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Thermodynamic Properties of Solubility for Nitrophenyl Derivatives of Furfural Oxime in Organic Solvents

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Abstract. Enthalpies and entropies of dissolution in acetonitrile, propan-2-ol and ethyl acetate were determined from the results of temperature dependence of solubility for 5-(2-nitro phenyl)-2-furyl oxime, 5-(3-nitro phenyl)-2-furyl oxime and 5-(4-nitro phenyl)-2-furyl oxime. Sublimation enthalpies and entropies were determined using integral effusion Knudsen method; adjustment of these values to 298K was conducted. Using these values the thermodynamic properties of solvation in the investigated systems were calculated. The influence of physical properties of the solvent on dissolution of the investigated compounds was analyzed.

Keywords: 5-(2-nitro phenyl)-2-furyl oxime, enthalpy, entropy, solubility, sublimation, solvation

1 Introduction

Heterocyclic compounds are very common in nature. Most of them take part in biological processes. Phenyl-furanic fragment is present in a lot of substances which develop a wide range of biological activity. Lately, functional compounds with phenyl-furanic fragment are widely used in multi-component reactions that allow optimizing the resource usage and conducing the green chemistry concept. Most of the parameters for the processes of syntheses for these compounds were chosen using the method of probes and mistakes. Determination of thermodynamic properties for compounds with phenyl-furanic fragment allows to calculate energetic properties of their molecules and to decrease the energy usage at separate stages of processes of their synthesis, purification and use. Investigated in the current work furfural oximes are used as soil nitrification inhibitors [1], intermediates in the synthesis of medicines with tuberculostatic [2], antifungal [3] properties, and for many syntheses of disubstituted furan derivatives[4]. Phenyl derivatives of furfural oxime show antispasmodic [5], vasodilator [6], cardiotropic [7] and antiviral [8] properties. Most processes with their participation take place in solvents. That's why thermodynamic properties of furfural oxime and its nitrophenyl derivatives solubility are needed for optimization and calculation of energy balances for processes of synthesis, purification and application of these compounds, which has become the main aim of this work.

2 Experimental

Structural formulas of 5-(2-nitro phenyl)-2-furyl oxime (A), 5-(3-nitro phenyl)-2-furyl oxime (B) and 5-(4-nitro phenyl)-2-furyl oxime (C) are shown in Figure 1.

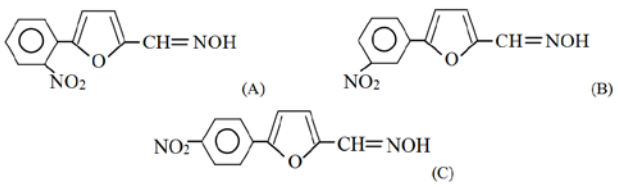

Figure 1. Structural formulas of the investigated compounds

The synthesis of investigated compounds was conducted by the method, shown in Figure 2.

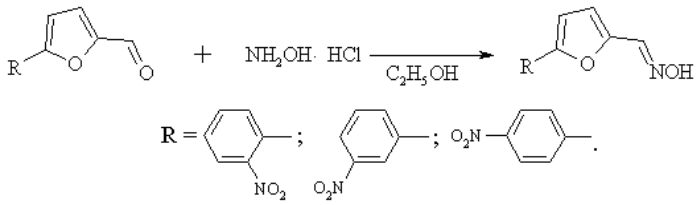

Figure 2. Synthesis of the investigated compounds

Mixture containing 0.023 mol of 5-(2-nitro phenyl)-2-furyl-carbaldehyde (for A), 5-(3-nitro phenyl)-2-furyl-carbaldehyde (for B) or 5-(4-nitro phenyl)-2-furyl-carbaldehyde (for C), 0.03 mol of hydroxylamine hydrochloride and 2 g of melted sodium acetate in 20 ml of ethanol was boiled during 4 hours. 30 ml of water was added after cooling with mixing. Obtained residue was filtered and recrystallized from ethanol.

The structure of the synthesized compounds was confirmed by NMR-spectroscopy results. ^{1}H NMR spectra were recorded using Varian 600 (600 MHz) spectrometer. DMSO and acetone were used as solvents. Chemical shifts (δ. ppm) are listed relatively to DMSO and acetone signal. ^{1}H NMR spectra data is listed in table 1.

Table 1. ^{1}H NMR spectra of the investigated compounds.

