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The Inhibition of Mild Steel Corrosion in an Acidic Medium by the Juice of *Citrus Paradisi* (Grapefruit)

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ABSTRACT

The corrosion inhibition of mild steel in HCl solution in the presence of the juice of *citrus paradisi* (grapefruit) in the temperature range 30-50°C was studied using the weight loss technique. The juice of *citrus paradisi* was found to act as a corrosion inhibitor in the acid environment. The inhibition efficiency increases with increase in inhibitor concentration but decreases with an increase in temperature. The inhibition is attributed to the adsorption of a component in the juice onto the surface of the mild steel.

Keywords: Citrus paradisi; mild steel; corrosion inhibition; adsorption

INTRODUCTION

Iron and its alloys (e.g. steels) are exposed to the action of acids in industry. Processes in which acids play a very important part are acid pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid de-scaling [1,2]. The exposures can be most severe but in many cases, corrosion inhibitors are widely used in industry to prevent or to reduce the corrosion rates of metallic materials in these media.

Because of the toxic nature and high cost of some chemicals currently in use it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered as a good source for this purpose [3]. The possible replacement of some expensive chemicals as corrosion inhibitors for metal in acid cleaning process by naturally occurring substances of plant origin has been studied, amongst others by Hosary and Saleh [3].

Natural products of plant origin contain different organic compounds (e.g. alkaloids, tannins, pigments, organic and amino acids) and most are known to have inhibitive action [3,4]. In our earlier communication [5] it was found that *cocos nucifera* (coconut) juice inhibits the corrosion of mild steel in hydrochloric acid solution (HCl). Ekpe et al. [5] and Saleh et al. [6] used the aqueous extracts of some natural products (fruits, fruit shells, leaves, seeds) as corrosion inhibitors of some metals.

Citrus species are utilized in many industries for the production of the various brands of citrus juices [7]. The juice is also rich in vitamin C, folic acid and significant quantities of other vitamins, pectins, flavonoids among others [7,8]. In particular, nootkatone contributes to the bitter flavour of the grapefruit [7]. Nitrogenous compounds are also present to the extent of 0.05 – 1.0% mostly as free amino acids – asparagines, alanine, arginine, aspartic acid, glutamine, glutathione, histidine, betaine, cysteine, proline, serine and stachydrine [5,7, 8]. The principal acid in citrus fruits is citric acid (80 – 90% of the total acids). Others are malic, tartaric, benzoic, succinic, quinic, oxalic and formic acid [7].

The fruit juice of *citrus paradisi* may be of use in the production of non-toxic inhibitors to replace toxic corrosion inhibitors. For example, species present in the juice of *citrus paradisi*, especially nitrogen containing organic compounds, may adsorb on the metal and block the active sites on the surface, thereby reducing the corrosion rate in acid environment. The aim of this study was, therefore, to determine the inhibition efficiency of the fruit juice of *citrus paradisi* as an inhibitor for the corrosion of mild steel in 0.5M HCl. Weight loss technique was employed to carry out the measurements.

EXPERIMENTAL PROCEDURES

Material Preparation

The composition and preparation of mild steel coupons are described in detail as reported previously [10]. All test solutions were prepared from analytical grade reagents and double-distilled water. The *citrus paradisi* juice was used as an additive for this investigation. The additive concentration of 0.5, 1.0, 1.5, 2.0 and 2.5% volume/volume percent (v/v) were prepared in 0.5M HCl (corrodent) solutions at 30, 40 and 50°C.

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Weight loss measurement

Previously weighed mild steel coupons were immersed in 250ml open beakers containing 0.5M HCl solution (blank) without additive, and with additive concentrations of 0.5, 1.0, 1.5 2.0 and 2.5% in 0.5M HCl. The variation of weight loss was followed at 3 hour intervals progressively over15 hours at 30, 40 and 50°C. The procedure for weight loss determination was similar to that reported previously [9,10].

The inhibition efficiency (1%) was determined from [11]:

$$I\% = (W_b - W_i) / W_b \times 100\% \qquad \ldots (1)$$

Where W_b and W_i are the weight loss of mild steel per unit area (mg cm^{-2}) of coupons in the corrodent (blank) and corrodent-inhibitor systems.

