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CORROSION OF ARMCO IRON IN $HClO_4$ SOLUTION IN MIXED WATER-ALCOHOL SOLVENTS. I. POTENTIAL EFFECT OF SOLVENT

ARMCO iron anodic dissolution in $HClO_4$ solutions in mixed water-alcohol solvents (MeOH, EtOH, PrOH-1, PrOH-2, Etdiol, Prdiol-1,2) has been investigated by means of potentiodynamic (v = 0.002 V method. The contributions of the liquid junction potential $(\Delta_w^s \varphi_L)$ and of the standard potentials scale shifts $(\Delta_w^s \mu_{H^+}^{\ominus})$ in the corrosion potential shifts between water and mixed solvents $(\Delta_w^s \varphi_{corr}$ have been determined.

The mechanism of electrochemical anodic dissolution of iron in aqueous H_2SO_4 and $HClO_4$ solutions containing non specific adsorbed ions has been described in a number of publications [1-7]. It is generally agreed that hydroxyl ions play a major role in this process. Depending on the degree of energetic heterogeneity of the polycrystalline surface of the iron electrode, a catalyzed or noncatalyzed mechanism is proposed. In the rate determining step of the electrode reaction, a decisive role is played by active $FeOH^+$ complexes.

The process of anodic dissolution of iron becomes more complex when it takes place in electrolyte solution in mixed solvents consisting of water and nonaqueous solvent miscible with water. The complexity of the process results from the following effects:

1^o Adsorption of the molecules of nonaqueous solvent on the electrode surface. The problem has received considerable attention of investigators, mainly in terms of the theory of inhibitive action;

2° Adsorption of solvent molecules leads to a shift of zero charge potential of the metal (${}_{Fe}E\delta = 0$);

3° Molecules of the nonaqueous solvent participate in the formation of active complexes. The mechanism of electrode reaction has been proposed in this case for only a few mixed solvents: water with DMSO [8,9] water with DMF [10], and water methanol (MeOH)[10] and ethanol (EtOH)[11];

4° Changes in the values of electrode potentials characterizing the reaction are the sum of the interactions between solvent dipoles and the electrode ($\Delta_{s_2}^{s_1} g_{dip}$) and the change of the standard free enthalpy of ion solvation during transfer from one solvent to the other ($\Delta_{s_2}^{s_1} \mu_i^{*}$). The construction of the electrochemical cell may also cause the value of the liquid junction potential difference ($\Delta_{s_2}^{s_1} \varphi_L$) to contribute to the measured potential difference.

The chief concern of the present study was the last of the above mentioned problems, which comprises the set of effects commonly referred to as the solvent effect in electrode reaction.

Experimental

The study of the electrochemical corrosion of ARMCO iron in $HClO_4$ solutions in mixed water-aliphatic alcohols solvents was conducted using "Tacussel" equipment (PRT 10.5 potentiostat, "Servovit" linear sweep generator, "Logalex" logarithmic amplifier, and "Sefram" XY recorder).

An Fe-ARMCO electrode "Prolabo" 99.99 % in the form of wire 2.5 cm long and 0.05 cm in diameter was annealed in an electric oven at T = 1220 K for τ = 4 hrs in a hydrogen atmosphere, cooled in hydrogen atmosphere, and polished electrochemically in 1 M $HClO_4$ in dimethyl eter of ethylene glycol ("diglym") at 258 K. Following rinsing with water, the electrode was subjected to another course of the above thermal treatment. It was then mounted in a Teflon holder and inserted in a tri-electrode measuring cell. The space of the working electrode was separated from the counter electrode space (Pt) by means of porous glass. All measurements were conducted in solutions deaerated with argon (99.99 %) at 298 K.

The measuring cells were set according to the following schemes:

(A) : Fe |0.5 M $HClO_4$ (mixed solvent)| aqueous electrolytic bridge| SCE,

$$\text{(B)}: \text{Fe}\,|\underbrace{0.5\text{ M HClO}_4\,|\text{electrolytic bridge}|\,10^{-2}\text{ M LiCl, AgCl}}_{\text{in the mixed solvent}},\ \text{Ag}$$

In the cell (A) the classical electrolytic bridge(KNO_3 : KCl = 4 : 1)was used. The measuring cell and this bridge was separated by the cell including the mixed solvent under investigation.

Use was made of mixed solvents of with ethanol, propanol-1 (PrOH-1), propanol-2 (PrOH-2), ethandiol (Etdiol), and propandiol-1,2 (Prdiol). All alcohols, manufactured by "Carlo Erba", were p.a. and the concentrations used ranged from 0 to 94 mole %.

The working electrode employed in one of the measurements was annealed, polished electrolytically, subjected to cathodic polarization, brought to equilibrium potential, activated at that potential for two minutes, and then subjected to cathodic polarization again. The solution was replaced pneumatically, and the measurement proper was conducted at the sweep rate of polarization potential of $v = 0.002\ V\ s^{-1}$ yielding polarization curve lg I = f(E). The above heat treatment procedure applied to the electrode ensured reproducibility of results within 3 %.