Compound	Chemical shifts, δ, ppm
A	^{1}H NMR (600 MHz, Acetone – *d*6) δ 6.96 (d, J = 3.5 Hz, 1H, fur). 7.41 (d, J = 3.5 Hz, 1H, fur), 7.47 (s, 1H, CH), 7.64 (t, J = 8.7, Hz, 1H, C_6H_3), 7.78 (t, J = 8.1, Hz, 1H, C_6H_3), 7.88 (d, J = 8.0 Hz, 1H, C_6H_3), 7.91 (d, J = 7.2 Hz, 1H, C_6H_3), 11.20 (s, 1H, NH).
B	^{1}H NMR (600 MHz, DMSO) δ 7.32 (d, J = 3.3 Hz, 1H, fur), 7.43 (d, J = 3.3 Hz, 1H, fur), 7.68 (s, 1H, CH), 7.74 (t, J = 8.0 Hz, 1H, C_6H_4), 8.19 (d, J = 7.7 Hz, 1H, C_6H_4), 8.24 (d, J = 7.9 Hz, 1H, C_6H_4), 8.53 (s, 1H, C_6H_4), 8.05 (s, 1H, NOH)
C[1]	^{1}H NMR (600 MHz, DMSO): δ 12.10 (s, 0.18H, *syn*-OH), 11.56 (s, 0.82H, *anti*-OH), 8.30 (m, 2H), 8.10 (s, 0.82H, *anti*-CH), 8.00 (d, J = 8.9 Hz, 0.36H, *syn*-C_6H_4), 7.97 (d, J = 8.9 Hz, 1.64H, *anti*-C_6H_4), 7.67 (s, 0.18H, *syn*-CH), 7.45 (d, J = 3.6 Hz, 0.18H, *syn*-fur), 7.41 (d, J = 3.6 Hz, 0.82H, *anti*-fur), 7.36 (d, J = 3.6 Hz, 0.18H, *syn*-fur), 6.91 (d, J = 3.6 Hz, 0.82H, *anti*-fur)

Purity of the compounds was confirmed by the results of chromatography using Agilent 1100 HPLC with diode matrix and mass-selective detector on Zorbax SB-C18 column, 4.6mm×15mm, eluent A – acetonitrile-water with 0.1% TFA (95:5), no impurities were found. Solvents were purified using fractional distillation with further identification by refraction index (1.3726 for ethyl acetate (ref. – 1.3724), 1.3463 for acetonitrile (ref. – 1.3460) and 1.3774 for propan-2-ol (ref. – 1.3776)); using gas-liquid chromatograph "LHM-08D" with thermal conductivity detector the contents of main component were confirmed to be 99.9% mol.

Dissolution of substances was carried in three-neck flask equipped with a thermometer and stirrer. The substance was kept in solvent at room temperature for two days before the beginning of experiments. Mixing time was 45 minutes at a temperature of experiment, the permanence of which (± 0.1K) was reached using a water thermostat. The rate of stirring (50 rpm) was selected so that all solid phase was in the suspended state. Sampling was performed after complete precipitation of solid particles. To confirm the balance experiments were conducted in the both modes of temperature ascending and descending. The absence of hysteresis loop on the curve of the temperature dependence of the solubility reaffirmed achieving a state close to equilibrium. The mass of saturated solutions was determined by mass difference of cups before and after sampling weighted on the VLR-20 scales with an accuracy of 0.00005 g. Then the cups were placed in the oven, where the solvent evaporated at 323-333 K until the

[1] *syn*:*anti* conformers correlation is 9:41 (~1:4.55)

cup reached constant weight. The mass of solid residue was determined by weight difference between the cup with sample and the cup before sampling.

Solute mass (m_2), solubility in mol fractions (x_2), and temperature (T) of the experiments are listed in table 2 along with the coefficients of Schroeder's equation, obtained during experimental data processing. Here and hereafter experimental data was processed using the least squares method with Student's coefficient of 95% level of confidence.

