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THERMODYNAMIC STUDY OF THE ANTI-CORROSION PROPERTIES OF DICIANDIAMIDE IN AN ACID ENVIRONMENT

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Abstract: The article investigates the corrosion protection properties of N20 grade steel in a 0.5 M HCl solution of dicyandiamide (DTSDA). The study examines the gravimetric analysis of corrosion protection properties at different temperatures and concentrations. The adsorption of the inhibitor onto the metal surface is analyzed using Frumkin, Tyomkin, and Langmuir isotherms. By employing the Langmuir isotherm, the equilibrium constant, Gibbs energy, enthalpy, and entropy values of the adsorption process are determined.

Keywords: Dicyandiamide, corrosion inhibitor, gravimetric method, Langmuir isotherm, Gibbs energy, enthalpy, entropy.

Introduction. Inhibitors are commonly used for corrosion protection to decrease the corrosion rate of metals and alloys exposed to aggressive environments in industrial settings [1,2]. N20 steel, known for its special properties and affordability, finds extensive usage in various industries. However, long-term use of N20 steel presents challenges, particularly its low resistance to corrosion in acidic environments. Corrosion inhibitors have been investigated in several studies as a means to slow down the corrosion rate [3]. The utilization of inhibitors is an effective and practical method for safeguarding mild steels and metals from corrosion, particularly in acidic solutions where oxidation processes are prevalent [4].

Metal materials are widely used in the production industry and construction. However, their corrosion in industrial settings can cause environmental damage and pollution [5]. To address this issue, there is a growing focus on developing new

multifunctional inhibitors that can prevent chemical, electrochemical, microbiological corrosion, as well as salt deposition, while ensuring environmental safety. Industrially developed countries have made progress in using and developing various multifunctional inhibitors, such as those based on phosphate and phosphonic acids, organophosphate derivatives [6], and their complexes with polyelectrolytes and metal ions [7]. Research has been conducted on the corrosion of steel samples in different environments using newly developed oligomeric salts derived from organic compounds [8]. The results showed that the protective effect of these salts increased with higher molecular mass and hydrocarbon radicals.

Materials. Protection of N20 steel from corrosion is a pressing problem in the field of materials science, chemistry and technology. Steel N20 belongs to the family of carbon steels, its composition is as follows: Fe 98%, Sr ≤0.25%, Su ≤0.30%, Ni ≤0.30%, Mn 0.35–0.65%, As 0, 08%, Si 0.17–0.37%, S 0.17–0.24%, R ≤0.035% and S ≤0.040%. Before the experiment, the metal samples were cleaned and polished using various sandpapers (from 400 to 1200). The clean metal plates were then washed three times with distilled water and alcohol, after which they were dehydrated with acetone and air dried. All experiments were carried out in a background solution of 0,5 M hydrochloric acid at temperatures of 303, 313, 323 and 333 K. The N20 steel sample chosen for gravimetric studies had the shape of a plate measuring 2 cm wide, 3 cm high and 3 mm thick.

Research methods. The gravimetric method is intended to determine the corrosion rate of metals in environments with and without an inhibitor depending on the change in mass [9]. This method determines the degree of corrosion under conditions of different concentrations and in a certain temperature range. After keeping the samples in working solutions for 5 days, the corrosion products are removed and the corrosion rates are determined in an environment without an inhibitor (W_o) and in its presence (W_{inh}) (1).

$$\boldsymbol{W = \frac{(m_1 - m_2)\cdot 10000}{S\cdot \tau}} \quad (1)$$

where: W – corrosion rate (g/cm²·hour), m_1 and m_2 – mass of the plate before and after the experiment (g), S – surface of the plate (cm²), t – time of the experiment (hour).

Based on the values of $\mathbf{W_o}$ and $\mathbf{W_{inh}}$, the braking coefficient γ (2), the degree of protection $\boldsymbol{\eta}$ (3) and the degree of surface filling $\boldsymbol{\theta}$ (4) are found by the following equations:

$$\boldsymbol{\gamma = \frac{W_0}{W_{inh}}} \quad (2)$$

$$\boldsymbol{\eta = \left(1 - \frac{W_{inh}}{W_o}\right)\cdot 100\%} \quad (3)$$

