Inhibition of aluminium reaction in aqueous sodium hydroxide solution

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Phenol and its derivatives inhibit the dissolution of aluminium in aqueous NaOH solution with increased efficiency in the sequence: phenol, *p*-nitrophenol, *p*-aminophenol.

The postulated mechanism of inhibition is based on the donor-acceptor properties of the system metal—organic substance, on the arrangement of the electrons in the molecule under the action of prevailing mesomeric effects of function groups on the aromatic rings.

The expressive increase of inhibition efficiency of *p*-aminophenol in the presence of added Ca^{2+} ions is explained by preferred adsorption of these ions on the metal surface, consecutive shielding of its negative charge and thereby the facilitation of binding the organic molecule on the surface. Another explanation takes into consideration the possibility of creation of Ca^{2+} complexes with protective properties.

Фенол и его производные подавляют растворение алюминия в водном растворе NaOH с возрастающей эффективностью в ряду: фенол, п-нитрофенол, п-аминофенол.

Постулируемый механизм ингибирования основан на донорно-акцепторных свойствах системы металл—органическое соединение, на размещении электронов в молекуле под воздействием преобладающих мезомерных эффектов функциональных групп на ароматических кольцах.

Существенное повышение эффективности ингибирования у п-аминофенола в присутствии добавок иона Ca^{2+} объясняется предпочтительной адсорбцией этих ионов на поверхности металла и, вследствие этого, экранированием его отрицательного заряда, а, таким образом, облегчением присоединения органической молекулы к поверхности. Другое объяснение принимает во внимание возможность образования комплексов с Ca^{2+}, обладающих защитными свойствами.

Although there is a great number of papers, *e.g.* [1—12], dealing with the inhibition of aluminium reaction in aqueous NaOH solution, and although great attention is paid to the protection of metals against corrosion, the problem of inhibition of considered reaction has not been studied to such extent as to make a wider application of suitable inhibitors possible in the praxis.

In paper [13] we have studied the kinetics and mechanism of aluminium reaction in aqueous NaOH solution. The present paper links up to the cited one and deals with the inhibition of this reaction by some phenol derivatives from the viewpoint of explaining the mechanism of that action and considering its possible application by pickling of aluminium during its surface finishing.

When selecting phenols as the inhibitors of Al reaction in NaOH solution we have taken into account, that organic substances which have in their molecule an aromatic ring or a heteroatom with a lone electron pair, exhibit good inhibition properties [4].

Experimental

The methods, described in paper [13] have been used with the exception that the experiments were realized in 300 cm^3 volume, under atmospheric air pressure and at 20 °C. The spectrally pure, polycrystalline aluminium (Johnson Matthey, London) has been used. The sample, the standardization of its surface, hydrodynamic conditions, the determination of dissolved amount of aluminium, were the same as in [13]. The distilled water has been used for preparation of the solutions and the chemicals used were of anal. grade (Lachema, Brno).

Since phenols are poorly soluble in water, the stock solutions have been prepared in diluted NaOH, so that its final concentration was 1 mole per dm^3. The concentration range for individual substances has been chosen as follows: concentration of phenol and *p*-nitrophenol being 1×10^{-3}—5×10^{-3} mol dm^{-3}, concentration of *p*-aminophenol 1×10^{-3}—4×10^{-2} mol dm^{-3}. The results are taken as an arithmetic mean of three independent measurements, the reproducibility of them being 4—7 %.

Results and discussion

Influence of phenol and its derivatives on the time behaviour of Al dissolution in aqueous NaOH solution

In 1 M-NaOH these substances were tested: phenol, *p*-nitrophenol, and *p*-aminophenol. When comparing the time courses of Al reaction in NaOH without and with the studied organic inhibitors (Fig. 1) it is evident that in general these substances decrease the reaction rate but they do not disturb the stationary
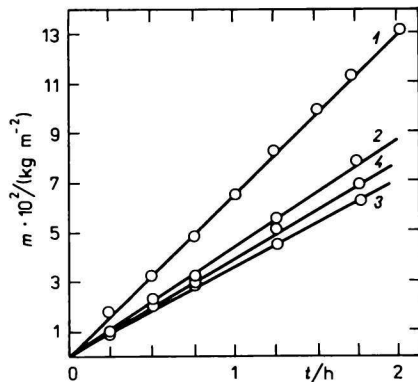
Fig. 1. Time course of aluminium reaction with 1 M-NaOH, $\theta = 25\ °C$, the inhibitor concentration being 5×10^{-3} mol dm^{-3}.
1. Without any inhibitor; 2. phenol; 3. p-nitrophenol; 4. p-aminophenol.

