

Effect of organic acids and bases on cathodic corrosion of aluminium in chloride solutions*

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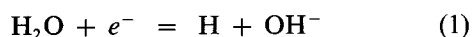
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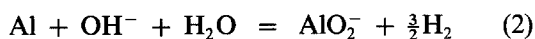
An attempt was made to inhibit cathodic corrosion of aluminium by the use of organic acids and bases. The corrosion is assumed to be caused by the effect of OH^- ions formed from water upon cathodic hydrogen evolution. This is known to result in hydration of the protective oxide film and chemical attack on the metal. Hence, organic substances were expected to inhibit the corrosion by consuming OH^- ions as well as by an adsorptive effect. The substances tested were HAc, HPro, HBut, HNic, TEA, Pyr, 3-Pic, 4-Pic, 3,5 Lut, 2,6 Lut, 2,4,6 Col, 4-HP, 2,4 AMP, 6,2 AMP, 2 AP and 3 AP. The best effect was achieved by TEA, 2,4 AMP and 2 AP, the potential window for low corrosion rate being extended by several hundred millivolts.

1. Introduction

Corrosion of aluminium has been a subject of numerous studies due to the importance of this material in contemporary civilization. It is well known that there is a potential region in which the rate of corrosion, even in such aggressive media as chlorides, is relatively small, of the order of $1 \mu\text{A cm}^{-2}$ (or $3 \times 10^{-4} \text{ mg cm}^{-2} \text{ h}^{-1}$ in material equivalent). In the absence of air or other 'depolarizer', or of an external electric field, aluminium in solution rests within this 'potential window' and, hence, is a very stable material. Yet, this window is limited on both the anodic and the cathodic side. At potentials of about -0.8 V with respect to the saturated calomel electrode (SCE) a sharp rise in anodic current occurs, with a resulting localized dissolution (pitting corrosion) [1]. On the cathodic side a similar phenomenon is observed. If the potential is driven negatively beyond about -1.4 V/SCE a sharp rise in current occurs [2], not only producing gaseous hydrogen but also causing dissolution of the metal by the chemical attack of hydroxyl ions formed in the same process. The interesting fact is that this dissolution is up to three times more efficient than that on the anodic side when calculated in terms of current efficiency [3], one aluminium atom being dissolved for each electron exchanged in the cathodic process, because the process consists of the reactions



and



Thus, the production and participation of OH^- ions is essential for the 'cathodic corrosion of alu-

minium'. Cathodic corrosion can be equally damaging as anodic in situations where the potential is driven negative (cathodic protection, electrophoretic deposition of paints and polymers). Hence, the possible inhibitive action of different substances is sought. This paper reports an attempt to obtain insight into the effect of organic acids and bases on the cathodic processes at this metal in chloride solutions.

2. Experimental details

High purity aluminium (99.999%, obtained by courtesy of Alcan International) was cut into cubes with 1 cm sides, and made into electrodes by pressing a copper wire into a hole on one side and then insulating all but one side with an epoxy resin. The open side was polished mechanically to a mirror finish, rinsed in alcohol and triply distilled water and stocked in a dessicator to attain its 'natural' oxide skin.

The electrochemical glass cell was of the usual type with provision for purging with purified nitrogen and thermostating. Aluminium electrodes could be introduced through the lid close to a Luggin capillary for connection with an SCE reference electrode. Platinum wire, enclosed in a tube with a glass frit, could be introduced into the same solution as the counter electrode.

The basic solution was 2 M NaCl made of reagent grade salt and triply distilled water, to which organic acids and bases were added in different concentrations. The additives used were as follows: acetic acid (HAc), propionic acid (HPro), butyric acid (HBut), nicotinic acid (HNic), triethanolamine (TEA), pyridine (Pyr), 3-picoline (3 Pic), 4-picoline (4 Pic), 3,5-lutidine (3,5 Lut), 2,6-lutidine (2,6 Lut), 2,4,6-collidine (2,4,6

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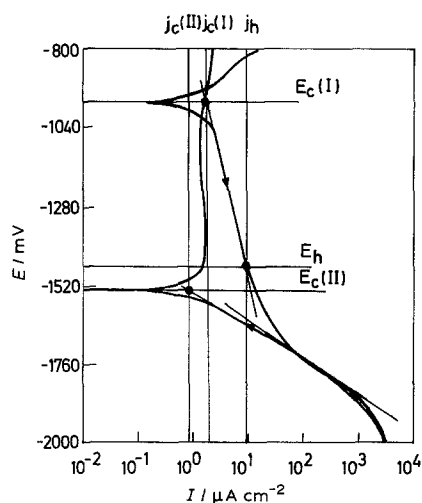


Fig. 1. Tafel plots of aluminium in 2 M NaCl solution obtained (↓) after some dwelling at the pitting potential and (↑) in the potential region between -1.8 and -2.0 V/SCE. E_c – corrosion potential, E_h – hydration potential, j_c – corrosion current density, j_h – deviation current density.

