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The influence of Cl^- on the passivity of Fe and Ni in acid organic solvents

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The influence of HCl on the anodic behaviour of Fe and Ni in DMSO/1 M H_2SO_4 depends on the water content of the solution. In completely anhydrous solutions the current density at the same voltage is in no case enlarged and pittings are certainly not observed. At water contents in the range 2–50% the two metals show pitting corrosion, but the current density at the same voltage is much lower than in aqueous solutions. The true anodic polarization measured with an interrupting potentiostat is very high and probably caused by a salt layer. It may be the source of the inhibition effect of DMSO. Fe in DMF/1 M H_2SO_4 has a similar anodic behaviour depending on the HCl concentration, but the polarization in this anhydrous solvent is much lower. The inhibition effect also seems to be lower.

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1. Introduction

Investigations on the anodic behaviour of iron and nickel in organic solvents with an interrupting potentiostat [1, 2] have shown that in completely anhydrous solvents (which have been investigated so far) a high polarization is found, which increases nearly linearly with the overall potential and may furnish a decrease of the current with increasing voltage (e.g. in dimethylsulphoxide). When we investigated the influence of different sulphuric acids such as H_2SO_4 itself, NH_2SO_3H, CF_3SO_3H, no significant distinction between the current–potential curves in the same solvent could be measured. In the present work the influence of hydrogen chloride on the anodic behaviour of Fe and Ni in 1 M H_2SO_4/dimethylsulphoxide (DMSO) and 1M H_2SO_4/dimethylformamide (DMF) with different water contents was studied, assuming that the chloride ions would have their typical effect on the anodic behaviour, such as pitting, in these solvents also.

2. Experimental

The solutions of DMSO/1 M H_2SO_4 and DMF/1 M H_2SO_4, prepared as previously [3], with different water contents (which was determined with the Karl Fischer method and to make the solvent utterly anhydrous, the rest of the water was converted with the corresponding quantity of SO_3) received the desired concentration of hydrogen chloride by passing anhydrous gaseous HCl or, in the case of higher water contents, by adding the necessary amount of aqueous hydrochloric acid. The samples of Fe and Ni were the same as previously used [3], embedded in polypropylene with a working surface of 0·5 cm^2 pre-treated in the same way as described in [3]. The electrochemical cell and the measuring device with an interrupting potentiostat is described elsewhere [1]. It was therefore possible to record the voltage- and current-dependent ohmic drop and by subtracting it from the overall voltage, the true polarization U_p could also be determined.

3. Results

The current–voltage curves in anhydrous solvents at a concentration of 0·1 M HCl, 1 M H_2SO_4 are practically the same as those obtained without HCl (DMF (100%), 1 M H_2SO_4 $\sigma = 240\ \Omega$ cm. DMSO (100%), 1 M H_2SO_4, $\sigma = 240\ \Omega$cm, 25° C); the current density i_p is even somewhat smaller than that without HCl (see Figs. 1a and b) when we compare the values of the current density at the same voltage in the normally passive region. In Fig. 1 the i–U curves of Fe in DMSO/1 M H_2SO_4 without (a) and with HCl (0·1 M) (b) are compared.

