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REACTION ORDER DETERMINATION IN THIOCYANATE SPECTROPHOTOMETRIC MEASUREMENT THROUGH EXTRACTION BY FORMATION OF ION PAIR WITH THIONINE

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In the article in order to study spectrophotometric measurement of thiocyanate through extraction by formation of ion pair with thionine, the partial and total order of reactions to the reactors were studied.

***Keywords*:** thionine, thiocyanate, spectrophotometry.

Introduction. In the present article by spectrophotometric method the order of reaction according to various factors of thionine, thiocyanate and hydrogen ion was studied. This reaction was studied through spectrophotometric measurement followed by the peak absorption of thionine in 600 *nm*. The optimized conditions were used in all parts of the experiment as shown in Tab. 1 [1–4].

Table 1

Optimized condition

[Thionine]	$1.566 \cdot 10^{-4}$ *mol/L*
pH	6–7
Solvent	isobutyl keton
Temperature	30°*C*
Time	240 *s*

The rate equation is as follows:

$$W = k[\text{thionine}]^n\,[\text{tiocyanate}^-]^{n'}\,[\text{H}]^{n''},$$

where k is the rate constant of the reaction; n, n', n'' are partial orders of the reaction with respect to different reactants of the reaction with respect to different reactants in the reaction.

Experimental Part. In order to determine the reaction order the optimized concentration of all materials except for the considered one should be kept constant. Thermal equilibrium of all solutions was reached by keeping them in 30°*C* for 30 *min*. Then the solutions were mixed in the 10 *mL* volumetric flask and

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the absorption of the solutions was recorded at 60 and 180 *s*. By using the changes in the absorption in accordance with the concentration, the order of reaction can be obtained. In all the phases of the experiment the material with analytical purity degree of concentration and double distilled water were used. In drawing the graph and extraction of the equation of the graph the least square was used.

The Determination of Reaction Order in Accordance with Thionine. In order to determine the reaction order in accordance with thionine the range of concentration was considered $3.48 \cdot 10^{-6}$–$1.566 \cdot 10^{-4}$ *M*. The rest of the parameters were kept constant. The differential absorption of 60 and 180 *s* was achieved. The results are illustrated in Tab. 2.

Table 2

Determination of the order of reaction in relation to thionine

[thionine] · 10^5, *mol/L*	ΔA	log [thionine]	logΔA
0.348	0.003	–5.458	–2.523
1.04	0.005	–4.983	–2.301
1.74	0.007	–4.759	–2.155
2.43	0.010	–4.614	–2.000
3.13	0.012	–4.504	–1.921
3.83	0.014	–4.417	–1.854
4.52	0.016	–4.345	–1.796
5.22	0.017	–4.282	–1.770
5.92	0.019	–4.228	–1.721
6.61	0.023	–4.180	–1.638
7.31	0.027	–4.136	–1.569
8.00	0.034	–4.097	–1.469
8.70	0.036	–4.060	–1.444
9.40	0.039	–4.027	–1.409
10.09	0.042	–3.996	–1.377
10.79	0.043	–3.967	–1.367
11.48	0.048	–3.940	–1.319
12.18	0.051	–3.914	–1.292
12.88	0.054	–3.890	–1.268
13.57	0.056	–3.867	–1.252
14.27	0.059	–3.846	–1.229
14.96	0.061	–3.825	–1.215
15.66	0.063	–3.805	–1.201

Considering the fact that concentration of all the factors was constant except for thionine, we have the equation:

$$W = k[\text{thionine}]^n\ [\text{SCN}^-]^{n'}\ [\text{H}]^{n''},$$

$K_1 = k\ [\text{SCN}^-]^{n'}\ [\text{H}]^{n''}$, $W = K_1[\text{thionine}]^n$, $\log W = \log K_1 + n\log[\text{thionine}]$.

By sketching the logarithmic graph of absorption changes in accordance with the log[thionine], the reaction order according to thionine was calculated 0.89.

