306.8	22.80	8.26	312.5	45.25	9.41
293.4	35.30	5.97	297.8	24.20	6.52	306.8	24.60	8.18	316.5	37.55	10.08
294.8	25.65	6.30	297.8	25.45	6.54	306.8	38.60	8.27	316.5	47.75	10.22
294.8	25.90	6.23	301.5	26.90	7.47	310.1	27.90	8.73	316.5	59.35	10.32
$\ln x_2 = (2.11 \pm 0.17) - (2119 \pm 52) \cdot 1/T$											
Ethylacetate											
293.4	7.60	3.61	303.4	11.55	4.56	306.7	25.15	5.14	312.5	14.45	5.70
293.4	8.55	3.57	303.4	15.40	4.40	306.7	25.35	4.95	312.5	16.85	5.60
293.4	8.70	3.53	303.4	16.25	4.52	306.7	27.35	5.05	312.5	17.75	5.59
293.5	13.60	3.51	303.6	14.05	4.58	308.8	17.10	5.07	316.9	14.55	6.31
293.5	14.15	3.52	303.6	16.55	4.51	308.8	17.55	5.00	316.9	18.85	6.26
293.5	15.85	3.51	303.6	16.60	4.56	308.8	18.15	5.07	323.6	26.30	7.51
297.6	13.50	3.96	304.5	12.80	4.61	312.0	15.90	5.57	323.6	26.80	7.43
297.6	16.00	3.89	304.5	14.45	4.71	312.0	18.95	5.62	323.6	38.55	7.41
297.6	20.45	3.92	304.5	14.90	4.72	312.0	19.05	5.55			
$\ln x_2 = (2.23 \pm 0.20) - (2314 \pm 61) \cdot 1/T$											
2-Propanol											
296.2	3.00	0.78	309.8	7.00	1.54	319.1	12.15	2.41	330.5	13.10	3.54
296.2	3.35	0.76	309.8	9.30	1.58	322.0	13.30	2.67	330.5	17.20	3.54
296.2	6.00	0.80	314.9	9.80	2.00	322.0	14.80	2.66	330.5	16.75	3.55
299.1	4.60	0.89	314.9	9.35	1.93	322.0	9.90	2.68	333.3	19.05	4.10
299.1	5.00	0.98	314.9	12.00	1.93	323.3	17.20	2.74	333.3	16.60	4.10
299.1	8.95	0.96	316.8	9.20	2.22	323.3	17.65	2.71	333.3	24.95	4.12
302.7	4.50	1.12	316.8	16.75	2.16	323.3	16.35	2.72	338.0	23.70	5.06
302.7	5.00	1.15	316.8	20.15	2.14	327.0	11.80	3.21	338.0	29.40	5.08
302.7	6.75	1.07	318.0	9.75	2.24	327.0	19.358	3.10	338.0	37.75	5.06
306.4	5.25	1.40	318.0	12.80	2.21	327.0	23.05	3.22	340.5	36.30	6.08
306.4	7.80	1.42	318.0	12.60	2.25	330.2	19.30	3.65	340.5	25.95	6.11
306.4	10.00	1.36	319.1	16.05	2.43	330.2	18.20	3.68	340.5	38.80	6.06
309.8	6.20	1.58	319.1	12.75	2.35	330.2	24.90	3.73			
$\ln x_2 = (7.76 \pm 0.27) - (4409 \pm 85) \cdot 1/T$											

Table 4

Thermodynamic parameters of compounds I and II solubility in the organic solvents at 298 K

Solvent	$x_2 \cdot 10^3$	$\Delta_{sol}H^0$	$\Delta_{mix}H^0$	$\Delta_{sol}S^0$	$\Delta_{mix}S^0$
		kJ/mol		J/mol·K	
Compound I					
Acetonitrile	0.508±0.015	33.93±0.56	6.9±1.9	51.0±1.7	0.6±2.9
Benzene	0.1997±0.0064	36.88±0.83	9.9±2.1	53.5±2.6	3.1±3.6
Dimethylketone	2.198±0.069	22.35±0.71	-4.6±2.0	24.1±2.3	-26.3±3.4
Ethylacetate	1.320±0.035	23.35±0.42	-3.6±1.9	23.3±1.3	-27.1±2.8
2-Propanol	0.1870±0.0042	42.17±0.81	15.2±2.1	70.3±2.6	19.9±3.6
Compound II					
Acetonitrile	1.515±0.042	25.72±0.72	-4.1±1.9	32.3±2.3	-26.9±3.4
Benzene	0.576±0.020	34.31±0.54	4.4±1.9	53.3±1.7	-5.9±2.9
Dimethylketone	6.73±0.16	17.62±0.43	-12.2±1.8	17.5±1.4	-41.7±2.8
Ethylacetate	3.95±0.10	19.24±0.51	-10.6±1.9	18.5±1.7	-40.7±3.0
2-Propanol	0.868±0.032	36.65±0.71	6.9±1.9	64.5±2.2	6.3±3.2

