Study on corrosion control of N80 steel in acid medium using mixed organic inhibitors

T Kumar, S Vishwanatham* & Emranuzzaman

Indian School of Mines University, Dhanbad 826004, India

Email: sunkari_v@yahoo.com

Effects of inhibitor mixtures (TVE-3A, TVE-3B and TVE-3C) containing formaldehyde in combination with phenol or cresol on corrosion behaviour of N80 steel in 15% HCl solution were investigated using weight loss and potentiostatic polarization technique. The influence of temperature (30-115°C) and time interval (6-24 h) in the absence and presence of inhibitors on corrosion of the steel in the acid has been studied. TVE-3B has shown the maximum inhibition of 68.6% at ambient temperature whereas maximum inhibition shown by TVE-3A and TVE-3C was found to be 62.2% and 65.7% respectively. The inhibition efficiency was found to gradually decrease with increase in temperature in the case of TVE-3A while TVE-3B and TVE-3C showed a further increase in the protection at higher temperatures (about 81% at 115°C). The protective efficiency of TVE-3B and TVE-3C is comparable with Grade-III (about 88% at 115°C) commercial inhibitor. Inhibition of corrosion is due to adsorption of inhibitors on the metal surface. The adsorption is found to obey Frumkin isotherm. FTIR study of the metal surface products after the corrosion inhibition tests reveal presence of non-linear poly phenyl species, no free carbonyl group indicating formation of a cross linked and three dimensional networking resulting in novalac resin or bakelite by condensation polymerization (acid catalyzed). Oxygen atom, (of –OH group in phenol or substituted phenol) may coordinate to Fe^{2+} on the metal surface resulting in a protective inhibitor layer. Thermal stability of the inhibitor mixtures was determined by DSC, which has shown that the compounds present in TVE-3A vaporize with increase in temperature while the compounds present in the case of TVE-3B and TVE-3C are thermally stable up to 200°C.

Keywords: Corrosion inhibitor, N80 Steel, Phenol, Cresol

Acidization of petroleum oil wells is an important stimulation technique for enhancing production. Hydrochloric acid (15-20%) solution is commonly used for the purpose. The 15% HCl used for acidizing process leads to severe corrosion of oil well casing, tubing and accessories. Corrosion inhibitors are added along with the acid to reduce the corrosion attack on the well equipment[1]. There are many other methods available to prevent the corrosion attack from such aggressive environments but one of the most economic methods is the application of corrosion inhibitors[2]. In previous works, various organic inhibitors have been used against the corrosion of iron and steel[3, 4]. The effective inhibitors used against the acidizing corrosion include acetylenic alcohol, aromatic α,β unsaturated aldehydes, nitrogen containing heterocylic compounds and quaternary salts[5-9]. In an earlier communication[10], phenol and its *o*- and *p*-substituents were reported for corrosion inhibition of N80 steel in 15% HCl solution. Some of the acidization inhibitors are effective only at high concentration. In the present work, three inhibitor mixtures (TVE-3A, TVE-3B and TVE-3C) consisting of formaldehyde and phenol compounds are evaluated to understand the inhibitive performance of the mixtures at relatively lower concentrations and the results are compared with Grade-II and Grade –III commercial acidizing inhibitors used against corrosion of the steel.

Experimental Procedure

N80 steel specimen [chemical composition: C (0.31%), S (0.008%), P (0.010%), Si (0.19%), Mn (0.92%), Cr (0.20%) and Fe (balance)] used in the study were of the size 6.0×2.0×0.3 cm. The corrosion experiments were carried out as per the standard experimental procedures of corrosion testing[11]. AR grade 37% HCl was used for the preparation of the acid solutions; volume of the test solutions used for the weight loss studies was 500 mL. The inhibitor mixtures studied in this work were: TVE-3A (formaldehyde:phenol::1:2), TVE-3B (formaldehyde:*o*-cresol::1:2) and TVE-3C (formaldehyde:*p*-cresol::1:2). Commercially available formaldehyde (Merck)) was used for the present study. It is sold as a saturated aqueous solution with concentration of around 37%

formaldehyde, stabilized with 10%-15% methanol. it is readily soluble in water(25°C)[12]. Phenol, *o*-cresol and *p*-cresol used in the preparation of the inhbitior mixtures were of AR grade (Merck). Aqueous solubility of phenol, *o*-cresol and p-cresol has been found to be 70, 26 and 23 g/L respectively (25°C)[13,14]. The concentration range of inhibitor employed was 0.1 to 0.8%(*v/v*) in the acid. The commercial inhibitors Grade-II and Grade-III reported in this work were received from Oil and Natural Gas Corporation, India. The methods of calculation of corrosion rate, percentage protection, activation energy, free energy of adsorption, enthalpy, entropy were the same as described earlier[9]