Results and discussion

The quasipotentiostatic curves lg I = f(E)obtained made it possible to determine the characteristics of the electrode processes with hydrogen depolarization and activated dissolution of iron. The Tafel slopes ${}_{Fe}b_+$ and ${}_{Fe}b_-$, which characterize the anodic and cathodic processes respectively, as well the order of the hydrogen ion depolarization reaction are collected in Table 1. As can be seen from those data, the Tafel coefficient of the anodic dissolution reaction is constant for all $HClO_4$ solutions in the mixed solvents. At the same time, its ${}_{Fe}b_+$ value, equal to 40 ± 5 mV/dec., suggests that anodic dissolution proceeds according to the catalyzed reaction mechanism [2-4,6].

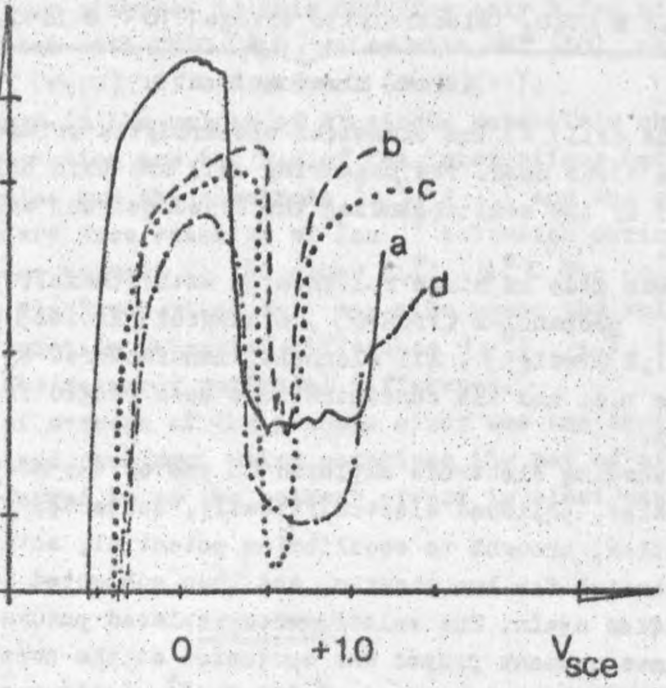

Fig. 1. Potentiodynamic ($v=1\cdot10^{-3}$ $V\cdot s^{-1}$) polarization curves of ARMCO iron in 0.5 M $HClO_4$ solutions: 1a) a - H_2O; b - 84 mol % EtOH; c - 84 mol % PrOH-2; d - 72 mol % Etdiol; 1b) Tafel's curves.

Measurements conducted in 0.5 M $HClO_4$ solutions in solvents with high alcohol content made it possible to obtain polarization curves [Fig. 1]. Similarities in the curves indicate that similar anodic iron dissolution mechanisms are involved. The absence of a current "plateau" in the range of polarization potentials corresponding to passivation processes seems to suggest that anodic oxidation of alcohol takes place, for monohydroxyl alcohols undergo anodic oxidation more readily than diols.

Table 1. Kinetics data of the Fe/Fe(II)reaction in $HClO_4$ (T = 298 K) in mixed water - alcohol solvents.

Solvent	$\frac{\partial \lg i_{corr}}{\partial c_{H^+}}$	b_+ [m V]	b_- [m V]
H_2O	1.0	40 ±2	120 ±10
H_2O - MeOH	0.9 ... 1.2	40 ±5	120 ±10
H_2O - MtOH	0.9 ... 1.2	40 ±5	120 ±10
H_2O - PrOH-1	0.9 ... 1.1	40 ±5	120 ±10
H_2O - PrOH-2	0.9 ... 1.1	40 ±5	120 ±10
H_2O - Etdiol	0.8 ... 1.2	40 ±10	120 ±20
H_2O - Prdiol	0.8 ... 1.4	40 ±10	120 ±20

