Derman S et al. / Portugaliae Electrochimica Acta 45 (2027) 575-582

Influence of Inorganic Electrolyte Solutions on the Cleaning of Steel Surfaces from Oil Contamination

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Received 05/08/2025; accepted 10/01/2026
https://doi.org/10.4152/pea.2027450515

Abstract

This article investigates the influence of inorganic electrolyte solutions on the efficiency of cleaning steel surfaces from oil contamination. Using an electrochemical method, it was demonstrated that electrolyte solutions, compared with pure water, significantly reduce free surface energy at the metal–solution interface due to the formation of a double electric layer and oxidation of the metal surface. However, complete cleaning is hindered by the presence of an oil barrier, the overcoming of which requires combined use of electrolytes and organic surfactants. Future research will be devoted to studying this combined effect on the cleaning process.

Keywords: degreasing; double electric layer; electrochemical method; electrolytes; interphase boundary; metal cleaning; surfactants.

Introduction•

Surface preparation of metals, particularly steel, is a fundamental stage that determines the quality of subsequent technological operations, whether electroplating, painting or the application of anti-corrosion protection. Even microscopic residues of oil contaminants can critically reduce adhesion, inevitably leading to defects and deterioration of operational properties of finished products. In this context, the search for ways to optimize cleaning compositions remains a priority task in applied electrochemistry.

Traditionally, industrial cleaning agents are complex systems comprising organic surfactants and inorganic electrolytes. While the functions of surfactants have been extensively studied, the mechanism of action of the inorganic component is often viewed simplistically. According to established concepts [1-4], the role of electrolytes is primarily limited to auxiliary functions: influencing colloidal

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•The abbreviation list is in page 581.

properties of surfactants (e.g., by lowering critical micelle concentration) or, in the case of alkaline media, chemically saponifying fats. However, this approach does not provide an exhaustive explanation of cleaning efficiency, particularly regarding chemically inert, non-saponifiable contaminants.

One believes that existing models overlook the crucial aspect that the cleaning process occurs at the three-phase "metal–oil–solution" interface. Consequently, direct influence of the medium's ionic composition on the energetic state of this interface cannot be ignored. This study verifies the hypothesis that electrolyte solutions can actively alter the system's free surface energy through the formation of an electric double layer and the initiation of oxidative processes on the metal surface. Understanding the nature of these interactions is essential for the development of advanced cleaning technologies.

Method

To verify the proposed mechanism and assess the contribution of inorganic compounds to the cleaning process, a series of experiments was conducted to remove model contaminants from steel surfaces. Two types of contaminants were used in the study: paraffin, for an integral assessment of cleaning quality; and decane, for a detailed study of physicochemical surface properties (wetting and interfacial tension). Quantitative assessment of surface cleanliness (S_{act}) was performed using electrochemical method described in [5]. The method is based on measuring current during potentiostatic nickel deposition. The logic of the measurement is that, since the galvanic process is only possible on conductive areas, the ratio of the recorded current to the current on a reference (fully clean) sample allows for the precise determination of the surface fraction free from the dielectric oil film.

To investigate the influence of the electric field on wettability, contact angles were measured in the three-phase "metal–solution–oil" system. Experiments were conducted on two different electrodes: mercury electrode -a 1 N Na_2SO_4 solution was introduced into a cell containing mercury. The potential was set relative to the potential of zero charge of mercury (0.23 V, NHE) using a potentiostat, changing it in 0.1 V increments. A microdose of decane (1 μL) was applied to the surface, and the shape of the resulting droplet was recorded on photographic film for subsequent analysis; steel electrode- the methodology was adapted for a solid body. A droplet of decane (1 μL) was applied directly to the steel sample, which was then immersed in the electrolyte. Electrode polarization was carried out from stationary potential in 0.1 V increments, recording changes in droplet shape using photographic method.

Additionally, to control for surface phenomena, interfacial tension at the "oil (decane)–solution" interface was determined using stalagmometric method. Stationary potential of steel was measured using a digital voltmeter relative to a silver chloride reference electrode.

Results

From thermodynamic considerations, detachment of contamination from a substrate occurs under the following conditions [6]:

$$\Delta G < 0,\ \gamma_{s/s} + \gamma_{o/s} < \gamma_{s/o} \qquad (1)$$

where ΔG is change in free surface energy upon detachment of contamination and $\gamma_{s}/_{s}$, $\gamma_{o}/_{s}$ and $\gamma_{s/o}$ represent interfacial tension values at the substrate–solution, oil–solution, and substrate–oil interfaces, respectively.