RESULTS AND DISCUSSION

Effect of *citrus paradisi* juice on the corrosion of mild steel in HCl solution

Figure 1 shows the variation of the weight loss with time for mild steel corrosion in 0.5M HCl and 0.5M HCl with various concentrations of *citrus paradisi* juice at 30°C. Similar trends were observed at 40 and 50°C. From the variation of weight loss with time of immersion in HCl solution without additive, compared with mild steel in HCl solution containing the additive at 30°C (Fig. 1), there is a general decrease in weight loss, signifying the inhibition of the acid corrosion of mild steel. The extent of the decrease in weight loss was found to depend on the concentration of additive. Figure 2 also confirms that the additive is a corrosion inhibitor; since there was a general decrease in corrosion rate (mg cm^{-2} h^{-1}). The corrosion rate as a function of additive concentration and at different temperatures (30 – 50°C) is shown in Figure 2. The corrosion rate decreases with increasing concentration of *citrus paradisi* juice at each of the temperatures. This confirms that the presence of the additive in 0.5M HCl solution inhibits the corrosion of mild steel by HCl and that the degree of corrosion inhibition depends on the amount of the *citrus paradisi* juice present.

Figure 3 illustrates the variation of the inhibition efficiency, I%, versus the concentration of the additive at 30, 40 and 50°C. The inhibition efficiency increases with increasing the concentration of the inhibitor. As shown in figure 3 inhibition efficiency increases with increase in concentration of the inhibitor up to 2.5%v/v at a maximum efficiency of 45.6%, 37.3% and 24.1% at 30%, 40 and 50°C respectively.

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Figure 3 shows the effect of increasing temperature from 30°C to 50°C on the inhibition efficiency. From the plot of the inhibition efficiency with concentration of the inhibitor and from the result given in Table 1, it was observed that the efficiency decreased with increasing temperature. On this basis it is suggested the inhibition mechanism is physi-sorption of the inhibitor on the metal surface.

Adsorption considerations

The surface coverage, θ, at each concentration of inhibitor was evaluated using the equation:

$$\theta = 1 - W_b/W_i \qquad \ldots \ (2)$$

Where W_b and W_i are the weight loss in corrodent and corrodent-inhibitor systems respectively at constant temperature.

The surface coverage data and corrosion rate are recorded in Table 2. The experimentally observed linear decrease in corrosion rate as seen in Table 2 with surface coverage, θ therefore supports the observation that the inhibitor inhibits corrosion by being adsorbed at the reaction sites on the mild steel surface [6]. A curtailment of these reaction sites would therefore lead to a reduction in the corrosion rate and this may be precisely how the inhibitor achieves inhibition by being adsorbed on the mild steel surface at the reaction sites

Figure 4 shows the plot of logarithm inhibition efficiency (I%) versus logarithm inhibitor concentration for the additive at 30, 40, and 50°C - a linear plot is obtained which obeys the Freundlish isotherm.

CONCLUSIONS

From the present investigation, the following conclusions can be drawn.

1. The efficiency of inhibition of mild steel in HCl is a function of the concentration of *citrus paradisi* juice.

2. The inhibition by this additive increased with increased additive concentration and decreased temperature.

3. *Citrus paradisi* fruit juice is a corrosion inhibitor for mild steel in HCl solution and can be used to replace toxic chemicals provided only modest (<50%) inhibition is required.

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TABLE 1: The effect of grapefruit (*citrus paradisi*) juice on mild steel corrosion in 0.5M HCl

Inhibitor Conc. v/v	Inhibitor efficiency (I%)		
	30°C	40°C	50°C
0.0%	–	–	–
0.5%	30.6	18.2	9
1.0%	33.3	21.4	10.3
1.5%	41.4	29.0	15.6
2.0%	43.1	34.1	20.3
2.5%	45.6	37.3	24.4

TABLE 2: Surface coverage, θ and corrosion rate during corrosion of mild steel in 0.5M HCl containing various concentrations of grapefruit (*citrus paradisi*) juice at 30°C

