CHAPTER IV

RESULTS AND DISCUSSION
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IV. 1: INTRODUCTION:

The application of Physical Chemistry to dye-adsorption problems was fairly at a crude level until the 1930's. A group of investigators, under T. Vickerstaff, began to establish the subject which seriously attracted the Physical Chemists, and his book, "The Physical Chemistry of Dyeing", published in 1950's, had a very great influence in attracting the interest of chemists. The subject of chemistry of dye-adsorption is very wide, complex and covers a vast literature. The Thesis inevitably touches upon the following: Chemical pretreatment of the hydrous oxides of tin and zirconium, study of the adsorption-desorption behaviour of some anionic and cationic dyes on the synthesised substrates of varying surphase-phase pH, and utilisation of the observations in column separation of certain synthetic dye-mixtures.

IV. 2: THE SURFACE OF HYDROUS TIN AND ZIRCONIUM OXIDE:

Stannic oxide (H2O) and Zirconium oxide (H2O) belong to the family of the quadrivalent element oxides, MO2. These hydrous oxides show acidic groups (Chapter I), and behave either as cation exchanger or
anion exchanger, depending upon the basicity of the central atom (M), and the strength of the M-O bond, relative to that of the -OH bond; provided that the -OH groups are the only Brønsted acidic groups present. The acidity scale of different oxides is established by comparison of the pH of the isoelectric points (pH$_i$). The acidic strength decreases in the order: SiO$_2$, MnO$_2$, SnO$_2$, TiO$_2$, ZrO$_2$, and so do the capacities for cation-exchange in basic media. The values of pH of the isoelectric point depend on the structure of the oxides, and especially on their crystallinity.

During the hydrolysis of many metal ions, positively-charged polymers are formed on the acid side of the isoelectric point, and negatively-charged polymers have been reported on the alkaline side. If these polymeric aggregates are arranged into an insoluble 3-dimensional network, anion-and cation-exchangers should result. If the counter-ions are negatively-charged, one speaks of an anion exchanger, and if they are positively-charged, of a cation-exchanger. In a useful exchanger, these counter-ions should be readily diffusible. The insoluble 'hydroxides' or hydrous oxides would be reminiscent of weakly acidic cation exchangers in the H-form or weakly basic exchangers in the free base form. Such a network would become charged on treatment with acids or bases.
It has been mentioned (Chapter I) that surface of hydrous tin oxide and zirconium oxide contain surface-hydroxyl groups which exhibit amphoteric behaviour because of the following reactions:

\[ \text{M} \rightarrow \text{M} + \text{OH}^- \quad \text{(1)} \]

\[ \text{M} \rightarrow \text{M}^- + \text{H}^+ \quad \text{(2)} \]

OR

\[ \text{M} \rightarrow \text{M}^+ + \text{OH}_2^- \quad \text{(3)} \]

\[ \text{M} \rightarrow \text{M}^- + \text{H}_2\text{O} \quad \text{(4)} \]

(species on the surface)

In the above equilibria, reactions (1) & (3), producing anion-exchange properties are favoured by low pH, whereas the reactions (2) & (4), which are favoured by high pH, result in cation-exchange characteristics. The anion-exchange to cation-exchange transition pH\(^{3,4}\) of HSO is 4.5 - 5.5, whereas the pH for HZO is 6 - 7.

It has also been said (Chapter I) that pre-treatment of the substrates with an amount of acid (HCl, H\(_2\)SO\(_4\)) or alkali (NaOH), insufficient to dissolve them, often yields the so-called basic and acid salts,
respectively. Treatment of the substrate HSO with NaOH may cover the surface with Na⁺ ions, whereas the acid-treatment of HZO will cover the surface with the acid-anions (Cl⁻, SO₄²⁻), as shown below:

\[ \text{Sn} - \text{OH} + \text{Na}^+\text{OH}^- \rightarrow \text{SnO}^- + \text{Na}^+ + \text{H}_2\text{O} \quad \ldots (5) \]

\[ \text{Zr} - \text{OH} + \text{H}^+\text{X}^- \quad \text{or} \quad \text{Zr}^+ + \text{X}^- + \text{H}_2\text{O} \quad \ldots (6) \]

\[ \text{Zr} - \text{OH} + \text{H}^+\text{X}^- \leftrightarrow \text{Zr}^+ + \text{X}^- + \text{H}_2\text{O} \quad \ldots (7) \]

The anions may either be covalently bound or present ionically (as hydrated ions), depending upon the nature of the anion. The anions may be replaced by other ions in water or other polar medium, and this may form the basis of sorption of the anionic dyes. Adsorption of the cationic dyes can take place by the replacement of Na⁺ by the dye-cations. Further, the formation of the ionised anion (X⁻) or cation (Na⁺) is favoured by an increase in the concentration of acid or alkali used for the pretreatment. It has also been remarked earlier that since Na⁺ and Cl⁻/SO₄²⁻ are usually much lower than H⁺ and OH⁻ ion, respectively (ion-selectivity series), they can be exchanged by other ingoing cations (e.g. dye-cations) or anions (like dye-anions).

The relative importance of cation- and anion-exchange properties is different for different oxides,
and it has been shown \(^6\) that Zr (IV) has more anion-exchange capacity in acidic solutions than Sn (IV), and the latter has more cation-exchange capacity in basic solutions. In view of this, HSO samples of surface pH 4.0 - 11.0, and HZO of surface-pH 1.0-7.0 were employed as substrates in the present study.

Nothing appears to be known of the adsorption of anionic dyes on chemically-pretreated HZO. A few studies of the adsorption of brilliant cresyl blue and safranine-T on HSO, treated with NaOH, has been reported recently \(^7\).

IV. 3: THE DYES:

All synthetic dyes, with few exceptions, are aromatic organic compounds. They may be divided into non-ionic and ionic (anionic & cationic). The molecules of ionic dyes are composed of two main parts, one of which is complex aryl radical, and it is the colour-imparting ion. If the balance of the charge on the dye-ion is positive, the dye is classed as 'cationic'. On the other hand, if the balance of the charge on this ion is negative, then the dye is classed as 'anionic' \(^8\). The second part of an ionic dye molecule is generally an inorganic ion of opposite charge to that of the colour-imparting aryl ion. (sometimes called gegenion). The function of the gegen-ion is to balance the charge on the dye-ion, and to render the dye water-soluble.
With few exceptions, anionic dyes are manufactured as metallic salts, and the vast majority of them are the sodium salts of sulphanic acids (such as Na^+D^-). In case of cationic dyes, the gegen-ion is usually the chloride ion. The majority of the anionic dyes may be regarded as amphoteric, since they possess side chains which are basic in reaction.

