STUDIES ON SURFACE PROPERTIES OF SOME HYDRATES

Theses Presented in Partial Fulfilment
of the Requirements for

THE MASTER OF SCIENCE DEGREE
IN CHEMISTRY

University College for Women - Ain Shams University,
Cairo.

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B.Sc. Special Degree

1973

The author dedicates this thesis to her husband and her parents who were always beside her .... spreading an air of confidence and encouragement.

بسم الله الرحمن الرحيم

Studies on Surface Properties of Some Hydrates.

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ACKNOWLEDGEMENT

The author expresses her thanks, and is also greatly indebted to Professor Dr. R. Sh. Mikhail, Professor of Physical Chemistry, Faculty of Science, Ain Shams University, Cairo, for his keen interest in the advancement of this work, his masterly guidance, his continuous encouragement and his helpful advice while carrying out the present work.

Finally she expresses her thanks and gratitude to Professor Dr. W.I. Awad, Chairman of Chemistry department, University College for women, Ain Shams University, and actually present in Baghdad University for his continous help in facilitating the conditions required for the present work.

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CHAPTER I

A. GENERAL INTRODUCTION

It has been estimated that three-fourths of the surface material on the crust of the earth is water. Animals, plants, as well as solid materials, contain a large proportion of combined water. This clarifies that water is in a permanent circulation in nature; and it is no more surprising to find extensive scientific studies on this material in the world.

It is well known that, water is widely distributed in its three states of matter: steam or aqueous vapor, liquid water, and solid ice or snow.

Water is chemically classified as a hydride of oxygen and the fact that it is a liquid at ordinary temperatures whereas hydride elements near oxygen in the periodic table are gases, indicates the existence of a special kind of interaction between neighboring molecules. These interactions explain the low density of liquid water compared to molecules of similar size, the abnormal increase in density from zero to + 4° and the abnormal mobility of proton and hydroxyl ions.

The structure of water has been studied by Bernal and Fowler, in 1933(1)(2), and they found that it is different at ordinary temperatures than at low temperatures.

Water exhibits a marked tendency to form additive compounds with other substances of the kind known as molecular compounds. This property is believed to be due to the electronic structure of the water molecule, which may be represented as - $H:\underset{..}{\ddot{O}}:H$ - and which thus contains two "lone-pairs" of electrons, which can form co-ordinate linkages. The most important of these compounds are the hydrates - particularly salt hydrates.

However, water is a convenient solvent for most salts during recrystallisation processes. Thus, by separating the pure compound from its solution, it may contain water of crystallisation, in other words hydrates are obtained.

It has been shown that in the group of simple alkali halides, the CO_3^{--}, SO_4^{--} of alkaline earths, Zn, Cd, Mg and transition elements the formation of crystalline hydrates is more pronounced as the ionic bonding of cations and anions in the anhydrous compound increases. Crystalline hydrates in covalent compounds are not known.

Thus a hydrate can be defined as a compound in the crystal of which discrete water molecules may be distinguished.

Hydration of positive ions is limited by the covalency rule, and when the permissible maximum is exceeded, Werner's suggestion of double water molecules occupying one coordination position is adopted.

