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Spectrochemical studies on charge transfer bands due to d^0, d^5 and d^{10} ions in a sodium silicate glass

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Titanium, vanadium and copper are normally present in glasses in their variable valency states but only Ti^{4+} ($3d^0$), V^{5+} ($3d^0$) and Cu^+ ($3d^{10}$) ions were found to exhibit charge transfer bands in glasses in the ultra-violet region of light. The molar extinction coefficients of these ions were calculated at their wavelength maxima in a $30Na_2O{\cdot}70SiO_2$ glass using Beer's-Bouger's equation and the intensities of their bands were found to lie of the order of around 10^3 gm mol lit^{-1}cm^{-1}. The values of the molar extinction coefficients for these ions were compared with those of Ce^{4+} ($5d^0$), Cr^{6+} ($3d^0$) and Fe^{3+} ($3d^5$) ions calculated earlier in $30Na_2O{\cdot}70SiO_2$ glass at their wavelength maxima in UV-region. The mechanism of electronic transition was suggested as L → M, M → L and M → L → M charge transfer available till date as a result of absorption of high energy UV-radiation extensively for d^0, d^5 and d^{10} ions respectively in glass depending upon the glass melting conditions. The low energy tail, of the UV-bands due to all these ions were found to obey Urbach's Rule in the present sodium silicate glass. The intensities of the charge transfer bands due to these ions are expected to depend upon their nature and symmetries, electronic configurations and wavelength of maximum absorption in the glass. *© 2001 Kluwer Academic Publishers*

1. Introduction

Charge transfer process due to unfilled, half-filled and completely filled d-state ions is an important and very useful phenomena occurring in crystals, solutions and glasses. The control of high energy radiations specially ultra-violet in commercial glasses such as sun glasses, art glasses, filters, window shielding glasses for observatory towers and high altitude buildings can be done by introducing the metal ions such as Cr^{6+}, Ce^{4+}, Ti^{4+}, V^{5+}, Fe^{3+} and Cu^+ in glasses. Nath *et al.* [1] had studied the ultra-violet absorption characteristics of hexavalent chromium in alkali silicate glasses as well as aqueous alkaline chromate solutions. In view of identical absorption spectra of glasses and solutions containing chromium, they identified the presence of Cr^{6+} ion as $[CrO_4]^{2-}$ complex ion in their alkali silicate glasses. They calculated the molar extinction coefficient of Cr^{6+} ion as 4.2×10^3 gm mol lit^{-1} cm^{-1} in a $30Na_2O{\cdot}70SiO_2$ glass and reported the intensity of the band at its wavelength maximum at around 370 nm. The value of molar extinction coefficient for Cr^{6+} ion as 4.2×10^3 gm mol lit^{-1} cm^{-1} at its λ_{max} at around 370 nm lies in the order of the intensity of the charge transfer bands. The mechanism of charge transfer was suggested as transfer of electron from oxygen ligand to Cr^{6+} ion to fill up its vacant $3d^\circ$-orbital in the glass. This phenomenon was very much analogous to L → M charge transfer process taking place in chromate solutions and crystals [2].

Sainz *et al.* [3] investigated the combined effect of TiO_2 and CeO_2 on the yellow colour formation in silicate glasses. The authors [3] studied the optical behaviour of glasses containing ions of cerium and titanium melted under moderate reducing conditions and suggested the Ce^{3+} and Ti^{4+} ions as the main colouring centres for yellow colour formation as per the following mutual redox interractions mechanism.

$$Ce^{4+} + Ti^{3+} \rightarrow Ce^{3+} + Ti^{4+} \qquad (1)$$

They studied the optical behaviour of glasses by spectrophotometry using the diffused reflectance powder technique to detect the ultra-violet bands for their coloured glasses under investigation and recorded the absorption spectra in UV-visible range as Kubelka-Munk function, F(R), equivalent to absorbance for reflectance spectra [3]. Despite this they did not determine the molar extinction coefficient of the colouring ions to ensure the mechanism of charge transfer bands responsible for intense yellow colour formation in glasses due to mixed redox interaction.

Wood and Remeika [4] reported the co-operative charge transfer bands within the two valence states of iron, namely ferrous and ferric, present in Yttrium iron garnet and they attributed it to Fe^{2+}—O—Fe^{3+} chromophore. Paul [5] has also studied the mechanism of charge transfer with mixed cerium-titanium redox in a sodium boroalumino silicate glass and suggested that the broad charge transfer arisen at round 29000 cm^{-1} (345 nm) is due to co-operative charge transfer within Ce^{3+}—O—Ti^{4+} coloured chromophore.

Steele and Douglas [6] suggested that in silicate glasses on one hand ferrous iron is responsible for charge transfer band in UV-region in between 200–230 nm with a molar extinction coefficient of 3.0×10^3 gm mol lit^{-1} cm^{-1} while on the other hand in silicate and borate glasses ferric iron has a strong charge transfer band with molar extinction coefficient of 7.0×10^3 gm mol lit^{-1} cm^{-1} centred at its wavelength maximum at around 230 nm in the UV-range. Although the authors [6] have calculated the intensities of their charge transfer bands but they could not clearly indicates the mechanism of charge transfer in their glasses containing ferrous and ferric iron. Singh *et al.* [7] reported a broad charge transfer band due to Ce^{4+} ion at around 225 nm in a $30Na_2O{\cdot}70SiO_2$ glass and calculated the intensity of the band in terms of molar extinction coefficient as 24.0×10^3 gm mol lit^{-1} cm^{-1} at its wavelength maximum. The mechanism was suggested as the transfer of electron from O^{2-} ligands to Ce^{4+} ion to fill up its vacant $5d^\circ$-orbital in a cerate group $[CeO_4]^{4-}$.

