Electrochemical Behavior of Mild Steel in Dimethyl Sulfoxide Containing Hydrochloric Acid

R.B. Rastogi,[*] **M.M. Singh, K. Singh and J.L. Maurya**

Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi-221005, India

Abstract

The corrosion behavior of mild steel in dimethyl sulfoxide containing various concentrations, i.e., 0.001, 0.005, 0.010, 0.015 and 0.020 M of hydrochloric acid has been studied in presence of 0.1 M tetra ethyl ammonium chloride as supporting electrolyte by applying electrochemical techniques. The results of these experiments have been supplemented by surface analysis of the samples exposed to corrosive solution under different experimental conditions. The electrochemical investigation was done potentiostatically by varying the concentration of HCl in DMSO and the experimental temperature as well.

Keywords : elecrochemical behavior, mild steel, DMSO-HCl mixture.

Introduction

Systematic investigations have been carried out on the kinetics and mechanisms of corrosion of metal and alloys in general in aqueous media [1-4], but their parallels in non-aqueous media are still quite rare[5-6]. In pure organic solvents, plastics and rubbers are the most vulnerable materials, but metals and alloys remain almost unaffected. The presence of water and acids in many of the organic solvents is reported [7-12] to have encouraged the corrosion of many metals. A great number of metal-organic solvent interfaces can exist [13-16] in view of the numerous organic solvents used either in laboratories or industries. During the last few decades, corrosion problem encountered in organic environments has been investigated [17-22] with particular attention on the anodic behavior of metals and their alloys. Anodic dissolution of copper in dimethyl formamide was investigated by Kostina *et al.* [13] and they reported the

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[*] Corresponding author. E-mail address: rashmi.apc@itbhu.ac.in

presence of two peaks in anodic polarization curves. Similar results have been found in water-ethanol solutions containing HCl [7-8]. Schwabe *et al.* [23] have reported anodic behavior of armaco iron in hydrous and anhydrous dimethyl sulfoxide (DMSO). A passive layer with a high barrier to charge transfer was reported [23] to have been formed on iron in hydrous DMSO (2% water), while in anhydrous DMSO, a salt like layer was formed [23], which resulted in a quick decrease in the anodic polarization.

A comprehensive and systematic investigation was carried out by Posadas and co-workers [24-26] on the kinetics and mechanism of iron dissolution and passivation in solutions of HCl and DMSO. The slope of Tafel curves increases continuously as the anodic polarization increases, and at constant anodic overvoltage there is a net increase of current on increasing the HCl concentration and temperature. The kinetics of the iron corrosion behavior in HCl-DMSO solution indicates a clear participation of the solvated proton. In this system, the anodic dissolution reaction is an inverse first order reaction with respect to hydrogen ion concentration, and in the electro deposition of iron, it is a first order reaction with respect to ferrous ion. The corrosion of metals and alloys in organic solvents exhibits a number of interesting features. The rate of corrosion is often found to be influenced by the solvent composition, structure, protolytic action, solubility of corrosion products and oxygen solubility. In general, rate factors such as concentration of reactants, temperature, presence of oxidizer and velocity of the environment are also important.

Mild steel is a well known structural material, particularly for large structures like storage tanks and pipelines, etc. In aqueous environments whether acidic or basic, its corrosion behavior is well studied; however, in non-aqueous solvents limited reports [27-32] are available. In view of inadequacy of work in non-aqueous media, the present investigation on corrosion behavior of mild steel in HCl-DMSO mixture has been undertaken.

Experimental

The working electrode specimens for electrochemical experiments were prepared from mild steel sheets having the following % composition :

C	Mn	Si	P	S	N	Cu	Cr	Fe
0.12	0.11	0.02	0.02	0.02	0.02	0.01	0.01	Remainder

The specimens were mechanically polished successively with 1/0, 2/0, 3/0 and 4/0 grades of emery papers. After this, the surface was thoroughly washed with soap, running tap water, distilled water and finally was degreased with acetone. The samples were dried and stored in a vacuum desiccator before immersing in the test solution. The solvent DMSO was first treated with alumina and then was distilled three times under reduced pressure, according to the reported method [16]. The water content was << 1% and no traces of organic impurities were detected. The solutions have been prepared by dissolving corresponding volumes

of standard hydrochloric acid in DMSO using 0.1 M tetraethyl ammonium chloride as supporting electrolyte.