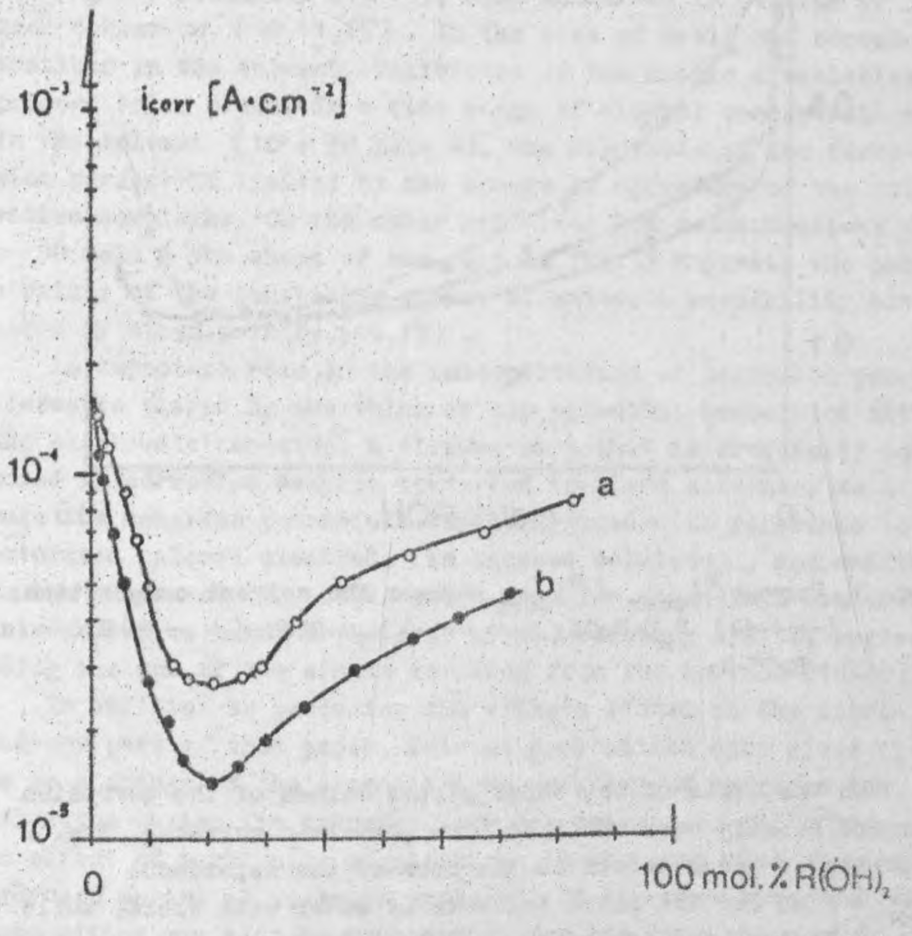

Fig. 2. Dependence i_{corr} = f(X) for ARMCO iron in 0.5 M $HClO_4$ solutions in mixtures: a - H_2O-Etdiol; b - H_2O-Pridiol-1,2

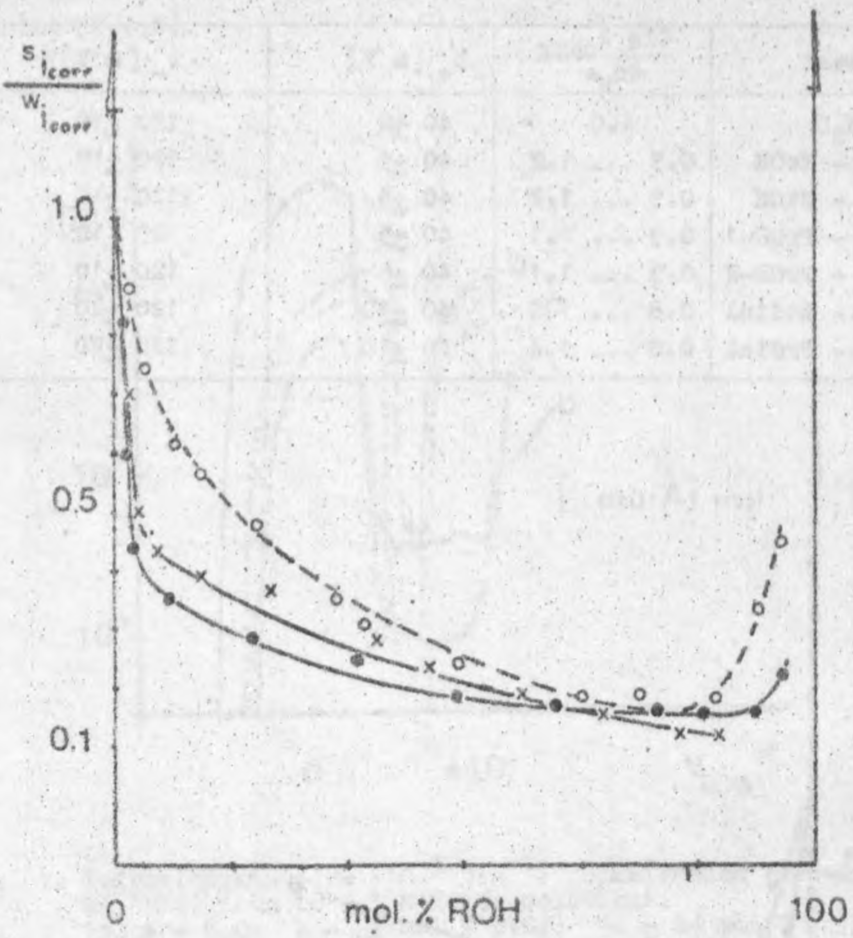

Fig. 3. Curves $^{s}i_{corr}$ / $^{w}i_{corr}$ versus the solvent composition: (-●-●-●-) H_2O-MeOH; (-o-o-) H_2O-EtOH; (— — —) H_2O-PrOH-2.