The dye molecules can also be described as made up of chromophore and auxochrome. A colligating is a special kind of auxochrome which can be either basic or acidic in nature. It can be positively or negatively charged. The most important basic colligators found in cationic dyes are, \( \overset{>}{\text{N}}^+ \), \( \overset{>}{\text{NH}} \) and \( -\text{NH}_2 \). The acid colligators found in anionic dyes are \(-\text{SO}_3^-\), \(-\text{SO}_3^\text{H}\), \(-\text{SO}_3^\text{Na}\), \(-\text{COOH}\), \(-\text{OH}\) and \(-\text{ONa}\).

The structural characteristics of the dyes taken up in the present work are discussed in IV.11.

IV. 4: MECHANISM OF ADSORPTION:

From the above discussion, it can be said that the organic electrolytes (the dyes) may be adsorbed by the chemically-pretreated substrates (HSO & HZO), probably by three mechanisms:

(i) A predominant ion-exchange of the single dye-ions,

(ii) Ion-exchange of aggregates of the dye-ions,
and, (iii) Covalent bond formation (chemisorption).

The exact mechanism in any given case is not known precisely, but it seems likely that all the three mechanisms may operate, although each to a different extent, depending upon: (a) the history of the oxide surface i.e., its surface-phase pH, (b) the acid or alkali used for its pretreatment, and hence, the anion or cation present thereon, and (c) properties of the dye.

The experimental observations are now taken up to explore a possible mechanism of adsorption, and to evaluate how far the alkali (NaOH) or acid (HCl, H_2SO_4) pretreatments bring about change in the sorption behaviour of the substrates.

IV. 5: TIME-VARIATION STUDIES:

The time required to attain equilibrium may throw light into the mechanism of adsorption. Generally, when the phenomenon occurs rapidly, the forces involved are considered to be coulombic (ion-exchange) and van der Waals forces. However, there are several ion-exchange processes in which the uptake is time-dependent.

(A) The studies with HSO:

The data (Tables 5 & 6, Figs. 3-5) indicate that adsorption of the cationic dyes from aq. solution is a fast process. Thus, at the pH of maximum sorption
(pH 8.5 MV, JR, pH 9.5 PS), 10 min-contact brings about 10-58% (MV), 28-65% (JR) and 33-75% (PS) adsorption of the dyes. The equilibrium appears to be established in 6 hr (MV) and 24 hr (PS & JR). The degree of adsorption with time appears to increase (Table 5) with increase in surface-pH (6.0 - 8.5). Thus, at pH 6.0 and the \([\text{Dye}]_0 = 1.80 \times 10^{-3} \text{ M}^{-1}\), 10 min-contact hardly shows 8% (MV), 6% (JR) and 1% (PS) adsorption. However, the degree of adsorption is quite marked at the lower concentrations of the dyes.

(B) The studies with H2O:

(a) HCl-treated H2O: (Tables 16 & 17, Figs. 12-14): The adsorption of the anionic dyes is quite marked in the early stages of adsorption. Thus, at the highest dye concentration (2.0\( \times \)10^{-3} \text{ M}^{-1}) and at surface-pH 3.0, the percentage-adsorption of the dyes in 10 min is: 15 (LG), 49 (OG) and 16 (NBB). However, at the lower dye-concentrations (say, 0.20\( \times \)10^{-3} \text{ M}^{-1}) the affinity for the substrate is quite more (25% LG & 85% NBB, 10 min). The equilibrium reaches in 24 hr (LG, NBB). OG at lower concentrations (< 0.80\( \times \)10^{-3} \text{ M}^{-1}) reaches the equilibrium state in 1 hr only.

(b) H_{2}SO_{4}-treated H2O: (Tables 18 & 19, Figs. 15-17): The data at pH of maximum adsorption (pH 5.0 LG & NBB, pH 4.0 OG, \([\text{Dye}]_0 = 2.0 \times 10^{-3} \text{ M}^{-1}, 10 \text{ min}) shows
38-50% sorption which reaches to 40-90% at the lower concentrations (Table 18). The equilibrium reaches in 24 hr (OG, NBB). The typical behaviour of LG at the dye concentration < $0.60 \times 10^{-3}$ m$^{-1}$ has been referred in Chapter III 'E'.

Thus, the greater degree of adsorption in short time-interval, especially at the lower dye concentrations, indicates ion-exchange nature of the sorption process. The possible reason for the slow attainment of equilibrium at the higher dye-concentrations may be the adsorption of large dye-ions, which exist as aggregates of a number of ions or molecules in aq. solution.

IV. 6: TEMPERATURE-VARIATION STUDIES:

The effect of temperature upon adsorption isotherms can throw light upon the mechanism of sorption. In general, adsorption by ion-exchange is athermic while chemisorption is usually exothermic with high values of heat of adsorption ($Q$). The extent of adsorption of solutes normally decreases with rise of temperature. However, some dye-stuffs show endothermic nature of adsorption also. This has been explained in terms of the adsorption of aggregates by the surface. This aspect is discussed at a later stage. The data is now examined in the light of the above.
The studies with HSO: The observations (Tables 9-11, Figs. 8-10) show that adsorption of MV (pH 6.0 - 8.5) and PS, JR (pH 6.0 - 11.0) in the temperature-range 30°-50°, is endothermic with 'Q' (iso-steric heat) values of 59-23·8kJ/mole. The apparent endothermic nature of the phenomenon may be due to association of the dye molecules in solution13,14 which disaggregate at higher temperatures. The dye-species reaggregate at the substrate surface during adsorption, either immediately before or at the moment of attachment to the surface. It is known that the dye-aggregation process is exothermic, and it does not explain endothermicity. The endothermic binding may be due to an increase in the number of species, responsible for adsorption, with temperature, as a consequence of uncoiling of the dye-aggregates in the substrate. The randomisation of such aggregated chains due to dye-substrate interaction would produce a considerable entropy gain, and this may be the cause coupled with an associated breaking of hydrogen bonds to give endothermic adsorption.

The heat of adsorption (in vapour phase) normally decreases with increasing amount adsorbed, and then tends to level out. The trends of 'Q' values (Table 11) are rather scattered. The general cause for a variable heat of adsorption are surface-
heterogeneity and adsorbate-adsorbate interactions\textsuperscript{15,16}. It, therefore, appears that a single reaction is not responsible for the 'Q' values. It is, therefore, likely that a combined effect of the following factors may contribute to the 'Q' values – more than one type of adsorption phenomenon, adsorbate-adsorbate interactions, solvent/adsorbent or adsorbate interactions. It has been reported in the literature\textsuperscript{17,18} that adsorption of large ions such as organic dyes on inorganic surfaces can take place by two distinct mechanisms, operating simultaneously. It may be said that the adsorbed molecules, after primary adsorption (ion-exchange) may proceed to diffuse into the micropores of the solid substrates.