The polarization experiments were carried out in a three necked double walled pyrex glass assembly. The cell was air-tight, containing an inlet with variable depth for nitrogen gas and an outlet with a calcium chloride tube attached to it. For applying different potentials across the reference and working electrodes, use was made of the Wenking model POS 73 potentiostat and steady state current values were recorded from the ammeter on the panel of the potentiostat. A rectangular working electrode with an exposed area of 2 cm^2 (both sides included) was inserted through a copper rod and fixed with the help of a screw. The rest of the surface of the electrode adjacent to the exposed area was coated with extra pure paraffin wax. A platinized platinum foil of size 1x1 cm^2, sealed in a glass tube, was used as the counter electrode. The contact was made through a platinum wire and mercury contained in the glass tube. The copper rod containing the working electrode as well as the glass tube of the counter electrode were kept in a fixed position. The potential of the working electrode was measured against a saturated calomel electrode. A Luggin capillary containing KNO_3 salt bridge was used to connect the reference electrode with the cell. It was kept very close to the electrode surface to minimize IR drop. The distance between the tip of the Luggin capillary and the working electrode was kept constant in all the cases, to ensure the reproducibility of the data.

The surface of the specimens after polarization experiments in DMSO-HCl solutions were studied by using a Scanning Electron microscope JEOL-JSM. The mild steel samples were mounted on the specimen stub and inserted in the evacuated chamber of the instrument at National Electron Microscope Laboratory, Department of Metallurgical Engineering, Institute of Technology, BHU. The microphotographs thus obtained at different magnifications viz. 70× and 700× were utilized to establish the mechanism of corrosion.

Results and discussion

Fig. 1 exhibits the variation in the open circuit potential (OCP) of mild steel at different concentrations of HCl in DMSO with respect to time. The OCP shifts towards more active direction with increase in time and ultimately attains a constant value. The time required for attainment of constant OCP values is a function of HCl concentration. In the concentration range from 0.001 M to 0.010 M, it takes about 30 minutes, whereas at higher concentrations the OCP becomes constant in about 10 minutes, only. The dependence of OCP on acid concentration at different temperatures is illustrated in Fig. 2. The OCP values invariably shift towards more active direction with increase in HCl concentration in DMSO. At 45 ℃, the shift is very rapid as the acid concentration is increased up to 0.005 M and then it shifts steadily and slowly with further increasing concentration. However, at lower temperatures, i.e. 25 ℃ and 35 ℃, a rapid shift is observed up to 0.015 M HCl. It is apparent from the above observations that active dissolution of oxide free mild steel occurs at all the concentrations of the acid, as well as at all temperatures. The tendency of mild steel to get corroded

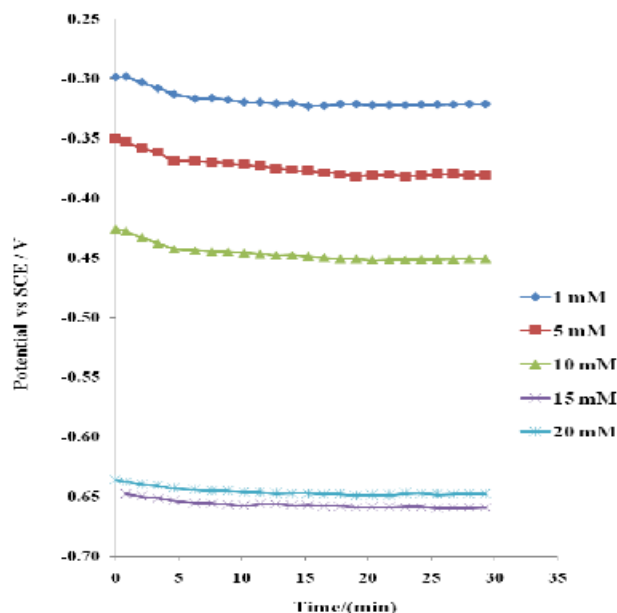increases with increase in concentration of hydrochloric acid in the referred solvent.

