ABSTRACT

FUNDAMENTALS OF
ADHESION OF ORGANIC COMPOUNDS AND AQUEOUS CLEANING OF GLASS AND METAL SURFACES: APPLICATIONS IN THE PHARMACEUTICAL AND CHEMICAL INDUSTRIES

by
Michel J. de Ruijter

In this thesis we studied the physics and chemistry of the adhesion of various classes of organic compounds to glass and stainless steel surfaces, by using diagnostic aqueous cleaning solutions and other techniques. We defined the thermodynamic requirements for aqueous cleaning based on extensive experimental and theoretical work. Novel cleaning diagrams are introduced, based on electrostatic interactions between organic compounds and solid surfaces, to facilitate the design of aqueous cleaning systems. We studied the mass transfer parameters for selected situations. The electrochemical Pourbaix-diagrams were used to explain the effect of hydrogen peroxide added to aqueous solutions and to avoid corrosion of solid surfaces during cleaning. On the basis of this work, we defined the necessary requirements for new non-stick materials to be developed. The use of such new materials should minimize the adhesion of organic materials to vessel surfaces.

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A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Environmental Engineering

Department of Civil and Environmental Engineering

May 1995

APPROVAL PAGE

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     Prevention.", presented at EPA 21st Annual RREL Research Symposium,
     Cincinnati, OH.

___. April 1995. "Interface/Materials, Applications in the Pharmaceutical
     Industry." *NJIT Research*, Newark, NJ.

___. August 1994. "Adhesion of Organic Materials to Vessel Surfaces Used in
     the Pharmaceutical and Chemical Industry.", presented at Proceedings of
     the 208th ACS National Meeting, Washington, DC.

de Ruijter, Michel J. July 1993. "Research into Diffusion Processes in LTA and
     FAU Zeolites with Isotopes." VUB Press, Brussels, Belgium. Thesis.

This thesis is dedicated to
Dr. Mohamed E. Labib and my wife Nancy.

ACKNOWLEDGMENT

TABLE OF CONTENTS

Chapter	Page

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(Continued)

CHAPTER 1

INTRODUCTION

Organic solvents are commonly used to clean vessels and equipment in the pharmaceutical and chemical industry. This organic-solvent cleaning generates a large volume of waste solvents and contributes to atmospheric emissions. Solvents are low molecular weight organic liquids such as aliphatic petroleum fractions, acetone, toluene and chlorinated hydrocarbons. They achieve cleaning of vessels and equipment because of their high solubility for dirt, greases and many organic residues. The majority of organic solvents have detrimental effects on the environment. Solvent emission has been investigated for its role in environmental health problems, stratospheric ozone depletion and smog formation. Questions concerning health and safety issues of such emissions include chronic and acute health effects, carcinogenicity and danger of explosions. In the pharmaceutical industry, cleaning solvents may account for 15 to 20 % of total volume of solvents used in all processes. After cleaning, the solvent waste generated is left for disposal, which is very costly.

The two main focuses in search for cleaner and safer technologies with respect to solvent cleaning include: (a) process changes to reduce the need for solvent cleaning, and (b) recycling steps that reduces the total solvent waste output. Our pollution prevention solutions to this problem include the use of alternative aqueous cleaning solutions (water-based) and the development of new equipment materials with non-stick surfaces that would minimize the adhesion of organic residues equipment surfaces (Ref. 10).

In order to remove or clean organic residue from a solid surface, the adhesion forces that bind organic residue to the surface must be overcome. In

order to understand cleaning and to develop cleaning parameters, we have to understand the adhesion of organic residue to solid surfaces. In this research we have used simple aqueous cleaning formulations to understand these adhesion phenomena. Such understanding is expected to provide novel technologies to reduce organic solvent use in industry.

1.1 Adhesion of Organic Material to Solid Surfaces

Earlier knowledge about the adhesion of organic materials to inorganic solid surfaces was based on the concept that polar components adhere better to surfaces. Recently, with the help of modern surface analytical tools, these concepts have become more specific in describing the conditions that influence adhesion. Actual chemical bonding between the organic compound and the surfaces was found to be necessary for strong adhesion (Ref. 9).

The acid-base or more generally the donor-acceptor interaction between the organic residue and the surface has been found to be responsible for the major portion of the adhesive bond. Two major concepts were advanced in the literature to quantify these donor-acceptor effects. First, new experimental methods were developed by Labib and Williams to relate the electron donicity of inorganic surfaces to their interaction to organic compounds and thus to adhesion (Ref. 9). The second concept was developed by Fowkes, who applied the Drago concepts of solvent interaction to solid surfaces and organic materials and relate them to adhesion (Ref. 7). Both approaches describe the chemical basis of adhesion in different ways.

On the basis of such understanding, organic compounds with ionizable functional groups such as carboxylic acid, hydroxyl and amine have been found to adhere strongly to metals. In this research, we are interested in surfaces and conditions that produce the minimum adhesion of organic materials to solid

vessel surfaces. Poor adhesion of organics is expected to produce less residue in the vessel after synthesis, and thus resulting in less cleaning. Ideally, we should minimize the adhesion of organic residue to equipment surfaces and render the cleaning possible with aqueous solutions. This would ultimately lead to the elimination of solvent cleaning practise.

1.2 Vessel Surfaces Used in the Pharmaceutical and Chemical Industries

The two most important materials used to make vessels and equipment in the pharmaceutical and chemical industries are stainless steel and glass. Sometimes Teflon or fluorocarbon materials are used in pumps, valves or transfer tubes.

The stainless steel used for this purpose has a high content of chromium, and is known for its corrosion resistance. Its ability to resist corrosion is attributable to a passivating surface film of chromium oxide, besides the natural film of iron oxides. This surface film is nonporous, self-healing and insoluble in wide pH regions. The minimum chromium content needed to achieve good protection is 12 %; but 18 % chromium is used. Other elements such as nickel, manganese, silicon and molybdenum are also present in the steel. In the pharmaceutical and chemical industries where often corrosive conditions exist, type 316 Stainless steel is widely used. It is well known that the thin layer of surface oxides dictates the adhesion of organic materials to the stainless steel (Ref. 2).

Most glasses contain silicon oxide as their major constituent. The glasses used for vessel surfaces in the pharmaceutical and chemical industries are chosen for their chemical and thermal-shock resistance. The adhesion of organic compounds to glass surfaces is usually attributed to reactions with the

silanol groups and adsorbed water molecules at the surface of glass.

1.3   Present Methods of Cleaning Validation

Cleaning validation in the pharmaceutical industry is regulated by the FDA and must be done between batches of synthesis or production runs.   Several techniques to validate cleaning are used in the pharmaceutical industry.   The main concern of the engineer in charge of cleaning the equipment is the degree of cleaning and not the cleaning process itself.   Visual inspection by trained technicians is widely used in the industry.   The engineer uses a flashlight to inspect the inside of a cleaned vessel as a routine procedure.   When organic deposits are seen, the cleaning procedure starts from the beginning until the degree of cleaning required by the FDA is satisfied.

A more rigorous method to validate cleaning in the pharmaceutical industry is the wipe or 'swab' test.   In this test, a soft tissue (mostly white cotton or filter paper) is moistened with high-purity solvent.   This tissue is used to swab an area of one hundred square centimeter clean.   The amount of organic contamination collected in the cloth (or the degree of cleanliness) is commonly determined by chromatographic or other appropriate technique.

For stainless steel, we used a combination of visual inspection and infrared spectroscopy to measure the level of cleaning.   For glass, we developed a new technique based on optical spectroscopy.   With the aid the latter technique we were also able to measure the change of cleaning performance solution as a function of pH, oxidation potential of a cleaning solution and to study the effect of temperature and time.   This has given us insight regarding the kinetics of the cleaning process.

1.4 Objectives of Work

We had three major objectives for this research. Our first objective in this thesis was to identify and select organic materials to be tested. Almost every imaginable organic is used in the chemical or pharmaceutical industry and will, in one way or another, end up to be cleaned after process. It is impossible to examine the adhesion and cleanability of all organic compounds used in the industry. Therefore we examined the adhesion mechanisms of several classes of organic materials to solid surfaces. To study a class of organic compounds, we choose one or two compounds to be tested for cleanability.

Our second objective was to understand adhesion and cleaning of selected organic materials in aqueous solutions. We examined the mechanisms of aqueous cleaning, without the addition of surfactants or other complex additives. Only three parameters were varied during this research. First, the pH of the solution is changed by the addition of appropriate buffer solutions. Second, the oxidation potential of the water is altered by the addition of hydrogen peroxide. Third, the temperature of the solution is varied to study the thermodynamic and kinetic aspects of cleaning. Theoretical treatments were developed to design aqueous cleaning systems for various organic/surface combinations.

Our ultimate objective was to predict parameters needed to design vessel surfaces with non-stick properties and to formulate prudent pollution prevention solutions to this problem.

1.5 Organization of the Thesis

In Chapter 2 we discuss the materials and techniques used and developed during this research to examine cleaning performance.

In Chapter 3, we have established theoretical relationships between the

thermodynamic parameters of the cleaning system: These parameters are the pH of the solution, the isoelectric point of the surface and the dissociation constant of the organic compound to be cleaned. We explain adhesion and cleaning in terms of equilibrium chemistry. We have also build a theoretical model for aqueous cleaning, on the basis of interface charging of the vessel surface and the organic layer (residue) adhering to it. In Chapter 3, we also present important kinetic and mass transfer aspects of the cleaning process.

In Chapter 4 and 5 we present and discuss the experimental results accomplished in this research, respectively. We were able to define the different parameters operating in the aqueous cleaning process and their impact on the cleaning of vessel surfaces. We showed the importance of the pH of the solution in the cleaning process and describe the adhesion of organic materials to solid surfaces from an equilibrium standpoint of view. In Chapter 5, we show how to construct and use electrostatic charge diagrams to determine pH regions of possible aqueous cleaning. We also discuss why the addition of hydrogen peroxide enhances aqueous cleaning.

Some critical features of materials and their surfaces with respect to aqueous cleaning are discussed in Chapter 5. During the cleaning process, the vessel surface should be restored in its initial state. The surface cannot be corroded or etched and the surface should again be passivated after cleaning. We discuss the use of the Pourbaix-diagrams to determine regions of cleaning, passivation, corrosion and etching. Pourbaix-diagrams are also used to explain the positive effect of hydrogen peroxide on cleaning and why in general, an oxidizing agent may be needed in a cleaning system. The critical parameters for the design of non-stick vessel surfaces have been identified in Chapter 5.

In Chapter 6, a summary of the work is given. The impact of the result on the design of cleaning systems is also discussed.

CHAPTER 2

EXPERIMENTAL PROCEDURES

In order to obtain consistent experimental results throughout this research, it was important to select appropriate materials and to establish reliable laboratory procedures. Several solid surfaces were chosen to represent vessel and equipment surfaces used in the pharmaceutical and chemical industry. Other solid surfaces were chosen to validate hypotheses and to achieve complete understanding of the phenomena involved in this work. Organic materials, representing several classes of organic compounds were selected to study adhesion of drugs to surfaces and to assess the cleaning of such surfaces in the aqueous environment. In this chapter we describe the methods used to characterize solid surfaces and the techniques used to measure cleaning performance. The methods presented here include new procedures that were specially developed for the purpose of this research.

2.1   Materials Selections

2.1.1 Selection of Vessel Surfaces

Most vessel surfaces used in the pharmaceutical industry are made from stainless steel or from steel cladded with glass or glass ceramics. Occasionally, teflon vessels are used. In this work we confined our study to steel and glass surfaces.

The stainless steel used in the pharmaceutical industry is the 316 L grade. This is a low carbon steel with high chromium and nickel content, and is known for its high corrosion resistance. In this research we used stainless steel

316 (SS 316) samples -- the high-carbon version of SS 316 L. Our stainless steel substrates were two inch square and one-sixteenth inch thick.

Several types of glass are used as liners for vessel surfaces. The glass types used in the pharmaceutical industry have several constituents and their composition is often proprietary. We examined the surface composition of a glass type that is common in the industry. This glass sample was provided by Pfaudler, Rochester, NY. Auger electron spectroscopy indicated that its composition is intermediate between conventional pyrex glass and high temperature glass (which is mainly silicon oxide). In this research, we used pyrex glass substrates having three inch square and one-eight inch thickness. For the optical spectrophotometric measurements, we used quartz cuvettes to represent a glass surface - quartz is pure silicon oxide. The cuvettes were 0.5 inch square and 1.75 inch high.

In order to validate our results with respect to aqueous cleaning, we also used surface samples made of aluminum, molybdenum, tantalum and titanium. All these samples were two by two inch in dimensions.

2.1.2 Selection of Organic Materials

It is virtually impossible to examine the adhesion and cleanability of all the organic compounds prepared in the pharmaceutical or chemical industries. In order to cover as many cases as possible, we selected materials to represent all classes of organic compounds. Our selection of organic compounds was based on the type of functional groups. It is expected that such functional groups determine the physical and chemical adhesion of the organic materials to a solid surface. Another major criteria of selection was the solubility of the organic compound in water. It is anticipated that water-insoluble organics are difficult to clean in aqueous cleaning. Carbohydrates, organic acids and bases,

esters and polymers were included in our study. The organic materials used in this research and some of their properties are summarized in Table 2.1.

Table 2.1 Selected materials and their characteristics.

Chemical Class	Compound used in Study	Melting-point (°C)	Soluble in water
carbohydrates	D-glucose	146	very good
low molecular acids	succinic acid	188	good
high molecular acids	stearic acid	71.2	no
amino aromatic acids	4-aminobenzoic acid	188	good
aromatic amines	diphenyl amine	52	no
esters	isoamyl acetate	-78	good
aromatic bases	8-hydroxy quinoline	76	slight
epoxy resins	bisphenol A + epichlorohydrin	-	no
ketones	cyclohexanone	-16	no
alcohols	glycerol	17.8	very good
silicon compounds	silicon grease	-	no

2.2 Surface Analysis of Steel and Glass Substrates

To understand the mechanism of adhesion between organic materials and solid surfaces, knowledge of the exact composition of such surfaces is necessary. We used X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and Fourier Transform Infrared spectroscopy (FTIR) to analyze the surfaces of some of the substrates used in this research.

In Auger electron spectroscopy (Ref. 4), Auger electrons are generated in the sample by an external electron source. The energy of the Auger electrons emitted from the surface is characteristic to the elements present. Auger electrons emitted from the top nanometer of the surface can be detected and analyzed. In other words, AES is a truly surface technique capable of uniquely characterizing the elemental composition of the surface of a solid. The basic components in AES equipment are: an ultrahigh vacuum chamber, an electron

gun for excitation, an electron energy analyzer and a computer. In AES, quantitative analysis is very difficult without standard specimen.

In XPS, the sample is bombarded with a low energy monochromatic X-ray beam. The electrons generated by XPS come from core orbits in the atoms located at the surface of the solids being analyzed. XPS gives the chemical composition of the surface at depths between 40 to 100 Å, depending on the density of the material.

Fourier transform infrared spectroscopy (FTIR) differs from traditional infrared spectroscopy in the way the data is calculated and presented (Ref. 14). In FTIR interferograms are recorded and the infrared spectra are computed from the interferograms via a fast Fourier transform algorithm. In our study FTIR was used in the reflection mode. This is referred to as grazing incidence reflection. This technique uses the reflection of an infrared beam at the surface of a solid substrate. To analyze organic films on solid surfaces, it is necessary that the underlying solid reflects the infrared radiation. In general, FTIR is used to analyze organic matter as explained in section 2.4.

All the analysis used in this research were performed at David Sarnoff Research Center, Princeton NJ, a subsidiary of SRI International, under the guidance of Dr. P.J. Zanzucchi and Mr. D.J. Szostak.

2.3 Techniques to Deposit Organic Residues on Substrates

In order to obtain a good adhering organic film (or residue), the solid substrates had to be perfectly clean. This is necessary to achieve the same substrate surface chemistry in all our experiments - a condition necessary for reliable interpretation of adhesion and cleaning results. Table 2.2 summarizes our procedures for cleaning the SS 316 and glass substrates (Ref. 13).

In our study, most organic compounds listed in table 2.1 were deposited from their concentrated solutions in a solvent. The solvents used are water, acetone and 2-propanol. Table 2.3 summarizes the deposition techniques used and describes the nature of the organic residue adhering to the solid substrates.

Table 2.2 Cleaning procedure for steel and glass.

316 SS	Glass
rinse with acetone hold in trichlorethylene for 30 seconds rinse with methanol rinse with acetone hold in hydrochloric acid for 30 seconds hold in nitric acid for 30 seconds rinse with hot deionized water rinse with acetone dry	wash with detergent hold in chromic acid for 30 seconds hold in hydrochloric acid for 30 seconds rinse with deionized water dry

In our general procedure, the substrates were kept in a boiling solution of the organic compound for one hour followed by drying under the flow of nitrogen gas.

Table 2.3 Different deposition techniques.

Material Selected	Preparation Method
Glucose and its dehydrated products	Dehydrated products were deposited on SS 316 from aqueous solutions followed by dehydration at 200°C. A strongly adhering, brownish residue was formed on the SS.
Succinic acid	Succinic acid was deposited on SS from a water solution, then heated at 100°C. A thick layer of white crystals was formed.

Table 2.3 (Continued).

Material Selected	Preparation Method
Stearic acid	Stearic acid was deposited on SS and glass from a boiling isopropanol solution. A thick layer of white spherical crystals was formed.
4-amino-benzoic acid	Deposited on SS from hot isopropanol solution. White crystals were formed.
Diphenyl amine	Deposited on SS and glass from warm isopropanol. Thick white crystals were formed
8-hydroxy quinoline	Deposited on glass from warm acetone solution. A layer of white crystals was formed.
Isoamyl acetate	Deposited on SS from acetone and heated at 200°C. Brownish layer was formed.
Bisphenol A + epichlorohydrin	Deposited cold on SS and dried.
Cyclohexanone	Deposited on hot SS (70°C). Solid residue was formed.
Silicon grease	Deposited cold on SS
Glycerol	Deposited on SS and heated at 200°C Sticky residue was formed.

The epoxy resin and silicone grease were deposited directly on the substrates at room temperature. In the cases of glucose, dehydrated sugars, glycerol and isoamyl acetate, the substrates with organic film were purposely heated to produce a water-insoluble residue. FTIR analysis was used to determine the chemistry of deposited glucose before and after heating.

2.4 Methods and Techniques to Measure and Quantify Cleaning

2.4.1 FTIR

The FTIR technique combined with grazing incidence reflection described in section 2.2, was used to detect small organic deposits on the surface of metals. To detect small concentrations of organics on the surface of a SS substrate, it was important to know the characteristic IR absorption bands of such compounds. For example, the broad and large peak resulting from the interaction of infrared light with the carbonyl group (C=O) that appears around 1700 cm^{-1}, is a indication that organics are present. Another important indicators include the peaks of organic hydroxy-group (C-OH) and carbon-hydrogen (C-H) absorption bands. The equipment used in this work was capable of producing high resolution infrared spectra. This allowed us to single out particular peaks in the FTIR spectrum. In our research, we compared the spectra of the organic compounds themselves, the perfectly clean steel and the cleaned sample between 400 and 5000 cm^{-1}. We also used FTIR to determine if the deposited organic residue was different in composition from the original organic compound.

We used reflection FTIR on steel surfaces. Although FTIR provided valuable information, it was difficult to use the technique to quantify the degree of cleaning on stainless steel substrates.

2.4.2 Visual Inspection Method to Determine Cleaning of Metals

Due to the difficulty in determining the level of cleaning by FTIR, we relied on visual inspection to establish our cleaning curves. By holding the sample against natural light, the smallest organic deposits could be seen on the surface

of metal substrates. We found visual inspection to be fast and that the average cleaning level over the whole sample area can be quantified.

We estimated the degree of cleaning by dividing the cleaned area by the total area of the sample. This method was used for both qualitative and quantitative evaluation of cleaning performance.

