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POTENTIOMETRIC INVESTIGATION OF MIXED LIGAND COMPLEXES OF Co(II), Ni(II) AND Zn(II) WITH THIOSALICYLIC ACID AND DIETHYLENETRIAMINE**

The formation of mixed ligand complexes of Co(II), Ni(II) and Zn(II) with thiosalicylic acid H_2SR and diethylenetriamine E in aqueous ethanol (50% v/v) was investigated by the potentiometric method at 298 and 313 K. The thermodynamic functions ΔF^o, ΔH^o and ΔS^o have been evaluated.

Thiosalicylic acid (H_2SR) belongs to physiologically important class of compounds called mercaptans. The growing importance of mixed complexes of transition metals with polyamines and biologically active compounds containing sulphur was the reason of our studies in this field. In literature there are only few papers on mixed complexes of H_2SR and ethylenediamine [1, 2]. As there were no data about such systems with diethylenetriamine, we considered worthwhile to extend our investigations to them.

The aim our present paper was the determination of stepwise stability constants of forming complexes in order to find out the tendency and paths of mixed chelates forming in systems consisting of Co(II), Ni(II) or Zn(II), diethylenetriamine (E) and thiosalicylic acid (H_2SR), including the evaluation of their thermodynamic functions ΔF^0, ΔH^0 and ΔS^0.

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EXPERIMENTAL

Reagents

Thiosalicylic acid H_2SR (Merck A. G.) was purified by recrystallization from methanol. Diethylenetriamine E (Schuhardt A. G.) was purified by vacuum distillation and used as its $HClO_4$ salt. Metal perchlorates were prepared by treating corresponding carbonates with perchloric acid. $M(ClO_4)_2$ solutions were standarized by complexometric method [3]. All the pH-metric titrations were carried out with carbonate - free NaOH solution.

Apparatus

The pH-metric titrations were performed under nitrogen in a water-jacketed thermostated beaker. pH measurements were made with a OP-208 Radelkis pH-meter equipped with a glass OP-0718 and OP-830 P calomel electrodes. The glass electrode was calibrated with buffers of pH = 4.008, 6.865 and 9.210 at 298 K. The NaOH solution was added from microburette.

Measurement method and calculation procedure

The procedure employed was to titrate a $M(II)$-H_2SR-E mixture of constant ionic strength ($\mu = 0,1$) in the presence of $HClO_4$ with standard NaOH at 298 and 313 K. Aqueous ethanol (50% v/v) was used as solvent. The sample volume was 50 cm^3.

For each system several series of titrations were performed. In each one, a constant concentration of two components was kept, while the concentration of third component was varied. From particular series of titration curves, the concentration of free uncomplexed components $[H_2SR]$, $[E]$ and $[M]$ were found as described in paper [4]. Having the concentrations we have calculated stability constants of complexes using MINIQUAD program [5].

The values of thermodynamic functions viz. free energy of formation ΔF^0, ligational enthalpy ΔH^0 and entropy changes ΔS^0 were evaluated using eqns (1)-(3) [6]:

$$\Delta F^0 = -2{,}303\ RT \log K \quad , \tag{1}$$

$$\Delta H^0 = \frac{2{,}303\ RT_1T_2(\log K_2 - \log K_1)}{T_2 - T_1} \tag{2}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta F^0}{T} \tag{3}$$

We have presumed the ΔH^0 values to be constant at the investigated 298-313 K temperature range.

RESULTS AND DISCUSSION

Potentiometric titration data suggest the formation of ternary complexes, which was confirmed by the results of calculations. The obtained stability constants are shown in Tab. 1.

Table 1

The values of parameters characteristic for stability of complexes forming in system $M(II)-H_2SR-E$

Metal ion	$\log\beta_{M(SR)E}$ (calc)	$\log\beta_{M(SR)E}$ (stat)	$\log X_{M(SR)E}$	$\Delta\log K_{M(SR)E}$	$\Delta_{M(SR)E}$
Co(II)	13.43	12.35	2.75	-0.49	1.08
Ni(II)	16.08	15.40	1.96	-1.83	0.68
Zn(II)	15.23	14.79	1.48	-1.88	0.44

Using evaluated stability constants concentration of metal complexes have been calculated from pH 4 to 10. These results plotted in Figs. 1-3 show that the mixed ligand complexes of [M(SR)E]-type are predominant species at higher pH values.