Col), 4-hydroxypyridine (4 HP), 2-amino-4 methylpyridine (2,4 AMP), 6-amino-2-methylpyridine (6,2 AMP), 2-acetylpyridine (2 AP) and 3-acetylpyridine (3 AP).

Electrochemical measurements were performed with a potentiostat (Par 273) driven by a computer (Comodore 128). Potential sweeps at a very low sweep rate (0.5 mV s^{-1}) were applied to aluminium electrodes starting from the pitting potential in the negative direction down to -2.0 V/SCE and back. The current response was converted to a logarithmic scale and the resulting Tafel plots, covering up to 6 orders of current density, were obtained on the plotter.

Weight loss measurements were made in a cell having both the cathode and the anode equal in the form of aluminium cubes. They comprised weighing both the cathode and the anode before and after holding the cathode at -1800 mV/SCE for up to 24 h and subsequently removing the corrosion products by a standard procedure with a mixture of 1.8% CrO_3 and 7 vol % H_3PO_4 at 80°C for 1 min.

3. Results

3.1. Polarization of aluminium in pure NaCl solution

The very slow scan applied to the system may be considered to simulate a steady state situation at each potential. Hence, quasi steady state Tafel plots resulted from scanning. A typical plot obtained in 2 M NaCl of pH 6.5, without any additives is shown in Fig. 1. A major difference should be noted between current responses to scanning in the cathodic and in the anodic direction. Driven from the pitting potential in the negative direction the electrode crosses the zero current potential, $E_c(\text{I})$, whereupon it enters a potential region of very slow increase in current (a linear Tafel relationship with a slope of the order 0.5 to 1 V dec^{-1}). Extrapolation of the Tafel line to the $E_c(\text{I})$ gives a corrosion current $j_c(\text{I})$, of the order of $1 \mu\text{A cm}^{-2}$. At

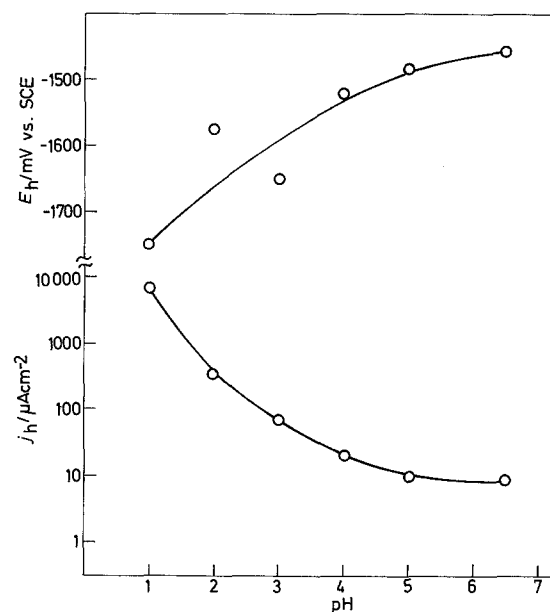


Fig. 2. pH-dependence of the hydration potential, E_h , and current density, j_h , in pure NaCl solution.

a potential of about -1.480 V/SCE, denoted as the hydration potential, E_h , a deviation of current from the linear Tafel line starts, leading to orders of magnitude larger current densities and a new linear portion of the Tafel plot tending to a slope of about 120 mV dec^{-1} .

After dwelling in the potential region between -1.8 and -2.0 V/SCE ('high cathodic potential' region – HCP) and correspondingly high current densities between 0.1 and 50 mA cm^{-2} for 800 s, the return of potential in the positive direction causes a divergence of the current response leading to a new corrosion potential significantly more negative than the initial one $E_c(\text{II})$, whereupon an anodic current of the order of $10 \mu\text{A cm}^{-2}$ persists to the end of the scan, i.e. for another 1200 s. Similar plots were obtained at decreasing pH values down to 1. However, a notable change in character occurs at pH below 6, the current–potential dependence tending to pH dependent limiting current densities. The dependence of E_h and j_h on pH is shown in Fig. 2. Table 1 gives examples of weight loss. It is

Table 1. Weight loss of aluminium at the cathode held at -1800 mV/SCE for 24 h compared to that at the anode polarized with the same current density