Table 2. Results of temperature dependence of solubility investigation

№	m_2, g	x_2	T, K	№	m_2, g	x_2	T, K
5-(2-nitro phenyl)-furyl-2-oxime							
Propan-2-ol							
1	0.02350	0.01591	308.2	18	0.03220	0.02273	319.6
2	0.02280	0.01572	308.2	19	0.03365	0.02276	319.6
3	0.02165	0.01589	308.2	20	0.03170	0.02273	319.6
4	0.02375	0.01649	309.6	21	0.03555	0.02398	321.2
5	0.02415	0.01638	309.6	22	0.03370	0.02409	321.2
6	0.02655	0.01748	311.5	23	0.03460	0.02385	321.2
7	0.02490	0.01726	311.5	24	0.03085	0.02251	319.2
8	0.02565	0.01737	311.5	25	0.03355	0.02235	319.2
9	0.02665	0.01849	313.4	26	0.03100	0.02208	319.2
10	0.02635	0.01836	313.4	27	0.01785	0.01218	299.5
11	0.02590	0.01820	313.4	28	0.01850	0.01214	299.5
12	0.02945	0.02025	315.9	29	0.01750	0.01238	299.5
13	0.02915	0.02004	315.9	30	0.01910	0.01298	302.3
14	0.02815	0.01973	315.9	31	0.01880	0.01315	302.3
15	0.03315	0.02167	317.6	32	0.01880	0.01286	302.3
16	0.03000	0.02153	317.6	33	0.02060	0.01448	305.8
17	0.03050	0.02155	317.6	34	0.02130	0.01435	305.8
$\ln x_2 = 5.75 \pm 0.25 - \cdot (3050 \pm 77)/T)$							
Acetonitrile							
1	0.04545	0.02159	294.3	18	0.06060	0.02981	305.4
2	0.04415	0.02108	294.3	19	0.05645	0.03205	308.5
3	0.04455	0.02106	294.3	20	0.06685	0.03199	308.5
4	0.04615	0.02235	296.6	21	0.06590	0.03202	308.5
5	0.04710	0.02236	296.6	22	0.06975	0.03460	310.6
6	0.04845	0.02216	296.6	23	0.06755	0.03432	310.6
7	0.04655	0.02336	297.9	24	0.07090	0.03432	310.6
8	0.04895	0.02355	297.9	25	0.07460	0.03670	312.2
9	0.04955	0.02329	297.9	26	0.07520	0.03667	312.2
10	0.04735	0.02514	300.6	27	0.07040	0.03664	312.2
11	0.05190	0.02533	300.6	28	0.04545	0.02193	295.1
12	0.04725	0.02503	300.6	29	0.04855	0.02201	295.1
13	0.05265	0.02752	302.7	30	0.04405	0.02216	295.1
14	0.05345	0.02796	302.7	31	0.04555	0.02547	301.1
15	0.05125	0.02726	302.7	32	0.06235	0.02514	301.1
16	0.06360	0.03072	305.4	33	0.05205	0.02504	301.1
17	0.06120	0.02997	305.4	-	-	-	-
$\ln x_2 = 5.61 \pm 0.34 - \cdot (2789 \pm 102)/T)$							
Ethyl acetate							
1	0.05610	0.05202	293.5	16	0.07720	0.06615	303.6

2	0.06010	0.05234	293.5	17	0.06885	0.06709	303.6
3	0.05510	0.05198	293.5	18	0.06480	0.06851	305.8
4	0.05935	0.05384	295.0	19	0.08165	0.06827	305.8
5	0.06370	0.05433	295.0	20	0.07040	0.06827	305.8
6	0.05690	0.05455	295.0	21	0.07295	0.07129	307.9
7	0.06835	0.05621	297.1	22	0.07675	0.07202	307.9
8	0.06390	0.05629	297.1	23	0.07285	0.07168	307.9
9	0.05965	0.05674	297.1	24	0.08150	0.07662	309.6
10	0.06895	0.05916	299.2	25	0.08575	0.07537	309.6
11	0.06545	0.05915	299.2	26	0.07800	0.07543	309.6
12	0.06135	0.05906	299.2	27	0.07995	0.08016	311.5
13	0.07010	0.06232	301.1	28	0.09125	0.08000	311.5
14	0.07085	0.06223	301.1	29	0.08220	0.08001	311.5
15	0.06425	0.06242	301.1	-	-	-	-
$\ln x_2$=4.26±0.21 − · (2118±63)/T)							
5-(3-nitro phenyl)-furyl-2-oxime							
Propan-2-ol							
1	0.00355	0.00249	305.0	13	0.00615	0.00401	315.0
2	0.00420	0.00264	307.0	14	0.00550	0.00404	315.0
3	0.00370	0.00254	307.0	15	0.00690	0.00456	317.1
4	0.00445	0.00300	308.9	16	0.00705	0.00503	319.5
5	0.00435	0.00296	308.9	17	0.00710	0.00478	319.5
6	0.00420	0.00293	308.9	18	0.00670	0.00479	319.5
7	0.00460	0.00315	310.6	19	0.00765	0.00521	321.6
8	0.00480	0.00326	310.6	20	0.00765	0.00530	321.6
9	0.00455	0.00323	310.6	21	0.00750	0.00526	321.6
10	0.00540	0.00351	313.1	22	0.00860	0.00598	323.6
11	0.00510	0.00356	313.1	23	0.00725	0.00581	323.6
12	0.00590	0.00401	315.0	24	0.00945	0.00576	323.6
$\ln x_2$=9.28±0.55 − · (4666±173)/T)							
Acetonitrile							
1	0.00565	0.00252	302.5	15	0.00735	0.00359	310.9
2	0.00535	0.00249	302.5	16	0.01025	0.00430	315.0
3	0.00520	0.00247	302.5	17	0.00870	0.00437	315.0
4	0.00640	0.00276	304.6	18	0.00845	0.00429	315.0
5	0.00585	0.00274	304.6	19	0.01030	0.00479	317.1
6	0.00565	0.00269	304.6	20	0.00975	0.00471	317.1
7	0.00670	0.00304	306.5	21	0.01005	0.00481	317.1
8	0.00645	0.00303	306.5	22	0.01095	0.00511	319.3
9	0.00630	0.00298	306.5	23	0.01100	0.00510	319.3
10	0.00745	0.00333	308.8	24	0.01120	0.00507	319.3
11	0.00690	0.00332	308.8	25	0.01195	0.00561	321.6
12	0.00710	0.00332	308.8	26	0.01225	0.00561	321.6
13	0.00830	0.00366	310.9	27	0.01205	0.00566	321.6
14	0.00770	0.00360	310.9	-	-	-	-
$\ln x_2$=7.73±0.22 − · (4150±67)/T)							
Ethyl acetate							
1	0.00815	0.00707	298.1	23	0.01410	0.01187	315.8
2	0.00810	0.00722	298.1	24	0.01320	0.01208	315.8
3	0.00950	0.00780	300.6	25	0.01310	0.01175	315.8

