On the pseudo-hyperbolic behavior of charge transfer resistance–temperature dependence in corrosion behavior of Nickel based glass alloy

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Temperature plays an important role in promoting the corrosion of metals. The Arrhenius plot can interpret the corrosion rate-temperature dependence, where the Arrhenius behavior gives a geometrical meaning and makes explicit a positive or negative linear dependence of charge transitivity and temperature. In addition, according to the Arrhenius interpretation, it represents the energy that the molecule in the initial state of the process must acquire before it can take part in the reaction, whether it is a physical, or a chemical process. Taking into account the deviation from the linearity, we have extended the Arrhenius-type expression by one term in $1/T^2$ and we have given some physical meaning to the new related coefficients for which it is found that they depend closely on the number of acid hydrogen atoms in the polyacid for the corrosion and passivation of the Nickel based metallic glass alloy of the composition Ni$_{82.3}$Cr$_7$Fe$_3$Si$_{4.5}$B$_{3.2}$. Moreover, we can consider that the deviation to the Arrhenius linear behavior as a super-Arrhenius behavior. In addition, a mathematical analysis of the trend of experimental scatter points of the charge transfer resistance with temperature permits us to reveal an interesting homographic behavior which leads us to suggest an original empirical model with only two optimal adjustable parameters, as well as a new pseudo-power dependence of the number of hydrogen atoms in the polyacid.

Generally, in corrosive electrolytic solution, metals get oxidized at anode and charges (electrons) are transferred through electro-circuit. This process is known as charge transfer, and any resistance in the charge transfer process is known as charge transfer resistance ($R_{ct}$). The Stern-Geary equation (describing the relationship between the polarization resistance ($R_p$) and the corrosion current density ($i_{corr}$)), which derived because of the mixed potential theory of Wagner and Traud, relates the corrosion current (corrosion rate) to the inverse of the resistance to charge transfer\textsuperscript{1-5}. In other words, corrosion rate is also reflected in terms of corrosion current density ($i_{corr}$). For this, corrosion rate can be quantitatively measured by means of polarization resistance techniques\textsuperscript{2,6-9}.

In most chemical reactions, an increase in temperature is accompanied by an increase in reaction rate due to the increase of kinetic energy and speeds up the chemical reaction\textsuperscript{10,11}, and the corrosion reaction rate doubles for each 10 °C rise in temperature. Therefore, it is important to take into consideration the influence of temperature when analyzing why metals corrode. The effect of temperature on the corrosion rate can be analyzed in terms of activation energy from Arrhenius behavior for the overall corrosion process\textsuperscript{12-18}.

If the corrosion rate is only controlled by the metal oxidation process, then the corrosion rate will increase exponentially with an increase in temperature following an Arrhenius relationship. The equation was first proposed by Van't Hoff (1884), in 1889 Svante Arrhenius provided a physical justification and interpretation for it\textsuperscript{19,20}.

Generally, for the majority of experimenters, the charge transfer resistance–temperature dependence is treated by linear regression of the Arrhenius behavior by the plot of the logarithm of the charge transfer resistance versus the reciprocal of absolute temperature.

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Nevertheless, we have noted that there is some feeble deviation to the linearity for numerous works, which
exceed the experimental errors bar. To fix this observation we will proceed in two manners in the present work.

(i) we will extend the Arrhenius type-equation by a supplementary term in \((1/T^2)\) to reduce the discrep-

ancy with the experience and test the deviation to the Arrhenius linearity if it can be classified as a sub-

Arrhenius or super-Arrhenius behavior for the studied system. In addition, we will model the effect of

the protons number in polyacid on the Arrhenius parameters.

(ii) Regarding the trend of experimental scatter points of the charge transfer resistance with temperature

that likes a hyperbolic behavior, we will mathematically investigate this variation and suggest an original

homomorphic model with only two optimal adjustable parameters for which we try to give some physical

significance.

We note the present work is a theoretical continuation and modeling of our principally experimental previous

work results\(^2\) where all experimental data are presented and discussed in terms of apparent activation energies,

active, and passive, as well as the enthalpies and entropies of the dissolution process.