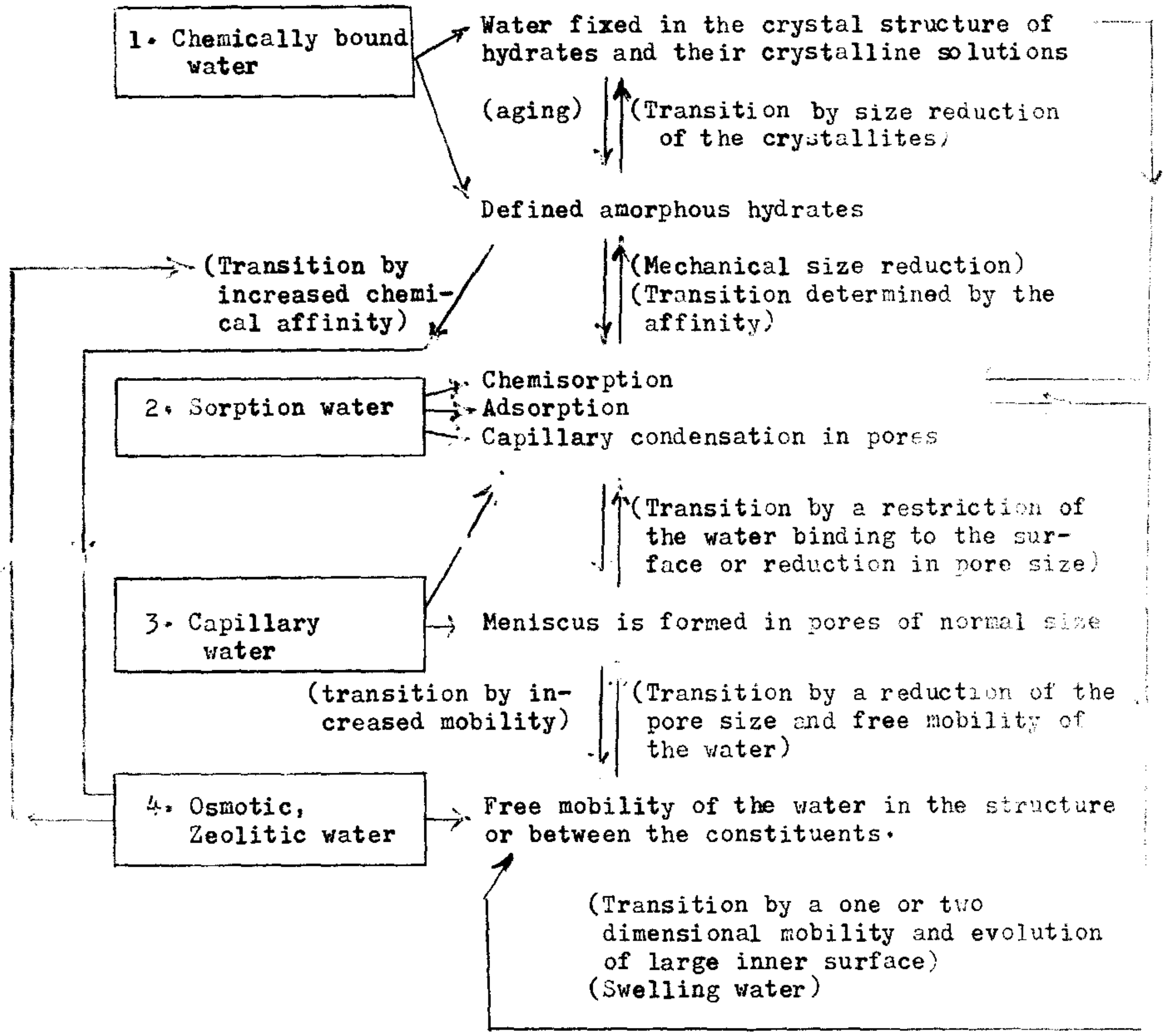
Sidgwick$^{(3)}$ concluded that, hydration of negative ions is exceptional but well established in certain cases. This is applicable for the hydrated sulfates containing odd numbers (1,5,7) of water molecules. It was assumed that one water molecule is definitely associated with the sulfate ion; it is now known that this is not the case, but there is another modern view for the arrangement of bonds to the odd water molecule; thus in case of $CuSO_4 \cdot 5H_2O$ for example, the metal ion is 6-coordinated; although there are only five water molecules for every cupric ion, yet, the fifth is not attached to the cation. Instead, the coordination group around the cupric ion is composed of four water molecules, and two oxygen atoms of the sulfate ion, and the fifth water molecule is held between the water molecules attached to the cation and the oxygen atoms of the sulfate ion. In other words, compounds of the type $MSO_4 \cdot H_2O$ where M= Mg, Zn, Cu, etc. are derivatives of mesosulfuric acid (H_2SO_5) rather than metasulfuric acid (H_2SO_4) and they should be represented as $MSO_4(OH)_2$ rather than $MSO_4 \cdot H_2O$.

A characteristic of most hydrates is that the removal of water leads to the collapse of the crystals, the structure of the anhydrous material bearing no simple relation to that of the hydrate. On the other hand, there are certain crystals which has the remarkable property of absorbing water, and this water can be subsequently removed without radically altering the crystal; i.e. reversible hydration or dehydration may take place without alteration in the size of the unit cell.

The above classification is quite general, a more specific classification, has been proposed by Gruner, Bernal, Konta and

Barrer. Gruner, in 1948(4), differentiated between chemically bound water, sorption water, capillary water, and finally osmotic zeolitic water. This is shown in the following diagram.

Gruner's Classification



Bernal in 1951(5), suggested another classification, in which he paid particular attention to the arrangement of water molecules. This classification can be summarized as follows :

A. <u>Nesohydrates</u>

(i) Isolated water molecules, for example $AlF_3 \cdot \frac{1}{2}H_2O$

(ii) Cation co-ordination shells, for example $Ba(H_2O)Cl_2$

(iii) Cation co-ordination shells filled, for example $Ni(H_2O)_6SO_4$

(iv) Water in excess of cation, for example $Cu(H_2O)_4SO_4(H_2O)$

(v) Acid hydrates, for example $(COOH)_2 \cdot 2H_2O$

B. <u>Phyllohydrates</u>

(i) Water in layers bound by ions, for example $CaSO_4 \cdot 2H_2O$, apophyllite

(ii) Water in layers bound by hydroxyl ions, for example vermiculite, montmorillonite and halloysite .

C. <u>Inohydrates</u>

(i) Water along continuous non intersecting channels, for example attapulgite, sepiolite.

(ii) Water along continuous intersecting channels, for example chabasite, harmotome, faujasite and other zeolites.

D. <u>Tectohydrates</u>

Water forms continuous three dimensional net work, for example gas hydrate.

Konta, in 1952(6), modified Gruner's classification. He emphasized the importance of differentiating between chemically bound water, and free water, and between adsorbed water and capillary water