Differential changes of enthalpy ($\Delta_{sol}H^0$) and entropy ($\Delta_{sol}S^0$) of the solution are calculated using the coefficients from Table 3 according to Eqs. (1) and (2). The results of the calculation are presented in Table 4.

$$\Delta_{sol}H^0 = R \cdot B \quad (1)$$

$$\Delta_{sol}S^0 = R \cdot A \quad (2)$$

where R – absolute gas constant, J/mol·K; A and B – constants of the equation $\ln x_2 = A - B/T$.

Calculated thermodynamic parameters of solutions $\Delta_{sol}H^0$ and $\Delta_{sol}S^0$ (Table 4) involve the process of solution forming ($\Delta_{mix}H^0$; $\Delta_{mix}S^0$) and phase transfer of the crystal compound to the liquid phase of the solution ($\Delta_{fus}H^0$; $\Delta_{fus}S^0$), see Eqs. (3) and (4).

$$\Delta_{sol}H^0 = \Delta_{mix}H^0 + \Delta_{fus}H^0 \quad (3)$$

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

Enthalpies of fusion ($\Delta_{fus}H^0$) are calculated according to Eq. (5), where correction for weight loss during fusion is taken into account [6]:

$$K \cdot S = q_{fus} + q_{vap} = m_0 \cdot \Delta_{fus}H + \Delta m_{vap} \cdot \Delta_{vap}H \quad (5)$$

where q_{fus} and q_{vap} – amount of heat absorbed during fusion and vaporization, respectively, J; m_0 – weight of the sample at the moment of fusion, g; Δm_{vap} – weight loss of the sample during the period to determine area S , g; $\Delta_{fus}H$ and $\Delta_{vap}H$ – specific enthalpies of fusion and vaporization at the fusion temperature, respectively, J/g; K – coefficient of heat transfer for the correspondence between the process heat efficiency and response as a peak area under DTA curve, J/K·s. The coefficient K was determined in [6] using standard solutions of silver nitrate, biphenyl, adipic and benzoic acids: $K \cdot 10^2 = 3.668 - 1.128 \cdot 10^{-2}T + 2.723 \cdot 10^{-5}T^2$; $S^2 = 5.96 \cdot 10^{-7}$.

Enthalpies of fusion of the investigated compounds obtained by derivatography are given in Table 5.

The change of entropy at fusion temperature is calculated according to Eq. (6):

$$\Delta_{fus}S_{T_{fus}} = \frac{\Delta_{fus}H_{T_{fus}}}{T_{fus}} \quad (6)$$

The obtained experimental values belong to different temperatures, because the values of $\Delta_{sol}H^0$ and $\Delta_{sol}S^0$ were calculated within the range from 293 to 342 K (Table 4), the values of $\Delta_{fus}H^0$ were determined at fusion temperatures (Table 5). So, to generalize the obtained results and to calculate thermodynamic parameters $\Delta_{mix}H^0$ and $\Delta_{mix}S^0$ at 298 K it is necessary to recalculate $\Delta_{fus}H^0$ and $\Delta_{fus}S^0$ using Eqs. (7) and (8) [7]:

$$\Delta_{fus}H_T = \Delta_{fus}H_{T_{fus}} \left[1 + \frac{T - T_{fus}}{1.35 \cdot T_{fus}} \right] \quad (7)$$

$$\Delta_{fus}S_T = \Delta_{fus}S_{T_{fus}} \left[1 + 0.74 \cdot \ln \frac{T}{T_{fus}} \right] \quad (8)$$

The values recalculated at 298 K are presented in Table 4.