Materials and methods

The material chosen for the study was Nickel based metallic glass alloy of the composition Ni\(_{82.3}\)Cr\(_{7}\)Fe\(_{3}\)Si\(_{4.5}\)B\(_{3.2}\)

weight percent (wt%) from Vacuumschmelze. The experimental data of our previous paper\(^2\) on the effect of

temperature ranging from (20 to 80) °C on corrosion and the electrochemical behavior of the glassy alloy in HCl,

H\(_2\)SO\(_4\), and H\(_3\)PO\(_4\) were used in this study. Full details are described in previous paper\(^2\).

Deviations to the Arrhenius-type equation

Arrhenius-type equation. Activation energy \((E_a)\) is strictly combined with kinetics of chemical re-

actions. The effect of temperature on reaction rates is calculated using the Arrhenius equation. A common sense

is that at higher temperatures, the reactants molecules colliding probability becomes higher and the reaction

proceeds faster. The bond cleavages and rearrangements of molecules generally increase as temperature rises.

This is through the collision theory, transition state theory or a chemical reaction.

The Swedish chemist Svante Arrhenius was the first who combined the concepts of activation energy and

the Boltzmann distribution law into one relationship. This described as the Arrhenius equation. The familiar

Arrhenius equation, Eq. (1) is given as follows\(^2\):

\[
R_{ct} = A_{ct} e^{\frac{E_a}{R T}}
\]  

(1)

where \(E_a\) is the activation energy, \(A_{ct}\) is the pre-exponential factor which, is also known as the frequency fac-
tor, and it mathematically represents the limiting theoretical value of the charge transfer resistance at infinite

temperature. This factor is also interpreted as an entropic factor which, it is presenting the frequency of colli-
sions between reactant molecules at a standard concentration. Noteworthy, although \(A_{ct}\) is often described as

temperature independent, but it is actually dependent on it. This is because \(A_{ct}\) is related to molecular collision,

which is a function of temperature.

These two Arrhenius parameters are generally supposed both constants practically independent of tempera-
ture. The logarithm form of the preceding equation can be expressed as follows:

\[
\ln R_{ct} = \ln A_{ct} + \frac{E_a}{R} \times \frac{1}{T}
\]  

(2)

The plot of \((\ln R_{ct})\) as a function of the reciprocal of absolute temperature \((1/T)\) gives approximately a handy

straight line (Fig. 1a, b and c) whose slope is equal to \((E_a/R)\) and the intercept on the ordinate is equal to \((\ln A_{ct})\).

The results of the linear regression for the three acids are presented in the Table 1.

Observing the variation of the two Arrhenius parameters \((E_a\) and \(\ln A_{ct}\)) which are in the opposite senses
(Table 1), we have thought about inspecting their mutual dependence\(^2\) by plotting one parameter against the

second for the three studied polyacids H\(_2\)B. In fact, the Fig. 2 shows interesting causal correlation for which the

quasi-linearity inter-dependence can be expressed as follows:

\[
E_a = E_{a0} + t_0 \cdot (-R\ln A_{ct})
\]  

(3)

where \(E_{a0} (= 21.64 \text{ kJ} \cdot \text{mol}^{-1})\) is the activation energy corresponding the null value of the entropic factor (i.e. at

the limiting case of absence of any acidic proton), and the slope \(t_0 (= 304.45 \text{ K})\) is equivalent to an absolute tempera-
ture characteristic of the studied system at such conditions, and which can be also named as current Arrhenius

temperature\(^2\). Moreover, we notice that \((t_0)\) has an ambient value (31.3 °C). We can give then an inspiration for

future investigators to think about the probable optimal value of working temperature.

