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PEROXYMOLYBDATES PREPARATION, CHARACTERIZATION AND MILD STEEL CORROSION INHIBITION

C. M. MUSTAFA, D. A. BEGUM AND M. MOHIUDDIN

Department of Applied Chemistry and Chemical Technology, University of Rajshahi, Rajshahi 6205, Bangladesh

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Six peroxymolybdates were prepared by varying pH (5, 6 & 7) and ratio between hydrogen peroxide and molybdate (2:1 & 1:1). These were characterized as mono-, di-, mixed and polymerized peroxymolybdates. The best corrosion inhibition of mild steel in simulated cooling water (SCW) was obtained by diperoxymolybdate. This shows the beneficial effect of peroxy group addition to molybdate. Other peroxymolybdates did not show improved corrosion inhibition compared to the molybdate. This was due to the decomposition of these peroxymolybdates before reaching the mild steel surface. With citric acid, peroxymolybdates provided highly improved corrosion inhibition of mild steel in SCW and the best result was obtained with monomeric monoperoxymolybdate. These results as well as the mechanisms of corrosion inhibition were discussed.

Key words: Mild steel, Peroxymolybdate, Corrosion inhibitor.

Introduction

The importance of soluble molybdate compounds as corrosion inhibitor has greatly increased due to stringent restrictions on the effluent disposal problem associated with the effective chromate-based corrosion inhibitors. Early reports [1-3] show that molybdate was effective and comparable to chromate in the aerated aqueous system. It has been established in recent works [4,5] that molybdate is only effective in the presence of oxygen. It is explained [6] that weak oxidizing property of molybdate is responsible for weak corrosion inhibition in de-aerated media.

Peroxymolybdate compounds possess important role in catalytic oxidation and are stronger oxidizing substances than molybdate [7]. These compounds, due to strong oxidizing property, may provide better corrosion inhibition to the metal in the aqueous system. Citric acid was reported [8] to have corrosion inhibition property for mild steel and was claimed to improve the inhibition efficiency of molybdate [9].

From the above perspectives peroxymolybdate compounds have been prepared, characterized and investigated as corrosion inhibitors, with or without the addition of citric acid, for mild steel in the aqueous system. Weight loss method has been adopted for the measurement of corrosion rate. The reliability of the method was enhanced by using spectrophotometric method for measuring the soluble iron produced during corrosion.

Experimental

Chemicals and reagents. All chemicals used for this work were of analytical grade and no effort was made to purify them further.

Preparation of peroxymolybdates. Peroxymolybdate compounds were prepared [7,10] by slow addition of 30% hydrogen peroxide in aqueous 1M sodium molybdate solution with constant stirring for a period of one hour. This was then evaporated to 1/10th of the original volume at $65 \pm 5^\circ\text{C}$. The crystalline peroxymolybdates were filtered and washed with absolute alcohol. Six different products were prepared by the reaction of hydrogen peroxide with sodium molybdate at pH values 5, 6 and 7 and at H_2O_2 -Mo ratios 2:1 and 1:1. IR spectra of the compounds (as KBr discs) were measured with a Pye-Unicam SP3-3000 IR Spectrophotometer.

Corrosion experiments. Inhibitor solutions were made by dissolving 500 ppm peroxymolybdates and molybdate in distilled water or in simulated cooling water (SCW) (Composition: 495 ppm NaCl, 520 ppm Na_2SO_4 , 170 ppm NaHCO_3 and 66 ppm Na_2CO_3) alone or with 500 ppm citric acid [11,12]. pH of each solution was adjusted to 8.5 by using either dilute solution of NaOH or H_2SO_4 . Corrosion measurements were carried out on 1 mm thick and 4 cm by 4 cm sized commercial grade mild steel coupons. The coupons were abraded with a fine grade emery paper to remove adhered dirt and rust, polished on a polishing wheel using Griffin's fast cutting grade 5/50 alumina powder, cleaned with running tap water and degreased with acetone. Air dried coupons were stored in a desiccator containing silica gel for subsequent experiment.

