CHAPTER II

EXPERIMENTAL
CHAPTER-II

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The chapter deals with the experimental procedure for the preparation of $\text{HClO}_4$, $\text{HNO}_3$, $\text{HCl}$, $\text{H}_2\text{SO}_4$ and $\text{CH}_3\text{COOH}$-treated hydrous zirconium oxide samples (HZO) and alkali-treated Tin oxide samples (HSO) of varying surface-phase pH. Nitrophenols and amino acids were used as adsorbates. Adsorption desorption procedure, pH of aqueous solution of the solutes and electrolytes along with certain essential features of the adsorbents like surface area, hydroxide ion-exchange capacity, anion content, have also been determined.

The chemicals used were of analytical purity, unless otherwise mentioned. For the preparation of solutions and their dilutions, deionised water, which was further glass distilled, was employed. The glass apparatus used were of Corning/Pyrex type. Temperatures are reported in °C. pH measurements were made with "SYSTRONICS" Digital pH-meter, Model No. 335 (accuracy ± 1%). Colorimetric measurements were carried out with "SPEKOL" spectrocolorimeter (Carl-Zeiss, accuracy 0.5%). A single-pan balance was employed for weighing.

For measurement of volume of the solutions, calibrated pipettes with highest accuracy and reproducibility were used. Some of these were:
(1) 'FISHER' brand volumetric pipettes with accuracy for different capacity as shown below:

<table>
<thead>
<tr>
<th>Capacity (cm³)</th>
<th>Accuracy (cm³)</th>
<th>Capacity (cm³)</th>
<th>Accuracy (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 to 2</td>
<td>± 0.006</td>
<td>3 to 6</td>
<td>± 0.001</td>
</tr>
<tr>
<td>10</td>
<td>± 0.02</td>
<td>20 to 25</td>
<td>± 0.03</td>
</tr>
<tr>
<td>50</td>
<td>± 0.05</td>
<td>100</td>
<td>± 0.08</td>
</tr>
</tbody>
</table>

(2) 'OXFORD Macro Set Transfer-pipetting Systems' to handle 1 to 10 cm³ solutions with 0.5% full scale precision.

(3) Repipet II Dilutors and Dispensers with 0 to 5 and 0 - 10 cm³ reagent dispensers and having reproducibility of 0.2%.

II.1: PREPARATION OF ADSORBENTS:

Chemical pretreatment of hydrous oxides, resulting in evokement of ion-exchangeable sites, has been advocated. To investigate the deeper aspects of the concept, and to explore further its utility in the field of chromatography, H₂O has been selected for chemical pretreatment with acids (HClO₄, HNO₃, HCl, H₂SO₄ and CH₃COOH), and H₂O with aqueous alkali (NaOH). The substrates so obtained, and with varying surface-phase pH, were used to study the change in the sorption-desorption behaviour of some anionic and cationic species from aqueous solutions. In the present work, pH
of the adsorbent means surface-phase pH, which is the bulk pH, when diluted with distilled water to 1%-equivalent H2O or HSO.

II.1-A: SYNTHESIS OF HYDRATED ZIRCONIUM OXIDE (H2O):

II.1-A.1: Preparation:

Hydrated zirconium oxide was prepared by adding 0.1M-aqueous ammonia to 0.1M-zirconium oxychloride solution in 0.1M-HCl (2:1 v/v), as reported by Singh and Tandon (1). The precipitated zirconium oxide was kept in contact with the mother liquor at room temperature for 5-days for ageing. Then the precipitate was filtered, washed several times with water until free from chloride ions. pH of the wash-liquid was 9.0. The product was air-dried at 30 ± 2° and then heated at 110 ± 2° to a constant weight. The dried material was sieved through 100-200 mesh.