Concentration of inhibitor v/v%	Surface Coverage, θ	Corrosion rate (mg cm^{-2} h^{-1})
0.5%	0.31	0.174
1.0%	0.33	0.167
1.5%	0.41	0.147
2.0%	0.43	0.142
2.5%	0.46	0.136

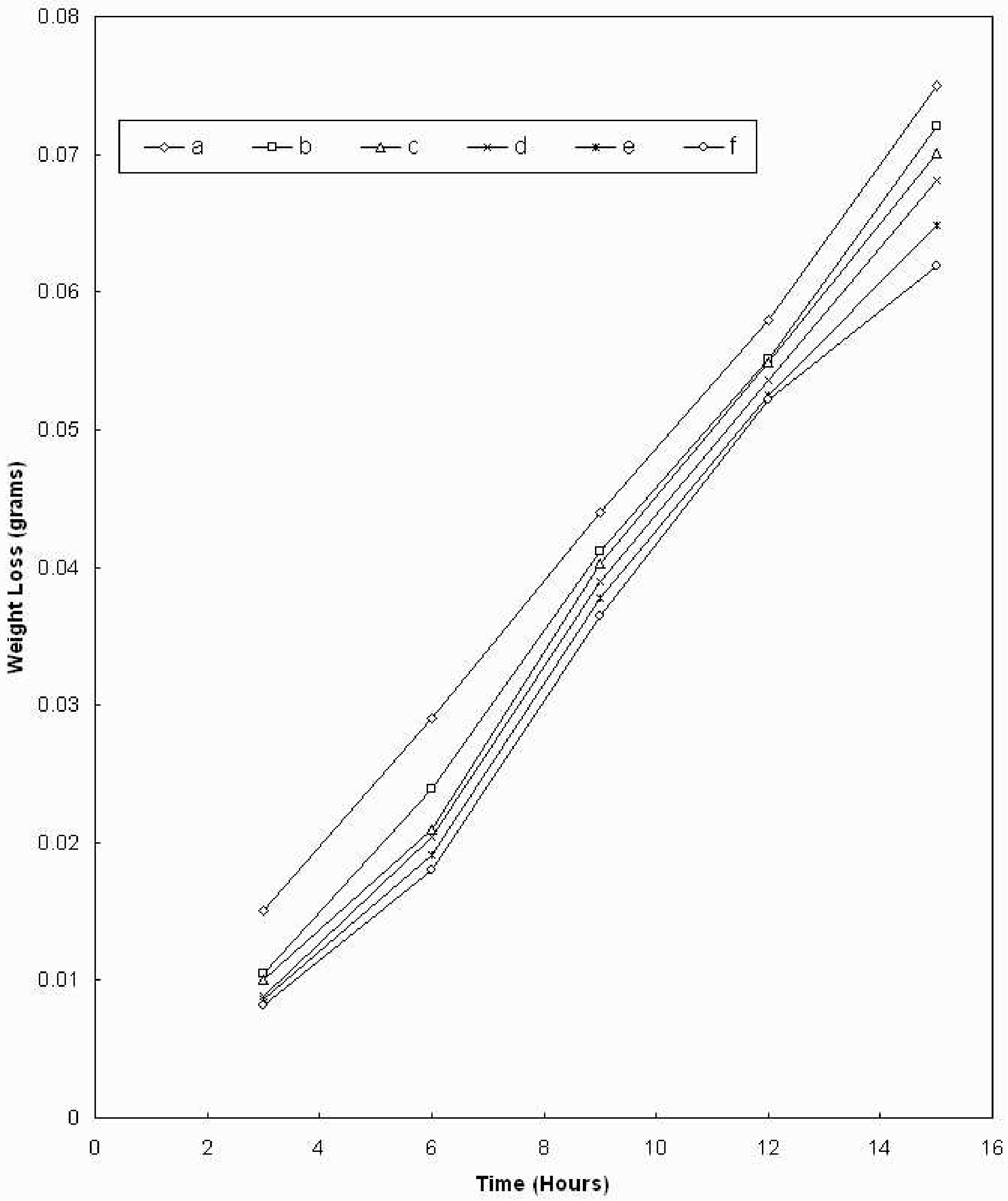

Figure 1: Variation of weight loss with time for mild steel coupons in 0.5M HCl solution containing various concentrations of *citrus paradisi* fruit juice: (a) 0.0% v/v, (b) 0.50%v/v, (c) 1.0%v/v, (d) 1.50%v/v, (e)2.0%v/v and (f) 2.5% v/v