Furthermore these figures show the true polar-

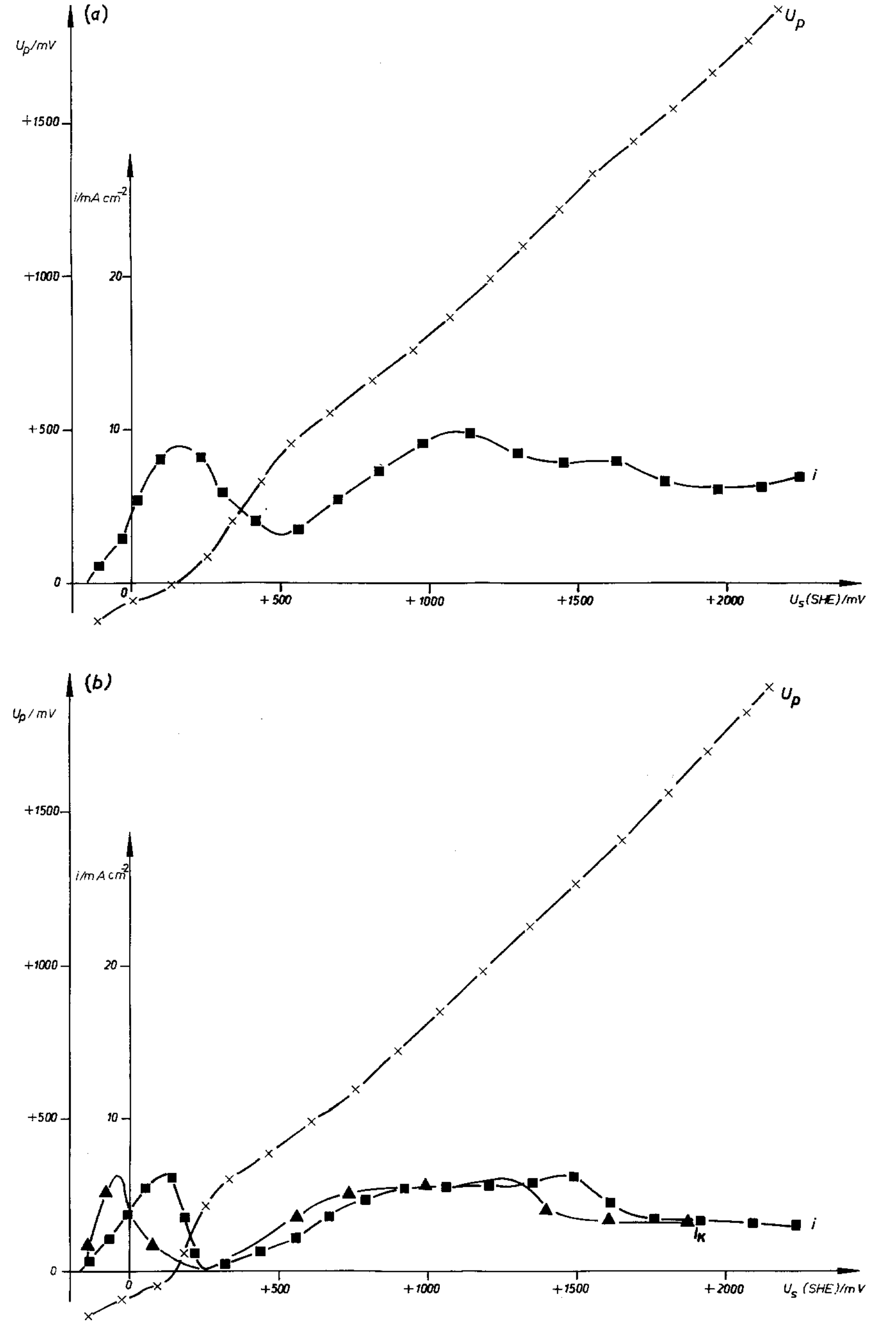

Fig. 1. (a) Anodic behaviour of Fe in DMSO (100 wt%), 1 M H_2SO_4. (b) Anodic behaviour of Fe in DMSO (100 wt%), 1 M H_2SO_4; 0·1 M HCl.

ization U_p calculated from the nominal voltage U_s and the ohmic drop U_K determined with the potentiostat during an interrupting time of 10 μs

$$U_p = U_s - U_K.$$

The curves were obtained by potentiodynamic measurement and recording; $\dot{U}_s = 20\,\mathrm{mV\,min^{-1}}$. The i_K-curves give the current density with automatic iR compensation, the i-curves without. As is seen in Table 1 at a water content of 2% Fe has

Table 1. Influence of HCl in 1 M H_2SO_4, DMSO, H_2O (Fe, $T = 25°$ C)

