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CATIONIC EFFECT IN THE REDOX REACTION BETWEEN $[AuCl_4]^-$ AND $[HSO_3]^-$ IONS

KINETYCZNY EFEKT KATIONOWY W REAKCJI REDOKS POMIĘDZY JONAMI $[AuCl_4]^-$ ORAZ $[HSO_3]^-$

In this work the analysis of the influence of the concentration of chloride salts on the changes in the rate constants of redox reaction between $[AuCl_4]^-$ and $[HSO_3]^-$ is performed. It is shown, that changes in the value of the rate constant k depend strongly on the kind of a cation added to the reacting system. This effect results from the variation of several factors which are considered in the text, i.e. cationic radius, the type of the cation and hydration number.

W pracy dokonano analizy wpływu stężenia różnych soli chlorkowych na zmianę stałej szybkości k reakcji redoks pomiędzy $[AuCl_4]^-$ oraz $[HSO_3]^-$ ze szczególnym uwzględnieniem rodzaju kationu tej soli. Wykazano, że wzrost stałej k zależy silnie od rodzaju kationu dodanego do układu reakcyjnego i wynika ze zmian wartości promienia jonowego oraz liczby hydratacyjnej danego kationu.

1. Introduction

One of the important problems to be solved in the future is the processing and recycling of the precious metals from various kinds of wastes discharged from the industry. For example, except for the production of pure gold from the minerals, its recycling from the scrap materials becomes very important. One of the most frequently used methods in the recovery of gold is leaching it from the scrap materials, and next, the reduction of the gold salt in the aqueous solution in order to precipitate the metallic phase of Au. As a result, pure gold is obtained. In order to be able to carry out this process we should know its optimal conditions (e.g. pH, temperature, concentration of reagents, etc.) under which the Au phase precipitates. This parameters should be

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selected on the basis of the knowledge of the kinetics and the mechanism of such a reaction. As an example, investigations on the reduction of gold(III) complexes in the aqueous chloride solution can be given [1]. In that work the $NaHSO_3$ as the reductant was used. On the basis of the obtained results, the kinetic equation and the mechanism of that reaction were suggested.

The key parameter experimentally determined during the kinetics investigations is the "rate constant" (k) of the reaction (e.g. reduction). In the case of precipitation of Au metallic phase from the aqueous solutions, the k value for the gold(III) reaction of reduction has an influence on the size of obtained Au particles. It is connected with the rate of formation of a number of metallic nuclei appearing during the gold(III) reduction. The size of precipitated Au particles, which is rate dependent, determines the possibility of their filtration.

The term "constant" suggests, that the value of k is constant for the given reaction. It is true but only under precisely determined conditions (e.g. temperature, concentration of reagents, etc.). The rate constant can change when the ionic strength (I) of the solution is changed. This known dependence ($k = f(I)$) is described by Brönsted-Bjerrum (B-B) formula, which can be used as a convenient tool for analysing the mechanism of reaction. It informs us about the charge of reacting species [2].

However, the experimentally obtained value of the rate constant may change not only due to the change of the ionic strength in the solution, but also due to the change of the kind of salt used to keep I constant. One can learn from the literature that for a reaction running in the presence of a large amount of salt composed of the multivalent ions, the reciprocal repulsions between reagents and the salt ions are present [3-6]. Such interactions strongly influence the possibility of using the B-B formula to determine the charges of reacting species.

During experiments many authors use different kind of neutral salts like NaCl, $NaClO_4$, KCl, in order to keep I = const., which apparently have different influence on the value of the rate constant obtained for the same reaction [7, 8]. Therefore it is clear, that in order to be able to predict the size of precipitated Au, to compare the values of the rate constants obtained for the same reaction, and to deduce the charges of reacting molecules correctly we need to know both: the value of ionic strength and the kind of salt in the environment where the reaction takes place.

It can be summarized that I and kind of a salt used are really important factors influencing the rate constant of the reaction.