(B) The studies with HZO: (Tables 23-28; Figs. 22-26):

The adsorption on HCl-treated samples (pH 1.0 - 7.0, Table 23, 24) is endothermic with 'Q' values of 40 to 62 kJ/mole (Table 25). The behaviour on H\textsubscript{2}SO\textsubscript{4}-treated samples (Tables 26, 27) is exothermic, and the 'Q' values are -7.5 to -42 kJ/mole (Table 28). As discussed in the case of adsorption of the cationic dyes on HSO, a single reaction does not appear to be responsible for the adsorption phenomenon.
IV. 7: SURFACE-pH OF SUBSTRATES AND ADSORPTION:

(A) The studies on HSO:

It has already been mentioned in the beginning of this chapter and chapter I that the effect of pre-treatment of tin oxide with NaOH is to convert it from the $H^+$-form to $Na^+$-form, and this form leads to much-more favourable equilibrium than that of the latter form. Further, the ionically-bound sodium content of tin oxide appears to increase continuously with increasing pH. Thus, the cation-content of HSO becomes essentially negligible at pH $< 4.0$, and maximum at pH $11.0$. The data in Table 1 show that the $Na^+$ ion-content and the $H^+$ ion-exchange capacity of the tin oxide samples range from $0.01 - 0.80$ mg-ion/g and $0.08 - 1.10$ meq/g, respectively for substrates of surface pH $4.0 - 11.0$.

At higher pH values, the $H^+$ ions of the substrate tend to dissociate from the oxygen of surface $-OH$, leaving a net $-ve$ charge on the surface. This will attract the dye-cations. As the pH is lowered, additional $H^+$ ions may associate with the surface $-OH$, leaving a $+ve$ charge on the surface, as shown below:

\[ \text{SnO}^- \rightleftharpoons \frac{+H^+}{-H^+} \text{SnOH}^0 \rightleftharpoons \frac{+H^+}{-H^+} \text{SnOH}_2^+ \ldots (8) \]

Surface at high pH \hspace{1cm} Surface at low pH.
The experimental observations of this study are reported in Tables 7 & 8 and Figs. 6 & 7. It is observed that the degree of adsorption depends on the surface-pH of HSC; it increases in the pH-range 5.0 - 8.5 (MV, JR) and pH 5.5 - 9.5 (PS). However, a gradual decrease in sorption occurs at pH > 8.5 (JR) and pH > 9.5 (PS). MV gets precipitated at pH > 8.5. Maximum sorption is shown at pH 8.5 (MV, JR) and pH 9.5 (PS). The adsorption behaviour of the dyes with respect to pH may be explained as per equation (8).

In the favourable range of adsorption, the dyes appear to be adsorbed predominantly by ion-exchange, as also indicated by L-type isotherms (JR, PS). However, the isotherms of MV are of S-type. The S-shape represents the case in which it becomes easier for the molecules to get adsorbed, as adsorption proceeds. Molecules already adsorbed enter into inter-molecular binding, and assist further adsorption. The species taking part in adsorption upto pH ~ 8.5 (MV, JR) and pH 9.5 (PS) appear to be the dye-cations, and above these pH, the proportion of the dye-cations decreases, resulting in the decrease of adsorption. It is to be mentioned here that tin oxide has been treated with quite concentrated aq. NaOH (Chapter II). If it is assumed that the alkali is leached out from the oxide surface at high pH values, the alkali-ions may compete for the surface; resulting in decrease in the
degree of adsorption (pH > 8.5 JR, pH > 9.5 PS). Also, the content of the Na⁺-ions on the surface (Table 2) decreases at low surface-pH values, resulting in substrates having no affinity for the dyes (pH < 5.0 MV, JR and pH < 5.5 for PS). The maxima in the isotherms at pH 8.5 (MV, JR) and pH 9.5 (PS) may be due to strong adsorbate-adsorbate and/or solute-solvent interactions, in comparison to that of the adsorbate-adsorbent interaction. It is likely that the alkali-ions on the substrate surface may also compete for the surface at pH of maximum sorption. Maxima in the adsorption isotherms of cationic dyes have also been reported⁹ to indicate their association in solution.

Percentage-adsorption versus pH values for the dyes (Fig. 7) also indicate their adsorption in different phases.

(B) The Studies on H₂O:

(a) HCl-treated H₂O:

It has been shown (Table 20, Figs. 18 & 19) that adsorption of the anionic dyes increases with decrease in pH of the substrates (OG, NBB pH 7.0 to 3.0, LG pH 7.0 to 2.0), and maximum sorption (not 100%) occurs at pH 2.0 (LG) and pH 3.0 (OG, NBB). It is also observed that sorption of NBB gradually decreases at pH < 3.0. However, OG exhibits decreasing
adsorption at pH 3.0 - 2.0, followed by increase in the phenomenon at pH 2.0 - 1.0. Adsorption of LG, however, remains constant at pH < 2.0. Further, the rate of Cl⁻-dye anion-exchange appears to be proportional to the concentration of ingoing ions (at higher dye-concentrations). The adsorption by anion-exchange appears to occur in two stages - rapid exchange of the dye-anions (simple or micelles) at sites followed by slow exchange at sites within the substrate.

It has been shown (Table 2) that ionically-bound Cl⁻ ion-content of H₂O decreases with increasing pH (pH 7.0 - 3.0, 0.005 - 0.05 mg-ion/g), and so adsorption of the dyes is minimum at pH 7.0. Further, the observations can also be interpreted by the protonation and exchange reactions taking place at higher pH as shown below:

\[ \text{Surface at high pH:} \quad Zr - O^- \xrightarrow{+H^+} Zr - OH^- \xrightarrow{+H^+} Zr - OH_2^+ \quad \cdots (9) \]

Thus, at high pH-values, the H⁺ ions of the Zr - OH of the substrate tend to dissociate from the oxygen, leaving a -ve charge on the surface. So, the dye-anions will be repelled, and the adsorption is checked. As the pH is lowered, additional H⁺ may associate with
the -OH, leaving a net +ve change which will attract the dye-ions, and also the adsorption is favoured.

At pH < 3.0, concentration of the chloride ions on the H2O surface and also in the adsorption bath increases, and the ionic species responsible for adsorption decrease. Further, there may be competition between the dye molecules and the undissociated acid molecule (HCl), which result in decrease of adsorption. Thus, the affinity of the dyes decreases at pH < 3.0.