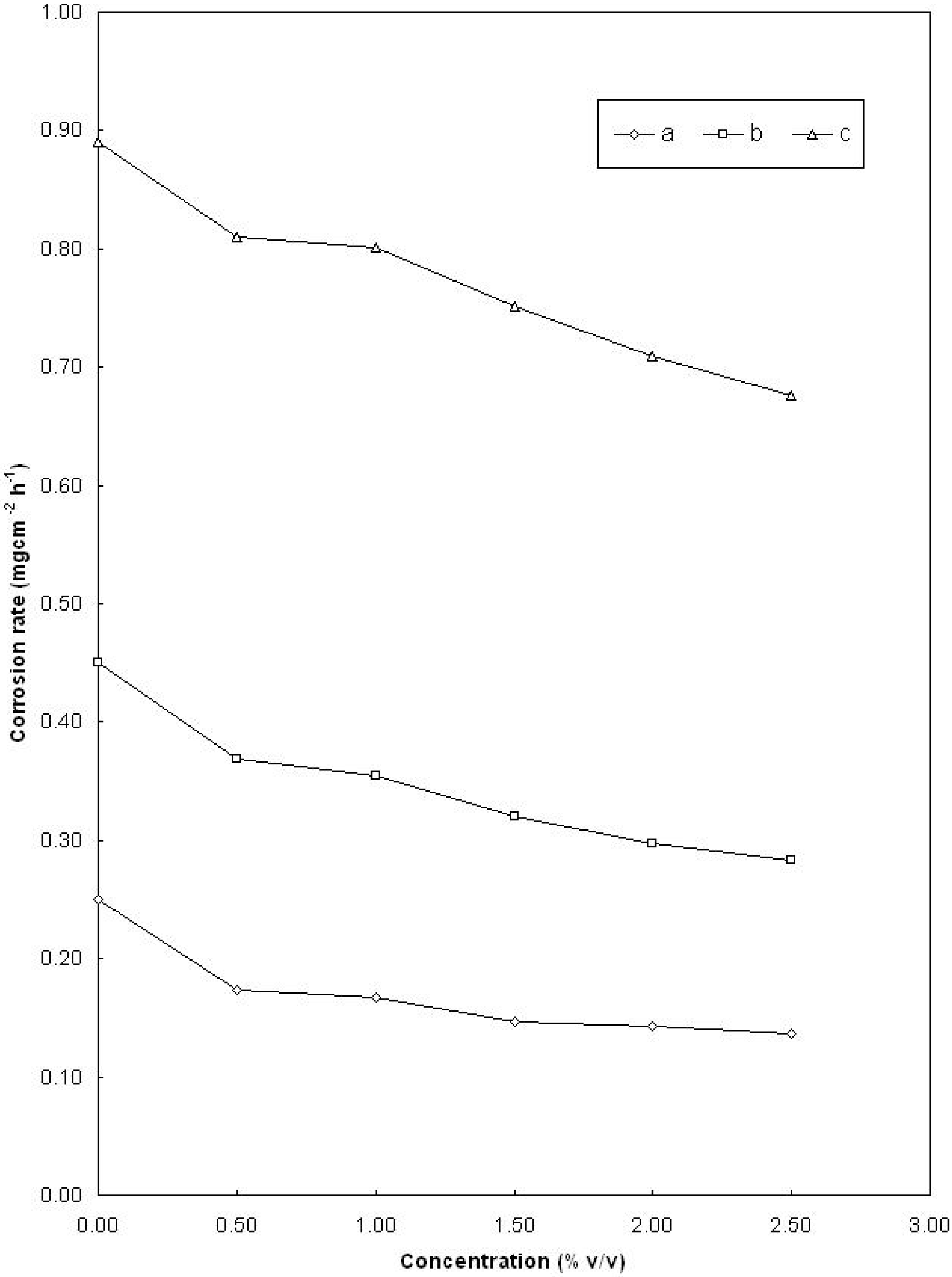

Figure 2: Variation of the corrosion rate with the concentration of *citrus paradisi* fruit juice for mild steel in 0.5MHCl at different temperatures: (a) 30°C (b) 40°C and (c) 50°C