We can conclude that there is a close causal correlation (Fig. 3) between the Arrhenius parameters \((E_a\) and

\(-R\ln(A_{ct}))\) and the thermodynamic parameters \((\Delta H\) and \(\Delta S\)), respectively, for glassy Ni\(_{82.3}\)Cr\(_{7}\)Fe\(_{3}\)Si\(_{4.5}\)B\(_{3.2}\) alloy
corrosion. In the same context, to confirm that the entropic factor of Arrhenius \(-R\ln(A_{ct})\) is equivalent to an

entropy\(^2\), the Fig. 3b shows a clear causal correlation between the activation entropy \(\Delta S\) \((/\text{J} \cdot \text{K} \cdot \text{mol})\) determined

from impedance measurements in our previous work\(^2\) and the logarithm of the entropic factor of Arrhenius
\(-R\ln(A_{ct})\) \((/\text{J} \cdot \text{K} \cdot \text{mol})\) for the three polyacids HCl, H\(_2\)SO\(_4\), and H\(_3\)PO\(_4\) at atmospheric pressure. Moreover, the slopes values of
the two straight lines of Fig. 3 are very near the unit (1.06 and 1.04) which means that \((E_a\) and \(\Delta H))\) and
\((-R\ln(A_{ct}))\) and \(\Delta S\)) have approximately the same value of gap or “jump” when the number of protons
(x) of the acid changes by one unit. We add that the Arrhenius parameters represent the movement between two energy levels related to transition state, while the thermodynamic parameters, as a state functions, represent the movement between two energy levels related to equilibrium thermodynamic states.

The highest $R^2$-square value (Table 1, Fig. 1c) indicates that in the case of triacid (H$_3$PO$_4$) the temperature dependence practically follows the Arrhenius behavior. Nevertheless, in the case of monoacid (HCl), we observe clear discrepancy with the Arrhenius linearity. In addition, the deviation of experimental points (Fig. 1a) to the straight line is systematic in nature and not random, which shows that the phenomenon, represented by variation of the logarithm of charge transfer resistance ($\ln R_{ct}$) as a function of the inverse of the reciprocal temperature ($1/T$), is not linear and we should extend the Arrhenius-type equation or think about another non linear model.

In the following sections, we will present a new empirical expression reducing to a large degree the discrepancy with the experimental data points.

Extended Arrhenius-type equation. Observing the trend of points in Fig. 1, we clearly see that there is feeble net deviation from the linearity of the Arrhenius behavior. For that, we suggest, as optimization by non-linear regression, to fit simply the experimental results ($\ln R_{ct}$) vs. $(1/T)$ with only a polynomial of second degree, which it can be expressed as follows:

$$\ln R_{ct} = a_0 + a_1 \times \left(\frac{1}{T}\right) + a_2 \times \left(\frac{1}{T}\right)^2$$

where $a_i$ are optimal adjustable parameters. To give certain physical meaning of these parameters, the Eq. (4) can be re-expressed as follows:

$$\ln R_{ct} = \ln A_0 - E_1 R \times \left(\frac{1}{T}\right) + E_2^2 R^2 \times \left(\frac{1}{T}\right)^2$$

We note that due to the concavity of the curves in Fig. 1, the second term of Eq. (4) must be negative, that is why we have inserted a minus sign in Eq. (5) to have positive physical parameters. Table 2 presents values of the corresponding parameters.
To help giving preliminary physical significances to the parameters of Eq. (5), we have tested the Eq. (3) on the

\[ y = 21.6362 + 0.30445x \]  
\[ R = 0.999855 \]

- \( R \cdot \ln(A) \) / J·K\(^{-1}\)·mol\(^{-1}\)
- \( E_a / \text{kJ/mole} \)
- \( HCl \)
- \( H_2SO_4 \)
- \( H_3PO_4 \)

**Figure 2.** Correlation between the activation energy \( E_a \) (kJ/mol) from polarization and impedance measurements\(^2\) and the entropic factor of Arrhenius – \( R \cdot \ln(A)/\Omega\cdot\text{cm}^2 \) / (J/K·mol) for the three acids HCl, H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\) at atmospheric pressure.

**Figure 3.** Correlation between the entropic factor of Arrhenius – \( R \cdot \ln(A)/\Omega\cdot\text{cm}^2 \) / (J/K·mol) and the thermodynamic parameters for glassy Ni\(_{82.3}\)Cr\(_7\)Fe\(_3\)Si\(_{4.5}\)B\(_3.2\) alloy corrosion; (a): with the activation enthalpy \( \Delta H \) (kJ/mol) and (b): with the activation entropy \( \Delta S \) (J/K·mol) determined from impedance measurements in previous work\(^1\) for the three polyacids HCl, H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\) at atmospheric pressure.