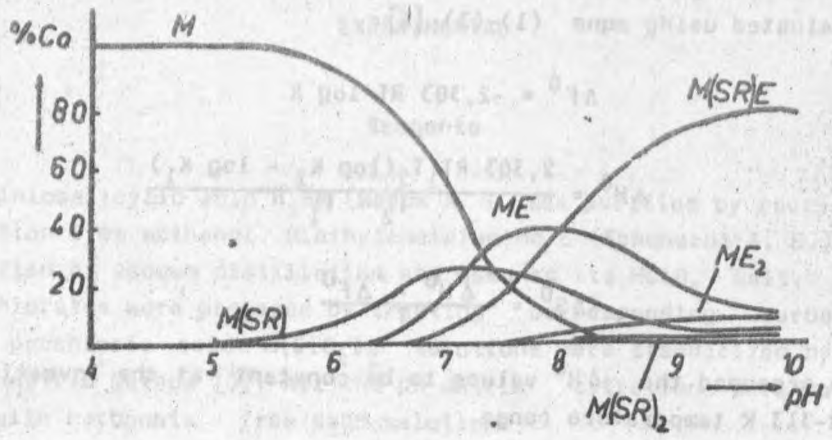

Fig. 1. Variation with pH of the composition a solution (1 : 1 : 1) Co(II)-H_2SR-E

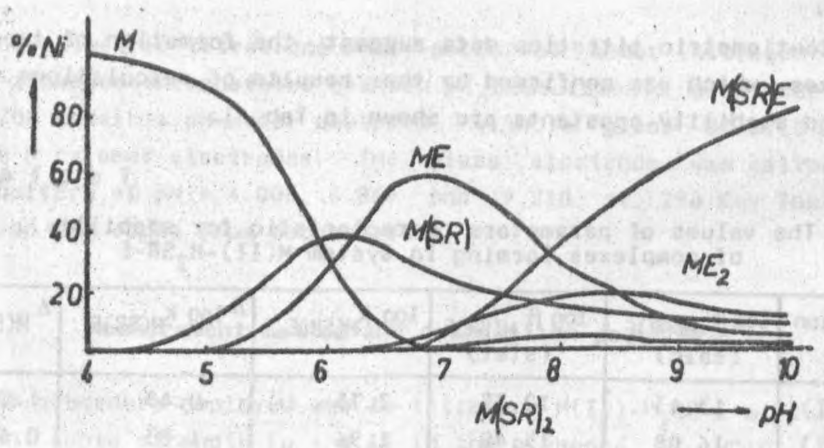

Fig. 2. Variation with pH of the composition of a solution (1 : 1 : 1) Ni(II)-H_2SR-E

Factor $\Delta \log K_{M(SR)E}$ given by expression (4):

$$\Delta \log K_{M(SR)E} = \log \beta_{M(SR)E} - (\mathrm{lcg}\, K^{M}_{M(SR)} + \log K^{M}_{ME}) \qquad (4)$$

is the measure of tendency for forming the ternary complexes by the stepwise addition according to eqns (5)-(6) or (7)-(8) (the charges of ions are ommitted):

$$M + SR = [M(SR)] \qquad (5)$$

$$[M(SR)] + E = [M(SR)E] \qquad (6)$$

$$M + E = [ME] \qquad (7)$$

$$[ME] + SR = [M(SR)E] \qquad (8)$$

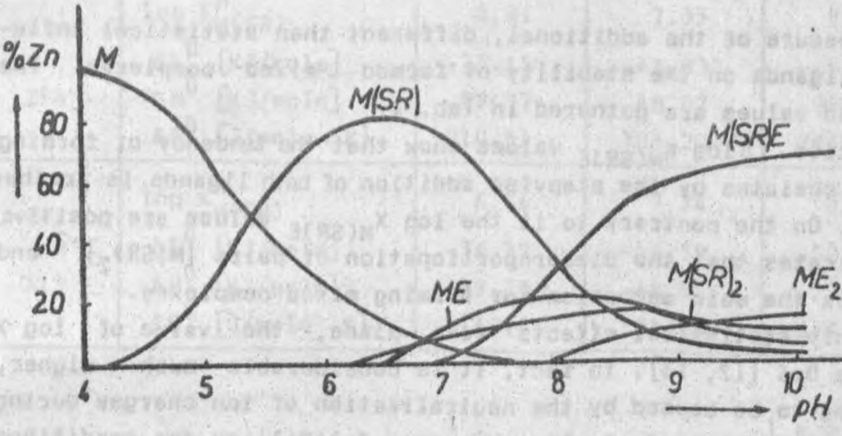

Fig. 3. Variation with pH of the composition of a solution (1 : 1 : 1) Zn(II)-H_2SR-E

Taking into account, that the stability of complexes of $[M(SR)_2]^{2-}$ and $[ME_2]^{2+}$ are relatively high, the dissproportionation of these complexes according to the equation (9) seems to be very likely way of forming mixed complexes:

$$[M(SR)_2]^{-2} + [ME_2]^{2+} = [M(SR)E]^0 \qquad (9)$$

The tendency for it can be measured by factor log $X_{M(SR)E}$ [7] given by the expression (10):

$$\log X_{M(SR)E} = 2 \log \beta_{M(SR)E} - (\log \beta_{M(SR)_2} + \log \beta_{ME_2}) \qquad (10)$$