Polarisation experiments were carried out using Elico potentiostat model CL-95. All potential values were recorded on the saturated calomel (SCE) scale. Infrared studies were carried out using Perkin Elmer FTIR spectrometer model 1760X. The constituents of the mixed organic inhibitors (formaldehyde and phenol substituent) were mixed in the ratio of 1:2. About 1 mL of concentrated HCl was added to 25 mL of the inhibitive mixture solution and was refluxed with continuous stirring at 80°C for about 8 h. After refluxing, a sticky solid substance was obtained that was analysed by FTIR. Differential scanning calorimeter (DSC) studies were carried out using Perkin Elmer model DSC-7. For this study, 25 mL of solution of the inhibitor mixture was taken in a 100 mL flask and 1 mL of HCl was added to the solution and stirred by a magnetic stirrer for about 30 min at room temperature.

Results and Discussion

Based on weight loss measurements, the corrosion rates and the values of percentage inhibition (PI) for various concentrations of the inhibitors after 6 h of immersion at room temperature (25±1°C) are given in Table 1. TVE-3B has shown the maximum inhibition of 68.6% at inhibitor concentration of 0.8% whereas maximum PI shown by the commercial inhibitors Grade-II and Grade-III at the same concentration was found to be 87.2% and 84.2% (Table 2) respectively. The protective efficiency of the inhibitors has been found to be in the following order:

Grade- II > Grade- III > TVE-3B > TVE-3C >TVE-3A

The degree of surface coverage (θ) of steel surface by different concentrations of inhibitors was calculated using the following equation:

$$\theta = [W_o - W_i] / W_o$$

where W_o and W_i are weight loss of the metal in absence of the inhibitor and presence of the inhibitor respectively. The plots of θ versus log C displayed characteristic S- shape (Fig. 1) indicating that the adsorption process of the inhibitors on the metal surface obeys the Frumkin isotherm.
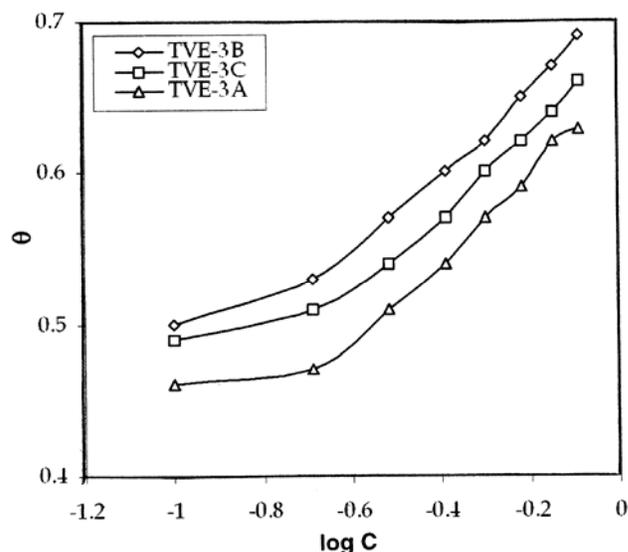

Fig. 1—Frumkin isotherm for adsorption of mixed organic inhibitors on steel in 15% HCl

Table 1—Percentage inhibition of N80 steel in 15% HCl in presence of mixed organic inhibitors at different concentration