**Table 2.** Optimal Arrhenius parameters \((E_i\) and \(\ln A_0)\) from non-linear regression of Eq. (2).

| Acid     | \( \ln A_0 \) | \( E_1 \) | \( E_2 \) | \( R \)-square |
|----------|----------------|----------|----------|----------------|
| HCl      | 38.2266        | 217.76   | 18.999   | 0.99929        |
| H\(_2\)SO\(_4\) | 19.708        | 153.79   | 17.779   | 0.99987        |
| H\(_3\)PO\(_4\) | -2.1065       | 56.450   | 14.547   | 0.99753        |

To help giving preliminary physical significances to the parameters of Eq. (5), we have tested the Eq. (3) on the
where \( \left( \frac{\partial \ln R_{ct}}{\partial (1/RT)} \right) \) is known as the deformation function’s flexibility in the deformed Arrhenius equation (Eq. 8) for the charge resistance–temperature dependence.

\[
E_a(T) = A_{ct} \left[ 1 + d \cdot \frac{E_0}{RT} \right]^d
\]  
(8)

where \( E_0 \) is the height or the amount of the potential energy barrier and \( d \) is known as the deformation parameter for which the sign will indicate the nature of deviation to the Arrhenius linearity. The advantage of this deformed Arrhenius equation is that we can discuss the rate constant in terms of a single parameter. The expression of Eq. (8) represents both the Arrhenius and non-Arrhenius behaviors of charge transfer resistance \( R_{ct}(T) \). For positive values of \( d \), super-Arrhenius behavior is observed while for negative values of \( d \), sub-Arrhenius is observed. For values of \( d \) neighboring \( 0 \), we observe the classical Arrhenius behavior (Eq. 1) and the \( E_0 \)-value tends to the Arrhenius activation energy \( E_a \) (Table 1). Then, we can mathematically demonstrate the following expression:

\[
E_a(T) = \lim_{d \to 0} A_{ct} \left[ 1 + d \cdot \frac{E_0}{RT} \right]^d = A_{ct} e^{\frac{E_0}{RT}}
\]  
(9)

For which we re-find the Eq. (1) form.

Moreover, for very feeble deviation, where the \( d \)-values are small, we can write the Eq. (6) (in accordance with Eq. (8)) in asymptotic expansion and, as a limit of succession, we can approximately write the following expression:

\[
E_a(T) \approx E_0 + \frac{d \cdot E_0^2}{RT}
\]  
(10)

The Eq. (10) can be reformulated in terms of the reciprocal of \( E_a(T) \) (i.e. \( \gamma(T) = 1/E_a(T) \)) as follows:

\[
\gamma(T) \approx \alpha - d \cdot \frac{1}{RT}
\]  
(11)

where \( \alpha \) is the inverse of Arrhenius–Eyring energy obstacle to charge transfer in the case of (H\(_3\)PO\(_4\)).

Table 3. Optimal adjustable parameters (\( \alpha \) and \( d \)) from linear regression of Eq. (11).

| Acid     | \( \alpha \) | \( d \) | \( R \) |
|----------|--------------|--------|--------|
| HCl      | 0.1416       | 0.31964| 0.99929|
| H\(_2\)SO\(_4\) | 0.04882   | 0.09689| 0.9987 |
| H\(_3\)PO\(_4\) | 0.025334  | 0.041189| 0.99753|

Parameters \( E_a \) and \( \ln A_{ct} \) we find practically the same behavior depicted in Fig. 2 where the slope \((T_0 = 482.66 \text{ K})\) a current Arrhenius temperature with a \( R \)-square 0.9949.

We can notice an improvement of the correlation coefficient \( (R \)-square) proving that there effectively is classification of the goodness of fit comparing with the results of Table 1 (i.e. in the Table 2, the quality is the best in the case of the mono acid HCl) we can attribute this effect to the conflict between the amount and parity of the chosen polynomial degree and, the experimental bar error of each acid, where the triacid \( (\text{H}_3\text{PO}_4) \) has two corresponding weak acids \( (\text{H}_2\text{PO}_4^- \text{ and HPO}_4^{2-}) \). We note that the width of studied temperature range play also an effective role for this fact.