This information was the reason to carry out research on the kinetics of reduction reaction of $[AuCl_4]^-$ ions using $NaHSO_3$ in the presence of different kinds of chloride salts. In this work, the influence of cations (chosen from the I and II group of the periodic table) on the rate constant of the reaction of reduction was tested. The changes of the rate constant values were estimated as well as the analysis of factors influencing these changes was performed.

2. Experimental

a) Materials Preparation

$HAuCl_4$ solution was prepared by dissolving pure Au (chemical purity — 99.99%, obtained from Mennica Państwowa, Poland) in aqua regia. After several evaporations of this solution and dilution of the obtained solid in distilled water, the starting substrate was obtained which was next used for solutions preparation with require content of gold(III). Salt solutions were prepared by dissolving a suitable amount of adequate chloride compound (AnalaR) and mixed with the gold(III) solution. The constant value of pH in the solution was adjusted using hydrochloric acid on the similar level as it is used in the KGHM hydrometallurgical technology. Such solutions were protected from the sunlight. $NaHSO_3$ solution was prepared by dissolving a proper amount of $Na_2S_2O_5$ (AnalaR) in distilled water just prior to experiment.

b) Experimental Procedure and Apparatus

Using the SX.18MV-R Rapid Mixing Spectrophotometer (from Applied Photophysics, U.K.) working in the UV-Vis range (from 190 to 900 nm) with the 0.5 cm optical path, the stopped- flow methods were employed for kinetic studies. All measurements were carried out in thermostated silica cuvette. Due to applied Peltier system, the temperature of the measurement cell was kept constant (25°C) in the range ±0.1°C.

The experiments consisted in the mixing of reagents in the reactor, which was UV-rayed with the beam of the wavelength of 315 nm. The detection system automatically recorded changes of absorbance with time. Concentration vs. time curves obtained in this manner were the basis for the determination of respective rate constants of reduction reactions of gold(III) complexes. Their values were calculated from experimental data using OLIS software [9].

3. Results

On the basis of the previously obtained results concerning the kinetics of reduction of gold(III) chloride complexes using acid sulfite, the mechanism and the rate equation of the reaction was suggested [1]. It was shown that the first stage of the reduction process can be described with the reaction:

$$[AuCl_4]^- + [HSO_3]^- \xrightarrow{k} SO_3^{\bullet -} + [AuCl_3]^- + H^+ + Cl^- \tag{1}$$

for which the rate equation has the formula:

$$-\frac{dC_{[AuCl_4]^-}}{dt} = kC_{[AuCl_4]^-}C_{[HSO_3]^-}, \tag{2}$$

where: $C_{[AuCl_4]^-}$ and $C_{[HSO_3]^-}$ — concentrations of the reagents, k — the rate constant of the reaction (1).

To fulfill the conditions of the pseudo-monomolecular reaction, in all experiments the large excess of the reductant was used ($C_{[HSO_3]^-} : C_{[AuCl_4]^-} = 37.5 : 1$). Under this condition the equation (1) has a form:

$$-\frac{dC_{[AuCl_4]^-}}{dt} = k_{obs}C_{[AuCl_4]^-}, \tag{3}$$

where:

$$k_{obs} = kC_{[HSO_3]^-}. \tag{4}$$

Experimental measurements of the rate constants (k_{obs}, k) were performed in different salt solutions. The results obtained, gathered in Tables 1 and 2, showed that the value of k changes with the change of the salt used to keep I = const during experiments.

The analysis of the data gathered in Tables 1 and 2 showed that in the solutions where the concentration of the cations gradually increased, the rate constants of reaction (1) increased too. The observed dependencies are shown in the Fig. 1, where the concentration was substituted by the ionic strength. For the cations from the I group of the periodic table one can see that the increase of the rate constant is compatible with the trend: $Li^+ < Na_+ < K^+$. In the case of cations from the II group, the effect of reaction (1) acceleration is bigger, and is in agreement with the trend: $Ca^{2+} < Mg_{2+} < Sr^{2+}$.