Solvent (DMSO : H_2O)	*HCl* (M)	$\mathcal{E}_R$ (mV versus SHE)	$\mathcal{E}_p$ *region* (mV versus SHE)	i_p (mA cm^{-2}) *at* $U_s = + 1500$ *mV versus SHE*	$\mathcal{E}_{tr}$ (mV versus SHE)	U_p *at* $U_s = + 1500$ *mV versus SHE*	*Remarks*
100:0	0	− 160	–	8	–	+ 1300	no passivity
100:0	0·10	− 170	–	6	–	+ 1270	no passivity
98:2	0	− 210	+ 300 to + 650	0·012	+ 1950	+ 1500	
98:2	0·05	− 230	+ 200 to + 900	0·035	+ 1920	+ 1500	
98:2	0·10	− 230	+ 400 to + 1100	0·050	+ 1900	+ 1500	
85:15	0·10	− 230	+ 500 to + 650	0·025	+ 1850	+ 1500	
85:15	0·20	− 260	+ 500 to + 1200	0·1	+ 1820	+ 1500	
85:15	0·30	− 260	+ 650 to + 1350	0·2	+ 1800	+ 1500	
80:20	0·05	− 230	+ 400 to + 600	0·01	+ 1880	+ 1500	
80:20	0·10	− 230	+ 400 to + 600	5	+ 1830	+ 1470	
75:25	0·10	− 240	–	20	–	~ 1250	no passivity } irregular
50:50	0·10	− 220	–	43	–	~ 1000	no passivity } i fluctuations
0:100	0·10	− 180	–	250	–	+ 100	no passivity

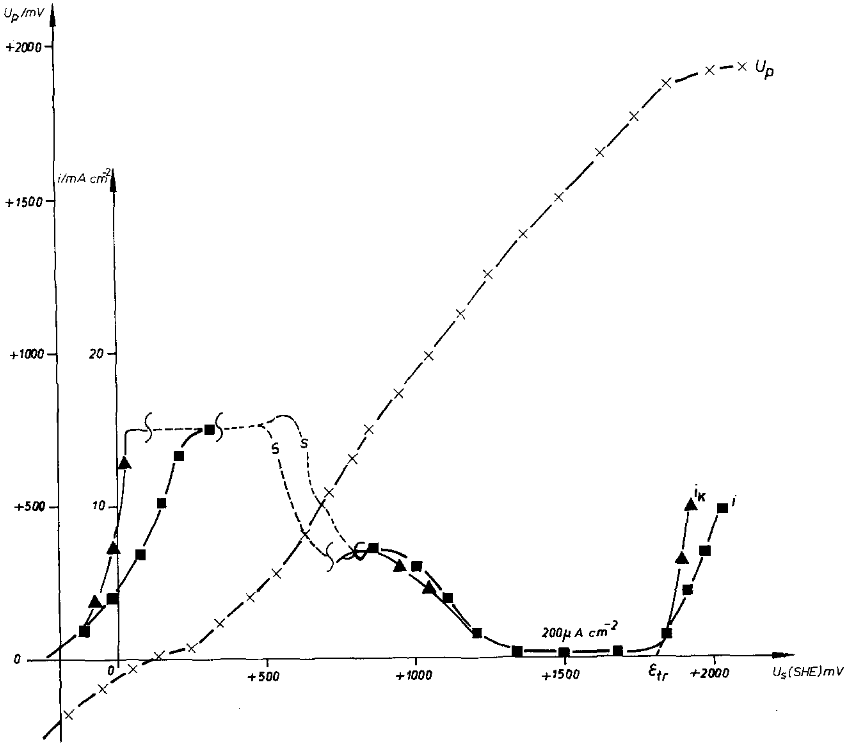

Fig. 2. Anodic behaviour of Fe in DMSO:H_2O (85:15), 1 M H_2SO_4, 0·3 M HCl. s: region of vibrations amplitude (max.): 20 mA cm^{-2}.

already become passive but the 'passive current' increases with the content of HCl. Ni in 98 wt% DMSO/1 M H_2SO_4 has the same current density with 0·1 M HCl as without HCl (see Table 2). In these tables the resting potential $\mathcal{E}_R$, the region of passivity $\mathcal{E}_p$, the potential of the rise into the transpassive state $\mathcal{E}_{tr}$, which may be considered as the critical (see Fig. 2) pitting potential, the current density i mA cm^{-2} at $U_s = +1500$ mV (SHE) and the true polarization U_p at the same overall voltage are also given. In DMSO with 15 wt% H_2O, Fe remains 'passive' up to 0·3 M HCl for a current density in the corresponding aqueous solution of more than 1000-fold higher.

At 75 wt% DMSO/0·1 M HCl only, one cannot speak of a passive state, but the current density at 1000 mV (SHE) is much smaller than that in H_2O, 1 M H_2SO_4. This behaviour may also be seen in the diagrams (Figs. 2–4). Ni remains 'passive' up to 50 wt% DMSO/0·1 M HCl, for a current density in H_2O/1 M H_2SO_4, 0·1 M HCl at 1000 mV (SHE) (see Fig. 5) is more than 40-fold higher. The polarization in the 1 : 1 mixture is high.