Electrolyte	pH	Weight loss/mg		Recorded current/mA	Cath./An. weight loss
		cathode	anode		
2 M NaCl	5.06	26.9	42.7	2.5	0.63
+0.5 M HAc	2.26	0.2	2.6	0.25	0.08
+0.1 M HAc	2.58	0.7	3.4	1.0	0.20
+0.05 M HAc	3.14	11.7	23.4	2.5	0.50
+0.005 M HAc	3.28	16.5	28.9	3.0	0.57
+0.001 M HAc	3.46	14.6	25.6	3.0	0.57
+0.1 HPro	2.57	0.7	6.5	1.0	0.11
+0.05 HPro	2.76	1.5	7.8	1.22	0.19
+0.005 HPro	3.22	3.3	10.0	1.44	0.33
+0.001 HPro	3.53	6.0	11.8	1.78	0.51

seen that in the pure NaCl the cathodic weight loss was comparable to the anodic one, their ratio being 0.63.

Characteristic features of all the recorded cathodic Tafel plots obtained in 2 M NaCl solutions without and with the addition of the organic acids and bases are shown in Table 2.

3.2. Effect of organic acids on the polarization properties of aluminium

The addition of organic acids to the NaCl solution produces major changes in the Tafel plot. This is exemplified by the plots, shown in Fig. 3, obtained after the addition of 0.5 M HAc. The characteristic of the plot compared to that in pure NaCl solution is that E_c is shifted in the positive direction and that j_c is significantly larger. The Tafel slopes in the low cathodic potential (LCP) region are much higher and E_h is shifted in the negative direction by 50 to 100 mV. The striking difference arises in the plots obtained after the system dwelt in the HCP region. These exhibit a corrosion potential no different to the original one. The return polarization curve virtually coincides, in the HCP region, with that obtained in the cathodic sweep to a potential close to E_h , whereupon it runs parallel to the latter, but at significantly lower current density. The difference is largest in the presence of HBut, where some shift of E_c in the negative direction is also observed.

As the highest current attained in the presence of the acids at -2.0 V/SCE is larger than that in pure NaCl solution, and because of the exponential nature of the current-density-potential relationship, the amount of electricity passed during the dwell in the HCP region is more than proportionally larger. Thus, during the 800 s of dwell in pure NaCl solution about 220 mC cm^{-2} of cathodic charge is transferred while in the presence of the acids this amounts to over 800 mC cm^{-2} .

As the concentration of an acid is lowered a limiting current region appears, as shown in Fig. 4 for the HPro. This limiting current is proportional to the concentration of the acid. Before it there is a continuous decrease in the Tafel slope. At the end of the limiting current plateau there is again an increase in current density and this potential is denoted here as E_h . It is seen in Fig. 5 to be substantially more negative than that in pure NaCl solution.

The presence of the organic acids is seen in Table 1 to substantially reduce the weight loss compared to that in pure NaCl solution. The cathodic-to-anodic weight loss ratio is seen to increase with decrease of acid concentration and increase of pH.

3.3. Effect of organic bases

3.3.1. Triethanolamine. As seen in Fig. 6 the presence of TEA affects the Tafel plot for aluminium in NaCl solution at a concentration as low as 1 mM. Comparing with Fig. 1 it is seen that the Tafel slope in the LCP

region remains virtually the same, but with j_c and subsequent cathodic currents larger by one order of magnitude. E_h is shifted in the negative direction by about 300 mV. As shown in Table 2, further addition of TEA does not increase the effect, the E_h exhibiting a relatively small dispersion of points. One persistent feature is the appearance of a current maximum (hump) in the potential region around $E_p = -1.50$ V/SCE. As this peak is overcome the polarization curve continues its high slope trend which it followed before the peak.

3.3.2. Pyridine. A characteristic of pyridine is that it has an effect at very low concentration (0.001 M) but the effect is very small compared to TEA and a slight concentration dependence is found. Tafel plots exhibit rather poor reproducibility. Still, as seen in Fig. 7, an entirely different picture is obtained than that in pure NaCl solution, for two values of pH (adjusted by adding HCl). A current hump is also observed at about -1.35 V/SCE. If the hump is neglected and the change of slope is observed, it can be seen (Fig. 7) that it occurs at $E_{h,a} = -1.508$ at pH 6.5 and $E_{h,b} = -1.679$ V/SCE at pH 1. Generally, the slopes in the LCP region are lower at the lower pH than at the higher one.

It is interesting to note that, although at the lower pH and at one and the same potential throughout both the LCP and the HCP regions, the recorded current densities are significantly larger than those at the higher pH, close to the corrosion potential the opposite situation arises and the corrosion current at the lower pH is smaller than at the higher one.