On the basis of the Tafel slopes values of the corrosion current density were obtained (for geometric surface). Fig. 2 illustrates these values in the form of the dependence $i_{corr} = f(X)$ for the mixed solvents of water with diols, while Fig. 3 depicts the dependence $\frac{^{s}i_{corr}}{^{w}i_{corr}} = f(X)$ for the mixed solvents of water with monohydroxyl alcohols.

The plots of Fig. 2 exhibit a minimum of i_{corr} values for media containing ~ 20 mole % alcohol. It has to be kept in mind here that this corresponds to the composition of many cooling mixtures (50/50 vol %) commonly employed in industrial equipment. The increased value of the corrosion current density for solvents containing more than 20 mole % diol may be attributed e.g. to the complexing effect of the organic component [12].

The $\frac{s_{i_{corr}}}{w_{i_{corr}}} = f(X)$ plots shown in Fig. 3 have shapes typical of electrodic reaction inhibited by electrically neutral organic molecules [13-15], also confirmed in studies of iron corrosion [10,11,16]. In the case of small ROH concentrations in the solvent, inhibition of the anodic dissolution process takes place. In a wide range of alcohol concentrations in the solvent (10 ÷ 90 mole %), the magnitude of the corrosion current is limited by the change of structure of the solvation complexes. On the other hand, for ROH concentrations of > 90 mole % the shape of the plot in Fig. 3 suggests the possibility of the inhibiting effect of water, a possibility also noted by other authors [16,17].

An impostant role in the interpretation of corrosion processes is played by the value of the potential associated with the electrodic reaction, a cirsumctance that is frequently ignored in corrosion studies conducted in mixed solvents. As a ruke the reaction potentials are determined with reference to saturated calomel electrode (in aqueous solution), and shifts in the values of the electrodic reaction potentials are then interpreted as being a property of the reacting system, neglecting the sum of the efects deriving from the solvent [18-20].

In addition to producing the effects listed in the introductory part of this paper, solvent composition also gives rise to a change of the standard free enthalpy of hydrogen ion solvation during its transfer from one solvent to the other, an effect of particular significance in the case when standard hydrogen potential scale is employed. At the same time, solvent composition may also be responsible for the appearance of liquid-liquid interface in the measuring cell. If the latter effect occurs, account has to be taken of the difference in the liquid junction potential($\Delta\, ^{s_1}_{s_2}\, \varphi_L$) appearing at the interface.

An attempt to deal with the above problems was made by Bacarella and Sutton [11] taking account of the work of Popovych [21], Izmailov and Aleksandrov [22,24], and Grunwald [25-27] on the "degenerate proton activity coefficient".

For the measuring cell set in accordance with the scheme adopted from the paper [11]:

$$(C)\quad \text{Fe, } H_2(1\text{ atm})|0.5\text{ M } H_2SO_4\text{ (EtOH - HOH)}\| E'^{s}_{L} \|$$

$$\text{or Pt}$$

$$\| 0.5\text{ M } H_2SO_4 \| E^{w}_{L} \| \text{ KCl}_{sat.aq.}, Hg_2Cl_2, \text{ Hg}$$

where

$$E'^{s}_{L} + E^{w}_{L} = E^{s}_{L} \qquad (1)$$

The magnitude of the corrosion process potential is given by equation:

$$E^{s}_{Fe} = E^{s}_{cell} + E^{s}_{L} + E_{SCE}\ , \qquad (2)$$

where, in turn, E^{s}_{cell} is an experimental value.

The magnitude of E^{s}_{L} was determined by measuring the potential difference in the cell [11]:

$$(D)\quad \text{Pt, } H_2|\ H^+, \text{(EtOH-HOH)}\| E^{s}_{L} \| \text{ KCl}_{sat.aq.}, Hg_2Cl_2Hg\ .$$

The difference in the Galvani potentials proposed by Bacarella and Sutton [11] is equal to

$$\phi_M - \phi_{SCE} = E^{s}_{cell} = \left(\phi_M - \phi_{s_1}\right) + \left(\phi_{s_1} - \phi_{s_2}\right) + \left(\phi_{s_2} - \phi_{SCE}\right) \qquad (3)$$

where $(\phi_M - \phi_{s_1}) = E^{s}_{M}$ is the difference in the Galvani potentials between a point on the metal(Fe or Pt) and some point S_1 in the solution phase, $(\phi_{s_1} - \phi_{s_2}) = - E^{s}_{L}$ is the potential difference at the liquid-liquid interface between the mixed solvent and saturated aqueous solution of KCl (cf. eqn. 1), and $(\phi_{s_2} - \phi_{SCE}) \equiv - E_{SCE}$ is the difference in the Galvani potentials for the reference electrode relative to aqueous KCl solution.