(b) H2SO4-treated H2O:

The results (Table 22 and Figs. 20) show that the adsorption of the dyes on H2SO4-treated H2O increases with decrease in surface-pH of the substrate (LG and NBB pH 7.0 - 5.0, OG pH 7.0 - 4.0). Maximum adsorption (although not 100%) occurs at pH 5.0 (LG, NBB) and pH 4.0 (OG). Also, decrease in sorption with pH occurs. Thus, the adsorption of LG and NBB decreases at pH < 5.0 while that of OG takes place at pH < 4.0. Thus, in the favourable range of adsorption (LG & NBB pH 5.0 - 7.0, OG pH 4.0 - 7.0), the solutes are essentially the ionic species. At pH < 5.0, the concentration of SO4^2- ions on the substrate surface and also in the adsorption bath increases, and the ionic species taking part in the adsorption decrease. At pH > 7.0, the proportion of SO4^2- ions diminish, resulting in decrease of adsorption.
Percentage adsorption versus pH values for the dyes on the substrate (Fig. 21) also indicate adsorption of the dyes in different phases (monodispersed & aggregates).

IV. b: REVERSIBILITY OF ADSORPTION

One can judge operation of the ion-exchange behaviour by:

(a) The effect of inorganic salts added to the adsorption bath (i.e., adsorption in competitive systems),

and,

(b) behaviour of the loaded adsorbates with desorbents.

IV. c: Adsorption in presence of electrolytes

This study incorporates the effect of addition of aq. solution of inorganic salts to the adsorption bath. To analyse the situation, one has to consider the possible interactions between the competing adsorbates, under the situation studied in the present work.

When more than one strongly binding adsorbate is present in a system, involving electrostatic interaction as the driving force for adsorption, then adsorption of each ion may affect that of the others in several ways like:
Percentage-adsorption versus pH values for the dyes on the substrate (Fig. 21) also indicate adsorption of the dyes in different phases (monodispersed & aggregates).

IV. 8: **REVERSIBILITY OF ADSORPTION:**

One can judge operation of the ion-exchange behaviour by:

(A) The effect of inorganic salts added to the adsorption bath (i.e., adsorption in competitive systems),

and,

(B) Behaviour of the loaded adsorbates with desorbents.

IV. 8:'A': ** ADSORPTION IN PRESENCE OF ELECTROLYTES:**

This study incorporates the effect of addition of aq. solution of inorganic salts to the adsorption bath. To analyse the situation, one has to consider the possible interactions between the competing adsorbates, under the situation studied in the present work.

when more than one strongly binding adsorbate is present in a system, involving electrostatic interaction as the driving force for adsorption, then adsorption of each ion may affect that of the others in several ways like:
(i) Change in the surface potential.

(ii) Competition between the ions for the available binding sites on the substrate.

(iii) Bridging.

(i) Let 'A' be the ion whose adsorption behaviour is being investigated in presence of the competing ion 'C'. Adsorption of 'C' may enhance or diminish the electrostatic contribution for adsorption of 'A', and this depends on the relative net-charge on 'A' and 'C', and the complete stoichiometry of the reactions.

For instance, take adsorption of \( \text{C}^{2+} \) ions from solution which may increase, decrease or do not affect the charge in the interfacial region:

\[
\text{MO}^- - \text{A}^+ + \text{C}^{2+} \rightarrow \text{MO}^- - \text{C}^{2+} + \text{A}^+ \quad \text{(10)}
\]

Increases

\[
\text{MO}^- - \text{A}^+ + \text{C}^{2+} + \text{H}_2\text{O} \rightarrow \text{MO}^- \text{COH}^- + \text{A}^+ + \text{H}^+ \quad \text{(11)}
\]

Decreases

\[
\text{MO}^- - \text{A}^+ + \text{C}^{2+} + \text{H}_2\text{O} \rightarrow \text{MO}^- \text{COH}^+ + \text{A}^+ + \text{H}^+ \quad \text{(12)}
\]

No effect

In reaction (10), the surface potential increases because a divalent ion replaces a monovalent ion. In reaction (11) and (12), the divalent ion hydrolyses when it adsorbs but stoichiometry is the same. However, there is no change in surface potential.
in reaction (12) but the solution-pH will change. The adsorbed ions (C) in reaction (11) are away from the surface than in reaction (12). This causes a slight, but non-zero decrease in the potential of the interphase region. Numerous such reactions could be proposed to convey the same point i.e., the charge on an ion in solution is not necessarily a good indicator of how it will affect surface potential, when it adsorbs. This point has to be considered in competitive adsorption studies because sorption of one cation can enhance sorption of another cation or diminish sorption of an anion.

(ii) In addition to the above electrical interactions, the strongly binding adsorbates may compete for available sites, resulting in decrease of the tendency of each ion to adsorb. Also, some adsorbates may take up more space or more sites than the others, and this becomes important when one considers the large dye-ions versus the small inorganic ions.

(iii) Bridging is that phenomenon in which specific chemical interactions allow the ion 'C' to bind itself simultaneously to the surface as well as to the ion 'A', even though no surface - to - A bond is formed. This situation can be described by two limiting cases. In one case, a soluble A-C complex binds as a single entity or is formed at the surface, yielding a discrete
adsorbed species. In other case, the ion 'C' may form a surface precipitate to which ion 'A' adsorbs, and so the presence of the original adsorbent becomes irrelevant, except as a site for precipitation of 'C'. Adsorption of 'A' is then expected to be similar to its adsorption in a system containing only precipitated 'C' and no other solid.

Let the data be examined in the light of the above probabilities.

(a) The Studies on H3O:

The studies conducted for the influence of the cations: Na⁺, Ba²⁺ and Al³⁺ (in the adsorption bath) on the adsorption of cationic dyes in aq. medium reveal that:

(i) The presence of the cations decreases the adsorption of the solutes, and the order of retarding influence is: Al³⁺ > Ba²⁺ > Na⁺.

(ii) The cations are less effective in retarding the adsorption at the pH of maximum sorption of the dyes. However, their influence becomes more pronounced above and below this pH.

In the light of the above explanation, it can be said that the action of the cations is one of the repulsion between the dye-cations and the inorganic cations at the surface of the substrates, and
competition between them for ionic sites, and not merely due to ionic size. The operation of alternative covalent bond mechanism, especially at higher pH values, is shown by relatively smaller effect of the electrolytes on the degree of adsorption (Table 12).

