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Boron-Coordinated Compounds with Polyols and Inhibitation of Metal Corrosion

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Abstract **- Based on the results of chemical analysis, thermoanalytical curves and IR absorption spectra the resulting product proves the individuality and chemical formula of sodium mannitolborate $C_6H_{12}O_6B(OH)_2]$. From the specific electric conductivity (25±0,1^0 C) and optical rotation angle data (18 +2^{0}C) in the polyol-boric acid-water systems the stability constants of sodium mannitolborate were calculated using the classic laws of electrochemistry. The results show that the most stable are two anions - mannitoldiborate [Mannitol B_2]$^{-2}$ and mannitolborate [Mannitol B]$^-$, which exists in the alkaline and neutral parts of the systems at the total concentrations of 0.25, 0.5 and 0.75 M [1]. We provide the use of sodium mannitolborate as a corrosion inhibitor in combination with additives for steel and non-ferrous metals (aluminium, copper, brass) in water and water-ethylene glycol mixtures (1:1). We investigated the corrosion within the temperature range of 20-70 ^{0}C and under dynamic conditions. With reference to the corrosion gravimetric measurements, sodium mannitolborate is an excellent inhibitor in water media for steel, copper, brass, aluminium and its combination with other additives influences insignificantly the corrosion protection degree (98-88%). Therefore, sodium sorbitolborate itself is effective at all investigated concentrations and can be used in water media to prevent corrosion Sodium mannitolborate and additives in water-ethylene glycol media (1:1) shows, that sodium mannitolborate is effective inhibitor of corrosion for steel and under optimal conditions inhibition effenciency reaches 95% (2,0 g/l). The compositions G and H on the base of sodium mannitolborate are very effective for steel (protection effect 97%, 99%) accordingly. Sodium mannitolborate and compositions do not protect copper and aluminium. The composition with sodium mannitolborate H is very effective for brass (protection effect 95%).**

Keywords **- corrosion inhibitor, mannitolborate, water, cooling media**

INTRODUCTION

Boron compounds, especially borax, are widely used as part of several compositions for inhibiting corrosion in water, but their efficiency is low and great concentrations must be used – up to 7% for steel. The role of borax is only to maintain the pH of the solution constant – that is to attach the buffer properties to the solutions in which the protected metal (steel) constructions act. The attained inhibition effectiveness of borax in artesian water at 70^{0}C is 10, 30, 65 % at corresponding concentrations, g/l : 1,2 3,5 , all of the sodium sorbitolborate in the same conditions is 93-98 % at corresponding concentration 1-2 g/l must be used [2]. We propose the boron compounds of other type – the salts of boron coordination compounds, where ligands are polyhidroxy organic acids or polyols. In the coordination compounds of tetracoorinated boron are not toxic, as sorbitol and mannitol forming ones are food products or remedies as calcium gluconate.

Inhibiting mixtures are known, the compositions of which include polyoxycompounds, such as sorbitol, mannitol, pentaerythritol and others [3,4]. Products of interactions of some polyoxycompounds with boratione, for example, sodium sorbitol borate, sodium xylitol borate are inhibitors of steel corrosion in aqueous media [5]. Therefore, it is practically useful to investigate the interaction of D-mannitol with sodium tetraborate, synthesize and extract these compounds and study their inhibiting action not only on steel but on non-ferrous metals as well, such as aluminium, copper, brass.

EXPERIMENTAL

Sodium mannitolborate has been synthesized by the interaction of equimolar quantities of D-mannitol and sodium tetraborate when heated. This dihydrate of sodium mannitol borate $Na[C_6H_{14}BO_8]\cdot 2H_2O$ is a colourless and vitreous matter well soluble in water, ethyleneglycol and propylenglycole.

Experimental data, %: B 3.90; Na 8.08; H_2O 12.90.

Calculation data, %: B 3.81; Na 8.10; H_2O 12.68.

Thermal decomposition of the complexes was investigated using a derivatograph (Paulic, Paulic, Erday) at a heating rate of 10 ^{0}C per minute (Fig.1). IR absorption spectra were taken by a spectrometer SPECORD using tablets with KBr (Fig.2).