Measurement of the potential difference in cell (D) leads to the determination of acidity as a measure of proton activity in water at a given point in time:

$$p^A = -\lg a_{H^+} = -\lg c_{H^+} \cdot y^s_{H^+} \cdot f_{H^+} \quad , (4)$$

where $y^s_{H^+}$ is the conventional molar lyonium ion activity coefficient in solvent S, and f_{H^+} is the "degenerate proton activity coefficient" measured for infinitely dilute solution relative to water as the reference state [11].

Since, at the same time, for aqueous solutions

$$-\lg a_{H^+} = -\lg c_{H^+} \cdot y^s_{H^+} = \mathrm{pH} \, , \qquad (5)$$

Bacarella and Sutton in effect obtained:

$$E^s_L = 0.06 \lg (c_{H^+} \cdot y^s_{H^+} \cdot f_{H^+}) - (E_{cell(Pt)} + E_{SCE}) \quad (6)$$

In the discussion that followed immediately after the publication of the study under consideration, Schwabe [28] categorically dismissed any possibility of determining the absolute scale of acidity under the conditions described by the authors [11]. Accepting Schwabe's objection, we can state the following: - the quantity E^s_L (eqn. 1), which Bacarella and Sutton [11] term "liquid junction potential" comprises the liquid junction potential difference proper and the diffusion potential at the $KCl_{sat.aq.}$ | 0.5 M H_2SO_4 interface. It can be easily found, by the method of succesive approximations and making use of Planck's theory [29] , that the diffusion potential at that interface is some milivolts and may be practically neglected;

- the magnitude of the liquid junction potential difference at the 0.5 M H_2SO_4 (EtOH-HOH)‖0.5 M H_2SO_4(HOH) interface cannot be accurately determined directly from SEM measurement in the proposed cell (C). There are, however, a number of indirect procedures for determining the value of $\Delta^s_w \varphi_L$ in the function of solution composition [21,30,31] . Calculations can be approproately based only on very similar and independently obtained $\Delta^{s}_{w}\varphi_{L} = f(X)$values;

- the degenerate proton activity coefficient determined by Izmailov [22-25] and Grunwald [25-27] is, in effect, a measure of changes in the standard free enthalpy of hydrogen ion solvation during its transfer from the mixed or nonaqueous solvent to water $\Delta^{s}_{w}\mu_{H^{+}}^{\ominus}$. At the same time, it is a measure of the shift of the standard hydrogen potential scale. Using different methods, Izmailov [22-25], Strehlov [32], and Parsons [33], as well as the present author [30,31] have all determined the value of $\Delta^{s}_{w}\mu_{H^{+}}^{\ominus}$ for water-alcohol media and obtained satisfactory agreement of the results.

Fig. 4 shows the plots of $\Delta^{s}_{w}\varphi_{L} = f(X)$(curve 1) and $\Delta^{s}_{w}\mu_{H^{+}}^{\ominus} = f(X)$(curve 2) obtained for the solvents used in the present study;

- in the left-hand branch of cell (C) as proposed by Bacarella and Sutton, the value of the reference is $^{s}\mu_{H^{+}}^{\ominus}$. The value of E_{SCE} in the right-hand branch is also referred to arbitrary zero of the hydrogen scale, i.e. also to $^{w}\mu_{H^{+}}^{\ominus}$.

Summing up the above, the "liquid junction potential" of Bacarella and Sutton [11] is the sum of diffusion potential, liquid-liquid potential difference $\Delta^{s}_{w}\varphi_{L}$, and the potential difference resulting form change of the standars free enthalpy of hydrogen ion solvation. The values of E^{s}_{L} obtained by Bacarella and Sutton and those determined in our own research [30,31] for the sum $\Delta^{s}_{w}\varphi_{L} + \Delta^{s}_{w}\mu_{H^{+}}^{\ominus} = f(X)$ are listed in Fig. 5.

Fig. 6 illustrates the values of the differences in the experimentally obtained corrosion potentials plotted in the function of solvent composition. The φ_{L} $\Delta^{s}_{w}E_{corr}$ in the figure applies to the value obtained from measurement in the cell containing liquid-liquid interface (A), while $\Delta^{s}_{w}E_{corr}$ is for the result obtained from measurement in cell (B). In the latter cell, the calculation of the silver chloride silver electrode potentials in the mixed solvents in each case relative to the hydrogen scale zero point adopted for each solvent was based on the literature values of $E^{o}_{AgCl,Ag}$ and activity coefficients [34-37]. Taking account of the sum