The Tafel plots for the return sweep after dwelling in the HCP region (not shown in Fig. 7), and even at less negative potentials (down to -1.6 V/SCE) virtually coincide with those obtained at cathodic going potentials. Yet in the LCP region the plots diverge and an anodic component becomes significant, giving a corrosion potential far more negative than the original one (between -1.3 and -1.5 V/SCE) and an anodic current density of up to $50 \mu\text{A cm}^{-2}$, persisting during the entire potential return, which takes, e.g. at pH 1, some 1000 s (about 50 mC cm^{-2} of anodic charge). Also, no current hump is recorded.

3.3.3. Pyridine derivatives. Addition of all the pyridine derivatives was investigated in solutions of pH 6.5. The effect of methylpyridines (picolines) and dimethylpyridines (lutidines) appear to depend on the position of the methyl-group in at least one feature — the current hump. Thus, the 4-Pic and 2,6-Lut exhibit the hump as well as other features of the Tafel plot much in the same way as the Pyr itself, except that the effects increase with increasing concentration (up to 0.05 M) and E_h occurs at significantly more negative potentials. In the case of 4-Pic the hump, as well as current densities at the same potentials, decrease with increasing additive concentration. The hump is lost at 0.05 M of additive in the solution. A similar situation is found with 2,6-Lut except that the hump vanishes

Table 2. Characteristic features of the cathodic Tafel plots of aluminium in 2_M NaCl, without and with addition of some organic acids and bases

Substance	c/M	pH	E_c	$j_c/\mu\text{A cm}^{-2}$	E_h	$j_h/\mu\text{A cm}^{-2}$ note
NaCl	2	6.5	-960	1.5	-1460	9
		5	-1170	4	-1482	10
		4	-1145	12	-1520	21
		3	-1240	8	-1652	70
		2	-995	210	-1575	350
		1	-950	2300	-1750	7200
+ HAc	0.5	2.55		20	-1541	71
+ HPro	0.5	3.12		20	-1500	54
+ HBut	0.5	3.60		20	-1467	39
+ TEA	0.001	6.5	-902	17	-1750	422
	0.005	6.5	-902	38	-1732	442
	0.007	6.5	-946	26	-1794	681
	0.01	6.5	-955	26	-1750	562
	0.05	6.5	-980	15	-1760	280
	average			-937 ± 28	24 ± 7	-1757 ± 16
+ Pyr	0.001	6.5		6	-1500	18
		1		2.5	-1679	380
	0.01	6.5		13	-1491	15
		1	-1020	8	-	-
+ 3-Pic	0.005	6.5	-952	3.7	-1530	54
	0.05	6.5	-911	4.7	-1420	24
+ 4-Pic	0.001	6.5	-1015	15	-1500	100
	0.01	6.5	-920	7	-1562	46
	0.05	6.5	-1060	9	-1562	46
+ 2,6-Lut	0.005	6.5	-970	17.4	-1520	191
	0.05	6.5	-1170	6.7	-1750	268
+ 2,4,6-Col	0.005	6.5	-855	5.5	-1510	31
	0.05	6.5	-820	10	-1680	280
+ 4-HP	0.005	6.5	-980	7.0	-1480	14
	0.05	6.5	-975	5.7	-1640	110
2,4 AMP	0.001	6.5	-884	25	-1678	649
	0.005	6.5	-897	38	-1732	610
	0.005		-1180	7.0	-1770	160
	0.007	6.5	-942	14.7	-1785	486
	0.01	6.5	-928	12.7	-1768	618
	0.05	6.5	-910	21.5	-1768	421
	0.05	6.5	-925	4.0	-1840	340
	average			-952 ± 50	17 ± 8	-1763 ± 33
+ 6,2 AMP	0.005	6.5	-825	10.0	-1520	70
	0.05	6.5	-835	7.5	-1665	110
+ 2 AP	0.001	6.5	-898	10	-1717	158
			-861	15	-1776	562
	0.005	6.5	-871	5.7	-1755	422
			-910	15	-1723	619
	0.007	6.5	-837	10	-1640	478
			-892	15	-1759	825
	0.01	6.5	-880	5.5	-1623	147
			-883	10	-1750	464
	0.05	6.5	-968	10	-1822	360
			-919	19.5	-1763	649
average			-891 ± 24	12 ± 4	-1732 ± 45	435 ± 164
HNic	0.005	6.5	-830	7.0	-1400	10
	0.05	6.5	-830	7.5	-1305	14