For Fe the potential $\mathcal{E}_R$ and that of the transpassive rise $\mathcal{E}_{tr}$ are normally more negative with HCl; the $\mathcal{E}_p$ region is more positive with HCl. As in the earlier papers [1–4] we use the 'passivity' definition of C. Wagner: decay of I with increasing U_s. In the anhydrous DMSO solutions the true polarization U_p increases nearly proportional to the nominal potential, independent of the HCl content (Figs. 1a and b). However, when no passivity is reached, the polarization U_p is relatively low; the high ohmic drop is caused by the high current density in the solution of low conductivity (see Figs. 3 and 4 and Tables 1 and 2). In DMSO: H_2O (50:50), 1 M H_2SO_4, 0·1 M HCl (Fig. 3) the U_p values at high U_s could not be determined because of the irregular current fluctuations. As demonstrated by Tables 1 and 2 the polarization caused by passive layers in solvent–water mixtures is nearly equal at the nominal voltage of + 1500 mV. In 100 wt% DMSO the polarization is somewhat smaller, but as previously shown [4] this passivity is fundamentally different from the passivity in the presence of water on account of its very short decay-time after disconnection of the applied voltage.

Table 2. Influence of HCl in 1 M H_2SO_4, DMSO, H_2O (Ni, $T = 25°$ C)

Solvent (DMSO : H_2O)	*HCl* (M)	$\mathcal{E}_R$ (mV versus SHE)	$\mathcal{E}_p$ *region* (mV versus SHE)	i_p (mA cm^{-2}) *at* $U_s = +1500$ *mV versus SHE*	$\mathcal{E}_{tr}$ (mV versus SHE)	U_p *at* $U_s = +1500$ *mV versus SHE*	*Remarks*
100:0	0	+ 250	+ 400 to + 550	0·6	–	+ 1485	no passivity
100:0	0·1	– 50	+ 450 to + 650	0·6	–	+ 1250	no passivity
98:2	0	+ 50	+ 550 to + 650	0·04	+ 1770	+ 1500	
98:2	0·1	– 20	+ 450 to + 630	0·5	+ 1670	+ 1480	
95:5	0·1	– 50	+ 730 to + 950	1	+ 1720	+ 1460	
90:10	0·1	– 30	+ 750 to + 950	1·6	+ 1650	+ 1452	
50:50	0·1	+ 30	+ 570 to + 750	22	+ 1770	+ 1450	
0:100	0·1	+ 50	–	400	–	+ 900	no passivity

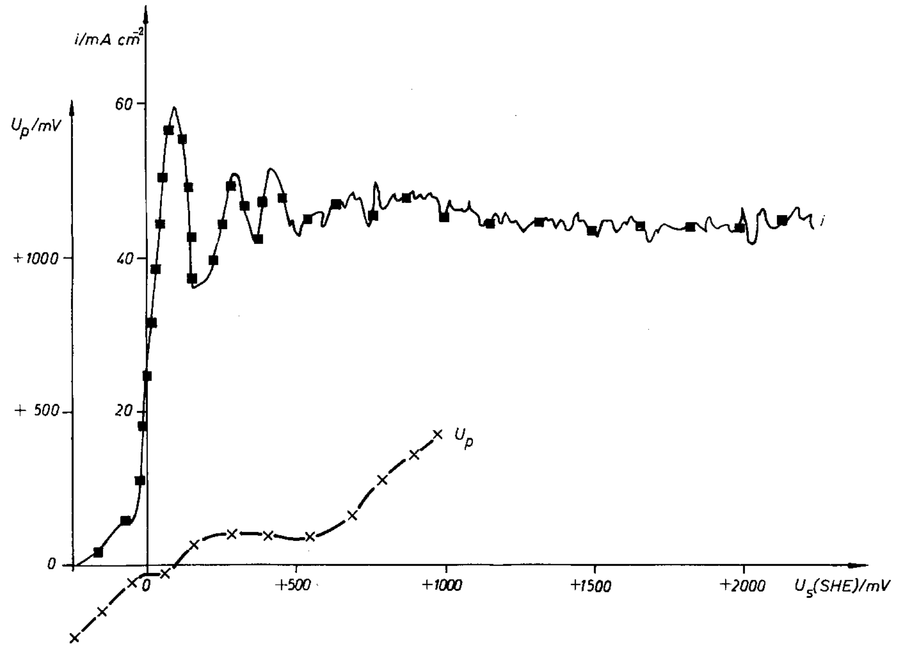

Fig. 3. Anodic behaviour of Fe in DMSO:H_2O (50:50), 1 M H_2SO_4, 0·1 M HCl.

