Study of thallium iodide dissolution kinetics in aqueous sodium iodide solutions in production conditions

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The kinetics of thallium iodide dissolution in sodium iodide solutions at concentration of the latter ranging from 0.6 to 6.3 mol/dm^3 has been investigated. An essential time-depended variation of thallium iodide dissolution rate has been established. Consideration of thallium iodide solubility dependence on sodium iodide concentration under varying experimental conditions has evidenced the presence of two parallel processes. The first is an equilibrium one and is connected with formation of thallium ion complex with iodide ions. The second process is non-equilibrium one and is due to interaction with iodine.

Изучена кинетика растворения иодида таллия в растворах иодида натрия, концентрация которых изменялась от 0,6 до 6,3 моль/дм^3. Установлено существенное изменение скорости растворения иодида таллия во времени. Изучение кривых зависимости растворимости иодида таллия от концентрации иодида натрия при варьировании условий эксперимента позволило обнаружить наличие двух параллельно протекающих процессов: равновесного, связанного с комплексообразованием ионов таллия с иодид-ионами, а также неравновесного, обусловленного взаимодействием с иодом.

Technological solutions being formed in the production of scintillation detectors on the basis of NaI(Tl) (washing liquids from growth units, solutions formed at crystal cutting using water jets, etc.) contain, besides the tap water components (calcium, magnesium iron, and other salts), a fine-grain thallium iodide suspension as well as sodium iodide in concentrations from 10 to 100 mg/dm^3 [1]. Such technogenic solutions should not be discarded because those are a source of valuable secondary raw materials (TlI, I$_2$) as well as are highly toxic (thallium belongs to substances of 1st danger class).

Before [2], the TlI behavior features in sodium iodide or cesium iodide have been studied. Basing on temperature dependences of dissolved thallium iodide concentration (C_{TlI}) at different NaI and CsI concentrations, as well as on C_{TlI} on the iodide ion concentration at different temperatures, it

has been shown that the temperature influences the TlI solubility more heavily than the I$^-$-ion excess does. The influence of I$^-$ ion, in its turn, appears either as that of an ion of the same kind in the TlI dissolution equilibrium, or as that of a complexing agent. The effect of time was not considered before at the same temperature conditions. Meanwhile, in production conditions, the above-mentioned solutions are accumulated and stored for rather prolonged periods. In that connection, the purpose of this work was to study the dissolution kinetics of thallium iodide in aqueous solutions of sodium iodide.

The studies were made using model systems approximating as well as possible the production conditions. To that end, a set of solutions was prepared where the sodium iodide (special purity grade) was varied within a wide range (Table 1) at variable

Table 1. Model system compositions

Series No.	TlI sample mass, g	Solution volume, dm³	Sample mass, g		Concentration, mol/dm³	
			NaI	NaClO₄	NaI	NaClO₄
1	2.0	1.0	88.59	–	0.6	–
2	2.0	1.0	236.23	–	1.6	–
3	2.0	1.0	354.35	–	2.4	–
4	2.0	1.0	590.58	–	3.9	–
5	2.0	1.0	944.92	–	6.3	–
6	2.0	1.0	88.59	416.33	0.6	3.4
7	2.0	1.0	590.58	12.25	3.9	0.1

