

Joanna Masłowska*, Józef Szmich*

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

Potentiometric studies of the M(II)-thiosalicylic acid(H₂A)-polyethylenepolyamine (E) systems (where: M = Ni, Co or Zn ions, E-ethylenediamine, diethylenetriamine or triethylenetetraamine) in ethanol-water NaClO₄ solutions ($\mu = 0,1$) reveals the formation of ternary complexes of [MAE]⁰ type. The log K_{form} and ΔG^0 values of these complexes were calculated at 25°C. The constitution of formed complexes was determined as well as the order of their stabilities in term of polyethylenepolyamines and metal ions.

Thiosalicylic acid (TSA) has two possible coordination sites, sulphhydryl (-SH) and carboxyl (-COOH) groups. Sulphur is known to form weak $\pi M \rightarrow L$ bonds, whereas $M \rightarrow O$ bonds are σ in character. Ligands with sulphur donor atoms are classified as soft bases and those with oxygen donor atoms as hard bases [1]. This is the reason why the formation of simple and mixed transition metal chelates of TSA has gained an interest in recent years [2-10]. In the present study an attempt has been made to investigate the complex formation of Ni(II), Co(II) and Zn(II) with TSA and polyethylenepolyamines such as: ethylenediamine (en), diethylenetriamine (dien) and triethylenetetraamine (trien).

* Institute of General Food Chemistry, Technical University of Łódź, Poland.

EXPERIMENTAL

Reagents

Thiosalicylic acid (Marck A. G.) was purified by crystallization from methanol. Polyamines (en, dien, trien) (Schuchardt A. G.) were purified by vacuum distillation and used as their salts with HClO_4 (en \cdot 2HClO_4 , dien \cdot 3HClO_4 and trien \cdot 4HClO_4 , resp.). $(\text{Ni}/\text{ClO}_4)_2$, $\text{Co}(\text{ClO}_4)_2$ stock solutions were prepared according to procedure [11] and standardised using EDTA [12, 13]. All the pH titrations were carried out with carbonate-free NaOH solution. Ethanol-water 50 : 50 (V/V) solutions were used and constant ionic strength ($\mu = 0.1$) was maintained by NaClO_4 .

Apparatus

pH measurements were performed with precision, digital OP-208 pH-meter Radelkis, equipped with a glass OP-0718P and calomel OP-0830P electrodes. Radelkis buffers of pH 2.15, 7.05 and 9.21 were employed. Potentiometric titrations were performed under purified nitrogen, supplied on to the bottom of the water-jacketed beaker at 25° .

Measurements and calculation procedure

The measurements were carried out as described in previous papers [14-16]. Several series of titration curves were made. pK values of ligands calculated from their titration curves by C h a b e r e k and M a r t e l l method [17] are presented in the Tab. 1.

Figure 1 shows the titration curves for the systems: $0.001 \text{ M}(\text{II}) - 0.01 \text{ TSA} - 0.01 \text{ HClO}_4 - 0.079 \text{ NaClO}_4 - \text{H}_2\text{O}$ (where $\text{M} = \text{Ni}, \text{Co}$ and Zn). From these curves, the stability constants of simple complexes have been calculated using B j e r r u m method [18] modified by C a l v i n and W i l s o n [19] (Tab. 2). Zinc (II) complexes are colourless, Ni(II) - dark-violet and Co(II) - dark-brown.

Table 1
Ligand acid dissociation constants

Ligand	pK_1	pK_2	pK_3	pK_4
TSA H_2A	5.14	9.52	-	-
H_2en^{2+} ^a	7.10	9.70	-	-
H_3dien^{3+} ^b	4.55	9.95	10.18	-
H_4trien^{4+} ^c	3.85	6.67	9.20	9.92

a, b, c Ref. [14, 15, 16] - respectively.

