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Effects of some thioureas on the dissolution of aluminium alloys in nitric acid

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A study has been made on the inhibitive efficiency of some thioureas (urea, thiourea, phenylthiourea and naphthylthiourea), in the concentration range 0.0025 to 2%, in relation to dissolution of some aluminium alloys (1060, 1100, 3003 and 5052) in 20% nitric acid solution at temperatures of 25, 35 and 45° C. It was found that the structures of the thioureas affected the inhibitive efficiency but the mechanism of inhibition remained the same. The compounds exhibited maximum protection in the concentration range 0.025 to 0.03%. A gradual lowering in the efficiency of the compounds above the concentration of 0.03% has been observed. At the concentration of 1.5%, urea appears to be a corrosion accelerator and causes localized attack on the alloy surface; the other compounds still showed some degree of inhibition. The additives were most efficient towards 1060 alloy, followed by 1100, 3003 and 5052 alloys. The protecting power of all the compounds other than urea was found to improve with increase in temperature. All the compounds appeared to inhibit corrosion by adsorbing at cathodic sites. A distinctive hump (i.e. a current maximum) is observed in the steady-state potentiostatic anodic polarization curves of the alloys. This hump is found to be affected by the inhibitors. At higher concentrations, the compounds act as cathodic depolarizers, which is confirmed by measuring steady-state corrosion potentials and cathodic polarization diagrams.

1. Introduction

Aluminium alloys are used as reaction vessels in many industries where nitric acid is a direct reactant or is produced as a by-product. In very high and low concentrations of nitric acid, the corrosion rate of aluminium alloys is not very great, but in the concentration range 20–40%, the rate of corrosion of commerical-grade 1100 alloy is of the order of 4.0 mm yr^{-1} even at room temperature [1]. The rate is much increased with increase in temperature. In our earlier papers, we have reported that some organic compounds act as inhibitors for the aluminium–nitric acid system [2–6]. In the present work the inhibitive effects of some substituted thioureas are determined and a possible mechanism for their action is suggested.

2. Experimental

Nitric acid, BDH Analar grade, was used for the preparation of the solutions. Thiourea and urea were also of this grade, while phenylthiourea and naphthylthiourea were synthesized in the laboratory by standard methods and their purities confirmed by their sharp melting points. The solutions were prepared in doubly distilled water. Aluminium alloys in sheet form were supplied by M/S Hindalco, Mirzapur (UP), India, with compositions as given in Table 1.

Specimens used for the weight-loss experiments measured 75 mm x 50 mm. They were polished successively with 1/0 to 4/0 grades of emery paper, followed by cleaning with benzene and

Table 1. Percentage of alloying elements in the aluminium sheet

Alloy	*Si*	*Fe*	*Mn*	*Mg*	*Cu*
1060	0.12	0.02	0.04	–	–
1100	0.13	0.52	0.068	0.021	0.01
3003	0.16	0.58	0.78	–	–
5052	0.17	0.04	–	2.30	–

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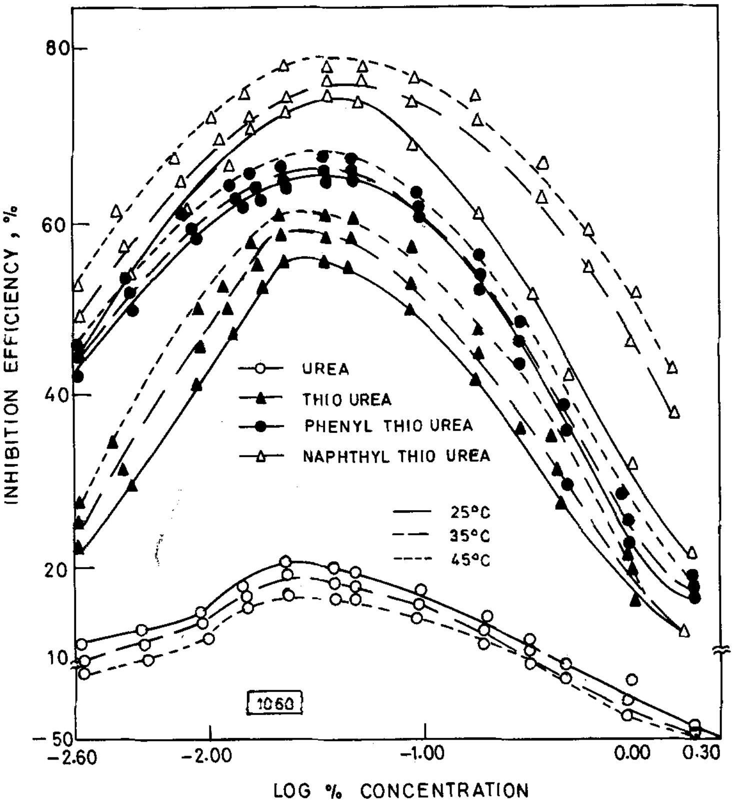

Fig. 1. Variation of percentage efficiency with concentration of inhibitor for alloy 1060.