(Series 1–5) or constant (Series 6, 7) ionic strength. A large excess of thallium iodide (special purity grade) was used to provide the heterogeneity of systems under study. During the experiment (for 5.5 months), the solutions were kept at 20±0.5°C in a STBV-1000-IV thermobaric chamber. The solutions were mixed thoroughly every day. To study the TlI dissolution kinetics, the settled solutions were sampled (avoiding roiling) 1, 3, 14, 28, 42, 56, 84, 112, 140 and 164 days after the model systems preparation. The sample preparation included a heat treatment of an aliquot first in the presence of nitric acid (special purity grade) to remove iodine and then in the presence of hydrogen peroxide (chemical purity grade) and sulfuric acid (special purity grade) until sulfuric acid vapor was removed. The dry residues were dissolved in ammonium acetate buffer solution (pH 4.8). The alternating current voltammetry [3] was used to measure the dissolved TlI concentration. The anodic oxidation currents were recorded in the single-drop polarography mode using a UPS special polarographic unit at linear voltage sweep within −0.9 to −0.2 V range. The measurements were made using a valve-type stationary mercury electrode (REKT) [4] as the indicating one, silver chloride electrode as the reference one, and platinum electrode as the auxiliary one. The statistical processing of a large experimental data set has shown that in the analysis procedure, the method provides linear calibration plots within two or three decimal orders of thallium concentration. The reproducibility of the determination results is characterized by relative standard deviation (S_r) values of 0.02 to 0.11 for thallium concentrations of $4.05 \cdot 10^{-4}$ to $1.6 \cdot 10^{-6}$ mol/dm³, respectively. The lower determination limit is $2 \cdot 10^{-7}$ mol/dm³. The *t*-test evidences that within the aforemen-
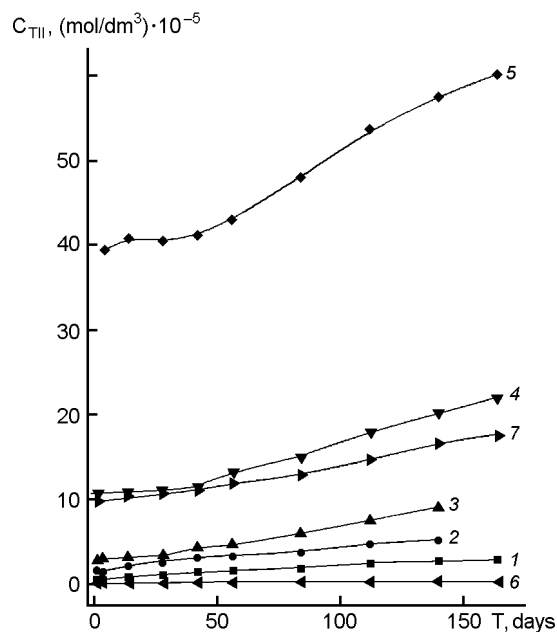

Fig. 1. Thallium (I) dissolution kinetics in sodium iodide solutions at variable (*1–5*) and constant (*6*, *7*) ionic strength. C_{NaI} (mol/dm³): 0.6 (*1*), 1.6 (*2*), 2.4 (*3*), 3.9 (*4*), 6.3 (*5*); 0.6 mol/dm³ NaI + 3.4 mol/dm³ NaClO₄ (*6*); 3.9 mol/dm³ NaI + 0.1 mol/dm³ NaClO₄ (*7*).

tioned concentration range, the systematic error at $P = 0.95$ is insignificant.

The kinetic dependences of dissolved thallium iodide concentration in sodium iodide solutions based on the data obtained are presented in Fig. 1. The curves are seen to be different for different NaI concentrations both in series with variable ionic strength (curves *1–5*) and in series where the ionic strength was kept constant using NaClO₄ additives (curves *6* and *7*). At NaI concentrations not exceeding 2.4 mol/dm³, the dependences obtained are approximated by linear regression equations with parame-

Table 2. Linear regression parameters for $C_{TII} = a + bt$ dependences[*]

Ser. No.	Time interval days	C_{NaI}, mol/dm^3	C_{NaClO4}, mol/dm^3	n	$a + \Delta a$	$b + \Delta b$	r
1	1...164	0.6	–	10	0.67 ± 0.05	0.015 ± 0.001	0.986
6	1...164	0.6	3.4	10	0.16 ± 0.01	0.005 ± 0.001	0.964
2	1...140	1.6	–	9	1.7 ± 0.1	0.025 ± 0.001	0.985
3	1...140	2.4	–	9	2.4 ± 0.1	0.045 ± 0.002	0.993
4	1...42	3.9	–	5	10.6 ± 0.2	0.021 ± 0.006	0.985
	42...164	3.9	–	6	8.2 ± 0.3	0.055 ± 0.003	0.998
7	1...42	3.9	0.1	5	9.7 ± 0.1	0.032 ± 0.004	0.913
	42...164	3.9	0.1	6	8.7 ± 0.3	0.055 ± 0.003	0.998
5	3...42	6.3	–	4	40 ± 1	0.06 ± 0.03	0.898
	42...112	6.3	–	4	33 ± 1	0.18 ± 0.01	0.998
	112...164	6.3	–	3	40 ± 2	0.13 ± 0.02	0.998

[*]C_{TII} in (mol/dm^3)·10^{-5}; time t, in days; n, number of experiments carried out at a fixed time point (within the range indicated), the result for each experiment is calculated from 3 parallel trials; Δa, Δb, the confidence interval half-width for average value of a and b parameters, calculated at confidence probability $P = 0.95$; r, the linear correlation coefficient.

