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INFLUENCE OF TEMPERATURE ON THE STABILITY OF 2-ETHYLIMIDAZOLE AU (III) COMPLEXES

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Abstract. *This article deals with the complexation of gold (III) with 2-ethylimidazole at a temperature range of 278-328 K by potentiometric titration. The reduction of the Au/$[AuCl_4]^-$ system potential during the titration process at all temperatures under study indicates a reduction of the equilibrium concentration of $[AuCl_4]^-$ and their coupling into complexes. The non-linearity of the dependence of E on lgC_L is characteristic for the systems in which stepwise complexation occurs. We calculated the common stability constants of the complexes $[Au(2\text{-}EI)Cl_3]$ and $[Au(2\text{-}EI)_2Cl_2]Cl$ (at 298 K $lg\beta_1 = 6.14\pm0.06$; $lg\beta_2 = 13.18\pm0.08$). The stability of the complexes grows with increasing of temperature. The temperature factor affects the stability of the bisubstituted complex to a greater extent (at a rise in temperature by 50 °C the stability of the bisubstituted complex increases by 2.69 log units, at the same temperature interval the stability of the monosubstituted complex increases by 1.32 log units).*

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Introduction

In this paper we reviewed data on the chemistry of gold compounds in solutions [1]. Based on the authors' own and literature data, the authors showed that the standard potential of the Au^{3+}/Au system is (1.0±0.003) V. It was shown that the hydrolysis process of $AuCl_3 + H_2O \leftrightarrow [AuCl_3OH]^- + H^+$ proceeds when the pH is increased. The stability of dimercaptide Au(III) complexes in solution using the Au/$[AuCl_4]^-$system is reported by the authors of [2]. We experimentally determined the standard potential of Au^{3+}/Au system at different concentrations of $[AuCl_4]^-$ and $[Cl]^-$ and found that the value of E^0 varies in the range 1.013-1.041 V. Using pH-metric titration the authors of [3] studied the substitution of chloride ions in $[AuCl_4]^-$ by OH^- in aqueous solution at 298 K. The equilibrium constants of the complex particles are as follows: $lg\beta_1 = 7.87$; $lg\beta_2 = 14.79$; $lg\beta_3 = 20.92$ and $lg\beta_4 = 25.98$. The replacement of chloride ions by ethylenediamine (en) and diethylamine (dien) ammonia at 298 K in $[AuCl_4]^-$

spectrophotometrically and potentiometrically was reported by the authors of [4]. For the equilibrium $AuCl_4^- + NH_3 = AuCl_3(NH_3) + Cl^-$ the equilibrium constant is $lg\beta_1 = (6.73\pm0.09)$ V and the standard potential of the system $(Au(NH_3)_4^{3+}/Au^0)$ = 0.52 V. The equilibrium constants for the substitution of $AuCl_4^-$ for ethylenediamine are $lg\beta_1 = 16.2$ and $lg\beta_2$ I = 27.7 and for diethylamine $lg\beta_3 = 22.7$. The authors of [5] studied the Cl^- substitution equilibrium of $[AuCl_4]^-$ into pyridine (py),2.2-dipyridyl (bipy) and 1.10-phenanthroline (phen) by the spectrophotometric method in acidic solution. Considering the protonation constants of amines for the equilibrium $AuCl_4^- + L = AuLCl_i^{3-i} + (4-i)Cl^-$ the equilibrium constants are: $lg\beta_1$ = 3.3(py), 8.2(bipy), 9.5(phen).

The potentiometric titration method is still one of the most frequently used methods for determining the composition and stability constants of complex compounds at different temperatures [6-9]. In [10] composition and thermodynamic characteristics of 1-furfurylidenamino-1,3,4-triazole complexes of gold (III) at 278–318 K have been calculated. It was found that the stability of the complexes reduces with increasing temperature. An increase of temperature also affects the number of forming complex particles. We can determine the stability of three complex particles at the temperature range 288–308 K and only two at 318 K. In [11] the complexation of $H[AuCl_4]$ with 2-methylimidazole at different temperatures using $Au/[AuCl_4]^-$ system was studied. In this work the authors studied the effect of gold hydrolysis on the electrode potential of the $Au/[AuCl_4]^-$ system. It was shown that the interaction of $H[AuCl_4]$ with 2-methylimidazole produces three complex particles proceeds with the emission of heat. By potentiometric method the authors of [10, 12] found that gold (III) with triazole and benztriazole forms four complex particles which stability decreases with increasing temperature. The authors of [13] present data on reversibility of $Au/[AuCl_4]^-$ system, ionization constant of 2-ethylimidazole and complexation of $[AuCl_4]^-$ with 2-ethylimidazole at 298 K. Complexing proceeds as follows by the general equation

$$[AuCl_4]^- + n(2\text{-EI}) \leftrightarrow [Au(2\text{-EI})_nCl_i]^{3-i} + (4 - i)Cl^-$$

the composition and total formation constants of the three complex particles can be determined.