Differential values $\Delta_{mix}H$ and $\Delta_{mix}S$ calculated according to Eqs. (3) and (4) (Table 4) characterize the interaction of the components in the solution. Their positive and negative values are connected with the type of intermolecular bonds, including hydrogen bonds between component and solution molecules [8]. The molecules have electron-donor (carbonyl, nitrile) and electron-acceptor (hydroxy, amine) groups capable to form hydrogen bonds, the energy of which is 15–20 kJ/mol for strong bonds and 4–6 kJ/mol – for weak bonds [9]. It is known [10, 11] that high specific enthalpy of vaporization partly confirms the formation of strong hydrogen bonds. For this purpose the enthalpy of vaporization of the compounds **I** and **II** determined by thermogravimetry were recalculated for 298 K according to the method given in [12] and enthalpies of vaporization of the solvents were taken from [11]. The results are presented in Table 6.

Table 5

Enthalpies of fusion of compounds I and II

m_0 , g	Dm_{vap} , g	S , K·s	q_{vap} , J	$D_{fus}H_{T_{fus}}$, kJ/mol	$D_{fus}H_{298}$, kJ/mol	$D_{fus}S_{T_{fus}}$, kJ/mol	$D_{fus}S_{298}$, kJ/mol
Compound I;				$T_{fus} = 480.8 \pm 1.5$ K; $K = 0.04539$ J/K·s			
0.2005	0.0023	704.5	1.038	36.77	26.41	76.5	49.4
0.1987	0.0022	718.3	0.963	37.93	27.25	78.9	50.9
0.2026	0.0021	731.8	0.922	37.98	27.28	79.0	51.0
Average value:				37.6 ± 1.7	27.0 ± 1.9	78.1 ± 2.3	50.4 ± 2.5
Compound II;				$T_{fus} = 461.0 \pm 1.1$ K; $K = 0.04255$ J/K·s			
0.1839	0.0009	690.1	0.3445	39.79	29.8	86.3	58.4
0.1997	0.0006	752.1	0.2109	40.16	29.4	89.0	60.2
0.2017	0.0007	777.2	0.2468	41.04	30.3	87.1	59.0
Average value:				40.3 ± 1.6	29.8 ± 1.8	87.5 ± 2.1	59.2 ± 2.3

Table 6

Enthalpies of vaporization and energy of intermolecular interaction at 298 K (kJ/mol)

Molecular mass, g/mol	Compound	$\Delta_{vap}H_{298}^0$	Hypothetic alkane $\Delta_{vap}H = E_{disp}$	$E_{dum} + E_H$
41.05	Acetonitrile	33.45±0.21 [5]	15.5±1.8 [11]	17.9±2.0 [11]
58.07	Dimethylketone	30.5±1.5 [5]	24.4±3.2 [11]	6.1±4.7 [11]
60.06	2-Propanol	45.0±2.0 [5]	23.0±3.7 [11]	22.0±5.7 [11]
78.11	Benzene	33.9 ± 1.0 [5]	28.7±2.3 [11]	5.2±3.3 [11]
88.10	Ethylacetate	35.1±2.0 [5]	32.1±3.7 [11]	3.0±5.7 [11]
238.25	I	134.1±1.1	85.4±3.7	48.7±4.8
252.27	II	123.4±1.8	90.7±4.7	32.7±6.5

The compound vaporization is accompanied by destroying all intermolecular bonds provided by dispersive, dipole-dipole interactions and hydrogen bonds [10, 13]. If we assume that the intermolecular interaction in alkanes is provided only by dispersive forces, then the difference between enthalpy of vaporization of the investigated compounds and alkane with the same molecular mass gives the energy of dipole-dipole interaction and hydrogen bonds. Enthalpies of vaporization for hypothetic alkane were calculated in [11] and given in Table 6. To calculate the enthalpy of vaporization of hypothetic alkanes with the molecular mass of dissolved compounds, we chose three alkanes [5]: $C_{16}H_{34}$ $M = 226.44$ g/mol, $\Delta_{vap}H_{298} = 81.3 \pm 1.6$ kJ/mol; $C_{17}H_{36}$ $M = 240.47$ g/mol, $\Delta_{vap}H_{298} = 86.0 \pm 2.1$ kJ/mol; $C_{18}H_{38}$ $M = 254.49$ g/mol, $\Delta_{vap}H_{298} = 92.0 \pm 2.6$ kJ/mol. The difference between the enthalpies of vaporization for the compounds **I**, **II** and hypothetic alkane refers to the energy of dipole-dipole and hydrogen bonds in the investigated compound. The calculation results are presented in Table 6.

