Hydrocarbon-soluble inhibitors of metal corrosion. Part 3. Dependence of the inhibitive efficiency and adsorptivity of oleic acid amides and salts on their physicochemical parameters

A.I. Altsybeeva, E.A. Tronova and V.V. Burlov

OOO NPO NEPhTEKhIM, ul. Pulkovskaya 10, St. Petersburg, 196158 Russian Federation
E-mail: altsybeeva@yandex.ru

Abstract

Correlation analysis of the dependence of the inhibitive efficiency (determined from electrochemical measurement data) and adsorption capability (determined from the changes in the junction potential difference upon formation of an adsorption film on a metal from inhibitor solutions) on the physicochemical parameters has been performed for a number of amides and salts obtained from the same amines and differing in the number and arrangement of nitrogen atoms in the molecules. A prediction is given for the efficiency of a mono-substituted piperazine amide − a corrosion inhibitor for carbon steel and copper.

Key words: *correlation analysis, efficiency prediction, oleic acid amides and salts.*

Let us analyze the dependence of the inhibitive efficiency and electron-donating capability of amides and salts on the main physicochemical parameters of the inhibitors.

Tables 1 and 2 list the corrosion and adsorption parameters and the main physicochemical parameters of oleic acid amides and salts.

Table 1. The main corrosion, adsorption and physicochemical parameters of oleic acid amides.

Amide of:	γ	ΔJPD steel	$q\,(N_{sp^3})$	$q\,(O_{sp^3\,ring})$	$q\,(O_{sp^2})$	Σq	π	μ
Hexylamine	4.6	154	−0.212	−	−0.372	−0.584	9.36	4.0
Cyclohexylamine	12.5	203	−0.216	−	−0.363	−0.579	8.83	3.6
Morpholine	104	256	−0.155	−0.222	−0.373	−0.750	6.47	3.0
Piperidine	100	98	−0.165	−	−0.375	−0.540	7.15	3.6
Piperazine (mono)	7.35 calc. 163.72	94	−0.168 −0.172	−	−0.375	−0.715	5.06	3.7

Table 2. The main corrosion, adsorption and physicochemical parameters of amine salts of oleic acid.

Salt of:	γ	ΔJPD steel	$q(N_{sp^3})$	$q(O_{sp^3 ring})$	$q(O_{sp^2 salt})$	$q(O_{sp^3 salt})$	Σq	π	μ
Hexylamine	9.9	103	+0.406	–	–0.325	–0.281	–0.200	3.63	2.5
Cyclohexylamine	8.3	148	+0.361	–	–0.376	–0.326	–0.341	3.82	2.0
Morpholine	28.1	195	+0.351	–0.219	–0.353	–0.372	–0.593	–1.24	1.4
Piperidine	35.4	111	+0.341	–	–0.354	–0.393	–0.406	–1.49	3.3
Piperazine (mono)	55.5	41	+0.347 –0.176	–	–0.306	–0.374	–0.509	–4.49	2.8

The following designations are used: q is electronic charge, π is hydrophobicity (calculated Hansch π-constant), Σq is total electron density on the heteroatoms, μ is dipole moment, γ is the corrosion inhibition coefficient for steel based on electrochemical measurements, ΔJPD (steel) is the junction potential difference upon adsorption on steel. The molecular masses of the amides are similar (from 349 to 365), so similarity of their molecular sizes can be assumed and its variation can be neglected in subsequent considerations. The same is true for salts (MM from 367 to 383).

The calculated parameters were taken from [1]. The cathodic and anodic polarization curves in the presence of inhibitors were recorded in a solution containing 30 mg/dm^3 NaCl and 10 g/dm^3 Na$_2$SO$_4$. The inhibitor film on specimen surfaces was formed in 1% solution of an inhibitor in isopropanol (amides) or in an aqueous emulsion containing 1 g/dm^3 of an inhibitor (salts). A steel specimen was kept for 60 min in an isopropanolic solution or in an aqueous emulsion, then dried for 60 min in air, and immediately placed into the cell for recording of polarization curves. Electrochemical measurements were carried out on carbon steel 20 using the common procedure, in a standard electrochemical cell with divided anodic and cathodic spaces. Platinum auxiliary electrodes were used. The potential of the working electrode was measured relative to a saturated silver chloride electrode ($E = 0.202$ V). All potentials in the text are given with respect to saturated silver chloride electrode. Polarization curves were recorded in the potential range from −1.25 V to 0.05 V in the positive direction, without preliminary cathodic activation of the electrode.

