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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Prognostication of the Anticorrosive Activity in the Series of Pentenylarylamines and Their Industrial Introduction

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Abstract—Quantum-chemical parameters and regression analysis were used to predict and synthesize a number of compounds with the highest inhibiting activity in the series of pentenylarylamines. For the compounds with the highest inhibiting activity, tri-2,4,6-(1'-methyl-2'-butenyl)aniline and di-2,6-(1'-methyl-2'-butenyl)-4-methylaniline, technical documentation was developed and their inhibiting activity in media as close as possible to real oilfield conditions were performed. On the basis of results of these tests, the given compounds are recommended for pilot tests.

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The correlation between the structure and inhibiting properties has been extensively studied [1–3]. Of particular interest in recent years has been use, for this purpose, of quantum-chemical calculations of molecule properties [4–6], depending on which a tendency toward an increase in the inhibition efficiency can be revealed. However, examples of obtaining optimal structures with the highest inhibiting activity cannot be found in these publications.

It has been shown that alkenylanilines readily accessible via condensation of anilines with hydrohalogenated 1,4-adducts of piperilene or cyclopentadiene are potential corrosion inhibitors [7, 8]. However, the dependence of the anticorrosive activity on structural parameters has not been studied for compounds of this series.

The goal of our study was to examine the relationship between the electronic structure of molecules and their corrosion inhibiting activity in the series of pentenyl derivatives of aniline, predict and synthesize optimal corrosion inhibitors, and introduce compounds with the highest anticorrosive activity into industrial practice.

EXPERIMENTAL

Pentenylarylamines were synthesized by the known procedures [7]. Anticorrosive studies were performed in conformity with GOST (State Standard) 9.506–87 [9]. The maximum anticorrosive activity was evaluated by the degree of protection Z (%) in conformity with GOST 9.506–87, determined by the formula

$$Z = \frac{V_{ko} - V_{ki}}{V_{ko}} \times 100,$$

where V_{ko} and V_{ki} are the metal dissolution rates in media without and with an inhibitor, respectively (g m^{-2} h^{-1}).

As witness samples served steels 20, the amounts of the compounds being tested were 0.033 M, and the temperature of the hydrochloric acid solution was maintained at 25 ± 1°.

The quantum-chemical parameters [energy of higher occupied molecular orbitals, E_{HOMO} (a.u.); energy of

lower unoccupied molecular orbitals, E_{LUMO} (a.u.); negative charge on the nitrogen atom, Q_{min} (a.u.); electrophilicity index W; and dipole moment μ(D)] were calculated using PC GAMESS 7.15 software [10] in the B3LYP/6-31G(d, p) approximation [11, 12].

The calculation results were visualized and preliminarily processed using ChemCraft 1.5 software [13].

All the structures calculated in this study were subjected to optimization and are stationary points on the potential-energy surface (PES), which was confirmed by solution of a vibrational problem: for minima on the PES, the diagonalized Hessian matrix contains only positive terms.

We used hydrochloric acid solutions as corrosive media. Preliminary corrosion tests demonstrated that the optimal hydrochloric acid concentration for the chosen compounds is its 16% solution. At low hydrochloric acid concentrations (1–12%), we have a gross experimental error, and at high concentrations (20–22%), the corrosion system does not react on structural changes for the simplest aromatic amines.

To study the anticorrosive properties of pentenylarylamines, we chose monosubstituted pentenylarylamines synthesized by the known methods [7]. Table 1 lists the calculated electronic properties of mono pentenylarylamines and the degrees of corrosion protection, determined for these compounds.

An analysis of the results we obtained demonstrated that the strongest correlation dependence is observed in this set of parameters for the negative charge on the nitrogen atom. For the whole selection of mono pentenylarylamines **I**–**IX**, the correlation coefficient R^2 is 0.54 (Table 2). In a stage-by-stage exclusion of *ortho*-substituted pentenylarylamines **VI** and **VIII** from the general selection, the correlation coefficient increases (R^2 = 0.59) and reaches a value of 0.95 upon exclusion of *ortho*-substituted pentenylarylamines) and reaches a value of 0.95 upon exclusion of ortho-substituted pentenylarylamines **II**, **III**, **VI**, and **VIII** from the general selection.