The effectiveness of used inhibitors to reduce corrosion was expressed as inhibition degree and protection degree from the weight loss of specimens in uninhibited and inhibited water, results given in Table 1 and water-ethylene glycol (1:1 solutions in Table 2 respectively. The protecting action of the inhibitor was determined from the formula: $E= [(v - v_1)/v].100\%$, where v is the metal corrosion rate without inhibitor (g/m^2.h); v_1 is the metal corrosion rate with inhibitor (g/m^2.h). The efficiency of protection was evaluated from the coefficient of corrosion retardation: $\gamma = v/v_1$,

where v is the metal corrosion rate without inhibitor (g/m^2.h); v_1 is the metal corrosion rate with inhibitor (g/m^2.h).

The corrosion experiments were carried out at dynamic conditions at 20-70 ^{0}C in water and water- ethylene glycol media (1:1). Duration of experiments was 336 hours. Samples of the following materials underwent corrosion tests: steel 08PC (% mass: C 0.07; Si < 0.03; Mn 0.27; P 0.0022; S 0.03; Ni < 0.2); aluminium (% mass Cu 3.8; Mg 1.2; Mn0.3; Ni< <; copper M-1; brass Л63); dimensions 40.0 x 20.0 mm. The samples were placed in special vessels for corrosion tests, which were filled with 300 ml of the tested liquid, plugged

hermetically with a cover, heated at 20^0 C and 70^0 C.. In 336 hours of exposing to the tested solutions, the samples were taken out, cleaned with a soft brush, washed in sequence with distilled water and ethanol, dried and weighted. By measuring the change in sample mass, the corrosive action of the tested liquid was determined. The metal specimen arrangement in corrosion cell was as follow: copper, brass, steel, aluminium and the average weight loss was determined for each metal. After corrosion test the corrosion products were removed using a standard procedure [6]. Various compositions were developed for water media: D - sodium mannitolborate (MB),SiO_2 (1,0;0,2) g/l, E – MB+HMF (1.0;0.5) g/l, F - MB,SiO_2, $Na_2B_4O_7$) (1.0;0.2;3.0) g/l and for water ethylene glycol (1:1) media: G – MB, SiO_2, $Na_2B_4O_7$P (alkali metal salt) (2.0;0.2;3.0;2.5) g/l, H – MB, SiO_2 ,P (alkali metal salt), sodium benzoate (2.0;0.2;3;2.5.0;5.0)g/l.

RESULTS AND DISCUSSION

Fig.1. displays thermogravimetric curves of sodium mannitolborate decomposition. When being heated at 10^0C/min, two molecules of crystallization water are lost within the 80-120 ^{0}C temperature range. The DTG and DTA curve exhibits an endothermic minimum. The mass loss, herewith, is 12.9% (12.68 in calculation). When heated to 220 ^{0}C, sodium mannitol borate loses two molecules of constitution water which appears due to condensation of OH groups in boron atom. The mass loss in this case is 25.4%, calculation 25.37%. Within the 220-420 °C temperature range, three more molecules of constitution water are lost in several stages – 57.1% (57.08% in calculation). At further heating, the organic compound of a molecule oxidizes. The DTA curve exhibits an exothermal maximum.

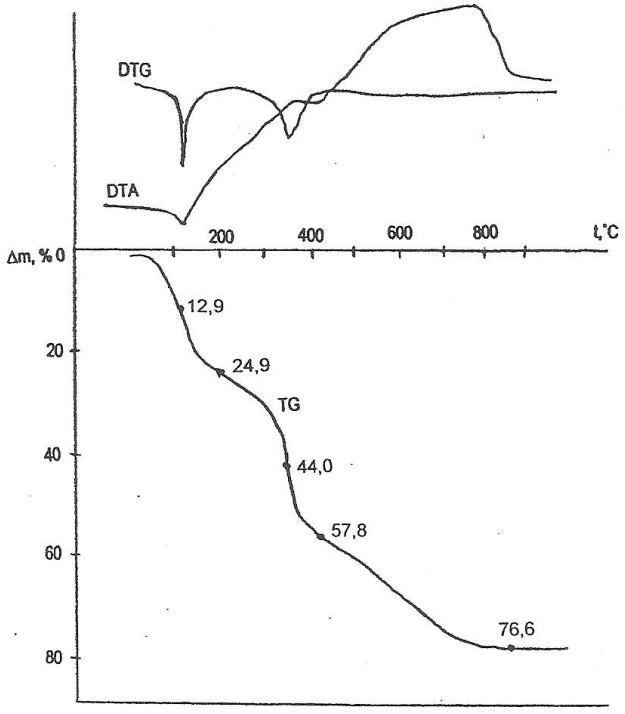

Fig.1. Thermogravimetric curves of sodium mannitolborate decomposition.