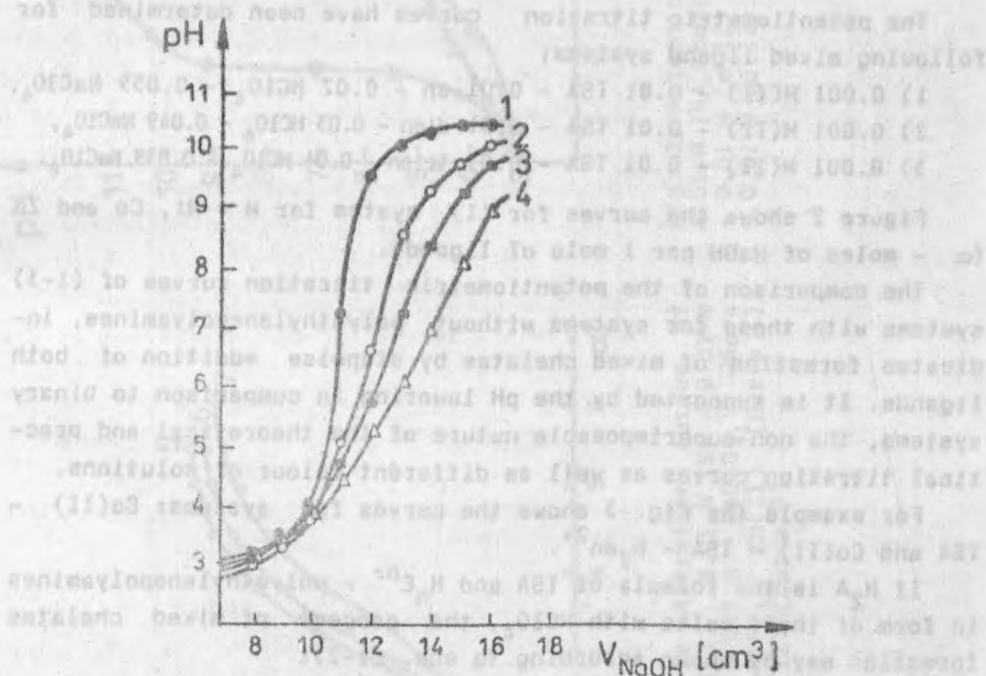


Fig. 1. Potentiometric titration curves of TSA in absence and presence of M(II)

Curve 1: 0.01 M TSA - 0.01 M $HClO_4$ - 0.08 M $NaClO_4$. Curve 2: 0.001 M $Co(II)$ - 0.01 M TSA - 0.01 M $HClO_4$ - 0.079 M $NaClO_4$. Curve 3: 0.001 M $Ni(II)$ - 0.01 M TSA - 0.01 M $HClO_4$ - 0.079 M $NaClO_4$. Curve 4: 0.001 M $Zn(II)$ - 0.01 M TSA - 0.01 M $HClO_4$ - 0.079 M $NaClO_4$.

Table 2

Stability constants of the binary TSA complexes of [MA] and [MA₂] type

Metal ion	$\log \beta_1$	$\log \beta_2$
Co(II)	5.8 ± 0.2	4.1 ± 0.2
Ni(II)	6.9 ± 0.2	4.2 ± 0.2
Zn(II)	8.2 ± 0.3	

The potentiometric titration curves have been determined for following mixed ligand systems:

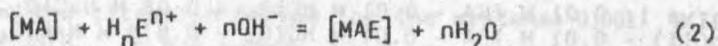
- 1) 0.001 M(II) - 0.01 TSA - 0.01 en - 0.02 HClO₄ - 0.059 NaClO₄,
- 2) 0.001 M(II) - 0.01 TSA - 0.01 dien - 0.03 HClO₄ - 0.049 NaClO₄,
- 3) 0.001 M(II) - 0.01 TSA - 0.01 trien - 0.04 HClO₄ - 0.039 NaClO₄.

Figure 2 shows the curves for (1) system for M = Ni, Co and Zn (α - moles of NaOH per 1 mole of ligand).

The comparison of the potentiometric titration curves of (1-3) systems with those for systems without polyethylenepolyamines, indicates formation of mixed chelates by stepwise addition of both ligands. It is supported by the pH lowering in comparison to binary systems, the non-superimposable nature of the theoretical and practical titration curves as well as different colour of solutions.

For example the Fig. 3 shows the curves for systems: Co(II) - TSA and Co(II) - TSA - H₂en²⁺.