$$\boldsymbol{\theta = \left(1 - \frac{W_{ing}}{W_o}\right)} \quad (4)$$

Thermodynamics of adsorption. For a more complete description of the adsorption characteristics of the inhibitor under study on the steel surface, thermodynamic values were calculated through the adsorption isotherms of Langmuir (5) [10], Frumkin (6) and Temkin (7):

$$\boldsymbol{\frac{C_{инг}}{\theta} = \frac{1}{K_{ads}} + C_{ing}} \quad (5)$$

$$\frac{\theta_{grav}}{1-\theta_{grav}} exp(-2f\theta_{grav}) = K_{ads}C_{inh} \quad (6)$$

$$exp(f\theta_{inh}) = K_{ads}C_{inh} \quad (7)$$

where: C_{inh} is the inhibitor concentration in solution (mg/l), θ is the degree of complete coverage, K_{ads} is the adsorption equilibrium constant.

The Langmuir isotherm provides more information about the mechanism of interaction between the steel surface and the inhibitor. Using the value of K_{ads} determined from the relationship between C_{inh} and C_{inh}/θ using the Langmuir isotherm, the standard Gibbs energy [11] of adsorption ΔG^{o}_{ads} was determined in the temperature range 303 – 333 °C according to equation (8):

$$\Delta G^{0}_{ads} = -RTln(1000K_{ads}) \quad (8)$$

where: K_{ads} – the adsorption equilibrium constant, R – 8,314 J/mol•K, T – temperature (K), the amount of water in the solution is 1000 (g/l).

$$\Delta G^{0}_{ads} = \Delta H^{0}_{ads} - T\Delta S^{0}_{ads} \quad (9)$$

Using equation (9), a graph of the dependence of ΔH_{ads} on temperature is plotted, and the values of ΔH_{ads} and ΔS_{ads} are found at the point of intersection with the ordinate axis and along the tangent of the straight line [12].

Understanding the activation kinetics and thermodynamics of the corrosion process provides crucial insights into the mechanisms of action of inhibitors [14]. This is achieved by determining the activation energies of inhibitors through measuring corrosion rates at various temperatures and concentrations [14]. The activation energy is calculated by comparing corrosion rates in the presence and absence of an inhibitor, using the Arrhenius equation (10):

$$W_{grav} = A\, exp\left(\frac{-E_a}{RT}\right) \quad (10)$$

where: Ea - activation energy (kJ/mol), R - universal gas constant (8.314 J/mol•K), T - temperature (K), A - pre-exponential Arrhenius coefficient.

Based on the corrosion rates obtained at different temperatures and concentrations, a linear graph is plotted showing the relationship between log W and 1000/T [15]. The slope of this line is then determined. The tangent of the angle α (tgα) in this graph is linked to the activation energy by the equation: tgα = -Ea / (2.303•R).

To calculate the values of activation enthalpy (ΔH_a) and entropy (ΔS_a) [16], utilize the transition state equation (11) along with the graphical representation as described in reference [17]:

$$W_{grav} = \frac{RT}{Nh}\, exp\left(\frac{\Delta S_a}{R}\right)\, exp\left(-\frac{\Delta H_a}{RT}\right) \quad (11)$$

where: h - Planck's constant (6.626•10−34 m2kg/s) and N - Avogadro's constant.

The activation enthalpies are determined from the slopes of the graph, using the equation tgα = –ΔHa / (2.303 * R), where tgα is the tangent of the angle α in the graph. The activation entropy is found at the point of intersection with the ordinate axis [log (R/Nh) + (ΔSa / 2.303 * R)].

Results. To obtain additional information about the protection mechanisms, the coating of DCDA inhibitor on the surface of N20 steel was studied as a function of

concentration at 50, 100, 150 and 200 mg/L at different temperatures (see Table 1). With increasing concentration, an increase in inhibitor protection ($\eta_{Grav.}$) and surface coverage ($\theta_{Grav.}$) was observed. This is explained by the fact that more inhibitor molecules cover more corrosion centers and reduce the corrosion process.

Table 1. Corrosion efficiency of the DCDA inhibitor in a background solution at various temperatures and concentrations.