Extrapolation of linear cathodic and anodic regions in the polarization curves in semi-logarithmic coordinates gave the free corrosion potential (E_{cor}) and the logarithm of corrosion current density (lg i_{cor}) in the intersection point of the linear regions. The current densities were used to calculate the corrosion inhibition coefficients (γ_i) and the corresponding protection effects (Z_i) using the formula:

$$\gamma_i = \frac{i}{i'} \tag{1}$$

The electron work functions from the metal were determined using the capacitor method with direct reading of the junction potential difference (JPD). The «Поверхность-ИИ» ("Poverkhnost'-I1") instrument is a miniaturized high-sensitivity digital electrometer intended for measurement of the difference of surface potentials between the metal surface studied (M) and the measuring electrode (ME). Metal specimens of Steel 10 and M1 copper sized $50 \times 50 \times (2-3)$ mm were polished, degreased with hexane, and dried for 5 min in air. After that, the first JPD was measured (JPD_1). After JPD_1 was measured, the specimen was placed into a 1% isopropanolic solution of an inhibitor, kept there for 1 h, then removed from the solution, transferred into a desiccator with calcium chloride, and kept there for 1 h. After drying in the desiccator, the second JPD was measured (JPD_2), and the specimens with adsorbed inhibitor were again placed into a desiccator. The total time difference between the first two measurements followed by ΔJPD determination was 2 h.

Approximation of experimental data for compliance with certain mathematical relationships was carried out using the MATLAB 6.5 vector-matrix laboratory. The "SVD" operator was not required in these approximations. To achieve the minimum calculation errors, it was sufficient to use direct algebraic mathematical processing of source data with 1st and 2nd degree polynomials.

The resulting polynomials of degrees $1\ldots s$ in have the following general scalar form:

$$y_p = b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + .. + b_5 x_1^2 + b_6 x_2^2 + b_7 x_3^2 + b_8 x_4^2 + .. + b_k x_1^s \qquad (2)$$

and allow one, if required, to perform easy fast computations on a calculator based on approximation coefficients $b_1, b_1, \ldots b_k$.

The calculation was carried out by direct algebraic mathematical processing of source data using the following designations:

> F – calculated starting parameter Y,
> $DF = F - Y$ – calculated error of the computations,
> A – summary table of computation results,
> B – approximating polynomial coefficients.

A 1st degree polynomial proved to be sufficient for high accuracy computations.

Computation program:

```
% source data loading %
load amidy11.mat;
% computed dependences %
X=[X1,X2,X3,X4,X5];
% computation of approximating polynomial coefficients %
B=X/Y;
% computation of γ %
F=X*B;
% determination of computation error %
DF=F-Y;
```

```
% summary table of computation results %
A=[Y,F,DF];
```

Let us consider the following variants of correlation.

Variant 1.

Oleic acid amides

The general equation has the form: $\gamma = f(\Delta\text{JPD}, q_{N_{sp^3}}, q_{O_{sp^2}}, \pi, \mu)$.

Table 3. Source data for the computation.

Amide of:	Designations					
	Y	X1	X2	X3	X4	X5
	γ	ΔJPD steel	$q(N_{sp^3})$	$q(O_{sp^2})$	π	μ
Hexylamine	4.6	154	−0.212	−0.372	9.36	4.0
Cyclohexylamine	12.5	203	−0.216	−0.363	8.83	3.6
Piperidine	100	34	−0.165	−0.375	7.15	3.6
Morpholine	104	256	−0.155	−0.373	6.47	3.0

Table 4. Computation results.

Matrix A			Coefficients B
Y	F	DF	
4.6	4.2763	1.4388e–013	−0.10619
12.5	12.902	−2.8422e–014	0
100	100.02	1.4211e–013	−1029.2
104	103.85	−5.6843e–014	−34.049
			−10.8

Data for piperazine amide that had low efficiency due to poor solubility, which is considerably lower than that required to form an inhibitor film, was not used in the calculations. The poor solubility is apparently because the final product contains a considerable admixture of piperazine diamide that is poorly soluble in the majority of organic solvents.

The calculated inhibition coefficient for piperazine is:

$$Y(\gamma) = -0.10619 \cdot 94 - 1029.2 \cdot (-0.375) - 34.049 \cdot 5.06 - 10.8 \cdot 3.7 = 163.72.$$

Oleic acid salts

The general equation has the form: $\gamma = f(\Delta \text{JPD},\ q_{N_{sp^3}},\ q_{O_{sp2}},\ \pi,\ \mu)$.

Table 5. Source data for the computation.

Salt of:	Designations					
	Y	**X1**	**X2**	**X3**	**X4**	**X5**
	γ	**ΔJPD steel**	$q\,(N_{sp^3})$	$q\,(O_{sp^3\,salt})$	π	μ
Cyclohexylamine	8.3	129	0.361	−0.326	3.82	2.0
Hexylamine	9.98	103	0.406	−0.281	3.63	2.5
Morpholine	33.3	92	0.351	−0.372	−1.24	1.4
Piperidine	35.4	111	0.341	−0.393	−1.49	3.3
Piperazine (mono)	55.5	41	0.347 −0.176	−0.374	−4.49	2.8

Table 6. Computation results.

Matrix A			Coefficients B
Y	**F**	**DF**	
8.3	8.345	0.044965	−0.24873
9.98	9.9441	−0.03586	0.053182
33.3	33.274	−0.02566	−137.16
35.4	35.396	−0.00426	−2.0764
55.5	55.523	0.022789	1.8149

Variant 2

Oleic acid amides

The general equation has the form: $\Delta \text{JPD} = f(q_{N_{sp^3}},\ q_{O_{sp2}},\ \pi,\ \mu)$.