II.1-A.2: Composition:

Zirconium as zirconium dioxide in the original H2O was estimated colorimetrically by Alizarin red 'S'-method (2). It contained 59% ZrO₂. For the estimation of water of crystallization in the H2O samples, about 1.0 g H2O was weighed accurately in silica crucible, ignited at 800° and weighed. The difference in the weight was the amount of water lost, and the weight of the residue was the amount of anhydrous zirconium oxide. From this result, the water of crystallization was calculated by the method of Alberti et al (3). The weight loss at 800° is 41%, which corresponds to
the formula \( \text{ZrO}_2 \cdot 4.7\text{H}_2\text{O} \). This composition has also been reported by Hallaba et al \((4)\).

II.1-A.3: Surface-phase pH:

0.25 g of the \( \text{H}_2\text{O} \) sample was shaken with water (25 ml) for 30 min, allowed to settle, decanted, and pH of the liquid was determined. pH of the aqueous extract was found to be 8.4. This has been taken as surface-phase pH or surface-pH of the sample.

II.1-A.4: Chemical stability:

For determination of the stability of \( \text{H}_2\text{O} \) in acids, about 500 mg accurately weighed sample was kept in contact with 100-ml of the acid (\( \text{HClO}_4 \), \( \text{HNO}_3 \), \( \text{HCl} \), \( \text{H}_2\text{SO}_4 \) and \( \text{CH}_3\text{COOH} \)) of various concentrations for 24 hr with intermittent shaking. The amount of zirconium dissolved was estimated by Alizarin red 'S'-method \((2)\). The sample is fairly stable in the acids. However, the sample showed solubility of \( \leq 0.6\% \) in 2N solution of the acids used for the pretreatment.

II.1-A.5: Preparation of acid-treated \( \text{H}_2\text{O} \) of varying surface-phase pH:

The \( \text{H}_2\text{O} \) prepared was subjected to chemical pretreatment with \( \text{HClO}_4 \), \( \text{HNO}_3 \), \( \text{HCl} \), \( \text{H}_2\text{SO}_4 \) and \( \text{CH}_3\text{COOH} \) of varying strengths. 25-g of the sample was taken in a number of stoppered bottles, and shaken with 50-cm\(^3\) of the acid of varying strength \((0.01 - 2.0\text{N})\) for 24 hr at room temperature \((30 \pm 2\text{C})\). The supernatant-liquid was decanted and the
solid-phase repeatedly washed with water till the washings were free from the acid-anions \((\text{ClO}_4^-, \text{NO}_3^-, \text{Cl}^-, \text{SO}_4^{2-}\) and \(\text{CH}_3\text{COO}^-.\)). The samples were dried at \(110\pm2\degree\) to a constant weight, and the surface-phase pH was determined. The details are recorded in Table 1.

II.1.B: **SYNTHESIS OF HYDRATED TIN OXIDE (HSO):**

(i) **Preparation:**

Tin oxide used for the preparation of samples of varying pH was first prepared by oxidising high purity tin foil (BDH AnalaR) with hot 35% w/w nitric acid. The hydrous precipitate formed was thoroughly washed with distilled water through a glass filter, until the final \(pH\) of the filtrate \(\sim 3\), dried at \(110\pm2\degree\) for 12 hrs in an electric oven and pulverized in an agate mortar, sieved through 100-400 mesh and stored in dry amber-coloured bottle. The \(\text{pH}\) of 1%-aqueous extract was 3.0 which was taken as the surface-phase \(\text{pH}\) of the sample.

II.1-B.1: **Composition:**

Tin as tin oxide was determined idiometrically in the original HSO sample. It was found to contain 82.5% of SnO2. To determine the water of hydration, the same procedure was adopted as for H2O. From the result, the water of crystallization was calculated by the method of Alberti et al (3). Chemical composition of the hydrated tin oxide sample was found to be SnO2 : H2O as 1:1.62.
Sen and Ghatuary (5) have also reported the same composition.

The HSO sample was fairly stable in water and NaOH (0.5N). However, with higher concentrations of the alkali (NaOH) used for the pretreatment, slight solubility was observed. Thus, the solubility was 0.2%, 0.5% and 0.8% in 1.0N, 1.5N and 2.0N-NaOH solution, respectively.