Figure 1. Variation of open circuit potential of mild steel in different concentrations of HCl in DMSO with time at 25 ℃.

The potentiostatic anodic polarization behavior of mild steel in solutions containing 0.001, 0.005, 0.010, 0.015 and 0.020 M of HCl in DMSO with 0.1 M tetraethyl ammonium chloride as the supporting electrolyte has been studied at different temperatures. Figs. 3-5 illustrate the anodic polarization behavior of mild steel in different concentrations of HCl in DMSO at 25, 35 and 45 ℃, respectively. Well defined Tafel regions followed by distinct limiting current densities are observed at all concentrations of HCl in DMSO at each temperature. It is further observed that the potential range for the validity of Tafel relation gets shortened with increase in the concentration of acid.

The influence of HCl concentration on the anodic polarization behavior of mild steel at 25 ℃ is demonstrated by the curves in Figs. 3-5. It is observed that the nature of the polarisation curves does not alter with the change in the acid concentration. However, with increase in the acid concentration, the curves are shifted in the direction of increasing current density with respect to the curve for the preceding concentration. The values of corrosion current density (i_{corr}), corrosion potential (E_{corr}), limiting current density (i_L), Tafel slope of anodic curve ($ß_a$) and corrosion rate calculated from the polarization curves at different concentrations of HCl in DMSO have been listed in Table 1 at 25, 35 and 45 ℃. These data reveal that as the concentration of HCl increases from 0.001 M to 0.020 M, the i_{corr} values gradually increase whereas E_{corr} becomes more negative. The increase in corrosion current and decrease in corrosion potential with increasing concentration of HCl indicate that the rate of corrosion of mild steel should increase with increasing the concentration of the acid in DMSO. The limiting current density which is the measure of maximum corrosion rate attainable during the

accelerated test is also found to be concentration dependent, having its maximum value for 0.020 M HCl in DMSO.
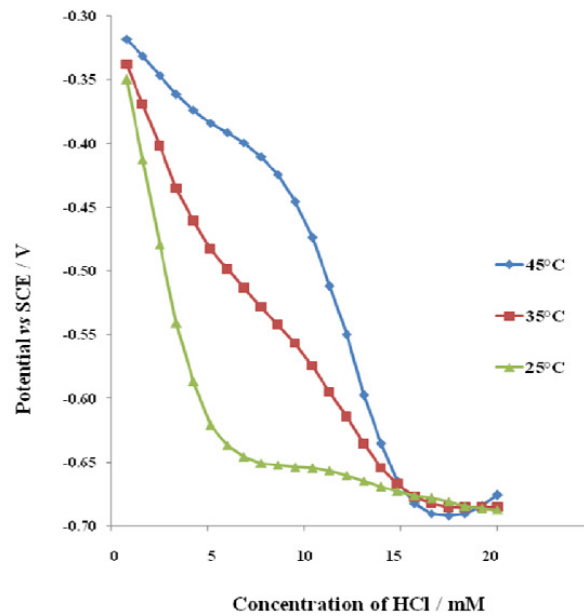