Inhibitor	Percentage inhibition (%) for concentration (%, *v/v*) of							
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
TVE-3A	46.2	47.0	51.0	54.3	57.1	59.4	61.6	62.2
	(202.2)	(199.1)	(184.1)	(171.9)	(161.2)	(151.5)	(144.3)	(142.0)
TVE-3B	50.5	54.3	57.2	59.6	62.2	64.6	67.3	68.6
	(186.1)	(138.5)	(160.9)	(151.7)	(142.0)	(133.1)	(122.9)	(118.1)
TVE-3C	48.5	51.6	54.3	56.6	58.3	61.6	64.3	65.7
	(193.5)	(181.8)	(171.9)	(163.2)	(156.8)	(144.3)	(134.1)	(129.0)

Values in parentheses indicate corrosion rate (CR) in mpy; corrosion rate for the blank (CR°)=375.8 mpy

Table 2—Effect of exposure period on percentage inhibition of inhibitors (0.8%) against corrosion of N80 steel in 15%HCl

Exposure period (h)	Percentage inhibition (%)				
	Grade-II	Grade-III	TVE-3A	TVE-3B	TVE-3C
6#	62.2	68.6	65.7	87.2	84.2
	(142.0)	(118.1)	(129.0)	(48.2)	(59.1)
12#	65.3	70.2	67.7	88.5	86.1
	(95.1)	(81.6)	(88.5)	(31.5)	(38.1)
18#	67.7	71.8	69.3	90.4	87.6
	(67.3)	(58.7)	(63.9)	(20.0)	(25.8)
24#	68.9	73.6	71.2	93.3	89.5
	(56.5)	(47.9)	(52.3)	(12.2)	(191.1)

At room temperature; values in parentheses indicate corrosion rate in mpy

The mixed organic inhibitors as well as the commercial inhibitors brought about appreciable decrease in corrosion rate of metal in the acid solution even after long exposure (Table 2). In the case of 12 h exposure test, PI of TVE-3A, TVE-3B, TVE-3C, Grade-II and Grade- III (at 0.8%) was 65.3, 70.2, 67.7, 88.5 and 86.1% respectively. PI of all the inhibitors further increased slightly ($\approx$ 3%) after 24 h test in the acid solution. The increase in PI with time may be attributed to the formation of a barrier film, which prevents the attack of acid on the metal surface[15]. The corrosion rate increased both in presence and absence of the inhibitors with increase in temperature.

PI of TVE-3B and TVE-3C was found to increase with increase in temperature up to 115°C (Table 3). The inhibition offered by TVE-3A gradually increased with increase in temperature up to 60°C (PI=69.8%) but it was decreased at higher temperature (PI=60.2% at 90°C), which might be due to initiation of vaporization of the constituents of the mixture at higher temperatures as evidenced by the observation of the DSC study. Investigation on inhibition performance of TVE 3A at 115°C was not carried out. In case of commercial inhibitors, PI increased with increase in temperature up to 90°C, while it was slightly decreased at 115°C. When compared with TVE-3A, TVE-3B or TVE-3C, inhibition performance of the commercial inhibitors was slightly better (Grade-II; PI=91.5%; Grade-III PI=88.0%) at 115°C. The increase of PI with rise in temperature may be discussed on the basis that the energy involved is the net change of the endothermic desorption of the small H_2O molecules and exothermic adsorption[16] of large organic additive molecules as represented by

$$Org_{(aq)} + XH_2O_{(s)} \Leftrightarrow Org_{(s)} + XH_2O_{(aq)}$$
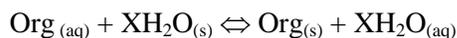
where X is the size ratio, which is the number of water molecule of the organic adsorbate. The kinetics of the metal oxidation in the acid medium may involve adsorbed water molecules ($Fe.H_2O_{ads}$) and displacements of the adsorbed water molecule by the inhibitor species, which in turn may affect the corrosion inhibition process[17,18]. The values of energy of activation (E_a) were calculated from the slopes of the Arrhenius plots of log k versus $1/T$, where k is the corrosion rate and T is the absolute temperature. The activation energy of all the inhibitors was lower than the value obtained in absence of inhibitor that may suggest that inhibitors do not change the temperature coefficient of the reaction rate but are firmly held on the metal surface or due to chemisorption[19] of the inhibitor molecule on the metal surface. Similar results have been reported with pure iron[20]. Putilova *et al.*[21] explained that this behaviour is due to presence of inhibitor, that when chemisorbed at high degree of coverage, the rate determining step in the dissolution of the metal becomes the diffusion process through the layer formed by adsorbed inhibitor and corrosion products, hence a lower temperature coefficient is observed. Sastri[22] explained that chemisorption takes place more slowly than physical adsorption. On the basis of the magnitude of the free energy for adsorption obtained for these inhibitors it may be said that Grade-II] inhibitor is more strongly adsorbed than any other inhibitor.

