EFFECT OF IONIZING RADIATIONS ON SOME ION EXCHANGE RESINS

THESIS

Submitted to University College for Girls
Ain Shams University
In Partial Fulfilment of the
Requirements for the
Degree of M. Sc.
In
(Chemistry)

By
Nabela Ahmed Mahmoud Maziad
(B. Sc)

National Centre for Radiation
Research and Technology
Atomic Energy Authority

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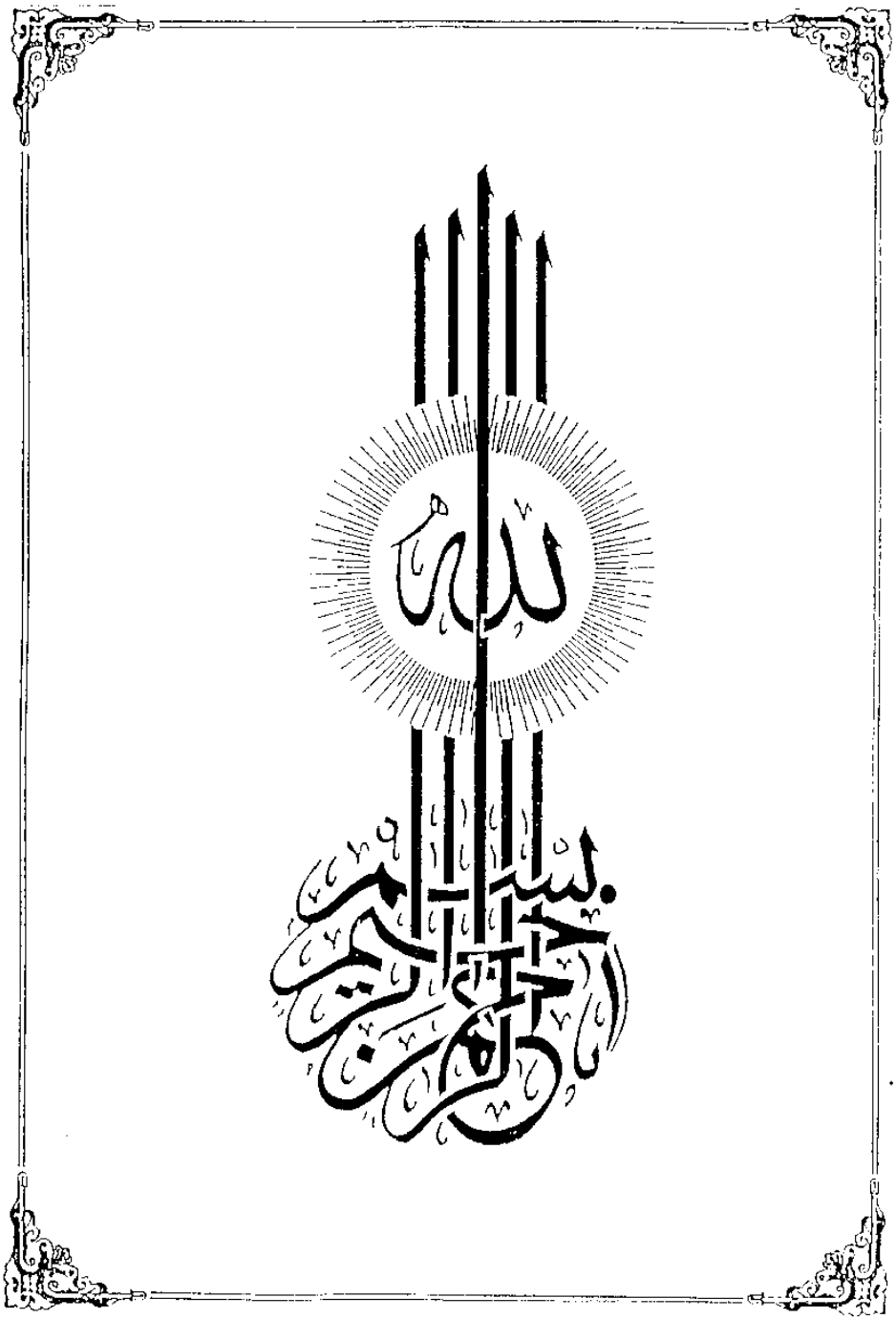

EFFECT OF IONIZING RADIATIONS ON SOME ION EXCHANGE RESINS

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NOTE

The candidcte has attended courses for one year, covering the Following Topics .

1- Photochemistry

2- Spectroscopy

3- Electrochemistry

4- Adv. chem. Reaction

5- Surface. chemistry

6- Polymer. chemistry

7- Kinetic and catalysis

8- Quantun chemistry

9- Thermodynamics

10- Instrumental analysis

She has successfally passed a written examination in these courses in partial fulfillment for the degree of Master of science.

Approved

vice - dean for graduate studies

AIM OF WORK

It would be difficult at present to find a branch of industry which could dispense with the use of ion exchangers. They are used in chemical, metallurgical and food industries, in the manufacture of antibiotics, purification of water, etc. During the past four decades ion-exchange technology has assumed particular importance in connection with the processing of solutions containing radioactive elements. Such use of ion exchange resins has its own typical features, since ionizing radiations produce changes in the physical and physiochemical properties of the ion exchangers. Irradiation of the resins is accompanied by changes in their exchange capacity, swelling tendency, selectivity of sorption, exchange kinetics, etc. At high integral doses (above 10^8 rad) the decrease in the original capacity, caused mainly by the cleavage or destruction of ionogenic groups, as well as the contamination of the processed solutions by the products of radiation-chemical decomposition of the sorbents, may be so considerable that the resins can no longer be employed in the processing of radioactive solutions.