4	0.00850	0.00746	300.6	26	0.01555	0.01282	318.0
5	0.00860	0.00779	300.6	27	0.01435	0.01285	318.0
6	0.01145	0.00808	302.7	28	0.01405	0.01277	318.0
7	0.00775	0.00788	302.7	29	0.01670	0.01335	319.6
8	0.00880	0.00810	302.7	30	0.01415	0.01320	319.6
9	0.01070	0.00876	304.6	31	0.01430	0.01327	319.6
10	0.00955	0.00854	304.6	32	0.01725	0.01388	321.6
11	0.00950	0.00863	304.6	33	0.01505	0.01363	321.6
12	0.01125	0.00930	306.6	34	0.01560	0.01399	321.6
13	0.01055	0.00926	306.6	35	0.01680	0.01524	323.6
14	0.00990	0.00907	306.6	36	0.01780	0.01509	323.6
15	0.01195	0.00985	308.9	37	0.01635	0.01512	323.6
16	0.01130	0.00967	308.9	38	0.01810	0.01538	325.6
17	0.01100	0.00986	308.9	39	0.01700	0.01512	325.6
18	0.01240	0.01058	311.4	40	0.01645	0.01538	325.6
19	0.01160	0.01051	311.4	41	0.01850	0.01652	327.4
20	0.01375	0.01140	313.7	42	0.01865	0.01638	327.4
21	0.01245	0.01123	313.7	43	0.01780	0.01652	327.4
22	0.01260	0.01100	313.7	-	-	-	-
$\ln x_2$=4.41±0.17 − · (2792±52)/T)							
5-(4-nitro phenyl)-furyl-2-oxime							
Propan-2-ol							
1	0.00365	0.00261	314.6	24	0.00720	0.00492	333.1
2	0.00300	0.00257	314.6	25	0.00640	0.00474	333.1
3	0.00255	0.00256	314.6	26	0.00710	0.00484	333.1
4	0.00365	0.00258	316.7	27	0.00200	0.00143	300.9
5	0.00375	0.00267	316.7	28	0.00230	0.00156	303.2
6	0.00450	0.00299	318.5	29	0.00225	0.00160	303.2
7	0.00425	0.00299	318.5	30	0.00205	0.00162	303.2
8	0.00405	0.00292	318.5	31	0.00260	0.00172	306.2
9	0.00365	0.00310	320.6	32	0.00280	0.00185	306.2
10	0.00475	0.00316	322.3	33	0.00235	0.00172	306.2
11	0.00470	0.00317	322.3	34	0.00285	0.00190	308.7
12	0.00520	0.00353	324.1	35	0.00595	0.00398	326.9
13	0.00540	0.00358	324.1	36	0.00580	0.00391	326.9
14	0.00480	0.00355	324.1	37	0.00545	0.00403	326.9
15	0.00515	0.00368	326.1	38	0.00625	0.00452	330.0
16	0.00570	0.00369	326.1	39	0.00350	0.00447	330.0
17	0.00475	0.00361	326.1	40	0.00770	0.00525	333.9
18	0.00600	0.00415	328.3	41	0.00730	0.00522	333.9
19	0.00600	0.00427	328.3	42	0.00735	0.00508	333.9
20	0.00595	0.00424	328.3	43	0.00870	0.00555	336.3
21	0.00670	0.00445	330.9	44	0.00790	0.00567	336.3
22	0.00635	0.00448	330.9	45	0.00750	0.00551	336.3
23	0.00615	0.00438	330.9	-	-	-	-
$\ln x_2$=6.23±0.28 − · (3846±89)/T)							
Acetonitrile							
1	0.00945	0.00406	294.9	20	0.01265	0.00692	312.1
2	0.00850	0.00404	294.9	21	0.01640	0.00734	314.3
3	0.00865	0.00404	294.9	22	0.01560	0.00734	314.3