II.2.C: SYNTHESIS OF ALKALI-TREATED HSO OF VARYING SURFACE-PHASE pH:

Treatment of hydrous oxides, like tin oxide, with an amount of alkali insufficient to dissolve them, often yields acid salts, which are expected to be cation-exchangers, if the cations of the alkali (counter-ions) are not built into the net work and thus, exchange activity would be imparted to the solid, as shown below:

\[ \text{SnOH} + \text{Na}^+ \text{OH}^- \rightleftharpoons \text{SnO}^- + \text{Na}^+ + \text{H}_2\text{O} \quad \ldots \ldots (1) \]

Tin oxide samples of pH 4.0 - 11.0 were then prepared by treating the above \( \beta \)-form of the tin oxide with varying concentrations of NaOH (Table 2). The following method was adopted for the purpose. The tin oxide sample (25 g) was covered separately with different concentrations of NaOH (50 cm\(^3\)) at 30 ± 2\(^\circ\). The samples were kept over-night and occasional shaking was done. Afterwards, the supernatant liquid was decanted. The solid-phase was repeatedly washed
with 50-cm³ portions of distilled water, till the washings had a desired and constant pH (Table 2). A little of the washed sample was dried at 110 ± 2° for 30 min. and 0.25 g of Cl⁻ was shaken with water (25-cm³) for 30 min, allowed to settle, decanted and pH of the liquid (preliminary pH) determined. Now the remaining solid was dried at 110 ± 2° for 12 hr, stored in air-tight, amber-coloured bottles, and kept in a desiccator over fused calcium chloride. The results obtained and the conditions followed are shown in Table 2.

II.2: SURFACE AREA:

The relative surface area of a solid plays an important role in its sorptive properties, and also helps to determine whether it can function as an adsorbent in chromatography. Thus, surface area of some of the pretreated HZO samples and HSO samples was determined by the standard "continuous flow method"(5). The surface area analyser used for the purpose was the one fabricated by Bhat and Krishnamoorthy (7) of the Analytical Chemistry Division of Bhabha Atomic Research Centre, Trombay. The analyser measures the quantity of nitrogen gas physically adsorbed (at a fixed pressure of nitrogen, single point method) by the sample at liquid nitrogen temperature. From the quantity of nitrogen adsorbed, the monolayer capacity (the volume of gas need to coat the solid surface completely by a monomolecular gas layer) is calculated by the Brunauer-Emmet
Teller (B.E.T.) theory (8,9). The specific surface area is calculated from the monolayer capacity. The values are given in Table 1 and 2.

A review of the table shows a decrease in the surface area of the HZO sample on its treatment with acids. This effect is, however, more marked in the case of the HZO samples of lower values of surface-phase pH and in case of acetic acid treatment of the sample. However, NaOH-treatment of tin oxide does not appear to have a significant effect in changing its surface area.

II.3: ESTIMATION OF THE IONS PRESENT ON THE PRETREATED HYDROUS ZIRCONIUM OXIDE AND TIN OXIDE SAMPLES:

During the preparation of the pretreated HZO and HSO samples of varying pH, although an attempt has been made to remove the adhering acid or alkali completely from the samples by washing them repeatedly with water and drying at elevated temperatures, yet it is expected that considerable and varying amount of bound anions (ClO$_4^-$, NO$_3^-$, Cl$^-$, SO$_4^{2-}$ and CH$_3$COO$^-$ on HZO) or cation (Na$^+$ on tin oxide) may be present on them, which can play an important role in the adsorption-desorption behaviour of polar solutes. Thus, the anions (ClO$_4^-$, NO$_3^-$, Cl$^-$, SO$_4^{2-}$ and CH$_3$COO$^-$) and the cation (Na$^+$) present on the acid-treated HZO and alkali-treated HSO samples, respectively, were estimated as outlined below:
For the estimation of the anions (ClO$_4^-$, NO$_3^-$, Cl$^-$, and CH$_3$COO$^-$) on acid treated HZO, the sample (0.25 g) was equilibrated with 25 cm$^3$ of 1.0N NaOH solution for 24 hr, and the anion so extracted was estimated colorimetrically. Absorbance of the extract of the ion-associate of perchlorate with methylene blue in chloroform was measured at 655 nm, and the perchlorate content was found from the calibration curve (10). Phenol disulphonic acid was employed as reagent for nitrate estimation at 410 nm (11). The chloride estimation was done at 460 nm, using mercury (II) thiocyanate method (12), while for the estimation of acetate, the characteristic blue to green colour produced by the addition of lanthanum nitrate and ammonium hydroxide followed by iodine solution to the extract, was measured at 625 nm, against a reagent blank (13).

For the estimation of sulphate in sulphuric acid-treated HZO (pH 3.0 - 7.5), the sample (1.0 g) was transferred into a platinum crucible to which was added a mixture of (3 g) anhydrous sodium carbonate and sodium peroxide (0.2 g). It was fused at 1000-1050 ± 2° for 15 min. The fused mass was extracted with water and filtered. The sulphate present in the filtrate was estimated gravimetrically as barium sulphate (14).

The sodium present in NaOH-treated tin oxide samples (pH 6.0 - 11.0) was estimated by atomic absorption spectrophotometric method (15). For this, tin oxide sample (0.25 g)
was transferred to a 100 cm$^3$-Teflon beaker, squirted with distilled water to just moist the sample and then HF (10 cm$^3$) and HClO$_4$ (5 cm$^3$) were added, digested over night (covered) in a boiling water bath. The cover was removed and the contents evaporated. The operation continued until the solution fumes, first slowly, and then strongly for a period of 10 min, cooled, diluted with water and transferred to a 250-cm$^3$ volumetric flask. From the solution so obtained, sodium was estimated using "Varian atomic absorption spectrophotometer" Model No. AA 575. For the purpose, the volume proportion of lithium used as internal standard was kept constant in all calibration standards, because of the use of the internal standard as an index of sample concentration and unknown samples. The ionic content of the acid and H2O and alkali treated HSO samples are recorded in Table 1 & 2.

II.4: HYDROXIDE OR HYDROGEN ION-EXCHANGE CAPACITY MEASUREMENT:

As mentioned in Chapter I, the pretreatment of H2O with an acid like HClO$_4$, HNO$_3$, HCl, H$_2$SO$_4$ or CH$_3$COOH and HSO with an alkali like sodium hydroxide is expected to enhance their apparent ion-exchange capacity. Further, the effect of this pretreatment is expected to convert the oxide from the OH$^-$ and H$^+$-forms to respectively, the ClO$_4^-$, NO$_3^-$, Cl$^-$, SO$_4^{2-}$ or CH$_3$COO$^-$ and Na$^+$-forms, respectively. It is also pointed out that the evokement of ion exchangeable sites of these
hydrous oxides by the chemical pretreatments is also dependent on the hydronium-ion concentration. To estimate the effect of the pretreatment of HZO with acids and tin oxide with alkali in the manner described earlier, the hydroxide ion-exchange capacity of the different acid-treated HZO samples and the hydrogen ion exchange capacity of the various HSO samples were determined by batch operation. For this, HZO sample (1.0 g) was equilibrated with NaOH (100 cm$^3$, 0.1M) for 24 hr, and back titrated with standard HCl (0.1M). In case of HSO, the sample (1.0 g) was, however, equilibrated with aqueous HCl (100 cm$^3$, 0.1M) for 24 hr, and back titrated with standard NaOH (0.1M). The values obtained are shown in Table 1 and 2.