Analysis and review of the literature showed that, despite some experimental data, in general, the complexing of gold (III) with amide ligands in a wide temperature range is still an understudied area of coordination chemistry. Taking into account these gaps, we set the task to study the complexing of gold (III) with 2-ethylimidazole in a wide temperature range, to determine the composition, stability, thermodynamic characteristics and other parameters of the complex particles formed in solution.

Main body

Fig. 1 shows the experimental dependences of E on lgC_L, which are results of potentiometric titration. The reduction of the Au/[AuCl4]- system potential during the titration process at all temperatures under study indicates a reduction of the equilibrium concentration of $[AuCl_4]^-$ and their coupling into complexes.

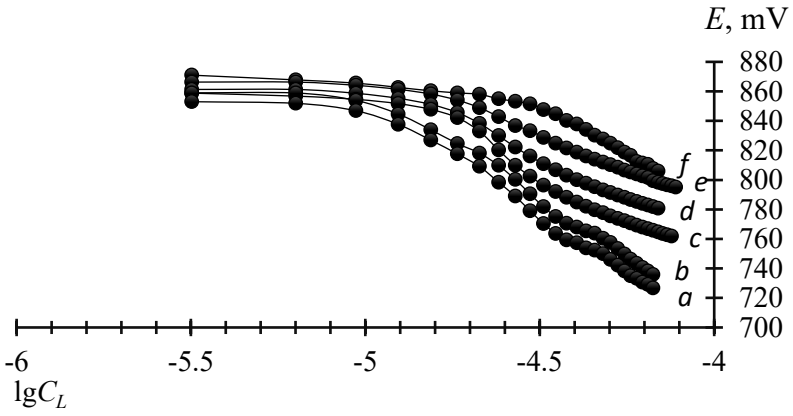

Fig. 1. Dependence of E on lgC_L for system H[$AuCl_4$] with 2-ethylimidazole at 278–328 K: *a* – 278 K; *b* – 288 K; *c* – 298 K; *d* – 308 K; *e* – 318 K; *f* – 328 K

The non-linearity of the dependence of E on lgC_L is characteristic for systems in which stepwise complexing occurs.

Table 1. The potential change of the Au/$[AuCl_4]^-$system with potentiometric titration of $[AuCl_4]^-$ 2-ethylimidazole, the equilibrium concentrations of the starting substances and the reaction products at 298 K calculated by the KEV software. $C_{2\text{-EI}} = 4\cdot10^{-4}$ mol/l; $C_{[AuCl4]} = 1\cdot10^{-5}$ mol/l

E, experimentally	*E*, theoretically	$[AuCl_4]^-\cdot10^{10}$ mol/l	[2-EI]·10^8 mol/l	$[Au(2\text{-EI})Cl_3]\cdot10^8$ mol/l	$[Au(2\text{-EI})_2Cl_2]^+\cdot10^7$ mol/l
870.1	869.5	-	-	-	-
868.0	867.4	84228.0	7.90229	91.6085	5.81114
867.0	865.6	67670.2	14.9802	139.522	16.7777
865.4	863.4	52406.7	22.4253	161.753	29.1180
862.0	860.7	38335.1	31.4746	166.067	41.9582
857.9	857.2	25656.7	44.0445	155.532	54.9901
852.4	852.6	14990.4	63.7275	131.482	67.2614
845.1	846.2	7027.14	100.219	96.9298	77.9799
836.7	837.8	2643.56	170.739	62.1225	85.1442
829.0	829.7	1031.14	278.430	39.5146	88.3174
822.8	823.2	481.691	409.862	27.1727	89.4010
817.6	817.7	254.769	564.405	19.7909	89.6661
813.5	813.6	156.143	720.263	15.4789	89.4960
809.9	809.9	102.061	889.654	12.4970	89.2482
806.9	806.9	71.3639	1061.17	10.4229	88.7863
804.4	804.2	52.2633	1237.01	8.89811	88.3579
802.0	801.9	39.9623	1410.85	7.75991	87.8840
799.9	799.8	31.2564	1589.83	6.83936	87.2848
798.1	797.9	25.2416	1763.83	6.12774	86.7620
796.4	796.2	20.5747	1947.64	5.51527	86.2279
794.8	794.6	17.1426	2126.94	5.01831	85.6810
793.4	793.2	14.5492	2301.22	4.60813	85.1246
792.0	791.9	12.3975	2484.70	4.23971	84.5636
790.8	790.6	10.7479	2661.19	3.93663	84.0956
789.7	789.5	9.41734	2833.28	3.67236	83.5233
788.6	788.4	8.26328	3014.25	3.42814	82.9489
787.6	787.4	7.34665	3187.53	3.22307	82.4703