In DMF (100 wt%) as in other anhydrous solvents [3] Fe is not passive and even a low HCl content somewhat decreases the current density at U_s = + 1500 mV (SHE) (Table 3). The polarization at this value of U_s is relatively low, even lower than in DMF–H_2O mixtures, where no passivation in the normal sense is observed (compare Figs. 6 and 7). Even at small water contents one can see from Table 3 the anodic behaviour of Fe in this solvent compared with DMSO.

When any rise after a low anodic current in the presence of HCl is observed, the potential $\mathcal{E}_{tr}$ ('pitting potential') is less positive than that without HCl and the move to lower values increases

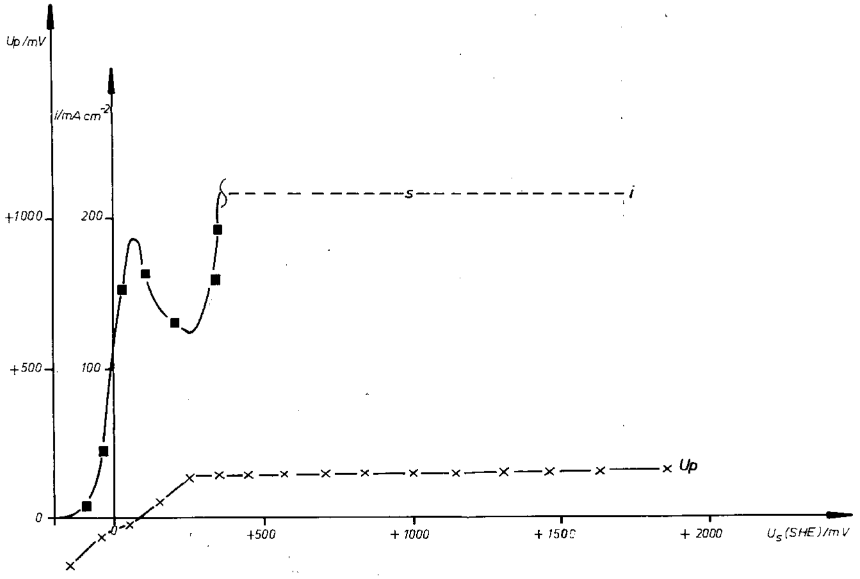

Fig. 4. Anodic behaviour of Fe in H_2O/1 M H_2SO_4, 0·1 M HCl. s: region of vibrations amplitude (max.): 310 mA cm^{-2}.

Table 3. Influence of HCl in 1 M H_2SO_4, DMF, H_2O (Fe, $T = 25°$ C)

Solvent (DMF : H_2O)	*HCl* (M)	$\mathscr{E}_{\mathrm{R}}$ (mV versus SHE)	$\mathscr{E}_{\mathrm{p}}$ *region* (mV versus SHE)	i_{p} (mA cm^{-2}) *at* $U_s = +1500$ *mV versus SHE*	$\mathscr{E}_{\mathrm{tr}}$ (mV versus SHE)	U_{p} *at* $U_s = +1500$ *mV versus SHE*	*Remarks*
100:0	0	−180	–	40	–	+ 500	no passivity
100:0	0·01	−150	–	36	–	+ 400	no passivity
100:0	0·10	−150	–	42	–	+ 330	no passivity
98:2	0	−230	+ 950 to + 1150	0·02	+ 1970	+ 1500	
98:2	0·01	−240	+ 650 to + 1070	0·04	+ 1970	+ 1500	
98:2	0·10	−250	+ 770 to + 1020	15	+ 1070	+ 1150	
85:15	0	−250	+ 400 to + 630	0·04	+ 1980	+ 1500	
85:15	0·01	−270	+ 650 to + 730	0·04	+ 1940	+ 1500	
85:15	0·30	−220	–	34·6		+ 850	no passivity
75:25	0·10	−250	–	32	–	+ 1050	no passivity
50:50	0·10	−250	–	31	–	+ 270	no passivity slow *i* fluctuations
0:100	0·10	−170	–	250	–	+ 100	no passivity