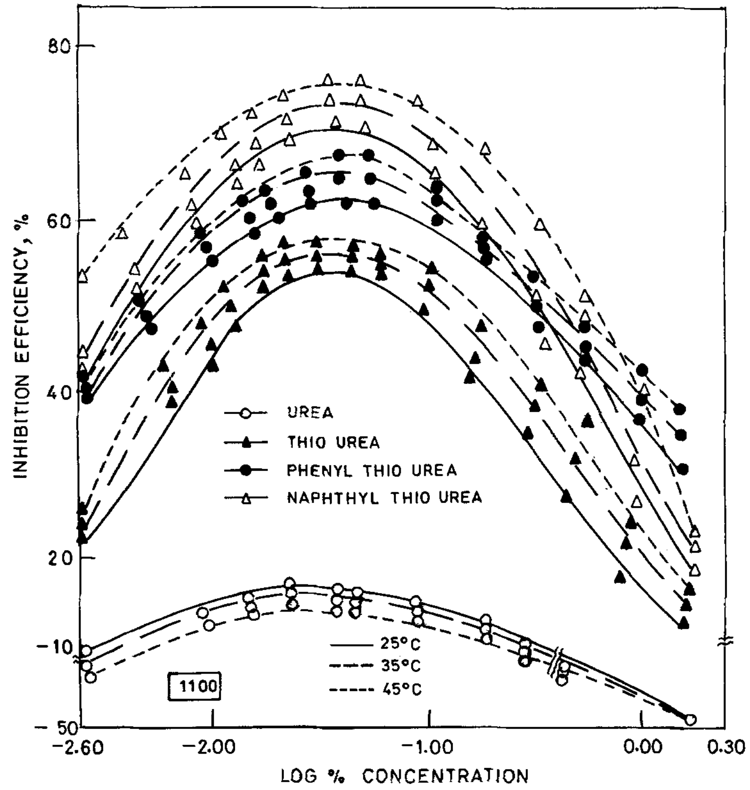

Fig. 2. Variation of percentage efficiency with concentration of inhibitor for alloy 1100.

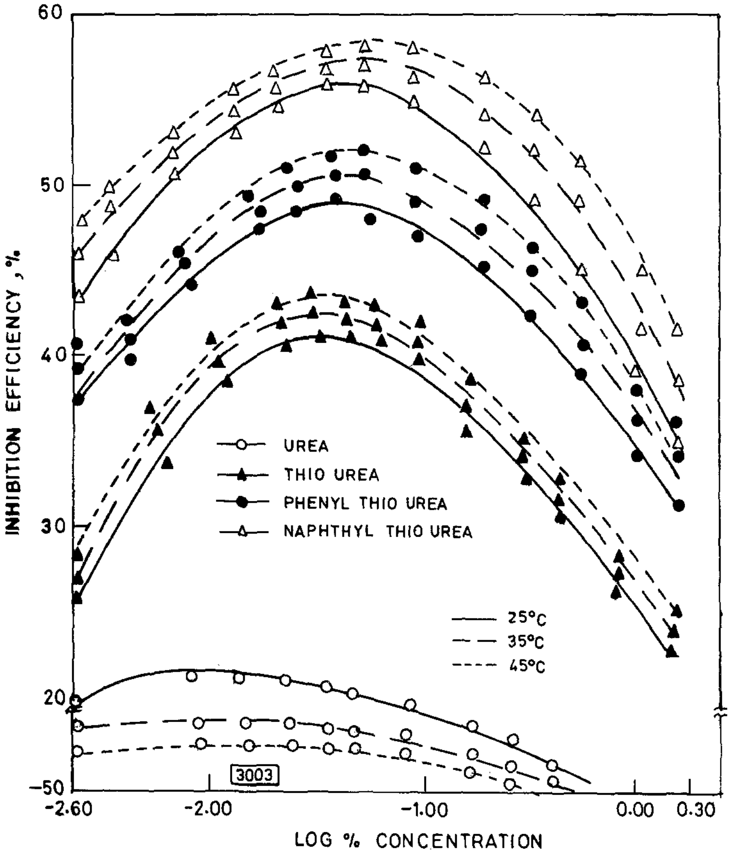

Fig. 3. Variation of percentage efficiency with concentration of inhibitor for alloy 3003.

soap, and finally with acetone, and were stored in a vacuum desiccator. The experiments were performed in 500 cm^3 Corning glass beakers (without lid), containing 300 cm^3 of 20% nitric acid solution (unless otherwise stated) at 25, 35 and 45° C containing different concentrations of the inhibitors. The weight losses were determined after cleaning the corroded specimens with 70% nitric acid for 5 min and then washing them thoroughly with distilled water and drying.