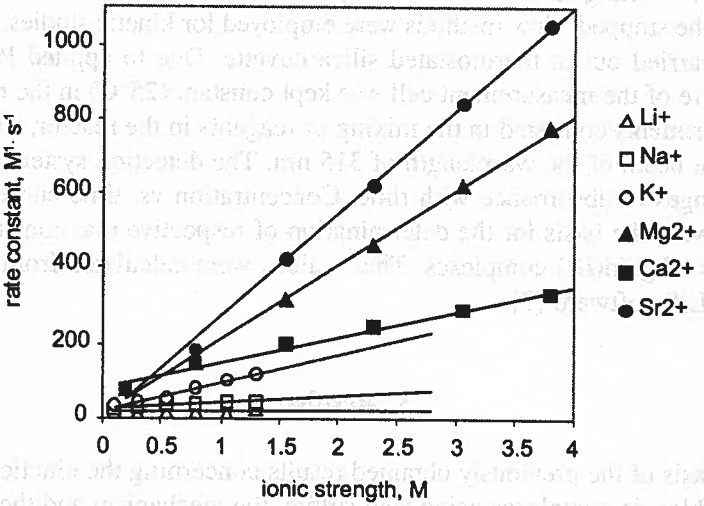

Fig. 1. Dependence of the rate constant vs. ionic strength for the reaction between $[AuCl_4]^-$ and $[HSO_3]^-$ in the presence of cations from the I and II group of the periodic table

TABLE 1

Values of the rate constants (k_{obs} and k) for the reaction between $NaHSO_3$ and $[AuCl_4]^-$ ions in the aqueous solution contating Li^+, Na^+, K^+ cations. Conditions: pH = 1.3, $C_{0,[AuCl_4]^-} = 5 \cdot 10^{-5}$ M, $C_{0,S(IV)} = 1.875 \cdot 10^{-3}$, temperature (25 ± 0.1)°C

Concentration of cation M	Ionic strength* I M	Rate constant (average of five) k_{obs} s^{-1}	Mean standard deviation σ s^{-1}	Rate constant (average of five) k^{**} $M^{-1} \cdot s^{-1}$	Mean standard deviation σ $M^{-1} \cdot s^{-1}$
1	2	3	4	5	6
K^*					
0.05	0.10	0.06459	± 0.00021	34.449	± 0.113
0.25	0.30	0.08074	± 0.00026	43.062	± 0.141
0.50	0.55	0.10284	± 0.00013	54.614	± 0.070
0.75	0.80	0.15258	± 0.00032	81.377	± 0.169
1.00	1.05	0.19199	± 0.00009	102.397	± 0.048
1.25	1.30	0.22438	± 0.00203	119.671	± 1.081
Na^*					
0.05	0.10	0.04037	± 0.0001	21.531	± 0.096
0.25	0.30	0.05394	± 0.0001	28.768	± 0.075
0.50	0.55	0.06597	± 0.0001	35.184	± 0.058
0.75	0.80	0.07426	± 0.0002	39.606	± 0.127
1.00	1.05	0.07848	± 0.0001	41.860	± 0.061
1.25	1.30	0.08302	± 0.0009	44.276	± 0.479
Li^+					
0.05	0.10	0.02862	± 0.00009	15.267	± 0.371
0.25	0.30	0.03351	± 0.00007	17.870	± 0.031
0.50	0.55	0.03321	± 0.00009	17.715	± 0.048
0.75	0.80	0.03417	± 0.00053	18.224	± 0.082
1.00	1.05	0.03315	± 0.00011	17.680	± 0.060
1.25	1.30	0.03564	± 0.00011	19.011	± 0.059

* — constant pH of solutions was adjusted using 0.05 M HCl. This value was taken into account during calculations of ionic strength.

** — k was obtained from the equation: $k_{obs} = kC_{S(IV)}$, where k_{obs} — observed rate constant, k — the rate constant of the second order reaction between $[AuCl_4]^-$ and sulfur (IV) ions, $C_{0,S(IV)}$ — concentration of reductant.