Polarization behaviour

Anodic and cathodic polarization curves for the steel in 15% HCl (in absence and presence of 0.8% of the inhibitor) at room temperature are given in Fig. 2. The shift in the cathodic and anodic partial curves in the presence of the inhibitors is due to adsorbed inhibitor species on the surface of the steel that affect both the anodic and cathodic areas. When compared with the values obtained in uninhibited hydrochloric acid solution, the open circuit potential for all the inhibitors remains in positive direction (Table 4). The shift in the positive direction indicates the interference of these inhibitors with the anodic partial processes. In case of all the inhibitor mixtures, the values of I_{corr} are found to decrease indicating corrosion inhibition. The variations in the values of b_a and b_c in the case of the inhibitors may indicate that both the anodic and cathodic processes are controlled and all the tested organic inhibitor mixtures are of mixed type inhibitors which predominantly control anodic reaction[23]. The values of

Table 3—Corrosion parameters of N80 steel in 15%HCl in the presence of inhibitors (0.8%) at different temperatures

Test period: 6 h

Inhibitor	Temp. (°C)	PI (%)	C.R.(k) (mpy)	E_a (KJ/mol)	ΔG_a (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)
Blank	30	-	478.6	38.294	-	35.774	-
	40	-	758.3		-		-
	50	-	1197.9		-		-
	60	-	1926.4		-		-
	80	-	9069.3		-		-
	90	-	13151.1		-		-
	115*	-	30393.2		-		-
TVE-3A	30	65.7	164.2	35.7688	4.4383	33.286	0.095
	40	66.2	256.3				
	50	68.0	383.2				
	60	69.8	581.9				
	80	65.0	3173.0				
	90	60.2	5233.8				
TVE-3B	30	71.3	137.4	34.9282	6.9638	32.409	0.084
	40	72.5	208.6				
	50	74.0	311.3				
	60	76.0	462.3				
	80	77.6	2031.7				
	90	78.4	2841.0				
	115*	81.2	5712.7				
TVE-3C	30	69.4	146.4	35.3590	5.2999	32.840	0.090
	40	70.2	225.9				
	50	71.2	345.0				
	60	73.1	518.1				
	80	74.3	2330.1				
	90	76.1	3142.4				
	115*	80.6	5896.3				
Grade-II	30	88.7	54.1	28.705	12.777	26.186	0.044
	40	90.6	71.3				
	50	91.2	105.4				
	60	92.5	144.5				
	80	94.3	517.1				
	90	95.8	552.3				
	115*	91.5	2581.0				
Grade-III	30	86.7	63.7	28.950	12.017	26.431	0.047
	40	88.2	89.5				
	50	89.5	125.8				
	60	90.7	179.2				
	80	92.1	716.0				
	90	93.4	867.5				
	115*	88.0	3644.3				

*Pressure =18 psi; test period =1 h

PI obtained by weight loss method were found to be in accordance with that of the polarization method.

FTIR study

Figures 3-5 show the infrared spectra of the inhibitor surface products obtained from N80 steel surface after 6 h corrosion test in 15% HCl. A shift in the band position in case of the metal surface product of TVE-3A, TVE-3B and TVE-3C in the range of 1620-1540 cm^{-1} (Table 5) is observed, while the spectra of the pure samples of TVE-3A, TVE-3B and TVE-3C showed a sharp peak between 1510 and 1507cm^{-1}

Table 4—Electrochemical parameters for N80 steel in 15% HCl containing 0.8% inhibitors