The polarization studies were carried out using flag-shaped, 10 mm x 10 mm electrodes, with a side tag of length 40 mm. Part of the tag adjacent to the electrode surface was blocked with paraffin wax. The experiments were carried out in a 200 cm^3 Pyrex glass cell containing 100 cm^3 of solution (with and without inhibitors). Different values of potential were impressed on the electrode surface using a Wenking (laboratory model) potentiostat and the resulting steady-state currents were recorded. All experiments were carried out in an air thermostat (± 0.2° C).

3. Results and discussion

Figs. 1 to 4 show the inhibition efficiencies exhibited by urea, thiourea, phenylthiourea and naphthylthiourea at different concentrations and temperatures towards the different aluminium alloys. Naphthylthiourea is found to be the most effective inhibitor, followed by phenylthiourea, thiourea and urea. The degree of inhibition afforded by various compounds is attributed to their basicity and the surface area projected by different inhibitors on the metal surface [7, 8]. All the inhibitors are most effective towards 1060 alloy followed by 1100, 3003 and 5052 alloys. This may be due to the presence of various alloying elements in the alloys which may influence the extent of the adsorption of the compounds on their surface. With the rise in temperature from 25 to 45° C inhibition efficiency increased for all the four alloys. Ivascanu and Sfilip [9] and Hoar and Holliday [10] have reported similar behaviour of the thioureas, but Putilova [11] observed a

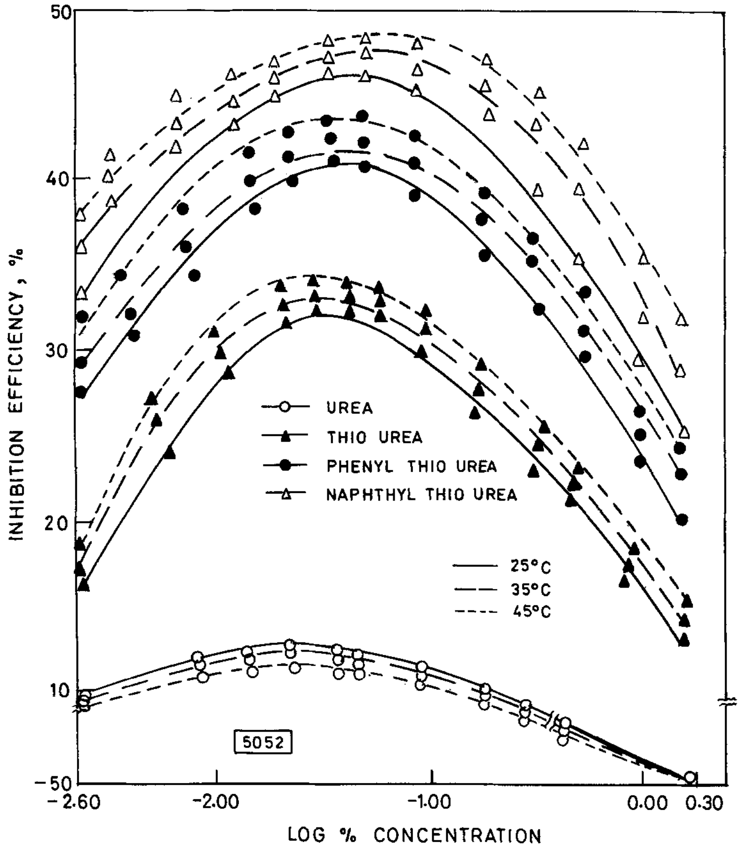

Fig. 4. Variation of percentage efficiency with concentration of inhibitor for alloy 5052.

reverse effect. We have also observed improvement in the inhibition efficiencies of thioureas with rise in temperature [2, 3]. Although there is no satisfactory explanation for this increase in the efficiency of the compounds, it seems probable that with increase in temperature, there occurs some chemical change in thiourea inhibitors leading to an enhancement in the electron density at the active centres which improves the effectiveness of the compounds.