TABLE 2

Values of the rate constants (k_{obs} and k^*) for reaction between $NaHSO_3$ and $[AuCl_4]^-$ ions in the aqueous solution contating Mg^{2+}, Ca^{2+}, Sr^{2+} cations. Conditions: pH = 1.3, $C_{0,[AuCl_4]^-} = 5^*10^{-5}$ M, $C_{0,S(IV)} = 1.875^*10^{-3}$, temperature (25 ± 0.1)°C

Concentration of cation M	Ionic strength* I M	Rate constant (average of five) k_{obs} s^{-1}	Mean standard deviation σ s^{-1}	Rate constant (average of five) k^{**} $M^{-1} \cdot s^{-1}$	Mean standard deviation σ $M^{-1} \cdot s^{-1}$
1	2	3	4	5	6
Mg^{2+}					
0.05	0.20	0.13798	± 0.00025	73.594	± 0.138
0.25	0.80	0.26381	± 0.00088	140.70	± 0.47
0.50	1.55	0.59211	± 0.00114	315.79	± 0.61
0.75	2.30	0.86278	± 0.00232	460.15	± 1.24
1.00	3.05	1.16282	± 0.00544	622.90	± 6.68
1.25	3.80	1.45976	± 0.01207	778.54	± 6.43
Ca^{2+}					
0.05	0.20	0.14016	± 0.00028	74.756	± 0.147
0.25	0.80	0.27126	± 0.00585	144.67	± 3.12
0.50	1.55	0.36832	± 0.01013	196.44	± 0.85
0.75	2.30	0.45989	± 0.00203	245.27	± 1.08
1.00	3.05	0.53983	± 0.00511	287.91	± 2.72
1.25	3.80	0.62778	± 0.00389	334.81	± 2.08
Sr^{2+}					
0.05	0.20	0.14549	± 0.00019	77.59	± 0.10
0.25	0.80	0.33861	± 0.00259	180.59	± 1.38
0.50	1.55	0.78995	± 0.00434	421.30	± 2.31
0.75	2.30	1.1717	± 0.0031	624.88	± 1.67
1.00	3.05	1.5752	± 0.0168	840.11	± 9.00
1.25	3.80	1.9736	± 0.0163	1052.58	± 8.69

* — constant pH of solutions was adjusted using 0.05 M HCl. This value was taken into account during calculations of ionic strength.

** — k was obtained from the equation: $k_{obs} = kC_{S(IV)}$, where k_{obs} — observed rate constant, k — the rate constant of the second order reaction between $[AuCl_4]^-$ and sulfur (IV) ions, $C_{0,S(IV)}$ — concentration of reductant.

Using the least square method, the empirical equations describing dependencies k = f(I) were determined, and are given in Table 3. All equations are linear though the concentration of the salt added exceeded dilute solution range.

TABLE 3

Empirical equations of dependence of the rate constants (k) vs. ionic strength (I) for reaction between $NaHSO_3$ and $[AuCl_4]^-$ ions in the aqueous solution containing different chloride salts

Chloride salt which supports I = const. in the solution	Empirical equation	
LiCl	$k = 2.142\,I + 16.16$	(5)
NaCl	$k = 18.38\,I + 22.64$	(6)
KCl	$k = 74.46\,I + 21.70$	(7)
$MgCl_2$	$k = 200.5\,I + 8.212$	(8)
$CaCl_2$	$k = 69.48\,I + 78.48$	(9)
$SrCl_2$	$k = 277.1\,I + 7.804$	(10)

However, the experimentally obtained data indicate that not only the concentration of the cation but also the kind of the cation changed the value of the rate constant of reaction (1). It is clearly seen in Figs. 2 and 3 that at constant ionic strength the size of the cation affected the rate constant k.

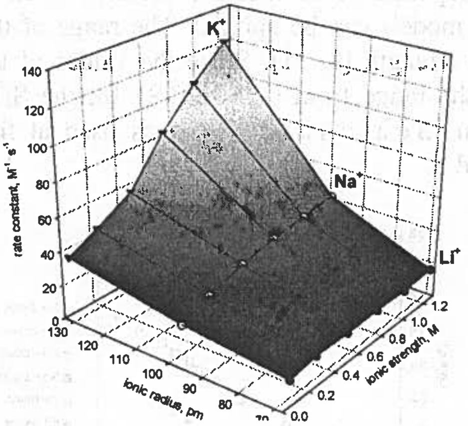

Fig. 2. 3D dependence of the rate constant vs. ionic radius and ionic strength for the reaction between $[AuCl_4]^-$ and $[HSO_3]^-$ — comparison of the k obtained in the presence of different kind of cations from the firts group of the periodic table: Li^+, Na^+, K^+ (values of ionic radius are from [10])