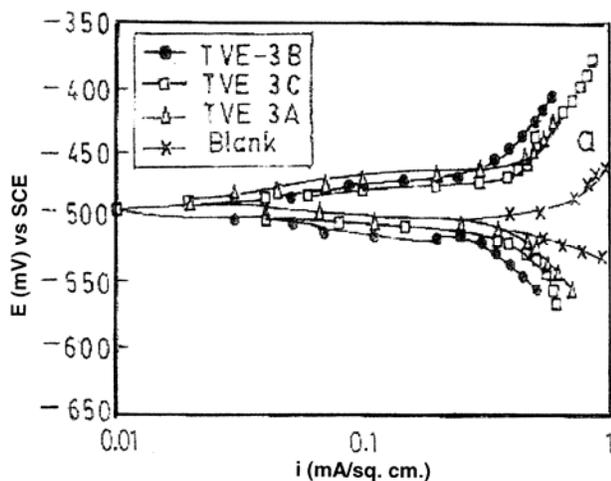| Inhibitor	Tafel slope mV/decade		I_{corr} mA	OCP mV	C.R. mpy	Percentage inhibition	
	b_a	b_c				From Tafel plot	From weight loss
Blank	150	140	0.7	-508	316.5	-	-
TVE-3A	134	138	0.27	-490	122.1	61.4	62.2
TVE-3B	120	146	0.23	-494	104.1	67.1	68.6
TVE-3C	122	140	0.25	-498	113.0	64.3	65.7

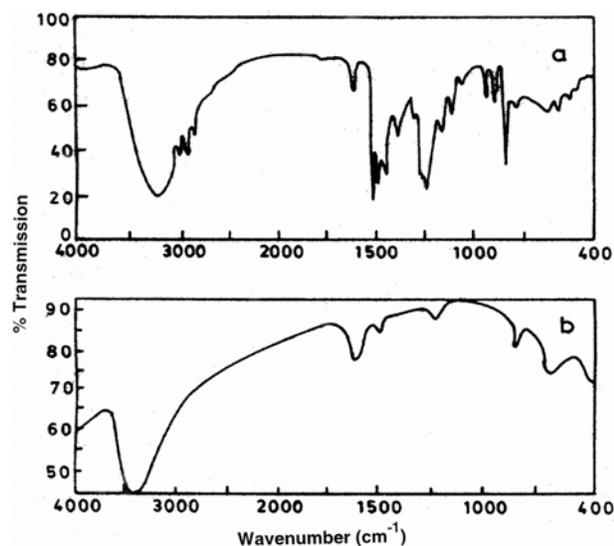Fig. 2—Polarisation curves of N80 steel in 15% HCl in presence of mixed inhibitors

Fig. 3—FTIR spectra of (a) pure TVE-3A and (b) inhibitor product formed on metal surface after inhibition test in the acid solution containing TVE-3A
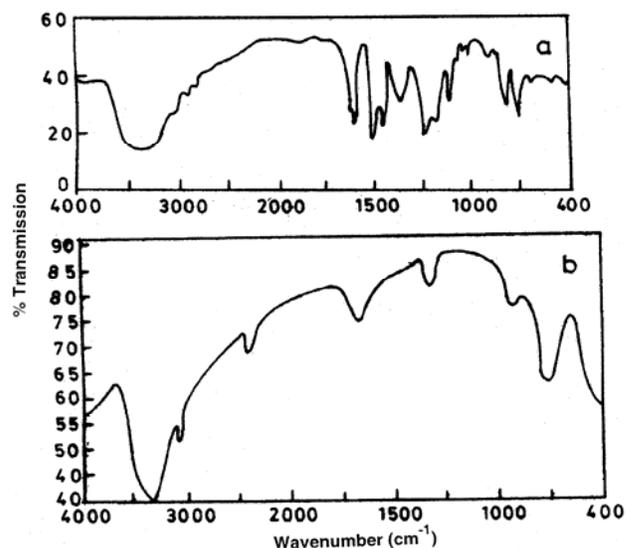