It is further seen from Figs. 1 to 4 that all the compounds are most effective at a concentration around 0.03%. Above this concentration a gradual lowering in the efficiencies of the inhibitors has been noted. At higher concentration of urea (> 1.5%), the compound acts as a corrosion stimulator towards all the four alloys studied but the other three inhibitors show some degree of inhibition even at this concentration. The percentage efficiencies have, however, appreciably diminished. The scanning electron microscopy surface studies of the specimen subjected to nitric acid solutions containing higher concentrations (2%) of the compounds exhibited the formation of severe pits on the surface of the alloys.

In order to understand the action of the inhibitors, the steady-state corrosion potentials were measured and cathodic polarization studies were carried out for the inhibitors. The plots for 1060 alloy are shown in Figs. 5a and b. The other alloys also had similar characteristics. It is seen from Fig. 5 that the corrosion potentials in the presence of the compounds initially increase in the active direction, then above 0.025% the potentials move in a negative direction. This result, in conjunction with the weight-loss data (Figs. 1 to 4), indicates that the compounds depolarize the cathodic reactions. This has further been confirmed by the cathodic polarization of one alloy (1060) in the presence of 2% of the compounds (Fig. 5b). An inspection of the polarization curves of the figure shows that the curves in the presence of the inhibitors are shallow as compared to the curve of the blank solution.

The cathodic and anodic polarization curves for 1060 alloy in the presence of 0.025% (opti-

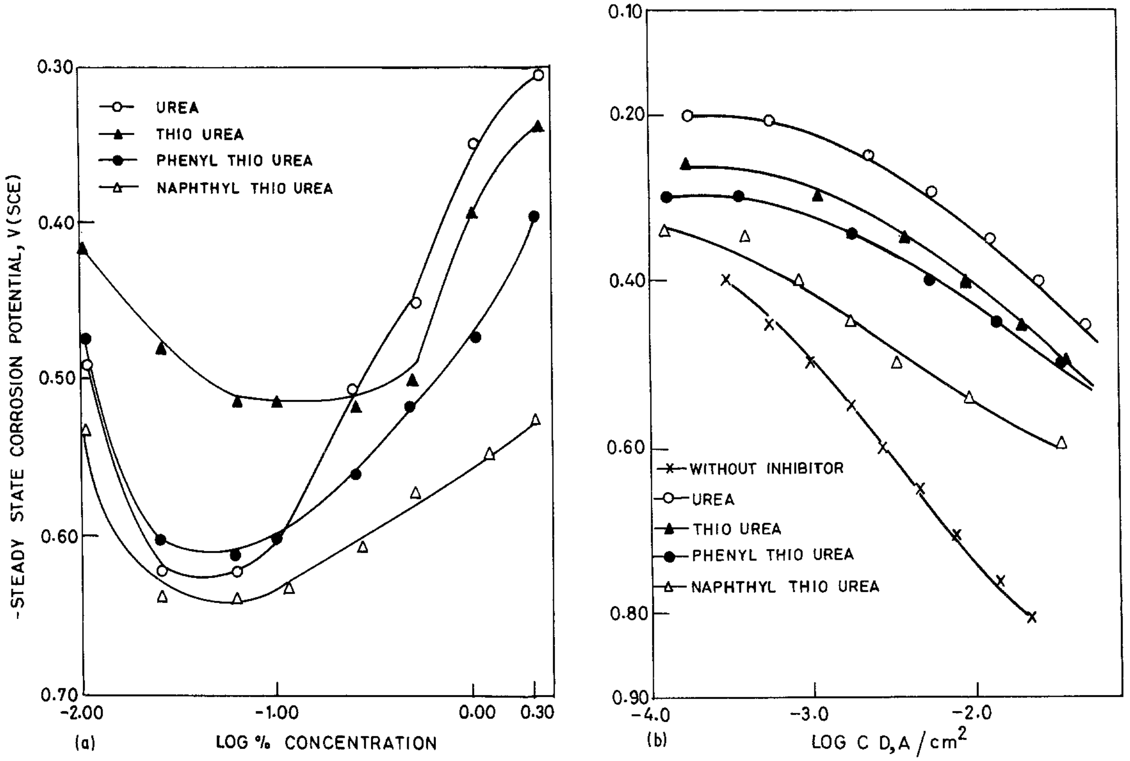

Fig. 5. (a) Variation of the steady-state corrosion potential with concentration of inhibitor. (b) Cathodic polarization diagrams in the presence of 2% of the compounds.