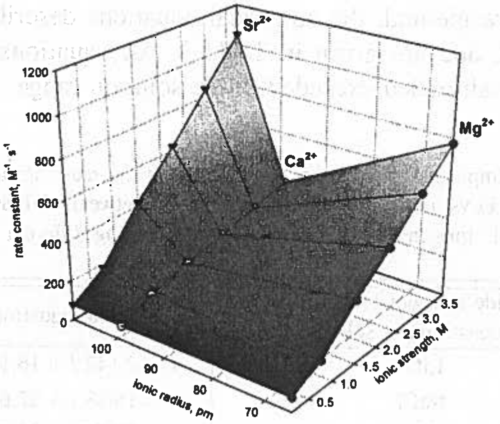

Fig. 3. 3D dependence of the rate constant vs. ionic radius and ionic strength for the reaction between $[AuCl_4]^-$ and $[HSO_3]^-$ — comparison of the k obtained in the presence of different kind of cations from the second group of the periodic table: Mg^{2+}, Ca^{2+}, Sr^{2+} (values of ionic radius are from [10])

4. Discussion

In order to find out the possible reason of the observed changes, the following facts were taken into account.

To describe the dependence of the rate constant k on the ionic strength I of the solution, different models can be applied. The range of their validity depends on the value of the ionic strength [3, 11]. Since the values of the ionic strength in our experiments were in the range from 0.15 to 3.85 M, the SIT model of Bronsted-Guggenheim-Scatchard [11] was used at first. Calculated data are presented in Fig. 4 and 5.

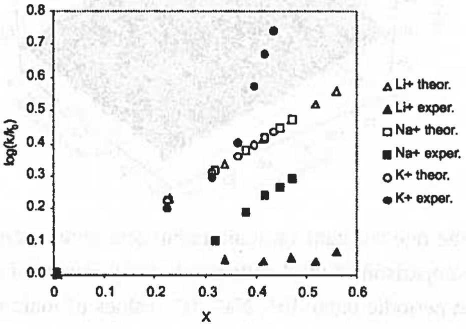

Fig. 4. Dependence of $\log\left(\frac{k}{k_0}\right)$ vs. $X = \frac{2Az_{complex}^2\sqrt{I}}{1+1.5\cdot\sqrt{I}} + (\varepsilon_{HCl}c_{HCl} + \varepsilon_{salt}c_{salt})$ for reaction (1) in the presence of Li^+, Na^+, and K^+ cations. $A = 0.509$ in aqueous solution, $z_{complex} = -2$ is the charge of activated complex in the reaction (1),$C_{HCl} = 0.05$ M, c_{salt} are from the Table 1, ε factors are from [12]

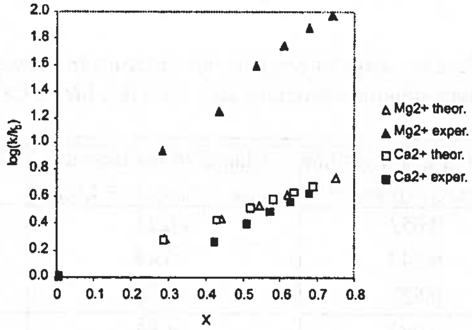

Fig. 5. Dependence of $\log\left({}^{k}\!/_{k_0}\right)$ vs. $X = \frac{2Az_{complex}^2\sqrt{I}}{1+1.5\cdot\sqrt{I}} + (\varepsilon_{HCl}c_{HCl} + \varepsilon_{salt}c_{salt})$ for reaction (1) in the presence of Mg^{+}, and Ca^{+} cations (for $SrCl_2$ we had no data). $A = 0.509$ in aqueous solution, $z_{complex} = -2$ is the charge of activated complex in the reaction (1),$C_{HCl} = 0.05$ M, c_{salt} are from the Table 2, ε factors are from [12]

This composition indicates that the SIT model does not describe precisely changes in the rate constants k in electrolytes in which chloride salts of Li, Na, K and Mg are present (except for $CaCl_2$).