However, some researchers interpret the sign of the deviation to the Arrhenius linearity as a sub-Arrhenius or super-Arrhenius behaviors. For this fact, we remember that the activation energy \( E_a \) (Table 1) can be generally expressed at constant pressure as follows:

\[
E_a(T) = \left( \frac{\partial \ln R_{ct}}{\partial (1/RT)} \right)_p
\]  
(6)

We note that in our case of polynomial form (Eq. 5) the activation energy \( E_a(T) \) can be expressed as follows:

\[
E_a(T) = 2E_a^2 \times \left( \frac{1}{RT} \right) - E_1
\]  
(7)

The positive slope \( (2E_a^2) \) in Eq. (7), confirmed by the positive concavity of curvature indicated in Fig. 1, leads us to conclude that we are in the case of super-Arrhenius behavior.

On the other hand, the deviation to the classic Arrhenius linearity can be more interpreted by the \( d \)-exponential function’s flexibility in the deformed Arrhenius equation (Eq. 8) for the charge resistance–temperature dependence.
confirms the feeble discrepancy with classical Arrhenius behavior indicated in Fig. 1c. We note that the value of \( d \) bears the same sign as the derivative of the activation energy \( E_a(T) \) with respect of the reciprocal of absolute temperature at constant pressure: \( \frac{\partial E_a(T)}{\partial (1/T)} \), or the second derivative of the charge transfer resistance \( R_{ct} \) with respect of the reciprocal of absolute temperature at constant pressure: \( \frac{\partial^2 R_{ct}(T)}{\partial (1/T)^2} \).

**Effect of the acid proton number on the model parameters.** The Table 2 shows that all of the three parameters of the Eq. (5) both decrease in a strictly monotonous way, which it inspires us to investigate possible relationship with the number of hydrogen \( (x_H) \) of the acid. Some different simulations for reducing the line’s curvature lead us to obtain the best linearization form expressed as follows:

\[
Y = Y_0(1 - \delta \cdot x_H^\beta)
\]

where \( Y \) is one of the three parameters \( (E_1, E_2 \text{ and } \ln A_0) \) of Eq. (5) and, \( Y_0, \delta \) and \( \alpha \) are three adjustable parameters. Results of this finding are shown by Fig. 4 and presented in Table 4.

This curious and interesting pseudo-power behavior of Eq. (12) leads us to give up the Arrhenius-type model and think about another mathematical form like the hyperbolic behavior.

In the same context, we have also done some different simulations for reducing the line's curvature which lead us to obtain the best linearization form for the two optimal adjustable parameters \( (\alpha \text{ and } d) \) of Eq. (11) (Fig. 5). We found that similar pseudo-power behavior obeying Eq. (12) is observed for \( \beta = -0.147 \), both for the two parameters \( (\alpha \text{ and } d) \) with excellent correlation coefficients (Fig. 5).

We conclude that the number of hydrogen \( (x_H) \) of the polyacid has an important effect, which can be quantified and modeled for eventual future estimation, or prediction and can open window to improve or develop some theories.

**Pseudo-hyperbolic behavior of charge transfer resistance with temperature**

The graphical representation (Fig. 6) of the charge transfer resistance \( (R_{ct}) \) as a function of temperature \( (T) \) shows a pseudo-hyperbolic behavior characterized by the tendency towards very low values when the temperature increases and a tendency towards very high values when the temperature decreases. To analyze this behavior, we will perform two linearization tests.

Nevertheless, in the case where the pseudo-hyperbolic behavior is followed, the value of the limiting temperature \( (T_{lim}) \) related to the vertical asymptote when \( (R_{ct}) \) tends to infinity and the value of the limiting charge transfer resistance \( (R_{lim}) \) when the temperature \( (T) \) tends to infinity, are unknown. For that, we will proceed to two linearization forms. We add that before finding these two linearization forms, we have tested graphically several different transformed independent-dependent variables dependencies, for which we can cite for example \( R_{ct} = f(1/T) \), \( 1/R_{ct} = f(T) \), \( 1/R_{ct} = f(1/T) \) and \( R_{ct} = T = f(T) \). All these mathematical functions exhibit non-linear forms.

