ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 4, 1985

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POTENTIOMETRIC STUDIES OF ASCORBINATE-TARTRATE MIXED COMPLEXES OF Fe(II), Co(II) AND Ni(II)

Mixed complexes of Fe(II), Co(II) and Ni(II) with ascorbic (H_2Asc) and tartaric acids (H_2Tart) were examined by the Lefebvre method of potentiometric surfaces. The formation of complexes with the composition: $[M(HAsc)(Tart)]^-$ (where M(II) = Fe, Co or Ni) was found; their stability was characterized and the values of $\log\beta_{111}$ in turn: 6.245 ±0.064, 4.748 ±0.077, 8.566 ± ± 0.100.

Introduction

One of our research interests are the studies aimed at the understanding of equilibrium processes in systems containing "biometal" ions and physiologically active compounds, playing part of bioligands [1-3]. To the former agents belong, among other things, organic acids including ascorbic acid $C_6H_8O_6$ (H_2Asc), known as vitamin C[4] and tartaric acid $C_4H_6O_6$(H_2Tart). Ascorbic acid takes part in many fundamental biochemical processes, hence simple ascorbinate complexes were the subject of our previous studies [5-8].

The present paper is devoted to potentiometric investigation of mixed complexes of some transition metals with ascorbic and tartaric acids. Simple complexes of metals with tartaric acid, similarly to simple complexes with ascorbic acid, show not too high stability [9]. The stability of mixed complexes with both this acids has not been known as yet. Therefore we have undertaken electrochemical examinations of systems containing ascorbic and tartaric acids and Fe(II), Co(II) and Ni(II) ions.

Experimental

Reagents and solutions

The following reagents and solvents were used in the investigations: $FeSO_4 \cdot 7H_2O$, analar grade produced by POCh, Gliwice, perchlorates $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ prepared from analar reagents by the method described previously [1-3, 5-8, 10]. The concentration of metal ions in the alkaline solutions was measured by the complexometric methods. Ascorbic acid $C_6H_8O_6$, analar grade, manufactured by Polfa - Kraków and tartaric acid $C_4H_6O_6$, analar grade, produced by POCh - Gliwice, were used in the form of solutions prepared, as required, from weighed portions of solid reagents for successive titrations. The pH values of the solutions were adjusted with $HClO_4$ solution (Jenapharm - GDR) and NaOH (POCh - Gliwice) prepared from analar reagents. The ionic strength of one solutions under investigation was maintained constant ($\mu = 1.0$) by means of a standard $NaClO_4$ solution prepared from analar reagent produced by Reachim, SU. The calibration of pH-meter was made with buffers with pH from 1 to 10 produced by Radelkis or POCh - Gliwice. All the solutions were prepared with demineralized water with a conductivity below 0.2 μs.

Apparatus

Potentiometric measurements were made with the use of an Automatic Titrimeter OP-506 (Radelkis) with a combination electrode (calomel electrode + glass electrode) of the type OP - 8071-1/A (Radelkis). The readings of potentials of a titrated system were taken from the voltage scale with an accuracy to ± 0.5 mV. It was found experimentally that the relationship E = f(pH) is a rectilinear one within the pH range from 1 to 10, and the number of mV for a unit of pH corresponds to the theoretical value [11]. Titration was made in a 200 cm^3 closed airtight glass vessel under nitrogen at $20 \pm 0,5^{\circ}C$. The solutions were agitated on titration with a magnetic stirrer OP-912/3 (Radelkis).

Measurement method

A system containing two acids was investigated: ascorbic acid (H_2Asc) and tartaric acid (H_2Tart), which acted as ligands, and ions of such metals as Fe(II), Co(II) or Ni(II). As was previously stated [3, 6-8], the Lefebvre method of potentiometric surfaces allows to calculate equilibrium concentrations of components $[M^{2+}]$, $[HAsc^-]$, $[Tart^{2-}]$ at each titration point. In series of measurements the initial concentration of only one reagent was changed. Then for each system, three series of measurements were carried out with the following changes taken place in turn: in I series: initial concentration of metal ions from 0.0 to 0.02 mole/dm^3, in II series: initial concentration of H_2Asc from 0.03 to 0.07 mole/dm^3 and in III series: initial concentration of H_2Tart from 0,04 to 0,06 mole/dm^3. The remaining parameters as: ionic strength ($\mu = 1.0$), initial volume of solution ($V_o = 100$ cm^3), initial concentration of hydrogen ions ($[H^+] = 0{,}03$ mole/dm^3) and concentrations of the two remaining complexoforming substances in the given series were constant.