It is also interesting to note, that the equations given by the Brönsted-Bjerrum (B-B),

$$\log\left({}^{k}\!/_{k_0}\right) = 2z_{[AuCl_4]^-}z_{[HSO_3]^-}A\left(\sqrt{I}\right) \tag{11}$$

and

$$\log\left({}^{k}\!/_{k_0}\right) = 2z_{[AuCl_4]^-}z_{[HSO_3]^-}A\left({}^{\sqrt{I}}\!/_{1} + \sqrt{I}\right) \tag{12}$$

which can be applied to systems with the ionic strength less than (or equal to) 0.001 and 0.1 M respectively [3], in all cases predict correctly the linear dependence between k and I (Fig. 6 and 7) obtained from our experiments.

It can be seen however that slopes of those dependencies differ from the theoretical ones. Therefore, from equations (11) and (12) the charge of the activated complex formed during the reaction can be estimated. According to the mechanism proposed in [1], the charges of reagents should be equal to "– 1" ($z_{[AuCl_4]^-} = z_{[HSO_3]^-} = -1$). Hence, the charge of the activated complex ($z_{complex}$) should be the sum of the charges of reagents ($z_{[AuCl_4]^-} + z_{[HSO_3]^-} = -2$). Values of that charge and reacting ions ($z_{[AuCl_4]^-}$ and $z_{[HSO_3]^-}$) can be estimated from respective slopes (it was assumed that $z_{[AuCl_4]^-} = z_{[HSO_3]^-}$, and in aqueous solution $A = 0.51$,). The results of these calculations are gathered in Tab. 4.

TABLE 4

Estimated values of the effective charge of reagents, for the reaction between $[HSO_3]^-$ and $[AuCl_4]^-$ ions in the aqueous solution containing Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} cations

Type of cation in the solution	Slope of a straight line $2z_{[AuCl_4]^-}z_{]HSO_3]^-}A$	Charge of the reactant $z_{reactant} = z_{[AuCl_4]^-} = z_{[HSO_3]^-}$	Charge of the complex $z_{complex}$
Li^+	0.052	- 0.23	- 0.5
Na^+	0.248	- 0.49	- 1
K^+	0.627	- 0.78	- 1.5
Mg^{2+}	2.773	- 1.65	- 3.3
Ca^{2+}	0.764	- 0.87	- 1.7
Sr^{2+}	3.555	- 1.77	- 3.7

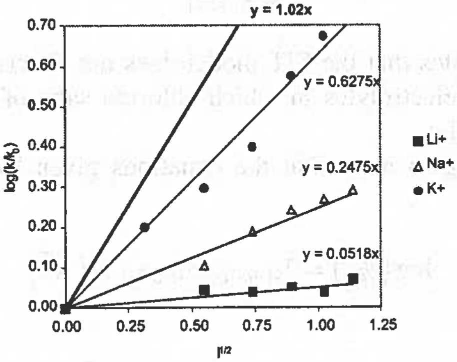

Fig. 6. Dependence of $\log\left(k/k_0\right)$ vs. square root of ionic strength for reaction (1) in the presence of Li^+, Na^+, and K^+ cations

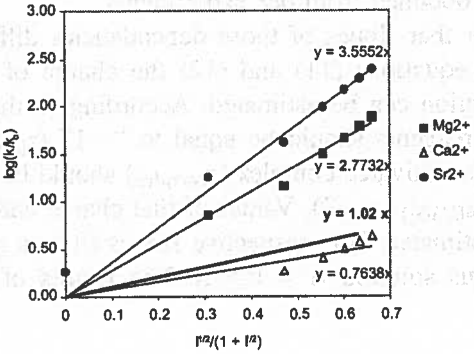

Fig. 7. Dependence of $\log\left(k/k_0\right)$ vs. $\left(\sqrt{I}/1+\sqrt{I}\right)$ for reaction (1) in the presence of Mg^{2+}, Ca^{2+}, and Sr^{2+} cations

The results indicate that the total charge of the activated complex is not equal to "—2" but depends on the cation added to the solution.