II.5: PURIFICATION OF ADSORBATES:

Two types of adsorbates have been used in the present investigation, i.e., (i) nitrophenols: 2,4-dinitrophenol and 2,4,6-trinitrophenol (picric acid) (BDH) and (ii) Three types of amino acids: (A) acidic amino acids: aspartic acid (BDH) and glutamic acid (BDH), (B) neutral amino acids: glycine (BDH) and DL-Serine (E. Merck), and (C) basic amino acids: (L(+)−arginine (E.Merck) and L(−)−histidine (E. Merck). The nitrophenols and amino acids were used after recrystallizations from ethanol−water mixture (1:1, v/v). In case of the nitrophenols, the recrystallization was continued, until their melting point was sharp and in
agreement with the literature value i.e., 112.9° (INP) and 121.9° (PA). The purified samples of the nitrophenols were dried at 80 ± 1° for 12 hr to remove moisture.

In case of amino acids, the crystallization was continued, till the absorbance was constant, and the chromatography showed the presence of only one component. The purified samples were dried at 105 ± 2° for 12 hr, and stored over drierite. The structure and other details of the adsorbate are shown in Fig. 1. The abbreviation INP, PA, Asp, Glu, Gly, Ser, Arg and His have been adopted for convenience to represent 2,4-dinitrophenol, picric acid, Aspartic acid, glutamic acid, glycine, serine, Arginine and Histidine, respectively.

II.6: ESTIMATION OF THE ADSORBATES:

The stock solution of each adsorbate of a particular concentration was prepared by dissolving its required amount in water or 90% ethanol (in case of neutral and basic amino acids) as shown in Table 3.

From the stock solution (2.00 m mol dm⁻³) 80, 60, 50, 40, 30, 20, 10, 5 cm³ solutions were withdrawn, and each was diluted to 100 cm³ in calibrated volumetric flasks with water or 90% ethanol. In case of nitrophenols, further, out of the diluted solutions, 2.0 cm³-portions were withdrawn from each flask, mixed with 2.0 cm³ of 1.0N caustic soda solution, and then diluted suitably. The absorbance was measured at 385 nm against water as blank.
For the estimation of the amino acids, 2.0 cm$^3$-portions of the diluted solutions were withdrawn from each flask and transferred into a 25 cm$^3$ graduated tube with B-14 quick-fit cap, to which 2.0 cm$^3$ sodium acetate-EDTA buffer solution* was added, followed by the addition of 2 cm$^3$ of 0.4% (w/v) solution of ninhydrine (E. Merck, G.R.) in absolute alcohol and mixed well. A blank was prepared, substituting water for the solute solution. After addition of the reagent was complete, all the tubes were shaken to ensure mixing and then fitted with small air condenser and placed in a vigorously boiling water bath for 30 min, after refluxing began, to generate the colour. The tubes were then removed from water bath, air condenser was detached from each, and 4.0 cm$^3$ 75% (v/v) ethanol were added. The tubes were placed in a water bath for cooling for 5 min. Finally, the volume was made up to 10 cm$^3$ with 75% ethanol and all the tubes capped and then shaken vigorously for 30 seconds to oxidise hydridantin and to remove its red colour. After standing at room temperature for 30 min, absorbance measurements were taken at 570 nm against a blank with a Spekol spectrocolorimeter.

Colour is enhanced by addition of disodium-ethylene diamine tetra-acetic acid and it also improves reproducibility by eliminating trace metal interferences (16). EDTA is dissolved in 0.2 M sodium acetate solution and the buffer so obtained when used, maintains the pH 5.0, which is the optimum pH needed for colour generation for the amino acids and glutathione (17).