Analysis of the relationship between the inhibiting activity of the compounds under study and the effective charge on the nitrogen atom shows that the larger the latter (in absolute value), the more pronounced the anticorrosive properties of a compound. Based on this

Table 1. Quantum-chemical parameters of alkenylarylamines and trisubstituted pentyl- and pentenylarylamines and their degrees of protection

Compd.	Compound	E, a.u.		W	Q_{max}	Q_{min}	μ, D	Z_{exp}	Z_{calc}
		HOMO	LUMO		a.u.			%	
I	*N*-(1-Methyl-2-butenyl)aniline	–0.1869	0.0124	0.0191	0.330	–0.60	1.852	69.4	71.7
II	*O*-(1-Methyl-2-butenyl)aniline	–0.1869	0.0124	0.0191	0.330	–0.600	1.852	71.0	71.7
III	*N*-(1-Methyl-2-butenyl)-3-метилaniline	–0.1850	0.0165	0.0176	0.283	–0.61	1.916	72.1	–
IV	*N*-(1-Methyl-2-butenyl)-3-methylaniline	–0.1852	0.0137	0.0185	0.334	–0.601	1.662	72.9	72.1
V	*N*-(1-Methyl-2-butenyl)-4-methylaniline	–0.1819	0.0128	0.0184	0.325	–0.6	1.552	73.8	–
VI	*O*-(1-Methyl-2-butenyl)-4-methylaniline	–0.1879	0.0069	0.021	0.256	–0.667	1.616	76.1	–
VII	*N*-(1-Methyl-2-butenyl)-2,4-dimethylaniline	–0.1802	0.0164	0.0171	0.276	–0.61	1.627	78.0	75.2
VIII	*O*-(1-Methyl-2-butenyl)-2,4-dimethylaniline	–0.1865	0.0113	0.0145	0.125	–0.676	1.505	84.9	–
IX	*n*-(1-Methyl-2-butenyl)aniline	–0.1927	0.0075	0.0214	0.352	–0.657	1.576	93.0	91.6
X	2,4,6-Tri(1'-butenyl)aniline	–0.1882	0.0181	0.0194	0.155	–0.666	1.428	94.9	94.7
XI	2,4,6-Tri-(3'-butenyl)aniline	–0.1877	0.0139	0.0187	0.174	–0.672	1.325	97.75	96.8
XII	2,6-Di-(1'-methyl-2'-butenyl)-4-methylaniline	–0.1837	0.0063	0.0207	0.255	–0.678	1.689	97.87	98.9
XIII	2,4,6-Tri-(1'-methyl-2'-butenyl)aniline	–0.1858	0.0057	0.0212	0.255	–0.678	1.898	98.0	98.9

Table 2. Results of preliminary corrosion tests of compounds **XII** and **XIII**. Experimental conditions: 15% hydrochloric acid solution as model medium, temperature 90°C, exposure duration 1 h

Compound	Dosage, wt %	Degree of protection, %
XII	0.5	96.6
	1.0	97.3
	2.0	97.4
	3.0	98.0
	4.0	98.4
	0.5	98.8
XIII	0.5	97.0
	1.0	97.6
	2.0	98.0
	3.0	98.4
	4.0	98.8
	5.0	99.1

prognosis, we synthesized 2,4,6-tri-(1'-methylbutyl) aniline (**X**), 2,4,6-tri-(3'-methylbutyl)aniline (**XI**), 2,6-di-(1'-methyl-2'-butenyl)-4-methylaniline (**XII**), and 2,4,6-tri-(1'-methyl-2'-butenyl)aniline (**XIII**). Table 2 lists electronic properties and degrees of corrosion protection under the action of the above compounds. The full set of compounds can be described with satisfactory accuracy by the correlation equation $Z = -137.44 - 348.61Q_{min}$.

Using the regression equation for the negative charge on the nitrogen atom, we calculated the degrees of corrosion protection for compounds **I–XIII** under study. It can be seen in Table 1 that the experimental and calculated degrees of corrosion protection for the compounds synthesized coincide within experimental error and standard calculation errors.

Based on the results of our study and on the fact that all the components used to synthesize compounds with the highest inhibiting activity (**XII**, **XIII** are industrially manufactured, we decided to organize industrial manufacture of these compounds and recommended to perform preliminary corrosion tests in media as close as possible to the real industrial conditions.

