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Note

Inhibitive Effect of Nicotine and Related Compounds toward Corrosion of Copper in Potassium Persulphate Solutions

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Inhibitory action of nicotine, nicotinic acid and nicotinamide towards corrosion of copper in 0.1 mol dm^{-3} $K_2S_2O_8$ solution has been investigated. The order of efficiency was found as follows: nicotinic acid > nicotine >nicotinamide. Nicotinic acid afforded 94% protection at 30 °C. Its efficiency was found independent of the temperature.

Desai and coworkers[1–3] studied the corrosion of various types of brass and the inhibition of corrosion in 0.2 mol dm^{-3} $K_2S_2O_8$ solutions. In the present investigation an attempt has been made to study the influence of molecular structure of nicotine and related compounds on the corrosion of copper in 0.1 mol dm^{-3} $K_2S_2O_8$ solutions.

EXPERIMENTAL

Copper specimens of size 6 × 3 cm (26 s. w. g.) were used. Preparation, testing and cleaning procedures were described previously[1]. For weight loss data 250 cm^3 of a 0.1 mol dm^{-3} $K_2S_2O_8$ solution were taken for the immersion of each specimen. Experiments were carried out at (30 ± 0.5) °C and (60 ± 0.5) °C. The potassium persulphate used was a Merck product. The solution of nicotinic acid was prepared in ethanol. The reproducibility of the percentage efficiency was ± 2%.

For the galvanostatic studies the copper specimes used had an effective area of 4 cm^2 (2 × 2 cm^2), the length of the handle being 4 cm. The handle, the back of the test coupons, and the platinum auxiliary electrode were coated with perspex and wax. The external current was supplied from a storage battery. The results are represented graphically in Fig. 1.

RESULTS AND DISCUSSION

Weight loss data are given in Table I. In the case of nicotine the inhibitive power slightly increases with increasing concentration of the compound and remains constant with increasing temperature. It is a poor corrosion inhibitor. It afforded only 38 and 36% protection at 30 and 60 °C, respectively. Nicotinamide afforded less inhibition than nicotine, *i. e.* only 25% protection at 30 °C, but its inhibitive power increased at 60 °C. The protective value slightly increases with an increase in concentration. Nicotinic acid acted as a very effective inhibitor at a concentration of 4.0×10^{-3} mol dm^{-3} (94 and 95% protection at 30 and 60 °C, respectively). Its inhibitive power increases with increasing concentration.

The galvanostatic measurements (Fig. 1) showed that in the case of nicotinic acid, the cathodic polarization was remarkable, the anodic polarization being negligible. The inhibition is predominantly under cathodic control.

In the present work, it is observed that the corrosion rate of copper in potassium persulphate solution increases rapidly with increasing temperature

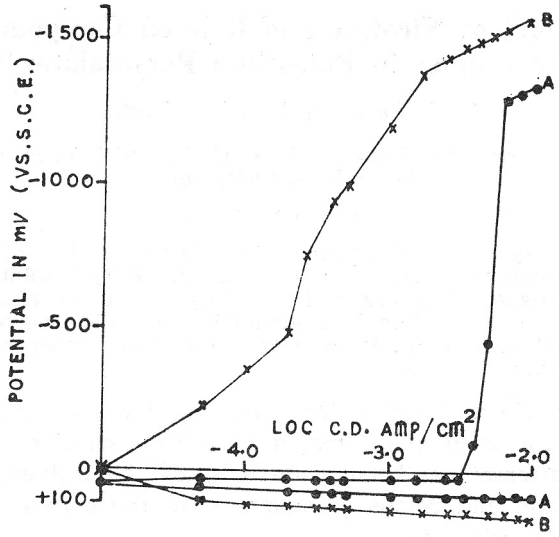

Fig. 1. — Effect of current densities on cathode and anode potential of copper: AA′ — 0.1 mol dm^{-3} $K_2S_2O_8$; BB′ — 0.1 mol dm^{-3} $K_2S_2O_8$ + 4.0 × 10^{-3} mol dm^{-3} nicotinic acid

TABLE I.

Weight loss data on inhibitory action of nicotine and related compounds towards corrosion of copper in 0.1 mol l^{-1} $K_2S_2O_8$