For preparation of sodium acetate-EDTA buffer solution, 0.41020 g of anhydrous sodium acetate and 1.25 g of EDTA were dissolved in water, and the volume is made up to 250 cm$^3$. 
II.7: **ADSORPTION PROCEDURE:**

0.10 g HZO or HSO sample of a particular pH was transferred carefully into 10-cm³ volumetric flasks. To each of these flasks, 10 cm³ of diluted adsorbate solutions (0.10 to 2.00 m mole dm⁻³) were added. The flasks were initially shaken, placed in thermostat at the desired temperature for different time intervals. The intermittent shaking of the flasks was done manually. After a definite period, 5-cm³ of the aliquot were withdrawn from each flask, centrifuged and then from 2.0 cm³ of this solution, the adsorbate concentrations (Ce, end concentration) estimated spectrophotometrically. The amount adsorbed (x) was taken as the difference of Co – Ce, where Co is the initial concentration.

II.8: **ADSORPTION IN PRESENCE OF ELECTROLYTES:**

In order to explore the possible mechanism of adsorption, study of the influence of the presence of some strong electrolytes (NaNO₃, Na₂SO₄ and Na₃PO₄) on adsorption was also conducted with nitrophenols. In case of acidic, neutral amino acids the electrolytes used are NaNO₃, Mg(NO₃)₂ and Al(NO₃)₃ for neutral and basic amino acids. The concentration of the adsorbate and the electrolytes were the same i.e. 2.00, 0.80 and 0.20 m mole dm⁻³. These conditions allow the anions (NO₃⁻, SO₄²⁻ and PO₄³⁻) and cations (Na⁺, Mg²⁺ and Al³⁺) to compete for the adsorption
sites on HZO and HSO surfaces. The general procedure adopted was as follows: 5.0 cm$^3$ of adsorbate solution (4.00, 1.60 and 0.40 m mole dm$^{-3}$ in case of amino acids and 2.00 and 0.40 m mole dm$^{-3}$ for nitrophenols) was transferred to 10 cm$^3$-volumetric flasks, and to each of them 1.0 cm$^3$ of the electrolyte solution in water or 90% ethanol (20.00/10.00 and 2.00 m mole dm$^{-3}$) was added. Then the volume was made up to the mark with water. Now, into each of them, 0.10 g of the adsorbent was added. The flasks were shaken and placed in thermostat at 30 $\pm$ 1$^\circ$ for 24 hr. The end concentration, and hence the amount of the solute adsorbed was estimated as usual.

II.9: DESORPTION STUDIES:

Desorption behaviour of a solute may give an insight as to what extent the adsorbed species are replaceable from the substrate, and also the selectivity of different desorbing agents. The term "selectivity" means knowledge of the interactions of the adsorbed species with inorganic ions, used as desorbing agents.

The procedure followed for desorption studies was to equilibrate the adsorbate with the substrate, then to reduce the concentration of the solutions, followed by addition of the desorbing agent. The amount of the adsorbate remaining with the solid, was recorded. Thus, the pre-treated HZO and HSO of varying pHw were selected as substrate
to study the equilibrium at 30 °C (24 hr). The initial strength of the solutes was: 2.00, 0.80 and 0.20 mol dm⁻³. After an interval of 24 hr, 3 cm³ of the solution from each flask were pipetted out, centrifuged and estimated for the "end concentration".

The flasks left with 5 cm³ solutions, were again made up to the mark with the solution of the desorbent (5 cm³) and kept in thermostat at 30°C for 1 hr. After this interval, 5 cm³ of the aliquot was withdrawn from each flask, centrifuged and estimated. This procedure has been referred to as "first dilution". The solution left in the flask was again given the same treatment with the desorbing agent for an interval of 1 hr, hereafter called "final dilution".

Aqueous or 90% ethanol solutions of sodium nitrate, sulphate and phosphate of different concentrations (0.1 - 0.001 M) have been used as desorbent in the studies with acidic amino acids and nitrophenols, while the desorbents used for the studies of neutral and basic amino acids were the solutions of the nitrate of sodium, magnesium and aluminium (0.01 - 0.001 M) in 90% ethanol.

II.10: pH of the sorbates and electrolytes in water/90% Ethanol:

In all the above sorption-desorption studies, the hydronium ion concentration of the solution is of
considerable importance. So, the pH of the amino acids and nitrophenols solutions (2.00 mmole dm$^{-3}$) and those of the electrolytes, used in aqueous and 90% ethanol medium were measured. The data are shown in Table - 4.