Figure 2. Variation of open circuit potential of mild steel with concentration of HCl in DMSO at different temperatures.
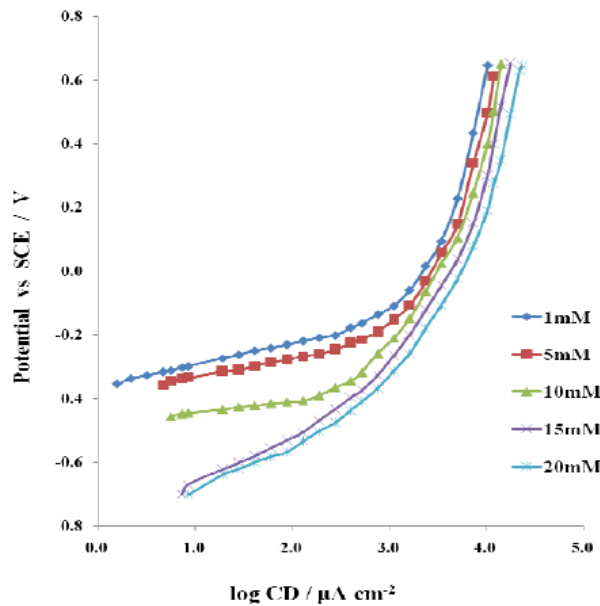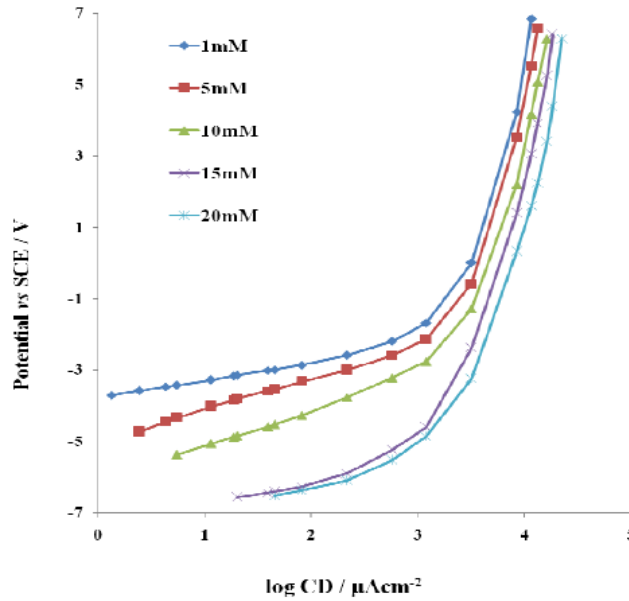

Figure 3. Anodic polarization behavior of mild steel in presence of different concentrations of HCl in DMSO at 25 ºC.

The observed increase in corrosion rate with increase in HCl concentration may be attributed to the change in the specific conductance of the HCl-DMSO system. It has been reported [5] that the solution of HCl in DMSO behaves in a manner similar to that of aqueous HCl solution. HCl is believed to dissociate in DMSO following the chemical equation

$$DMSO + HCl \rightarrow DMSOH^+$$

Thus, a gradual increase in the specific conductance of HCl-DMSO system should occur with increase in molar concentration of HCl in DMSO, due to increase in number of ions. Such an increase in conductance of HCl-DMSO solution in the range of the studied concentration of HCl during the present investigation has already been reported. In the light of this it becomes imperative that at each potential during the anodic polarization, the observed current density should increase with rise in concentration of HCl, which is the present case.

Figure 4. Anodic polarization behavior of mild steel in presence of different concentrations of HCl in DMSO at 35 ºC.
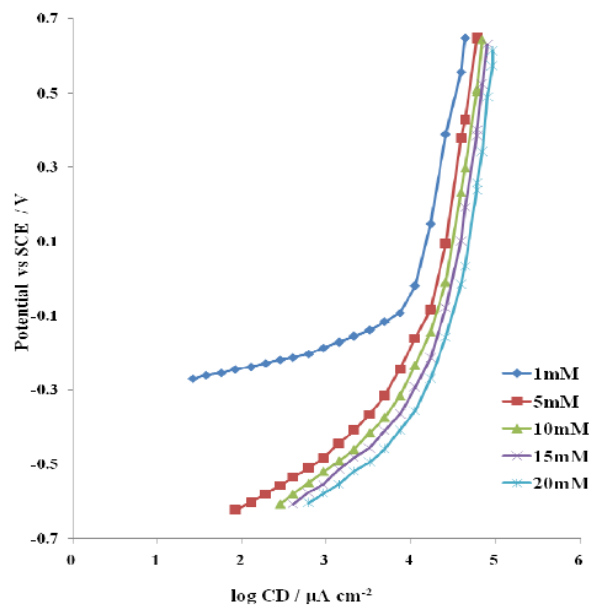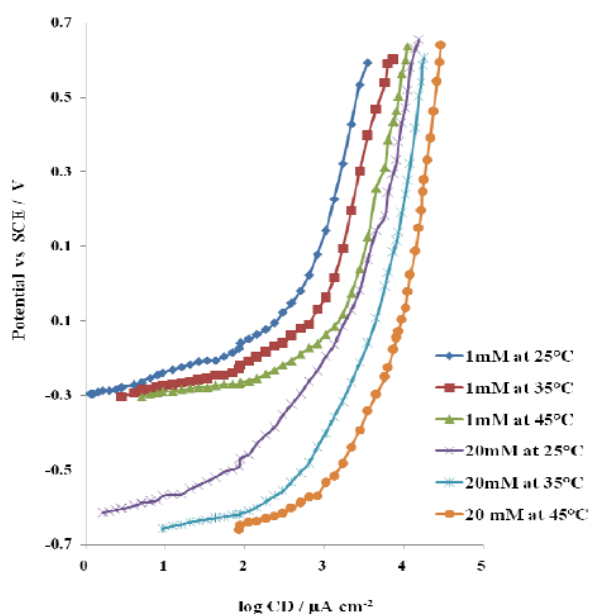