2.4.3 Optical Spectroscopy to Determine Cleaning of Glass

In search of a quantitative method to measure cleaning performance for glass substrates, we developed a new technique based on optical spectroscopy. Visible light spectrometry is used in analytical chemistry to determine the concentration of compounds in solutions. In conventional analysis, the solution of interest is placed in a glass cuvette, and the absorbance (or transmission) is measured. Incoming light is absorbed by the solution according to Beer's law,

$$A = \log (I_0 / I) = k\,C \qquad (2.1)$$

with A = absorbance
I_0 = intensity of incoming light
I = intensity of light transmitted light
C = concentration of absorbing material in solution
k = positive constant.

In equation 2.1, the concentration C is the mass of absorbing material present in the cuvette, divided by the volume of solution in the cuvette (V). If we assume the volume of the solution to be constant, we can rewrite the formula as

$$A = \log (I_0 / I) = k'\,m \qquad (2.2)$$

with k' = k / V = positive constant
m = mass of absorbing material present.

Equation 2.2 expresses a positive linear relationship between the mass of absorbing matter present in the cuvettes and measured absorbance.

In our optical method, we deposited the organic compounds on the outside of the quartz cuvettes and left the cuvettes empty. The incoming light, as shown in figure 2.1, passed through two layers of organic matter, before being measured.

I_0 I

monochromatic
light source

cuvette with
organic deposits

photospectrometer
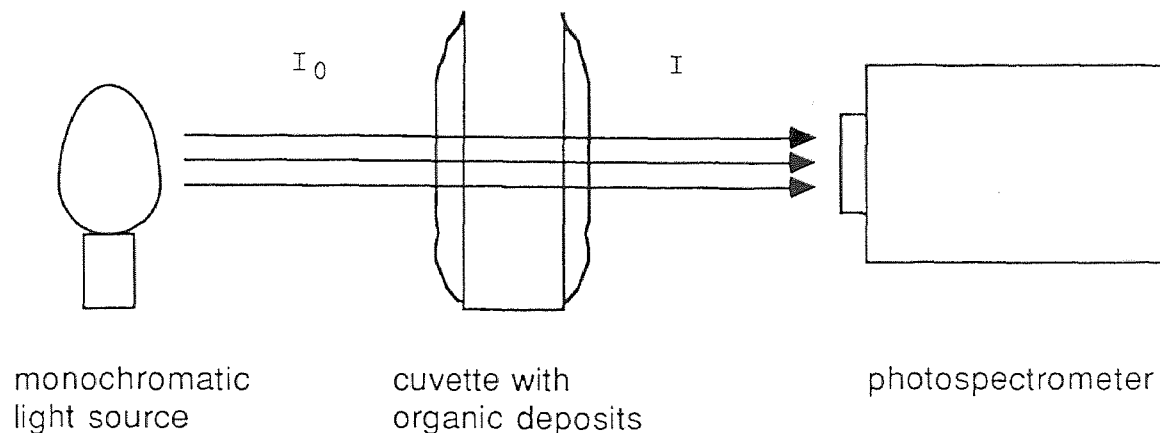
Figure 2.1 Photomeasurement of absorbance of organic deposits.

Using equation 2.2, it is now possible to calculate the mass of deposited organic matter by measuring the absorbance. Since the difference in the mass of deposited material before and after cleaning is equal to the cleaning performance, it is possible to calculate cleaning performance from absorbance data (see section 2.5).

We used an ultraviolet and visible light spectrometer made by Gilford Instruments, model 240, connected to a digital absorbance meter, model 410. In our measurements we used light with a wavelength of 400 nanometer. This gave good peaks for all the examined organics. The area on the cuvette covered by visible light was about one centimeter square.

2.5 Procedures Used to Establish Cleaning Curves

In several cleaning experiments, the pH of the cleaning solution defined the regions of possible cleaning. In order to determine the cleaning behavior at different pH conditions, we established the so called 'cleaning curves'. In a cleaning curve, the cleaning performance versus pH is plotted. Because the temperature and time of cleaning are two very important parameters of cleaning performance, care was taken to insure that the temperature is constant and that the time of cleaning is equal for all samples during the measurement of cleaning curves

As discussed earlier, we used two main methods to quantify cleaning, namely visual inspection for stainless steel and visible light spectroscopy for glass. In visual cleaning, the cleaned area is compared with the total area of the sample to determine the cleaning performance. Cleaning performance is expressed in percent -- i.e., zero percent means no cleaning and 100 % means perfectly clean.

For glass, the linear relationship between cleaning performance and absorbance of visible light was used to establish the cleaning curves. Since the absorbance values are relative, two initial conditions need to establish a unique relationship between absorbance and cleaning. In analogy with the visual measurements, we state that perfectly clean is one hundred percent cleaning performance, and no mass loss during cleaning is zero percent cleaning performance. We used the following linear equation to calculate cleaning performance from absorbance data.

$$C_p\ (\%) = (A_0 - A_t) / (A_0 - A_c) \times 100 \qquad (2.3)$$

with $C_p\ (\%)$ = cleaning performance in percent

A_0 = absorbance before cleaning
A_t = absorbance at time t (after cleaning)
A_c = absorbance of perfectly clean cuvette

A_c was measured after thoroughly cleaning with acetone. With this method it was also possible to study cleaning performance versus cleaning time.

2.6   Microscopic Examination and Adhesion Assessment

In addition to XPS, AES and FTIR to analyze the surface chemistry, and optical light absorbance to measure cleaning, we used optical microscopy to examine the samples. By using a microscope, we were able to confirm if macroscopic cleaning correspond to microscopical cleanliness.

CHAPTER 3

ADHESION OF ORGANIC COMPOUNDS TO
SOLID SURFACES - THEORETICAL TREATMENT

As indicated in chapter 1, the adsorption of organic compounds to many solid surfaces is dominated by the chemical behavior of surface oxides and hydroxides. There are two ways to describe this adhesion phenomenon. The first involves equilibrium chemistry between the surface and the organic molecules. The second is based on electrostatic interaction between the organic compound and the surface. In section 3 and 4, some kinetic and mass transfer aspects of cleaning are discussed.

3.1   Introduction

Atoms at a solid surface are only partly bonded to atoms in the bulk inside the solid. Such surface atoms thus possess residual valences on their outerside surface that are often saturated by forming surface oxides and hydroxides. These surface oxides and hydroxides are responsible for the adsorption of foreign molecules onto the surface. Adsorption is traditionally classified into physical adsorption and chemisorption. Chemisorption takes place when there is a strong chemical bonding between the adsorbed molecules and the atoms of the surface. If there is only a weak interaction between the adsorbate molecules and the atoms in the solid surface, the adsorption is considered physical adsorption. Chemisorption is considered to be irreversible, while physical adsorption is considered to be reversible.

In the aqueous environment, the residual valences of surface atoms reacts with water and oxygen to form surface oxides and hydroxyl groups . It is

estimated that about 2 to 6 hydroxyl groups per square nanometer are present on a clean smooth oxide surface (Ref. 8). A natural, clean surface usually contains several layers of water, that are hydrogen-bonded with the underlying hydroxylated surface.

Several adhesion mechanisms can be cited for the adhesion of organic compounds to solid surfaces. Besides Van der Waals forces and hydrogen-bonding, acid-base or more generally electron donor-acceptor interactions are the most common mechanisms for adhesion (Ref. 9).

3.2   Isoelectric Point of a Surface

The hydroxyl groups at a solid surface can be ionized at the solid-water interface, according to the following equilibriums (Ref. 2)

$$=MOH + H^+ <==> =MOH_2^+ \tag{3.1}$$

and

$$=MO^- + H^+ <==> =MOH \tag{3.2}$$

with $=M$ representing the metal or glass surface.

As can be seen, the ionization of a hydroxylated surface depends on the concentration of protons present in solution, and thus the pH of the solution. For oxides, there exists a specific pH at which the number of positive charges on the surface equals the number of negative charges. This pH value is defined as the isoelectric point of the surface (IEP). If the pH of the solution in contact with the solid surface is lower than the IEP, than the solid surface is charged positively. If the pH of the solution is higher than the IEP, the surface will be negatively charged. In acid-base terminology, a low IEP (<7.0) indicates an acidic oxide surface, while a high IEP (>7.0) indicates a basic surface.

Surface reactions are often expressed by means of acid-base equilibria. In analogy with the Bronsted acid-base theory, the following equilibrium constants can be defined respectively,

$$K_1 = [\equiv MOH_2^+] / [\equiv MOH] [H^+] \tag{3.3}$$

and

$$K_2 = [\equiv MOH] / [\equiv MO^-] [H^+] \tag{3.4}$$

Multiplication of both equilibrium constants results in the following,

$$K_1 K_2 = [\equiv MOH_2^+] / [\equiv MO^-] [H^+]^2 \tag{3.3}$$

Taking the logarithm of both sides, and knowing that

$$- Log [H^+] = pH \tag{3.4}$$

gives

$$Log (K_1 K_2) = Log ([\equiv MOH_2^+] / [\equiv MO^-]) + 2 pH \tag{3.5}$$

When the pH of the solution equals the IEP, the number of positive and negative charges are equal and thus

$$Log (K_1 K_2) = 2 IEP$$

or, assuming symmetry about the IEP gives

$$\boxed{K_1 = K_2 = 10^{IEP} \tag{3.6}}$$

In acid-base reactions, hydrogen-bonding is a common intermediate. In the next sections we describe hydrogen-bonding by $\equiv MOH...HOOCR$ in the case of an acid (RCOOH) bonding to the surface, and $\equiv MOH...R$, in case we are dealing with a base (R) bounded to the surface.

3.2.1 Cleaning Organic Acids of Solid Surface

In the case of the aqueous cleaning of an organic acid deposited onto a hydroxylated surface we can write down the following equilibria

$$=MOOCR + H_2O \iff =MOH...HOOCR$$

and

$$=MOH...HOOCR \iff =MOH + H^+ + RCOO^- \tag{3.7}$$
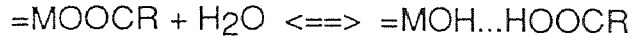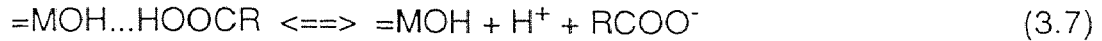
To clean the surface, the above equilibrium has to be shifted to the right-hand side. This equilibrium is in fact the combination of two reaction. The first reaction is

$$=MOH...HOOCR \iff =MOH_2^+ + RCOO^- \tag{3.8}$$
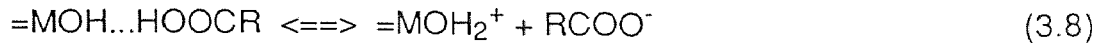
which can be approximately described by the equilibrium constant K_a

$$K_a = [RCOO^-] [H^+] / [RCOOH] \tag{3.9}$$

or

$$pK_a - pH = Log ([RCOOH] / [RCOO^-]) \tag{3.10}$$

To shift reaction (3.8) to the right, the pH of the cleaning solution has to be above the pK_a of the acid -- Condition 1.

The second reaction is

$$=MOH_2^+ \iff =MOH + H^+ \tag{3.11}$$

Combining (3.3) and (3.6) the next equation is derived

$$IEP - pH = Log ([=MOH_2^+] / [=MOH]) \tag{3.12}$$

To shift reaction (3.11) to the right, the pH of the cleaning solution has to be above the IEP -- Condition 2.

Combining conditions 1 and 2, to shift reaction (3.7) to the right, and thus to clean the surface from an organic acid, the pH of the cleaning solution has to be above both the pK_a of the acid and the isoelectric point of the oxide surface. In summary,

$$pH > IEP \text{ and } pK_a ===> \text{cleaning}$$
$$pH < IEP \text{ or } pK_a ===> \text{no cleaning}$$

These theoretical conclusions have been verified by experiments (see chapters 4 and 5).

3.2.2 Cleaning Organic Bases of Solid Surface

To clean an organic base off a solid hydroxylated surface in an aqueous environment, the following equilibrium has to be shifted to the right.

$$=MOH...R + H_2O <==> =MOH + R + H_2O \qquad (3.13)$$
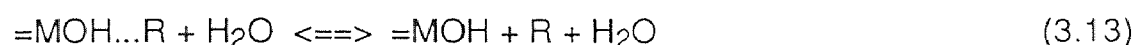
Again the reaction can be seen as the combination of two reaction. First, the equilibrium of following reaction has to be shifted to the right.

$$=MOH...R <==> =MO^- + HR^+ \qquad (3.14)$$

which can be described with the following equilibrium constant.

$$K_a = [R][H^+] / [HR^+] \qquad (3.15)$$

with $K_a = 10^{-14} / K_b$, in analogy with regular acid-base interactions. Equation (3.15) is rewritten as

$$pK_a - pH = Log([HR^+] / [R]) \qquad (3.16)$$

To shift reaction (3.14) to the right, the pH should be below the pK_a of the base deposited -- Condition 1.

Secondly, the next equilibrium should be shifted to the right.

$$=MO^- + H^+ <==> =MOH \qquad (3.2)$$

From reaction (3.2) and equations (3.4) and (3.6) is the following derived.

$$IEPS - pH = Log([=MOH] / [=MO^-]) \qquad (3.17)$$

To shift reaction (3.2) to the right, the pH of the solution should be lower than the pK_a of the base -- Condition 2.

Combining the two necessary conditions 1 and 2 results in the following rules to clean an organic base off a hydroxylated solid surface.

pH < IEPS and pK_a ===> cleaning

pH > IEPS or pK_a ===> no cleaning

3.2.3 The Isoelectric Points of Solid Substrates

Isoelectric points of surfaces can be measured in many different ways. Electrokinetic methods including electroosmosis, streaming potential and electrophoresis, and direct measurements by potentiometric titration are important. An excellent overview of experimental data about IEP can be found in Reference 11.

Another way to estimate IEP of surfaces in aqueous environments is to use the Pourbaix-diagrams (see also Chapter 5). Originated by Pourbaix, potential-pH diagrams are computed by electrochemical data (Ref. 12). Lines in Pourbaix-diagrams combine oxidation-reduction equilibria with acid-base equilibria. The IEP is in general presented by a vertical line in the Pourbaix-diagrams, showing the transition of a neutral solid into a charged species. Table 3.1 summarizes the IEP of the solids used in this research.

Table 3.1 Isoelectric points of solids in water at 25 °C.

Solid Surface	Active Component	Isoelectric Point
Steel	Fe_2O_3, Fe_3O_4, Cr_2O_3	8.5
Quartz	SiO_2	2.5
Molybdenum	MoO_3	3.7
Aluminum	Al_2O_3	9.0
Titanium	TiO, TiO_2, Ti_2O_3	6.0
Tantalum	Ta_2O_5	5.2

3.3 Interfacial Repulsion and Attraction Forces

When two charged particles come close together, they influence each others surface potential, resulting in repulsive and attractive forces between the two particles (Ref. 16). The repulsive energy V_R for two identical particles is given by:

$$V_R = B\varepsilon k^2 T^2 a\gamma^2 \exp(-\kappa H) / z^2 \qquad (3.18)$$

with V_R = repulsive potential energy
  B = constant
  ε = permittivity of medium
  kT = thermal energy
  a = radius of spheres
  z = counter-ion charge number
  κ = inverse of diffuse double layer thickness
  H = distance between spheres,

and with γ a function of the surface potential of the particles and H the distance between the particles. In case of two different particles, the repulsion energy is function of the product of the surface potentials of both particles.

Attractive forces, or dispersion forces are given by:

$$V_A = -Aa / 12H \qquad (3.19)$$

with V_A = attractive potential energy
  A = Hamaker constant,

independent of the surface potentials. The total interaction between the particles is the sum of the repulsive and attractive forces that act upon both particles. Figure 3.1 shows the net interaction between two particles as a function of the distance between the particles. Depending on the repulsive energy, the particles will repel each other (1) or attract each other (2).

An organic layer adhering to a solid surface can be seen as the combination of two flat plates, very close to each other. Both layers are charged at their interface. In the case of adhesion, the two layers attract each other. During the cleaning process, we want the two layers to repel each other.

Therefore V_R has to be positive and large enough to overcome the diffusive forces, so that the net interaction is positive (repulsive). If we assume that the repulsive energy-equation for two flat plates close to each other has the same form as equation 3.18, the product of both surface potentials has to be positive and large enough. Therefore the two surfaces should have the same charge sign. Although we do not know the actual calculation, we can state that, depending on the charging of the two layers, cleaning will or will not occur (see chapter 5).
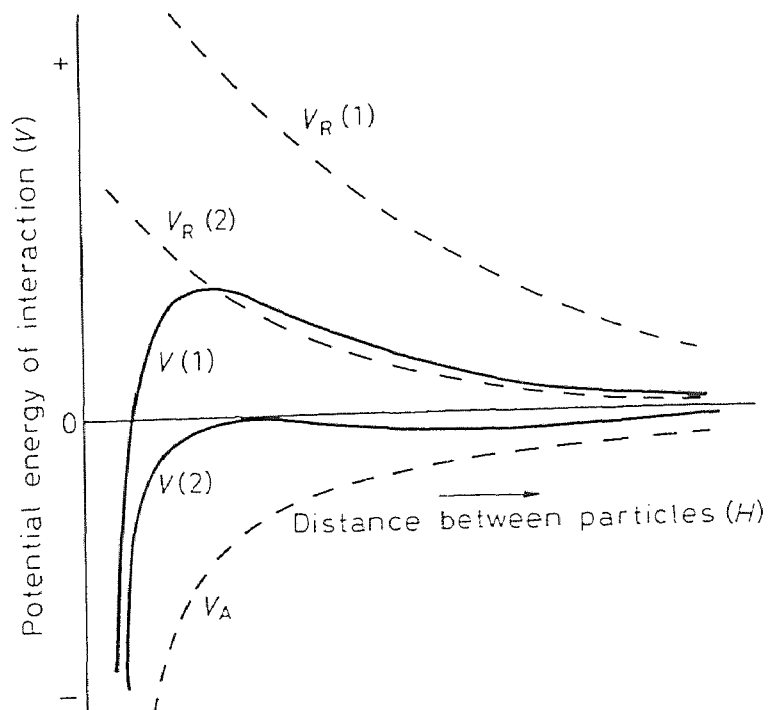
Figure 3.1 Total interaction energy curves, V(1) and V(2), obtained by the summation of an attractive curve V_A, with different repulsion curves $V_R(1)$ and $V_R(2)$, (Ref. 16).

3.4 Mass Transfer Treatment of the Cleaning Process

In the previous sections, the thermodynamic equilibrium conditions for cleaning are considered. If the cleaning solution does not satisfy these conditions, no cleaning is possible. If the thermodynamic conditions are satisfied, the kinetics

of cleaning become important with respect to cleaning rates. The kinetics of cleaning can be described by the flux of material leaving the surface. We define the flux as the mass of organic material that passes through a control surface parallel to the surface per time unit (Figure 3.2). The units of flux are kilogram per square meter per second.

We assume the solid surface as a flat plate, and we view cleaning as the removal of the deposited organic material from the surface into the solution.

solution

control surface A_s

N_a

organic deposit, M

solid surface
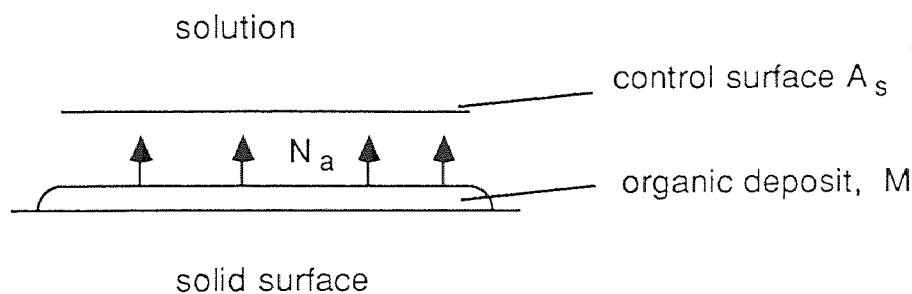
Figure 3.2 Flux of organic material from surface into solution.

The flux is thus

$$N_a = M / A_s\, t \tag{3.20}$$

with N_a = flux [kg / m^2 s]
      M   = mass of organic material leaving the surface [kg]
      A_s = surface area the cleaning is applied to [m^2] = constant
      t   = cleaning time [s]

which indicate that the flux is represented by the derivative of the change of mass against time. Combined with equations 2.2 and 2.3 the next relation can be derived

$$Cp(\%) = C\, t \tag{3.21}$$

where C [s^{-1}] is representative for the flux. The value of C is calculated by measuring the slope in the different (Cp(%),t)-curves.