ters (determined by least square method) presented in Table 2. At NaI concentrations above 2.4 mol/dm^3, a significant non-monotonous increase of TlI solubility during the whole experiment is observed. As a result, the curves are subdivided into several sections. At $C_{NaI} = 3.9$ mol/dm^3, there are two such sections, while at $C_{NaI} = 6.3$ mol/dm^3 (near to saturation), three ones. Each section is approximated by a linear regression equation, that is evidenced by the correlation coefficients rather close to unity (see Table 2). The average slope values b for those sections are significantly different according to t-criterion at $P = 0.95$. This evidences a variable rate of TlI dissolution. The system seems to remain non-equilibrated even after 164 days.

The curves of TlI solubility as a function of sodium iodide concentration constructed basing on the results obtained 1 day (Fig. 2, curve *1*) and 140 days (Fig. 2, curve *2*) after the model system preparation are essentially of the same shape but differ by a certain variable quantity ΔC characterizing the TlI concentration increase that seems to be associated with competing processes.

It is of interest to compare the dependences obtained in this work with the dependence (Fig. 2, curve *3*) constructed using data from [5] where another approach was used to study the influence of alkali iodides on TlI solubility. That approach consisted in that the TlI solubility was determined by
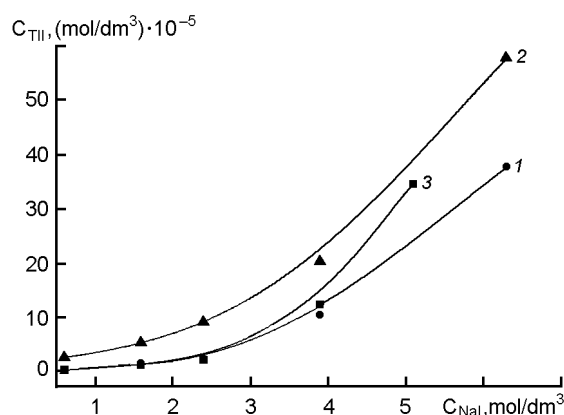

Fig. 2. Thallium iodide solubility curves in sodium iodide solutions. Data obtained in this work after 1 day (*1*) and 140 days (*2*) after the model system preparation; data from [5] (*3*).

titration of solutions containing different I$^-$ concentrations with TlNO$_3$ solution until stable cloudiness. Nephelometry was used to indicate the final point. Fig. 2 shows a good coincidence between curves *1* and *3* for NaI solutions at concentrations not exceeding 2.4 mol/dm^3. It is evident that the same TlI solubility values can be obtained under different experimental conditions (TlI dissolution in this work and precipitation in [5]) only in an equilibrium system. Thus, it can be supposed that in the systems under study, the equilibrium in the TlI dissolution

Table 3. Results of TlI dissolved in model systems prior to and after Na_2SO_3 introduction

| C_{NaI}, mol/dm³	C_{NaClO4}, mol/dm³	C_{TlI}, (mol/dm³)·10⁻⁵					
		1*	140* + 1**	28*	140* + 24**	140*	164*
0.6		0.6	0.4	1.2	0.6	2.7	2.8
0.6	3.4	0.2	0.2	0.2	0.2	0.2	0.3
1.6		1.6	1.6	2.7		5.2	
2.4		2,4	2.2	3.6		9.0	
3.9		10.5	8.7	10.9	9.1	20.2	22.0
3.9	0.1	9.7	9.9	10.6	9.2	16.7	17.6
6.3		37.8	38.0	40.5	39.3	57.5	60.2

* time (days) after the model system preparation

** time (days) after the introduction of 0.1 g/dm³ Na_2SO_3 into the system kept for 140 days

and Tl(I) iodide complexing processes is attained already in the 1st day:

$$TlI <\!\!-\!\!> Tl^+ + I^-, \qquad (1)$$

$$TlI + (n-1)I^- <\!\!-\!\!> TlI_n^{(n-1)}. \qquad (2)$$
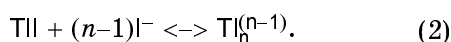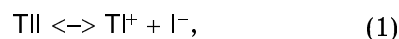
Besides, in real conditions, a partial oxidation of I^- with air oxygen is possible:

$$4I^- + O_2 + 4H^+ <\!\!-\!\!> 2I_2 + 2H_2O. \qquad (3)$$
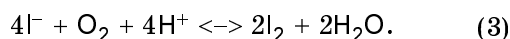
This has been evidenced also during the experiment as the color change of the solutions from light yellow to yellowish-brown, the color intensity being the higher, the higher NaI concentration is. The complex anion I_3^- and free iodine being formed may also be involved in TlI dissolution. To eliminate that process, an excess sodium sulfite has been added to model system kept for 140 days. The sulfite interacts with iodine according to the following scheme:

$$SO_3^{2-} + I_2 + H_2O <\!\!-\!\!> SO_4^{2-} + 2HI. \qquad (4)$$
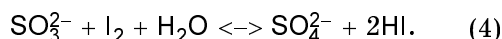
The comparison of determined dissolved TlI amounts prior to and after sodium sulfite addition (Table 3) has shown that after iodine was reduced, the system were returned essentially to the state corresponding to the 1st day of the initial experiment. Thus, the time-depended variation of TlI dissolution rate has been found to be due to the presence of free iodine in the systems.

There is no unambiguous interpretation of interaction between iodine and univalent thallium. The equilibrium calculation for solutions containing only Tl^+ and free iodine

$$Tl^+ + I_2 <\!\!-\!\!> Tl^{3+} + 2I^- \qquad (5)$$
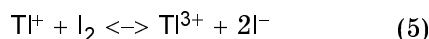
shows that the Tl^+ oxidation with iodine is impossible. A theoretical equilibrium calculation in $TlI–NaI–H_2O–O_2$ system that could confirm the probability of Tl^{3+} formation is hindered due to the absence of reliable complexing constants for uni- and trivalent thallium. A sensitive test for trivalent thallium can be provided by its precipitation as poorly soluble hydroxide. The thallium (III) concentration in equilibrium
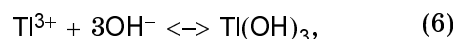
$$Tl^{3+} + 3OH^- <\!\!-\!\!> Tl(OH)_3, \qquad (6)$$
$$lgK_s = 34.1 \quad [6]$$

as calculated using the scheme by Komar' [7] is $1.3 \cdot 10^{-9}$ mol/dm³. In the model solution containing 6.3 mol/dm³ of sodium iodide, thallium concentration is $6 \cdot 10^{-4}$ mol/dm³, that is, exceeds more than by 5 decimal orders the equilibrium one. This amount is sufficient for precipitation. However, even traces of cloudiness were not observed in the solution under study. Thus, in our experimental conditions where the iodide ion concentration exceeds considerably the free iodine one, the equilibrium (5) seems to be shifted strongly to the left. The time-depended change in the TlI dissolution rate in the presence of excess iodide ion is like to be due to formation of $TlI–I_2$ complex according to reaction

$$TlI + I_3^- <\!\!-\!\!> TlI \cdot I_2 + I^-. \qquad (7)$$
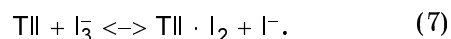
Thus, basing on the study of thallium iodide dissolution kinetics in NaI solutions, the time-depended change of the dissolution rate has been established. Comparing the TlI solubility dependences on NaI concentration obtained by us with those described in lit-

erature [5] as well as using the results of an experiment including elimination of iodine influence, we have established the presence of two parallel processes. The first one is associated with Tl^+ complexing with I^- ions and is an equilibrium process. The second one, presenting TlI interaction with a complex anion I_3^- (the concentration of the latter being increased in time), causes a non-equilibrium of the system as a whole. The found regularities can be used to suppress the TlI solubility in real technological solutions that are open systems having a large contact area with atmospheric air.

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Вивчення кінетики розчинення іодиду талію у водних розчинах іодиду натрію у промислових умовах

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Вивчено кінетику розчинення іодиду талію у розчинах іодиду натрію, концентрація яких змінювалася від 0,6 до 6,3 моль/дм³. Встановлено суттєве змінення швидкості розчинення іодиду талію за часом. Вивчення кривих залежності розчинності іодиду талію від концентрації іодиду натрію при варіюванні умов експерименту дозволило виявити наявність двох процесів, що протікають паралельно: рівноважного, пов'язаного з комплексоутворенням іонів талію з іодид-іонами, а також нерівноважного, обумовленого взаємодією з іодом.