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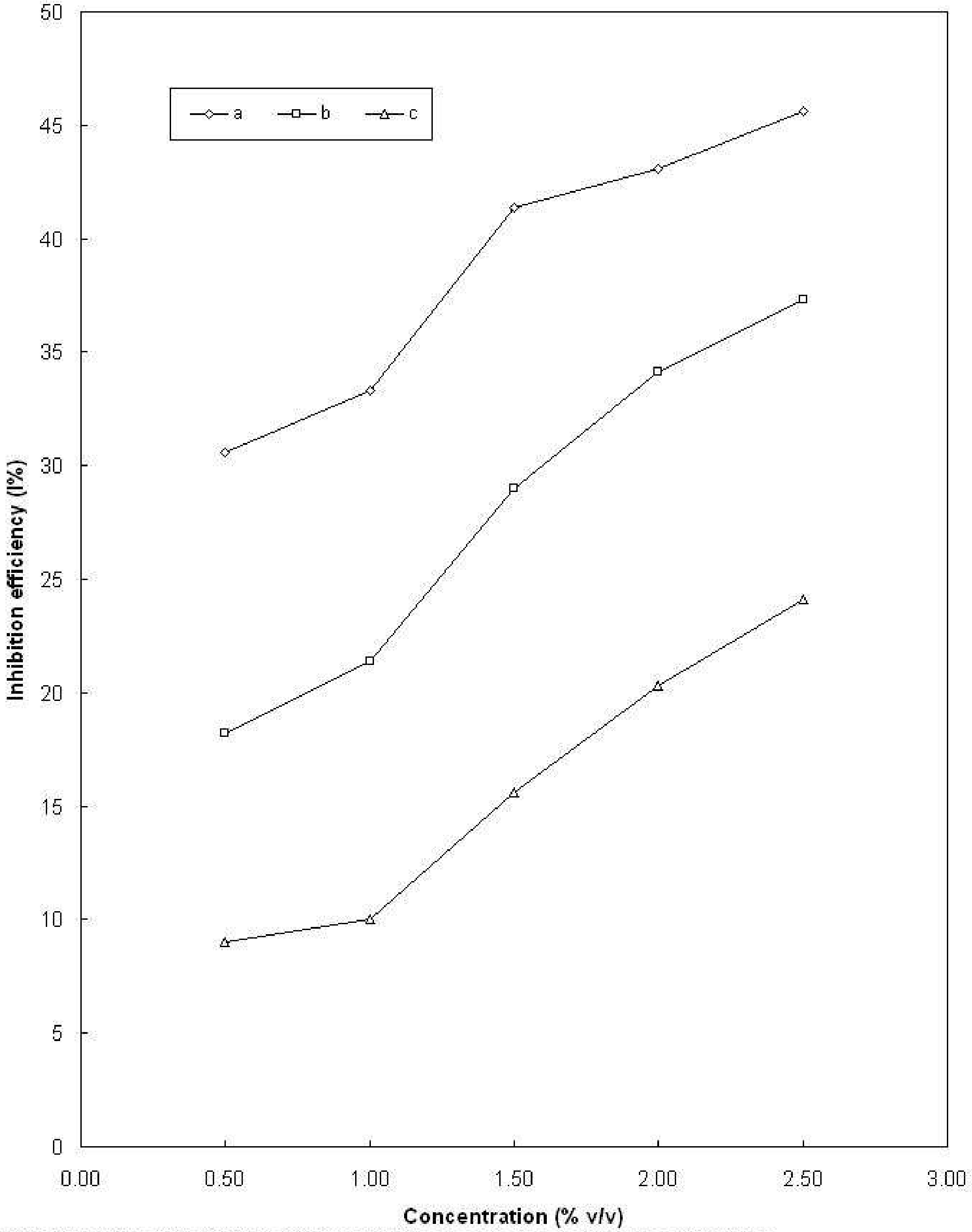