Table 7. Source data for the computation.

Amide of:	Designations				
	Y	**X1**	**X2**	**X3**	**X4**
	ΔJPD steel	$q\,(N_{sp^3})$	$q\,(O_{sp^2})$	**π**	**μ**
Hexylamine	154	−0.212	−0.372	9.36	4.0
Cyclohexylamine	203	−0.216	−0.363	8.83	3.6
Morpholine	256	−0.155	−0.373	6.47	3.0
Piperazine	94	−0.168	−0.375	5.06	3.7
Piperidine	34	−0.165	−0.375	7.15	3.6

The computation program is provided for approximation with a 2nd order polynomial because approximation with a 1st order polynomial results in considerable computation errors:

```
% source data loading %
load amidy31.mat;
% computed dependences %
X=[X1,X2,X3,X4,X1.^2,X2.^2,X3.^2,X4.^2];
% computation of approximating polynomial coefficients %
B=X/Y;
% computation of ΔJPD %
F=X*B;
% determination of computation error %
DF=F - Y;
% summary table of computation results %
A=[Y,F,DF];
```

Table 8. Computation results.

Matrix A			Coefficients B
Y	**F**	**DF**	
154	154	−5.0022e–012	0
203	203	−4.0927e–0s12	−5218.2
			−674.13
256	256	−1.5916e–012	672.3
94	94	−4.5475e–013	0
			0
34	34	−1.3642e–012	50.813
			−163.64

Oleic acid salts

The general equation has the form: $\Delta JPD = f(q_{N_{sp^3}},\ q_{O_{sp2}},\ q_{O_{sp^3 salt}},\ \pi, \mu)$.

The computation error is completely similar to that presented in Variant 1 (amides) for approximation with a 1st order polynomial.

Table 9. Source data for the computation.

Salt of:	Designations					
	Y	**X1**	**X2**	**X3**	**X4**	**X5**
	ΔJPD steel	$q\,(N_{sp^3})$	$q\,(O_{sp^2 salt})$	$q\,(O_{sp^3 salt})$	π	μ
Hexylamine	103	0.406	−0.325	−0.281	3.63	2.5
Cyclohexylamine	129	0.361	−0.376	−0.326	3.82	2.0
Piperidine	111	0.341	−0.354	−0.393	−1.49	3.3
Morpholine	92	0.351	−0.353	−0.372	−1.24	1.4
Piperazine	41	−0.176	−0.306	−0.374	−4.49	2.8

Table 10. Computation results.

Matrix A			Coefficients B
Y	**F**	**DF**	
103	103	−2.8422e−014	−45.699
129	129	8.5265e−014	4685.1
111	111	1.1369e−013	−5128.8
92	92	−1.7053e−013	79.358
41	41	5.6843e−013	−34.02

Variant 3

Oleic acid amides

The general equation has the form: $\Delta JPD = f(q_{N_{sp^3}},\ q_{O_{sp2}}, \pi, \mu)$.

The computation program is completely similar to that presented in Variant 2 (amides) for approximation with a 2nd order polynomial because approximation with a 1st order polynomial results in considerable computation errors.

Table 11. Source data for the computation.

Amine	Designations				
	Y	X1	X2	X3	X4
	ΔJPD copper	$q\,(N_{sp^3})$	$q\,(O_{sp^2})$	π	μ
Cyclohexylamine	121	−0.216	−0.363	8.83	3.6
Morpholine	83	−0.155	−0.373	6.47	3.0
Piperidine	79	−0.165	−0.375	7.15	3.6
Hexylamine	72	−0.212	−0.372	9.36	4.0
Piperazine	42	−0.172	−0.375	5.06	3.7

Table 12. Computation results.

Matrix A			Coefficients B
Y	F	DF	
121	121	−4.5475e−013	0
83	83	1.1369e−013	2090
			29.441
79	79	−1.1369e−013	453.68
			0
72	72	2.2737e−013	0
			−1.2121
42	42	0	−70.915

Conclusions

1. The results of electrochemical studies and junction potential difference measurements indicate that oleic acid amides and salts are electron donors in case of adsorption on steel and predominantly inhibit the anodic metal ionization reaction.

2. A relationship has been shown between the inhibiting and electron-donating capability of the amides and salts synthesized, on the one hand, and the main physicochemical parameters, namely, the electron density on the hetero atoms responsible for adsorption on metals, as well as hydrophobicity and dipole moments of molecules, on the other hand.

3. It has been shown that it is possible to approximate the dependences of the inhibitive efficiency and adsorption capability of oleic acid amides and salts with high reliability and with minimum computation errors.

References

1. A.I. Altsybeeva, V.V. Burlov and E.A. Tronova , *Int. J. Corros. Scale Inhib.*, 2014, **3**, no. 3, 160. doi: [10.17675/2305-6894-2014-3-3-160-166](10.17675/2305-6894-2014-3-3-160-166)

◆ ◆ ◆