CHAPTER 4

EXPERIMENTAL RESULTS

In this chapter, we systematically present all results of this investigation. First the surface composition of stainless steel and glass was characterized. Second, the cleaning of organic compounds of steel and glass were determined. Thirdly, the cleaning performance of stearic acid on aluminum, molybdenum, tantalum and titanium is described. Finally, the influence of the temperature on cleaning performance is given. All methods used to obtain these results are described in chapter 2. The results will be fully discussed in chapter 5.

4.1 Surface Analysis of Stainless Steel and Glass

The surface chemistry of steel and glass is important to understand the adhesion of organic compounds to surfaces and to define the cleaning mechanisms of such solid surfaces. We used XPS, AES and FTIR to analyze SS 316. AES was the only technique used to characterize the surface composition of glass samples.

4.1.1 Stainless Steel

Figure 4.1 shows the XPS elemental scan of SS 316 surface. Prior to the analysis the sample was cleaned according to the procedure described in Table 2.2. Iron, chloride, nickel, oxygen, chromium and carbon are all present at the surface of SS 316. Figure 4.2 shows the elements detected by Auger electron spectroscopy in the surface of clean SS 316. Peaks of chloride,

carbon, nitrogen, oxygen, chromium, iron, and nickel are present according to AES.

994.45 6.36E+04	C (KLL)
742.42 5.24E+04	O(kVV)
576.56 2.12E+04	Cr
531.32 2.38E+04	O(Is)
406.38 4.86E+03	Hi, N
285.76 5.79E+03	C(Is)
199.55 4.58E+03	Cl(Lp)
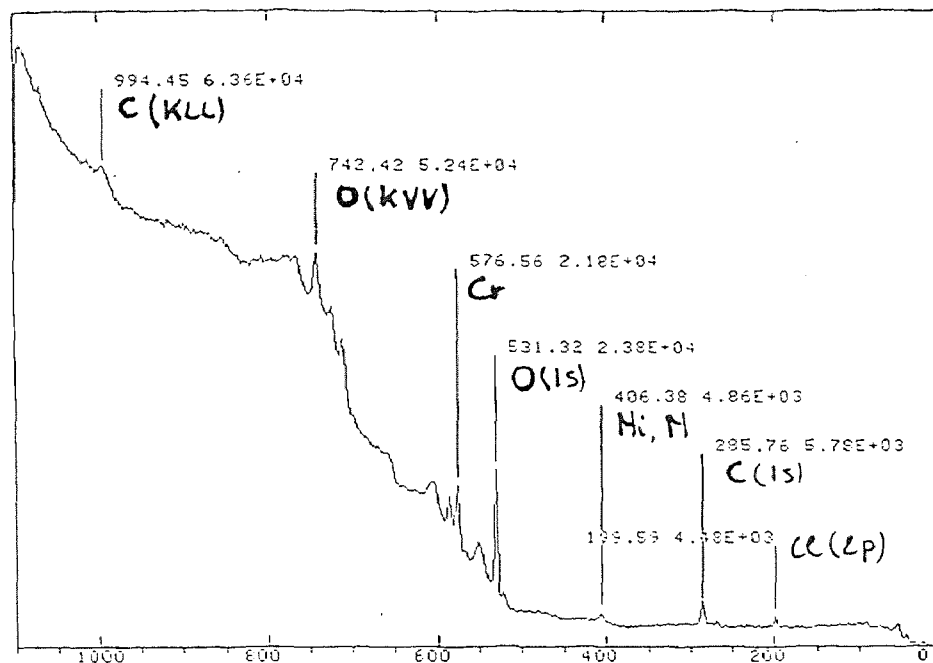
Peak Number	Position (eV)	Element (electron)
1	55	iron (3p)
2	200	chloride (2p)
3	286	carbon (1s)
4	407	nickel
5	531	oxygen (1s)
6, 9, 10	552, 606, 659	iron (Lmm)
7, 8	577, 587	chromium (2p3/2)
11	711	iron (2p)
12	742	oxygen (KVV)
13	994	carbon (KLL)

Figure 4.1 XPS of clean SS 316.

Table 4.1 shows a comparison between the bulk composition of SS 316 (Ref. 2) and its surface composition. The latter was calculated from the relative peak heights from Figure 4.2 multiplied by their relative sensitivities. It is clear

that the surface composition of the stainless steel is completely different from its bulk composition.
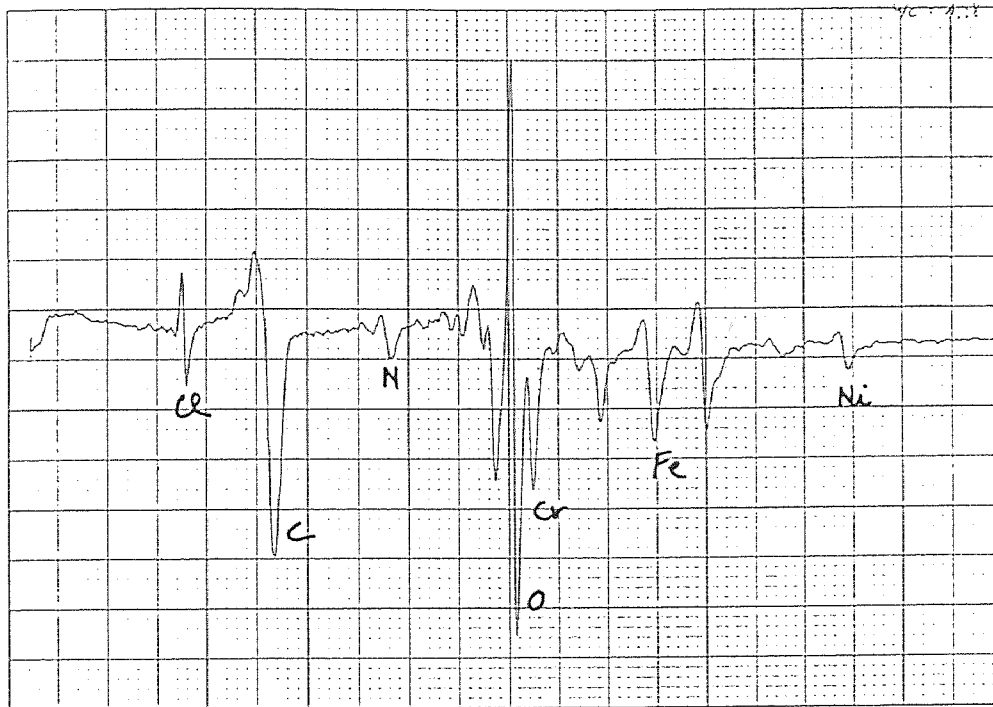
Figure 4.2 Auger electron spectroscopy of clean SS 316.

Table 4.1 The bulk- and surface composition of SS 316.

Element	Bulk Composition* (%)	Surface Composition (%)
iron	65	19
chromium	16 - 18	10
nickel	10 - 14	2
molybdenum	2 - 3	0
manganese	2	0
silicon	1	0
oxygen	0	37
carbon	0.08	27
nitrogen	0	2
chloride	0	3

* from Metals Handbook, 9th ed. Vol 13

While the bulk composition is dominated by iron and the other metals, the surface composition is dominated by oxygen and carbon. The carbon on the surface of stainless steel is due to adsorption of CO_2 and organic carbon from the atmosphere. The chloride present at the surface is probably a residue left behind from the cleaning where hydrochloric acid was used. The most important element close to the surface is oxygen; it has three possible sources. First, the oxygen is present in the form of metal oxides, as explained in chapter 3. Second, residual water is adsorbed to the surface. Thirdly, it is present in carbon dioxide, adsorbed to the surface.
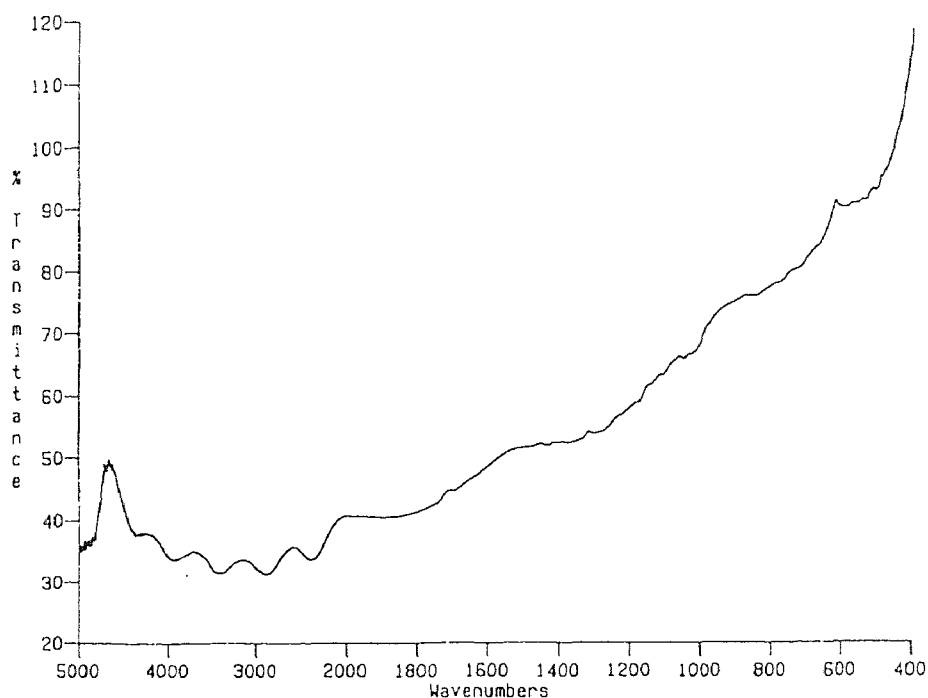
Figure 4.3 FTIR of clean SS 316.

The FTIR spectrum (Figure 4.3) was used as a reference spectrum. The FTIR spectra of organics deposited on steel, is the combination of the spectra of clean steel and pure organic.

4.1.2 Glass

Figure 4.4 shows the Auger electron spectrum of Glassteel 5015, obtained from Pfaudler, Rochester, NY. The main constituents on the surface of this glass are oxygen and silicon. Only small peaks of calcium, boron, potassium, iron and carbon are seen.
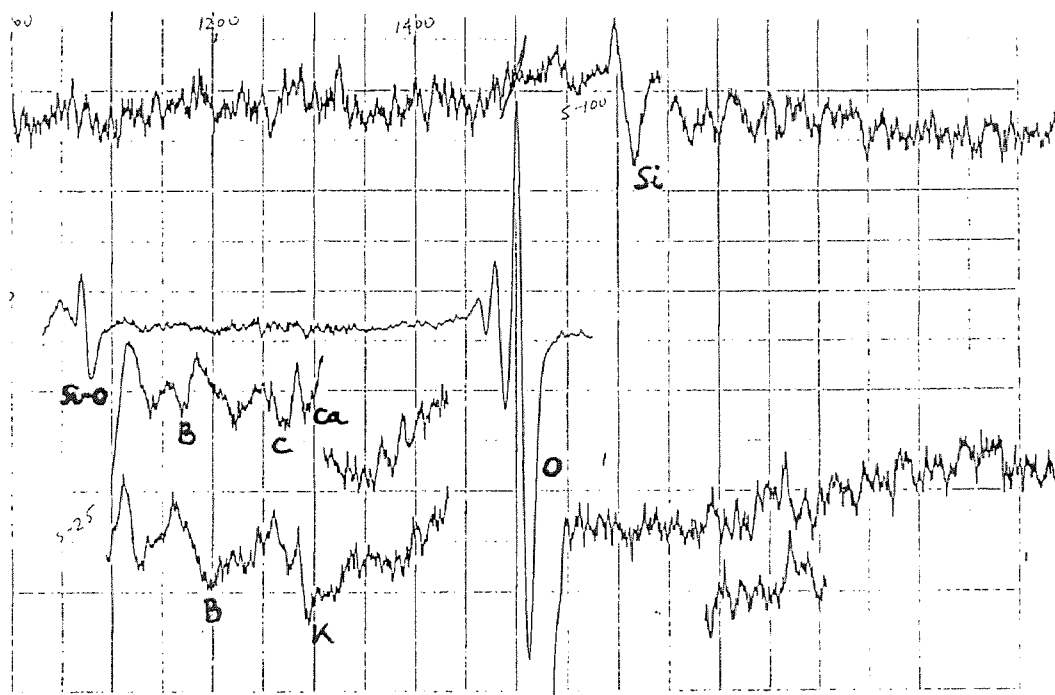
Figure 4.4 Auger electron spectrum of Glassteel 5015.

Table 4.2 shows the composition of several commercial glass types used in the industry. The glass code is a number originated by the Dow Corning Company, and is used in the industry to identify various glass types. According to our analysis, Glassteel 5015 is a high temperature glass with a high silicon oxide content. In our experiments, we used pyrex glass and quartz. We do not expect the surface chemistry of glass to be largely affected by the minor addition of chemicals. There are some differences between glass and quartz, especially in their dissolution properties. While quartz starts dissolving in water at a pH of about 9, Pyrex does not etch until pH 11.

Table 4.2 Approximate composition of commercial silicate glasses (wt %).

Type	Glass Code	SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	CaO	BaO
general	7740	81	2	13	4			
general	7760	78	2	15	3	1		
pharmaceutical	7800	72	6	11	7	1	1	2
high temperature	7913	96.5	0.5	3				
laboratory ware	G20	76	5	7	6	1	1	4

4.2 Cleaning Organic Residues from Stainless Steel Surface

The performance of cleaning organic deposits from steel was measured by visual inspection. The cleaned area was divided by the total area, to give a value of cleaning performance in percent. We measured the cleaning performance of D-glucose, succinic acid, stearic acid, 4-aminobenzoic acid, diphenyl amine, isoamyl acetate, cyclohexanone, glycerol, silicon grease and an epoxy resin at various pH conditions. The results are summarized in section 4.4.

4.2.1 D-Glucose and Dehydrated Carbohydrates

The D-glucose was deposited by holding the stainless steel sample in a one molar solution of D-glucose in water at 100°C for two hours. An amorphous, sticky and thick layer was formed. Figure 4.5 shows the FTIR spectrum of D-glucose on SS 316. All peaks compare well with the spectrum of pure D-glucose in bulk, except for the peak at 1700 cm^{-1}. This peak is due to an aldehyde functional group. The ring structure of D-glucose is in a natural equilibrium with a linear structure containing an aldehyde group. The D-glucose was easily cleaned with a cold water rinse.

A dehydrated sugar residue was prepared in the same manner as above by placing the stainless steel substrate in the oven for one hour at 200°C. This

time the sample was covered with a yellow-brownish layer. In this case the FTIR spectrum showed signs of a second peak in the same region, indicating decomposition into an carboxylic acid. This sample was not cleanable in pure water. We were able to clean the sample in a solution of 30 % hydrogen peroxide in water at ph 5.5, at 60°C. It took ten minutes before the sample was completely clean. A similar sample was also cleanable in a 2.5 % chlorox (NaOCl) solution at room temperature. After one week, the stainless steel sample we cleaned with chlorox was corroded. A third sample was cleaned easy at room temperature with the following cleaning solution: 4.5 % hydrogen peroxide and 4.5 % ammonium hydroxide in water (pH=11.3).
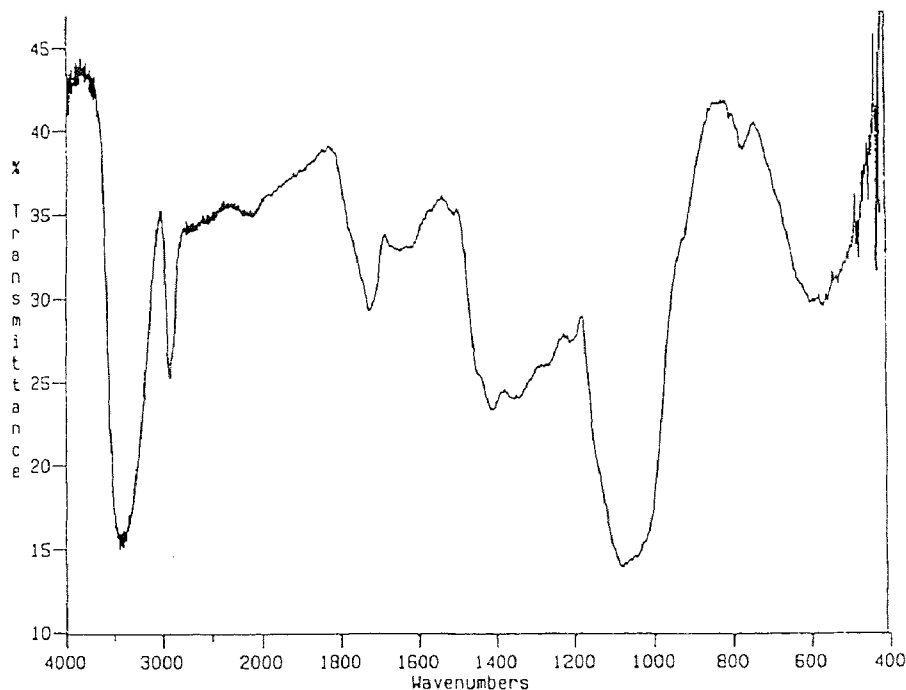
Figure 4.5 FTIR spectrum of D-glucose on SS 316.

4.2.2 Succinic Acid and 4-Aminobenzoic Acid

A sample with succinic acid was prepared from a one molar solution at 100°C. A thick layer of white crystal covered half of the sample. The sample was easily cleanable with a cold water rinse.

The sample with 4-aminobenzoic acid was prepared from a 0.5 molar solution with 2-propanol, for 1 hour at about 70°C. White crystals were formed on the sample. This sample was easy cleanable with a cold rinse of water.

4.2.3 Isoamyl Acetate, Glycerol and Cyclohexanone

A substrate held in a solution of 0.5 molar amyl acetate in acetone at 80°C for two hours did not show any residue. We were able to form a residue of amyl acetate on a stainless steel substrate by placing the solution on the substrate and let the acetone evaporate. The formed residue was easy cleanable with a cold water rinse. In order to make a more adhering film of amyl acetate, we heated the substrate in an oven at 180°C for one hour, and a brown, sticky residue was formed. This substrate was not cleanable in cold water, or warm water (60°C). The substrate was cleaned in the 4.5 % hydrogen peroxide, 4.5 % ammonium hydroxide in water solution at 60°C. In less than one minute all residue went into solution.

We deposited glycerol on stainless steel by holding a substrate in a one molar solution of glycerol and water at 80°C for one hour. The formed residue was cleanable with a cold water rinse. When a similar substrate was put in the oven for one hour at 200°C, a sticky residue was formed. This residue could not be cleaned by cold water. In warm water (60°C), the substrate became more clean, but the cleaning process took about 10 minutes. A solution of 4.5 % hydrogen peroxide with 4.5 % ammonium hydroxide in water at 60°C cleaned a similar substrate within one minute.

We were not able to deposit cyclohexanone from a solvent. Therefore we placed pure cyclohexanone on a warm substrate (70°C). A clear solid residue was formed. This residue was not cleanable with cold or warm water. It

was easy cleanable in with the hydrogen peroxide-ammonium hydroxide solution, at 60°C. In less than one minute all residue was cleaned.

4.2.4 Cleaning of Epoxy Resin and Silicon Grease from SS Surface

We deposited an epoxy resin layer on stainless steel. The two epoxy components, namely bisphenol A and epichlorohydrin were mixed onto the substrate and left to dry. A sticky, clear layer was formed. The substrate was only cleanable in the hydrogen peroxide/ammonium hydroxide solution at 70°C, if scrubbing was provided.

Silicon grease was placed immediately onto the stainless steel substrate to make an adhering film. It was not cleanable in cold or hot water. It cleaned slowly in hydrogen peroxide-ammonium hydroxide solution (70°C). It took about ten minutes to obtain perfect cleaning.

4.2.5 Cleaning of an Organic Acid - Stearic Acid

Stearic acid was deposited from a one molar, 2-propanol solution at about 70°C for two hours. A thick, white hydrophobic layer was formed on the substrate. Cleaning was found to be a pH-dependent process. Figure 4.6 shows the pH conditions where the substrates were cleanable in water, and in water-hydrogen peroxide solution (4.5 %), both at 55°C. All the cleaning curves were obtained after ten minutes of cleaning.