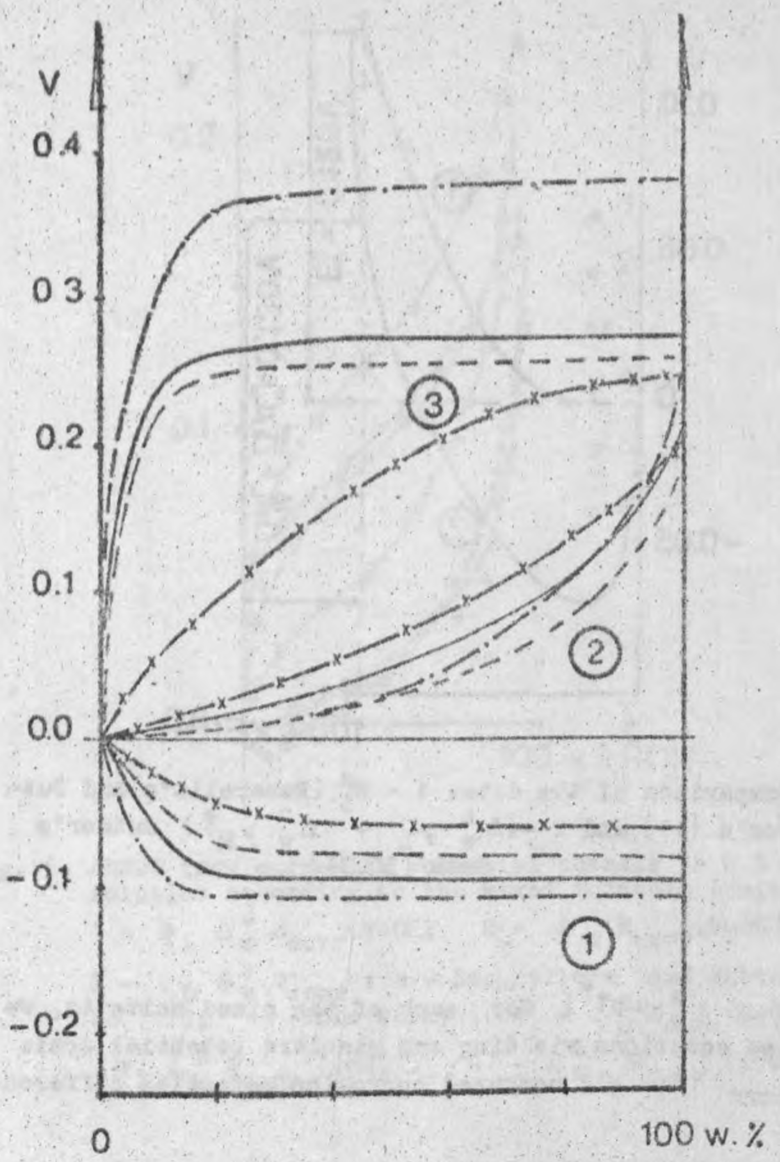

Fig. 4. Potential changes curves: 1 - $\Delta_w^s \varphi_L = f(X)$; 2 - $\Delta_w^s \mu_{H^+}^{\ominus} = f(X)$; $\Delta_w^s g_{dip} = f(X)$ for mixed solvents (– – – –) H_2O - MeOH; (———) H_2O-EtOH; H_2O-PrOH-2 ; (–x–x–). H_2O - Etdiol

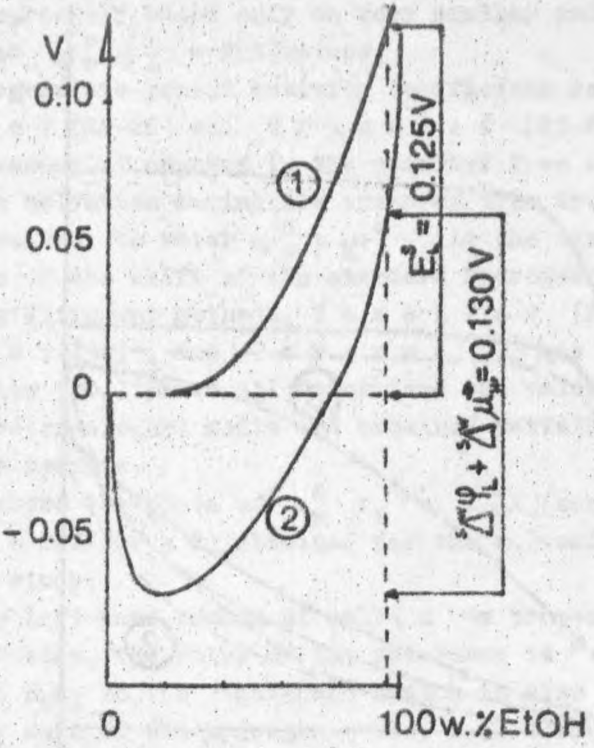

Fig. 5. Comparison of the data: 1 - E_L^s (Bacarella's and Sutton's [11] and 2 -($\Delta_w^s \varphi_L + \Delta_w^s \mu_{H^+}^{\ominus}$) author's data [30,31]