T, K	C, mg/l	W, (mg/cm²·h)	γ	η, %	θ
	-	1,0672	-	-	-
	50	0,2582	4,130	75,79	0,7579
303	100	0,2105	5,066	80,26	0,8026
	150	0,1454	7,334	86,37	0,8637
	200	0,0894	11,928	91,62	0,9162
	-	1,1741	-	-	-
	50	0,3111	3,772	73,49	0,7349
313	100	0,2749	4,269	76,58	0,7658
	150	0,1823	6,438	84,47	0,8447
	200	0,1716	6,839	85,38	0,8538
	-	1,2509	-	-	-
	50	0,3728	3,356	70,20	0,7020
323	100	0,3381	3,701	72,98	0,7298
	150	0,3102	4,034	75,21	0,7521
	200	0,2674	4,679	78,63	0,7863
	-	1,3748	-	-	-
	50	0,4809	2,860	65,03	0,6503
333	100	0,4542	3,028	66,97	0,6697
	150	0,4334	3,173	68,48	0,6848
	200	0,3989	3,447	70,99	0,7099

As the temperature increases, the corrosion rate and the level of protection of the inhibited system decreases. At a temperature of 303 K, the level of protection in concentrations of 50-200 mg/l was 75.79-91.62%, and at a temperature of 313 K $\eta_{Grav.}$ the value was 73.49-85.38%, 70.20-78.63% at a temperature of 323 K and 65.03-70.99% at a temperature of 333 K (Table 1).

