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THE GROWTH OF ELECTROCHEMISTRY IN THE UNIVERSITY OF COIMBRA FROM THE BEGINNING TO THE PRESENT[a)]

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The study of Chemistry at the University of Coimbra began with the 1772 reform, normally known as the Pombaline reform (after the Marquis of Pombal, King Joseph I's Prime Minister). This was a profound reform of the University and among its great innovations the study of the experimental sciences is one of them. A new Faculty was then created - the Faculty of Philosophy - dedicated to these sciences. The fourth year of the philosophical course, the last one, was occupied with the chair of chemistry "Theoretical and Practical Chemistry".

The same reform also stipulated the construction of the "Laboratorio Químico" intended for the practice of chemistry. The building was in fact concluded in three years which is remarkable for the time. For two centuries it served as the centre of chemistry studies of the University of Coimbra.

The progresses registered in chemistry until the end of the eighteenth century may be considered satisfactory for the starting of a new science in a small country without much scientific tradition and did not contrast much with the development of this science in the rest of Europe, busy with the conflict between Lavoisier's chemistry and the phlogiston theory.

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a) Based on the invited lecture delivered at the Celebratory Session of the 5th Anniversary of the Portuguese Electrochemical Society, Lisbon, 1989.

Accepted by the end of the century in the whole of Europe, the new chemistry developped at an impressive rate and so at the end of the XIX century, chemistry was a well established science, comprising a large number of specialities, with strong ties to other sciences and with a prominent position in the economy and in the life of society.

Contrasting with the rest of Europe, the scientific progress in our country during the nineteenth century was very small. Therefore at the end of the century our scientific backwardness was very great. Though not the only responsible factors, the wars and social conflicts in which Portugal was involved along this time, were unquestionably important causes.

Our scientific activity only had some expression after the middle of the century and even so restricted to analytical work concerning mineral waters, and products of economic and pharmaceutical interest.

The lack of laboratory equipment did not allow the setting up of modern practical teaching at a time when this was of fundamental importance to the development of chemistry as an experimental science, which indeed it is. It was only by 1860 that some scientific equipment and teaching aids were acquired and the previous building adapted to the needs of the modern chemistry.

The lectures being less dependent on financial ressources, always kept an acceptable level as one can see from the adopted text books and from the acquisitions of journals and books for the library.

In such a situation, one could not expect any meaninful activity in the area of electrochemistry. However, after the 1840's some acquisions were registered of material used for the manufacturing of batteries and for laboratory experiments such as water electrolysis.

The attention given to electrochemistry in lectures by the middle of the century should be mentioned. The 1844 reform introduced into the philosophical course, for the first time, some chemical specialities. The course had gone from only one chair of chemistry to three, one of them being "Chemical Philosophy" lectured by Prof. Simões de Carvalho.[1] His lectures were organized from the leading authors and above all, from original papers published in the scientific journals. In the book he wrote in 1851 a great development of acid, base and salt concepts was given as well as of the electrochemical theories about chemical affinity of Davy, Ampere and Berzelius.[2]

Another noteworthy work was a dissertation presented by Alvaro Basto as a candidate to a professorship position at the Faculty of Philosophy. The book entitled, 'Introduction to the theory of electrolytic dissociation' deals with osmotic pressure theory of Van't Hoff and with the electrolytic dissociation theory of Arrhenius.[4] It is an updated monographic study about electrolyte solutions.

In fact, the updated knowledge of Alvaro Basto concerning solution chemistry is clear in his texbooks about analytical chemistry.

A new period of the development of electrochemistry started in the 1920's with Egas Pinto Basto.[5] At this time some equipment was acquired for laboratory classes of physical chemistry and for research too. This instrumentation included apparatus for electrical measurements, electromotive forces and electrical conductivity determinations.

This period marks the beginning of a new era in the life of the "Laboratório Quimico" owing to the importance given to research as a means to reach an international scientific standard.

Pinto Basto published some interesting papers about mineral waters where together with some experimental results obtained by himself he presented an interpretation of results obtained by several authors based on the modern theories of ionic solutions.[6]

The scientific activity related to electrochemistry increased with Couceiro da Costa[7] who immediately after the Second World War acquired equipment for teaching and research. Most of this equipment was for potentiometric and conductimetric studies and included a glass pH meter the well known Beckman Model G. Beforehand, pH was measured with acid-base indicators,

or in the more recent past, by the quinhydrone electrode. The majority of the work of Couceiro da Costa was on physical and analytical chemistry but he published also a few papers on electrochemistry both theoretical and practical.[8]

As a natural result of scientific expansion, by the end of the 1950's a new phase began in electrochemistry at Coimbra, which may be characterized by pursuing of research in electrochemical systems and not only in electrochemistry as an applied science as before. The first papers of this phase were concerned with the equilibrium and kinetics of ion-exchange reactions in synthetic resins. A few years later the research field was extended to the solid/solution interface involving mainly inorganic solids and ionic solutions.

During the next decade research activities spread to polarography and to ion selective electrodes. Neither technique was directed towards the analytical field, but rather to the structure of the solutions and interfaces and mechanisms of electrode processes.

The first years of the 1970's were very important for the development of electrochemistry in Coimbra and we believe for science in Portugal as a whole. At that time, decisions were made about scientific policy and financial support granted which led to a considerable increase in activity through the organization of research projects, training of researchers in the country and abroad, and acquisition of equipment.

One should not include in an historic rectrospective recent scientific activity, because it is impossible to assess with certainty the contribution which it will give to the progress of science and to the

institutions where it is carried out. However, as it is the aim of this exposition to cover the activity in the area of electrochemistry to the present day we will give a brief summary of the work done in recent years.

