١٠٨٢٣ | ٣

ION EXCHANGE CHARACTERISTICS
OF HYDROUS TIN OXIDE

Thesis Submitted

By

A
EL-SAID IBRAHIM SHABANA

(M.Sc. in Chemistry)

Atomic Energy Authority , Cairo , Egypt

15966

To

Faculty of Science
Ain Shams University

رسالة

For

The Degree of Doctor of Philosophy
in Chemistry

(1987)

Central Library - Ain Shams University

TO

SARA

My Daughter

Central Library - Ain Shams University

بسم الله الرحمن الرحيم

Central Library - Ain Shams University

ION EXCHANGE CHARACTERISTICS OF
HYDROUS TIN OXIDE

Thesis Advisors	Approved
Prof. Dr. N.M.Guindy	Nabila M. Guindy
Prof. Dr. S.S.Abd El-Reheim	....
Prof. Dr. N.Z. Misak	....
Ass. Prof. Dr. N.Sh. Petro	....

Nabila M. Guindy
Prof.Dr.N.M.Guindy
Head of Chemistry Department
Faculty of Science-Ain Shams University

Central Library - Ain Shams University

ACKNOWLEDGEMENT

The author is grateful to the Authorities of the International Atomic Energy Agency, Vienna, Austria, for financial support under Research Contract No. 2716/R2/RB, which provided for many facilities and in particular the numerous analyses performed in this work.

The author wishes to express his deepest gratitude to Prof.Dr.N.M.Guindy, Head of the Chemistry Department, Faculty of Science, Ain Shams University and to Prof.Dr.S. S.Abd El-Reheim, Chemistry Department, Faculty of Science, Ain Shams University, for sponsoring this work at the university, their kind help and encouragement.

The author is greatly indebted to Prof.Dr.N.Z.Misak, Professor of Physical Chemistry, Nuclear Research Centre, Atomic Energy Authority, for suggesting the problem, his continuous guidance, sincere help and valuable discussion during all the stages of this work.

The author wishes to express his thanks to Dr.N.Sh. Petro, Assistant Professor of Physical Chemistry, Lab. of Surface Chemistry and Catalysis, National Research Centre, for her kind help and useful discussions on the evaluation of the surface characteristics of all the samples, and to Prof. Dr.B.S.Girgis, Professor of Physical Chemistry, National Research Centre, Lab. of Surface Chemistry and Catalysis for his kind help and sincere advice.

Central Library - Ain Shams University

Thanks are also due to Dr.I.M.El-Naggar, Lecturer of Physical Chemistry, Nuclear Research Centre, Atomic Energy Authority, for his kind help and kind co-operation during all the stages of the work.

The author wishes to extend his thanks to Prof.Dr.A. S.Emara, Head of the Chemistry Department, Nuclear Research Centre, Atomic Energy Authority, for his kind support and encouragement. The author wishes to thank also all the colleagues of the Nuclear Chemistry Department for their kind co-operation.

Central Library - Ain Shams University

CONTENTS

CHAPTER I

INTRODUCTION

page

Central Library - Ain Shams University

CHAPTER II

EXPERIMENTAL

CHAPTER III

RESULTS AND DISCUSSION

Central Library - Ain Shams University

CHAPTER I

INTRODUCTION

I,1. INTRODUCTORY OUTLINE

Ion exchange by natural Soils(1) has been known since the nineteenth century. At the beginning of the twentieth century, both natural and synthetic aluminium silicates were used for softening water and treating sugar solutions. Later on, synthetic crosslinked polystyrene cationic and anionic resins were prepared and had the advantage of chemical stability. Resins are used for a variety of purposes including separations, recoveries, deionization and catalysis.

The structure and ion exchange properties of organic resins are given in many books, specially those of Kunin (1) and Helfferich(2). For natural and synthetic inorganic exchangers references is made to the books of Helfferich(2), Amphlett(3), Grim(4), the review articles of Pekarek and Vesely(5), and the review articles in the recent book edited by Clearfield(6,7).

Recently, many inorganic ion exchangers have been prepared and studied. These materials are composed mainly of the following groups : hydrous oxides , acidic salts of multivalent metals, salts of heteropolyacids , insoluble ferrocyanides and synthetic clays and zeolites.