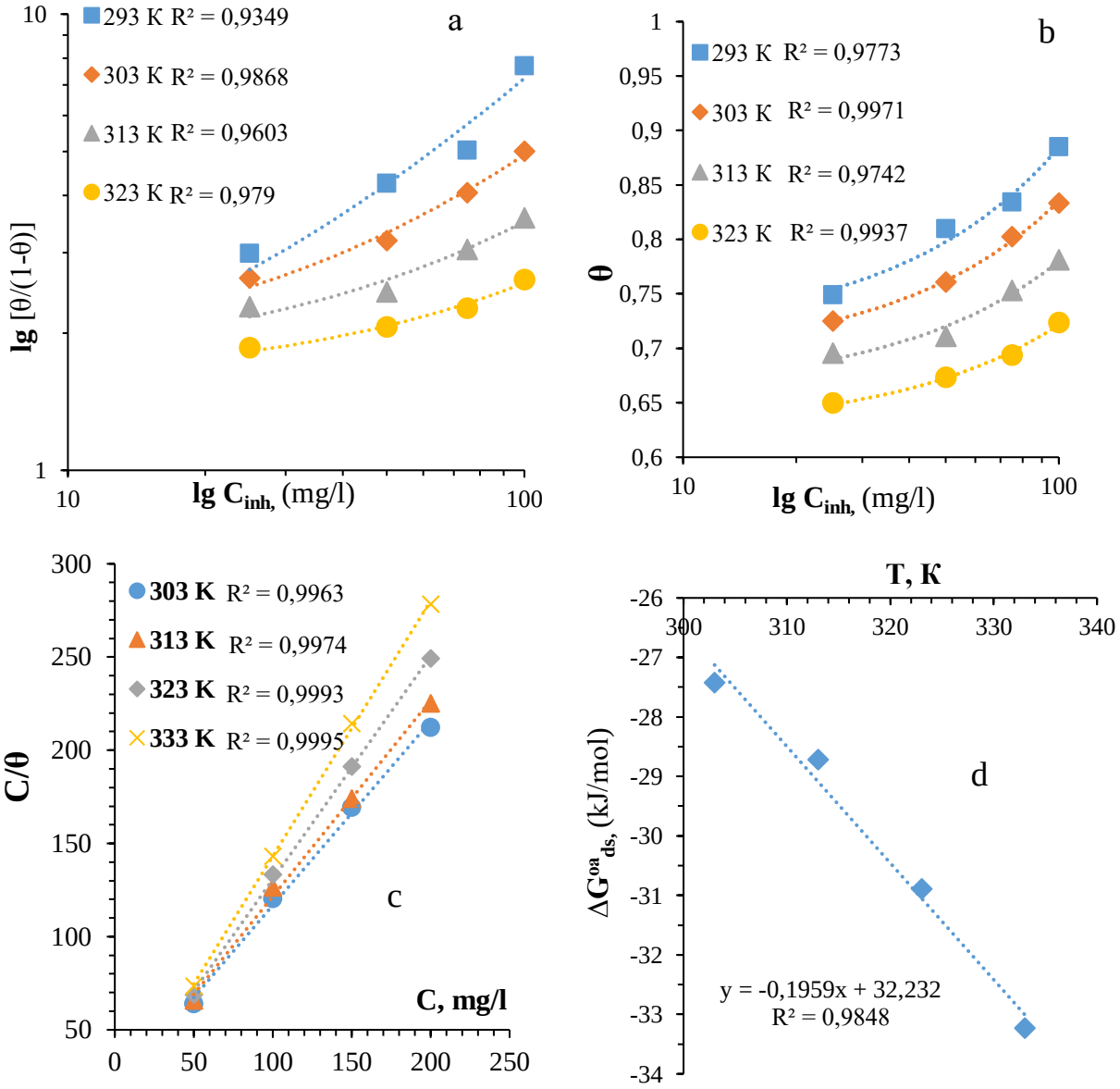

Figure 1. Frumkin (a), Temkin (b) Langmuir adsorption isotherms (c) and Ellingham diagram (d) of DCDA on a metal surface.

In order to comprehensively understand the adsorption mechanism of the DCDA inhibitor on the steel surface, Frumkin, Temkin, and Langmuir isotherms were examined. Analysis of the correlation coefficient (R^2) from these isotherms revealed that the adsorption of the inhibitor on the metal surface is not accurately described by the Frumkin and Temkin isotherms (Fig. 1a, 1b). However, the correlation coefficient indicated a consistent alignment with Langmuir's theory of monomolecular adsorption (Fig. 1c).

The correlation coefficient derived from the linear form of the Langmuir isotherm supports the adherence of the process to Langmuir's theory of monomolecular adsorption (Fig. 1a). With increasing temperature, the decrease in the Gibbs energy value during the adsorption process suggests its spontaneous nature (refer to Table 2).

Table 2. Thermodynamic functions of the adsorption process in a background solution with the participation of DCDA.

T, K	K_{ads}	R^2	ΔG_{ads}	ΔH_{ads} kJ/mol	ΔS_{ads}, kJ/mol
303	53,6682	0,9983	-27,42	32,109	0,1954
313	62,3830		-28,72		
323	99,6115		-30,89		
333	163,961		-33,23		

Conclusions. Furthermore, the graphical calculation using the Ellingham diagram indicates a change in standard enthalpy (ΔH_{ads} = 32.11 kJ/mol) during the adsorption process, signifying its exothermic nature (Fig. 1d).

Alongside the standard enthalpy change, a standard entropy change was also identified (ΔSads = 0.195 J/mol) (refer to Table 3). The adsorption process results in an increase in disorder due to the rapid formation of the interaction complex with inhibitor molecules compared to the action of water on the steel surface, leading to a positive value for entropy.

References

1. Rajabov Yu.N., Akbarov H.I. Aminotiokarbamid asosidagi oligomer ingibitorlar sintezi va po'lat bilan ta'sirlashish termodinamikasi // SamDU Ilmiy axborotnoma 2021-yil, 5-son (129) 14-20 b.

2. Turaeva H.K., Rajabov Y.N., Akbarov X.I. Electrochemical study of (Z)-4-(tert-butylamino)-4-oxobuten-2-acid synthesis and inhibition properties // Scientific and Technical Journal of NamIET. Namangan-2022. Volume-7, Issue-2. ppm. 173-178.

3. Berdimurodov E., Kholikov A., Akbarov K., Guo L., Kaya S., Verma K., Dagdag O. New and green corrosion inhibitor based on new imidazole derivate for carbon steel in 1 M HCl medium: experimental and theoretical analyses // International Journal of Engineering Research in Africa. – Trans Tech Publications Ltd, 2022. – T.58. – C. 11-44.

4. Rajabaliyev N., Rajabov Yu., Nig'matillayeva M., Akbarov X. Disiandiamid ingibitorining Lengmyur izotermasi yordamida termodinamik tadqiqoti // "Замонавий физик-кимёвий тадқиқот усулларининг илмий ва ишлаб чиқариш соҳасидаги интеграцияси" Республика илмий-амалий конференцияси. Тошкент–2023. 198-199 b.

5. Berdimurodov E., Eliboyev I., Berdimuradov K., Kholikov A., Akbarov K., Dagdag O., Arrousse N. Green β-cyclodextrin-based corrosion inhibitors: Recent developments, innovations and future opportunities //Carbohydrate Polymers. – 2022. – C. 119719.

6. Berdimurodov E., Kholikov A., Akbarov Kh., Guo L., Abdullah A.M., Elik M. A gossypol derivative as an efficient corrosion inhibitor for St2 steel in 1 M HCl+ 1 M KCl: An experimental and theoretical investigation //Journal of Molecular Liquids. – 2021. – T. 328. – C. 115475.