Enthalpies of vaporization are proportionate to the energies of intermolecular interactions of different compounds in the solution (Table 6). Thus, the solubility of the investigated compounds in 2-propanol and benzene is endothermic (Table 4). The reason is that the energy of different bonds opening in solvents and investigated compounds is not equalized by the energy of a new bonding between the solvent and solute molecules. The proton-donor properties of the compound **II** are better compared with those of the compound **I**. This fact is confirmed by negative values of differential enthalpies of mixing with solvents having proton-acceptor properties.

4. Conclusions

The thermodynamic properties and differential heats of solution determined for 2-cyano-3-[5-(phenyl)-2-furyl]-2-propenamide and 2-cyano-3-[5-(4-methylphenyl)-2-furyl]-2-propenamide may be used to optimize the processes of synthesis, purification and processing with their participation.

References

- [1] Fürstner A., Castanet A., Radkowski K., Lehmann C.: J. Org. Chem., 2003, **68**, 1521. <https://doi.org/10.1021/jo026686q>
- [2] Holla B., Akberali P., Shivananda M.: Farmaco, 2000, **55**, 256. <https://doi.org/10.1021/jo026686q>
- [3] Williams D., Lee M.-R., Song Y.-A. *et al.*: J. Am. Chem. Soc., 2007, **129**, 9258. <https://doi.org/10.1021/ja072817z>
- [4] Karateev A., Koryagin A., Litvinov D. *et al.*: Chem. Chem. Technol., 2008, **2**, 19.
- [5] <http://webbook.nist.gov>
- [6] Sobechko I., Van-Chin-Syan Yu., Gorak Yu. *et al.*: Rus. J. Phys. Chem., 2015, **89**, 919. <https://doi.org/10.1134/S003602441506028X>
- [7] Sobechko I., Prokop R., Gorak Yu. *et al.*: Voprosy Khim. i Khim. Techn., 2013, **4**, 12.
- [8] Smirnova N.: Molekuliarnye Teorii Rastvorov. Khimiya, Leningrad 1987.
- [9] Pimental G., Mak-Klelan O.: Vodorodnaya Sviaz. Mir, Moskva 1964.
- [10] Raid K.: Kurs Fizicheskoi Organicheskoi Khimii. Mir, Moskva 1972.
- [11] Sobechko I.: Voprosy Khimii i Khim. Techn., 2014, **5-6**, 48.
- [12] Sobechko I.: Chem. Chem. Technol., 2016, **10**, 27.
- [13] Sobechko I., Gorak Yu., Van-Chin-Syan Yu. *et al.*: Izvest. Vysshikh Uchebn. Zavedeniy, Khim. i Khim. Techn., 2015, **58**, 45.

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ТЕРМОДИНАМІЧНІ ВЛАСТИВОСТІ РОЗЧИНІВ 2-ЦІАНО-3-[5-(ФЕНІЛ)-2-ФУРИЛ]- 2-ПРОПЕНАМІДА ТА 2-ЦІАНО- 3-[5-(4-МЕТИЛФЕНІЛ)-2-ФУРИЛ]-2- ПРОПЕНАМІДА В ОРГАНІЧНИХ РОЗЧИННИКАХ

Анотація. Визначено температуру плавлення 2-ціано-3-[5-(феніл)-2-фурил]-2-пропенаміда та 2-ціано-3-[5-(4-метилфеніл)-2-фурил]-2-пропенаміда та їх температурну залежність розчинності в ацетонітрилі, бензені, диметилкетоні, етилацетаті, 2-пропанолі. За температурною залежністю розчинності розраховані диференційні ентальпії та ентропії їх розчинення. З урахуванням ентальпії плавлення розраховані ентальпії та ентропії змішування досліджених речовин при 298К. Проаналізовано вплив міжмолекулярних взаємодій в досліджених розчинах на розчинність досліджених речовин та їх ентальпії змішування.

Ключові слова: ентальпії розчинення й змішування, ентропія розчинення й плавлення; диференційний термічний аналіз.