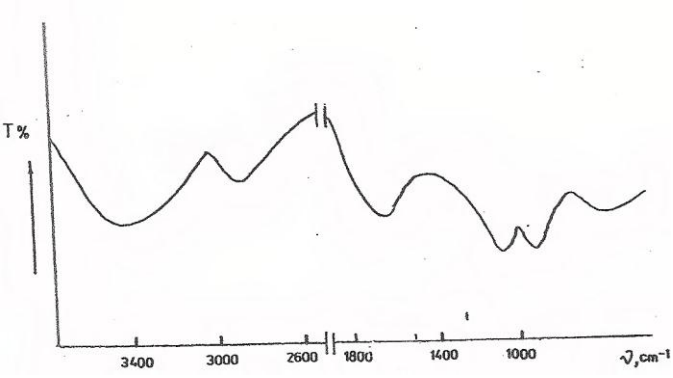

Fig.2. IR absorption spectra of sodium mannitolborate

TABLE 1

STEEL AND NON-FERROUS METALS CORROSION INHIBITION BY SODIUM MANNITOLBORATE (MB) AND WITH OTHER ADDITIONS IN WATER MEDIA

Inhibitor	Concentration of sodium mannitolborate, g/l	Meral	Inhibition degree, γ	Protection degree E, %
-	-	Steel	1,0	-
Sodium	0,5		2,2	53,7
mannitolborate	1,0		2,3	56,2
„	1,5		4,1	75,7
„	2,0		10,0	90,0
„	3,0		13,3	92,5
D	1,0		32,7	96,9
E	1,0		1,9	47,3
F	1,0		53,0	98,1
-	-	Copper	1,0	-
Sodium	0,5		7,2	86,1
mannitolborate	1,0		5,9	82,9
„	1,5		7,0	85,8
„	2,0		5,0	80,1
„	3,0		5,8	82,9
D	1,0		4,7	78,8
E	1,0		1,2	15,5
F	1,0		3,9	74,1
-	-	Brass	1,0	-
Sodium	0,5		3,0	66,7
mannitolborate	1,0		5,5	81,9
„	1,5		4,4	77,2
„	2,0		8,9	88,7
„	3,0		3,8	73,4
D	1,0		2,8	64,4
E	1,0		0,8	-23,8
F	1,0		4,6	78,2
-	-	Alumi-	1,0	-
Sodium	0,5	nium	0,8	-27,9
mannitolborate	1,0		0,27	-268,0
„	1,5		0,76	-24,0
„	2,0		0,75	-33,1
„	3,0		0,27	-272,6
D	1,0		6,45	84,5
E	1,0		2,4	58,8
F	1,0		6,3	84,1

The combustion of the organic compound completes at 900 ^{0}C. Upon calcination, the residue is a sodium metaborate (experiment: 23.4%, calculation: 23.19%).

The IR absorption spectra show (Fig.2) the presence of tetracoordinated boron in the compound: the light absorption strip at 940-960 cm^{-1} and the light absorption strip at 1050 cm^{-1} are related to the primary alcohol group, and at 1660 cm^{-1}

they exhibit the presence of crystallization water in the compound. The absorption strips at 2840-2880 cm^{-1} are related to the valence oscillations of CH_2 groups. A broad absorption strip at 3460 cm^{-1} is determined by the hydrogen bonds of OH groups.