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**Table 4.** Optimal Arrhenius parameters \( (Y_0, \delta \text{ and } \beta) \) from non-linear regression of Eq. (12).

| Parameter | \( Y_0 \) | \( \delta \) | \( \beta \) |
|-----------|----------|----------|----------|
| \( E_1 \) | 1.30     | 0.1125   | 1.30     |
| \( E_2 \) | 1.75     | 0.2495   | 1.75     |
| \( \ln A_0 \) | 2.95 | 0.09545  | 2.95     |
| \( R_{square} \) | 0.999912 | 0.99999   | 0.999999 |

**Figure 4.** Variation of the three adjustable parameters \( (E_i \text{ and } \ln A_0) \) of Eq. (5) as a function of the number of hydrogen \( (x_H) \) of the acid.
behavior. Nevertheless, we find only two further expressions \( T \cdot R_{ct} = f(R_{ct}) \) and \( T \cdot (R_{ct} + R_1) = f(R_{ct}) \) showing a good linearity which we will develop in the following section.

First linearization form. This form consists to test the linearization in the positive branch of the prospective parabola by testing the product \( T \cdot R_{ct} \) as a function of \( R_{ct} \) to situate approximately the position and arrangement of the curve. The following figures (Fig. 7) show an excellent apparent linearity that can be expressed as follows:

\[
TR_{ct} = a_0 + a_1 \cdot R_{ct}
\]

(13)

Taking into account the dimensional equations, we set \( a_0 = T_0 \) and \( a_1 = T_0 \cdot R_0 \). We then obtain a more significant hyperbolic form, which can be expressed as follows:

\[
R_{ct} = \frac{R_0 T_0}{T - T_0}
\]

(14)
where $R_0$ and $T_0$ are two optimal adjustable parameters, which are equivalent to a charge transfer resistance and temperature, respectively. Values of these parameters are given in the Table 5. However, the $R_0$-value mathematically represents the value that the charge transfer resistance can take, when the temperature ($T$) reaches twice the value of $T_0$ while the Fig. 6 and Table 5 indicates a certain discrepancy leading us to speculate that the real phenomenon is probably described by a more complexing parabola or another mathematical form which is consolidated by the fact that the limiting temperature value ($T_0$) is very near to the minimum temperature (293.15 K) of the investigated temperature range. On the other hand, at very high temperature, the model of Eq. (14) indicates that the charge transfer resistance tends to a very low value, showing that the corrosion is accentuated.

### Second linearization form.

This form consists to test the linearization in the negative branch of the prospective parabola by testing the product $T(R_{ct} + R_i)$ as a function of $R_{ct}$ to situate approximately the position and arrangement of the curve and its asymptotes and where $R_i$ is a free adjustable parameter. The following figures (Fig. 8) show an excellent apparent linearity, which can be expressed as follows:

$$T(R_{ct} + R_i) = a_0 + a_1 \cdot R_{ct}$$  \hspace{1cm} (15)

Taking into account the dimensional equations, we set $a_1 = T_0$ and $a_0 = T_0 \cdot R_0$. We then obtain a more significant homographic form, which can be expressed as follows:

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**Table 5.** Optimal adjustable parameters’ values of Eq. (14), for each acid.

| Acid   | $T_0$ | $T_0$ | $R_0$ | R-square |
|--------|-------|-------|-------|----------|
| HCl    | 291.08 | 17.93 | 145.08 | 0.999912 |
| $H_2SO_4$ | 292.42 | 19.27 | 71.19  | 0.999936 |
| $H_3PO_4$ | 292.73 | 19.58 | 93.53  | 0.999912 |

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**Figure 7.** Linear correlation between the product temperature-charge transfer resistance $T \cdot R_{ct}$ and the charge transfer resistance $R_{ct}$ for each acid.

**Figure 8.** Linear dependence between the product $T(R_{ct} + R_i)$ of Eq. (15) and the charge transfer resistance $R_{ct}$ for each acid.
where $R_0$, $R_1$ and $T_0$ are three optimal adjustable parameters, which are equivalent to two charge transfer resistances and temperature, respectively. Values of these parameters are given in the Table 6.