Results and discussion

In a system, in which, beside a metal ion, ascorbic and tartaric acids are included, the concentration of complexoforming ions increases with the change in H^+ ions brought about by the titration with standard NaOH solution as a result of the acid dissociation. In the case of ascorbic acid, within the pH range 1-7 these are $HAsc^-$ ions ($pK_1 = 4{,}23$; $pK_2 = 11.32$ [14, 15]), and in the case of tartaric acid these are $Tart^{2-}$ ions ($pK_1 = 2.9$, $pK_2 = 4{,}1$ [9, 16]). Under such conditions, beside the complexes ions of simple ions of the investigated metals with these ligands, mixed complexes are formed with participation of both ligands. Assuming that a mixed complex is formed in the investigated system, the simplest one with composition 1 : 1 : 1, one complete number or metal ions which was introduced to the solution participate in the investigated pH range in the following forms (1):

$$\left[M^{2+}\right]_o = \left[M^{2+}\right] + \left[MHAsc\right] + \left[M(HAsc)_2\right] + \left[MTart\right] + \left[MHAscTart\right] \quad (1)$$

and the complexoforming anions from corresponding acids - in the forms (2) and (3).

$$\left[HAsc^-\right]_o = \left[HAsc^-\right]\left(1 + \frac{[H^+]}{K_1^A}\right) + \left[MHAsc\right] + \left[M(HAsc)_2\right] + \left[MHAscTart\right] \quad (2)$$

$$\left[Tart^{2-}\right]_o = \left[Tart^{2-}\right]\left(1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1K_2}\right) + \left[MTart\right] + \left[MHAscTart\right] \quad (3)$$

Knowing the stability constants of simple complexes of the investigated metal ions with ascorbic and tartaric acids, it is possible to calculate the concentrations of these complexes at the given pH, and consequently to find the concentration of the mixed complex MHAscTart from equation 1-3 [17]. The value of stability constant β_{111} of the mixed complex was calculated from the following relationship (4):

$$\beta_{111} = \frac{[MHAscTart]}{[M^{2+}][HAsc^-]\ [Tart^{2-}]} \quad (4)$$

presented in a logarithm form by equation (5):

$$\log \beta_{111} = \log\left[MHAscTart\right] + p\left[M^{2+}\right] + p\left[HAsc^-\right] + p\left[Tart^{2-}\right] \quad (5)$$

The concentrations of uncombined metal ions and ligands, in a complex, required to calculate the stability constant of a mixed complex, were obtained from potentiometric data. Fig. 1a-c shows, as an example, the titration curves obtained in three measurement series for the system containing Co(II), H_2Asc and H_2Tart. The shifts of successive curves in the given series are a measure of the complexation processes taking place in the gi-