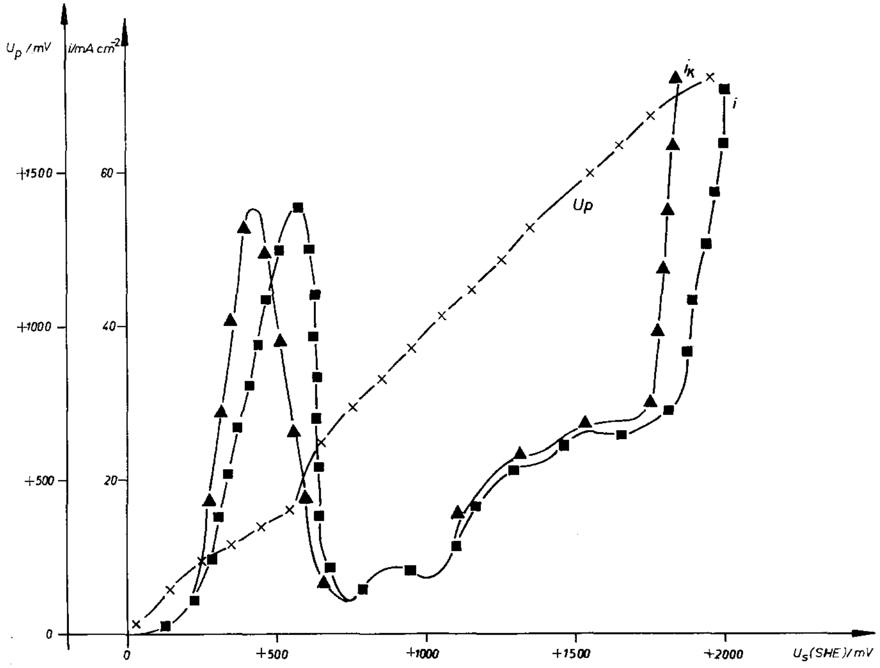

Fig. 5. Anodic behaviour of Ni in DMSO:H_2O (50:50), 1 M H_2SO_4, 0·1 M HCl. $\Delta U_s/\Delta t = 20\,\mathrm{mV\,min^{-1}}$.

with concentration of HCl, at least for Fe (Tables 1 and 3). Ni (Table 2) shows no obvious displacement of $\mathcal{E}_{tr}$, because shortly after the decay the current begins to rise with a different slope (see Fig. 5). The first rise has a value of $\mathcal{E}_{tr} = +1000$ mV.

However all the measurements with Fe and Ni in DMSO–H_2O mixtures prove that up to DMSO: H_2O = 50:50 this solvent inhibits the pitting corrosion, since the current density at the same voltage is much smaller than in aqueous solutions. The same is true for DMF and Fe, but the inhibiting effect seems not to be so strong; Ni in DMF, HCl, H_2O has to be proved. Whereas in completely anhydrous DMSO and DMF/HCl there are no distinct pittings,

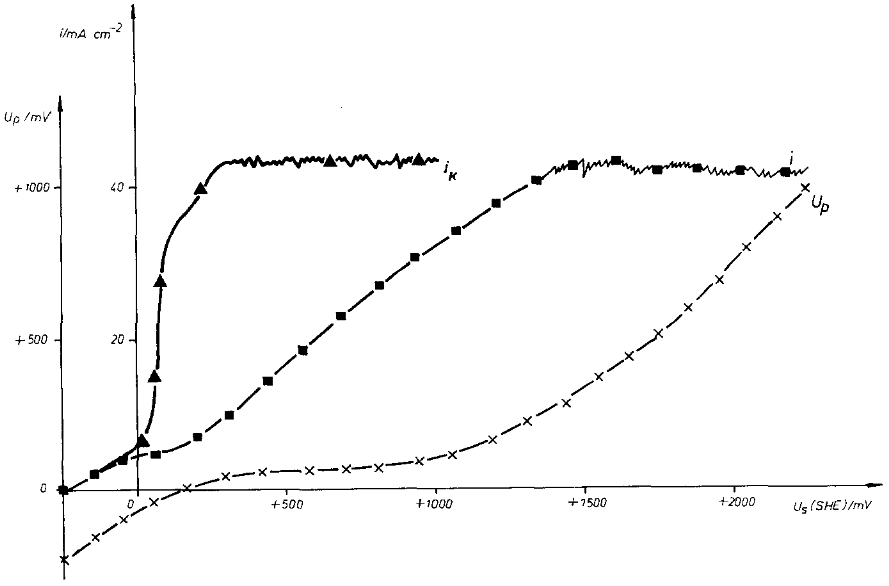

Fig. 6. Anodic behaviour of Fe in DMF (100wt%), 1 M H_2SO_4, 0·1 M HCl.