TABLE 2

STEEL AND NON-FERROUS METALS CORROSION INHIBITION BY SODIUM MANNITOLBORATE (MB) AND WITH OTHER ADDITIONS IN WATER – ETHYLENE GLYCOL SOLUTIONS

Inhibitor	Concentration of sodium mannitolborate g/l	Meтal	Inhibition degree, γ	Protec-tion degree E, %
-	-	Steel	1,0	-
Sodium mannitolborate	0,5		10,04	90,00
„	1,0		11,22	91,09
„	1,5		4,40	77,29
„	2,0		18,88	94,70
„	2,5		6,55	84,73
G	3,0		21,36	95,32
H	2,0		35,75	97,20
	2,0		45,35	99,78
-	-	Copper	1,0	-
Sodium mannitolborate	0,5		0,74	-35,35
„	1,0		0,76	-32,32
„	1,5		0,44	-125,25
„	2,0		0,42	-138,38
G	2,5		0,45	-122,29
H	3,0		0,51	-97,98
	2,0		0,79	-27,27
	2,0		1,38	27,27
-	-	Brass	1,0	-
Sodium mannitolborate	0,5		2,80	64,25
„	1,0		1,86	46,38
„	1,5		2,31	56,76
„	2,0		2,38	57,97
G	2,5		2,96	66,18
H	3,0		3,21	68,84
	2,0		1,86	46,14
	2,0		18,00	94,44
-	-	Alumi-nium	1,0	-
Sodium mannitolborate	0,5		0,30	-230,54
„	1,0		0,50	-98,80
„	1,5		0,67	-49,70
„	2,0		0,72	-39,52
G	2,5		0,31	-217,96
H	3,0		0,54	-83,83
	2,0		1,02	2,40
	2,0		0,97	-2,99

Table 1 illustrates the results of corrosion tests for steel and non- ferrous metals in the presence of sodium mannitolborate and additives in water media. For steel in the presence of Na mannitolborate protection degree against corrosion achieves 95% (concentration 2.0 g/l), composition H practically completely protect steel against corrosion (protection degree effective for brass 9599.8%). For copper the corrosion protection degree does not strongly depend on the inhibitor concentration. In the composition F is 78%. The sodium mannitolborate is ineffective for aluminium. The best results for aluminium were obtained with compositions containing silicates of alkali metals (composition D and F). The protection degree reaches 84.5%. Table 2 illustrates the results of corrosion tests for steel and non-ferrous metals in the presence of sodium mannitolborate and additives in water-ethylene glycol media (1:1). Therefore, sodium mannitolborate itself is effective at all investigated concentrations and can be used in water-ethylene glycol mixtures to prevent corrosion and at the concentration of 2.5 g/l the protection degree reaches 98%. Sodium mannitolborate and compositions G and H on its base are effective inhibitors for steel and brass and under optimal conditions inhibition effenciency reaches 99.8%%. The sodium mannitolorate and compositions do not protect copper and aluminium, there is a need to use other additives and sodium mannitolborate-based compositions.

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Ināra Zariņa, Roza Ignaša. Bora koordinācijas savienojumi ar polioliem un metālu korozijas inhibēšana
Izpētīta kompleksu veidošanās sistēmā D-mannīts- Na tetraborāts – ūdens, pielietojot izomolārās sērijas, ņemot par pamatu šķīduma elektrovadītspēju (25 +0.2^{0}C) un optiskās aktivitātes (18 +2^{0}C) izmaiņas pie kopējās koncentrācijas 0.25, 0.5 and 0.75 M. Pēc īpatnējās elektrovadītspējas (25±0,1^0 C) un novirzes no polarizācijas griešanās leņķa aditivitātes, noteikta divu komplekso anjonu eksistence: mannitodiborāts [Mannits B_2]$^{-2}$ un mannitoborāts [MannitsB]$^-$ Uz šo pētījumu pamata no D-mannīta un Na tetraborāta sintezēts Na mannitoborāts (molārā attiecībā 1:1). Pēc elementāranalīzes datiem iegūtais savienojums atbilst formulai Na[$C_6H_{12}O_6B(OH)_2$]. Pēc IK absorbcijas spektru un termiskās analīzes datiem noteikta kompleksā savienojuma struktūrformula. Iegūtais savienojums ir balta stiklveida viela, labi šķīst ūdenī, etilenglikolā, propilenglikolā. Na mannitolborāts kā metālu korozijas inhibitors ir videi draudzīgs un atbilst zaļo korozijas inhibitoru grupai. Pārbaudītas Na mannitoborāta (MB) inhibējošās īpašības uz tērauda un krāsaino metālu (Cu, Al, misiņš) paraugiem atsāļotā ūdenī atkarībā no koncentrācijas: 0,5; 1,0; 1,5; 2,0; un 3 g/l.. Pierādīts, ka palielinoties MB koncentrācijai no 0,5 līdz 3 g/l tērauda korozijas ātrums pakāpeniski samazinās un aizsardzības efekts (E%) sasniedz 92,5% pie inhibitora koncentrācijas 2 g/l. Vara paraugu