In each experiment the pH was kept constant by adding the appropriate buffer to the cleaning solution. At low pH, no cleaning was obtained, with water or with the hydrogen peroxide solution. At higher pH, the substrates in the hydrogen peroxide solution were perfectly cleaned in 10 minutes. The sudden change in behavior occured at pH about 8.5 for pure water as cleaning solution and at pH 8.0 in the hydrogen peroxide solution.

Figure 4.6 Cleaning performance for stearic acid on SS 316 versus pH of solution, in water and hydrogen peroxide solution (4.5%) at 55°C. Measured after ten minutes.

4.2.6 Cleaning of Organic Base - Diphenyl Amine

Diphenyl amine was deposited on SS 316 as a thick, hydrophobic layer from a 2-propanol solution. The residue was neither wettable nor cleanable by cold water. When we raised the temperature above 52°C, the diphenyl amine melted and could be cleaned. Figure 4.7 shows the pH regions where cleaning took place, both in water and in hydrogen peroxide (4.5 %) solution at 45°C. In water, the substrates were only partly cleanable at very high pH. In the hydrogen peroxide solution, the substrates were perfectly cleanable at high pH (Figure 4.7). At lower pH, all amine was stripped off the surface, but the surface did not looked clean at all.

Figure 4.7 Cleaning performance for diphenyl amine on SS 316 versus pH of solution, in water and hydrogen peroxide solution (4.5%) at 45°C. Measured after ten minutes.

4.3 Cleaning of Glass Surfaces

All the experimental results regarding glass surfaces are measured with the optical spectrometer method, described in chapter 2. With this optical method we could measure cleaning performance as a function of time, pH and other variables.

4.3.1 Cleaning of Stearic Acid from Glass Surface

Stearic was deposited as a thick hydrophobic layer on glass. The stearic acid residue was not cleanable in cold water. Figure 4.8 shows the cleaning performance as a function of pH.

Two distinct performance regions are identified. Below 4.0, stearic acid was not cleanable in warm water; however very slowly cleaning in the hydrogen peroxide solution was observed. Above pH 6, the samples were perfectly

cleaned after five minutes in the hydrogen peroxide solution, and partially cleaned in pure water alone. In the absence of hydrogen peroxide, the pH had to be raised above 8.0 before the samples could be cleaned in the aqueous solutions. In this case, a significant change in cleaning performance occured above pH 5. In addition hydrogen peroxide was found to enhance cleaning, as we have found for stainless steel.
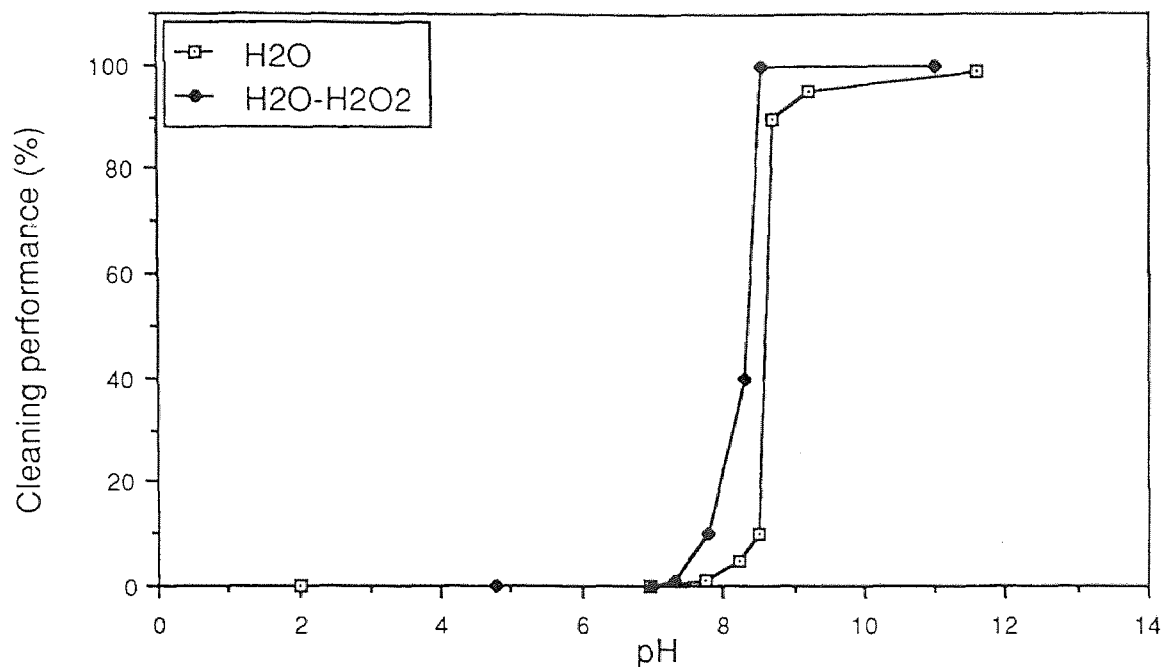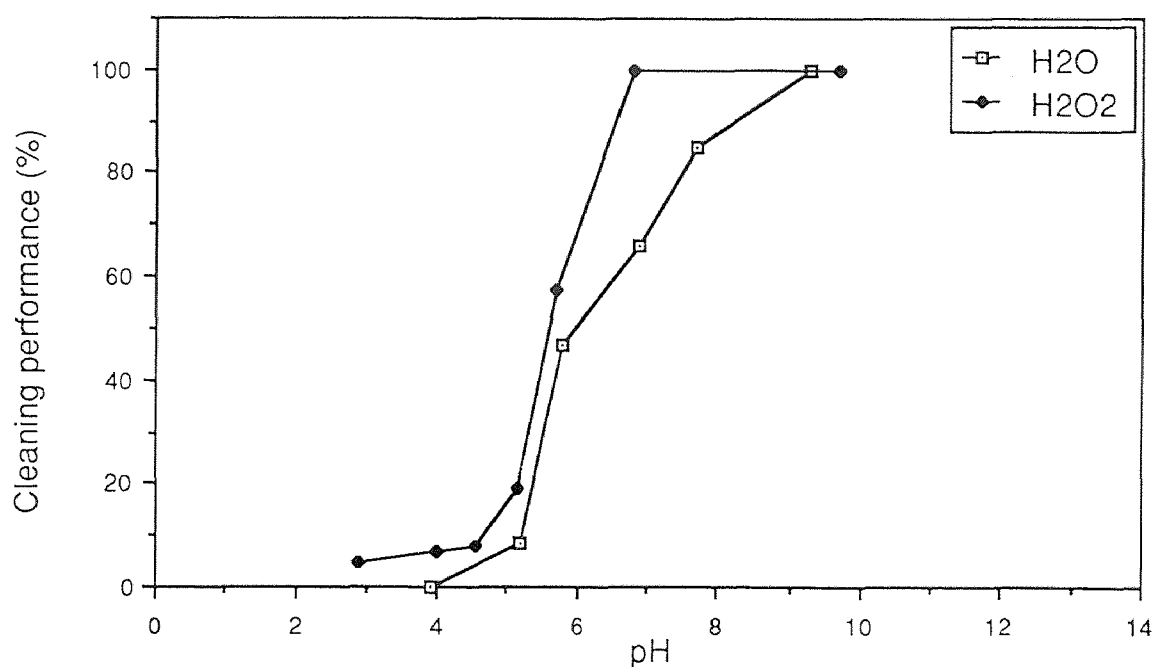

Figure 4.8 Cleaning performance for stearic acid on glass versus pH of solution, in water and hydrogen peroxide solution (4.5%) at 55°C. Measured after five minutes.

Figure 4.9 and figure 4.10 show the cleaning performance as a function of time at different pH conditions. In the absence of hydrogen peroxide, it seems that after a time of constant cleaning, no additional cleaning occured.

The speed of initial cleaning and the ultimate cleaning level accomplished depended strongly on the pH of the solution. The higher the pH, the faster and more complete cleaning was achieved.

Figure 4.9 Cleaning performance for stearic acid on glass versus time in water at 55°C. Measured at different pH.

Figure 4.10 Cleaning performance for stearic acid on glass versus time in hydrogen peroxide solution (4.5 %) at 55°C. Measured at different pH.

In the presence of hydrogen peroxide, the initial cleaning rate increased with increasing pH and thus making the pH the dominant parameter in this process. Comparing the results in Figures 4.9 and 4.10, hydrogen peroxide seems to speed up the cleaning. This point will be elaborated upon in chapter 5.

4.3.2 Cleaning of Diphenyl Amine from Glass Surface

Diphenyl amine was deposited on glass using the same method employed on steel. Again a thick white layer was formed. Figure 4.11 shows that diphenyl amine was not cleanable in hydrogen peroxide solution, except in solutions with pH below 2. Above pH 9 the quartz was easily cleaned due to etching of the quartz in basic solutions.

Figure 4.12 indicate an almost constant cleaning rate of diphenyl amine off glass depending on the pH of the cleaning solution.
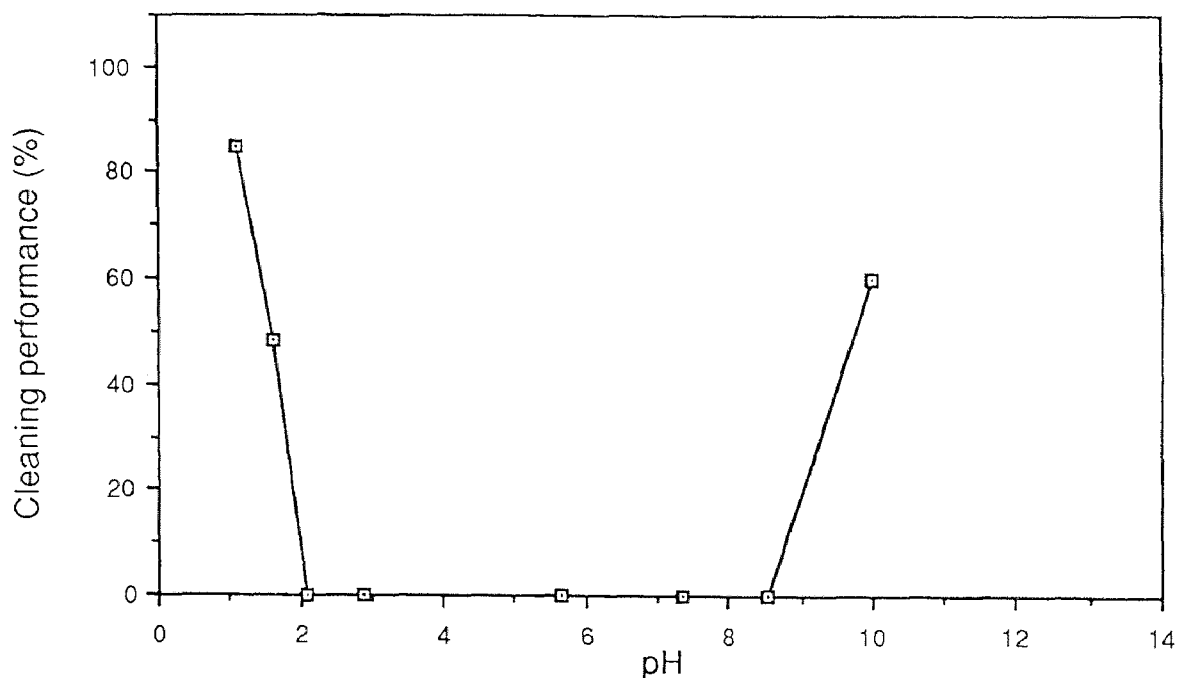
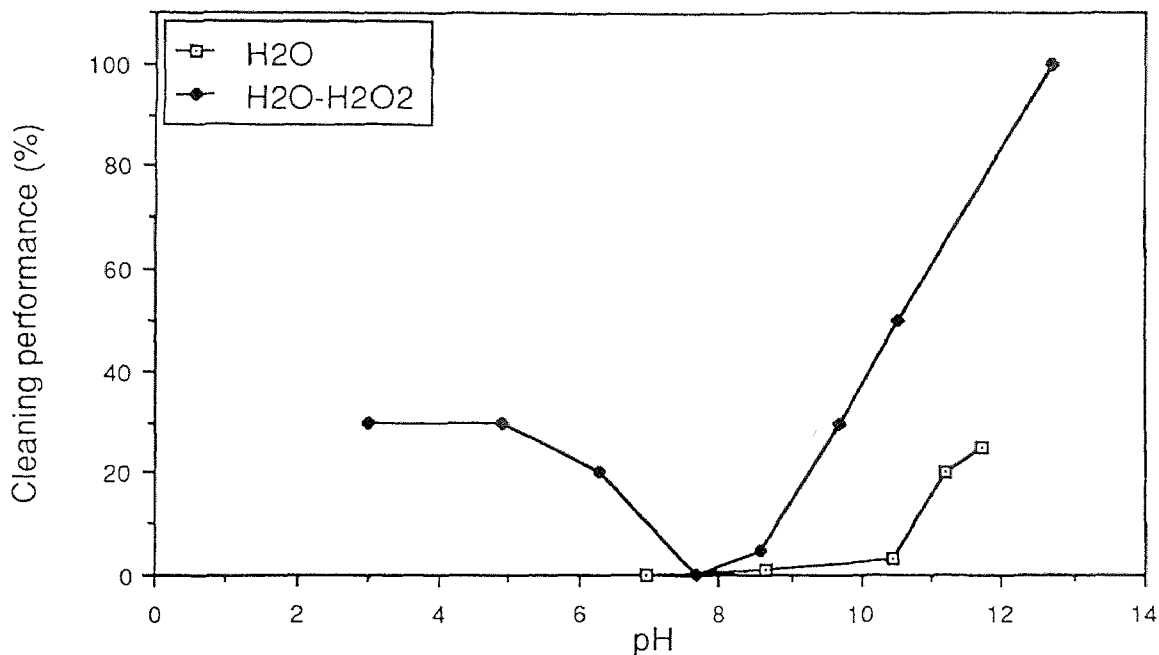Figure 4.11 Cleaning performance for diphenyl amine on glass versus pH in hydrogen peroxide (4.5 %) solution at 45°C. Measured after five minutes.
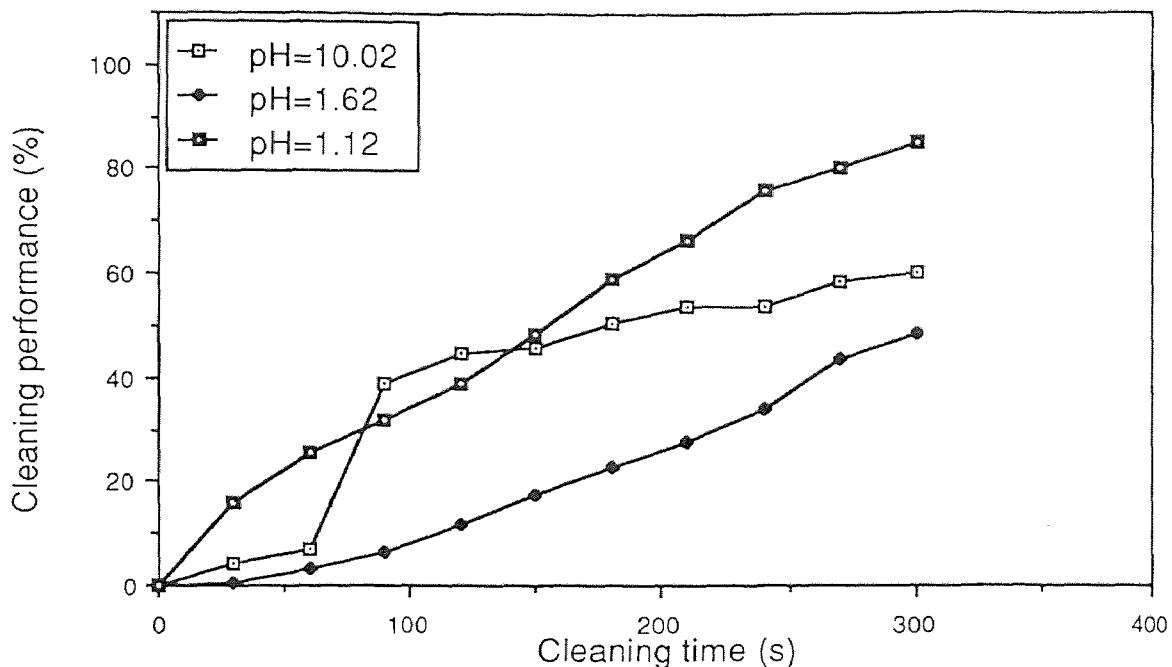
Figure 4.12 Cleaning performance for diphenyl amine on glass versus time in hydrogen peroxide solution (4.5 %) at 45°C. Measured at different pH.