Figure 3: Variation of the inhibition efficiency with the concentration of *citrus paradisi* fruit juice for mild steel in 0.5MHCl at different temperatures: (a) 30°C (b) 40°C and (c) 50°C

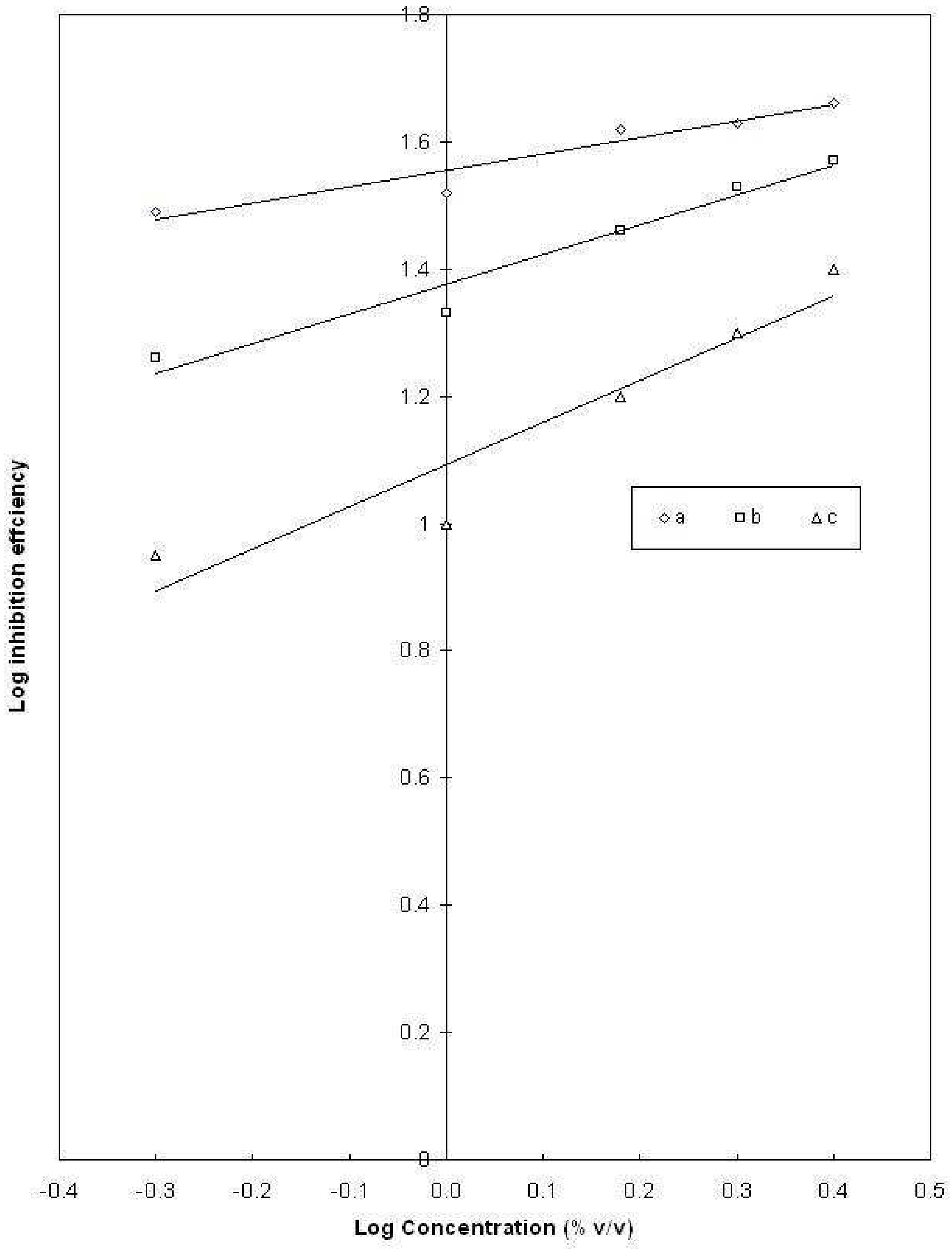

Figure 4: Plot of Log inhibition effieciency with log inhibitor concentration at different temperatures: (a) 30°C (b) 40°C and (c) 50°C