

POTENTIOMETRIC INVESTIGATION OF MIXED-LIGAND COMPLEXES OF Co(II), Ni(II) AND Zn(II) IONS WITH THIOSALICYLIC ACID AND ETHYLENEDIAMINE

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Formation of mixed-ligand complexes of Co(II), Ni(II) and Zn(II) ions with thiosalicylic acid (H_2SR) and ethylenediamine (en) in aqueous ethanol (50 vol. %) was investigated by the potentiometric method at 298, 313 and 328 K at the ionic strength of 0.1 ($NaClO_4$). The thermodynamic functions ΔG^0 , ΔH^0 and ΔS^0 have been evaluated at these temperatures.

It has been suggested by Kumari et al.¹ that thiosalicylic acid (H_2SR) and ethylenediamine (en) form mixed complexes with Ni(II) and Zn(II) ions. We have proved their results to be right^{2,3}. The aim of the present work was to determine the stepwise stability constants of complexes forming in a system consisting of Co(II), Ni(II) or Zn(II), ethylenediamine (en) and thiosalicylic acid (H_2SR), including the evaluation of their thermodynamic functions ΔG^0 , ΔH^0 and ΔS^0 .

EXPERIMENTAL

Thiosalicylic acid H_2SR (Merck A.G.) was purified by recrystallization from methanol. Ethylenediamine (en) (Schuhardt A.G.) was purified by vacuum distillation and used as its $HClO_4$ salt. Metal perchlorates were prepared by treating of corresponding carbonates with perchloric acid. $M(ClO_4)_2$ solutions were standardized by means of the complexometric method⁴. All the pH-metric titrations were carried out with carbonate-free NaOH solution. The pH-metric titrations were performed under nitrogen in a water-thermostated beaker with the use of 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 a microburette. The procedure employed was to titrate $M(II)-H_2SR$ and $M(II)-H_2SR-en$ mixtures (where: $M(II) = Co(II), Ni(II)$ or $Zn(II)$) with standard NaOH solution at 298, 313 and 328 K. Aqueous ethanol (50 vol. %) of ionic strength 0.1 ($NaClO_4$) was used as the solvent. The sample volume was 50 cm³. For each system several series of titrations were performed. In each one, a constant concentration of two components was maintained, while the concentration of the third compound was varied. From particular series of titration curves, the concentration of free uncomplexed components: $[H_2SR]$, $[en]$ and $[M(II)]$ were found as described in paper³. From these concentrations we have calculated stability constants of complexes using MINQUAD program⁵.

Values of thermodynamic functions, such as free energy of formation ΔG^0 , ligational enthalpy ΔH^0 and entropy changes ΔS^0 were evaluated using the Eqs (1)–(3).

$$\Delta G^0 = -2.303RT \log K \quad (1)$$

$$\Delta H^0 = \frac{2.303RT_1 T_2 (\log K_2 - \log K_1)}{T_2 - T_1} \quad (2)$$

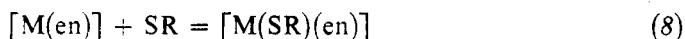
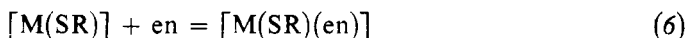
$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (3)$$

RESULTS AND DISCUSSION

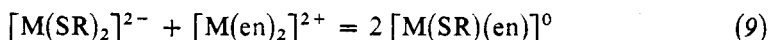
Potentiometric titration data suggest the formation of ternary complexes, which was confirmed by stability constants shown in Table I. Using the calculated stability constants, the concentration of metal chelates has been evaluated for pH values from 4 to 10. These dependences, shown in Fig. 1, demonstrate that the mixed-ligand complexes of $[M(SR)(en)]$ type are predominant type at higher pH range. Factor $\Delta \log K_{M(SR)(en)}$ given by expression (4):

$$\Delta \log K_{M(SR)(en)} = \log \beta_{M(SR)(en)} - (\log K_{M(SR)} + \log K_{M(en)}) \quad (4)$$

is the measure of tendency for forming the ternary complexes by the stepwise addition according to Eqs (5)–(6) or (7)–(8) (the ion charges are omitted).



The concentrations of $[M(SR)_2]^{2-}$ and $[M(en)_2]^{2+}$ are substantially high and thus, their disproportionation according to the Eq. (9) seems to be a very probable way of forming mixed complexes.



The tendency for such disproportionation can be expressed by a factor $\log X_{M(SR)(en)}$ given by the expression (10).

$$\log X_{M(SR)(en)} = 2 \log \beta_{M(SR)(en)} - (\log \beta_{M(SR)_2} + \log \beta_{M(en)_2}) \quad (10)$$

Since statistical effects form an essential factor for mixed ligand complexes stabilization⁶, we have calculated the statistical stability constants

$$\log \beta_{M(SR)(en)}(\text{stat.}) = \log 2 + 1/2 (\log \beta_{M(SR)_2} + \log \beta_{M(en)_2}). \quad (11)$$

The $\Delta \log \beta_{M(SR)(en)}$ value given by the Eq. (12):

$$\Delta \log \beta_{M(SR)(en)} = \log \beta_{M(SR)(en)}(\text{calc.}) - \log \beta_{M(SR)(en)}(\text{stat.}) \quad (12)$$

is the measure of additional, different from statistical influences of ligands on the stability of mixed complexes. The calculated values are summarized in Table I.