Figure 5. Anodic polarization of mild steel in different concentrations of HCl in DMSO at 45 ºC.

Table 1. Corrosion parameters of mild steel in different concentrations of HCl in DMSO at different temperatures.

Conc./ mmol dm^{-3}	E_{corr} /(mV)			i_{corr} /(μA/cm^2)			i_L/(mA/cm^2)			Ba/ (mV/decade)			Corrosion rate/ (mpy)		
	25 ℃	35 ℃	45 ℃	25 ℃	35 ℃	45 ℃	25 ℃	35 ℃	45 ℃	25 ℃	35 ℃	45 ℃	25 ℃	35 ℃	45 ℃
1	-350	-340	-310	9.16	17.45	42.92	49.41	54.65	57.40	96	122	183	3.90	7.43	18.28
5	-370	-460	-630	18.90	42.80	93.16	50.78	55.26	59.87	124	146	207	8.05	18.23	39.69
10	-460	-530	-640	35.73	72.01	139.71	51.83	56.82	60.20	146	162	230	15.22	30.68	56.53
15	-670	-650	-660	56.70	120.00	194.07	53.14	57.40	61.27	168	187	257	24.15	51.13	82.69
20	-680	-660	-670	78.53	182.00	365.07	55.14	58.54	62.13	190	200	280	33.46	77.55	155.55

The effect of temperature on the anodic polarization behavior is exhibited by the curves in Fig. 6 plotted for 0.001 and 0.020 M HCl at the three experimental temperatures. It may be realized from the figure that at a given concentration of HCl, the nature of polarization curves essentially remains unaltered on increasing the temperature of the system. However, at a constant overvoltage, a net increase of anodic current is observed as temperature increases. Thus, as the temperature of the system is increased, the corrosion rate at each concentration of the solution is expected to increase. This behavior can again be explained on the basis of temperature dependence of specific conductance data [17]. Accordingly, the specific conductance of HCl-DMSO systems in presence of the supporting electrolyte tends to increase with temperature at a given composition. The increase in specific conductance with temperature is responsible for the enhanced current densities at each anodic potential.

Figure 6. Anodic polarization of mild steel in presence of 1 and 20 mM HCl at different temperatures.

The cathodic polarization behavior of mild steel in different concentrations of HCl-DMSO system has been illustrated in Fig. 7-9 at 25, 35 and 45 ℃, respectively. It is noted from these figures that the cathodic polarization curves at different concentrations from 0.001 and 0.020 M, are similar. The potential