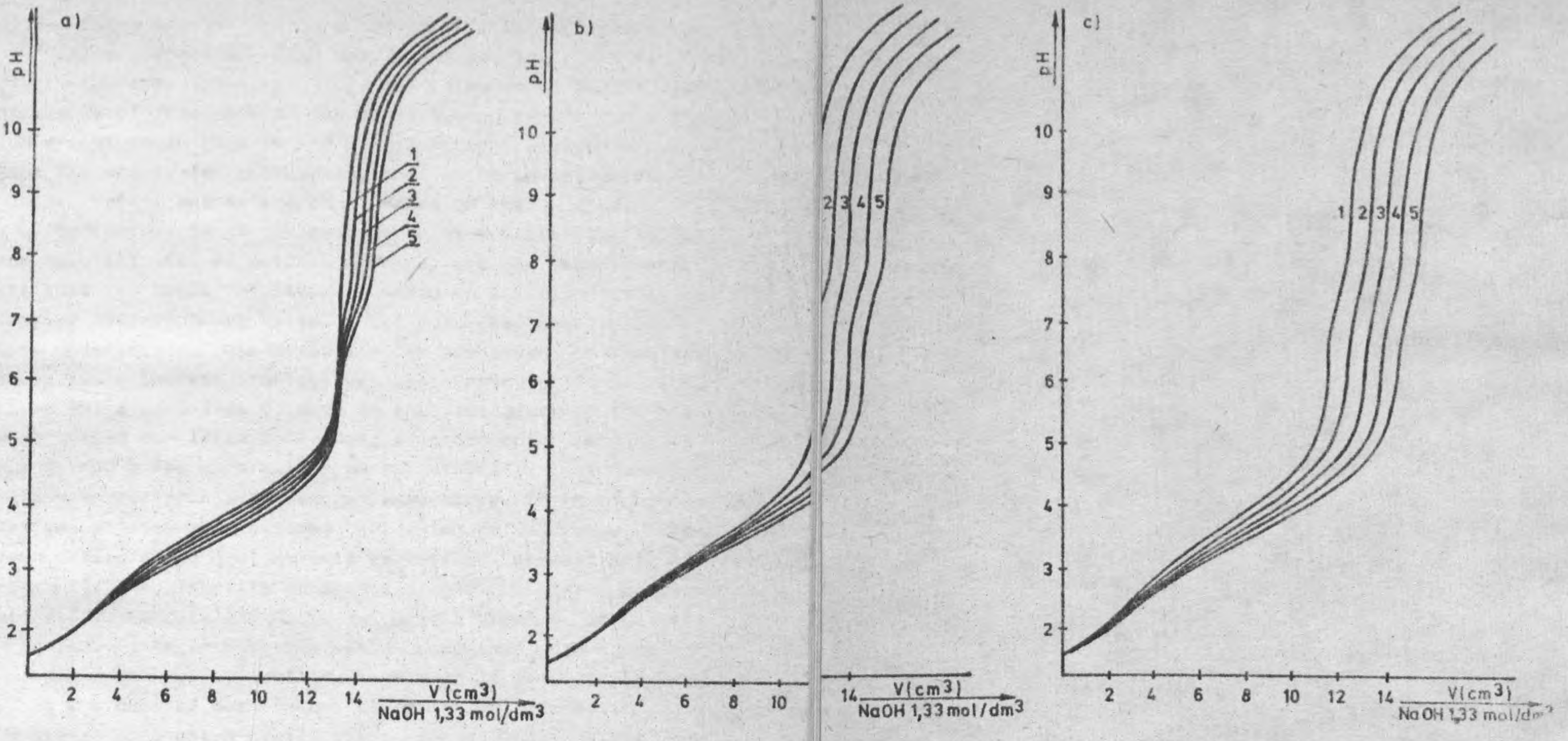

Fig. 1. Titration curves in the system: Co(II) H_2Asc - H_2Tart - $NaClO_4$ - $HClO_4$ - H_2O

a) $[H_2Asc]_o$ = $[H_2Tart]_o$ = 5 . 10^{-2} mol/dm^3, $[Co(ClO_4)_2]_o$ = - 0.0; 2 - 5 . 10^{-3} ; 3 - 1 . 10^{-2}; 4 - 1.5 . 10^{-2};
5 - 2 . 10^{-2} /dm^3

b) $[Co(ClO_4)_2]_o$ = 1 . 10^{-2} mol/dm^3, $[H_2Tart]_o$ = 5 . 10^{-2} mol/ $[H_2Asc]_o$ = 1 - 3 . 10^{-2}; 2 - 4 . 10^{-2}; 3 - 5 . 10^{-2};
4 - 6 . 10^{-2}; 5 - 7 0^{-2} mol/dm^3

c) $[Co(ClO_4)_2]_o$ = 1 . 10^{-2} mol/dm^3, $[H_2Asc]_o$ = 5 . 10^{-2} mol/d $[H_2Tart]_o$ = 1 - 4 . 10^{-2}; 2 - 4.5 . 10^{-2}; 3 - 5 . 10^{-2};
4 - 5.5 . 10^{-2}; 5 - . 10^{-2} mol/dm^3