For the corrosion experiment coupons were suspended in 400 ml inhibitor solution in a 500 ml stoppered conical flask for the specific periods. Care was taken that the coupons were completely immersed in the solution and did not

touch side walls or bottom of the beaker. At the end of soaking adhered solid corrosion products were scrubbed in the inhibitor solution with a nylon brush. The solid mass was dissolved with HCl and heated (whenever necessary). Iron concentration in the solution, due to corrosion, was measured with an ANA Model 75 Spectrophotometer (Tokyo Photoelectric Co.Ltd., Japan) using thiocyanate method given elsewhere [13,14]. Corrosion rate in mdd ($\text{mg dm}^{-2}\cdot\text{day}^{-1}$) was calculated from total amount of iron in mg in the solution (due to corrosion), total surface area of the coupon in dm^2 , and soaking time in days. Corrosion potentials of the mild steel coupons were measured by a digital multimeter (Hioki 3236 Digital Hi Tester, Japan) using saturated calomel electrode (SCE) with a Luggin probe. All corrosion measurements were carried out atleast in duplicate.

Results and Discussion

Characterization of Peroxymolybdates. Table 1 shows conditions for the preparation of peroxymolybdates. Peroxymolybdates I, II and IV were pale yellow crystalline compounds, and others were white crystals. It has been reported [7,10,15] that number of peroxy groups (mono to tetra or mixed peroxy groups) in the peroxymolybdates depend on the hydrogen peroxide to molybdate ratio and pH of the solution. High ratio and pH lead to the formation of higher peroxymolybdates. In this work three pH values (5, 6 & 7) and two H_2O_2 -Mo ratios (2:1 & 1:1) were used for the preparation of six compounds. As not more than four stoichiometric peroxy compounds are possible in monomeric state, therefore, it is likely that some of the prepared compounds contain mixed peroxy groups or are polymeric. Figure 1 shows planar representation of molybdate and four possible peroxy-molybdates. It is evident that atleast for tetra- and triperoxy compounds both double and ionic bonds of molybdate are utilized in the peroxy formation. In the literature peroxy formation is mentioned through both of these bonds [16].

TABLE 1. CONDITIONS FOR THE PREPARATION OF PEROXYMOLYBDATES.

Conditions for preparation			
H_2O_2 -Mo ratio	pH	Colour	Compound
2	5	Pale yellow	Peroxymolybdate I
2	6	Pale yellow	Peroxymolybdate II
2	7	white	Peroxymolybdate III
1	5	Pale yellow	Peroxymolybdate IV
1	6	white	Peroxymolybdate V
1	7	white	Peroxymolybdate VI

The temperature was $30\pm 2^\circ\text{C}$

IR data of the prepared peroxymolybdates are shown in Table 2. The band at 920.5 cm^{-1} , attributed to $(\text{Mo}=\text{O})$ mode [17] was found for all compounds except peroxymolybdate III. Metal peroxy grouping gives rise to three diagnostic vibrational modes. Bands at 840.5 cm^{-1} , 630.5 cm^{-1} and 555.60 cm^{-1} were observed in all compounds. These are due to $\nu(\text{O}-\text{O})$, $\nu(\text{Mo}-\text{O})_{\text{asym}}$ and $\nu(\text{Mo}-\text{O})_{\text{sym}}$ modes respectively as reported elsewhere [18,19], and indicate the presence of peroxy group in all of the six compounds. For compounds I, II, and IV two more bands at 775.80 cm^{-1} and 445 cm^{-1} were obtained. These are attributed to $\nu(\text{Mo}-\text{O}-\text{Mo})_{\text{asym}}$ and $\nu(\text{Mo}-\text{O}-\text{Mo})_{\text{sym}}$ modes [20] and reveal polymerization of these peroxymolybdates through oxygen bridge.