region in which cathodic polarization curves could be plotted depends upon the concentration of HCl and particularly at higher concentration this region is quite narrow. This behavior is exactly what is expected in terms of large shift in OCP with concentration of HCl. Further, these curves are gradually and bodily shifted towards higher current density region with increase in HCl concentration from 0.001 and 0.020 M.
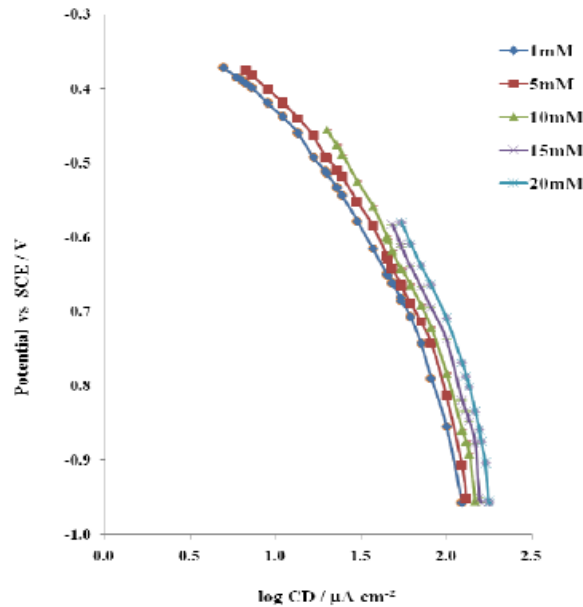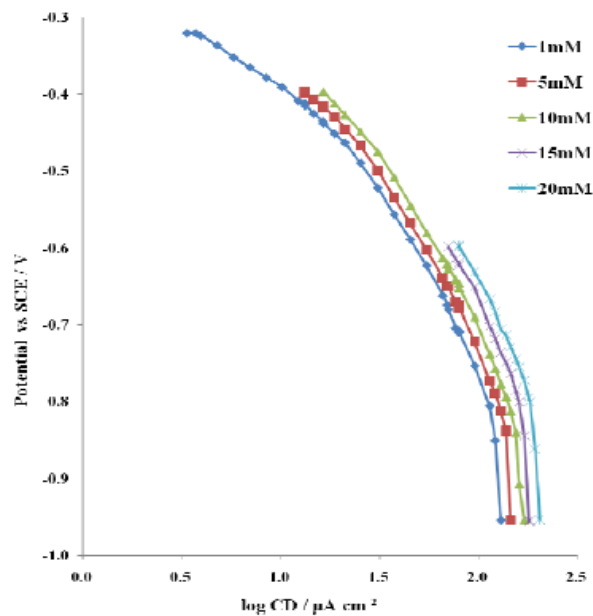

Figure 7. Cathodic polarization of mild steel in different concentrations of HCl in DMSO at 25 ºC.

Figure 8. Cathodic polarization behavior of mild steel in different concentrations of HCl in DMSO at 35 ºC.
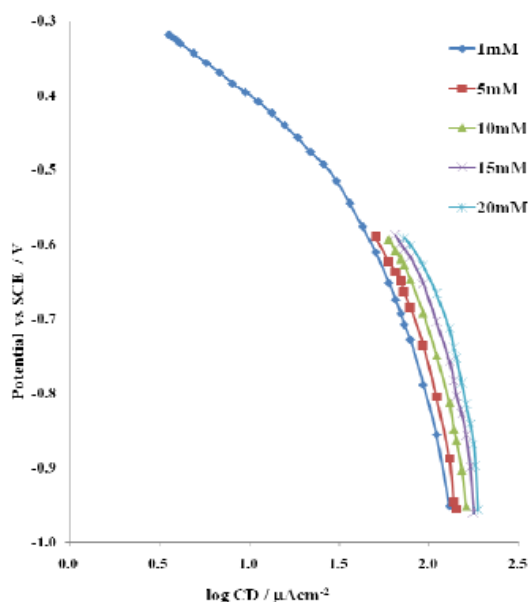
Figure 9. Cathodic polarization behavior of mild steel in different concentrations of HCl in DMSO at 45 ºC.

The continuous shift in cathodic polarization curves towards higher current density side with increase in temperature follows a pattern similar to that observed in the case of anodic polarization. Thus, it is possible to attribute this shift in cathodic polarization curve to the increase in conductance of HCl solution in DMSO with increase in the acid concentration. The increase in conductance is related with increase in total ionic concentration, i.e., concentration of both chloride and hydrogen ions. Since cathodic polarization behavior indicates acceleration in cathodic rate with acid concentration, it could be very well said that hydrogen ion discharge is the most likely cathodic reaction, as is often the case with aqueous acid solutions. The mechanism of hydrogen evolution reaction based on the suggestions of Posadas *et al.* [5-7] can be written as:

$$DMSOH^+ + Fe\ (e) \rightarrow Fe\ (H) + DMSO$$

$$Fe\ (H) + Fe\ (H) \rightarrow Fe + H_2$$
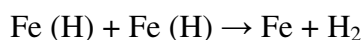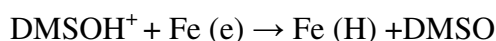
Dependence of the rate of hydrogen evolution on the concentration of HCl indicates that first step is the rate determining step.