Determination of Reaction Order in Accordane with Thiocyanate. In this phase according to the previous method and in order to determine the reaction order in relation to concentration of thiocyanate, we should take all the conditions constant and the concentration of thiocyanate should be changed. So, $1.72 \cdot 10^{-5}$ till

$3.796 \cdot 10^{-5}$ of thiocyanate concentration was used. The concentration of other factors was used in the optimized concentration and the absorption was recorded in two times of 60 and 180 *s* (Tab. 3).

Table 3

The determination of the order of reaction in relation to thiocyanate

$[SCN^-] \cdot 10^6$, *mol/L*	ΔA	log $[SCN^-]$	logΔA
1.724	0.001	–5.763	–3.000
3.448	0.002	–5.462	–2.699
5.172	0.002	–5.286	–2.699
6.896	0.003	–5.161	–2.523
8.620	0.004	–5.064	–2.398
10.34	0.006	–4.985	–2.222
12.07	0.007	–4.918	–2.155
13.79	0.009	–4.860	–2.046
15.52	0.010	–4.809	–2.000
17.24	0.012	–4.763	–1.921
18.96	0.013	–4.722	–1.886
20.69	0.013	–4.684	–1.886
22.41	0.015	–4.650	–1.824
24.14	0.016	–4.617	–1.796
25.86	0.016	–4.587	–1.796
27.58	0.017	–4.559	–1.770
29.31	0.018	–4.553	–1.745
31.03	0.020	–4.508	–1.699
32.76	0.021	–4.485	–1.678
34.48	0.021	–4.462	–1.678
36.20	0.022	–4.441	–1.658
37.93	0.023	–4.421	–1.638

Considering that the concentration of all factors except thiocyanate were constant, we have the rate equation as

$$W = k\,[\text{thiocyanate}]^n\,[SCN^-]^{n'}\,[H]^{n''},$$

$K_2 = k\,[\text{thiocyanate}]^n\,[H]^{n''}$, $W = K_2[SCN^-]^{n'}$, $\log W = \log K_2 + n' \log[SCN^-]$.

By sketching the logarithmic graph of absorption changes in accordance with the log[thiocyanate], n', which is the order according to thiocyanate was calculated 1.074.

Determination of Reaction Degree in Accordance with pH. Here, in order to determine the reaction order in relation to pH, all the conditions should be kept constant and only pH should be changed. So in this solution different concentrations pH 1 till pH 7 were used. For the rest of the factors, the optimized concentrations were used. Finally, absorption in two times of 60 and 180 *s* was recorded (Tab. 4).

Considering the concentrations of all factors except pH were constant, we have the rate equation of:

$$W = k[\text{thionine}]^n\,[SCN^-]^{n'}\,[H]^{n''},$$

$K_3 = k\,[\text{thionine}]^n\,[SCN^-]^{n'}$, $W = K_3[H]^{n''}$, $\log W = \log K_3 + n'' \log[H]$.

Table 4

Determination of the order of reaction in relation to pH

pH	ΔA	log $[H^+]$	logΔA
1.0	0.008	–1.0	–2.097
1.5	0.009	–1.5	–2.046
2.0	0.011	–2.0	–1.959
2.5	0.012	–2.5	–1.921
3.0	0.013	–3.0	–1.886
3.5	0.014	–3.5	–1.854
4.0	0.015	–4.0	–1.824
4.5	0.017	–4.5	–1.770
5.0	0.018	–5.0	–1.745
5.5	0.019	–5.5	–1.721
6.0	0.021	–6.0	–1.678
6.5	0.021	–6.7	–1.678
7.0	0.022	–7.0	–1.658

By sketching the changes of absorption in accordance with the log $[H^+]$, then n'', which is the reaction order according to H^+ was calculated –0.072.

After drawing logarithmic graph, the logarithm of absorption changes According to log$[H^+]$, we have obtained reaction order in relation to concentration of H: $n'' = -0.072, \quad r = 0.982$.

Considering the obtained result, the total order of reaction consists of $n + n' + n'' = 0.890 + 1.074 - 0.072 = 1.892$.

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