It appears that no peroxymolybdate was formed through ionic oxygens of the molybdate, as no noticeable shifts of $\nu(\text{O}-\text{O})$, $\nu(\text{Mo}-\text{O})_{\text{asym}}$ and $\nu(\text{Mo}-\text{O})_{\text{sym}}$ modes were observed

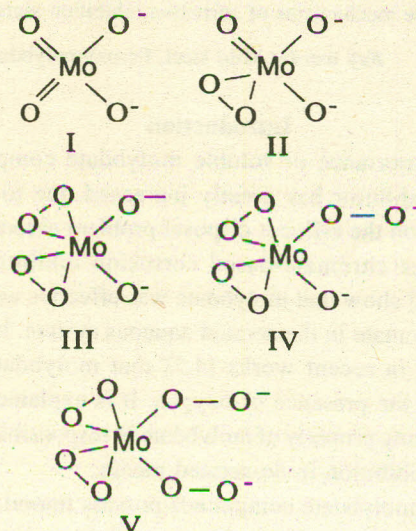


Fig. 1. Peroxymolybdates -- Preparation, characterization, and mild steel corrosion inhibition.

TABLE 2. INFRARED SPECTRAL DATA FOR PEROXYMOLYBDATES.

Compound	Band maxima, cm^{-1}					
	(Mo=O)	(O-O)	(Mo-O)	(Mo-O)	(Mo-O-Mo)	(Mo-O-Mo)
Peroxymolybdate I	920(s)	480(m)	635(m)	555(w)	780(m)	445(w)
Peroxymolybdate II	920(ms)	845(m)	635(m)	555(br)	780(m)	445(w)
Peroxymolybdate III	-	845(s)	635(ms)	560(br)	-	-
Peroxymolybdate IV	920(s)	840(m)	630(m)	555(w)	775(m)	445(w)
Peroxymolybdate V	925(s)	845(m)	635(m)	560(w)	-	-
Peroxymolybdate VI	925(m)	845(m)	635(m)	560(br)	-	-

Relative band intensities denoted by s = strong; ms = medium strong; m = medium; br = broad and w = weak.

in any of the six compounds. The absence of $\nu(\text{Mo}=\text{O})$ mode only in peroxymolybdate III indicates formation of diperoxymolybdate in the case of this compound. In this work this compound was prepared from the solution having maximum H_2O_2 -Mo ratio of 2:1 and maximum pH value of 7.0. IR data did not show whether or not the compound prepared from a particular solution was a mixture of mono- and diperoxymolybdates, and the extent of such mixing. It is quite likely that peroxymolybdates V and VI prepared from the solution containing hydrogen peroxide and molybdate at a ratio 1:1, and at pH values 6 and 7 are either monoperoxymolybdates or mixtures of mono- or diperoxymolybdates. Thus, peroxymolybdate III is diperoxo, peroxymolybdates V & VI are mono- or mixtures of mono- or diperoxo, and peroxymolybdates I, II and IV are polymerized peroxy compounds.

The corrosion behaviour of mild steel in the presence of 500 ppm peroxymolybdate in distilled water is depicted in Fig. 2 as a function of soaking time. The result is also shown when 500 ppm molybdate was present. Peroxymolybdates I and II show lower corrosion rate than molybdate when soaking time was low. For all peroxymolybdates, except peroxymolybdate III, corrosion rate increased with the increase of soaking time. In molybdate corrosion rate decreased and in peroxymolybdate III it remained unchanged with soaking time. Molybdate inhibited mild steel corrosion better than other peroxymolybdates after 10 days soaking. All peroxymolybdates exhibited different corrosion inhibition behaviour. This indicates that no two of them are identical in composition.