Since the statistic effects are essential factor for mixed ligand complexes stabilization [8-11] we have also calculated the statistical stability constants

$$\log \beta_{M(SR)E}(\text{stat}) = \log 2 + 1/2(\log \beta_{M(SR)_2} + 1/2 \log \beta_{ME_2}) \qquad (11)$$

The difference $\Delta_{M(SR)E}$ given by the expression (12):

$$\Delta_{M(SR)E} = \log \beta_{M(SR)E}(\text{calc}) - \log \beta_{M(SR)E}(\text{stat}) \qquad (12)$$

is the measure of the additional, different than statistical influence of ligands on the stability of formed mixed complexes. The calculated values are gathered in Tab. 1.

Negative $\Delta \log K_{M(SR)E}$ values show that the tendency of forming of mixed chelates by the stepwise addition of both ligands is rather moderate. On the contrary to it the $\log X_{M(SR)E}$ values are positive, what indicates that the dissproportionation of pairs $[M(SR)_2]^{-2}$ and $[ME_2]^{2+}$ is the main mechanism for forming mixed complexes.

If only statistical effects take place, the value of $\log X$ should be 0.6 [12, 13]. In fact, it is considerable much higher, what seems to be caused by the neutralization of ion charges during dissproportionation. So in the pH range fullfilling the conditions of forming simple 1 : 1 metal-ligand complexes, the participation of ternary complexes in solution is small, but at the higher pH values, when 1 : 2 metal-ligand complexes can be formed, mixed ligand complexes dominate in the solution.

The stability order of mixed complexes in term of metal ion is in a good egreement with Irving-William series [14]:

$$\text{Co(II)} < \text{Ni(II)} > \text{Zn(II)}$$

The calculated thermodynamic functions for the formation of mixed complexes by the stepwise addition according to eqns (5)-(6) are given in Tab. 2 and 3. It can be seen that the addition of H_2SR as well as E is accompanied with high negative F^0 values, what prove very strong driving force for complex formation. The addition of H_2SR is endothermic on contrary to the egzothermic addition E to $[M(SR)]$. The entropy positive changes fovour the complex formation. ΔS^0 values are much higher for the addition of the first ligand (H_2SR) than the second one (E). The values of $\Delta_{M(SR)E}$

Table 2

[M(SR)] complexes thermodynamic functions

Temp. [K]	Calculated value	Complex		
		[Co(SR)]	[Ni(SR)]	[Zn(SR)]
298	$\log K^{M}_{M(SR)}$	5.81	7.33	8.19
	ΔF^0 [KJ/mole]	-33.15	-41.83	-46.73
	ΔH^0 [KJ/mole]	29.77	48.82	29.19
	ΔS^0 [J/mole · K]	210.91	304.20	244.70
313	$\log K^{M}_{M(SR)}$	6.06	7.74	8.41
	ΔF^0 [KJ/mole]	-36.32	-46.39	-50.41
	ΔH^0 [KJ/mole]	29.77	48.82	29.19
	ΔS^0 [J/mole · K]	211.15	304.18	244.73

Table 3

[M(SR)E] complexes thermodynamic functions

Temp. [K]	Calculated value	Complex		
		[Co(SR)dien]	[Ni(SR)dien]	[Zn(SR)dien]
298	$\log K^{M}_{M(SR)}$	7.62	8.75	7.04
	ΔF^0 [KJ/mole]	-43.48	-49.93	-40.17
	ΔH^0 [KJ/mole]	-26.20	-33.34	-22.62
	ΔS^0 [J/mole · K]	57.99	55.67	58.89
313	$\log K^{M}_{M(SR)E}$	7.40	8.47	6.85
	ΔF^0 [KJ/mole]	-44.35	-50.77	-41.06
	ΔH^0 [KJ/mole]	-26.20	-33.34	-22.62
	ΔS^0 [J/mole · K]	57.99	55.69	58.91

(Tab. 1) are positive, what confirm that investigated metal ions are better stabilized by two different, than by two ligands of the same kind. The high values of evaluated thermodynamic functions may be attributed to the high strength of the metal-sulphur and metal-nitrogen bonds.

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POTENCJOMETRYCZNE BADANIA MIESZANYCH KOMPLEKSÓW Co(II), Ni(II) I Zn(II) Z KWASEM TIOSALICYLOWYM I DIETYLENOTRIAMINĄ

Przy użyciu metod potencjometrycznych badano powstawanie mieszanych kompleksów Co(II), Ni(II) i Zn(II) z kwasem tiosalicylowym (H_2SR) i dietylenotriaminą (E) w roztworach etanolowo-wodnych (50% v/v) w temp. 298 i 313 K. Obliczono towarzyszące powstawaniu kompleksów zmiany funkcji termodynamicznych: ΔF^o, ΔH^o i ΔS^o.