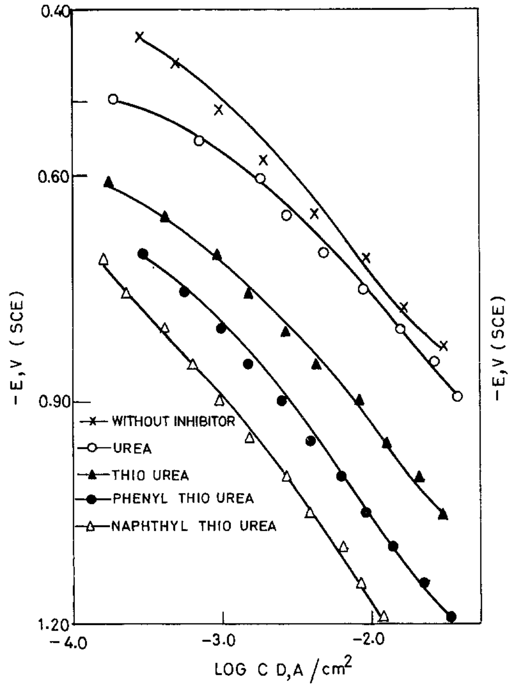

Fig. 6. Cathodic polarization diagrams in the presence of 0.025% of the compounds.

mum concentration as judged from weight-loss studies) of the inhibitors are shown in Figs. 6 and 7. It may be noted that in the presence of each of the compounds the polarization curves are almost parallel to the curve for the blank solution. This indicates that the adsorption of the inhibitors (at lower concentrations) in the double layer does not change the mechanism of the cathodic and anodic reactions occurring at the metal surface. The cathodic curves in the presence of the inhibitors have been shifted towards the active direction indicating their predominant action at the local cathodes. The inhibited anodic curves have been found to be shifted towards the left, i.e. in the lower current density region, which may be attributed to the presence of a protective film of inhibitor on the metal surface. The critical current density required for the passivation of aluminium alloys has been found to be lowest in the presence of naphthylthiourea followed by phenylthiourea, thiourea and urea, which is exactly in the same order as observed by the weight-loss technique.

Current densities required for the passivation

Table 2. Minimum current density required for the passivation of aluminium alloys in the absence and presence of 0.025% of the inhibitors. Temperature: 25° C

Inhibitor	*Current density required for passivation* (mA cm^{-2})			
	1060	*1100*	*3003*	*5052*
Blank solution	1.050	0.970	0.900	0.950
Urea	0.950	0.950	0.885	0.925
Thiourea	0.850	0.885	0.825	0.900
Phenylthiourea	0.750	0.800	0.775	0.875
Naphthylthiourea	0.600	0.725	0.725	0.850

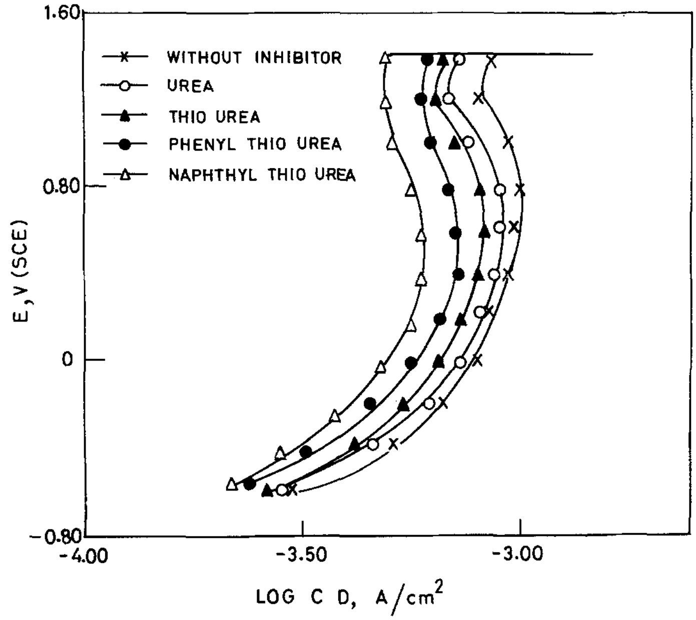

Fig. 7. Anodic polarization curves in the presence of 0.025% of the inhibitors.

of the alloys in the absence and the presence of 0.025% of the inhibitors, at a temperature of 25° C, have been summarized in Table 2. It is found that the lowering of the current densities is pronounced in the case of 1060 alloy followed by 1100, 3003 and 5052 alloys, the percentage efficiency afforded by the inhibitors for the alloys is also in the same order (Figs. 1 to 4).

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