TABLE I

The parameters characteristic for the stability of ternary complexes of $[M(SR)(en)]$ type. ($T = 290$ K)

Metal ion	$\log \beta_{M(SR)(en)}$ (calc.)	$\log \beta_{M(SR)(en)}$ (stat.)	$\log X_{M(SR)(en)}$	$\log K_{M(SR)(en)}$	$\Delta \log \beta_{M(SR)(en)}$
Co(II)	11.09	10.55	1.68	-0.42	0.54
Ni(II)	13.47	12.99	1.56	-1.52	0.48
Zn(II)	12.65	12.52	0.86	-1.25	0.13

TABLE II

Thermodynamic functions of formation of $[M(SR)]$ type complexes

T, K	Co(II)	Ni(II)	Zn(II)
		$\log K_{M(SR)}$	
298	5.81	7.33	8.19
313	6.06	7.74	8.41
328	6.28	8.11	8.63
		$\Delta G^0, \text{kJ/mol}$	
298	-33.15	-41.83	-46.73
313	-36.72	-46.39	-50.41
328	-39.44	-50.94	-54.21
		$\Delta H^0, \text{kJ/mol}$	
298-313	29.77	48.82	29.19
313-328	28.83	48.49	30.14
		$\Delta S^0, \text{J/mol K}$	
298	210.91	304.20	244.70
313	211.15	304.18	244.73
328	208.14	303.14	257.17

TABLE III
Thermodynamic functions of formation of $[M(SR)(en)]$ type complexes

T, K	Co(II)	Ni(II)	Zn(II)
$\log K_{M(SR)(en)}$			
298	5.28	6.14	4.46
313	5.11	5.89	4.26
328	4.96	5.72	4.07
$\Delta G^0, kJ/mol$			
298	-30.13	-35.04	-25.45
313	-30.63	-35.30	-25.53
328	-31.15	-35.93	-25.56
$\Delta H^0, kJ/mol$			
298-313	20.24	29.77	23.81
313-328	19.66	22.28	24.90
$\Delta S^0, J/mol K$			
298	33.19	17.68	5.50
313	33.19	17.67	5.55
328	35.03	41.61	0.66

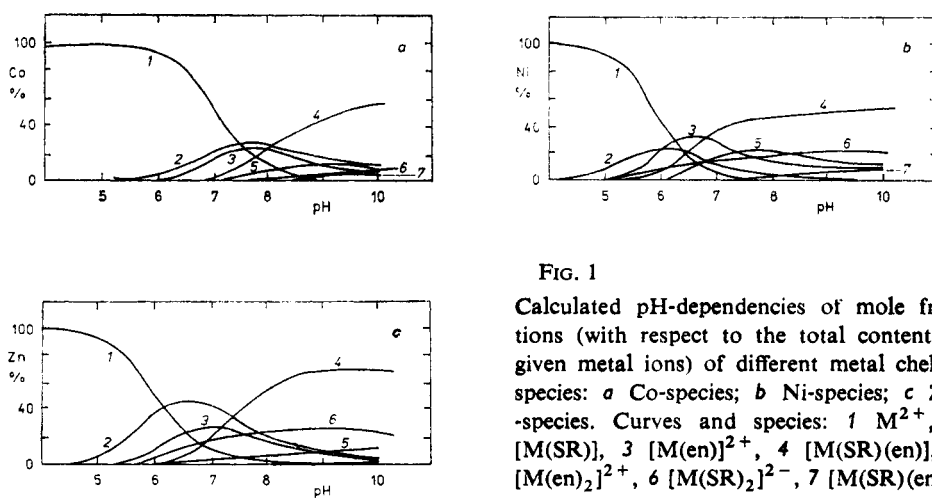
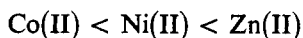


FIG. 1

Calculated pH-dependencies of mole fractions (with respect to the total content of given metal ions) of different metal chelate species: *a* Co-species; *b* Ni-species; *c* Zn-species. Curves and species: 1 M^{2+} , 2 $[M(SR)]$, 3 $[M(en)]^{2+}$, 4 $[M(SR)(en)]$, 5 $[M(en)_2]^{2+}$, 6 $[M(SR)_2]^{2-}$, 7 $[M(SR)(en)_2]$

Negative $\Delta \log K_{M(SR)(en)}$ values show that the tendency for forming mixed ligand chelates by the stepwise addition of both ligands is rather moderate (low, small). On the contrary, the values of $\log X_{M(SR)(en)}$ are positive indicating the disproportionation of pairs $[M(SR)_2]^{2-}$ and $[M(en)_2]^{2+}$ as the main mechanism of forming mixed complexes. They are much higher than statistical value $\log X = 0.6$ (ref.⁷) which seems to be caused by the neutralization of ion charges during the disproportionation. At the pH range fulfilling the conditions for forming simple 1 : 1 metal–ligand complexes, participation of ternary complexes in solution is small but at the higher pH range, when 1 : 2 metal–ligand complexes can be formed mixed chelates dominate in the solution. The stability order of these ternary complexes is in good agreement with Irving–Williams series⁸:



Calculated thermodynamic functions for the process of formation of mixed complexes are given in Tables II and III.

The H_2SR addition as well as en is accompanied with high negative ΔG^0 values, which proves very strong driving force for complex formation. Addition of H_2SR is endothermic, in contrast to the exothermic addition of en to $[M(SR)]$. The entropy positive changes favour the chelate formation. ΔS^0 values are substantially higher for addition of the first ligand (H_2SR) than of the second one (en). The values of $\Delta \log \beta_{M(SR)(en)}$ (Table I) are positive which confirms that investigated metal ions are better stabilized by two different than two same ligands. High values of the thermodynamic functions may be attributed to the strength of M–N and M–S bonds.

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