For compounds **XII** and **XIII**, we developed production procedures and technical specifications (TU) 2458-007-20833127–2009 "Yural-3K corrosion inhibitor." We performed at Federal state health-protection institution "Center for Hygiene and Epidemiology at the Republic of Bashkortostan" toxicological tests of these compounds belonging to third class of hazard according to GOST 12.1.007. We obtained a sanitary-epidemiological statement from the department of the Federal Service for Supervision of Consumer Rights Protection and Human Welfare for the Republic of Bashkortostan. The reagent was registered at the Federal agency for technological control and metrology, Federal State Enterprise "Standardization, Metrology, and Certification Center of the Republic of Bashkortostan."

Preliminary studies of the inhibiting activity of the reagent in corrosive media as close as possible to those under real industrial conditions were performed at the chemical laboratory of the department for complication control of crude-oil production at OOO "RN-UfaNIPIneft'." The inhibiting activity of the given compounds was studied in a 15% hydrochloric acid solution at a temperature of 90°C by the standard procedure with steel 20. The results of these tests are listed in Table 2.

The results of preliminary corrosion tests in corrosive media as close as possible to those under real industrial conditions demonstrated that compounds **XII** and **XIII**, taken in amounts of 0.5–5.0 wt %, have a 97–99% degree of protection. According to the results of these tests, the compounds are recommended for pilot tests.

The predicted compounds **XII** and **XIII** were synthesized by the known procedure described in [7], and their spectral characteristics were presented in the same report. Compounds **X** and **XI** were synthesized for the first time.

2,4,6-Tri-(1'-methylbutyl)aniline (X) was synthesized by hydrogenation of compound **XIII** on skeleton nickel in an alcoholic solvent [14]; n_{D20} 1.5856. Found (%): C 83.05, H 12.24, N 4.60. $C_{21}H_{37}N$. Calculated (%): C 83.10, H 12.29, N 4.61.

IR spectrum, ν, cm^{-1}: 3420, 3490 (NH_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.72–0.97 m (9H, $3CH_3$), 1.17–1.28 m (9H, CH_3), 1.45–1.55 m (6H, $3CH_2$), 1.64–1.75 m (6H, $3CH_2$), 2.72–2.80 (3H, 3CH), 3.56 br.s (2H, NH_2), 6.77 s (2H, ArH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.4 ($3CH_3$); 20.7 ($3CH_3$); 21.8 ($3CH_2$); 33.2 ($3CH_2$); 40.0 (3CH); 121.7, 132.0, 137.4, 138.6 (C-arom).

2,4,6-Tri-(3'-methylbutyl)aniline (XI) was synthesized by the Friedel–Crafts alkylation of 4-(1-meth-

ylbutyl)aniline produced by the known method [7] with isoamyl chloride in the presence of $AlCl_3$; n_{D20} 1.5815. Found (%): C 83.05, H 12.24, N 4.60. $C_{21}H_{37}N$. Calculated (%): C 83.10, H 12.29, N 4.61.

IR spectrum, ν, cm^{-1}: 3425, 3493 (NH_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88–0.89 m (12H, $4CH_3$), 0.96–0.98 m (3H, CH_3), 1.16–1.18 m (3H, CH_3), 1.23–1.48 m (8H, $4CH_2$), 1.58 m (CH, 2H), 2.20–2.24 m (4H, CH_2), 2.59 (1H, CH), 4.38 br.s (2H, NH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.19 (CH_3); 20.7 (CH_2); 22.67 (CH_3); 27.90 (2CH); 28.36 ($2CH_2$); 28.70 (CH_2); 41.34 ($2CH_2$); 43.90 (CH); 128.09, 132.16, 144.86, 146.11 (C-arom).

CONCLUSIONS

(1) Quantum-chemical parameters were calculated for prognostication of the inhibiting activity in the pentenylarylamine series.

(2) A number of compounds with the highest inhibiting activity were synthesized with consideration for the results of a regression analysis for the negative charge on the nitrogen atom.

(3) It was shown that the calculated degrees of corrosion protection coincide with experimental values within experimental and standard calculation errors.

(4) Compounds with the highest anticorrosive activity, 2,4,6-(1'-methyl-2'-butenyl)aniline and 2,6-di-(1'-methyl-2'-butenyl)-4-methylaniline, were recommended for pilot tests.

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