Table 1 shows the potential change of the Au/$[AuCl_4]^-$system with potentiometric titration of $[AuCl_4]^-$ 2-ethylimidazole, the equilibrium concentrations of the starting substances and the reaction products at 298 K calculated by the KEV software.

We entered potentiometric titration data, the concentration of $[AuCl_4]^-$ and 2-ethylimidazole at each titration point and the protonation reaction of 2-ethylimidazole into the KEV software to determine the composition and stability of the formed complex particles. The model takes into account the following equilibria:

$$H^+ + L = HL^+ \quad (1)$$

$$[AuCl_4]^- + L = [AuLCl_3] + Cl^- \quad (2)$$

$$[AuCl_4]^- + 2L = [AuL_2Cl_2]^+ + 2Cl^- \quad (3)$$

$$[AuCl_4]^- + 3L = [AuL_3Cl]^{2+} + 3Cl^- \quad (4)$$

$$[AuCl_4]^- + 4L = [AuL_4]^{3+} + 4Cl^- \quad (5)$$

$$H^+ + OH^- = H_2O \quad (6)$$

It should be noted that processing of the potentiometric titration data in the temperature range 278–328 K with the KEV programme shows satisfactory results in the reactions for the formation of the two complex forms (2) and (3). Table 2 shows the results of the calculation of the common stability constants. The reliability of the determination of the constants is confirmed by the satisfactory coincidence of the experimentally found potential values with the theoretical ones (see Table 1).

Table 2. Values of the common stability constants of 2-ethylimidazole gold (III) complexes

T, K	$lg\beta_{1[AuLCl3]}$	$lg\beta_{2[AuL2Cl2]+}$
278	5.88±0.08	12.24±0.09
288	6.05±0.07	12.76±0.08
298	6.14±0.06	13.18±0.08
308	6.55±0.07	13.86±0.06
318	6.88±0.08	14.41±0.05
328	7.20±0.09	14.93±0.06

The table shows the growing of stability of the complexes with increasing temperature. The temperature factor has a greater effect on the stability of the bisubstituted complex. At a rise in temperature by 50 ^{0}C the stability of the bisubstituted complex increases by 2.69 log units, at the same temperature interval the stability of the monosubstituted complex increases by 1.32 log units.

Recalculation of the common constants into step constants shows, that in the whole studied temperature range stability of the bisubstituted complex is greater than stability of the monosubstituted one (at 298 K $lgK_1 = 6{,}14$; $lgK_2 = 7{,}04$), that does not exactly correspond to the theory of stepwise complex formation. The greater stability of the bisubstituted complex as compared to the monosubstituted one may be explained by the fact that the chloride ligands located in $[Au(2\text{-EI})Cl_3]$ in the *trans*-position to the 2-ethylimidazole molecule are more easily replaced by a subsequent 2-ethylimidazole molecule.

The found common stability constants at different temperatures were used to determine the thermodynamic functions of complex formation by the temperature coefficient method. By the equation

$$lg\beta_i^0 = \frac{-\Delta H}{2{,}3R} \cdot \frac{1}{T} + \frac{\Delta S}{2{,}3R}$$

we graphically determined ΔH and ΔS (Fig. 2), the Gibbs energy was calculated using the equation $\Delta G = \Delta H - T\Delta S$.

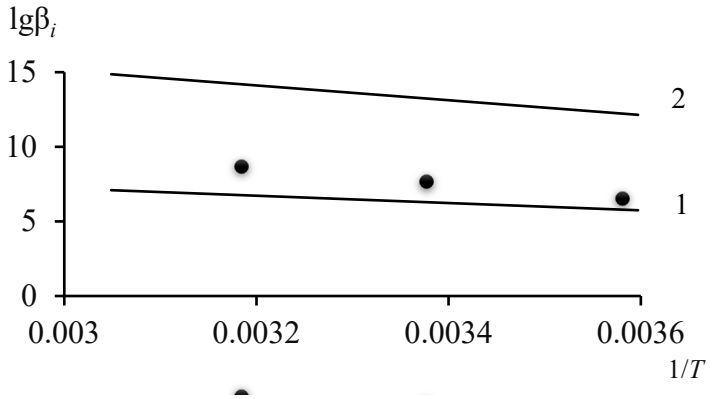

Fig. 2. Dependence of $lg\beta_i$ from $1/T$ for complexes $[Au(2\text{-}EI)Cl_3]^0$ (1) and $[Au(2\text{-}EI)_2Cl_2]^+$ (2)

Table 3 presents the values of thermodynamic functions for the formation of gold (III) complexes with 2-ethylimidazole.