Using Eq. (1), it is possible to determine which factors contribute to an increase in cleaning efficiency when moving from water to inorganic electrolyte solutions. Dissolution of electrolyte components into the bulk of oil phase, followed by their adsorption at the oil–solution interface, is unlikely; therefore, $\gamma_{s/o}$ can be considered constant. As shown by data in Table 1, transition from water to electrolyte solutions results in virtually no change in $\gamma_{o/s}$.

Table 1: Interfacial tension at the oil (decane) – 0.1 N solution boundary.

Solution	**H_2O**	**NaOH**	**NaCl**	**$NaClO_4$**	**Na_2SO_4**
$\gamma_{o/s} \times 10^3$, N/m	51	51,5	51,7	51,3	51,5

Thus, the observed increase in cleaning efficiency when replacing water with inorganic electrolyte solutions (Fig. 1) is explained by the fact that these solutions cause a more substantial reduction in free surface energy at the substrate–solution interface.

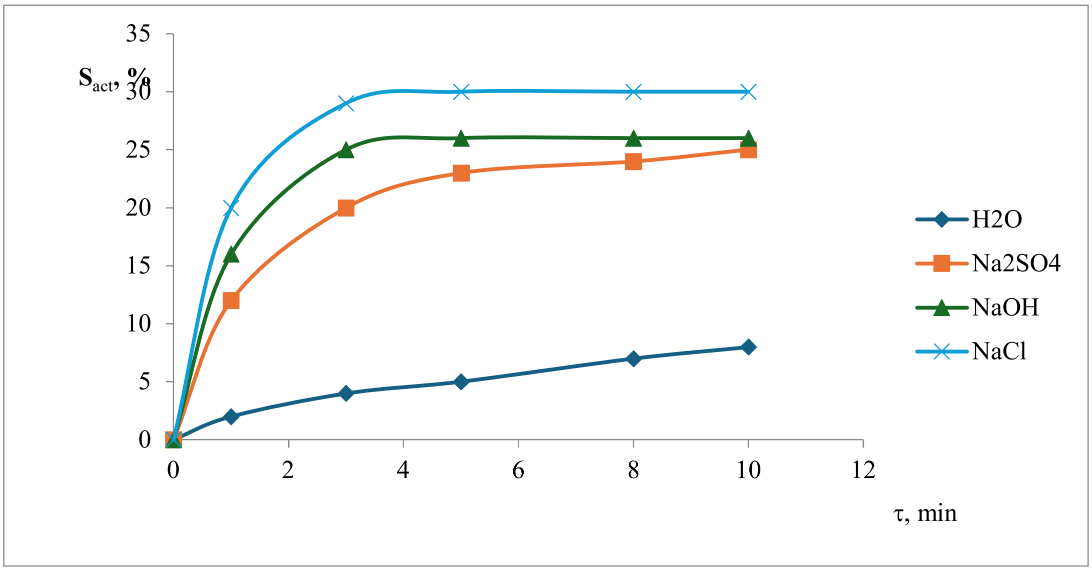

Figure 1: Dependence of the degree of steel cleaning on degreasing time (c = 0.1 g-eq/l, T = 600 ºC).

Discussion

Let one consider the factors determining the energetic state of this interface. In particular, it is necessary to account for the electrostatic factor associated with the presence of a double electric layer (DEL) at the metal–solution interface. DEL can be represented as a parallel-plate capacitor whose capacitance depends on electrolyte concentration [7].

In the case of mercury and other liquid or molten metals, dependence of interfacial tension at the metal–solution boundary on the surface charge density and potential is described by Lippmann equation [7]:

$$d\gamma_{s/s}/dE = -q \qquad (2)$$

where q is charge density and E is potential.

According to [2], the value of $\gamma_{s/s}$ reaches its maximum in the absence of surface charge. As potential deviates from potential of zero charge ($E_{q=0}$), $\gamma_{s/s}$ decreases, which facilitates the fulfillment of thermodynamic condition for detachment of contamination from the cleaned surface (see Eq. (1)).

The above considerations form the basis of the cleaning mechanism for metallic surfaces proposed in [8]. The possibility of such a mechanism is confirmed by the dependence of the contact angle in the mercury–decane 1 N Na_2SO_4 system on potential (Fig. 2).