($\Delta_w^s \varphi_L + \Delta_w^s \mu_{H^+}^{\ominus}$) for each of the mixed solvents, we can propose equations yielding one standard potential scale ($\Delta_w^s \varphi_{corr}$) for all measured corrosion potential differences.

$$\varphi_L \Delta_w^s E_{corr} = \Delta_w^s \varphi_{corr} + \Delta_w^s \varphi_L + \Delta_w^s \mu_{H^+}^{\ominus} \quad (7)$$

$$\Delta_w^s E_{corr} = \Delta_w^s \varphi_{corr} + \Delta_w^s \mu_{H^+}^{\ominus} \quad (8)$$

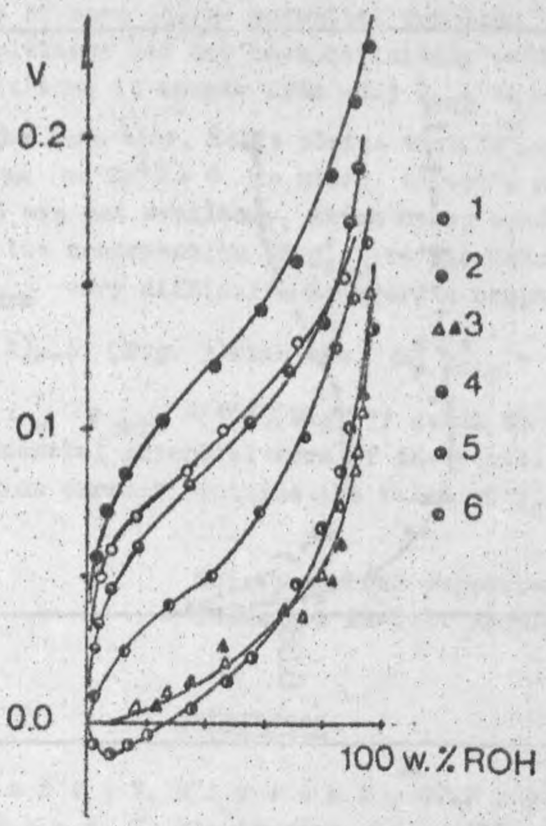

Fig. 6. ARMCO iron corrosion potential changes in 0.5 M $HClO_4$ solution according to the mixed solvents composition:
1 - $\varphi_L \Delta^s_w E_{corr}$(MeOH); 2 - $\Delta^s_w E_{corr}$(MeOH);
3 - $\varphi_L \Delta^s_w E_{corr}$: ▲ - Bacarella's and Sutton's data [11]; △ -this work; 4 - $\Delta^s_w E_{corr}$(EtOH);
$\varphi_L \Delta^s_w E_{corr}$(PrOH-2); 6 - $\Delta^s_w E_{corr}$ (PrOH-2);

The values of $\Delta^s_w \varphi_{corr}$ calculated on the basis of the proposed equations (7) and (8) in the function of solvent composition are collected in Fig. 7.

The quantity g^s_{dip} is the potential effect of the interactions between solvent dipoles and the electrode metal. The concept has been extensively discussed by Jakuszewski [38], Trasatti [39], and Bockris [40]