Specimen size 3 × 6 cm, duration 15 min, temperature (30 ± 0.5) °C

Concentration of compounds mol dm^{-3}	Nicotine		Nicotinamide		Nicotinic acid	
	Loss mg	% Inhibition	Loss mg	% Inhibition	Loss mg	% Inhibition
0.0	81.0	—	81.0	—	81.0	—
4.0 × 10^{-4}	55.0	32	70.0	14	30.0	63
8.0 × 10^{-4}	54.4	33	66.0	15	24.2	70
1.2 × 10^{-3}	53.2	34	64.8	20	21.3	74
2.0 × 10^{-3}	51.0	37	63.0	21	14.7	82
4.0 × 10^{-3}	50.0	38	60.8	25	4.0	94
					Temperature: (60 ± 0.5) °C	
0.0	220	—	220	—	220	—
4.0 × 10^{-4}	147	33	150	32	154	30
8.0 × 10^{-4}	146	34	149	32	39.4	82
1.2 × 10^{-3}	145	34	145	34	29.0	87
2.0 × 10^{-3}	144	35	144	35	15.0	93
4.0 × 10^{-3}	140	36	143	35	10.0	95

i. e. from 30 to 60 °C. The possibility of correlating structural characteristics with the inhibitive properties of the substances under study is justified by the fact that the metal–inhibitor interactions are based on chemisorption. The electron density of the organic polar group that can be considered as the reaction centre for the occurence of adsorption is obviously important, since it is possible to assume a bond of Lewis acid-base type, generally with the inhibitor as the electron donor and the metal as the electron acceptor. The strength of this bond depends on the characteristics of both adsorbent and adsorbate. In the present cases the nitrogen atom in regarded as the reaction centre of the chemisorption process. Hackerman[5] concluded that the greater the percentage of orbitals of the lone electrons on the nitrogen atom the more effective is the inhibitive action.

Nicotine gives quite poor inhibition compared to nicotinic acid. In nicotine, the adsorption should take place through the nitrogen atom in the six--membered ring, since the approach to the nitrogen in the five-membered ring may be sterically hindered, because of the —N—CH_3 substitution. The low inhibitive power of nicotine can be attributed to the low electron density on nitrogen because of delocalization of the electrons towards the ring.

In the case of nicotinamide the amide group has a less negative inductive effect compared to the —COOH group in nicotinic acid, and hence the electron density on the nitrogen of nicotinamide is smaller than on that of nicotinic acid.

In nicotinic acid —COOH group in β-position has a negative inductive effect. Therefore the electron density on nitrogen atom will be increased and hence the inhibitive action will also increase compared to the other two compounds.

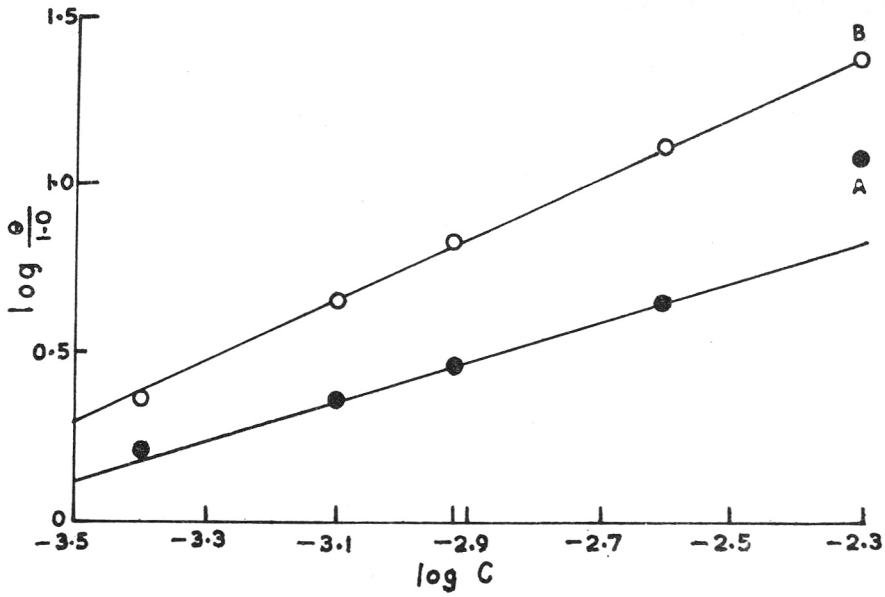

Fig. 2. — Langmuir's adsorption isotherms for nicotinic acid: A — at (30 ± 0.5) °C; B — at (60 ± 0.5) °C

Nicotinic acid has been found to be more effective than the other two compounds, hence the graph of log (C/mol dm^{-3}) *vs.* log $\frac{\Theta}{1-\Theta}$ was plotted (Fig. 2) in the case of nicotine, where Θ is the fraction of active sites of the metal surface covered by the adsorbed inhibitor (Θ was calculated by dividing the percentage of inhibition by hundred). The straight linear relationship between adsorption and log concentration of inhibitor supports Langmuir's adsorption isotherm. In the case of nicotinic acid the adsorption increases slightly at higher temperature.

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SAŽETAK

Inhibicijski učinak nikotina i srodnih spojeva na koroziju bakra u otopinama kalijeva persulfata

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Istraživan je inhibicijski učinak nikotina, nikotinske kiseline i nikotinamida na koroziju bakra u 0.1 mol dm^{-3} otopini $K_2S_2O_8$ i nađen redoslijed efikasnosti: moć od 94% pri 30 °C. Njezina efikasnost ne zavisi o temperaturi.

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