7. Ражабов Ю., Ниғматиллаева М., Акбаров Х. N20 маркали пўлатни коррозиядан ҳимоя қилишда дициандиамид ингибиторининг адсорбцион хоссалари // «Кончилик ва металлургия фанининг долзарб масалалари» мавзусидаги республика илмий-амалий анжумани. Олмалиқ-2023. 141-142 б.

8. Рахмонов Ж.А., Ражабов Ю.Н., Акбаров Х.И. Пўлат коррозиясига қарши ингибиторларнинг кинетик ва термодинамик тадқиқоти // “Kimyo va kimyo ta’limi muammolari” mavzusidagi respublika ilmiy-amaliy anjuman materiallari. Qo‘qon–2022. 123-124 б.

9. Akbarov Kh.I., Eshmamatova N.B., Fayzullaev N.I., Kalyadin V.G., Azimov L.A. Synthesis and Physico-Chemical Properties of Oligomeric Inhibitors of Corrosion on the Base of Nitrogen, PhosphorousContaining Compounds // International Journal of Advanced Science and Technology. Vol. 29, No. 5, (2020), -C. 6489–6506.

10. Okewale A.O., Adesina O.A. Kinetics and Thermodynamic Study of Corrosion Inhibition of Mild Steel in 1.5M HCl Medium using Cocoa Leaf Extract as Inhibitor // J. Appl. Sci. Environ. Manage. Vol. 24 (1) January 2020. –C. 37-47. https://dx.doi.org/10.4314/jasem.v24i1.6

11. Berdimurodov E., Kholikov A., Akbarov Kh., Guo L., Abdullah A., Elik M. A gossypol derivative as an efficient corrosion inhibitor for St2 steel in 1 M HCl + 1 M KCl: An experimental and theoretical investigation // Jour. of Molecular Liquids 328 (2021) 115475. doi.org/10.1016/j.molliq.2021.115475

12. Berdimurodov E., Kholikov A., Akbarov Kh., Guobao Xu., Aboubakr M.A., Morteza H. New anti-corrosion inhibitor (3ar,6ar)-3a,6a-di-p-tolyltetrahydroimidazo[4,5-d]imidazole-2,5(1h,3h)-dithione for carbon steel in 1 M HCl medium: gravimetric, electrochemical, surface and quantum chemical analyses // Arabian Journal of Chemistry-2020. doi: https://doi.org/10.1016/j.arabjc.2020.08.025

13. Berdimurodov E., Kholikov A., Akbarov Kh., Obot I., Guo L. Thioglycoluril derivative as a new and effective corrosion inhibitor for low carbon steel in a 1 M HCl medium: Experimental and theoretical investigation // Journal of Molecular Structure MOLSTR 130165. doi.org/10.1016/j.molstruc.2021.130165

14. Akinbulumo O., Odejobi O., Odekanle E. Thermodynamics and adsorption study of the corrosion inhibition of mild steel by Euphorbia heterophylla L. extract in 1.5 M HCl. // Results in Materials 5 (2020) 100074. doi.org/10.1016/j.rinma.2020.100074

15. Berdimuradov K., Berdimurodov E., Eliboev I., Azimov L., Rajabov Y., Mamatov J., ... & Akbarov K. Imidazole-and Imidazoline-based Corrosion Inhibitors //Handbook of Heterocyclic Corrosion Inhibitors. – CRC Press, 2023. – C. 55-73.

16. Borikhonov B., Kholikov A., Akbarov K. Elyor Berdimurodov, Khasan Berdimuradov, Ilyos Eliboev, Lazizbek Azimov, Yusufboy Rajabov, Jaykhun Mamatov. Covalent and noncovalent surface functionalization of nanomaterials (for enhanced solubility, dispersibility and corrosion prevention potential) //Corrosion Prevention Nanoscience: Nanoengineering Materials and Technologies. – 2023. – C. 37.

17. Berdimurodov E., Berdimuradov K., Eliboev I., Azimov L., Rajabov Y., Mamatov J., Akbarov K. Chemical Methods of Heavy Metal Management—Filtration, Ion Exchange, and Electrolysis //Heavy Metals in the Environment: Management Strategies for Global Pollution. – American Chemical Society, 2023. – C. 229-245.

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