Table 3. Values of thermodynamic functions for the complexation reactions of gold (III) with 2-ethylimidazole

Reaction of complex formation	ΔH, kJ/mol	ΔS, J/(mol·K)	ΔG, kJ/mol
$[AuCl_4]^- + (2EI) \leftrightarrow [Au(2EI)Cl_3]^0 + Cl^-$	38.66±0.75	233.3±4.78	-30.87±0.38
$[AuCl_4]^- + 2(2EI) \leftrightarrow [Au(2EI)_2Cl_2]^+ + 2Cl^-$	94.96±1.33	574.1±2.63	-76.15±0.17

By Table 3 the formation of both complex forms produces with the releasing of energy. Such a change in the heat content of the system has a negative effect on the spontaneous course of the complexing reaction. Positive changes in ΔS ensure the direction and spontaneity of the reaction to form 2-ethylimidazole complexes.

Fig. 3 shows as an example the distribution diagrams of mono- and bisubstituted gold (III) complex as a function of the concentration of 2-ethylimidazole at 308 K.

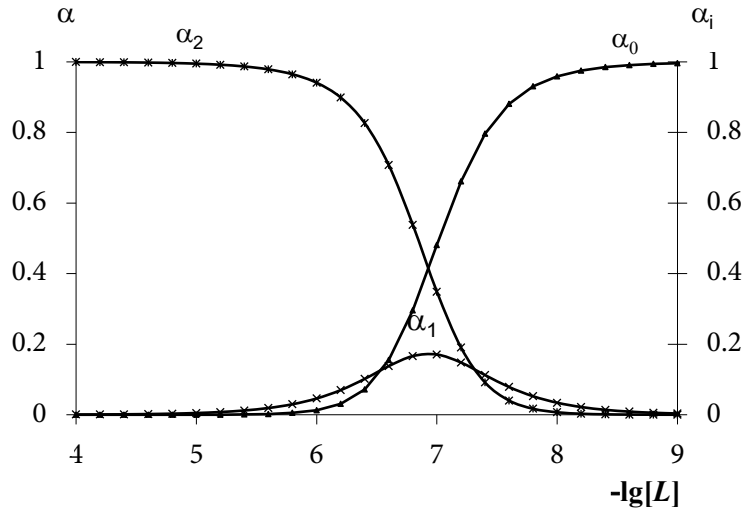

Fig. 3. Distribution curves of 2-ethylimidazole gold (III) complexes at 308 K, where α_0 – $[AuCl_4]^-$; α_1 - $[Au(2EI)Cl_3]$; α_2 - $[Au(2EI)_2Cl_2$

The analysis of the temperature dependence of the distribution function shows yield growing of complex forms with increasing temperature.

Experimental part

We used 2-ethylimidazole (2-EI) and $H[AuCl_4]$ as starting compounds. The $H[AuCl_4]$ solution was prepared according to the method described in [14]. The initial concentration of $H[AuCl_4]$ was $1 \cdot 10^{-5}$ mol/l, the concentration of 2-ethylimidazole was $4 \cdot 10^{-4}$ mol/l. To carry out a study of the interaction of $H[AuCl_4]$ with 2-ethylimidazole we used a galvanic cell with transfer: $Au/[AuCl_4]^- \| Ag,AgCl/Cl^-$. Potentiometric titration was carried out on a MI-150 pH-meter from a 5 ml half-microbiurette with a division value of 0.01 ml. In this research we used a weakly acidic $H[AuCl_4]$ solution (pH = 5) and an aqueous solution of 2-ethylimidazole (pH = 8.73). The concentration of chloride ions was 1 mol/l and was sustained by adding KCl to the solution. We created an ionic strength by adding sodium perchlorate (I = 0.05 mol/l) to the solution. We carried out potentiometric titration 4-5 times at each temperature. The system potential was set within 10-15 min. We kept the cell temperature constant with a water thermostat (±0.1 °C). The equilibrium concentrations of $[AuCl_4]^-$, 2-ethylimidazole, the resulting complexes and their stability constants were determined using the KEV program [15].

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