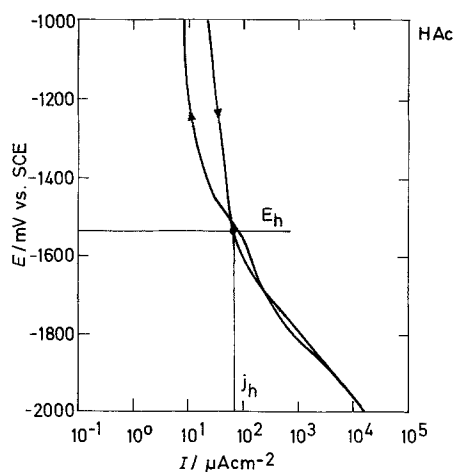


Fig. 3. Tafel plots of aluminium in 2M NaCl solution with the addition of 0.5M HAc (pH 2.55).

by 0.01 M of the additive. E_{cor} is shifted significantly in the negative direction. With the methyl-group in position 3(3-Pic) no current hump is observed. Also, contrary to all other bases which shift the E_{cor} in the negative direction compared to the pure NaCl solution, the 3-Pic shifts E_{cor} in the positive direction to the region around -0.9V/SCE .

In the presence of the tri-methyl pyridine (collidine) no current hump was observed at any concentration. A significant shift of E_{cor} in the positive direction was found. Other features of the Tafel plots are similar to those for the other pyridine derivatives.

Qualitative features of the Tafel plots of the other pyridine derivatives (4HP, 2,4 AMP, 2,6 AMP, 2 AP and 3 AP) were similar to those already described. The effects, however, appear to be much stronger than in the previous cases. Thus, E_h is found rather negative in 1 mM solutions and further increase in concentration produces virtually no effect. Hence, average values for the entire concentration range are calculated and given in Table 2.

The addition of nicotinic acid, as an example of a compound having both the acid and the basic function, was found to give similar effects as those of the other organic acids.

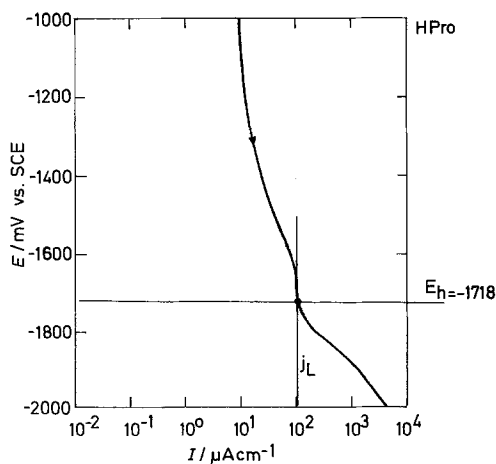


Fig. 4. Cathodic Tafel plot of aluminium in 2M NaCl solution with the addition propionic acid in a concentration of 0.05M.

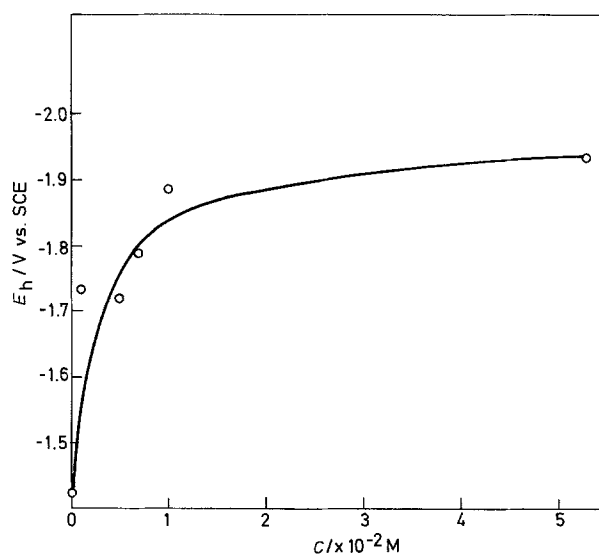


Fig. 5. Hydration potential of aluminium in 2M NaCl solution as a function of concentration of propionic acid added to the solution.

It is interesting to note that with both types of additive, although the current densities attained in the HCP region are significantly decreased with increasing concentrations of the additives, the anodic oxidation current of substances accumulated during dwell in the HCP region are larger in the larger concentration of both additives than in the lower ones.