Fig. 4—FTIR spectra of (a) pure TVE-3B and (b) inhibitor product formed on metal surface after inhibition test in the acid solution containing TVE-3B
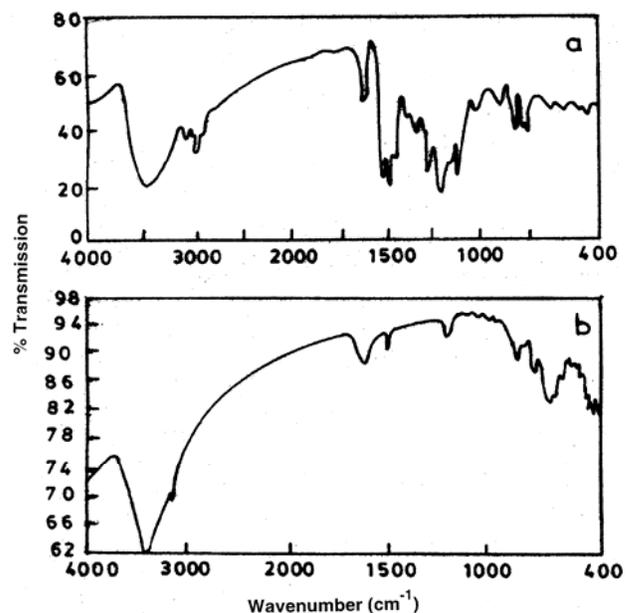

Fig. 5—FTIR spectra of (a) pure TVE-3C and (b) inhibitor product formed on metal surface after inhibition test in the acid solution containing TVE-3C

revealing[24-26] the presence of non-linear poly phenyl species, no free carbonyl group or no free –OH group in these inhibitor mixtures having formaldehyde and phenol/phenol derivative which may indicate formation of a cross linked and three dimensional net work resulting in novalac resin or bakelite by condensation polymerization (acid catalyzed). The spectrum of the metal inhibition product of TVE-3A, TVE-3B and TVE-3C showed a band at 3350, 3390 and 3360 cm^{-1} respectively, revealing the presence of –OH functional group of phenol in the organic mixtures. The spectrum of the metal inhibitor surface product revealed a shift in a band position of the functional group present in the inhibitor molecule to lower frequency (TVE-3A: from 3382 to 3350 cm^{-1}, TVE-3B: from 3419 to 3390 cm^{-1}, TVE-3C: from 3451 to 3360 cm^{-1}) when compared to that of the parent sample. This shift in the wave number may be attributed to the decrease of electron cloud density of the C-O bond present in the inhibitor molecule after adsorption on the metal surface. It may reveal that the oxygen atom of –OH group of the phenol or

Table 5—FTIR data and assignment of functional group of mixed organic inhibitors and the metal surface
products of the inhibitors

Inhiibtor	Band position (cm^{-1}) of pure sample tested	Band position (cm^{-1})of metal surface product	Functional group[22,23]
TVE-3A	3382	3350	O-H str. in phenol
	3021	3024	Aromatic C-H str.
	2918	-	CH$_2$ assymetric str. of R- CH$_2$-R '
	1596	1541	Ring mode
	1510	-	Non-linear poly phenyl
	1473	-	Sym. CH$_2$ bending of R- CH$_2$-R '
	1363	-	O-H in plane bending and C-O str.
	1230	1220	C-O str.
	816	845	Aromatic out of plane C-H bending
TVE-3B	3419	3390	O-H str. in phenol
	3011	3018	Aromatic C-H str.
	2916	-	CH$_2$ assymetric str. of R- CH$_2$-R '
	2853	-	CH$_2$ assymetric str. of aromatic – CH$_3$
	1611	-	Ring mode
	1507	1540	Non-linear poly phenyl
	1446	-	Sym. CH$_2$ bending of R- CH$_2$-R '
	1380	-	O-H in plane bending and C-O str..
	1261	1188	C-O str.
	816	820	Aromatic out of plane C-H bending
	750	740	Ortho di-substituted benzene
TVE-3C	3451	3360	O-H str. in phenol
	3013	3018	Aromatic C-H str.
	1508	1555	Ring mode
	1257	1190	C-O str.
	860	-	Aromatic out of plane C-H bending
	812	818	Ortho di-substituted benzene

substituted phenols co-ordinate to Fe^{2+} on the metal surface consequently decreasing the C-O bond strength.