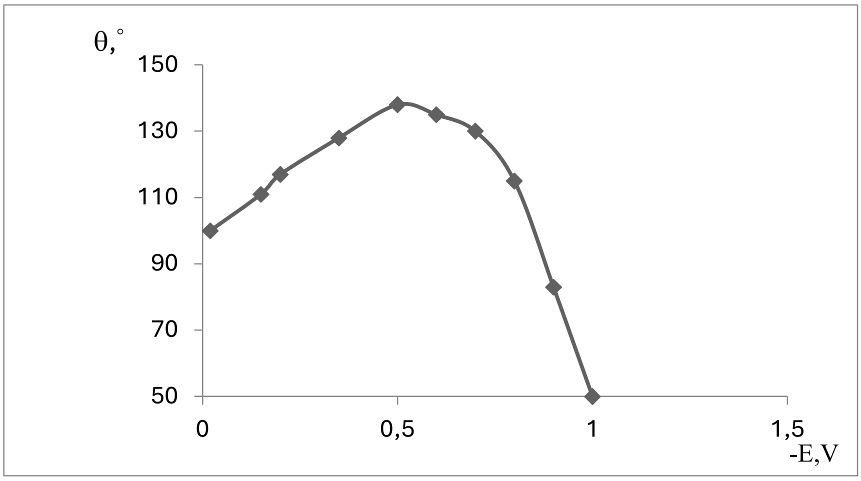

Figure 2: Dependence of the contact angle of wetting at the mercury-decane-1H Na_2SO4 interface on the electrode potential.

To some extent, this pattern also occurs for a copper electrode [8]. In the case of degreasing steel parts, considering the potential of zero charge of iron – in a Na_2SO_4 solution at pH = 5–6, $E_{q=0}$ for unoxidized iron is about –0.95 V *vs*. SCE [10, 11], and stationary potential of steel is around –0.6 V for 1 N Na_2SO_4 (Fig. 5) – it might be expected that cathodic polarization of a steel electrode would lead to oil spreading over the metal surface. However, as seen in Fig. 3, in the potential range from 0.6 to –1.0 V, contact angle in steel-decane 1 N Na_2SO_4 system remains constant.

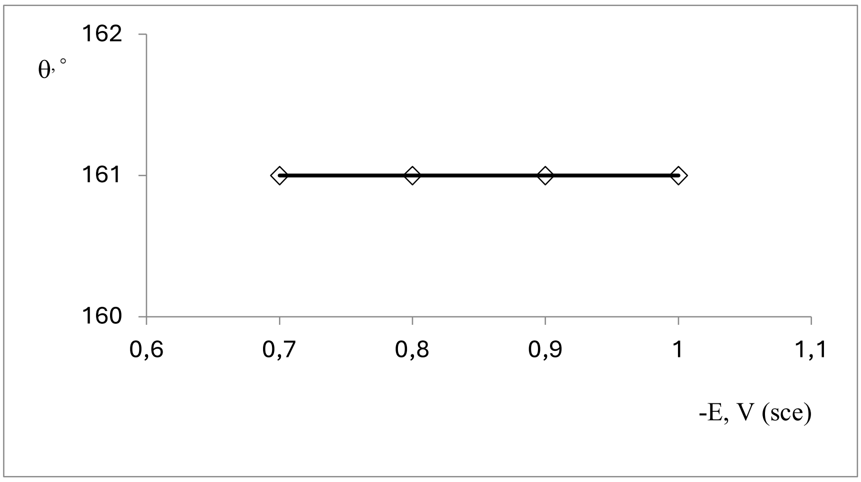

Figure 3: Dependence of the contact angle in the steel-decane-1H Na_2SO4 system on potential.

Cleaning degree of the metal also remains practically unchanged (Fig. 4).

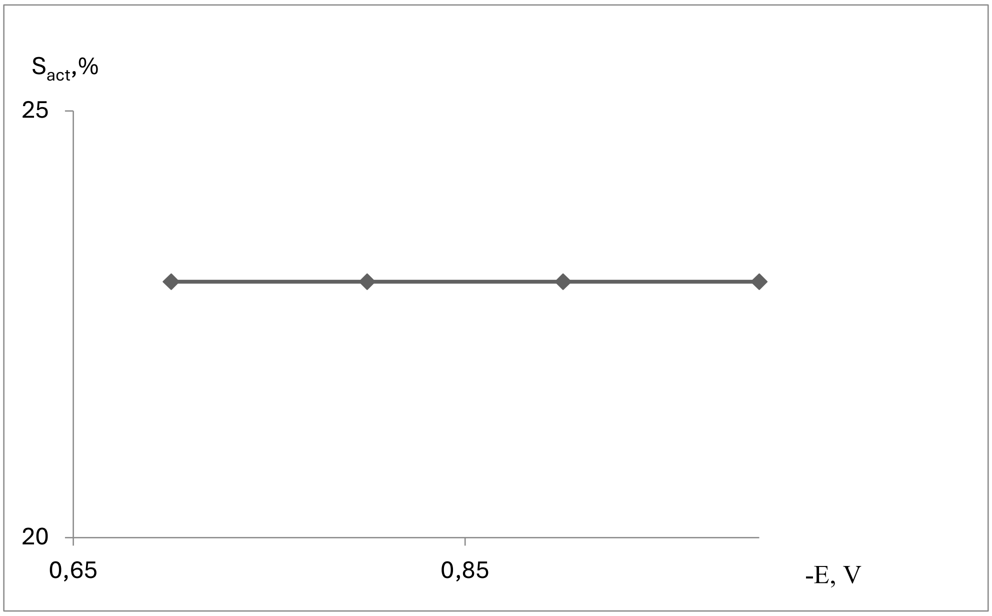

Figure 4: Dependence of the degree of steel purification on potential (background of 1 H Na_2SO_4).