4. Discussion

4.1. Polarization of aluminium in NaCl solutions

The Tafel plots proved to be good diagnostic tools for detecting the initiation of hydration of the oxide layer. The high slope at potentials between E_c and E_h (i.e. in the LCP region) at $\text{pH} > 6$ reflects discharge of water through the oxide film. In this region the increase of OH^- concentration, as a result of the balance between their production and diffusion away from the electrode, is too small to produce significant hydration of the oxide layer. However, beyond E_h this effect becomes

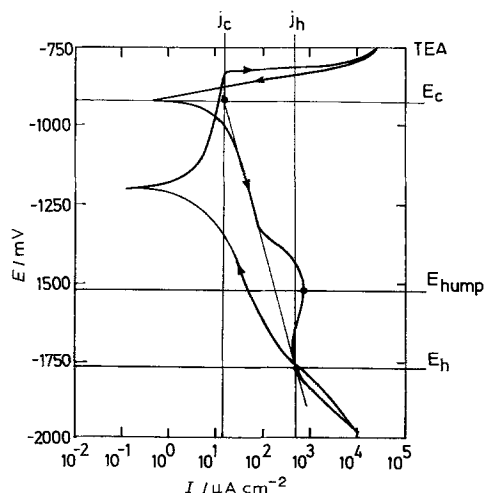


Fig. 6. Tafel plots of aluminium in 2M NaCl solution with the addition of 0.001M TEA recorded in the cathodic direction of change of potential (↓) and in the anodic one (↑).

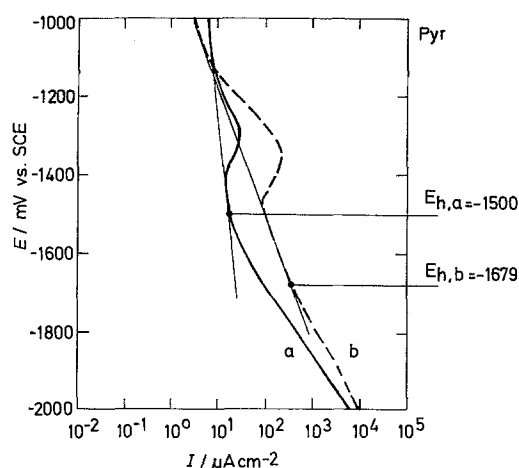


Fig. 7. Cathodic Tafel plots of aluminium in 2 M NaCl solution with the addition of 0.001 M Pyr and the adjustment of pH to two values, of 6.5 (a) and 1 (b).

significant. As the other linear portion of the Tafel plot is reached, the hydration of the oxide layer should be completed and hydrogen should be evolved at the bare metal surface. The slope in the range of 120 mV dec^{-1} indicates the usual mechanism of hydrogen evolution with the Volmer reaction as the rds. The corresponding formation of OH^- ions must produce the aforesaid chemical attack and cathodic corrosion of the metal.

The model is also supported by the weight loss measurements (Table 1), which show that the potential of -1800 mV/SCE is a potential beyond the hydration limit when chemical dissolution at the metal surface attains a similar intensity as that due to anodic dissolution at the other electrode.

Obviously the OH^- ions are formed only after the H^+ ions at the interface are exhausted by hydrogen evolution. Indeed the character of the Tafel plot (diffusion limiting current) at low pH indicates such exhaustion. Hence, it is to be expected that the cathodic current, j_h , needed to accomplish this should be proportional to the H^+ -ion concentration. This is seen in Fig. 8 to be roughly so at least in the low pH region (dashed line). The nonlinearity of the plot, i.e. ever larger currents needed for initiating hydration at higher pH values, can be understood in terms of an increased portion of OH^- ions leaving by diffusion.

4.2. Effect of addition of organic acids

All the three acids tested produce the same effect on the polarization of aluminium when starting from the corrosion potential at which the 'natural' oxide exists. Although there is a substantial increase in the corrosion current the increased slope of the Tafel plot, that is a higher resistance to discharge in the LCP indicates that in the presence of the acids the oxide layer either increased in thickness or decreased in conductivity or both. As both j_c and the Tafel slope have the same value in all acids they must be a consequence of acidity rather than of the organic character of the additives. Moreover a higher discharge rate through increased resistance indicates that the dis-

charge involves a different species, i.e. hydrogen ions rather than water. That this is so, is confirmed by the fact that at low acid concentrations there is the appearance of limiting currents (Fig. 4) which must reflect the slow transport of the acid molecules to the interface.

The hydration currents, j_h , imposed by the presence of the organic acids, when plotted against the pH which they produce in the solution, are seen in Fig. 8 to fall on a curve reflecting the effect of acidity in the pure NaCl solution. This indicates that it is only the active acidity of the organic acids rather than the acid capacity (total acidity), which affects the process of hydration which could be the case if the dissociation of the acids was very slow compared with the rate of discharge of H^+ -ions.

Availability of H^+ ions for discharge defers formation of OH^- from water and hence prevents hydration and cathodic corrosion.

Indeed, as seen in Table 1, in the presence of 0.5 M organic acids, the cathodic weight loss is reduced to the limits of error of the measurements. At lower acid concentrations, however, the weight loss ratio approaches that obtained in pure NaCl solution.