4	0.00995	0.00424	297.1	23	0.01445	0.00720	314.3
5	0.00860	0.00427	297.1	24	0.01740	0.00781	316.1
6	0.00915	0.00427	297.1	25	0.01635	0.00769	316.1
7	0.01000	0.00450	299.6	26	0.01615	0.00781	316.1
8	0.00955	0.00446	299.6	27	0.01980	0.00842	318.2
9	0.00955	0.00466	299.6	28	0.01665	0.00841	318.2
10	0.00995	0.00471	301.5	29	0.01715	0.00841	318.2
11	0.01030	0.00478	301.5	30	0.01940	0.00864	321.4
12	0.00995	0.00473	301.5	31	0.01865	0.00878	321.4
13	0.01230	0.00601	308.1	32	0.01725	0.00860	321.4
14	0.01245	0.00599	308.1	33	0.02180	0.00925	323.1
15	0.00980	0.00646	309.8	34	0.01805	0.00920	323.1
16	0.01380	0.00651	309.8	35	0.01825	0.00925	323.1
17	0.01310	0.00648	309.8	36	0.02140	0.01000	325.1
18	0.01685	0.00693	312.1	37	0.02020	0.00990	325.1
19	0.01450	0.00689	312.1	38	0.02035	0.00995	325.1
$\ln x_2$=4.36±0.22 – · (2919±69)/T)							
Ethyl acetate							
1	0.01075	0.00904	296.4	13	0.01230	0.01091	304.6
2	0.01025	0.00900	296.4	14	0.01215	0.01091	304.6
3	0.01020	0.00918	296.4	15	0.01365	0.01154	306.7
4	0.01135	0.00954	298.5	16	0.01380	0.01149	306.7
5	0.01055	0.00956	298.5	17	0.01230	0.01154	306.7
6	0.01050	0.00961	298.5	18	0.01380	0.01202	308.7
7	0.01170	0.00985	300.6	19	0.01415	0.01195	308.7
8	0.01100	0.00984	300.6	20	0.01320	0.01208	308.7
9	0.01170	0.01009	300.6	21	0.01410	0.01243	310.6
10	0.01235	0.01036	302.6	22	0.01415	0.01253	310.6
11	0.01180	0.01051	302.6	23	0.01355	0.01231	310.6
12	0.01385	0.01103	304.6	-	-	-	-
$\ln x_2$=2.28±0.23 – · (2070±70)/T)							

Graphical interpretations of the temperature dependences of solubility for the investigated compounds in chosen solutes (1 – propan-2-ol, 2 – acetonitrile, 3 – ethyl acetate) are shown in figures 3, 4 and 5.

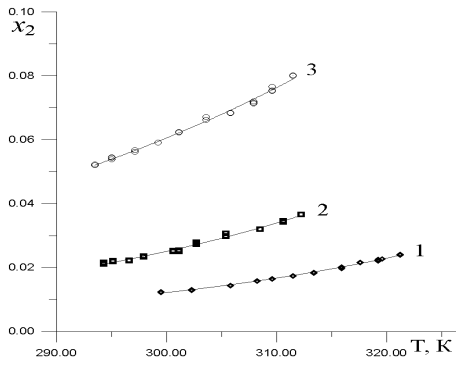

Figure 3. Temperature dependences of solubility for 5-(2-nitro phenyl)-2-furyl-oxime.

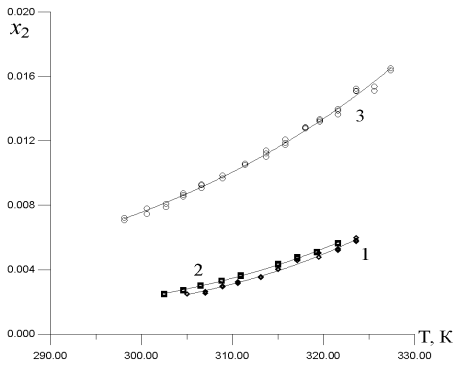

Figure 4. Temperature dependences of solubility for 5-(3-nitro phenyl)-2-furyl-oxime.

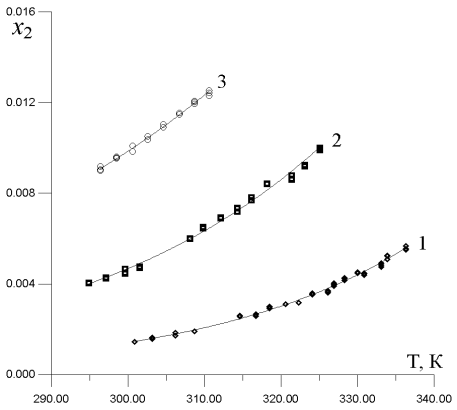

Figure 5. Temperature dependences of solubility for 5-(4-nitro phenyl)-2-furyl-oxime.