As happens in other Portuguese Universities, research in the Department of Chemistry is carried out within a framework of research lines integrated in a 'Centro de Química' of INIC (National Institute of Scientific Research). Working in electrochemistry there are from 1977, two research lines, *Structure of Solutions and Electrode Processes* and *Diffusition and Thermaldiffusion in Electrolyte Solutions*.

In the first, research projects in the following areas have been in progress:

i) *Structure of Solutions*. The main objective in this field has been the interpretation of solute-solvent interactions where one tries to elucidate, not only the general aspects of the interaction for each kind of group in the solute molecule (ionic, polar and non-polar) with various solvents, but also to study the mutual influence of the groups on solvation as well as the effect of the isomerism of the solute molecules. Although most attention has been given to aqueous solutions other solvents also have been studied.

Research in this field is basically fundamented, focussing on thermodynamic (volumetric and calorimetric) and transport (viscosity) properties.

ii) *Interfacial Phenomena*. In this area several projects have been carried out concerning ionic adsorption by inorganic solids (e.g. silica, alumina) from solutions. The adsorption phenomena have been followed by measuring surface and zeta potentials. Other types of solids are those used as ion sensors in manufacturing ion-selective electrodes (ex. Ag_2S). The techniques used in these studies are electrokinetic properties determined by microelectrophoresis and electroosmosis and potentiometric measurements.

iii) *Electrode Processes*. The work undertaken in this area has the objective of studying the mechanisms and kinetics of electrode processes in stationary and hydrodynamic, including flow-through, systems. Electrochemical systems investigated include the reduction of porphyrins in non-aqueous solvents and the corrosion of aluminium in acidic media. Also studied is the anodic oxidation of urea and carbamate herbicides and

redisolution voltammetry of various compounds, from mercury thin film and surface modified electrodes. Impedance and various voltametric techniques are used.

iv) *Electrocatalysis*. This topic deals with the investigation of the mechanism of electrode processes of technological interest such as the electroreduction of oxygen and the electrooxidation of alcohols. Special attention has been given to the electroreduction of oxygen. The mechanism of the reduction of oxygen on pure and modified surfaces of carbon and gold has been studied by using cyclic voltametry, rotating disc, rotating ring disc and pulse techniques.

v) *Bioelectrochemistry*. Recently a research project was initiated to develop electrochemical biosensors containing biological components to increase specificity. Immobilisation of enzymes on various supports with electrochemical detection of the enzyme reaction products has been investigated.

Several doctoral and master's theses have been conducted within this research line, which is, at this moment, constituted by six qualified researchers, three working for the Ph D degree and three others starting their research career.

In the second research line diffusion coefficients of electrolytes in aqueous solutions were measured with a new diffusion cell and ancillary equipment developed in this group.

Thermal diffusion an applications of Soret coefficients are used in the study of the structure of electrolyte solutions.

Compilation and assessment of thermodynamic and transport properties in electrolyte solutions presented in the form of books and computational data banks is another of the activities carried out.

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India. Four years later he came to Coimbra to complete his education. He got graduated and doctorate degrees at the local University and in 1920 he joined the staff of the 'Laboratório Químico'. In 1936 he became professor of physical chemistry. Since 1937 until his death he was the head of the Department. Couceiro da Costa had a very complete scientific culture in the fields of inorganic and physical chemistry. His physical chemistry course was advanced for the time. He had a critical mind and to his propensity for theoretical studies he allied that of a skilful experimentalist. He published many papers on physical and analytical chemistry and on the applications of these two branches of chemistry to mineral waters. Couceiro da Costa played a very important part in the scientific development of the Chemistry Department and in the planning of the New Building for Chemistry.

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O DESENVOLVIMENTO DA INVESTIGAÇÃO EM ELECTROQUÍMICA NAS UNIVERSIDADES E OUTRAS INSTITUIÇÕES LOCALIZADAS EM LISBOA

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1. INTRODUÇÃO

A investigação científica em electroquímica, na área de Lisboa, tem uma tradição relativamente recente se, apenas, se tiver em conta a existência de laboratórios disponíveis e minimamente estruturados e equipados para a realização permanente de projectos de investigação e, sobretudo, no que se refere à constituição de equipas de investigadores devidamente habilitados.

Apesar disso, particularmente, nos últimos vinte e cinco anos, a preferência de investigadores por esta área tem sido frequente e tem contribuido para um desenvolvimento rápido e fecundo da electroquímica como resultado dos impulsos dados por diferentes grupos que se foram constituindo, sobretudo, na Faculdade de Ciências e no Instituto Superior Técnico. Esta situação não aconteceu por acaso. Na verdade, no decurso da década de sessenta, tal resultou de duas circunstâncias que se conjugaram: existirem, nestas Escolas, alguns antecedentes no âmbito da electroquímica e no facto de ter sido adoptada, pelo, então, Instituto de Alta Cultura, uma política dinâmica que permitiu o envio de um número significativo de jovens para o estrangeiro para se especializarem em diferentes áreas, entre elas a que aqui se trata, bem como a concessão de subsídios a projectos liderados por pessoas que, em grande parte dos casos, revelaram o necessário dinamismo, espírito de iniciativa, criatividade científica e capacidade de liderança.

Tal processo teve sequência mais estruturada com a criação de numerosos Centros de Estudo, nas diferentes Universidades por razão da saída de dois despachos - 17/75 e 19/75 - no início de 1975 por iniciativa do, então, Secretário de Estado do Ensino Superior e Investigação Científica. Na sua sequência, dois grupos de investigadores das referidas Escolas Universitárias procuraram tirar proveito da nova legislação para solidificarem e ampliarem possibilidades nos seus objectivos de investigação e académicos. Foi assim que