The temperature limit values are lower than that of the first linearization, which shows that this technique has given better results. It can then be considered that this limiting temperature ($T_0$) corresponds to a very high value of the charge transfer resistances (Fig. 6) where the corrosion is practically slowed down.

Finally, we note that though the two homographic proposed models give specific parameters values of each acid, we have found that we can treat overall the three acids in the same time by only global parameters with reliable accuracy. Then, we obtain excellent linearization shown by (Fig. 9) for which, each the corresponding global optimal adjustable parameters are given by Table 7. It’s interesting to inspect in future the variation of these parameters for other systems in different conditions to more reveal their physical meaning.

**Arrhenius activation energy.** We note that we can estimate an average value of the Arrhenius activation energy from the Eq. (14) by considering that the linear Arrhenius behavior is not followed; and the Arrhenius-type equation (Eq. 2) must be expressed as follows:

$$\ln R_{ct} = \ln A_{ct}(T) + \frac{E_a(T)}{R} \left( \frac{1}{T} \right)$$

(17)
where the Arrhenius parameters $A_e$ and $E_a$ become dependent of temperature. For that to determine these parameters, we must consider the general definitions of Eq. (6) and not the slope of linear regression. 

$$E_a(T) = R \left( \frac{\partial (\ln R_{ct})}{\partial (1/T)} \right)_p$$

(18)

So, using Eqs. 14 and 18, we can obtain the following expression of the dependence of activation energy with temperature.

$$\frac{E_a(T)}{R} = \frac{T^2}{T-T_0}$$

(19)

Nevertheless, this expression can be transformed as follows to be easily integrated later for statistical handling:

$$\frac{E_a(T)}{R} = T + T_0 + \frac{T_0^2}{T-T_0}$$

(20)

To give an approximate estimation of the mean activation energy $E_a$ that should be obtained by classical linear regression we can apply the following reasoning. We can calculate the average value of the function $E_a(T)$ expressed by Eq. (20) over a temperature interval $[T_{min}, T_{max}]$ such as in our situation; $[293.15,353.15]$K, by the following expression:

$$\overline{E_a} = \frac{1}{T_{max} - T_{min}} \int_{T_{min}}^{T_{max}} E_a(T)dT$$

(21)

Which it can be adapted for Eq. (20) and can lead to a practical expression (Eq. 22) for an average value of activation energy without using direct linear regression of $\ln R_{ct}$ with $1/T$.

$$\overline{E_a} = R \left[ T_0 + \frac{T_{max} + T_{min}}{2} + \frac{T_0^2}{T_{max} - T_{min}} \ln \left( \frac{T_{max} - T_0}{T_{min} - T_0} \right) \right]$$

(22)

Nevertheless, we must notice that the small number of experimental data points and the existence of the corresponding errors can result in an average value of activation energy with a relative deviation about 10% or more.

**Conclusion**

Generally, for the majority of experimenters, the charge transfer resistance–temperature dependence is treated by linear regression of the Arrhenius behavior by the plot of the logarithm of the charge transfer resistance versus the reciprocal of absolute temperature.

Nevertheless, we have noticed that there is some feeble deviation to the linearity for numerous works, which exceed the experimental errors bar. To fix this observation and reduce the discrepancy between experimental and calculated values, we have proceeded in two manners.

(i). We have extended the Arrhenius type-equation by a supplementary term in $(1/T^2)$ to reduce the discrepancy with the experience and classify the nature of deviation as a super-Arrhenius behavior showing that the effective activation energy increases when the temperature decreases.

(ii). Regarding the trend of experimental scatter points of the charge transfer resistance with temperature, which likes a hyperbolic behavior, we have mathematically investigated this variation and suggested an original homographic model with only two optimal adjustable parameters for which we gave some physical meaning. In the same context, we have suggested a mathematical formula allowing to indirectly calculate the familiar Arrhenius activation energy using only the parameters of the homographic model for each acid or for overall the three acids.

(iii). In addition, in the present work, we discover interesting property, a causal correlation with the number of protons of polyacid, which can open a new theoretical field and encourage experimenters to validate this finding by the use of other acids in future investigation on different systems.

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