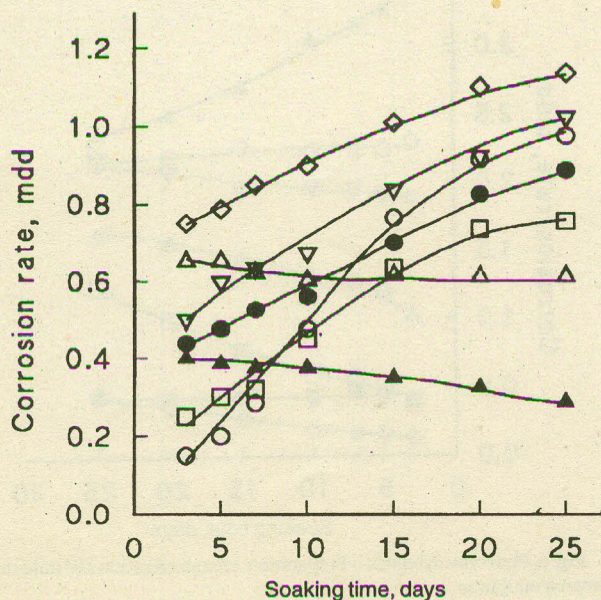


Fig. 2. Peroxymolybdates -- Preparation, characterization and mild steel corrosion inhibition.

The corrosion behaviour of mild steel in SCW is shown in Fig. 3. while that in SCW containing 500 ppm peroxymolybdates and molybdate are shown in Fig. 4. SCW is an aggressive medium due to appreciable amount of chloride (300 ppm) and sulphate (351 ppm) anions in it. Mild steel showed fairly high corrosion rate in this medium, which increased steadily with the increase of soaking time; and became as high as 40 mdd at 25th day of soaking. Corrosion rate significantly decreased in the presence of peroxymolybdates or molybdate in SCW, and this indicates that they have pronounced inhibition efficiency. The maximum corrosion rate was within 4.5 mdd in SCW in the presence of these inhibitors. Corrosion rates of mild steel increased in the case of

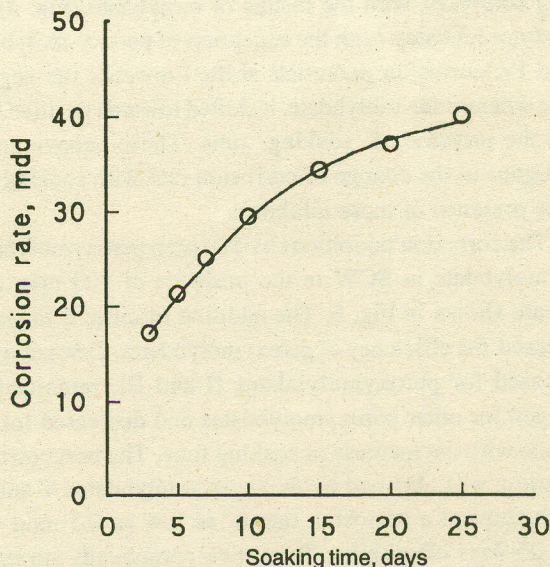


Fig. 3. Peroxymolybdates -- Preparation, characterization and mild steel corrosion inhibition.

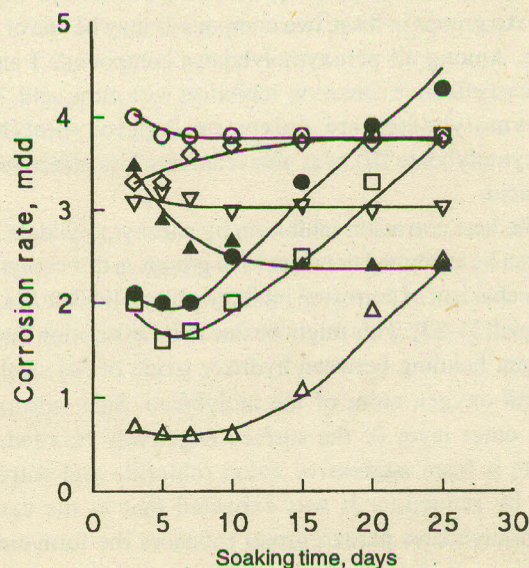


Fig. 4. Peroxymolybdates -- Preparation, characterization and mild steel corrosion inhibition.