(b) The studies on HZO:

The results (Table 29) indicate that the presence of the anions (NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$) in the adsorption bath decreases the adsorption of the anionic dyes. Nitrate is almost ineffective but SO$_4^{2-}$ and PO$_4^{3-}$ retard the adsorption significantly. Thus, the PO$_4^{3-}$ ions could inhibit 34-72% (H$_2$SO$_4$-treated HZO) and 22-67% (HCl-treated HZO) adsorption of the dyes. The explanation for these observations is the same as discussed for adsorption of cationic dyes on HSO.

IV. 8 'B': DESORPTION STUDIES:

As said in Chapter I, true ion-exchange processes are expected to be chemically reversible. Although obedience of the mass-action law has been established for certain exchange reactions on hydrous oxides; involvement of specific interactions with the oxide matrices has also been proposed when certain ions, notably polyvalent ones, are adsorbed. Hence, in these cases, complete chemical reversibility cannot be expected. Now the desorption data will be examined.
(a) The studies on HSO:

The desorption data (Tables13-15; Fig. 11) for the cationic dyes adsorbed on tin oxide of surface-pH 6.0 - 11.0 by aq. inorganic electrolytes (0.001 M - 1.0 M) show that:

(i) Desorption efficacy of the cations is in the order:

$$\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$$

(ii) Desorption increases with increase in the concentration of the electrolytes.

(iii) The extent of desorption also depends on the surface-pH of the substrate as well as the initial concentration of the dyes, taking part in adsorption. The desorption curves (Fig. 11) with Na$^+$ ions are almost linear but they are slightly curved for Ba$^{2+}$ and Al$^{3+}$ ions. The linearity is probably the consequence of weak exchanging power of the monovalent ion.

Thus, at the pH of maximum sorption (pH 8.5 MV, JR and pH 9.5 PS) and the higher dye concentration ($1.80 \times 10^{-3}$ ml$^{-1}$), it was observed that 9-40% (MV), 15-71% (PS) and 20-49% (JR) are desorbed with the desorbents. The values increase markedly, when their desorption is considered for the dyes adsorbed from dil. solutions (say $0.20 \times 10^{-3}$ ml$^{-1}$). It was observed that at this concentration, the percentage-desorption values increase to 40-100% (MV), 0-100% (PS) and 25-50% (JR).
These effective desorption values by the inorganic-cations point to the ion-exchange nature of the process. Atomic absorption spectrophotometric studies of sodium present on the substrate, before and after adsorption of the dyes (Table 37), show a decrease in sodium-content of the substrate, and so, the action can be presumed to be the ion-exchange of the dye-cations (simple or aggregated) with Na\(^+\) ions on the surface of the substrates. However, the two observations, suggesting some interaction of the dyes with the substrates are:

(a) Incomplete desorption with the electrolytes, especially at the higher dye-concentrations.

(b) Decrease in the degree of adsorption in the presence of electrolytes (IV.8). Further, as the dyes have the hydrogen-donor groups, they can also be adsorbed by hydrogen bonding to the surface with oxygen atoms by tin oxide, especially at higher surface pH of the adsorbent.

The lesser desorption at the lower pH of the substrates as compared to that of higher pH-substrates, also indicates operation of alternative covalent bond forces, making the process partially irreversible\(^2\).

(b) The studies on HZO:

The anionic dyes adsorbed on HZO (pH 3.0-7.0) could also be extracted significantly with inorganic-
anions (NO$_3^-$, SO$_4^{2-}$ and PO$_4^{3-}$), and as expected, the desorption efficacy was in the order: PO$_4^{3-}$ > SO$_4^{2-}$ > NO$_3^-$.

The degree of desorption was found to increase with increase in the concentration of the electrolytes (0.001 - 1.0 M) and surface-pH of the substrate (Tables 30-35). Thus, percentage-desorption values of the dyes adsorbed on HCl-treated HZO (pH 3.0, maximum sorption pH, [Dye]$_0$ = 2.00x10$^{-3}$ M$^{-1}$, with 1.0 M electrolytes are: 10-49 (LG), 12-65 (OG) and 23-87 (NBB). However, with the exception of LG, the degree of extraction increases considerably, when the dyes adsorbed at lower concentrations (say 0.20x10$^{-3}$ M$^{-1}$) are considered. Thus, with 1.0 M electrolytes, 75-100% OG and 50-75% NBB is extracted. LG, under these situations, hardly shows 21% desorption (Tables 30-32).

When the desorption data for the dyes adsorbed (2.0x10$^{-3}$ M$^{-1}$, pH 4.0, 5.0) on H$_2$SO$_4$-treated HZO (Tables 33-35) is considered, one observes that with 1.0 M electrolytes, the dyes extracted are: 22-31% (LG), 16-39% (OG) and 32-46% (NBB). Thus, the values are less as compared to their desorption from HCl-treated samples. At lower concentrations of the dyes (0.20x10$^{-3}$ M$^{-1}$), the desorption values are 36-71% (LG), 42-100% (OG) and 50-95% (NBB).
The inorganic anions, it appears probably compete with the dye-anions at the zirconium oxide surface for the ionic sites; making the process to be chemically reversible to a considerable extent. The lesser desorption in the lower pH-range, as compared to the higher surface pH values, again indicates operation of alternative covalent bond forces, making the process slightly irreversible, especially at lower surface-pH values.

IV. 9: ISOTHERMS:

The dye-species adsorbed on the substrates may cover the surface with a monolayer of the species, and as these species are large as compared to the original ions (Na⁺ on HSO and Cl⁻, SO⁴²⁻ on HZO), screening of the surface forces (to some extent) may occur. The monolayer may not be desorbed, if the screening is sufficiently good. The L-type isotherms, observed in the present study, indicate the formation of a monolayer of the adsorbed species, and strong affinity of the solutes for the substrates. Further, from the structural characteristics of the dyes, a flat orientation is likely to be the most-favoured one for these molecules. S-type isotherms have also been observed.

It is established that three important conditions, which are to be met for the applicability of Langmuir's treatment are:
(i) equivalent sites,
(ii) monolayer coverage, and
(iii) very little interaction between adsorbate molecules compared to adsorbate-adsorbent interaction.

Whenever, one or more of these basic conditions are not satisfied, the isotherms will deviate from the normal L-type. Thus, S-type curves of dyes on HSO and H2O, under conditions as mentioned above, may be due to:

(i) Concentration dependence of the activation energy for desorption of the species of the dyes, and/or
(ii) large negative contribution of the solvent or a second solute and
(iii) cooperative adsorption. The dye-species may be adsorbed packed in rows or clusters, through some form of interlocking of the adsorbed species.