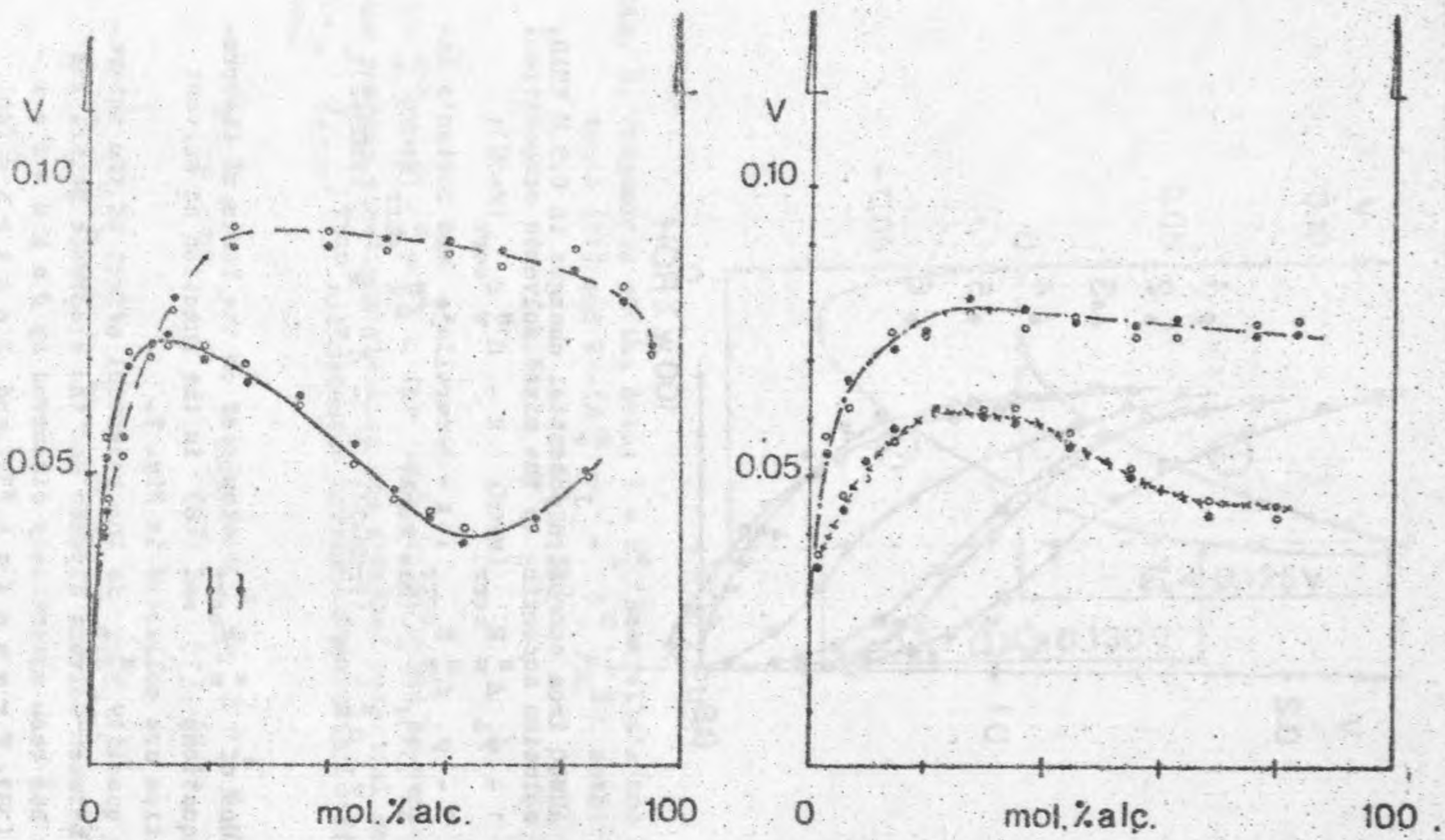

Fig. 7. The values of $\Delta_w^s \ \varphi_{corr}$ calculated form equations (7) - and (8) - according to the compositions of the solvents: (-----) H_2O - MeOH; (———) H_2O - EtOH; (-·-·-·) H_2O - PrOH-2; (—x—x—) H_2O - Etdiol .

for metallic electrode in zero charge potential.

The value of zero charge potential for iron $Fe^{E}\delta = 0$ in aqueous solutions has not been definitely established, and for H_2SO_4 solutions it ranges from -0.3 V_{SHE} to -0.37 V_{SHE} [41,42]. At the same time, Kelly claims that $Fe^{E}corr < Fe^{E}\delta = 0$. The values of $Fe^{E}\delta = 0$ in mixed solvents or nonaqueous solutions are not available, which makes credible interpretation of the contribution of g^{s}_{dip} to the determined value $\Delta^{s}_{w}\varphi_{corr}$ very difficult. However, a comparison of the $\frac{^{s}i_{corr}}{^{w}i_{corr}} = f(X)$plot (Fig. 3)with the $\Delta^{s}_{w} g^{s}_{dip} = f(X)$plot (Fig. 4) and $\Delta^{s}_{w}\varphi_{corr} = f(X)$(Fig. 7) seems to indicate that the exponential potential term of the equation describing the corrosion current contains the value of g^{s}_{dip}.

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KOROZJA ŻELAZA ARMCO W ROZTWORACH $HClO_4$ W MIESZANYCH ROZPUSZCZALNIKACH WODA-ALKOHOL. I. POTENCJAŁOWY EFEKT ROZPUSZCZALNIKA

Na podstawie quasipotencjostatycznych ($v = 0.002\ V \cdot s^{-1}$) krzywych polaryzacji wyznaczono parametry reakcji anodowego roztwarzania żelaza ARMCO w roztworach $HClO_4$ w mieszanych rozpuszczalnikach woda-alkohol (MeOH, EtOH, PrOH-1, PrOH-2, Etdiol, Prdiol-1,2). Do obliczenia wartości przesunięcia potencjału korozji ($\Delta_w^s \varphi_{corr}$) przy przejściu od wody do mieszanego rozpuszczalnika zaproponowano równanie uwzględniające przesunięcie skali potencjałów ($\Delta_w^s \mu_{H^+}^{\theta}$) i różnice potencjałów na granicy faz ciecz-ciecz ($\Delta_w^s \varphi_L$).