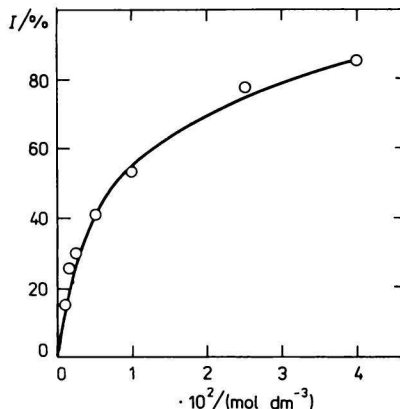Fig. 2. Dependence of inhibition efficiency of p-aminophenol on its concentration at Al dissolution in 1 M-NaOH, $\theta = 25\ °C$.

conditions of the reaction course. It means that for the given reaction conditions within the studied intervals the rate of reaction remains constant.

Influence of the inhibitor concentration

The information about inhibition properties of individual phenols can be obtained only by more detailed research of their influence on the reaction, under various reaction conditions.

First of all it is necessary to find out what is the action of the inhibitor concentration. This question can be solved on the basis of the graphical dependence in Fig. 2, which documents such dependence of inhibition efficiency on p-aminophenol concentration. Inhibition efficiency I has been calculated using the relation

$$I/\% = \frac{v_0 - v}{v_0} \cdot 100 \qquad (1)$$

where v_0 denotes the dissolution rate of Al in NaOH without an inhibitor, related to the area unit ($[v] = $ kg m^{-2} h^{-1}); v has the same meaning as v_0 but in the presence of an inhibitor.

The measured dependence $I = f(c_i)$ shows that the inhibition properties of individual phenols are different. When p-nitro- and p-aminophenol were used, the dissolution rate of Al in NaOH has been decreased with increasing inhibitor concentration down to the limiting value, while the inhibition efficiency of phenol

in the studied concentration range remained unchanged (Table 1). For the maximum inhibition effectiveness this inequality is valid

$$I_{ph} < I_{n-ph} < I_{a-ph}$$

But also this sequence cannot be taken as univocal, because the limiting efficiency of p-aminophenol has been reached at higher concentration $(c_i \geqslant 3 \times$

Table 1

Influence of concentration of phenols on aluminium dissolution rate in 1 M-NaOH, $\theta = 25$ °C

$10^3\ c_i$	Phenol		p-Nitrophenol		p-Aminophenol	
mol dm^{-3}	$\{v\}$	I	$\{v\}$	I	$\{v\}$	I
1.0	4.3	32.8	6.3	1.5	5.5	14.0
1.5	4.4	31.2	4.8	25.0	—	—
2.0	4.3	32.8	3.6	43.8	4.7	26.5
2.5	4.4	31.2	3.6	43.8	4.5	29.7
3.5	4.2	34.8	—	—	—	—
5.0	4.3	32.8	3.5	44.5	3.8	40.6
10.0	—	—	—	—	2.9	54.7
25.0	—	—	—	—	1.4	78.9
40.0	—	—	—	—	1.1	82.8

$\times 10^{-2}$ mol dm^{-3}) than by phenol and p-nitrophenol, the efficiency of which was practically unchanged already from $c_i = 2 \times 10^{-3}$ mol dm^{-3}.

The dependence for p-aminophenol, $I = f(c_i)$, can be quantitatively described by the relation, which is somewhat analogous to the adsorption isotherm

$$I = \frac{I_{max}\ \omega\ c_i}{1 + \omega\ c_i} \tag{2}$$

In the coordinates c_i/I vs. c_i it can be drawn as a straight line and from it $\omega = 201.2$ dm^3 mol^{-1}. p-Aminophenol can be therefore regarded as an adsorption inhibitor and the mechanism of its inhibition action taken as being adsorption-determined. Therefore we have turned our attention to p-aminophenol which inserted the best inhibition properties.