In the present study, the radiation-chemical stability of strongly basic anion exchanger of the polymerization type based on styrene-divinylbenzene copolymers with anchored quaternary ammonium

groups and a weakly basic anion exchanger of the polymerization type based on styrene-divinylbenzene copolymers with aliphatic amino groups was investigated. The radiation stability of the resins was assessed from the change in exchange capacity, loss in weight, change in swelling behavior and the formation of new exchange groups. The resins were irradiated in air and in vacuum, in the air-dry state and in solution and in the OH^-, Cl^- and NO_3^- forms. Nuclear magnetic resonance and electron spin resonance studies were carried out. The limits and possibility for the use of these two anion exchange resins in an intense radiation field are discussed.

CHAPTER (1)

INTRODUCTION

INTRODUCTION

To understand the radiation-chemical processes which take place in individual ion exchange resins in solution, a preliminary survey of the general problems of the radiation chemistry, which have a direct relevance to the radiolysis of these systems must be presented. Since the great majority of all-ion exchange resins used at present are high molecular organic compounds, their irradiation is accompanied by various radiation-chemical reactions typical of high polymers in general. Cross-linking, degradation, gas evolution, change in the degree of unsaturation, oxidation, change in physical and physico-chemical parameters. etc; all take place on the irradiation of ion exchange resins. It should be remembered, however, that ion exchangers in operation are exposed to ionizing radiations while in water or in aqueous electrolyte solutions. Reactions with the radiolysis products of the solutions the numerous intermediate reactions, reactions between the formed products with one another in various ways, and other secondary reactions may substantially affect the course of radiation-chemical reactions in the system resin-solution; in addition the presence of

functional groups in ion exchangers renders the mechanism of these reactions more complex. The general relationship governing the radiation chemistry of water and aqueous solutions and the radiation chemistry of high polymers will be briefly discussed.

RADIATION CHEMISTRY OF WATER AND AQUEOUS SOLUTIONS

A. RADIATION CHEMISTRY OF WATER

Under service conditions the radiolysis of ion-exchange materials takes place in aqueous solutions or electrolytes. When the system ion exchanger-solution is irradiated the effect of the radiation is both direct,i.e., due to the direct absorption of the radiation by the ion exchanger itself, and indirect. The indirect effect may be due to the transmission of the excitation or ionization energy by the water molecules to the sorbent, and also to the reaction between the products of radiolysis of water and aqueous solutions and the molecular, radical or ionic grouping of the sorbent. An oppositely directed energy transfer, i.e. from the excited or ionized groupings of the sorbent to the molecules of water or the solutes, may also take place. The radiolysis of water and aqueous solutions is accompanied by the formation of various reactive products, the first and foremost: hydrogen and OH radicals. The interaction of these radiolysis products with the ion exchanger intensifies, as a rule the radiation chemical damage and brings about a considerable decrease in the radiation resistance of the sorbent in aqueous solutions, as compared to its resistance when irradiated in the dry state.

According to the free radical theory of radiolysis of water, the action of ionizing radiation on water produces H-atoms, and OH radicals[1,2,3]

$$H_2O \text{ —^^^⟶ } H_2O^+ + e^- \quad (1)$$

$$H_2O^+ + H_2O \longrightarrow OH + H_3O^+ \quad (2)$$

$$e^- + H_2O \longrightarrow H + OH^- \quad (3)$$

$$H_2O \text{ —^^^⟶ } H_2O^* \longrightarrow H + OH^* \quad (4)$$

Thus, the radiolysis of water results in the formation of excited and ionized water molecules and electrons. Some of these particles lose their energies as a result of collisions with water molecules or become annihilated by neutralization.

$$H_2O^+ + e^- \longrightarrow H_2O \quad (5)$$

Reactions (1-3) are very fast, thus, depending on the kind and the energy of the ionizing radiation, reaction (1) takes 10^{-18} - 10^{-16} sec reaction (2) and (3) take 10^{-12} - 10^{-11} sec.[4] Reaction (4) is much slower; it takes 10^{-9} - 10^{-8} sec.[5] The OH radicals and H-atoms at sites of high consideration recombine as follows.[6]

$$H + H \longrightarrow H_2 \quad (6)$$

$$OH + OH \longrightarrow H_2O_2 \quad (7)$$

$$H + OH \longrightarrow H_2O \quad (8)$$

with the formation of molecular products of the radiolysis. Direct

formation of molecular products is possible by the collision of two excited water molecules or between an ordinary and an excited water molecule:[7]

$$2H_2O^* \longrightarrow H_2 + H_2O_2 \qquad (9)$$

$$H_2O + H_2O^* \longrightarrow H_2 + H_2O_2 \qquad (10)$$

Thus, the primary products of the action of ionizing radiation on water are H-atoms, OH radicals, hydrogen molecules and hydrogen peroxide molecules. They also include the hydroperoxide radical $HO_2^{\cdot}$, which is probably formed by the reaction[8]

$$H_2O_2 + OH \longrightarrow HO_2^{\cdot} + H_2O \qquad (11)$$

The yield of the hydroperoxide radical is very small and can be neglected in the case of reactions with low LET values (electrons, γ-quanta), but if the irradiated water contains dissolved Oxygen HO_2 is formed in high yields:

$$H + O_2 \longrightarrow HO_2 \qquad (12)$$

In addition to H_2O_2 and H_2, the radiolysis of pure water also yields small amounts of oxygen probably as a result of the following reactions[7]

$$OH + OH_2 \longrightarrow H_2O + O_2 \qquad (13)$$

$$H_2O_2 + HO_2 \longrightarrow H_2O + OH + O_2 \qquad (14)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (15)$$

During the irradiation of carefully purified water not containing