With regard to the hydrous oxides , the adsorption properties of oxides such as alumina and silica gels have been known long ago. Until recently, the major intrest in these

Central Library - Ain Shams University

materials was related to their use in analytical fields. Thus, the ion exchange behaviour of hydrous oxides remained for a long time somewhat shadowy because little attention was paid to the kinetics and thermodynamics of exchange on these materials.

The pioneering work in the field of the ion exchange properties of various hydrous oxides was done by the research group at Oak Ridge National Laboratory(8-10). Several review articles are now available on the ion exchange properties of hydrous oxides(3,5,15-18).

In fact, hydrous oxides as inorganic ion exchangers offer many advantages over organic resins. They exhibit good thermal and radiation stability. In addition, some hydrous oxides exhibit excellent selectivities for certain elements or groups of elements(7). Most of these hydrous materials can be prepared more easily and cheaply than organic resins. They have rigid structures which undergo little swelling or shrinking upon immersion in aqueous solution(7). They show resistive behaviour towards strong oxidizing reagents and organic solvents. Their major disadvantage is their lower resistance towards strong acid and base solutions at relatively high concentrations as compared with organic resins, although improved resistance can be obtained through aging or heating(7).

Hydrous oxides were reported to be useful in cation and anion separations, decontamination of waste water, and

Central Library - Ain Shams University

removal and separation of various radioactive nuclides from reprocessing solutions and sea water(5). Now, hydrous oxides are being recognized as efficient means for the separation of long-lived fission products from high-level and medium-level waste, waste disposal, and separation and purification of actinide elements from various sources(8-11). Ion exchange membranes that can be used for desalination of water have been made from hydrous oxides and hydrous oxide/phosphate mixtures(3,5).

I,2. KINETICS OF ION EXCHANGE :

As is well-known, when the rate of ion exchange is controlled by diffusion of ions in the liquid film adhering to the exchange particles, the rate increases with the increase of stirring velocity (till a certain limit of this velocity) and solution concentration. Besides, the rate is proportional to the first power of particle radius. For film diffusion control, the following equation applies(19-21) :

$$-\log (1-Q_t/Q_e) = Kt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where Q_t and Q_e are the amounts exchanged at time t and at equilibrium, respectively. Strictly speaking equation (1) is applicable for isotopic exchange or for the sorption of a trace ion but nevertheless it can be applied as a first approximation for ordinary batch ion exchange systems when the nature of the rate determining step is established(2).

When the exchange rate is governed by the diffusion of

Central Library - Ain Shams University

ions inside the exchanger particles, the rate of ion exchange is independent of solution concentration or stirring velocity and is proportional to the second power of the particle radius.

The following equation has been proposed for particle diffusion control when the sorbed ion is a microcomponent of the exchanger and the solution concentration is constant (21) or when the exchanger is transformed completely from one cationic form to the other cationic form (22) :

$$Q_t/Q_e = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n \pi^2 Dt/r^2} \quad ....(2)$$

D is the internal diffusion coefficient of the sorbed ion which is a microcomponent of the exchanger and is an effective internal diffusion coefficient of the system when the exchanger is transformed completely from one cationic form to the other , r is the particle radius and n is an integer number.

When a trace ion is exchanged from a finite solution volume in the presence of a large excess of another counter ion in both the exchanger and solution, the following equation gives the internal diffusion coefficient of the trace ion (2,23) :

$$Q_t/Q_e = \frac{w+1}{w} \left(1 - \frac{1}{\alpha - \beta} \left[\alpha \exp(\alpha^2 \tau)(1 + \text{erf}\, \alpha \tau^{1/2}) - \beta \exp(\beta^2 \tau)(1 + \text{erf}\, \beta\, \tau^{1/2}) \right] \right) \quad ....(3)$$

Where α and β are the roots of the equation :

$$x^2 + 3wx - 3w = 0 ,$$

Central Library - Ain Shams University

w is the ratio of the number of milliequivalents of the trace ion in the exchanger to that in the external solution, and

$$\tau = Dt/r^2$$

The following equation was used(20) at the initial stages of exchange for particle diffusion control in batch systems :

$$Q_t/Q_e = \frac{6}{r} \cdot \frac{Q_o}{Q_o - Q_e} \sqrt{\frac{Dt}{\pi}} \qquad \ldots\ldots\ldots\ldots(4)$$

Where Q_o is the initial amount of sorbed cation present in contact with an amount of exchanger containing an equivalent amount of the other ion, and D is a nominal diffusion coefficient.