The effect of temperature on the cathodic polarization curves is illustrated by the curves represented in Fig. 10 plotted for 0.001 and 0.020 M HCl at the three experimental temperatures. It may be noticed that there is no marked change on increasing the temperature of the system at a given concentration of HCl as far as the shape of the curves is concerned. However, at a constant overvoltage, a net increase of cathodic current is observed as temperature increases from 25 to 45 ºC. It is observed from the figure that the cathodic curves shift to higher current density on raising the temperature from 25 to 35 ºC is much greater than in the case of the corresponding curves between 35 and 45 ºC, respectively. The temperature dependence behavior of cathodic curves can also be influenced by the specific conductance of HCl solution in DMSO. From the literature values it

is observed that at constant concentration, specific conductivity increases with the temperature. On the basis of this it may be argued that the corrosion rate of mild steel at any given concentration of HCl in DMSO depends upon its conductance.
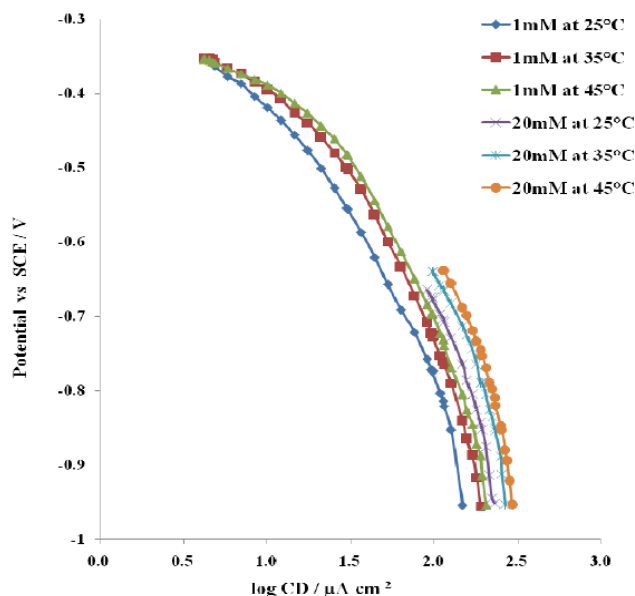

Figure 10. Cathodic polarization behavior of mild steel in presence of 1 mM and 20 mM HCl in DMSO at different temperatures.

The plot of log i_{corr} vs. 1/T in Fig. 11 is linear, indicating the activation controlled nature of the corrosion process. Further, the values of activation energy calculated on the basis of these plots are independent of the concentration of HCl and lie in the range of 75-80 kJ/mole. Thus, the increase in the concentration of HCl could enhance the corrosion rate merely by providing a more conducting medium. This conclusion is similar to that arrived at on the basis of anodic and cathodic polarization behavior.