ven system, being brought by the change in initial concentration of ions Co(II) (series I - Fig. 1a), H_2Asc (series II - Fig. 1b) and H_2Tart (series III - Fig. 1c). So calculated equilibrium concentrations of free ions in the investigated system, at the given pH are given in Fig. 2a and 2c illustrate analogous relationships for one system containing, beside the investigated organic acids, Fe(II) and Ni(II) ions. Based on these data, the values of concentration of one mixed complex MHAscTart, calculated from eqs. (1), (2) as well as from (3) are the same, which suggests that the number of ligands coming to a metal ion in this complex correspond to ratio 1 : 1 : 1. The final values of stability constants of this mixed complex are given in Tab. 1-3 for successively investigated systems containing Fe(II), or Co(II) Ni(II) ions. There is a lack of data, in the literature, on the stability of mixed complexes containing ascorbic acid as one of the ligands and a few information on the stability of similar complexes with tartaric acid. In our laboratory, we investigated equilibrium processes in systems containing Fe(II) ions, tartaric and oxalic acids [18] as well as Fe(II), tartaric and citic acids [2]. The stability constants simple and mixed complexes of Fe(II), Ni(II) and Co(II) with some organic acids are given in Tab. 4. As in seen the mixed complexes with H_2Asc and H_2Tart show much higher stability than that of the simple complexes. In the case of both acids, coordination takes place through oxygen atom which mostly gives ligands with a low degree of polarizability of the bond. The delocalized π electrons in the diene group of ascorbic acid cause the formation of ligands of a soft character or of a high degree of polarizability. In addition, both ascorbic and tartaric acids belong to two--donor ligands chelate character of both ligands can explain the high stability of the mixed complexes under investigation. A more detailed discussion on this subject will be possible after examination of other systems.

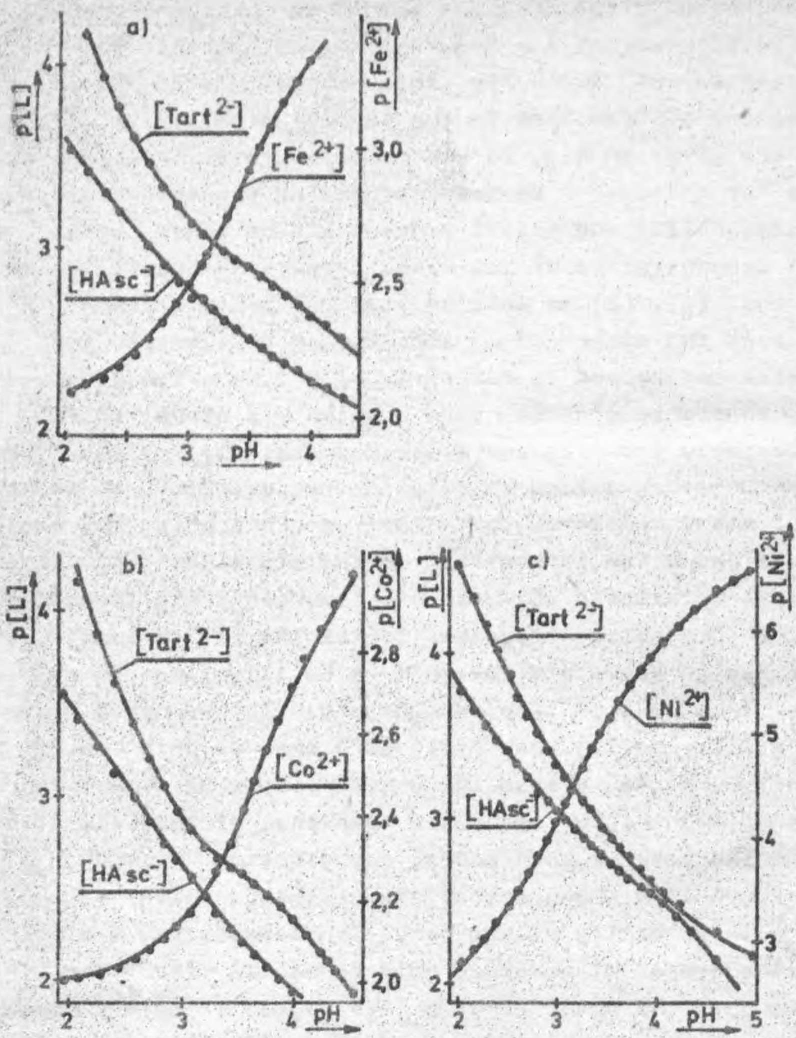

Fig. 2. Dependence of ligand and metal ion concentrations in the equilibrium on the pH of the system: M(II) - H_2Asc - H_2Tart - - $NaClO_4$ - $HClO_4$ - H_2O

a) M(II) = Fe(II); $[FeSO_4]_o = 1 \cdot 10^{-2}$ mol/dm^3; $[H_2Asc]_o$ = $[H_2Tart]_o = 5 \cdot 10^{-2}$ mol/dm^3

b) M(II) = Co(II); $[Co(ClO_4)_2]_o = 1 \cdot 10^{-2}$ mol/dm^3; $[H_2Asc]_o$ = $[H_2Tart]_o = 5 \cdot 10^{-2}$ mol/dm^3

c) M(II) = Ni(II); $[Ni(ClO_4)_2]_o = 1.01 \cdot 10^{-2}$ mol/dm^3; $[H_2Asc]_o$ = $[H_2Tart]_o = 5 \cdot 10^{-2}$ mol/dm^3