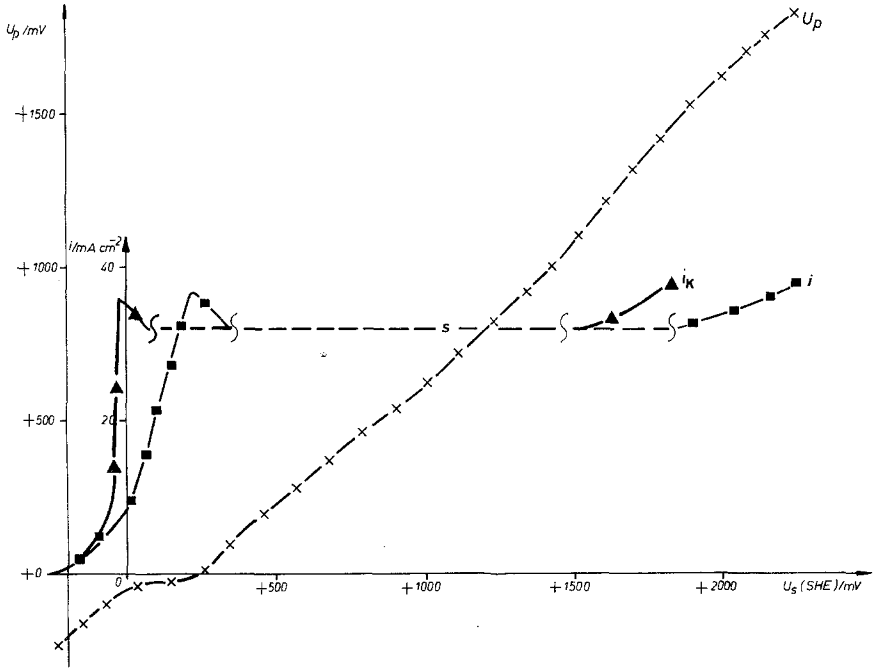

Fig. 7. Anodic behaviour of Fe in DMF : H_2O (75 : 25), 1 M H_2SO_4, 0·1 M HCl. s: region of vibrations amplitude (max.): 36 mA cm^{-2}.

they are formed in the presence of water (Fig. 8) and the diameter increases with the concentration of HCl, so that at high currents the attack seems to be uniform after a short time.

4. Discussion

When we consider the influence of HCl on the anodic behaviour of Fe and Ni in anhydrous solvents and at low water contents also, it seems possible to explain it by the preferential adsorption of Cl$^-$ or HCl over that of the solvents on the surface of the metals.

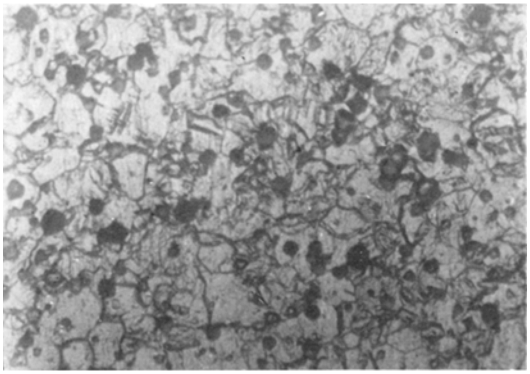

Fig. 8. Pittings on Ni in DMSO : H_2O (98 : 2) 1 M H_2SO_4, 0·1 M HCl. (× 285).