The factors (ii) and (iii) appear to contribute to the adsorption of the dyes, showing S-type isotherms, especially at higher solute concentrations.

The isotherms for the adsorption of cationic dyes on HSO (Fig. 3-10) are of L-, S- and H-type. MV mostly exhibits S-type isotherms whereas JR and PS show generally L-nature of the isotherms.

The studies of the anionic dyes on H2O also indicate L-, S-, and H-type isotherms. NBB generally
exhibits L-type isotherms whereas OG and LG show L- and o-type behaviour.

The maxima in the isotherm (Figs. 7, 19 and 21) may be due to stronger adsorbate-adsorbate and/or solute-solvent interactions, in comparison to that of adsorbate-adsorbent interaction. Such type of maxima have also been reported in the adsorption of dyes to indicate their association in solution\(^7,^9\).

**IV. 10: LINEAR PLOTS:**

The dyes are known to exist as aggregates of a number of ions or molecules in aq. solution with an equilibrium between the species and the simpler cations/anions of the dyes in solution. This has been shown for adsorption of ionic dyes, when adsorbed by ion-exchange on alumina\(^{23}\). The aggregation of the dye-species in the form of charged-micelles, can be shown by an examination of the amount of the dye adsorbed\(^{10,12}\). The plateau in adsorption isotherms is taken to represent the completion of monolayer (Ym). In the present study, the turning point in the isotherms are not well-defined, which may be due to low dye concentrations employed. Hence, 'Ym' values have been computed from the linear plots connecting \(m/X\) and \(1/B-X\) (Figs. 29-35), as suggested by Mathews\(^{24}\), and also employed by Jain\(^{25}\), Mishra\(^{26}\) and Moitra\(^{27}\). This has been shown as \((Ym)_L\).
It has also been proposed to use the value of surface area of the substrate, as determined by BET method, for the calculation of $Y_m$ values, using the relation:

$$S = Y_m \cdot N \cdot a \times 10^{-20}$$

Where, 'N' is the Avogadro number, 'a' the projection area of the solute (flat). Let the values ($Y_m$) determined be shown as ($Y_m)_S$.

In Table 36 is recorded the monolayer capacity, ($Y_m)_L$, ($Y_m)_S$ and maximum amount of the dye adsorbed ($X/m)_{max}$. The linear plots of MV adsorbed on HSO and OG adsorbed on $H_2SO_4$-treated HZO could not be obtained because of the S-nature of the isotherms.

The data (Table 36, Figs. 29-35) reveal that:

(A) The studies on HSO:

(i) In the concentration range studied, ($X/m)_{max}$ values of PS and Jr on HSO (pH 5.0 - 11.0) are generally close to the limiting values ($Y_m)_L$ except PS at pH 8.5, Jr at pH 8.5 and 9.5. ($Y_m)_L$ values have been computed from the linear plots.

In case of adsorption of PS (pH 5.0-11.0), the actual amount of the dye adsorbed and the ($Y_m)_L$ values are lower than the ($Y_m)_S$ values. This type of behaviour
is also shown by JR except at pH 8.5. The possible cause may be the adsorption of single dye-cations on HSO surface.

(ii) If one compares the \((\xi/m)_{\text{max.}}\) and \((Ym)_{L}\) values for the cationic dyes with \(H^+\) ion-exchange capacity of the HSO samples (Table 1), it is observed that the \((\xi/m)_{\text{max.}}\) and \((Ym)_{L}\) values are quite less as compared to the ion-exchange capacity of the HSO samples. Thus, even at very high concentration of the dyes, it appears that all the available ion-exchange sites are not occupied by the solutes.

(B) The studies on HZO:
(a) HCl-treated HZO:
In the pH range 3.0 - 7.0, \((Ym)_{L}\) and \((\xi/m)_{\text{max.}}\) values of LG are almost close but that of OG and NBB are higher. However, the values are lower than the \((Ym)_{S}\) values and the \(OH^-\) ion-exchange capacity (Table 2). This indicates adsorption of monodispersed dye-species on the substrates.

(b) \(H_2SO_4\)-treated HZO:
On account of the S-nature of the isotherms (LG, OG) most of the \((Ym)_{L}\) values could not be determined. However, the \((Ym)_{L}\) and \((\xi/m)_{\text{max.}}\) values of NBB are almost close.
IV. 11: STRUCTURAL CHARACTERISTICS OF THE DYES VERSUS ADSORPTION:

From the structure of the cationic dyes shown in Fig. 1, it is evident that MV is chiefly hydrochloride of pentamethyl p-rosaniline, and thus, it is a basic dye of the triphenyl-methane series, having the dye chromophore as a cation. It is closely related to crystal violet. The basic colligator (special type of auxochrome) found in MV is \( N^+ \). In water, the dye exists not as single ion or molecule but as aggregates of a number of ions or molecules. Such micelles may be ionised, although it is not necessary to assume that all ionisable groups in any micelle are dissociated. Phenosafranine is not exactly a dye but an adsorption indicator, and its use as a redox indicator has been studied by Steiehler et al.\(^2\), who have reported the following values for \( 10^{-4} \) M aq. solution at 30°:

\[
\begin{align*}
E^0 &= 0.280, \quad \text{Em} = 0.252 \\
pK_1 &= 4.96, \quad pK_2 = 5.78 \\
\text{Range of pH} &= 1.1 - 11.
\end{align*}
\]

The basic colligators found in its molecule are \(-\text{NH}_2\) and \(N^+\). Janus red is a cationic dye of the disazo-series having acid colligator \((-\text{OH})\), and it is one of the few dyes having trimethyl amino group as its side chain (auxochrome). The azo groups are
also present. The coverage factor (C.F.) for the dyes can be calculated using the relationship: 

\[ \text{C.F.} = 1.2 \times 10^{-7} \times (\text{ionic weight})^2 \]

The calculated values are PS (1.31), MV (3.66) and JR (6.01).

From the structure of anionic dyes shown in Fig. 2, it is evident that OG is a monosulphonate mono-azo dye, while NBB belongs to disulphonate diazo-group of dyes. LC has also a disulfonate group but lacks in the azo group. The coverage factor for the anionic dyes are: 2.8 (OG), 13 (LG) and 14.3 (NBB).

A few generalisations made by the earlier workers\(^{29}\) regarding adsorption of dyes may be cited at this stage.

(i) The greater the number of azo groups, the stronger is the adsorption. The affinity also increases with increase in molecular weight, number of sulphonate groups and double bonds in the dye molecule.