Figs. 12 and 13 show the micrographs of mild steel polished specimen and in 0.020 M concentration of HCl-DMSO system at 25, 35and 45 ºC, respectively. It is apparent from the photographs that the corrosion intensity increases with increase in temperature, which is in agreement with the results obtained from polarization studies.
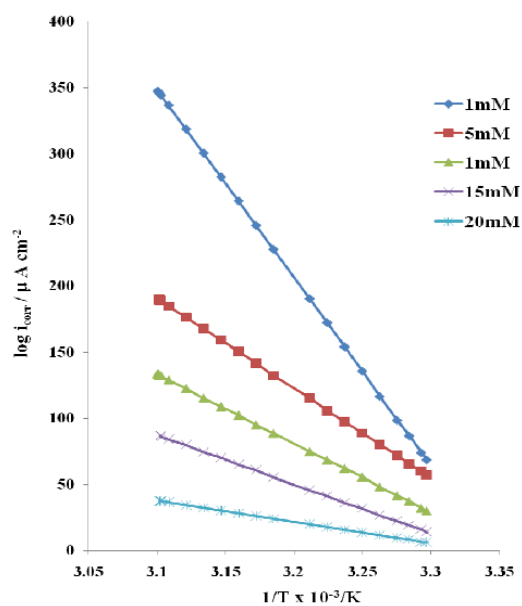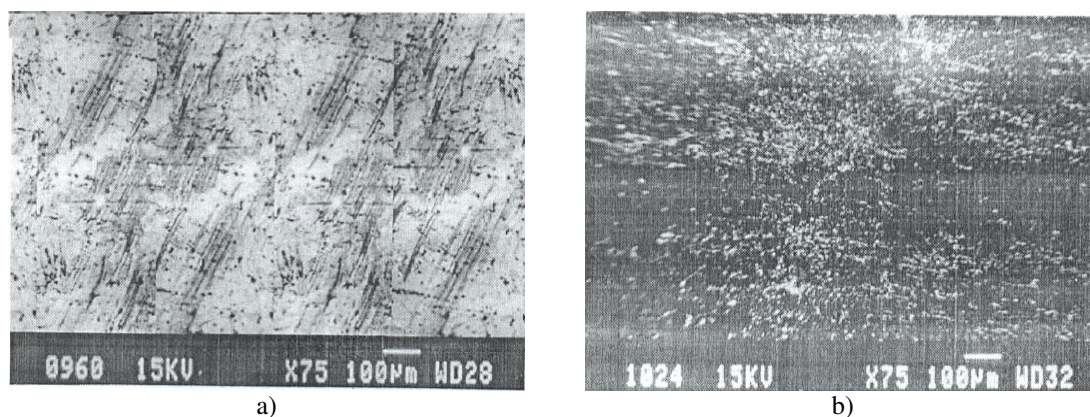
Figure 11. Evaluation of energy of activation.

Figure 12. Scanning electron micrographs of (a) mild steel polished specimen and (b) mild steel exposed to 0.020 M HCl-DMSO system at 25 ˚C.
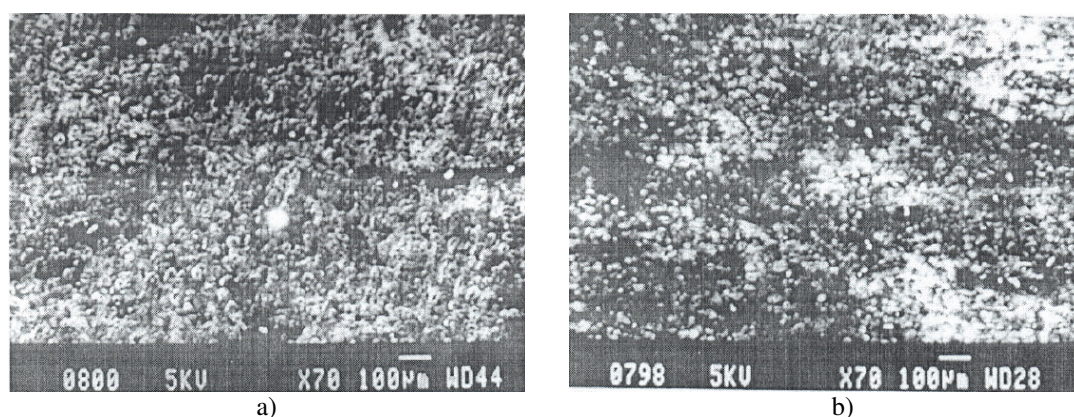

Figure 13. Scanning electron micrographs of mild steel exposed to 0.020 M HCl-DMSO system at (a) 35 ˚C and (b) 45 ˚C.

Conclusions

1. Active dissolution of oxide free mild steel in DMSO occurs at all concentrations of HCl and temperatures.

2. The tendency of mild steel to get corroded increases with increase in the concentration of HCl in DMSO as well as temperature.

3. The potentiostatic polarisation behavior at different concentrations of HCl and temperatures can be ascribed to the increase in specific conductance of the system.

4. The plot of i_{corr} vs. $1/T$ indicates the activation controlled nature of the corrosion process.

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