Apparently, the change of the "effective charge" is related to the size of the cation. The fact that the rate constant *k* depends on the ionic radii of added cation is not included into B-B equation. In the case of cations from the first group of the periodic table both reactants and the activated complex have their charges reduced according to the trend: the smaller the cation the bigger the reduction. This is demonstrated in Fig. 8, which shows that this dependence is linear.

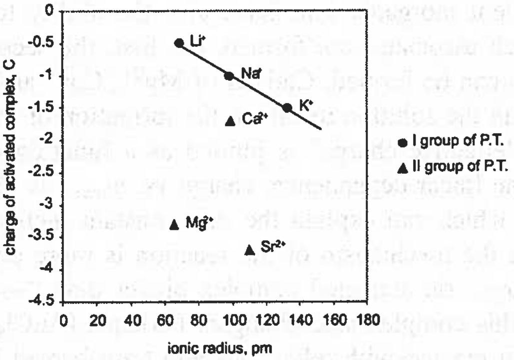

Fig. 8. Charge of intermediate complex in the reaction between $[AuCl_4]^-$ and $[HSO_3]^-$ vs. ionic radius of added cation (P.T. — Periodic Table, values of ionic radius are from [10])

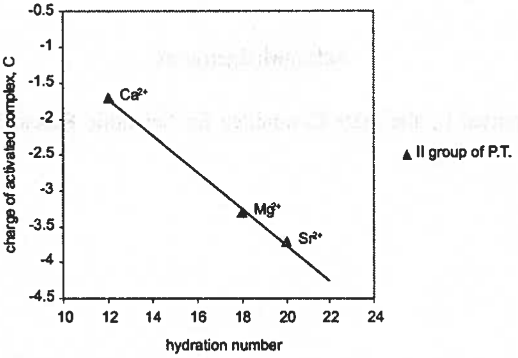

Fig. 9. Charge of activated complex in the reaction between $[AuCl_4]^-$ and $[HSO_3]^-$ vs. hydration number of added cation (P.T. — Periodic Table, values of hydration numbers are from [13])

The observed changes seem to be connected with the increasing hydration of the cation as its radius shrinks. Not only solvent molecules are effected but also reactant species. As the size of the cation increases, its effect on the surroundings weakens, and the charge of the activated complex is getting closer to the theoretical "–2" value. It can be speculated that with the CsCl addition the effect of the surroundings on the rate constant of reaction (1) would be close to nil.

However, the effect of the addition of the cations from the second group of the periodic table cannot be explained in the same way. No sensible correlation can be found between the charge and the ionic radii. It seems that in this case other factors must be taken into account. More attention requires the parameter, which is called hydration number of a cation ($n_{hydr.}$). It is known that monovalent inorganic ions have the ability to cause solvation of H_2O molecules in the so-called first hydration shell [3]. Cations Li^+, Na^+, K^+ considered in this work belong to this group. According to literature data [3, 13] multivalent inorganic ions have also the ability to associate with H_2O molecules. When such associates are formed, the first, the second and sometime the third hydration shells can be formed. Cations of Mg^{2+}, Ca^{2+} and Sr^{2+} belong to those ions. Their presence in the solution results in the formation of the first and the second hydration shells. If "effective charge" is plotted as a function of the total hydration number of the ion, the linear dependence, charge vs. $n_{hydr.}$, is obtained (Fig. 9).

The mechanism which can explain the rate constant increase in this case is not known. It seems that the mechanism of the reaction is more complicated. The value of the "effective charge" on activated complex bigger than "—2" suggests that with increased hydration this complex also changed. Perhaps, $[AuCl_4]^-$ and $[HSO_3]^-$ ions under given condition reacted with other ions and transformed into another activated complex with a higher charge. Since the rate of reaction also depends on how rapidly the reactant species can diffuse through the solution, viscosity measurements should help to distinguish if the reaction is under diffusion or activation control. This possibility however will be a subject of a future study.

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