(ii) An amino or hydroxy group is more effective when in the 2-position in the naphthalene nucleus than in 1-position. The o-hydroxy azo-dyes are adsorbed more strongly than the p-isomer. Giles et al.\(^{10}\) have also pointed out that for adsorption of anionic dyes on chromatographic alumina:
(i) The amount of the mono-disperse adsorbed dye-anions, representing a monolayer coverage on chromatographic alumina, should be inversely proportional to their cross-sectional area.

(ii) The amount of micelle-adsorbed anions should be inversely proportional to their basicity. The assumption made is that each sulphonate group exchanges with a chloride ion, of which there is a limited supply.

It may be said that size of the dye-ion may determine the degree of adsorption, as the ability of the ion to pack into the monolayer will differ. The molecular weight of the cationic dyes MV, PS and JR are 393.5, 322.79 and 460, respectively, and so JR-cations are expected to have greater affinity as compared to the others.

The $K_d$ values of the dyes (Table 38) indicate that in the pH range 7.0 - 11.0, JR has greater affinity than PS for $\Delta SO$ samples. However, MV (pH 7.0 - 3.5) has higher $K_d$ values as compared to the other dyes, and this may be due to participation of larger number of micelles of the dyes, as also shown by the S-nature of the isotherms.

The anionic dyes OG, LG and NBB have molecular weight 350, 577 and 617, respectively, and so NBB-anions should have greater affinity as compared to the other dyes.
The $K_d$ values (Table 38) of the dyes, when adsorbed on HZO (pH 3.0 - 7.0), show that on HCl-treated samples, OG has greater affinity as compared to LG and NB3 in the pH range 3.0 - 5.0 but LG indicates greater affinity in the pH range 6.0 - 7.0. This behaviour of LG may be due to its amphoteric nature.

The $K_d$ values (Table 38) of the anionic dyes, adsorbed on $\text{H}_2\text{SO}_4$-treated HZO of pH 3.0 - 7.0, again indicate the strongest affinity of OG for the substrates. The dyes LG and NBB follow the sequence:

$$\text{LG} > \text{NBB}$$

So, the general rules proposed above do not fit in exactly, when adsorption of the anionic dyes on acid-treated HZO are considered. This may again be due to the fact that adsorption of OG is micellar in nature, and also appears to involve chemical interactions to some extent. The S-nature of isotherms of OG also support the view.

IV. 12: CHEMICAL TREATMENT VERSUS ADSORPTION BEHAVIOUR:

The isoelectric point of HZO is 6-7. The acid-treatment, and hence the adsorbed anions ($\text{Cl}^-$, $\text{SO}_4^{2-}$), appear to lower the isoelectric pH, and thus, they modify the electrokinetic behaviour of the adsorbent.$^{30}$
Further, replacement of the OH\(^-\) ions from the surface by the anions may evoke the anion-exchange capacity, depending on the relative position of the anions in the ion-selectivity series i.e., OH\(^-\) > PO\(_4\)\(^{3-}\) > SO\(_4\)\(^{2-}\) > Cl\(^-\).

Since the Cl\(^-\) ion is much below in the series, it has much-lesser affinity for the HZO surface, and it can be easily exchanged by other ingoing dye-anions. This is shown by regular increase in adsorption with decrease in pH of the substrate.

The H\(_2\)SO\(_4\)-treatment appears to affect the surface of HZO in a different manner. The pretreatment may be lowering the isoelectric pH\(^{31}\). It may be lowered to a value in the vicinity of pH 4.0-5.0. This is indicated by the maximum adsorption of the dyes at pH 4.0 (OG) & pH 5.0 (LG, NBB). Further, as SO\(_4\)\(^{2-}\) ions have greater affinity for the surface\(^{32}\), and hence they may be competitive in influencing the process, quite considerably at lower pH values. At very low pH values (pH < 3.0), competitive adsorption between undissociated acid molecules and the product of the reaction between the dye and the acid may play very important part in decreasing adsorption affinity of the solutes for the substrate\(^{33}\). Thus, as compared to HCl-treatment, more sites, responsible for specific interaction, seem to be created by H\(_2\)SO\(_4\)-treatment of HZO.
The isoelectric point of HSO synthesised by the method (Chapter II) has been found to be 4.8 by Sen and Ghatuariy. Above the isoelectric point, HSO is expected to be a cation exchanger. This is found to be experimentally true (Chapter III A).

IV. Conclusion:

In short, it may be concluded that although pH plays an important part in the adsorption-desorption behaviour of polar solutes, like dyes, on chemically-pretreated substrates, like HSO & HZO, yet the adsorbed ions on the surface (Na⁺, Cl⁻, SO₄²⁻) also modify the electrokinetic behaviour of the adsorbents. Thus, in turn, can provide new surface behaviour of substrates.
### Table 36

Computation data of $\gamma_m$ (Amonolayer capacity) of the dyes adsorbed on "HSO₄⁻" and "HZO⁻" of varying surface - phase pH.

#### (A) Cationic Dyes (Mv, P3 and JR) on Alkali-Treated "HSO₄⁻"

<table>
<thead>
<tr>
<th>Surface-pH of &quot;HSO₄⁻&quot;</th>
<th>Methyl-Viol.-Lit. '68</th>
<th>Phenosafranine</th>
<th>Janus Red</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(X/m)max $\gamma_m$ *</td>
<td>(Y/m)$_L$ *</td>
<td>(Y/m)$_S$**</td>
</tr>
<tr>
<td>6.0</td>
<td>95 - 98</td>
<td>10 12</td>
<td>113</td>
</tr>
<tr>
<td>7.0</td>
<td>140 - 103</td>
<td>13 19</td>
<td>160</td>
</tr>
<tr>
<td>8.0</td>
<td>166 - 111</td>
<td>32 33</td>
<td>173</td>
</tr>
<tr>
<td>8.5</td>
<td>172 - 109</td>
<td>77 110</td>
<td>170</td>
</tr>
<tr>
<td>9.5</td>
<td>- -</td>
<td>105 111</td>
<td>-</td>
</tr>
<tr>
<td>10.5</td>
<td>- -</td>
<td>90 105</td>
<td>147</td>
</tr>
<tr>
<td>11.0</td>
<td>- -</td>
<td>67 94</td>
<td>144</td>
</tr>
</tbody>
</table>