Table 1

Experimental data for the calculation of stability constant β_{111} of the mixed complex in system: Fe(II) - H_2Asc - H_2Tart - $NaClO_4$ - H_2O; $\mu = 1.0$ t = 20°C, $[Fe^{2+}]_o = 1.10^{-2}$ mol/dm^3; concentr. ratio $[Fe^{2+}]_o : [H_2Asc]_o : [H_2Tart]_o = 1 : 5 : 5$

pH	$p[Fe^{2+}]$	$p[HAsc^-]$	$p[Tart^{2-}]$	$\log \beta_{111}$
2.66	2.2775	3.0117	3.4777	6.3667
2.77	2.3441	2.9213	3.3491	6.290
2.89	2.4150	2.8340	3.2372	6.216
2.99	2.4861	2.7570	3.1458	6.160
3.09	2.5613	2.7354	3.0792	6.182
3.18	2.6451	2.6820	3.0353	6.198
3.28	2.7333	2.6298	2.9979	6.220
3.38	2.8255	2.6577	2.9571	6.234
3.48	2.9097	2.5188	2.9054	6.225
3.57	2.9936	2.4671	2.8644	6.226
3.67	3.0774	2.4266	2.8634	6.277
3.76	3.1655	2.3882	2.8690	6.338
3.87	3.2494	2.3390	2.8657	6.374

$\log \beta_{111} = 6.254 \pm 0.064$

Table 2

Experimental data for the calculation of stability constant β_{111} of the mixed complex in system: $Co(II) - H_2Asc - H_2Tart - NaClO_4 - H_2O$; $\mu = 1.0$ $t = 20^{\circ}C$ $[Co^{2+}]_o = 1.10^{-2}$ mol/dm^3; concentr. ratio $[Co^{2+}]_o : [H_2Asc]_o : [H_2Tart]_o = 1 : 5 : 5$

pH	$p[Co^{2+}]$	$p[HAsc^-]$	$p[Tart^{2-}]$	$\log \beta_{111}$
2.85	2.1110	2.7716	3.0695	4.866
2.98	2.1400	2.6696	2.9365	4.757
3.10	2.1747	2.5683	2.8262	4.685
3.21	2.2096	2.4732	2.7383	4.619
3.32	2.2732	2.3832	2.6686	4.691
3.44	2.3418	2.2995	2.6238	4.757
3.54	2.4182	2.2251	2.5892	4.824
3.65	2.4928	2.1527	2.5330	4.831
3.76	2.5656	2.0835	2.4728	4.818
3.87	2.6389	2.0174	2.4078	4.793
3.98	2.7138	1.9536	2.3333	4.754
4.10	2.7878	1.8901	2.2482	4.695
4.23	2.8618	1.8312	2.1625	4.638

$\log \beta_{111} = 4.748 \pm 0.077$

Table 3

Experimental data for the calculation of stability constant β_{111} of the mixed complex in system: Ni(II) - H_2Asc - H_2Tart - $NaClO_4$ - H_2O; $\mu = 1.0$ $t = 20^{o}C$ $[Ni^{2+}]_o = 1.01 \cdot 10^{-2}$ mol/dm^3; concentr. ratio $[Ni^{2+}]_o : [H_2Asc]_o : [H_2Tart]_o = 1 : 5 : 5$

pH	$p[Ni^{2+}]$	$p[HAsc^-]$	$p[Tart^{2-}]$	log β_{111}
2.29	3.0368	3.5659	4.1727	8.680
2.40	3.1747	3.4780	4.0183	8.588
2.51	3.4221	3.3919	3.8688	8.508
2.61	3.4890	3.3184	3.7430	8.481
2.71	3.6558	3.2448	3.6221	8.457
2.81	3.8179	3.1712	3.5060	8.430
2.90	3.9895	3.1100	3.4137	8.449
2.99	4.1613	3.0513	3.3263	8.475
3.08	4.3328	2.9926	3.2437	8.595
3.17	4.5094	2.9362	3.1772	8.547
3.26	4.6861	2.8800	3.0957	8.595
3.34	4.8527	2.8410	3.0502	8.676
3.46	5.0098	2.7669	2.9320	8.639
3.55	5.1668	2.7254	2.8789	8.700
3.64	5.3238	2.6862	2.8293	8.766