4.3.3 8-Hydroxy Quinoline

8-Hydroxy quinoline deposited on glass was almost perfectly cleanable in warm water at every pH, except below 2.5 (figure 4.13). In H_2O_2 solution, the cleaning occurred perfectly between pH 2.05 and 9.9. When we tried to clean a sample in pure water with a buffer of pH 11.3, the organic was immediately cleaned of the glass surface, but the glass surface became dull in appearance. Apparently, the glass was etched by the highly basic solution. Figure 4.14 shows that the initial cleaning rates of cleaning do not depend strongly on the pH, except in very acid pH conditions. Compared to figure 4.15, we see that again in H_2O_2 solution the cleaning occurs faster, and it seems to be independent of the pH.
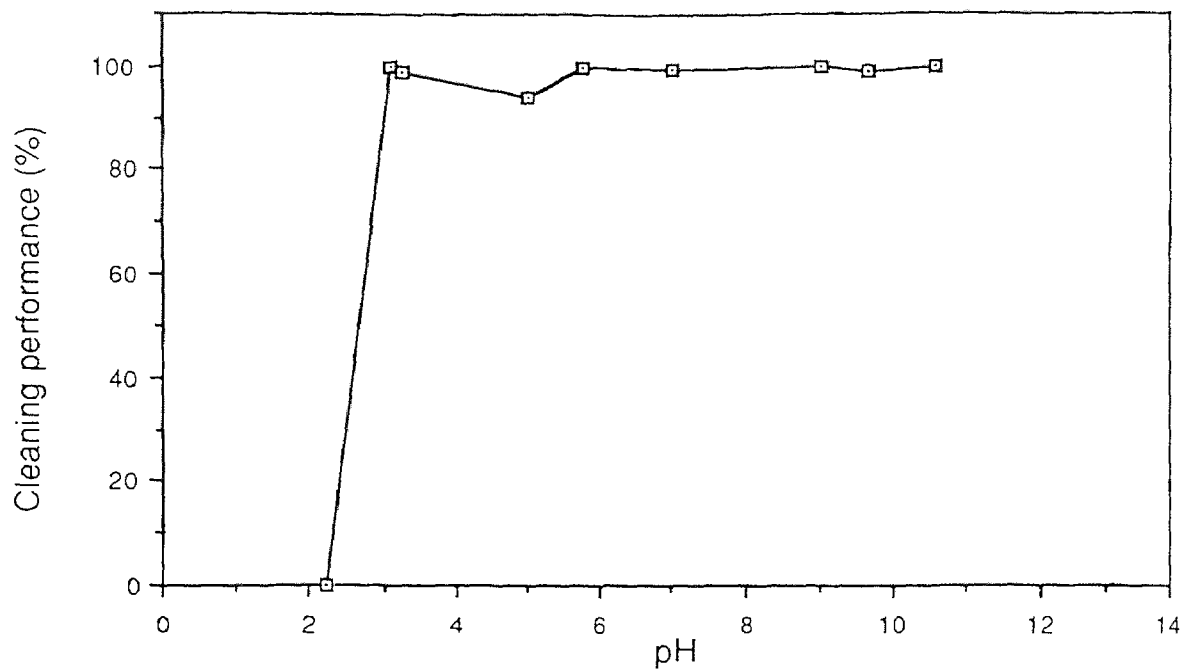
Figure 4.13 Cleaning performance for 8-hydroxy quinoline on glass versus pH in water at 55°C. Measured after five minutes.
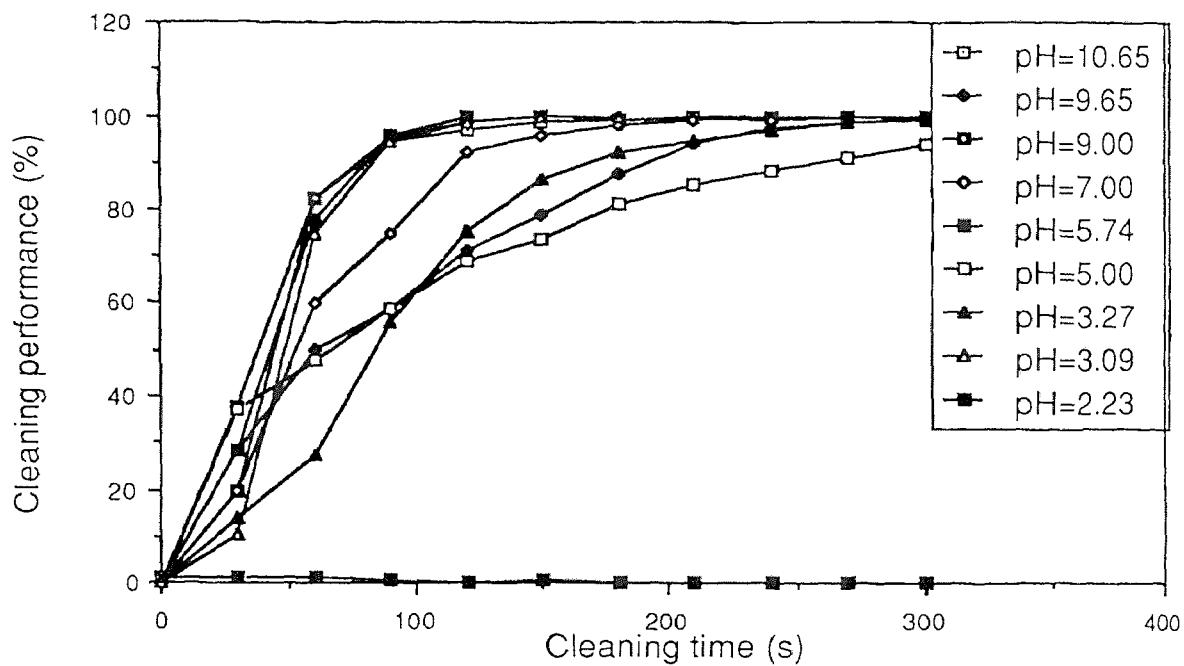
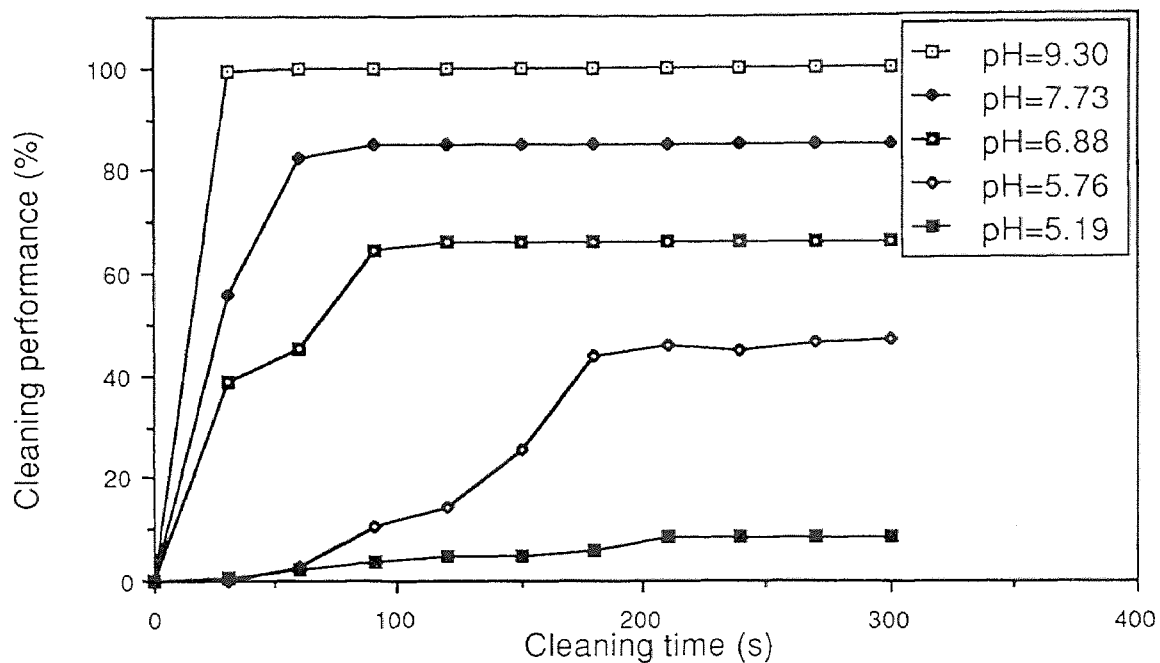**Figure 4.14** Cleaning performance for 8-hydroxy quinoline on glass versus time in water at 55°C. Measured at different pH.
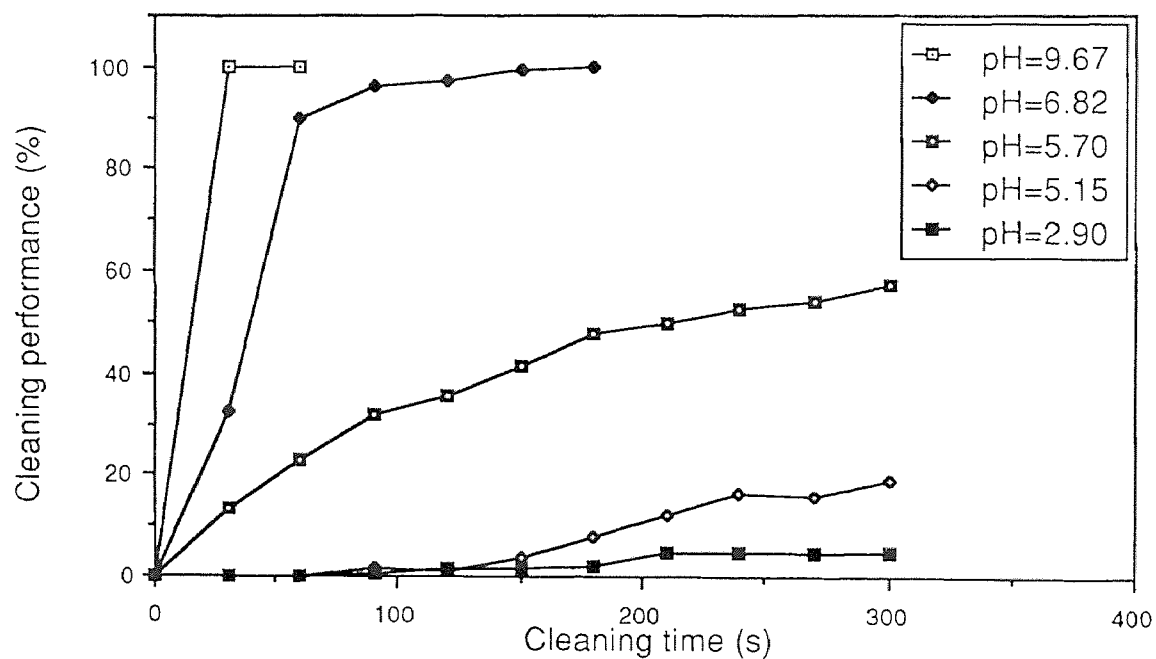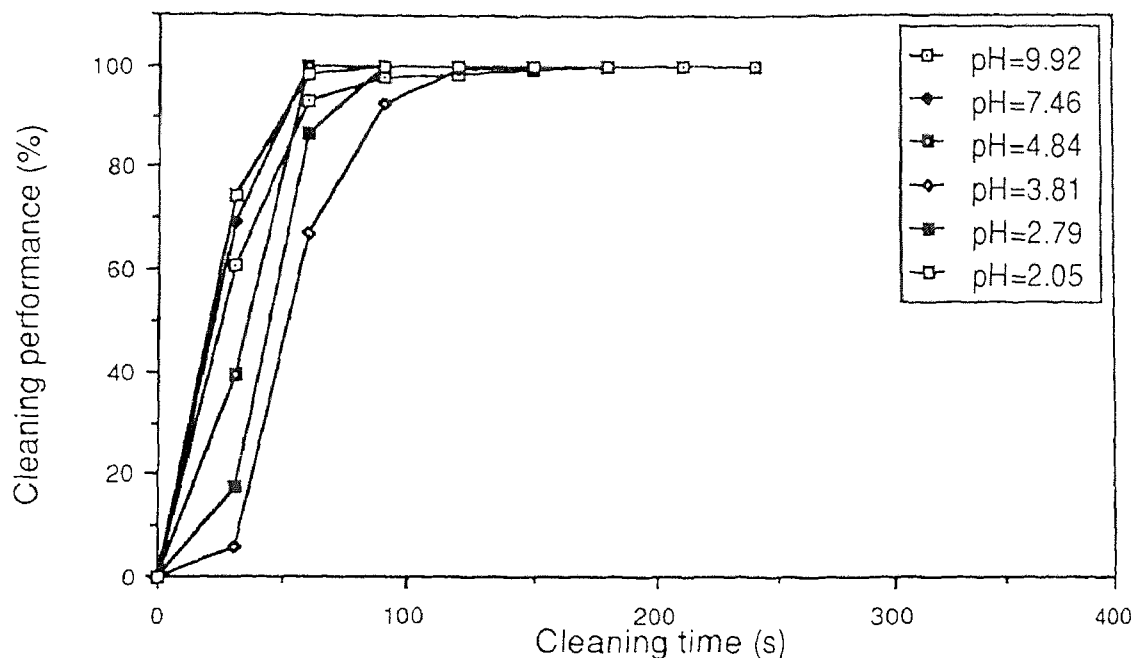
Figure 4.15 Cleaning performance for 8-hydroxy quinoline on glass versus time in hydrogen peroxide solution (4.5 %) at 55°C. Measured at different pH.

4.4 Summary

In table 4.3 a brief summary of all the cleaning results on steel and glass is given.

Table 4.3 Cleaning properties of different classes of compounds.

Class of Compounds	Functional Groups	Cleaning Proporties
Carbohydrates and dehydrated sugars Glucose	$R_1-R_2-R_3 \qquad R = O$ $\quad \mid$ $\quad O$ $\quad H$ Reacts as an electron donor to surface.	Glucose was easily cleanable in water off steel. Heated glucose was cleanable in oxidizingconditions. Basic conditions helped the cleaning.

Table 4.3 (Continued).
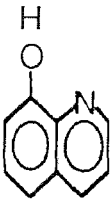
Class of Compounds	Functional Groups	Cleaning Proporties
Amino-aromatic amines 4-Aminobenzoic acid	H_2N —⟨O⟩— COOH Did not react to surface. Probably amphoteric.	Easily cleanable off steel in water.
Aromatic amines Diphenyl amine	HN (—⟨O⟩)$_2$ Reacted as a base to surface (pK=1.9).	Highly basic conditions were necessary to clean steel. At low pH, amine left the surface, but steel stays dull. Very high (>9) or very low (<2) pH was neccesary. Oxidizing agents helped.
Complex base 8-Hydroxy quinoline	H O N Reacted as a base. (pK$_1$=5.0, pK$_2$=9.81)	8-Hydroxy quinoline was perfectly cleanable off glass in water with pH>2.5, and hydrogen peroxide solution with pH>2.0.
Esters Amyl acetate	R_1- COO - R_2 Reacted as an electron donor, with possible forming of carboxylic group.	Ordinary amyl acetate was easy cleanable with water. Heated amyl acetate was cleanable off steel in a basic oxidizing solution.
Epoxy resin Bisphenol A + epichlorohydrin	(-R$_1$—⟨O⟩—OR$_2$-)$_n$ Complex interaction.	Resin was cleanable off steel in hot basic solution with oxidizing agent. Scrubbing had to be provided.

Table 4.3 (Continued).

Class of Compounds	Functional Groups	Cleaning Proporties
Ketons Cyclohexanone	R = O Electron donor.	Cleanable off steel in basic, oxidizing solution.
Silicon compounds Silicon grease	R - Si Complex reaction.	Slowly cleanable off steel in hot, basic and oxidizing solution.
Alcohol Glycerol	R - OH Some basic reaction. Transformation into carboxylic group is possible under influence of heat.	Ordinairy glycerol was easy cleaned off steel with water. Heated glycerol was cleanable in hot water. Basic and oxidizing conditions helped.

4.5 Cleaning of Organic Residues from Various other Metal Surfaces

In this section we describe the cleaning stearic acid from aluminum, molybdenum, tantalum and titanium substrates. All films were deposited from stearic acid concentrated in hot isopropanol. The cleaning performance was measured by visual inspection in all cases. All results are summarized in Figure 4.16

Stearic acid formed thick white crystals, adhering good to aluminum substrates. Cleaning in warm water (55 °C) in combination with the appropriate buffer was only possible at pH above 10 (Figure 4.16). In aqueous solutions with pH 11, the cleaning was very fast and complete, but the aluminum substrate was strongly corroded by the solution.

Stearic acid formed powderlike white crystals, loosely bounded to molybdenum substrates. The dry stearic acid could be scraped off the substrates by light mechanical action. In water however, the stirring action was

not enough to remove the deposited film. Only in water solutions with pH above 5 the stearic acid was displaced from the substrates into the water.
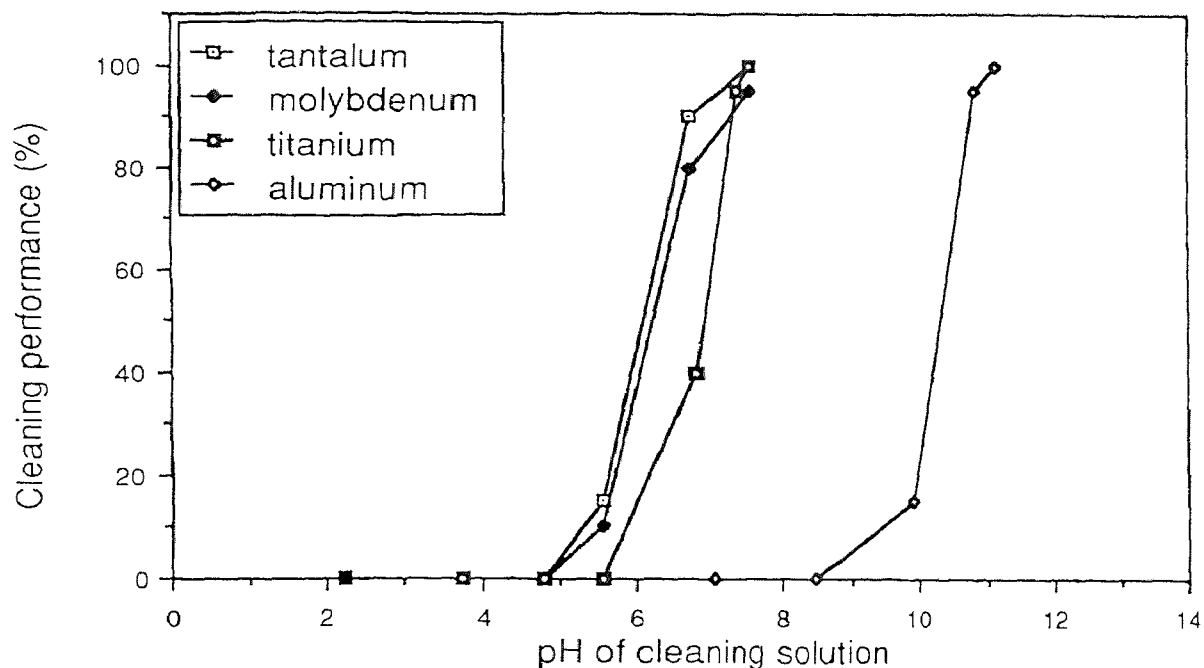
Figure 4.16 Cleaning performance in water and buffer solution for stearic acid on tantalum, molybdenum, titanium and aluminum versus the pH of the solution, after 10 minutes at 55 °C.

On tantalum, like on molybdenum, a loose layer of white crystals was formed on the substrates by stearic acid. The cleaning was possible in water with pH above 5.

Also on titanium a loose layer of powderlike stearic acid crystals was formed on the substrates. Cleaning action only occured in water with pH above 6.

4.6   Effect of Temperature on Cleaning

We have found the temperature to have an effect on the cleaning mechanisms in several ways. In general, we found that if the temperature of the cleaning

solution is raised above the melt temperature of the deposited organic residue, the cleaning proceeds faster and easier.

Figure 4.17 and figure 4.18 show how the cleaning of stearic acid depended on temperature. It is clear that temperature enhanced the cleaning and that it is an important cleaning parameter. The effect of the temperature on cleaning kinetics seems to be more significant in the presence of hydrogen peroxide - compare Figures 4.17 and 4.18. Apparently, the decomposition rate of hydrogen peroxide and its reactivity during cleaning is a highly temperature-dependent process. This will be further discussed in chapter 5.
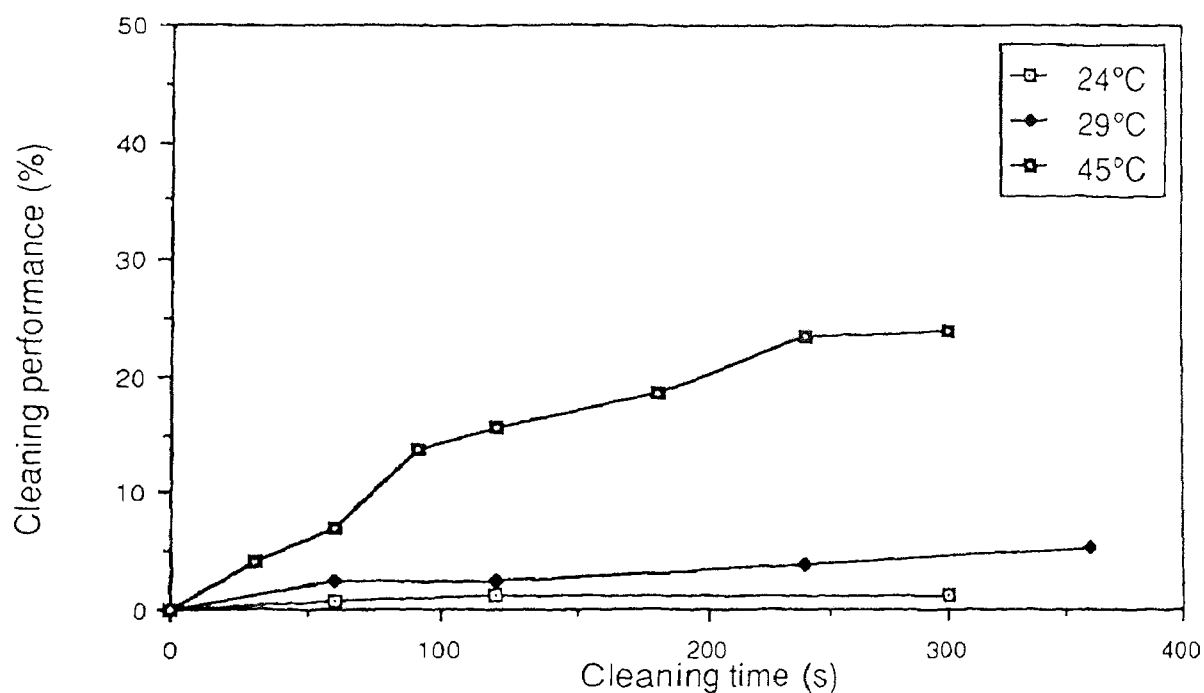
Figure 4.17 Cleaning performance for stearic acid on glass versus time in water at pH=7. Measured at different temperatures.
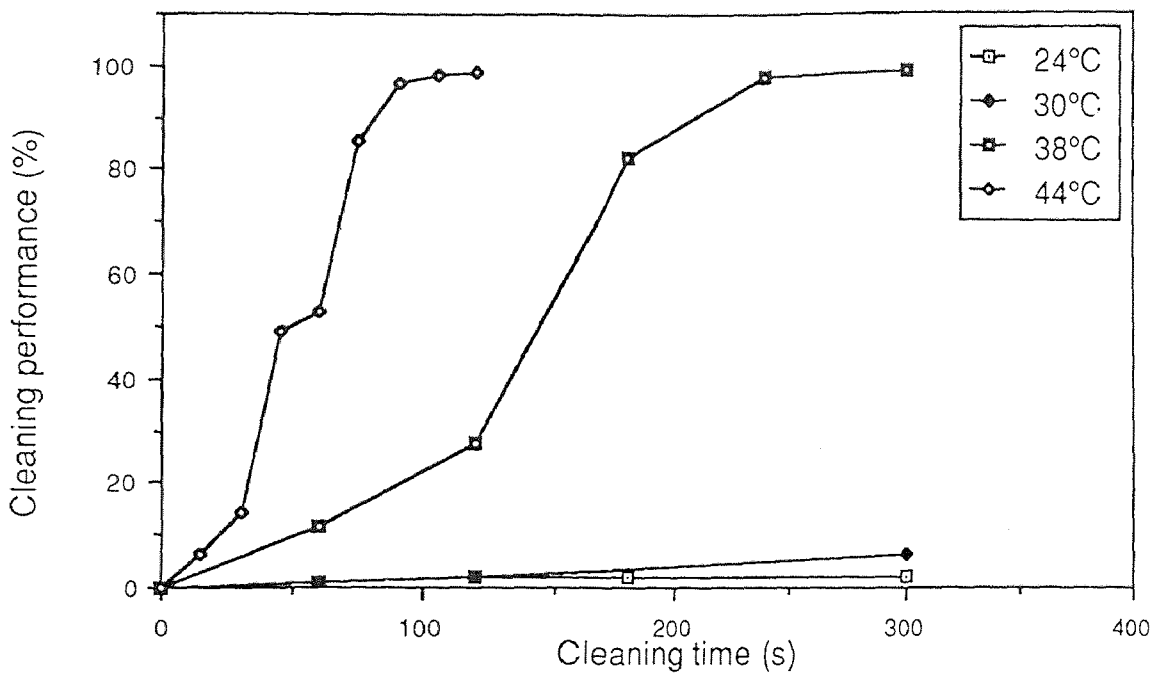
Figure 4.18 Cleaning performance for stearic acid on glass versus time in hydrogen peroxide solution (4.5 %) at pH=7. Measured at different temperatures.