Influence of medium aggressivity on the inhibition efficiency of p-aminophenol

For the p-aminophenol concentration $c_i = 10^{-2}$ mol dm^{-3} the dependence of Al dissolution rate on the concentration of aggressive component, *i.e.* on c_{NaOH} in

solution, which was in the range 0.5—5.0 mol dm^{-3}, has been investigated and the inhibition efficiency has been evaluated (Fig. 3). It passes through the minimum at $c_{NaOH} = 4$ mol dm^{-3}. When taking the aggressivity of NaOH alone, it has maximum at 5 M-NaOH.

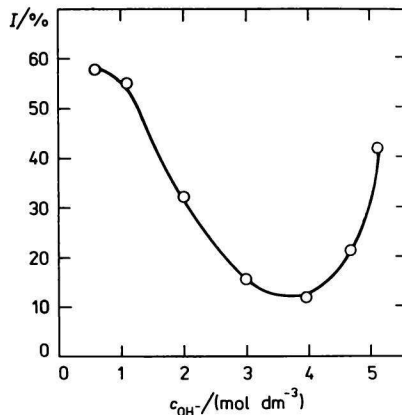Fig. 3. Dependence of inhibiting action of p-aminophenol on the NaOH concentration, $\theta = 25$ °C.

Influence of temperature on p-aminophenol inhibition efficiency

The dependence of Al reaction rate with 1 M-NaOH, inhibited with p-amino-phenol, has been investigated in the temperature range 25—45 °C. From the linearized temperature dependence log $\{v\}$ vs. $1/T$ the apparent activation energy and temperature coefficients (Table 2) have been evaluated. Comparing the systems pure [13] and inhibited it can be stated that the character of rate-deter-mining process does not change, i.e. the process occurs in the kinetic region also in the presence of inhibitor but with increased activation energy.

For qualifying the inhibition properties the deciding one is the ability of organic molecules to be adsorbed on the surface, which can be connected with donor properties of the molecule, i.e. with the total number of lone electron pairs which can be invested to forming the bond with Al surface atoms on one hand, and with

Table 2

Apparent activation energy and temperature coefficients of the aluminium dissolution rate in 1 M-NaOH with 10^{-2} M-p-aminophenol as an inhibiting agent

E^*		$\alpha = \dfrac{v_{\theta+10\,°C}}{v_\theta}$		
kJ mol^{-1}	θ/°C:	35—25	40—30	45—35
59.4		2.2	2.5	2.0

the magnitude of positive charge on the nitrogen atom of the functional group on the other.

If we consider the mechanism of inhibition it is necessary to take into account the structure of the molecule in the given reaction medium. The influence of alkaline medium on the phenols can be expressed by the equilibrium

$$C_6H_5OH + OH^- \rightleftharpoons C_6H_5O^- + H_2O \qquad (A)$$

which is shifted to the side of phenolates, having their negative charge delocalized between the benzene ring and oxygen atom (Fig. 4).
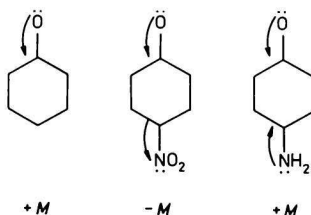

Fig. 4. Molecule of phenol, p-nitrophenol, and p-aminophenol with marked mesomeric effects.

For the adsorption and the inhibition too, the electron density on oxygen atom is substantial. The functional groups —NO$_2$ and —NH$_2$ have two types of action: they influence the electron density on oxygen atom on one hand and depress the electrostatic repulsion between the organic molecule, which represents an anion, and the negatively charged surface of the metal on the other one [14]. In this sense also the sequence of applied derivatives can be explained. Assuming that the strong $-M$ effect of —NO$_2$ group results in exhausting of electrons from the aromatic ring and thus also from the oxygen atom, *i.e.* it supports $+M$ effect of —OH group, then the molecule of p-nitrophenol is less electron-donating than the molecule of p-aminophenol, where $+M$ effect of the —OH group is compensated with $+M$ effect of —NH$_2$ group. The lowest effectiveness of phenol can be caused by the greatest repulsion, because its molecule does not contain the functional group with the positively charged centres.