#### (B) Anionic Dyes (Lg, QJ and NBB) on Acid-Treated "HZO⁻"

<table>
<thead>
<tr>
<th>Surface-pH of &quot;HZO⁻&quot;</th>
<th>Lissamine Green 'ON'</th>
<th>Orange II</th>
<th>Naphtol Blue-Black</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(X/m)max $\gamma_m$ *</td>
<td>(Y/m)$_L$ *</td>
<td>(Y/m)$_S$**</td>
</tr>
<tr>
<td>1.0</td>
<td>141 - -</td>
<td>155 217</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>141 - -</td>
<td>105 114</td>
<td>-</td>
</tr>
<tr>
<td>3.0</td>
<td>102 108 172</td>
<td>185 190 457</td>
<td>-</td>
</tr>
<tr>
<td>4.0</td>
<td>95 99 222</td>
<td>170 312 453</td>
<td>-</td>
</tr>
<tr>
<td>5.0</td>
<td>80 87 165</td>
<td>148 - 343</td>
<td>-</td>
</tr>
<tr>
<td>6.0</td>
<td>55 60 217</td>
<td>25 - 462</td>
<td>-</td>
</tr>
<tr>
<td>7.0</td>
<td>45 47 219</td>
<td>15 - 359</td>
<td>-</td>
</tr>
</tbody>
</table>

#### $\text{H}_2\text{SO}_4$ Treated "HZO⁻"

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_m$ *</th>
<th>$\gamma_m$ **</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>15 - -</td>
<td>14 - -</td>
</tr>
<tr>
<td>2.0</td>
<td>32 - -</td>
<td>18 - -</td>
</tr>
<tr>
<td>3.0</td>
<td>45 60 153</td>
<td>44 47 173</td>
</tr>
<tr>
<td>4.0</td>
<td>118 - 203</td>
<td>80 92 231</td>
</tr>
<tr>
<td>5.0</td>
<td>138 - 195</td>
<td>122 141 222</td>
</tr>
<tr>
<td>6.0</td>
<td>85 - 223</td>
<td>90 99 292</td>
</tr>
<tr>
<td>7.0</td>
<td>65 111 211</td>
<td>32 - 240</td>
</tr>
</tbody>
</table>

* Values computed from Linear-plots connecting $1/\gamma_m$ and $\gamma_m$.  
** Values computed from surface area values of the samples.  
(-) means the values could not be determined.
TABLE: 37

THE Na⁺-ION-CONTENT OF HYDROUS SnO₂ SAMPLES (BY AAS) BEFORE AND AFTER SORPTION OF CATIONIC DYES (MV, JR, PS).

'AAS' stands for Atomic Absorption Spectroscopy.

<table>
<thead>
<tr>
<th>Surface-Phase pH of SnO₂</th>
<th>Na⁺-ion-content before sorption (mg-ion/g)</th>
<th>Na⁺-ion-content after sorption (mg-ion/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>7.0</td>
<td>0.07</td>
<td>NIL</td>
</tr>
<tr>
<td>7.5</td>
<td>0.07</td>
<td>NIL</td>
</tr>
<tr>
<td>8.0</td>
<td>0.07</td>
<td>NIL</td>
</tr>
<tr>
<td>8.5</td>
<td>0.14</td>
<td>NIL</td>
</tr>
<tr>
<td>9.0</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>9.5</td>
<td>0.31</td>
<td>-</td>
</tr>
<tr>
<td>10.5</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>11.0</td>
<td>0.80</td>
<td>-</td>
</tr>
</tbody>
</table>

Dash (-) means the value not determined, as the dye gets precipitated at pH > 8.5.
FIG. 29: LINEAR PLOTS CONNECTING \( m/X \) AND \( 1/(B-X) \) IN LIQUID-SOLID SYSTEM (PHENOSAFRANINE ON NaOH-TREATED TIN (IV) OXIDE).
FIG. 30: LINEAR PLOTS CONNECTING \( \frac{m}{X} \) AND \( \frac{1}{(B-X)} \) IN LIQUID-SOLID SYSTEM (JANUS-RED ON NaOH-TREATED TIN (IV) OXIDE).
FIG. 34: LINEAR PLOTS CONNECTING m/X AND 1/(B-X) IN LIQUID-SOLID SYSTEM

LISASMINE GREEN B'N ON HCL-TREATED ZIRCONIUM (IV) OXIDE.

pH = 4.0
pH = 6.0
pH = 7.0
pH = 2.0
pH = 2.5
pH = 3.0
pH = 5.0
pH = 6.0

m/X (gram/mole)x10^3

1/(B-X) (litre/mole)x10^3
FIG. 82: LINEAR PLOTS CONNECTING \( m/x \) AND \( 1/(B-x) \) IN LIQUID-SOLID SYSTEM (ORANGE II ON HCl-TREATED ZIRCONIUM (IV) OXIDE).
FIG. 33: LINEAR PLOTS CONNECTING $m/X$ AND $1/(B-X)$ IN LIQUID-SOLID SYSTEM (NAPHTHOL BLUE BLACK ON HCL-TREATED ZIRCONIUM (IV) OXIDE).
FIG. 31: LINEAR PLOTS CONNECTING M/X AND 1/(B-X) IN LIQUID-SOLID SYSTEM

(LISSAMINE GREEN BIND ON HCl-TREATED ZIRCONIUM (IV) OXIDE).

M/X (gram/mole)x10^3

1/(B-X) (litre/mole)x10^3

pH = 7.0
pH = 6.0
pH = 5.0
pH = 4.0
pH = 3.0
pH = 2.5
pH = 2.0
pH = 1.0
pH = 0.0

0.0 0.08 0.16
0.12 0.22 0.32
0.20 0.30 0.40
0.18 0.28 0.38
0.16 0.24 0.32
0.14 0.22 0.30
FIG. 32: LINEAR PLOTS CONNECTING m/X AND 1/(B-X) IN LIQUID-SOLID SYSTEM (ORANGE II) ON HCl-TREATED ZIRCONIUM (IV) OXIDE.
FIG. 34: LINEAR PLOTS CONNECTING \( m/X \) AND \( 1/(B-X) \) IN LIQUID-SOLID SYSTEM (LISSAAGINE GREEN)

- \( pH = 3.0 \)
- \( pH = 7.0 \)

BN ON H2SO4-TREATED ZIRCONIUM (IV) OXIDE)

\[ m/X \text{ (g/mole)} \times 10^3 \]

\[ \frac{1}{16}X/\text{litrer/mole} \times 10^3 \]
FIG. 35: LINEAR PLOTS CONNECTING m/X AND 1/(B-X) IN LIQUID-SOLID SYSTEM (NAPHTHOL BLUE BLACK ON H2SO4-TREATED ZIRCONIUM (IV) OXIDE).
# LITERATURE CITED

**(CHAPTER - IV)**

<table>
<thead>
<tr>
<th>Reference</th>
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<th>Title</th>
<th>Page/Volume</th>
<th>Year</th>
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