4.3. Effect of organic bases

The effect of addition of organic bases to the NaCl solution, upon adjusting pH to 6.5 with HCl, is summarized in Fig. 9. Here, j_h is plotted against E_h (both being taken from Table 2) for pure NaCl and for different additives at two concentrations 0.005 M and 0.05 M. Average values and the average dispersion fields are given for the derivatives for which no concentration dependence is found.

Three groups of derivatives can be distinguished. The first, consisting of Pyr, as well as the 3-Pic, 4-Pic and HNic, gives relatively little effect on E_h even at the highest concentrations investigated. In two cases E_h was found to be even more positive than the values pertaining to the pure NaCl solution ($E_h = -1460$). Thus, in these cases little or no inhibition is observed either in delaying hydration or in decreasing the rate of hydrogen evolution at the oxide surface. On the contrary, j_h is generally significantly larger than in the case of pure NaCl solution. This indicates (a) that the additives do not exhibit buffering capacity with respect to OH^- ions and (b) that they affect the oxide layer (possibly reducing its thickness) so as to make electron tunnelling and water reduction easier than in the pure NaCl. In the case of 3-Pic the lack of buffering could be due to a very low concentration of the picolinium cation because of the low total concentration of 3-Pic and low degree of dissociation at the given pH. The HNic as a dual function compound has the dissociation constants of both functions too close to the pH 6.5 as to offer sufficient amount of either H^+ or of the corresponding cation, to be able to buffer the OH^- ions to a notable extent.

In the second group there are some pyridine derivatives (2,6 Lut; 2,4,6 Col; 4 HP; 6,2 AMP). They do

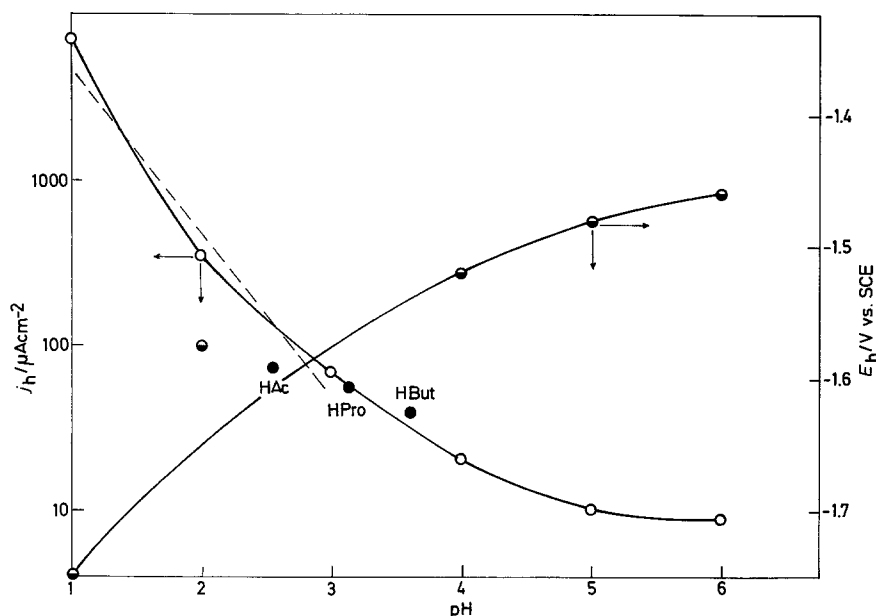


Fig. 8. pH-dependence of the hydration current in pure 2 M NaCl solution as well as in solutions containing 0.5 M of organic acids.

shift E_h to considerably more negative values than that for pure NaCl solution of the same pH, but only at relatively high concentration (0.05 M).

In the third group, consisting of TEA, 2,4 AMP and 2 AP, very efficient cathodic corrosion inhibitors are found which act at very small concentration (1 mM).

Cathodic hydrogen evolution current densities are significantly higher than in pure NaCl solution at all potentials between E_c and E_h . Nevertheless, no corrosion should occur, since discharge takes place through the oxide layer.

It should be noted that between the least efficient Pyr and the most efficient ones such as TEA or 2,4 AMP there is a difference in E_h of almost 300 mV and a difference in j_h of an order of magnitude. At the same time, between these compounds there is a difference in pK_B values of more than 2 units, Pyr being

a rather weak base (pK_B 8.81) in contrast to, for example, TEA (pK_B 6.23). Hence, at pH 6.5 the concentration of the buffering pyridinium ion is rather low, while TEA is virtually completely dissociated. Hence, most of the total buffering capacity of the latter must be used up by the OH^- ions evolved with the cathodic current, before free OH^- ions appear to attack the oxide layer. Thus, j_h reflects the limit of the buffering capacity. E_h on the other side is determined by the force needed to drive j_h .