$\log\beta_{111} = 8.566 \pm 0.100$

Table 4

Stability constants of simple and mixed complexes of Fe(II), Co(II) and Ni(II) with some organic acides

Composition	Method	Ionic strength	t [^{o}C]	log ß	Literature
$[FeHAsc]^+$	potentiometric	1.0	20	1.41	[8]
$[FeHAsc]^+$	potentiometric	3.0	25	0.21	[10]
$[Fe(HAsc)_2]$	potentiometric	1.0	20	2.30	[8]
$[Fe(Tart)]$	potentiometric	1.0	25	1.43	[19]
$[Fe(Tart)]$	potentiometric	1.0	20	1.14	[18]
$[Fe(Tart)_2]^{2-}$	polarographic	-	-	4.85	[20]
$[Fe(Tart)_2]^{2-}$	potentiometric	1.0	20	1.72	[18]
$[Fe(C_2O_4)]$	conductometric	0.0	18	3.70	[21]
$[Fe(C_2O_4)_2]^{2-}$	solubulity	-	-	6.87	[22]
$[Fe(HAsc)(Tart)]^-$	potentiometric	1.0	20	6.25	this work
$[Fe(Tart)(C_2O_4)]^{-2}$	potentiometric	1.0	20	1.41	[18]
$[FeCit\ Tart]^-$	potentiometric	1.0	20	1.91	[2]
$[CoHAsc]^+$	potentiometric	-	25	1.4	[23]
$[CoHAsc]^+$	potentiometric	1.0	20	1.06	[8]
$[Co(HAsc)_2]$	potentiometric	1.0	20	2.85	[8]
$[CoTart]$		0.5		2.1	[24]
$[CoHAscTart]^-$	potentiometric	1.0	20	4.25	this work
$[NiHAsc]^+$	potentiometric		25	1.05	[23]
$[NiHAsc]^+$	potentiometric	1.0	20	1.24	[8]
$[Ni(HAsc)_2]$	potentiometric	1.0	20	2.08	[8]
$[NiHAscTart]^-$	potentiometric	1.0	20	8.57	this work

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POTENCJOMETRYCZNE BADANIA ASKORBINIANOWO-WINIANOWYCH MIESZANYCH KOMPLEKSÓW Fe(II), Co(II) i Ni(II)

Metodą powierzchni potencjometrycznych Lefebvre badano mieszane kompleksy Fe(II), Co(II) i Ni(II) z kwasami askorbinowym (H_2Asc) i winowym (H_2Tart). Stwierdzono tworzenie się kompleksów o składzie: $[M(HAsc)(Tart)]^-$ (gdzie M(II) = Fe, Co i Ni) oraz scharakteryzowano ich trwałość. Wartości liczbowe log β_{111} wynoszą kolejno: 6,245 ± 0,064; 4.748 ± 0,077; 8,566 ± 0,10).

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ПОТЕНЦИОМЕТРИЧЕСКИЕ ИССЛЕДОВАНИЯ АСКОРБИНОВО-ВИНОГРАДНЫХ СМЕШАННОЛИГАНДНЫХ КОМПЛЕКСОВ Fe(II), Co(II) i Ni(II)

По данным метода потенциометрических поверхности Lefebvre исследовано смешаннолигандные комплексы Fe(II) Co(II) и Ni(II) с аскорбиновой кислотой (H_2Asc) и виноградной кислотой (H_2Tart). Установлено образование в растворе комплексов состава [M(HAsc)(Tart)](где M(II) = Fe, Co и Ni) и охарактеризовано их прочность. Найдены констацта образования комплексов возрастают по ряду:

Co(II) Fe(II) Ni(II)

$\log\beta_{111}$ = 4,748 ± 0,077; 6,245 ± 0,064; 8,566 ± 0,100