If H₂A is the formula of TSA and H_nEⁿ⁺ - polyethylenepolyamines in form of their salts with HClO₄, the process of mixed chelates formation may be shown according to eqs. (1-2):



The formation constants K defined by the expression (3):

$$K = \frac{[MAE]}{[MA][E]} \quad (3)$$

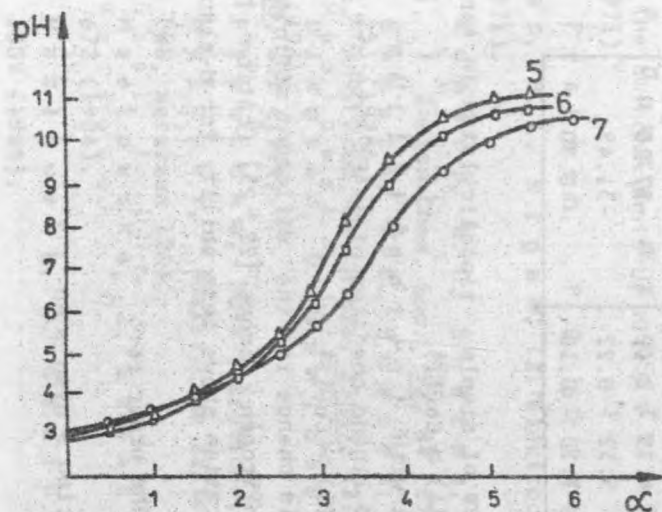


Fig. 2. Potentiometric titration curves of systems: 0.001 M M(II) - 0.01 M TSA - 0.01 M en - 0.02 M HClO_4 - 0.059 M NaClO_4 , where M(II) = Co(II) (curve 5), Zn(II) (curve 6) and Ni(II) (curve 7)

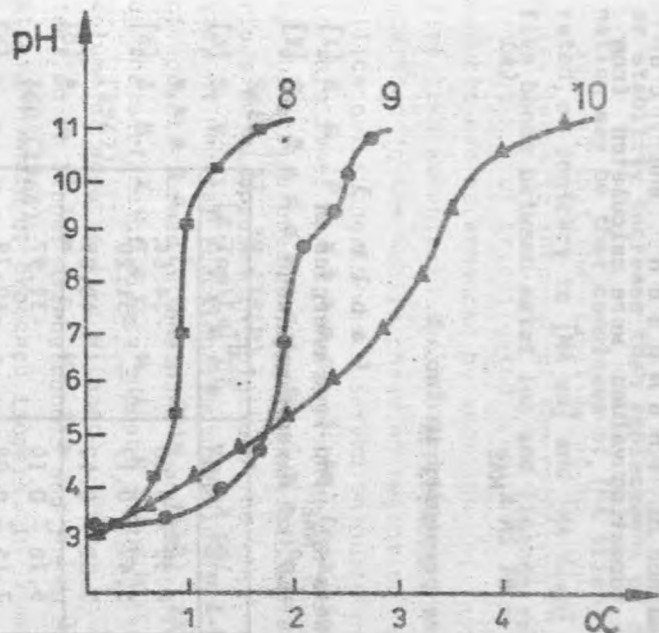


Fig. 3. Potentiometric titration curves: of 0.01 M TSA (curve 8) and systems 0.01 M TSA + 0.01 M Co(II) (curve 9) and 0.01 M TSA + 0.01 M Co(II) + 0.01 M en· 2HClO_4 (curve 10) ($\mu = 0.1$)

we have calculated by the method of Thompson and Loras [20]. Free energy formation values were calculated from equation (4):

$$\Delta G^{\circ} = RT \ln K_{MAE} \quad (4)$$

The evaluated values are presented in Tab. 3.

Table 3
Formation constants K_{MAE} and free energies of formation ΔG° of mixed complexes

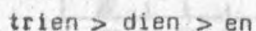
Complex	$\log K_{MAE}$	ΔG° [kJ/mol·K]
[CoAen]	4.32 ± 0.08	-24.64
[CoAdien]	5.47 ± 0.17	-31.20
[CoAtrien]	7.02 ± 0.12	-40.05
[NiAen]	5.78 ± 0.10	-32.97
[NiAdien]	7.15 ± 0.09	-40.79
[NiAtrien]	9.31 ± 0.18	-53.11
[ZnAen]	4.75 ± 0.12	-27.10
[ZnAdien]	5.52 ± 0.22	-31.49
[ZnAtrien]	7.10 ± 0.10	-40.50

The order of stabilities of simple tirosalicylates in term of metal ions is: Zn(II) > Ni(II) > Co(II).