peroxymolybdates II, III & VI remained more or less independent in the case of peroxymolybdates I, IV and V, and decreased in the case of molybdate with the increase of soaking time. Among all inhibitors the best corrosion inhibition in SCW was obtained by peroxymolybdate III. Figure 5 shows the change of corrosion potentials of mild steel with soaking time in SCW in the presence of peroxymolybdates and molybdate. Significantly higher potentials (positive potentials) were obtained in the presence of peroxymolybdates than those in the presence of molybdate. High corrosion potentials indicate better surface protection or more oxidizing condition on the surface. In this case the big shift of potentials towards positive value in the presence of peroxymolybdates might be due to more oxidizing conditions on the surface, as corrosion inhibition by peroxymolybdates were not improved when compared with the results of molybdate (Fig. 4). For peroxymolybdates, with the exception of peroxymolybdates I and IV, corrosion potentials shifted towards the negative value whereas for molybdate, it shifted towards positive value with the increase of soaking time. These behaviours are analogous to the change of corrosion rate with soaking time in the presence of these inhibitors.

The corrosion inhibitions by 500 ppm peroxymolybdates and molybdate in SCW in the presence of 500 ppm citric acid are shown in Fig. 6. The addition of citric acid greatly increased the efficiency of peroxymolybdates. Corrosion rates increased for peroxymolybdates II and III, remained unchanged for other peroxymolybdates and decreased for molybdate with the increase of soaking time. The best corrosion inhibition was obtained by the peroxymolybdates V and VI, which showed a corrosion rate of as low as 0.5 mdd even after 25 days of soaking. These two compounds are monomeric, and are likely to contain the lowest amount of peroxogroup among the six peroxymolybdates. The number of peroxo groups in these two compounds may be one or close to one. Among all peroxymolybdates compounds I and IV were least effective corrosion inhibitors with citric acid. These peroxymolybdates are polymeric. Diperoxymolybdate (peroxymolybdate III) was also relatively less effective with citric acid.

The best corrosion inhibition by peroxymolybdate III in SCW can be attributed to two peroxo groups in this compound. The mechanism of corrosion inhibition by molybdate has been explained [21-23]. This might be due to its adsorption through hydrogen bonding between hydroxy oxide of the steel surface and oxygen atom of the molybdate. Such adsorption makes outer layer of the surface negatively charged, and protects it from aggressive anion (chloride and sulphate) attack by repulsion. It was expected that in the case of peroxymolybdates peroxo group enhances the formation of

surface oxide and molybdate would, therefore, prevent aggressive anion attack producing two fold protections. However, this explanation did not hold for peroxymolybdates except peroxymolybdate III. This can be explained if it is assumed that the decomposition of less effective peroxymolybdates to molybdate and hydrogen peroxide occurs before reaching the surface. The hydrogen peroxide released in the solution may produce loosely adhered non-protective iron oxide/hydroxide on the surface. Once the surface is covered by non protective oxide layer, local acidity will grow underneath accelerating further corrosion. The increase of corrosion rate with soaking time in the presence of several