CHAPTER 5

DISCUSSION

For water-soluble organic compounds we found that water is a powerful cleaning agent, capable of achieving good removal of the organic residue from solid surfaces. If the organic material to be cleaned is not soluble in water (or if it is hydrophobic) other parameters are needed to accomplish good cleaning. pH Adjustment and the addition of an oxidizing agent were found to be essential in achieving satisfactory cleaning in all experiments. The combination water, hydrogen peroxide (4.5 %) and ammonium hydroxide (4.5 %), at pH around 11.3, effected the cleaning of many organic material deposited on steel. Increasing the temperature of the cleaning solution had positive effect on the cleaning.

In this chapter, the experimental results presented in chapter 4 will be compared with theoretical relations derived in chapter 3. The results are discussed in terms of thermodynamic conditions of cleaning and kinetic and mass transfer considerations.

5.1 Analysis of Solid Surfaces and Their Surface Chemistry

The surface composition of stainless steel is significantly different from its bulk composition. In addition to iron, chromium and nickel, the surface is dominated by oxygen in the form of oxides and hydroxides. The surface chemistry is mostly determined by the metal hydroxides (iron hydroxides and chromium hydroxides) present at the surface. In aqueous solutions, the dissociation of surface groups (hydroxides) and the dissolution of surface atoms are functions

of the pH of the solution and are the two major factors affecting chemical and physical processes at the solid/liquid interface.

The glass sample provided by a manufacturers of vessels used in the pharmaceutical industry (Glassteel 5015), is a high temperature glass with a high silicon oxide content. Traces of calcium, boron, potassium, iron and carbon are present at the surface. The surface chemistry of glass is mainly determined by the behavior of silicon oxide. The dissolution of SiO_2 and dissociation of silanol groups (-Si-OH) are also a function of the pH of the cleaning solution.

The dissociation of surface hydroxides in the aqueous environments is best described by the isoelectric point (IEP). The IEP is the point (on the pH-scale) at which the surface has a zero charge. In solutions with a pH below the IEP, the surface adsorbs protons from solution and becomes positively charged. The surface acts like a base. In solutions with a pH above the IEP, the hydroxide surface looses protons and becomes negatively charged. According to this definition, IEP is the combination of two reactions (see Chapter 3);

$$=MOH + H^+ \quad <==> \quad =MOH_2^+ \qquad (3.1)$$

and

$$=MO^- + H^+ \quad <==> \quad =MOH \qquad (3.2)$$
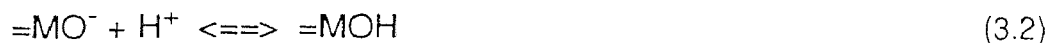
with $=M$ representing the metal or glass surface atoms.

Or, with K_1 and K_2 the respective equilibrium constants;

$$Log (K_1 K_2) = 2 \ IEP$$

which can be rewritten in

$$IEP = (pK_1 + pK_2) / 2 \qquad (5.1)$$

The IEP of solid surfaces were obtained from the literature (Ref. 11) or extracted from the Pourbaix-diagrams (Ref. 12) (see Section 5.6). The isoelectric points of the surfaces were given in Table 3.1. Steel and aluminum

have a high IEP (8.5 and 9.0 respectively), indicating they will adsorb protons in neutral waters. They are basic in nature.

Glass has a low IEP (2.5), indicating it will release protons in the neutral environments (pH = 7.0). Glass has an acidic character.

Table 3.1 Isoelectric points of solids in water at 25 °C.

Solid Surface	Active Component	Isoelectric Point
Steel	Fe_2O_3, Fe_3O_4, Cr_2O_3	8.5
Glass	SiO_2	2.5
Molybdenum	MoO_3	3.7
Aluminum	Al_2O_3	9.0
Titanium	TiO, TiO_2, Ti_2O_3	6.0
Tantalum	Ta_2O_5	5.2

Both steel and glass surfaces have top oxide and hydroxide layers, that determine their surface chemistry. Since these surface hydroxides dissociate like ordinary acids and bases, the surfaces are expected to react with organic acid and bases according to the classical acid-base theory (Ref. 9).

5.2 Adhesion and Cleaning of Organic Acid from Solid Surfaces

Stearic acid is insoluble in water and adheres strongly to steel and glass. The deposited stearic acid residue is hydrophobic and is not wettable by water. Since stearic acid is an organic acid, we can assume that it reacts with surface hydroxides of steel as it would react with an ordinary base. The carboxylic functional group of stearic acid reacts with the hydroxide group of the steel surface by releasing water. During the aqueous cleaning process, we want the acid to be replaced by water. Therefore, according to equilibrium chemistry, we

have to alter the pH of the solution until the affinity of surface hydroxides for the water is greater than the affinity of the surface hydroxides for the organic acid.

In Chapter 3 we derived equations showing that in order to clean an organic acid from steel, the pH of the aqueous solution has to be greater than the IEP of the steel and the pK_a of the acid. Our experimental results compare very well with our theoretical derivations. Figure 5.1 shows that the cleaning of stearic acid from steel (IEP=8.5) is only possible in solutions with pH above 8.0. Although in cleaning solutions with pH below 8.0 no cleaning occurs, in solutions with pH above 9.0 the cleaning is almost perfect after 10 minutes. Above pH 8.5, the water replaces stearic acid from the surface and effects good cleaning. The cleaning curve constructed in this case has a shape that resembles that of a typical titration curve. This is not surprising since both processes are based on the same principles, namely the equilibrium chemistry of acid-base reactions.

The situation for stearic acid adhering to glass is different. Glass is acidic in nature (IEP=2.5) and would preferentially react with bases. If the pH of the aqueous solution is below the pK_a of stearic acid (4.75), the adhering stearic acid is mostly undissociated. In this case, the water will not replace the stearic acid from the surface of glass. Under these pH conditions, the organic residue is hydrophobic and insoluble in water, and the net interface charge is zero (See below). If the pH of the cleaning solution is above the pK_a of stearic acid, the acid will dissociate and the water could preferentially bond to the surface hydroxide and replace the stearic acid from the surface. At this pH the interface is in net repulsion. Our theoretical prediction agrees well with this experimental result (Fig. 5.1). In aqueous solutions with pH below 4, no cleaning occured, while above pH 6 the cleaning was almost perfect after 10 minutes of immersing

the glass substrates in the solution. These experiments indicate the importance of electrostatic interactions at the interface on cleaning -- see section 5.4.

In summary, the cleaning of organic acids from solid surfaces is determined by the equilibrium chemistry between the surface hydroxydes, the organic acid and the water. The equilibrium is expressed in terms of IEP (surface), pK_a (acid) and the pH (cleaning solution). A solid surface will be cleaned from an organic acid if the affinity of the surface for water is greater than that for the organic acid. From our derivations in Chapter 3 and our experiments with stearic acid, we find the following to be necessary conditions for aqueous cleaning;

pH > IEP and pK_a ===> cleaning	(5.2)
pH < IEP or pK_a ===> no cleaning	(5.3)
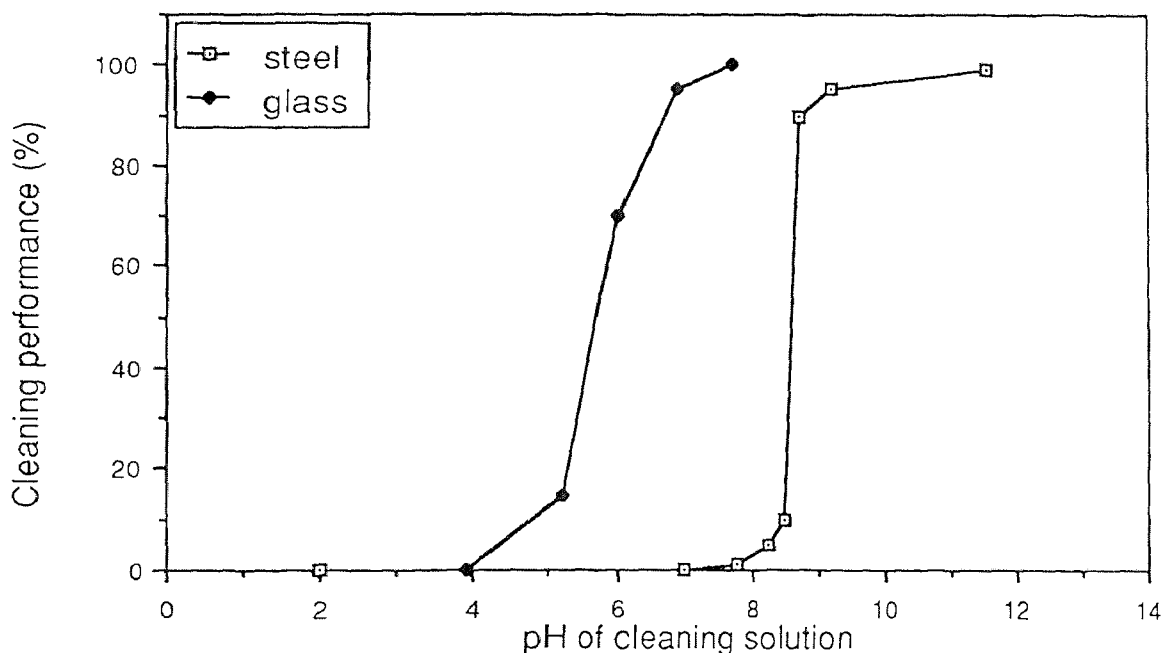
Figure 5.1 Cleaning of stearic acid on steel and glass, versus pH of cleaning solution in water and buffer solution at 55 °C. Measured after 10 minutes.

In other words, if the pH of the solution is greater than the IEP of the surface and the pK_a of the acid, the water will replace the organic acid on the surface. The acid will be physically removed from the surface, and the surface will be cleaned from the organic acid. When the pH is below the IEP or pK_a, the surface hydroxides preferentially react with the organic acid (or acid remains adhered to the surface) and the water will not be able to remove the acid. No cleaning occurs in this case. It should be noted that the above are thermodynamic conditions that must be satisfied in order to achieve cleaning.

To prove the generality of these conclusions, we tested the cleaning of stearic acid from aluminum, molybdenum, tantalum and titanium substrates. Figure 4.16 shows the cleaning performance of water at 55 degrees Celsius.
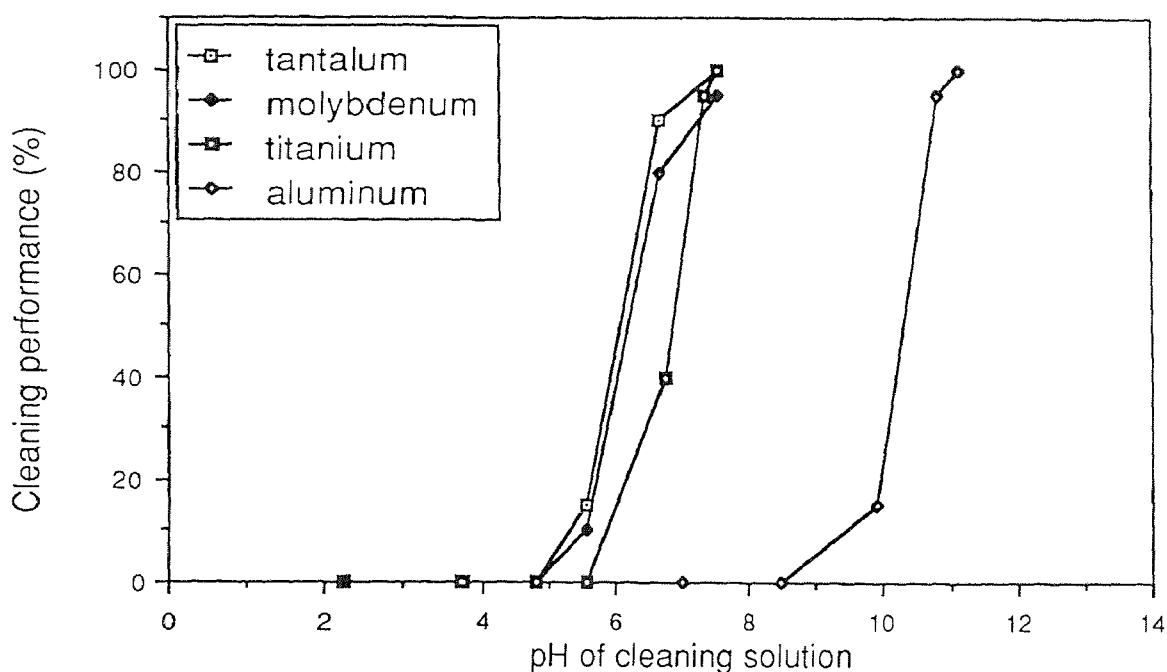
Figure 4.16 Cleaning performance in water and buffer solution for stearic acid on tantalum, molybdenum, titanium and aluminum versus the pH of the solution, after 10 minutes at 55 °C.

Aluminum (IEP = 9.0) is cleanable in water solutions with pH above 9. Titanium (IEP = 6.0) is only cleanable in solutions with pH above 6. Molybdenum (IEP = 3.7) and tantalum (IEP = 5.2) is cleanable in solutions with pH above 5. Again, if the IEP of the surface is greater than the pK_a of the acid, cleaning is possible in aqueous solutions with pH above the IEP. If the IEP is smaller than the pK_a of the acid, like in the case of molybdenum, the pK_a determines if cleaning is possible. These results strongly confirm our thermodynamic criteria for aqueous cleaning of an organic acid (equations 5.2 and 5.3). According to our knowledge, this is the first time this concept has been validated by experiment.

5.3 Adhesion and Cleaning of Organic Bases from Stainless Steel and Glass

Similarly we expect the adhesion of organic bases to be dictated by equilibrium chemistry. Organic bases are able to accept a proton and form a chemical bonding with a proton donor. Hydroxylated surfaces are able to act as proton donors, and thus react with an organic base. During the cleaning process, we want to replace the organic base with water. Therefore, the affinity of the surface for water must be greater than that for the organic base. From our derivations in Chapter 3, we found that to replace an organic base from the surface with water, the pH of the aqueous solution has to be lower than the IEP of the surface and the pK_a of the base (equations 5.4 and 5.5). Figure 5.2 shows our results with diphenyl amine deposited on glass and stainless steel.

$$pH < IEPS \text{ and } pK_a ===> \text{ cleaning} \qquad (5.4)$$

$$pH > IEPS \text{ or } pK_a ===> \text{ no cleaning} \qquad (5.5)$$

Diphenyl amine (pK_a = 1.9) is insoluble in water and forms a good adhering, hydrophobic residue on stainless steel and glass surfaces.
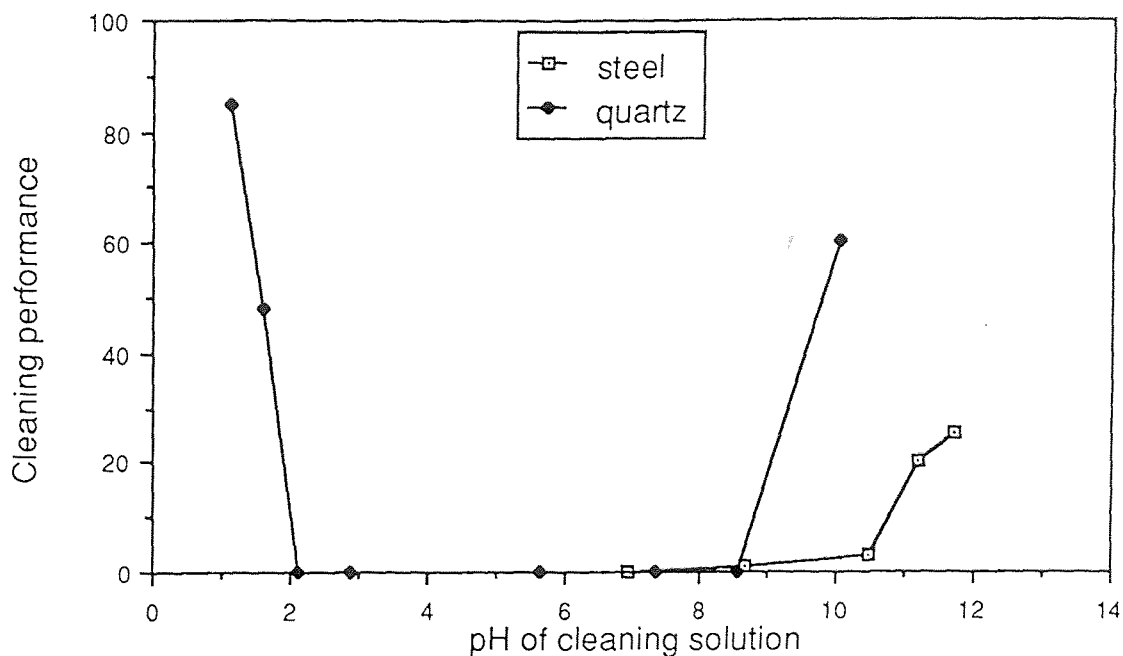
Figure 5.2 Cleaning of diphenyl amine versus pH of cleaning solution at 45 °C, on quartz with water-hydrogen peroxide (4.5 %) solution and steel in water-buffer solution.

Diphenyl amine adhering to glass (IEP = 2.5) was cleanable in aqueous solutions at a pH below 2.0. This again confirms our theoretical criteria setforth in equation 5.4 and 5.5. Below the IEP of glass and the pK_a of diphenyl amine, the water is more acidic than the surface and it is able to replace the organic layer. In this region the diphenyl amine is removed from the surface by the water and the glass is cleanable in aqueous solutions. At pH above the pK_a, water is more basic (or less acidic) than the organic base and the surface hydroxides will preferentially remain reacted with the organic base. In aqueous solutions with pH above 9 diphenyl amine was also cleanable from glass because of the dissolution of glass itself at such high pH conditions. At such

basic solutions the quartz or glass used in our experiments was etched and the top layers of silicon oxide surface become soluble.