Enthalpies ($\Delta_{sol}H^{I/S}$) and entropies ($\Delta_{sol}S^{I/S}$) of dissolution were calculated from the temperature dependence of the solubility of these substances in solvents using equation 1:

$$lnx_2 = \Delta_{sol}S^{I/S} / R ? \Delta_{sol}H^{I/S} / (R?T) \quad (1)$$

The results of calculations and the average temperatures of the studies range T_{sol} are listed in Table 3.

Table 3. Enthalpies and entropies of dissolution of the investigated compounds

Solvent	$\Delta_{sol}H^{I/S}$, kJ/mol	$\Delta_{sol}S^{I/S}$, J/mol · K	T_{sol}, K
5-(2-nitro phenyl)-furyl-2-oxime			
Propan-2-ol	25.36±0.64	47.8±2.1	310.4
Acetonitrile	23.19±0.84	46.6±2.8	303.3
Ethyl acetate	17.61±0.53	35.4±1.8	302.5
5-(3-nitro phenyl)-furyl-2-oxime			
Propan-2-ol	38.8±1.4	77.2±4.6	313.1
Acetonitrile	34.50±0.56	64.3±1.8	312.1
Ethyl acetate	23.22±0.43	36.7±1.4	312.8
5-(4-nitro phenyl)-furyl-2-oxime			
Propan-2-ol	31.97±0.74	51.8±2.3	318.6
Acetonitrile	24.27±0.57	36.3±1.8	310.0
Ethyl acetate	17.21±0.58	19.0±1.9	303.5

Temperature dependences of saturated vapor pressures and sublimation enthalpies were determined using integral effusion Knudsen method. Features of the installation, construction of cameras and membranes and the methodology of experiments were chosen according to recommendations [10].

Vacuum system of the installation reached the pressure of 0.1 Pa during 20±15 seconds during the experiment. Mass of the compound, evaporated during experiment (Δm) was determined from the mass difference of the camera, weighted before and after the experiment using VLR-20 scales with accuracy of ±0.00005 g. The accuracies of sample temperature (T) and effusion time (τ) were ±0.5 K and ±5 s respectively.

The reliability of the effusion installation was confirmed in a series of experiments with benchmark benzoic acid K-1 (content of main component 99.95%) in temperature range 322.7–354.1 K using a set of three membranes with orifice diameters 2.05, 2.10 and 2.15 mm respectively, and thickness 0.09 mm. Results of experimental determination of temperature dependence of saturated vapor pressure for benzoic acid were processed using the least squares method and approximated in a linear equation:

$$\ln P(Pa) = \left(33.72 \pm 1.81\right) - \left(10727 \pm 619\right) \cdot 1 / T; R = 0.9849$$

Sublimation enthalpy of benzoic acid, calculated from the equation, is equal to 89.2±5.1 kJ/mol (T_{sub}=343 K) and is in good accordance with the recommended value: 90.1±0.6 kJ/mol (T_{sub}=353K) from [11].

Methodology of saturated vapor determination for the investigated compounds is similar to the one for benzoic acid. Volatile impurities that could distort the results were removed on the first stage of experiment (surface formation). This stage was completed when the rate of mass loss was constant ±1% at the fixed temperature. Primary results of the effusion studies, saturated vapor pressure P of the investigated compound and temperatures of the experiments (T) are shown in table 4.