As shown in [11], dependence of $\gamma_{s/s}$ on potential for solid electrodes may differ from Lippmann equation, taking the form:

$$d\gamma_{s/s} /dE = q - dq/dS \qquad (3)$$

where dS is relative change in surface area during elastic deformation of the solid electrode.

The effect of elastic deformation (dq/dS) becomes significant when a layer of strongly adsorbed dipoles (e.g., water molecules chemisorbed on iron) forms on the electrode. Strong hydrophilicity of steel (iron) likely influences the possibility of spontaneous removal of contaminants due to electrostatic factor.

It is well known that when iron (steel) comes into contact with water and aqueous electrolyte solutions, the metal surface undergoes oxidation [12]. This oxidation process is complicated by the onset of passivation, when the transition of metal ions into the solution either stops or continues at a very slow rate.

Depending on the solution's pH, intermediate species such as $FeOH^+$, Fe_2OH^+, and Fe $(OH)_2$ form on the iron surface [13]. In alkaline solutions, the final products of anodic dissolution of iron include Fe $(OH)_2$ and the anion $HFeO_2^-$ [13].

These spontaneous processes are accompanied by a shift of the electrode's stationary potential in anodic direction (Fig. 5), and influence $\gamma_{s/s}$ value. Thus facilitates the fulfillment of the condition for spontaneous detachment of contaminants from the metal surface (see Eq. (1)).

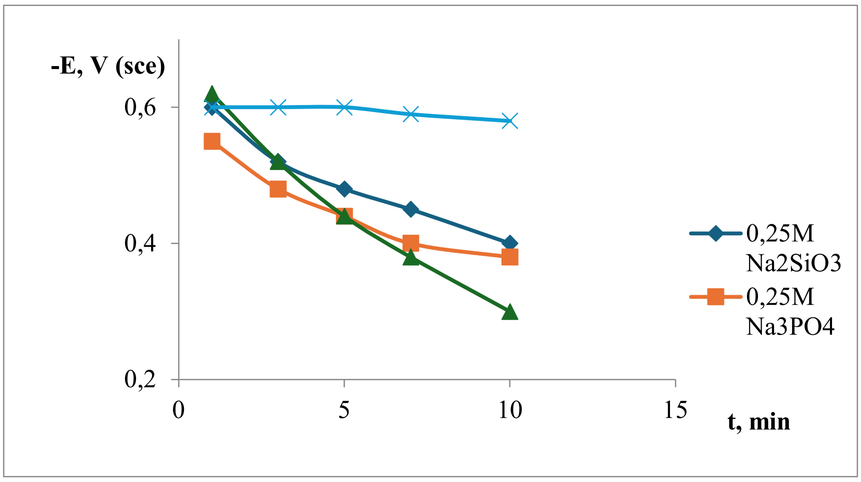

Figure 5: Dependence of the stationary potential of steel on processing time.

However, surface activity at the substrate–solution interface remains insufficient to achieve complete cleaning of the metal from contamination within the limited time allocated for this operation in the technological cycle. This is due to the fact that the contamination layer covering the metal surface acts as a barrier preventing contact between solution and substrate, as well as hindering surface reactions involved.

This barrier can be partially disrupted by kinetic energy of moving ions (e.g., due to high mobility of OH^- anions). Nevertheless, the main role is likely played by organic surfactants, which lower interfacial tension at the oil–solution boundary, thereby facilitating the fulfillment of condition (1) and reducing cohesive forces between individual oil particles (W_k):

$$W_k = 2\gamma_{o/s} \quad (4)$$

Conclusion

The conducted research shows that inorganic electrolyte solutions significantly enhance the efficiency of cleaning steel surfaces from oil contamination compared with pure water. It has been established that the main mechanism of this phenomenon is the change in free surface energy at the metal–solution interface, due to the formation of a double electric layer and spontaneous oxidation of the metal surface. Nevertheless, for complete and rapid cleaning, it is necessary to use inorganic electrolytes in combination with organic surfactants, which will be the subject of further research.

Authors' contributions

Derman S. and **Maryaskin Y. B.**: contributed equally to this work. **Maslak H. S.**: validation. **Chernousova N.**: visualization.

Abbreviations

DEL: double electric layer
S_{act}: surface cleanliness
SCE: saturated calomel electrode

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