Film diffusion control(2) is favoured by high capacity, low degree of crosslinking, small particle size, low concentration, inefficient agitation and by preference of the ion exchanger for the sorbed counter ion. The rate of the ion exchange step itself is usually very fast and does not determine the overall rate except when the exchanging ions form sluggishly reacting complexes with the functional groups , e.g. , in chelating resins. In the latter case, the ion exchange rate is independent of the exchanger particle size(21).

I,3. THERMODYNAMICS OF EXCHANGE :

The first approach to the thermodynamics of ion exchange is based on a Gibbs-Donnan equilibrium(24). According to this approach , we have the following equation for the uni-univalent exchange :

Central Library - Ain Shams University

$$AR + B^+ \rightleftharpoons BR + A^+ \;;$$

$$RT \log K_a = RT \log K + RT \log \frac{f_{B^+}}{f_{A^+}} - RT \log \frac{\gamma_{B^+}}{\gamma_{A^+}}$$

$$+ \frac{P}{2.3} (\bar{V}_B - \bar{V}_A) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

K_a is the thermodynamic equilibrium constant, f_{B^+} and f_{A^+} are the activity coefficients of the ions B^+ and A^+ in the exchanger salts BR and AR , respectively, γ_{B^+} and γ_{A^+} are the corresponding coefficients in solution, P is the osmotic pressure difference between the exchanger and solution phases , $\bar{V}_B$ and $\bar{V}_A$ are the partial molar volumes of the exchanger salts BR and AR, respectively , and K is the selectivity coefficient given by :

$$K = \frac{\bar{m}_{B^+} \cdot m_{A^+}}{\bar{m}_{A^+} \cdot m_{B^+}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where $\bar{m}_{A^+}$ and $\bar{m}_{B^+}$ are the molalities of A^+ and B^+ in the exchanger while m_{A^+} and m_{B^+} are their molalities in solution.

If the same reference state is chosen for the ions in both the solution and resin phases, we get the equation :

$$\log K_a = \frac{P}{2.3\ RT} (\bar{V}_A - \bar{V}_B) - \log \frac{f_{B^+}}{f_{A^+}} + \log \frac{\gamma_{B^+}}{\gamma_{A^+}} \ldots (7)$$

This approach was initiated by Gregor(25) for ion exchange resins and later by Bukata and Marinsky(26) for very open zeolites.

Central Library - Ain Shams University

Gaines and Thomas(27) gave the first thermodynamically most rigorous treatment of ion exchange. According to these authors, we have the following equation for uni-univalent exchange :

$$\log K_a = \int_0^1 \log K' d\, N_{BR} + \int_{a_w(N_{BR}=1)}^{a_w(N_{AR}=1)} n_w d \log a_w + \int_{a_w\ (N_{BR}=1)}^{a_w(N_{BR}=1)} (V_B / \tau - n_w) d \log a_w$$

$$- \int_{a_w(N_{AR}=1)}^{a_w(N_{AR}=1)} (V_A / \tau - n_w)\ d \log a_w \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where V_B and V_A are the equivalent volumes of the pure B- and A-forms of the exchanger, τ is the molar volume of water vapour, n_w is the number of moles of water of activity a_w associated with one equivalent of the exchanger, and K' is the selectivity coefficient K corrected for the solution phase activity coefficients. K is given by the equation :

$$K = N_{BR} . m_{A^+} / N_{AR} . m_{B^+} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where N_{BR} and N_{AR} are the mole fraction of the exchanger components BR and AR , respectively , and K' is given by the equation :

$$K' = N_{BR} \ . \ m_{A^+} \ . \ \gamma_{A^+} / N_{AR} . \ m_{B^+} \ . \ \gamma_{B^+} \ \ldots\ldots\ldots\ldots (10)$$

The first integral in equation (8) takes into consideration the dependence of the corrected selectivity coefficient K' on the exchanger composition. The second integral takes into consideration the variation of water sorption when going

Central Library - Ain Shams University