Table 4. Primary results of effusion studies

№	T, K	τ, s	First membrane		Second membrane		Third membrane	
			Δm, g	P, Pa	Δm, g	P, Pa	Δm, g	P, Pa
5-(2-nitro phenyl)-furyl-2-oxime								
1	387.1	7236	0.00555	0.3380	0.00575	0.3397	0.00610	0.3730
2	388.2	3640	0.00315	0.3819	0.00340	0.3999	0.00350	0.4261
3	396.6	3634	0.00710	0.8714	0.00760	0.9050	-	-
4	397.1	3659	0.00705	0.8599	0.00875	1.035	0.00885	1.084
5	377.4	10843	0.00355	0.1425	0.00450	0.1752	0.00395	0.1592
6	378.9	10838	0.00440	0.1770	0.00465	0.1815	0.00480	0.1939
7	381.3	10844	0.00655	0.2642	0.00635	0.2484	-	-
$\ln P = (-13449 \cdot 1/T \pm 921) + (33.8 \pm 2.4)$, $\rho = 0.9821$								
5-(3-nitro phenyl)-furyl-2-oxime								
1	402.5	7234	0.00477	0.2963	0.00500	0.3013	0.00490	0.3056
2	405.4	7240	0.00679	0.4229	0.00740	0.4472	0.00665	0.4160
3	406	7240	0.00771	0.4806	0.00790	0.4777	0.00790	0.4945
4	408.7	7235	0.00860	0.5382	0.00925	0.5616	0.00940	0.5908
5	410.2	7234	0.00835	0.5236	0.00845	0.5140	0.00815	0.5132
6	419.8	7222	0.01920	1.220	0.01735	1.070	0.01775	1.133
7	395.7	10822	0.00485	0.1997	0.00495	0.1977	0.00495	0.2046
8	407.2	10824	0.00925	0.3862	0.00910	0.3686	0.00935	0.3921
9	407.5	10825	0.01105	0.4615	0.01145	0.4639	0.01130	0.4740
10	394.1	10828	0.00335	0.1376	0.00350	0.1394	0.00340	0.1402
11	390	10827	0.00250	0.1021	0.00260	0.1030	0.00260	0.1067
$\ln P = (-13109 \cdot 1/T \pm 790) + (31.4 \pm 2.0)$, $\rho = 0.9736$								
5-(4-nitro phenyl)-furyl-2-oxime								
1	414.6	3619	0.00175	0.2205	0.00180	0.2200	0.00175	0.2215
2	418	3619	0.00250	0.3163	0.00245	0.3007	0.00245	0.3113
3	422.9	3696	0.00360	0.4486	0.00375	0.4534	0.00370	0.4630
4	425.1	3622	0.00380	0.4845	0.00425	0.5257	0.00410	0.5249
5	425.1	3626	0.00385	0.4903	0.00400	0.4942	0.00540	0.4988
6	428.9	3625	-	-	0.00545	0.6765	0.00390	0.6939
$\ln P = (-13664 \cdot 1/T \pm 797) + (31.5 \pm 1.9)$, $\rho = 0.9888$								

Graphical interpretation of temperature dependences of saturated vapor pressures for investigated compounds is shown in figure 6.

Values of sublimation enthalpies ($\Delta^g_{cr} H$) and entropies ($\Delta^g_{cr} S$), calculated from the linear form of Clapeyron-Clausius equation (2) of temperature dependence of saturated vapor pressure as well as average temperatures T_{sub} are listed in table 5.

$$\ln P = \Delta^g_{cr} S / R - \Delta^g_{cr} H / (R \cdot T) \quad (2)$$

Table 5. Sublimation enthalpies and entropies of the investigated compounds

Compound	Δ^g_{cr} *H,* kJ/mol	Δ^g_{cr} *S,* J/mol · K	T_{sub}, K
A	111.8±7.7	185±20	387.3
B	109.0±6.6	165±16	404.9
C	113.6±6.6	166±16	421.8

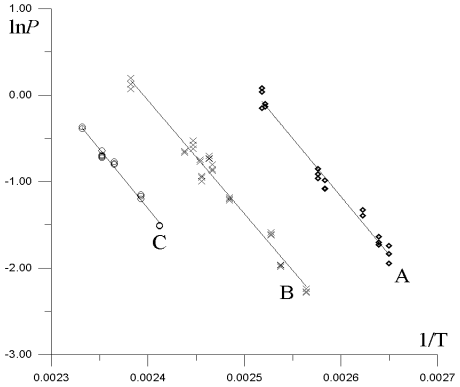

Figure 6. Temperature dependences of saturated vapor pressures for investigated compounds.

3 Discussion

Sublimation and dissolution enthalpies and entropies were determined in different temperature ranges conditioned by the properties of compounds and solvents. $\Delta^g_{cr} H$ and $\Delta^g_{cr} S$ needed to be adjusted to the average temperatures of solubility studies. Heat capacity changes ΔC_p during sublimation were crucial for these calculations. We couldn't determine these values experimentally, so the half-empiric method [12] was used for the purpose:

$$\Delta^g_{cr} H_{Tsol} = \Delta^g_{cr} H_{Tsub} + \left(0.259 \pm 0.041\right) \cdot M \cdot (T_{sub} - T_{sol}) \quad (3)$$

$$\Delta^g_{cr} S_{Tsol} = \Delta^g_{cr} S_{Tsub} + \left(0.259 \pm 0.041\right) \cdot \mathrm{In} \frac{T_{sub}}{T_{sol}} \quad (4)$$

where M – molecular weight of the compound (g/mol), T_{sub} – average temperature of vapor pressure studies, T_{sol} – average temperature of the solubility studies.