II.11: ELUTION STUDIES:

The usual goal in column chromatography is the adequate separation of a given sample mixture. In approaching this goal, one must have some quantitative measure of relative separation or resolution. Thus, in order to explore the utility of the results obtained by the sorption-desorption studies of the sorbates on acid-treated H$_2$O and alkali-treated H$_3$O, separation parameters were investigated. Different electrolytes solutions were used as elutants.

For this purpose, a known amount of the substrate (1.0 g) was introduced into a glass column (length 10 cm, i.d. 0.5 cm) with a sintered disc (number zero) support, and kept in contact (2 hr) with 1.0 cm$^3$ of the aqueous nitrophenol or ethanoic amino acid solution. The adsorbed solutes were then eluted with aqueous or 90% ethanol solution of the inorganic electrolytes (0.1M - 0.01M). The effluents were collected in fractions. The sorbate present in each fraction was then estimated as usual. From the results so obtained, different elution curves were drawn from which the possibility of separation of some sorbate mixture was explored.
II.12: CHROMATOGRAPHIC SEPARATIONS:

Finally, on the basis of the known values of the distribution coefficients of the adsorbates (adsorption-desorption studies) and the retention parameters (elution experiments) column separations of certain synthetic sorbates mixture (two or three component) were achieved. The solute mixture (1.0 cm³ of each solute) of a particular concentration was applied to the column (10 x 0.5 cm) and kept as such for 2 hr. The solutes were then eluted gradually with the eluents. The eluates collected were centrifuged and estimated colorimetrically to determine the percentage-recovery in each case.

The solutes in the eluates were confirmed by spot tests.
### TABLE 1

**SYNTHESIS AND COMPOSITION OF HYDROUS ZIRCONIUM OXIDE OF VARYING SURFACE-PHASE pH.**

<table>
<thead>
<tr>
<th>Surface-pH of oxide prepared</th>
<th>Strength of acid added for pretreatment (N)</th>
<th>pH of the wash liquid</th>
<th>Anion content of the sample (a eq. g⁻¹)</th>
<th>OH⁻ ion-exchange capacity (a eq. g⁻¹)</th>
<th>Surface area (S ± 2 m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.40</td>
<td>0.50</td>
<td>1.0</td>
<td>2.0</td>
<td>259</td>
</tr>
<tr>
<td>3.5</td>
<td>0.25</td>
<td>0.10</td>
<td>0.25</td>
<td>1.75</td>
<td>330</td>
</tr>
<tr>
<td>4.0</td>
<td>0.10</td>
<td>0.075</td>
<td>0.20</td>
<td>1.50</td>
<td>290</td>
</tr>
<tr>
<td>4.5</td>
<td>0.06</td>
<td>0.025</td>
<td>0.15</td>
<td>1.25</td>
<td>334</td>
</tr>
<tr>
<td>5.0</td>
<td>0.04</td>
<td>0.017</td>
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<td>0.08</td>
<td>305</td>
</tr>
<tr>
<td>5.5</td>
<td>0.02</td>
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<td>215</td>
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<td>6.0</td>
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<td>7.0</td>
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<td>0.015</td>
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<td>0.012</td>
<td>0.015</td>
<td>0.06</td>
<td>240</td>
</tr>
</tbody>
</table>

**Note:** (P) / [H₂O(P)]; (n) / [H₂O(n)]; (h) / [H₂O(h)]; (S) / [H₂O(S)]; and (a) / [H₂O(a)] stand for HClO₄, HNO₃, HCl, H₂SO₄ and CH₃COOH-treated H₂O, respectively.
TABLE - 2

DETAILS OF SYNTHESIS AND COMPOSITION OF HYDRATED TIN(IV)

OXIDE OF VARYING SURFACE-PHASE pH.