For the case of diphenyl amine deposited on stainless steel, the situation was complicated. From our theoretical criteria, we would expect the steel to be cleanable below the pK_a of diphenyl amine (1.9). We could not test the cleanability under these conditions because the steel surfaces becomes corroded in such acid solutions (see section 5.6). In solutions with pH above 11, the steel was not cleanable. We could however clean diphenyl amine with aqueous solutions by adding hydrogen peroxide. We will return to this point when we discuss the effect of H_2O_2.

In summary, the criteria (equation 5.4 and 5.5) for cleaning an organic base from a solid surfaces was followed during the cleaning of diphenyl amine from glass. We could not test the validity of our criteria for steel because the dissolution of iron at very low pH conditions.

5.4 Thermodynamic Criteria for Cleaning - Adhesion and De-Adhesion at Interfaces

In the previous sections, cleaning was approached from the microscopic point of view. To perform cleaning, each organic molecule adhering to the solid surface has to be replaced by a water molecule.

From the physics point of view, we consider the organic material as a charged solid layer, in close contact with another charged solid layer -- the steel or glass surface. The surface potentials of both layers may lead to attractive or repulsive conditions, as described in Chapter 3. The total electrostatic interaction energy between two layers is the sum of the repulsive and attractive energies. The repulsion energy term depends on the product of both surface

potentials. The attraction energy between two layers close to each other is independent of the surface potentials and is negative by definition.

In the case of an organic layer adhering to a solid surface (glass, SS, etc.), three conditions are possible:

1. If both surface potentials have opposite charges, the electrostatic energy (product of potentials) will be negative. This results in net attractive forces between the two surfaces. In this case the two surfaces will adhere or remain adhered to each other.

2. If both surface charges have the same sign (both positive or both negative), the electrostatic interaction term will be positive. If the repulsive energy is greater than the attractive dispersive energy, the two layers will repel each other and separate or de-adhere.

3. If one of the surface potentials is zero, that is if one of the two surfaces is not charged (not dissociated), the electrostatic interaction energy is zero, and the dispersion forces will become dominant which results in a net attractive force (adhesion, no cleaning).

If the condition at the interface between the organic residue and solid surface results in a net repulsion, the surface would be cleanable in the aqueous environment. Therefore, the two surfaces should have the same sign of charging for the cleaning to be possible.

In our experiments, we do not measure the exact value of the surface potentials of the solid surfaces or the organic layers. Therefore, we cannot calculate the exact repulsive forces or the net interaction. What we do know is where the surfaces are positively, negatively or zero charged. As explained above, a solid surface is positively charged in aqueous solutions with a pH below its IEP, is zero charged at its IEP and is negatively charged in solutions with pH higher than its IEP. An organic acid dissociates in solutions with a pH

above its dissociation constant, resulting in a negative surface in that pH region. Below the pK_a, the organic layer is neutral (no charges). For an organic base the situation is the opposite. In aqueous solutions with a pH below its pK_a, the organic layer is positively charged, while above the pK_a, the organic layer is zero charged (no dissociation).

This information is enough to determine if the two surfaces are in net repulsion or net attraction, or in other words, wether the solid surface is cleanable from the organic layer or not. In figure 5.3, the charge of the adhering surfaces is symbolized as a function of the pH of the cleaning solution. If a surface is positively charged, we set the charge at (+1), if a surface is negatively charged, we set the charge at (-1). For neutral surfaces the charge is zero. On the left hand side, we represent the case of stearic acid adhering to stainless steel. On the right hand side we give the charge curves for diphenyl amine adhering to glass. This depiction is essential to understand adhesion and cleaning phenomena.

The top curve (on the left hand side) represents the charging of the stainless steel surface. In aqueous solutions with pH below 8.5 (its IEP), the steel surface is positively charged (+1), above 8.5 the steel surface is negatively charged (-1). The middle curve is the symbolic charging of the stearic acid layer. Below pH 4.75 (its pk_a), stearic acid is neutral (not charged, not dissociated), resulting in a zero charge. In solutions with a pH higher than 4.75, stearic acid dissociates, resulting in a (-1) symbolic charge. The bottom curve (left) represents the net electrostatic interaction between the stainless steel surface and the organic layer of stearic acid -- it is the result the multiplication of the two previous curves. A positive net interaction indicates that repulsive forces are dominant between the two surfaces. In these regions the stainless steel is cleanable in aqueous solutions.
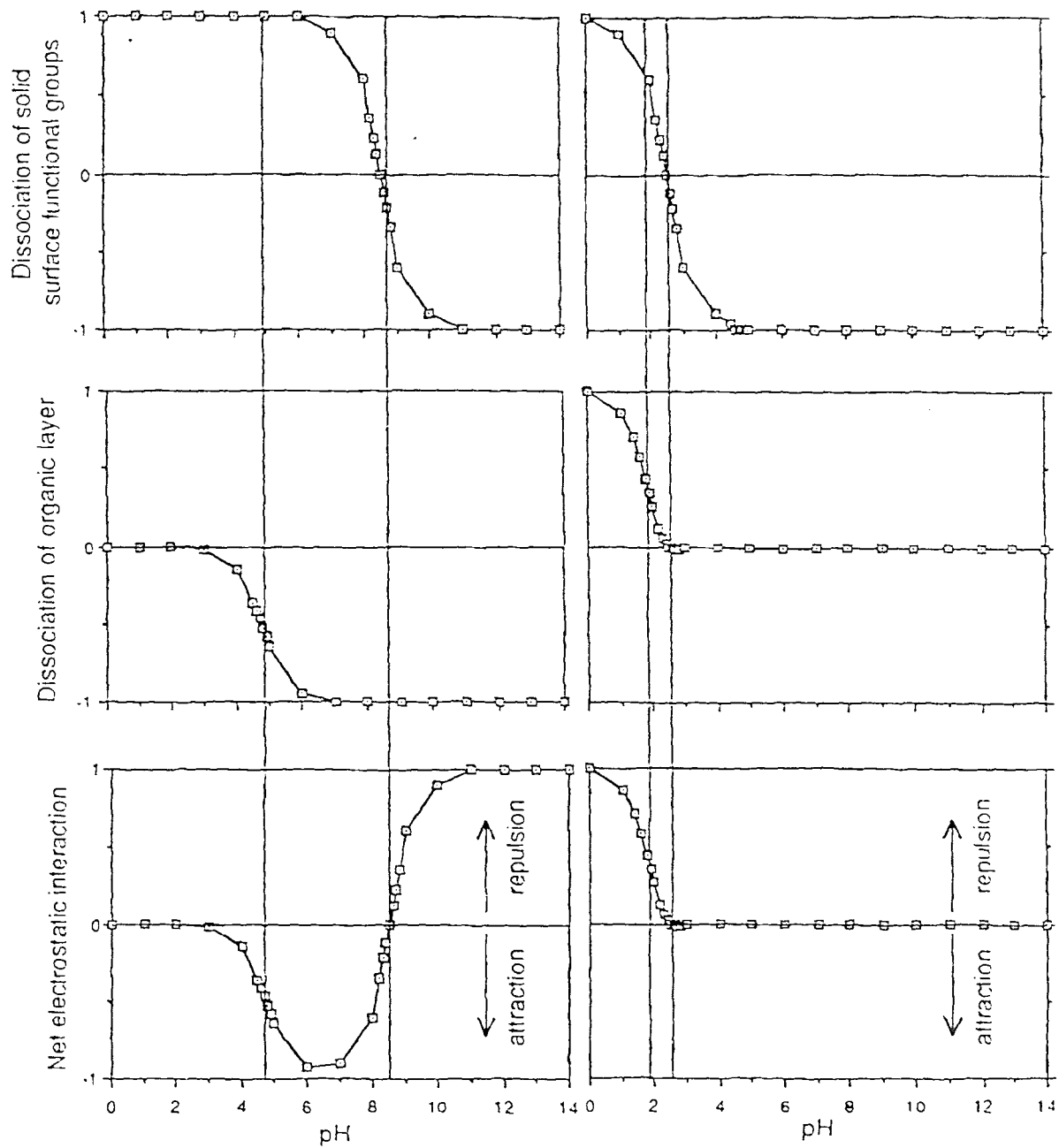
Figure 5.3 Charge diagrams of stearic acid on steel (left hand side) and diphenyl amine on glass (right hand side).

A negative or zero net interactions means that the two surfaces attract each other, and no cleaning will occur in aqueous solutions. In the latter case, the electrostatic term is zero and the dispersion attractive forces will dominate.

According to the net interaction curve, steel is cleanable in aqueous solutions with a pH above 8.5. This compares very well with our experimental results and is in agreement with our equilibrium calculations.

On the right hand side of figure 5.3 we followed the same procedure for diphenyl amine (organic base) adhering to glass. The first curve is the charge curve for glass (+1) in solution with pH<2.5; (-1) in solutions with pH>2.5). Diphenyl amine is positively charged (+1) in solution with pH<1.9 (its pK_a) and neutral above 1.9 (0 charge). The net interaction is again the multiplication of both curves. In aqueous solutions with pH below 1.9, the net interaction is positive (repulsive) and the diphenyl amine is cleanable in this pH region. In aqueous solutions with pH higher than 1.9, the net interaction is zero, resulting in a net attractive force between the organic residue and glass. Diphenyl amine is not cleanable in this pH region. This prediction compares very well with our experiments. Other net interaction curves can be constructed for other cases using the method described above.

This method of determining the pH regions of cleaning is convenient and fast. If surfactants are added to the cleaning solution, this method remains accurate in predicting pH regions of aqueous cleaning. Any organic material that can acquire charges in the aqueous environment, can be treated with this method. For organic material that are not functionalized, the prediction of this method may lead to designing appropriate cleaning processes, as we will show in section 5.5.

Both the equilibrium and electrostatic interaction methods predict the same thermodynamic cleaning criteria (IEP, pK_a and pH). Therefore both methods will predict the same pH regions of cleaning. They give the thermodynamic criteria for cleaning. If a cleaning solution falls outside these thermodynamic cleaning criteria, no cleaning is possible. If an aqueous

cleaning solution fulfills the thermodynamic criteria, cleaning is possible, if the rate of cleaning is high enough. The thermodynamic criteria are necessary conditions, kinetic conditions predict if cleaning is practical.

5.5 Kinetics and Mass Transfer Aspects of Aqueous Cleaning and the Role of Hydrogen Peroxide

5.5.1 Relationship between Thermodynamics and Mass Transfer Kinetics

While the thermodynamic conditions are necessary to determine cleanability, kinetic data is needed to determine the speed of cleaning. By developing the optical spectrometer technique to measure cleaning on quartz, we were able to measure the change in cleaning performance as a function of time. These measurements are an indication of the kinetics of the cleaning process -- the measure the rate of removal of organic residue from the surface. As explained in Chapter 3, the slope in these cleaning-time curves gives a relative value of flux -- the mass of material that leaves a unit surface area per unit time. The flux is a direct measurement of the rate of cleaning. All curves are shown in Chapter 4.

Figure 5.4 shows the variation of flux versus the pH of the cleaning solution for stearic acid deposited on quartz. It should be noted that flux = 1 means that a thick, good adhering film of stearic acid leaves the surface completely in 100 seconds. The flux depends largely on the pH of the cleaning solution. From the figure it can be seen that, in the thermodynamic favorable region, the difference between the pH and the pK_a of the stearic acid is the driving force in determining the cleaning flux for this system. The larger the difference, the faster cleaning occurs.
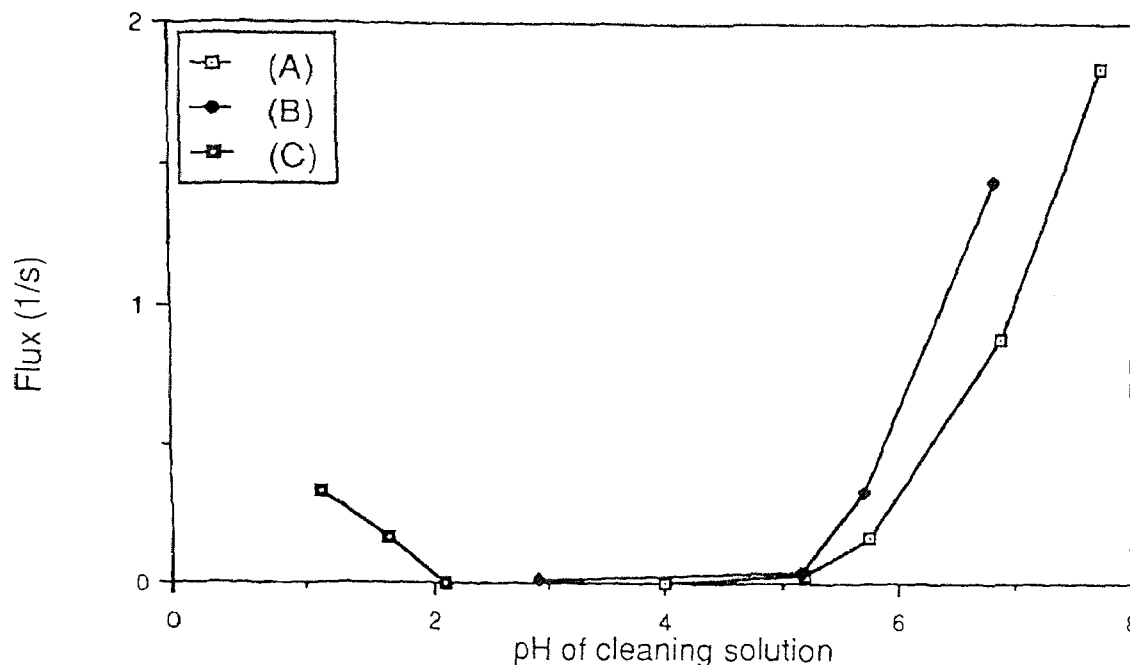
Figure 5.4 Flux of stearic acid leaving quartz substrates versus pH of cleaning solution, at 55 °C. In water-buffer solution (A) and water-hydrogen peroxide (4.5 %)-buffer solution (B). Flux of diphenyl amine in water-hydrogen peroxide (4.5 %)-buffer solution at 45 °C (C).

Figure 5.4 also shows how the cleaning flux of diphenyl amine depends on the pH of the cleaning solution. Although little data is available, the same phenomena is seen. In the thermodynamic favorable region for cleaning of the quartz-diphenyl amine system, that is below pH 1.9, the pK_a of diphenyl amine, the flux depends on the difference between the pH and the dissociation constant (the pK_a of the base).

In summary, in the thermodynamic favorable pH zone for cleaning, the rate of cleaning (flux) depends on the difference between the pH of the cleaning solution and the IEP of the surface (or the pK_a if it is the determinant factor). The larger the difference, the faster the cleaning is accomplished.

The addition of hydrogen peroxide (4.5 %) enhances the cleaning of stearic acid from quartz in the thermodynamic favorable pH zone (Fig 5.4). In solutions with pH below 5 (pH=4.75 is thermodynamic parameter for cleaning of

this system), no cleaning is accomplished, with or without the addition of H_2O_2. In solutions with pH higher than 5, the addition of H_2O_2 speeds up the cleaning process. For cleaning solutions with the same pH, the cleaning flux is higher for the solution with H_2O_2 than for pure water.

Although we could not accurately measure the flux of cleaning on steel surfaces, from Figure 4.6 it can also be seen that the addition of hydrogen peroxide enhanced the rate of cleaning of stearic acid from stainless steel. From these experiments we conclude that the addition of H_2O_2 acts not on the thermodynamic parameters, but does change the kinetic parameters positively. Hydrogen peroxide does not change the pH region of cleaning, determined by the thermodynamic parameters, nor does it change these parameters. In a solution with a pH outside the cleaning zone, no cleaning will be accomplished by the addition of H_2O_2.

5.5.2 Role of Hydrogen Peroxide on Mass Transfer Kinetics

The cleaning action of hydrogen peroxide can be divided into two classes:

(1) In the case of functionalized organic residue, the effect of hydrogen peroxide can be explained in different ways. First, H_2O_2 decomposes into water and oxygen gas at elevated temperatures. This decomposition occurs preferentially at the vessel surface. The gas bubbles generated immediately at the surface of the samples lift up the organic layer and thus enhance the removal of organic material. For this to happen, H_2O_2 first has to reach the surface to be cleaned. Therefore the cleaning solution has to be in the right pH zone. This explains why the effect of H_2O_2 is only kinematic. The steel surface acts as a catalyst for the H_2O_2 decomposition. Second, the H_2O_2 passivates the steel surface by creating a thick, homogeneous layer of iron oxide, and thus

preventing the organic material from redepositing at the surface (see section 5.6).

Figure 4.6 Cleaning performance for stearic acid on SS 316 versus pH of solution, in water and hydrogen peroxide solution (4.5%) at 55°C. Measured after ten minutes.

(2) In the case of an organic residue that can be functionalized by hydrogen peroxide, H_2O_2 acts as a strong oxidizer and is able to functionalize organic materials. Since functional groups are necessary to satisfy the thermodynamic conditions for cleaning, the creation of functional groups may be necessary in some cases. In Figure 4.7 is shown that the cleaning of diphenyl amine from steel is enhanced by the addition of H_2O_2. We attributed the higher cleaning rates in this case to the fact that hydrogen peroxide created additional charges (functional groups) on the diphenyl layer, which helped in forming an organic layer that can repel the steel surface at these pH conditions.
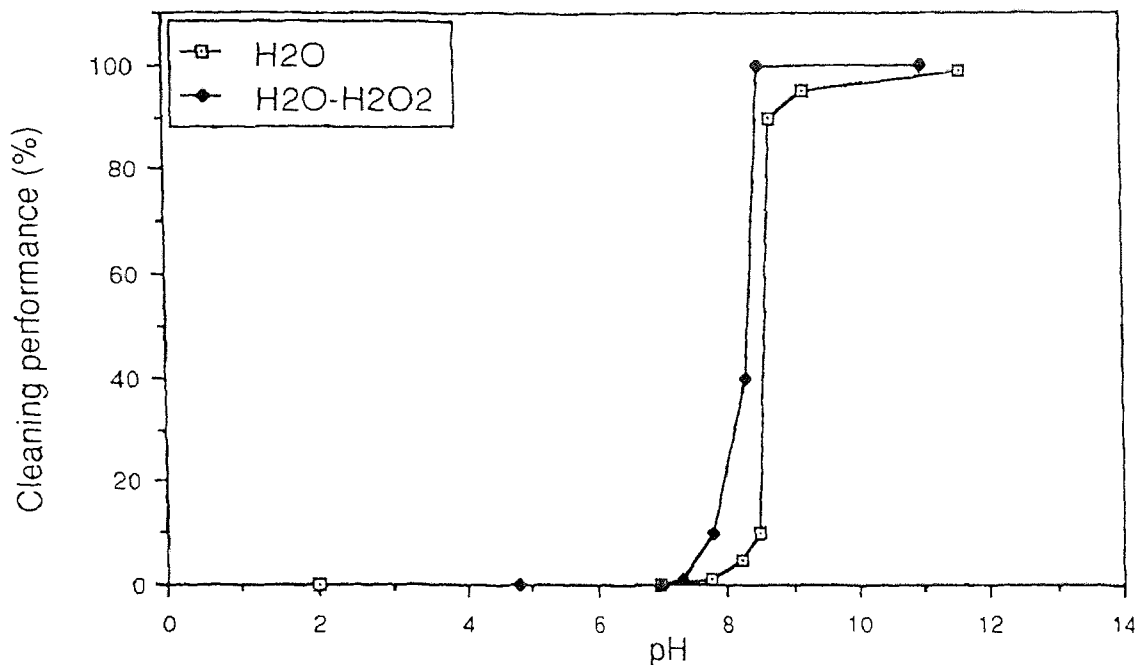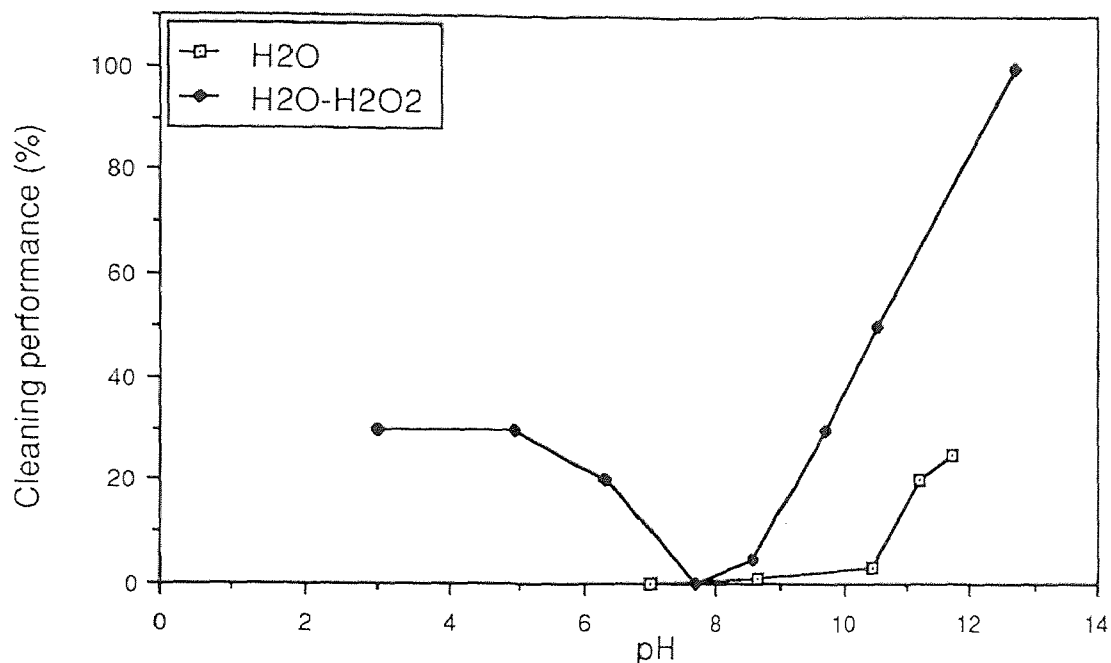
Figure 4.7 Cleaning performance for diphenyl amine on SS 316 versus pH of solution, in water and hydrogen peroxide solution (4.5%) at 45°C. Measured after ten minutes.