DSC study

DSC thermogram of TVE-3A (Fig. 6) indicates that the compounds of the organic inhibitor mixture were vaporized with increase in temperature. In case of TVE-3B (Fig. 7) and TVE-3C (Fig. 8), exothermic and endothermic peaks were observed between a particular temperature ranges. In case of TVE-3B one exothermic peak at 76.56 to 90.63°C and one endothermic peak at 103.12 to 173.46°C was observed while TVE-3C showed two endothermic peaks at 108.12 to 123.30°C and at 124.82 to 146.57°C. After rerun of all the above samples, the compounds that may form in the condensation process at that temperature could not be dissociated up to 200°C. When the sample holder containing these inhibitors was opened, some residue inside the sample holder was noticed that might indicate thermal stability of all the tested compounds.
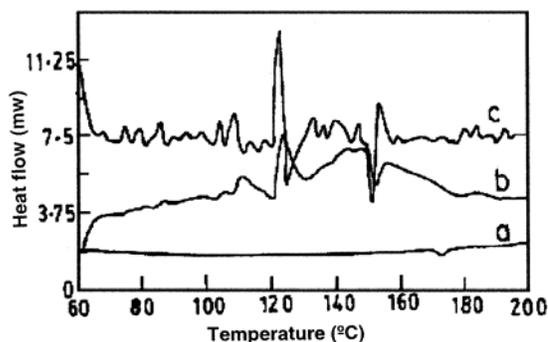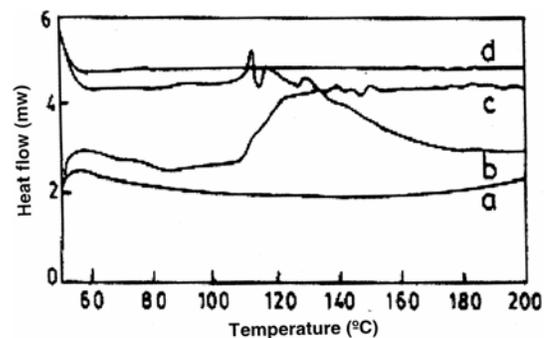

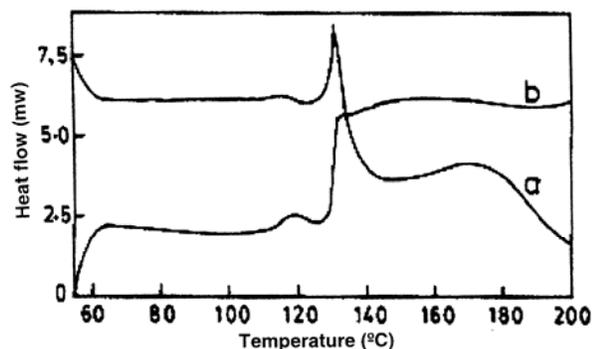Fig. 6—DSC thermogram of TVE-3A

Fig. 7—DSC thermogram of TVE-3B

Fig. 8—DSC thermogram of TVE-3C

Conclusion

All the tested mixtures inhibited the corrosion of the steel in 15% HCl medium. These inhibitor mixtures act as mixed type inhibitors, predominantly controlling anodic reaction and obey the Frumkin isotherm. TVE-3B has shown maximum inhibition of 68.6% at ambient temperature while it was 65.7% and 62.2% in case of TVE-3C and TVE-3A respectively. The inhibitor mixtures, TVE-3B and TVE-3C are found to be more effective in corrosion protection of the steel at higher temperatures (~81% at 115°C) and their protective efficiency is comparable with that of Grade-III (~ 88% at 115°C) commercial inhibitor. Grade-II inhibitor offered protection of about 92% at 115°C. However, in the case of TVE-3A, the protective efficiency gradually increased with increase in temperature up to 60°C and then showed a decrease in the inhibition efficiency (60.2% at 90°C). The inhibition efficiency of all the inhibitors showed significant inhibition (~ 70.0%) even after longer exposure time (24 h) in the acid. Presence of non-linear poly phenyl species (no free carbonyl group) was observed in the FTIR study of the metal surface products after the corrosion inhibition tests that may indicate formation of novalac resin or Bakelite by condensation polymerization. Oxygen atom, (of –OH group in phenol or substituted phenol) may co-ordinate Fe^{2+} on the metal surface resulting a protective inhibitor layer. DSC study revealed thermal stability of TVE-3B and TVE-3C organic mixture up to about 200°C.

Acknowledgement

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