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Thermodynamics of dissolution of functional derivatives of phenylfuran in organic solvents

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Orto-nitro derivatives of phenylfuran are used as starting materials in the synthesis of biologically active compounds. As is known, the synthesis and further purification of the obtained substances is carried out in organic solvents. To characterize the interaction of components in a solution, thermodynamic functions are used, namely, the degree of interaction of the components of the solution is judged by the enthalpy of dissolution ($\Delta_{sol}H$), and the degree of disorder of the system is judged by the change in entropy ($\Delta_{sol}S$).

Enthalpy and entropy of dissolution of 5-(2-nitrophenyl)-furan-2-carbaldehyde (I), 5-(2-nitrophenyl)-furan-2-oxime (II) 5-(2-nitrophenyl)-furan-2-carbaldehyde acid (III) 3-[5-(2-nitrophenyl)-2-furyl] acrylic acid (IV) 2-cyano-3-[5-(2-nitrophenyl)-2-furan] acrylic acid ethyl ester (V) in saturated solutions was determined by the temperature dependence of their solubility in organic solvents of different polarity.

The studied substances were obtained according to the procedures described in [1-5]. Acetonitrile, ethyl acetate, and iso-propanol were used as solvents. Before the experiments, the solvents were purified by fractional distillation followed by identification by refractive index; the presence of no more than 0.1%, mass of impurities in them was established by gas-liquid chromatography.

The dissolution of substances was carried out in a sealed glass vessel with a Teflon stirrer and a thermometer. The water temperature in the thermostat was maintained with an accuracy of ±0.1 deg. The stirrer rotation speed was 50 rpm, while the entire solid phase was in suspension. In preliminary

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experiments, it was found that with the selected mixing mode in all solvents, noticeable changes in solubility disappear after 40-45 minutes. In all subsequent experiments, the solutions were saturated for 180 minutes with constant stirring.

Using a pipette with a piston, samples were taken (in series of 2-3 samples) and transferred into weighing bottles, preliminarily weighed with an accuracy of ±0.0002 g. The bottles were quickly closed and weighed, thus determining the mass of the saturated solution. After weighing, the weighing bottles were slightly opened and dried to a constant weight in an oven with a temperature of 333-343K. After drying, the weight of the dry acid residue was weighed and its mole fraction was calculated. To confirm the establishment of equilibrium, experiments were carried out both in the mode of increasing the temperature and in the mode of decreasing it; the absence of a hysteresis loop on the curve of the temperature dependence of solubility convinces that equilibrium has been reached.

During the dissolution process, it was established that extremely dilute solutions (X_2 = 0.01 – 0.02) were formed in all the studied systems, which are similar in properties to ideal solutions. For extremely dilute solutions, the temperature dependence of the solubility of a solid substance in a liquid is calculated by equation (1):

$$\frac{d \ln X_2}{dT} = \frac{\Delta_{sol}H}{RT^2} \quad (1)$$

The thermal effect of the dissolution process of extremely dilute solutions was determined according to equation (5.5).

Taking this into account, temperature dependences of solubility were worked out by the method of least squares and presented in the form of a linear equation(2):

$$\ln X_2 = A - B/T \quad (2)$$

In the table 1 shows the temperature intervals in which the solubility (T1 – T2), K, coefficients of the linear equation A and B were studied.

Differential changes in enthalpy ($\Delta_{sol}H$) and entropy ($\Delta_{sol}S$) of dissolution were calculated according to equations (3) and (4) using the coefficients of the temperature dependence of the solubility of A and B (Table 1). The results of calculations are given in table. 1

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

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

where R is the universal gas constant, J/mol K.

Table 1

Thermodynamic parameters of solubility of studied substances in organic solvents

Substance	Temp. int., K.	A	- B	$\Delta_{sol}H$ kJ/mol	$\Delta_{sol}S$ kJ/mol
Acetonitrile					
I	276-322	10.88±0.22	4155±131	34.5±1.1	90.5±1.8
II	294-312	5.61±0.33	2786±100	23.16±0.83	46.6±2.7
III	301-319	3.26±0.77	2926±239	24.3±2.0	27.1±6.4
IV	279-323	4.28±0.30	3014±89	25.06±0.74	35.6±2.5
V	293-319	8.77±0.25	4402±77	36.6±0.64	72.9±2.1
ethyl acetate					
I	275-318	7.83±0.39	3317±117	27.6±1.0	65.1±3.2
II	293-311	4.26±0.21	2118±63	17.61±0.52	35.4±1.7
III	297-330	6.06±0.35	3597±120	29.9±1.0	50.4±2.9
IV	298-330	2.82±0.35	2254±108	18.7±0.9	23.4±2.9
V	305-330	9.02±0.31	4379±97	36.41±0.81	75.0±2.6
iso-propanol					
I	296-327	15.95±0.71	6732±224	56.0±1.9	132.6±5.9
II	299-321	5.75±0.24	3048±76	25.34±0.63	47.8±2.0
III	304-335	10.7±1.1	5129±346	42.6±2.9	89.0±9.1
IV	299-327	10.17±0.68	4857±212	40.4±1.8	84.6±5.7
V	298-326	17.0±1.0	7805±324	64.9±2.7	141,3±8,3

The thermodynamic parameters of solubility presented in the table characterize not only the process of solution formation (mixing of components), but also the phase transition of crystalline substances into the liquid phase of the solution.

Rather high values of the dissolution parameters of the studied substances in polar solvents are associated with their ability to form hydrogen bonds with the solvent.

References:

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