In our experiments, hydrogen peroxide was necessary to effectively clean cyclohexanone, amyl acetate, the epoxy resin and silicon grease from stainless steel substrates. In each case the cleaning was best accomplished in basic solutions, possibly because faster decomposition rates of H_2O_2 and effective functionalization of the organic residues in basic solutions.

5.5.3 Effect of Temperature on Mass Transfer Kinetics

Another important factor affecting the kinetic parameters of aqueous cleaning is the temperature of the cleaning solution. Figure 5.5 shows how the cleaning flux of organic material leaving the surface varied with the temperature during the cleaning of stearic acid from quartz in solutions with pH 7. These values are calculated from Figures 4.17 and 4.18. Increasing the temperature enhanced the rate of cleaning. The positive effect of the temperature is greater in the

water-hydrogen peroxide solution. This is probably due to additional dissociation of H_2O_2 and thus a greater activity on the surface at higher temperatures.
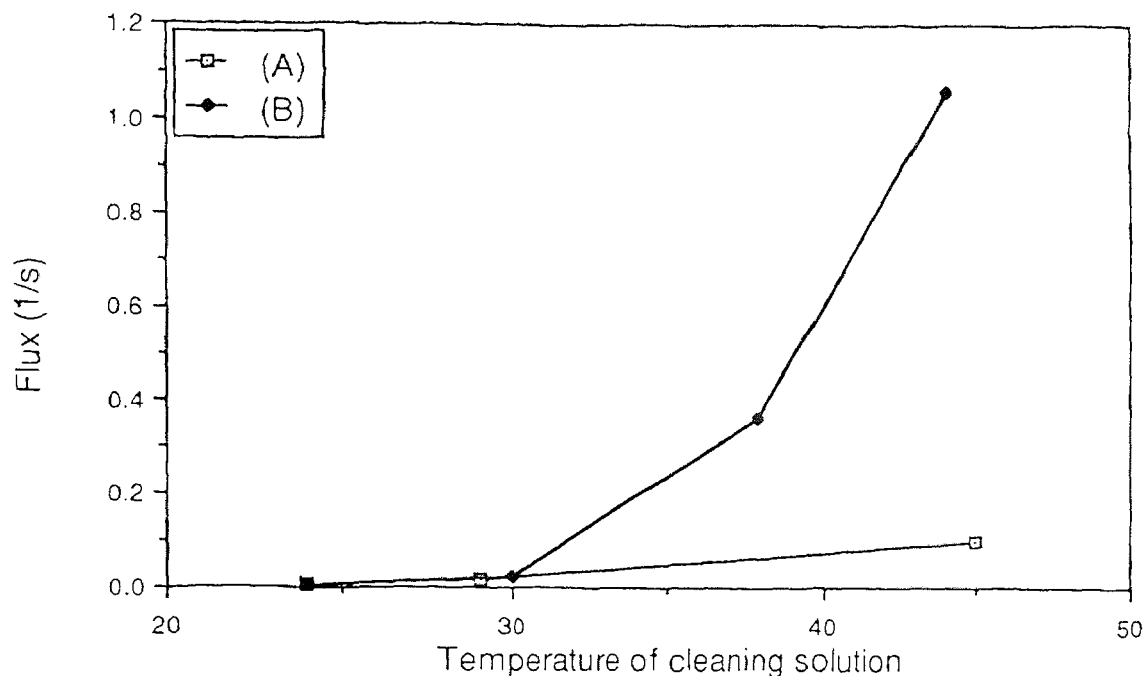
Figure 5.5 Flux of stearic acid leaving quartz substrates versus temperature in water-buffer solution (A) and hydrogen peroxide (4.5 %) solution (B), at pH=7.

5.6 Oxidation Potential, Corrosion and Passivation in Aqueous Cleaning - pH Regions to be Avoided

5.6.1 Effect of pH and Oxidation Potential on Cleaned Metal Surfaces

During the cleaning of stearic acid and diphenyl amine from steel in pure water, we noticed that although the organic layer was removed, the steel surface remained dull in solutions with pH between 8.5 and 11. Only if we raised the pH of the solution above 11 for stearic acid (see Fig 4.6 in previous section), the stainless steel surface regained its shininess. In experiments with hydrogen peroxide, we were not only able to clean the steel samples faster, but to obtain

the desired shininess -- almost immediately and without the need to raise the pH to 11.0.

We assume that the shininess of clean stainless steel is due to a homogeneous top layer of iron oxide (Fe_2O_3 or Fe_3O_4). This layer is known to passivate the steel and to protect the steel against further corrosion. This layer is formed naturally in contact with air or aqueous environments. In very basic solutions (pH>11) and with the help of an oxidizing agent (like H_2O_2), the oxidation of the top layer is faster and more homogeneous. A perfect protective thin oxide film (continues without holes) increases the shininess of the stainless steel.

This passivating process can also be the reason that in solutions containing H_2O_2, the cleaning of steel is faster and more complete compared to pure water at the same pH. When the organic residue leaves the surface, H_2O_2 immediately passivates the steel surface and creates the desired shinning appearance. This allows us to conclude that we must perform aqueous cleaning under appropriate pH-oxidation potential conditions needed for passivation.

An excellent tool to determine regions of passivation are the Pourbaix-diagrams (Ref. 12). Pourbaix-diagrams are electropotential-pH diagrams, expressing equilibria between possible electrochemical states of a surface. Most common are the Pourbaix-diagrams for metals in aqueous solutions. Figure 5.6 gives the Pourbaix-diagram of iron in water. The diagram can be divided into regions of immunity, corrosion and passivation. Iron corrodes in acidic water solutions, while in basic solutions form a passivating layer of Fe_2O_3 or Fe_3O_4.
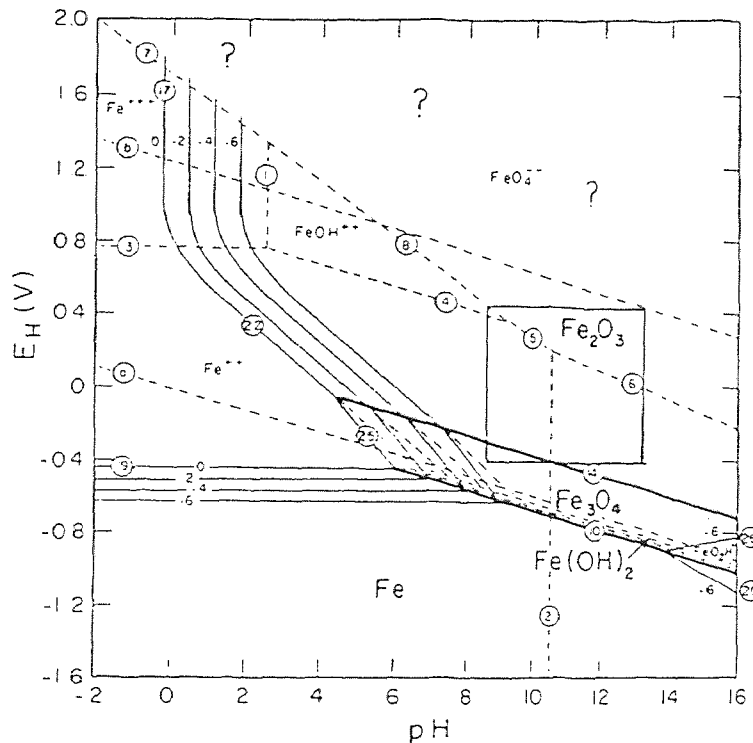
Figure 5.6 Pourbaix-diagram of iron in water, assuming passivation by films of Fe_2O_3 and Fe_3O_4, at 25 °C (Ref. 12). Box is passivating cleaning zone.

During the deposition of an organic onto stainless steel, the surface may be reduced (in the electrochemical sense), or the passivating film may be destroyed. In order to clean the surface, not only the organic layer has to be removed, but also the passivated film has to be restored in its initial, protective state. An oxidizing agent added to the cleaning solution helps to oxidize the steel surface and to restore its passivating oxide film. An oxidizing agent will raise the oxidation potential in the Pourbaix diagrams.

5.6.2 Corrosion Issues in Aqueous Cleaning

Several times during our experiments, we had to deal with the corrosion or etching of the solid substrates. Stainless steel was corroded when we attempted cleaning with a water-hypochloride solution. Aluminum was heavily

corroded in basic solutions (pH>10) due to dissolution of the oxide layer and quartz was etched in basic cleaning solutions (pH>9). Corrosion and etching occur when the solid surface becomes soluble in the surrounding liquid. Conditions of corrosion or etching are undesirable during the cleaning process. In designing cleaning systems, care should be taken to prevent corrosion or etching. The Pourbaix-diagrams can be used to determine zones of corrosion or dissolution. We have summarized the conditions for stainless steel and glass in this thesis

5.7 Understanding Adhesion
New Materials and Surfaces

As a result of surface reactions, organic materials adhere to vessel surfaces and form chemical bonding. These surface reactions may involve proton and/or electron transfers (Ref. 9). In general, if no exchange of protons is possible the adhesion may be accomplished by electron donor-acceptor reactions. The adhesion between hydroxylated surfaces and organic compounds is determined by acid-base reactions, electrostatic forces, Van der Waals and dispersion forces.

To reduce the amount of cleaning solution, or to use less aggressive cleaning solutions, new surfaces with non-stick characteristics may provide an attractive solution. If a vessel surface has non-stick characteristics towards the organic materials less organic residue will adhere to the surface. This should make the cleaning process easier and less costly. In other words, if the adhesion forces are smaller, the volume of cleaning solution will be smaller. Also, if we can decrease the adhesion forces between organic material and the vessel surface, environmentally friendly aqueous solutions can be used to

perform the cleaning, instead of the traditional solvents. We can therefore reduce organic solvent emission.

In order to reduce adhesion forces, the number of surface adsorption sites and their type need to be tailored. The hydroxyl-groups are the greatest source of surface adsorption sites. Reducing the number of hydroxyl-groups at the solid surface will have a positive effect on the cleanability of surfaces. This can be accomplished by different means for metals and glasses.

One way to reduce the number of active adsorption sites at the surface of steel is by nitriding. During nitriding of steel, residual valences on the outside of the steel surface are saturated in the forms of nitrides. Nitriding prevents the formation of oxides and hydroxides at the surface. Nitrides are known to be less reactive with organic compounds and should result in less adhesion of organic residue. Therefore nitrided steel is expected to be less reactive and to have a better cleanability in aqueous solutions. Care should be taken that new surfaces are no subject to corrosion or etching and that they should be abrasive-resistant. Future research should be pursued in this area.

In the case of glass, new surfaces can be made to render the number of silanol groups at the surface to be minimal. This can be accomplished by heat treating the glass materials and by tailoring the composition of glass. More research is required in this area as well.

CHAPTER 6

CONCLUSIONS

Pollution prevention is now viewed as the most prudent approach to minimize environmental emissions during manufacturing. This approach calls for redesigning production processes and adopting new strategies for waste minimization such as recycling and using new and advanced technologies. This research is an excellent example of such pollution prevention strategies to eliminate the use of organic solvent in cleaning and replace it with environmentally safe alternatives.

Here, we have employed the tools and techniques of advanced materials to address the problem of organic solvent cleaning in the pharmaceutical and chemical industries. Our approach is based on understanding the adhesion of organic residues to vessels and equipment surfaces and developing aqueous cleaning processes to replace the current organic solvent cleaning practice. The ultimate goal of this work is to define the parameters needed to make new generation of materials to build equipment for the pharmaceutical industry. The surfaces of such materials should have minimum adhesion to organic residues (non-stick) and should be safely cleaned with aqueous solutions.

We studied the physics and chemistry of adhesion of various classes of organic compounds to glass and stainless steel surfaces -- the two most common materials used to make vessels and equipment in the pharmaceutical industry. We used aqueous cleaning solutions with different properties to diagnose the adhesion and cleaning of organic compounds from glass and stainless steel surfaces. By employing this strategy, we have been able to define the thermodynamic requirements of aqueous cleaning and to make

conclusions regarding the requirements needed to develop novel materials with non-stick surface properties.

The surface chemistry of stainless steel and glass was found to depend on the chemistry of their surface oxides and hydroxides. The adhesion of organic compounds to such solid surfaces has been found by us to follow the generalized acid-base reaction, where the surface and organic compounds behave as acids or bases. Our extensive experimentation and testing have confirmed that this is indeed the major mechanism leading to the adhesion of organic materials to glass and stainless steel surfaces. The above facts have been supported by advanced surface characterization of glass and stainless steels using techniques such as FTIR, XPS and Auger electron spectroscopy, and by measuring cleaning behavior as function of pH, oxidation potential, temperature and various material surfaces. The acid-base interactions between the organic residue and the solid surface may be dominated by proton and/or electron transfer processes, depending on the functional groups of the organic molecules of the adhering residue.

This research consists of theoretical and experimental parts - Chapters 3 and 4, respectively. We derived several equations and relationships to illustrate various cases and scenarios. For organic residues with ionizable surface groups, we found that aqueous cleaning should follow chemical equilibrium calculations. Cases describing the adhesion and cleaning of organic acids and bases were used as examples. Using such equilibrium calculations, we defined the thermodynamic conditions necessary for achieving complete aqueous cleaning. The dominant parameters for such calculations were the pH, pK_a of the organic residue and the IEP of the solid surface. To accomplish complete cleaning of an organic acid, the pH of the solution should be higher than the pK_a of the acid and the IEP of the surface to be cleaned. For the case

of an organic base, we concluded that the pH of the cleaning solution must be less than the pK_a of the organic base and the IEP of the solid surface to effect complete cleaning. These theoretical predictions were tested by systematic experimentation as shown below.

The above theoretical treatment was essential to defining the pH regions where aqueous cleaning can be accomplished for various combinations of organic compounds and solid surfaces. To define such cleaning regions further, we expanded our theoretical treatment to predict interaction forces at the interface between the organic residue and the solid surface. Here, we used ionization equilibrium calculations of the organic compound and of the surface to compute the electrostatic interaction energy at the interface between the organic residue and the solid surface at various pH conditions. The application of such calculations has enabled us to define cleanability regions in the aqueous environment. Novel diagrams depicting the electrostatic interaction energy between the organic residue and the solid surface as a function of pH can now be easily constructed and used to design aqueous cleaning formulations for various cases. On the bases of such theoretical treatment, we concluded that the interface between the organic residue and the solid surface must be in a state of net electrostatic repulsion for the cleaning to be possible.

In the experimental part of this thesis, we studied the aqueous cleaning of several classes of organic compounds adhering to glass and stainless steel surfaces. Our experimental results agree with the theoretical predictions, especially for the cases where the functional groups of the organic residue are ionizable as a function of the pH. This was confirmed for the cases of stearic acid and diphenyl amine (organic base) of their surfaces of glass, stainless steel, aluminum, molybdenum, titanium and tantalum. Aqueous cleaning was

possible in each case provided the thermodynamic conditions for cleaning were satisfied.

One of the most challenging cases involved organic residues that were not ionizable as a function of the pH, and therefore could not satisfy the net electrostatic repulsion conditions in the aqueous environment. To achieve complete aqueous cleaning in such cases, the organic residue must become functionalized. We accomplished such functionlization by increasing the oxidation potential of the solution by adding hydrogen peroxide that effected the oxidation of the organic residue and created ionizable functional groups. Examples of this manipulation were used in the cleaning of diphenyl amine, epoxy resin, silicone grease and dehydrated carbohydrates. It should be noted that the thermodynamic conditions for aqueous cleaning must be met to achieve complete cleaning in the latter cases as well. The pH region where cleaning is possible when using an oxidizing agent are expected to depend on the type of functional groups created by this intentional oxidation. The cleaning of diphenyl amine, for example, was accomplished at higher pH in the present of peroxide which indicates the formation of functional groups that are ionizable under such pH conditions, possibly hydroxyl groups.

Kinetics and mass transfer rates are important to achieve practical aqueous cleaning. We studied the mass transfer parameters of the cleaning process for selected situations. We found that the thermodynamic condition for aqueous cleaning must be satisfied to achieve measurable cleaning flux rates. In the cleaning regions, cleaning rates were found be functions of temperature, difference between the pH of the cleaning solution and pK_a or IEP, and the concentration of the hydrogen peroxide. For metal surfaces, we found the rates of removing stearic acid from the surface depended mostly of the difference

between the pH of the cleaning solution and the pK_a or the IEP, but not on the type of metal itself.

A important factor was the state of the solid surface after completing the aqueous cleaning, especially with respect to corrosion, etching and shiny appearance. To avoid corrosion and etching of the solid surface, aqueous cleaning must be performed in pH regions where surface cannot be etched or corroded. We should avoid very high pH condition for glass and aluminum, and very low pH conditions for steel. With respect to the shiny appearance, especially for stainless steel, we confirmed by experiment that the surface of steel must be returned to its passivated condition. This the condition where the surface film of steel is uniformly oxidized and hydrated. We realized during our experimentation that the surface of steel appears dull even after the removal of organic residue from it. The steel surface returned to its shiny appearance after raising the pH >11.0, or by adding hydrogen peroxide in the solution. In view of our experiments, we could conclude that cleaning of steel must be accomplished in the passivated region, as depicted in the pH-oxidation potential diagrams constructed by Pourbaix. This new condition must be met when designing aqueous cleaning solutions and processes.

The theoretical and experimental results of this work are important in defining what is needed in new materials for building equipment and vessels for the pharmaceutical industry. The surface properties of new materials should have less interaction with organic compounds that should lead to low adhesion or non-stick properties. We predict that nitrided steel surface would passive to reaction with organic compounds compared to the surface or ordinary steel that is dominated oxide and hydroxide groups. Surface nitrides should be made at high temperatures and should be thick enough to avoid complications regarding delamination and corrosion. Other surface modifications of steel may

be needed to satisfy the above conditions. Similar principles apply to glass materials. The surface of new glass materials should be less reactive with organic compounds and should be less susceptible to etching in the aqueous environment. Such properties can be achieved by surface treatment of glasses to eliminate reactive silanol groups, or by new glass formulation achieving similar results. Such materials developments are challenging and require special investigation. This is an example of how recent environmental demands can drive new technologies. We believe that the development of novel materials that can be safely cleaned with less polluting aqueous solution would eventually transform the equipment manufacturing in the future.

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