From the kinetic point of view it is understandable that all these bases are better inhibitors than the organic acids, since the rate constants of association (between OH^- and the corresponding organic cation) are known to be many orders of magnitude larger than the rate constants of dissociation (preceding neutralization of OH^- by H^+ ions). Hence, the second

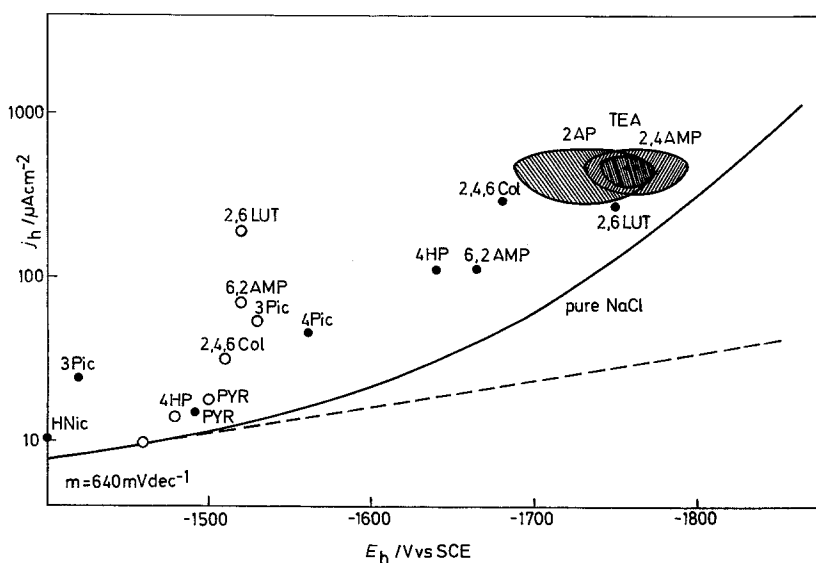


Fig. 9. Relationship between hydration current, j_h , and hydration potential, E_h , in pure NaCl solution and in the presence of different organic bases at pH 6.5 and at additive concentrations of 0.005 M (O) and 0.05 M (●).

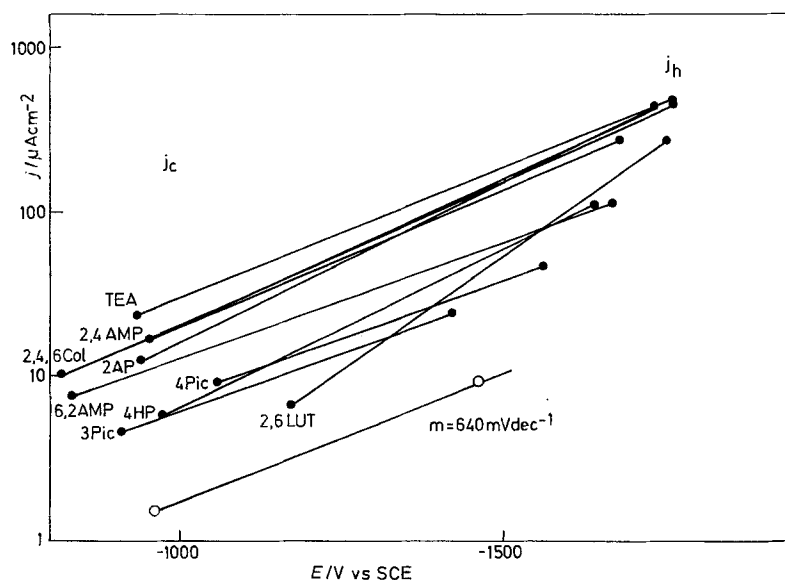


Fig. 10. Tafel plots for the cathodic process in the LCP region in pure NaCl solution (○) and in the presence of different organic bases (●) at pH 6.5.

and, in particular, the third group of organic bases as additives, may be considered as inhibitors of the cathodic corrosion of aluminium.

Some interesting conclusions can be drawn by reviewing the Tafel slopes of the cathodic process as in Fig. 10 (assuming linearity of $\log j$ between E_c and E_h). With the exception of only two additives (2,6 LUT and 4 HP), the presence of organic bases does not affect the Tafel slope. As the latter is determined basically by the resistance of the oxide film, this observation indicates that the additives change neither the thickness nor the conductivity of the film. The increase in the cathodic currents at any given potential, which in some cases amounts to over one order of magnitude, implies a catalytic effect of the additives on electron tunnelling through the film and water discharge.

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