In anhydrous solvents, the adsorption of the solvent with a following solid state reaction forming the salt of the metal is assumed [3]. As formerly supposed [4], the metal atoms of the surface react anodically with the anions of the solution without being dissolved before the anodic voltage is high enough and this form of passivation can be clearly distinguished from the passivation with water by oscillographic decay curves [4]. The higher polarity of DMSO compared with DMF [5] leads to a strong adsorption on the surface and so the anodic dissolution is inhibited: the current density of Fe at + 1000 mV (SHE) is 9·2 mA cm^{-2} in DMSO but ~ 40 mA cm^{-2} in DMF (without HCl, see Tables 1 and 3). In the presence of water one has to take account of not only its high polarity and strong adsorption but also its strong hydration energy with the surface cations and also the solid-state reaction forming the passive layer. So the competition of adsorption and hydration may lead to a different effect on the anodic dissolution in the active region (dependent on the metal and its exchange current density). At small water contents, without HCl the stronger adsorption of DMSO compared with DMF probably yields the much lower current density in the active region.

In the anhydrous solvents where HCl has no significant effect on the current density at + 1500 mV (SHE), Fe and Ni do not become passive. DMSO and DMF HCl solutions at low concentrations even seem to have an inhibition effect [6, 7]. Thus the current density at + 1000 mV (SHE) is nearly a half of that when the 1 M H_2SO_4, DMSO contains 0·1 mol HCl. But in the presence of water the specific adsorption of the Cl^- with the following hydration of the cations destabilizes the passive layer formed by the water, and when the HCl content is high this layer is not formed at all.

For every case in strong acid, anhydrous DMSO and DMF, the active dissolution of Fe and Ni (at least in DMSO) is essentially not influenced by HCl and no trustworthy pitting effect could be detected. That means that, in these conditions, no layer is formed even in the presence of oxygen [3] which can be destroyed by Cl^- or HCl.

The importance of the water for the formation of passive layers on Ni has been impressively evidenced by Auger electron spectroscopy with argon ion sputtering by Frankenthal and Kulpa [8] and for passive layers on Fe with X-ray photoelectron spectroscopy by Roberts and Wood [9].

Nevertheless high anodic polarizations are found especially in anhydrous DMSO for Fe and Ni, as can be seen in Figs. 1a and b and Tables 1–3. Since we can consider the large polarization as nearly proportional to the overall voltage (see Figs. 1a and b) at the beginning of the anodic voltage rise then it seems likely, because of the large Coulomb force between the surface cations and the anions in the solution, that a salt layer is formed by electrochemical or chemical reactions [3]. The high polarity of the DMSO molecules and their strong adsorption makes the anodic reaction with SO_4^{2-} or Cl^- more difficult than with the DMF molecules. The large excess of solvent molecules over anions makes this difference between the solvents independent of the anions. On the other hand, the individual solvation tendency of DMSO and DMF with respect to the cations may stabilize or dissolve a solid salt layer. Until now this has not been proved for enough solvents in order to give a definite explanation for the large differences between the anodic behaviour of Fe in the two aprotic solvents. That the anodic current density of Fe at the same true polarization is much higher than that of Ni in the solvents investigated was shown previously [4].

Furthermore it is not yet possible to designate quantitative relations between the electrochemical data of the current density–voltage curves and the related parameters of the solvents. For these data, for example, i_p, passivation potential, and so on can at best be reproduced under the same conditions [10, 11] only up to ± 10%. But it seems to us certain that water is necessary to produce this kind of passivity on iron and nickel, which has been well known since Faraday. This was also proved for the anodic behaviour of Fe in anhydrous methanol [3, 12]. The results of Brinzoi and Constantinescu [13] with carbon and stainless steel in methanol–water mixtures without and with HCl are no proof for the passivity of these steels in anhydrous methanol. When it is free of electrolyte the oxidation of the solvent

$$CH_3OH \rightleftharpoons CH_2O + 2H^+ + 2e^- \quad \mathcal{E}_H^0 = +0{\cdot}3\,V$$

can only give a rise of the current density. With HCl, stainless steel gives only a negative current–voltage characteristic in solutions with $CH_3OH : H_2O = 92:8$ but not at very small water contents. The potentials given in this work are measured moreover without taking into account the ohmic drop (specific conductivity of CH_3OH with 5 wt% H_2O, $3{\cdot}2 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$). That the minimum content of water necessary to produce passivity is different for each solvent was demonstrated earlier [3].

That oxide layers already existing on metals would have a real passivating effect without water in organic solvents seems questionable on the basis of the investigations of Garreau and Bonora [14] on the anodic behaviour of Al in ethanol and from our own, unpublished experiments with Al in DMF and DMSO.

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