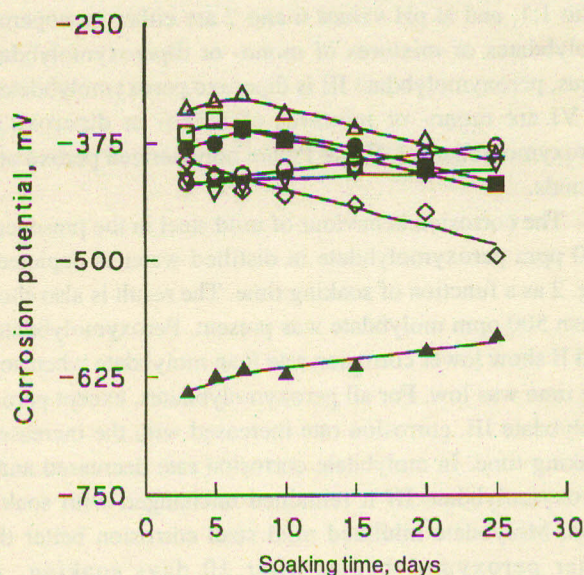


Fig. 5. Peroxymolybdates -- Preparation, characterization and mild steel corrosion inhibition.

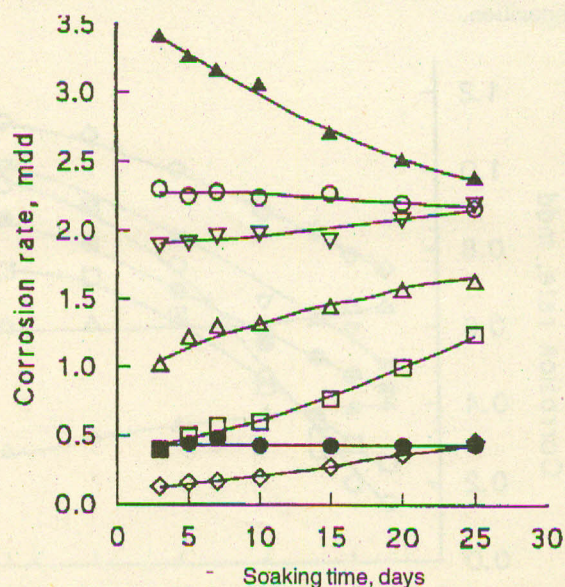


Fig. 6. Peroxymolybdates -- Preparation, characterization and mild steel corrosion inhibition.

peroxymolybdates may be due to this phenomenon. Little or no surface protection in the presence of several oxidizing agents including perborate and perbenzoic acid was explained [21] due to such non-protective oxide formation.

In the presence of peroxymolybdate and citric acid peroxymolybdate-citrate complex may form in the aqueous medium. Stabilization of peroxy groups by such complex formation was reported earlier [24]. The complex formation can hinder decomposition before adsorption on the surface. This may result in an increased supply of molybdate, oxidizing agent and citrate on the surface and produce synergistic corrosion inhibition. In this work the best corrosion inhibition was obtained by peroxymolybdates V and VI, which are supposed to be monomeric mono peroxymolybdate in nature. Thus, these two compounds may prefer to form complex with citric acid.

Conclusion

i) Diperoxymolybdate forms at pH 7 in the solution containing hydrogen peroxide and molybdate at a ratio 2. If ratio is 1 and pH is 5 or 6 mono or mixed peroxymolybdate forms. Peroxy group addition occurs through double bonded oxygen of the molybdate only. At pH 5 polymerization of the peroxy-molybdate occurs. Polymerization also occurs at pH 6 when H_2O_2 -Mo ratio is 2:1.

ii) Diperoxymolybdate is better corrosion inhibitor than other peroxymolybdates and molybdate in SCW. This shows the beneficial effect of the oxidizing group in the molybdate. For other peroxymolybdates corrosion inhibition is not so improved compared to that of molybdate. The decomposition of these compounds before reaching steel surface may be responsible for this.

iii) In comparison with molybdate, peroxymolybdates provide greatly improved corrosion inhibition with citric acid. This might be due to the stabilization of peroxy group by the complex formation with citric acid, and adsorption of the peroxymolybdate-citrate complex on the surface.

Work is in progress on the preparation of peroxymolybdate complexes with citrate or similar other ligands. Corrosion inhibition behaviours by them are being studied. The results of which will be published in near future.

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