It is in good agreement with Irving-Williams conclusion [21]. For the mixed ligand chelates of [MAE] type the order is following: Ni(II) > Zn(II) > Co(II).

The explanation for this change is the different affinity of these ions to sulphur and nitrogen atoms [22, 23] (cation Zn(II) with $3d^{10}$ electron configuration shows less ability for d-electrons engagement in the bond).

In term of polyamines the order is:



It is interesting, that replacement of en by dien causes smaller stability increase than replacement of dien by trien. The explanation may be that complexes of [MA trien] type are internally saturated, on contrary to [MA en] and [MA dien] complexes, with four and five bonds between metal ion and ligands respectively.

REFERENCES

- [1] R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).
- [2] R. Ramamani, S. Shanmuganathan, Current. Sci., 37, 39 (1968).
- [3] S. V. Larionow, V. M. Šulman, L. A. Podolskaja, Ž. Neorg. Chim., 9(10), 2333 (1964).
- [4] A. N. Kumar, H. L. Nigam, Ind. J. Chem. 5, 48 (1967).
- [5] A. N. Kumar, M. Katyai, J. Prakt. Chem., 33(3-4), 160 (1966).
- [6] M. V. Reddy, P. K. Bhattacharya, J. Inorg. Nucl. Chem., 32, 2321 (1970).
- [7] K. P. Dubey, M. K. Koul, Rev. Chim. Miner., 8, 819 (1971).
- [8] S. Prakash, P. C. Srivastava, A. M. Kumar, H. L. Nigam, J. Electrochem. Soc. India, 20, 101 (1971).
- [9] V. Kumari, R. C. Sharma, G. K. Chaturvedi, I. Indian Chem. Soc., 52, 84 (1975).
- [10] V. Kumari, R. C. Sharma, G. K. Chaturvedi, Rev. Roum. De Chimie, 23(8), 1275 (1978).
- [11] P. Ulmgren, O. Wahlberg, Acta Chim. Scand., A-28, 631 (1974).
- [12] H. Flaschka, EDTA-Titrations, Oxford 1964.
- [13] F. Welcher, Analityczne zastosowanie kwasu wersenowego, PWN, Warszawa 1963.
- [14] J. Masłowska, J. Szlich, Polish. J. Chem., 58, 672 (1984).
- [15] J. Masłowska, J. Szlich, Polish. J. Chem., 59, 1009 (1985).

- [16] J. Masłowska, J. Szmich, Zesz. Nauk. Pł., 41, 121, (1980).
- [17] S. Chaberek Jr., A. Martell, J. Am. Chem. Soc., 74, 5052 (1952).
- [18] J. Bjerrum, Metal Ammine Formation in Aqueous Solution, P. Haase and Son, Copenhagen 1941.
- [19] M. Calvin, K. Wilson, J. Am. Chem. Soc., 67, 2003 (1945).
- [20] L. C. Thompson, J. A. Loraas, Inorg. Chem., 2, 89 (1963).
- [21] H. Irving, R. J. P. Williams, J. Chem. Soc., 3533 (1953).
- [22] S. Ahrland, J. Chatt, M. R. Davies, Quart. Rev., 12, 265 (1958).
- [23] R. M. Tichane, W. E. Bennet, J. Am. Chem. Soc., 79, 1293 (1957).

Joanna Masłowska, Józef Szmich

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

Na podstawie potencjometrycznych badań układów: M(II)-kwas tiosalicylowy (H₂A)-polietylenopoliamina (E) (gdzie: M = Ni, Co i Zn, E-etylenodiamina, dietylenotrójamina i trietylenotetraamina) w wodno-etanolowych roztworach NaClO₄ ($\mu = 0,1$) w temp. 25 ± 0,1°C stwierdzono powstanie trójskładnikowych kompleksów typu [MAE]⁰. Wyznaczono ich skład oraz stałe tworzenia log K i wartości liczbowe energii swobodnej tworzenia ΔG^0 . Określono także szereg trwałości powstających kompleksów w zależności od polietylenopoliaminy i jonów metalu.