Combined action of p-aminophenol and Ca^{2+} ions on the reaction rate of Al with NaOH

The action of Ca^{2+} ions on Al dissolution in alkaline medium, especially the increase of this action in combination of organic molecules with Ca^{2+} ions is known [14].

The question has been investigated using $CaCl_2$ ($c = 10^{-2}$ mol dm^{-3}) in different-ly aggressive media (using NaOH with $c = 0.5$—5.0 mol dm^{-3}) at 25 °C. For comparison Fig. 5 shows separately the effect of p-aminophenol alone, the influence of Ca^{2+} ions alone, and the combined action of p-aminophenol and Ca^{2+} ions. As seen from Fig. 5, the added amount of Ca^{2+} acted at all NaOH concentrations, so as p-aminophenol, inhibitively, but at increased NaOH concentration this effect has been lowered. The most expressive inhibition· effect, regardless of medium aggressivity, has been reached using both Ca^{2+} ions and p-aminophenol.

The combined action of Ca^{2+} ions and p-aminophenol has been investigated at constant concentration of p-aminophenol and the varying concentration of Ca^{2+} salt and reversely (Fig. 6) in order to find the optimum ratio of Ca^{2+} and
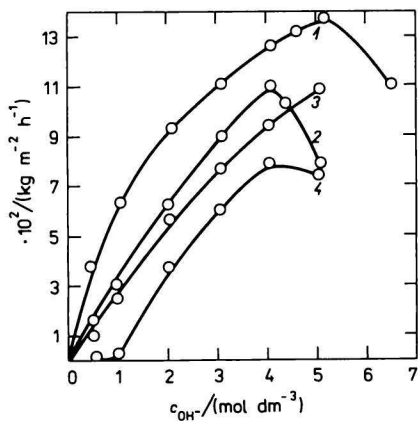

Fig. 5. Dependence of aluminium dissolution rate on the NaOH concentration, $\theta = 25$ °C.
1. Without any inhibitor; 2. 10^{-2} M-p-amino-phenol; 3. 10^{-2} M-Ca^{2+}; 4. 10^{-2} M-p-amino-phenol $+10^{-2}$ M-Ca^{2+}
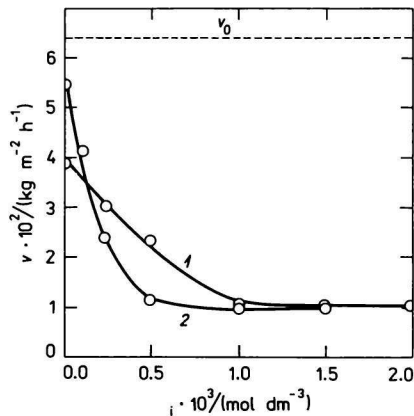
Fig. 6. Influence of concentration $c(Ca^{2+},$ p-aminophenol) on the dissolution rate of alu-minium at 25 °C.
1. $c = Ca^{2+}$ concentration for 1 M-NaOH $+ 10^{-3}$ M-p-aminophenol; 2. $c = p$-aminophenol con-centration for 1 M-NaOH $+ 10^{-3}$ M-$CaCl_2$.

p-aminophenol concentrations. The drawn dependences show the optimum ratio to be $1:1$. The marked increase of inhibiting action when using both the organic substance and calcium salt can be explained with the conjunction of electrostatic action and the donor-acceptor interactions [14]. The Ca^{2+} ions are preferentially adsorbed on the negative surface of aluminium. The negative charge of it is decreased (partly compensated), the adsorption of an organic anion is made easier and this anion creates the protective layer. Owing to the fact· that the ions Ca^{2+},

Al^{3+}, Cl^-, OH^- and the organic component are gathered in the phase boundary "surface—solution" it is probable that at optimum ratio of these components the chemisorbed complex compounds with protective properties are formed on the aluminium surface under the influence of the organic heteroatom and the Ca^{2+} cation.

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