Solution enthalpy $\Delta_{sol} H^{I/S}$ is the enthalpy of individual solute's I transfer from its standard state (solid for the investigated compounds) to solution in solvent S. Solvation enthalpy $\Delta_{solvat} H^{I/S}$ is the enthalpy of solute's I isothermal transfer from the ideal gas state to solution in solvent S. Sublimation enthalpy $\Delta^g_{cr} H$ is the enthalpy of solute I transfer from the solid state to the ideal gas state. The above listed properties follow the equation [9]:

$$\Delta_{sol} H^{I/S}{}_{Tsol} = \Delta^g_{cr} H_{Tsol} + \Delta_{solvat} H^{I/S}{}_{Tsol} \quad (5)$$

$$\Delta_{sol} S^{I/S}{}_{Tsol} = \Delta^g_{cr} S_{Tsol} + \Delta_{solvat} S^{I/S}{}_{Tsol} \quad (6)$$

The thermodynamic parameters of solvation are listed in table 6. Physical properties of the used solvents are listed in table 7.

In the row of solvents propan-2-ol – acetonitrile – ethyl acetate acceptor number A_N, which describes the solvents protonation ability, is decreasing (table 7), and the chemical consistency, which is characterized by free Gibbs energy (table 6) is increasing for all the studied systems. Oximes are likely to form intermolecular hydrogen bonds N: · · · HO. The more protonation ability of the solvent is, the

more these bonds it can destroy. Solvents with lesser A_N are of advisable use in chemical and technological processes involving these compounds.

Table 6. Thermodynamic properties of solvation for investigated compounds at T_{sol}

Solvent	T_{sol}, K	$\Delta_{solvat}H^{I/S}{}_{Tsol}$	$\Delta_{solvat}S^{I/S}{}_{Tsol}$	$\Delta_{solvat}G^{I/S}{}_{Tsol}$
5-(2-nitro phenyl)-furyl-2-oxime				
Propan-2-ol	310.4	-91.0±7.7	-151±20	-44.3±11
Acetonitrile	303.3	-93.7±7.7	-153±20	-47.2±11
Ethyl acetate	302.5	-99.3±7.7	-165±20	-49.5±11
5-(3-nitro phenyl)-furyl-2-oxime				
Propan-2-ol	313.1	-75.7±6.7	-104±17	-43.3±9.5
Acetonitrile	312.1	-80.1±6.6	-117±16	-43.7±9.3
Ethyl acetate	312.8	-91.2±6.6	-144±16	-46.2±9.3
5-(4-nitro phenyl)-furyl-2-oxime				
Propan-2-ol	318.6	-87.8±6.6	-131±16	-46.0±9.5
Acetonitrile	310.0	-96.0±6.6	-148±16	-50.0±9.5
Ethyl acetate	303.5	-103.5±6.6	-167±16	-52.9±9.5

Table 7. Physical properties of the used organic solvents

Solvent	T_{boil}, K	n_D^{20}	ε	μ, D	A_N	D_N
Propan-2-ol	355.4	1.3774	19.9	1.68	22.3	20.0
Acetonitrile	354.6	1.3463	37.5	3.5	18.9	14.1
Ethyl acetate	350.0	1.3724	6.02	1.85	9.3	17.1

The compensational effect between solvation enthalpies and entropies (figure 7), which depends on the reconstruction of intermolecular interactions between the solvents' and solutes' molecules, is also present in all of the investigated systems.

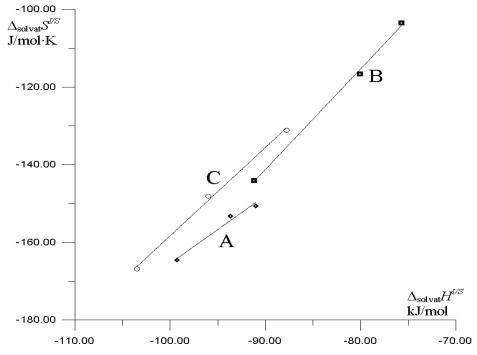

Figure 7. The compensational effect between solvation enthalpies and entropies.

Perhaps, it is caused by the partial destruction of hydrogen bonds of solute-solute and solvent-solvent types and the formation of new bonds of solvent-solute type. The larger number of investigated oxime-solvent systems is needed for the deeper explanation of this phenomenon.

4 Conclusions

The temperature dependences of saturated vapor pressures and temperature dependences of solubility for nitro phenyl derivatives of furfural oxime are well approximated by the linear forms of Clapeyron-Clausius (eq. 2) and Schroeder's (eq. 1) equations, respectively. Sublimation and dissolution enthalpies and entropies were reliably calculated using these equations. Solvation enthalpies entropies and Gibbs

energies were estimated from the obtained data. The presence of compensational effect between solvation enthalpies and entropies in the investigated systems was established. The increase of solubility with decrease of solvent's acceptor number is shown. From the chosen solvents ethyl acetate has the highest chemical consistency with oximes.

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