Time of contact: 24 hr
Surface-phase pH of HSO taken for pretreatment: pH 3.0
Temperature: 30 ± 1º
Volume of the alkali adsorbed for pretreatment: 50 cm³

<table>
<thead>
<tr>
<th>Surface-phase pH of the HSO prepared</th>
<th>Normality pH of the alkali used for liquid pretreatment (N)</th>
<th>pH of the H⁺ ion-exchange capacity (meq/g)</th>
<th>Amount of Surface cation area (S⁺, (Na⁺)(mg⁻m²/g) ion/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.0025</td>
<td>5.0</td>
<td>0.15</td>
</tr>
<tr>
<td>5.5</td>
<td>0.003</td>
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<td>0.18</td>
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<td>6.0</td>
<td>0.005</td>
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<td>6.5</td>
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<td>7.0</td>
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<td>0.80</td>
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<td>11.5</td>
<td>1.10</td>
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Dash (-) means the value not determined.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sorbate used</th>
<th>Mol. formula</th>
<th>Mol. wt.</th>
<th>Apparent dissociation constant*</th>
<th>Iso-electric point pI</th>
<th>Solubility in aq. medium**</th>
<th>Amount required for 2.00 m mol dm$^{-3}$ (g/dm$^3$)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>2,4-Dinitrophenol</td>
<td>C$_6$H$_4$N$_2$O$_5$</td>
<td>184.1</td>
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<td>3</td>
<td>Aspartic acid</td>
<td>C$_4$H$_7$O$_4$N</td>
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<td>1.88 3.65 (CONH) (NH$_3$)</td>
<td>9.60</td>
<td>2.77</td>
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<td>4</td>
<td>Glutamic acid</td>
<td>C$_5$H$_9$O$_4$N</td>
<td>147.08</td>
<td>2.19 4.25 (CONH) (NH$_3$)</td>
<td>9.67</td>
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<tr>
<td>5</td>
<td>Glycine</td>
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<td>2.34 9.60 (CONH) (NH$_3$)</td>
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<td>Serine</td>
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<td>L(+)-Arginine</td>
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<td>7.47</td>
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</table>

* Apparent dissociation constants at 25° determined on cells with liquid function;

** Solubility per 100 g of water at 25°.
<table>
<thead>
<tr>
<th>Solution</th>
<th>Aqueous medium Concentration</th>
<th>pH</th>
<th>90% ethanol medium Concentration</th>
<th>pH</th>
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<td><strong>Solute solution</strong></td>
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<td></td>
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<tr>
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<td>3.10</td>
<td>Glycine</td>
<td>2.00 mM</td>
</tr>
<tr>
<td>Picric acid</td>
<td>2.00 mM</td>
<td>3.00</td>
<td>Serine</td>
<td>2.00 mM</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>2.00 mM</td>
<td>3.35</td>
<td>Arginine</td>
<td>2.00 mM</td>
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<td>Glutamic acid</td>
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<td>Histidine</td>
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<td><strong>Electrolyte solution</strong></td>
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<td>Sodium Nitrate</td>
<td>0.01 M</td>
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<td>Sodium sulphate</td>
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<td>Sodium Phosphate</td>
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</table>
STRUCTURE OF THE AMINO ACIDS

ACIDIC AMINO ACIDS

Aspartic Acid - C_4H_7O_4N
mol. wt. = 133.06

Glutamic Acid - C_5H_9O_4N
mol. wt. = 147.08

NEUTRAL AMINO ACIDS

Glycine - C_2H_5O_2N
mol. wt. = 75.05

Serine - C_3H_7O_3N
mol. wt. = 105.06

BASIC AMINO ACIDS

Arginine - C_6H_14O_2N_4
mol. wt. = 174.14

Histidine - C_6H_9O_2N_3
mol. wt. = 155.09

STRUCTURE OF THE AMINO ACIDS

Fig. 1: THE SORBATES.
LITERATURE CITED