aizsardzības efektivitāte nav atkarīga no MB koncentrācijas un sasniedz 80-86%%, misiņa paraugu gadījumā optimālā MB koncentrācija ūdenī ir 2 g/l, aizsardzības efektivitāte sasniedz 88,7%. MB atsāļotā ūdenī neaizsargā alumīnija paraugus, bet pievienojot 0,2 g/l SiO_2 notiek spēcīga korozijas procesa bremzēšana un aizsardzības efektivitāte sasniedz 85%. Uz Na mannitolborāta bāzes ūdens videi izveidotas inhibitoru kompozīcijas D, E, F, tad ūdens – etilēnglikola videi – kompozīcijas G un H. Korozijas gravimetriskie pētījumi pierāda, ka nātrija mannitolborāts un kompozīcijas sasniedz teicamus rezultātus tērauda un krāsaino metālu (varš, misiņš, alumīnijs) korozijas inhibēšanā ūdens vidē.

Korozijas aizsardzības pakāpe tērauda paraugiem ūdens vidē sasniedz 98%, vara paraugiem - 86%, misiņa paraugiem - 81%, alumīnija paraugiem - 84%. Etilēnglikola vidē (1:1) sintezētais Na sorbitolborāts un izveidotās kompozīcijas ir efektīvi korozijas inhibitori tēraudam un aizsardzības pakāpe sasniedz 99%, misiņam - 94%, bet Na mannitolborāts un izveidotās kompozīzijas G un H neaizsargā vara un alumīnija paraugus.

Инара Зариня, Роза Игнаш. Координационное соединение бора с полиолами и торможение коррозии металлов

Изучено комплексообразование в системе D-маннит-Na тетраборат - вода, используя изомолязные серии. На основании данных удельной электропроводимости (25 ± 0,10 C) и отклонений от аддитивности поляризации вращения найдено два комплексных аниона: маннитолдиборат $[Маннит\ B_2]^{-2}$ и маннитолборат $[МаннитB]^-$ На основе изучения системы D-маннит и Na тетраборат разработан метод синтеза – от D-маннита и Na тетрабората получен маннитолборат натрия (молярное соотношение 1:1). На основании данных элементарного анализа, ИК-спектров и термогравиметрических резулътатов соединение соответствует формуле $Na[C_6H_{14}BO_8]\cdot 2H_2O$. Полученное соединение - белое, стеклообразное вещество, легко растворимое в воде, этиленгликоле, пропиленгликоле. Показано, что при увеличениеи концентрации маннитолбората натрия 0,5 до 3 г / л скорость коррозии стали постепенно уменьшается, и защитное действие (Е%), достигает 92,5% в ингибитора концентрации 2 г / л. Эффективность защиты меди не зависит от концентрации маннитолбората натрия и достигает 80-86%%, для латуни оптимальная концентрация маттитолбората натрия в воде 2 г / л, защита эффективности достигает 88,7%. Маннитолборат в водной среде не защищает алюминиевые образцы, но при добавлении 0,2 г / л SiO_2 происходит сильное торможение коррозионного процесса, и защитная эффективностъ достигает 85%. На базе маннитолбората натрия разработаны ингибиторные композиции D, Е. Ф (для водной среды) и G, Н для этиленгликоль-вода среды.

Гравиметрические исследования коррзозии стали и цветных металлов (медь, латунъ, алюминий) показывают, что маннитолборат натрия и композиции являются отличными ингибиторами для коррозии стальных образцов в водной среде и степень защиты составляет 98%, для меди 86%, для латуни, 81%, 84% для образцов алюминия. В среде этиленгликоля (1:1) Na маннитолборат и композиции D, Е эффективные коррозионные ингибиторы стали и степень защиты достигает (99%), латуни (94%), в то время Na маннитолборат и разработанные композиции на базе маннитолбората натрия G, Н не защищают медь и алюминий.