Several other investigations on the optical absorption characteristics of glasses containing transition metal ions and their role as redox with particular reference to vanadium, titanium and copper have been studied earlier also but a detailed picture on the mechanism of charge transfer bands in glasses had been lacking over past several years [8–21].

In view of this the present study was undertaken with pentavalent vanadium ($3d^\circ$), tetravalent titanium ($3d^\circ$) and monovalent copper ($3d^{10}$) present in a sodium silicate glass in order to calculate the intensities of their UV-absorption bands responsible for colouring characteristics of these ions as well as to suggest the mechanisms of charge transfer processes occurring in glasses.

2. Experimental

Sodium silicate glasses having molar composition $30Na_2O{\cdot}70SiO_2$ were selected as base glass composition. For preparing the glass batches, Analytical Reagent grade sodium carbonate and silicon dioxide powder were used. Desired concentrations of titanium, vanadium and copper were introduced in the batch in the form of AnalaR grade TiO_2, NH_4VO_3 and CuO. Sodium silicate glasses containing TiO_2 and CuO were melted in a 100 ml capacity platinum −2% Rhodium crucible kept in an electric globar rod furnace in air atmosphere at 1400°C. Since ammonium metavanadate is very corrosive towards the attack of platinum crucible as such glasses containing vanadium were melted in 100 ml alumina crucibles kept in the furnace at 1400°C. The temperature was controlled within ±10°C with an automatic R-type thermocouple temperature indicator-cum-controller. After approximately six hours of melting glasses were cast and poured onto an aluminium plate and after cooling they were crushed and remelted for an another period of four hours to ensure homogeneity. They were taken out of the furnace and poured into a rectangular mould onto an aluminium plate and annealed at 500°C for one hour. After grinding and polishing the absorption spectra of glass samples were recorded on an UV-Vis SICOSPEC-200GL recording spectrophotometer in ultra-violet range of light. Densities, thicknesses and refractive indices of the glass samples were measured. The glasses were chemically analysed for V^{5+} ion, total vanadium as pentavalent, Ti^{4+} ion, total titanium as tetravalent, cuprous copper and total copper as cupric spectrocolorimetrically [22, 23] using UV-Vis SICOSPEC-200GL digital spectrophotometer. The V^{3+} and Cu^{2+} ions were present in the sodium silicate glass as their V^{3+}/V^{5+} and Cu^{+}/Cu^{2+} redox pairs along with V^{5+} and Cu^{+} ions. Their concentrations were determined by the difference of total vanadium and V^{5+} ion ($[V^{3+}] = [\Sigma V] - [V^{5+}]$) and total copper and Cu^{+} ion ($[Cu^{2+}] = [\Sigma Cu] - [Cu^{+}]$) in the glass as presented in Table I.

TABLE I Molar extinction coefficients of Ti^{4+}, Cu^{+} and V^{5+} ions in a $30.Na_2O{\cdot}70SiO_2$ glass

Glass Sample No.	absorbance on Sicospec-200 GL Spectro-photometer	Wave length maxima (nm)	Thickness (cm)	V^{5+} ion	Total Vanadium as V^{5+} ion	V^{3+} ion = ΣV-V^{5+}	Total Titanium as Ti^{4-} ion	Cu^{+} ion	Total Copper as Cu^{2+} ion	Cu^{2+} ion = ΣCu-Cu^{+}	Molar extinction coefficient (ε) (gm mol $\text{lit}^{-1}\text{cm}^{-1}$)	Average (ε) (gm mol $\text{lit}^{-1}\text{cm}^{-1}$)	Error (%)
1a	0.258	250	0.124	-	-	-	0.0021	-	-	-	1.62×10^3		−1.9
2a	0.372	250	0.122	-	-	-	0.0032	-	-	-	1.65×10^3	1.65×10^3	0.0
3a	0.972	250	0.128	-	-	-	0.0073	-	-	-	1.64×10^3		−0.6
4a	0.928	250	0.126	-	-	-	0.0082	-	-	-	1.67×10^3		+1.2
1b	0.192	290	0.124	-	-	-	0.0021	-	-	-	1.13×10^3		0.0
2b	0.266	290	0.122	-	-	-	0.0032	-	-	-	1.12×10^3	1.13×10^3	−0.9
3b	0.587	290	0.128	-	-	-	0.0073	-	-	-	1.14×10^3		−0.9
4b	0.635	290	0.126	-	-	-	0.0082	-	-	-	1.12×10^3		−0.9
5a	1.920	240	0.198	-	-	-	-	0.019	0.046	0.027	1.29×10^3	-	+3.1
6a	2.470	240	0.181	-	-	-	-	0.028	0.057	0.029	1.23×10^3	1.25×10^3	1.6
7a	2.820	240	0.128	-	-	-	-	0.045	0.076	0.031	1.24×10^3		−0.8
8a	3.880	240	2.138	-	-	-	-	0.058	0.092	0.034	1.24×10^3		−0.8
5b	1.790	265	0.198	-	-	-	-	0.019	0.046	0.027	1.20×10^3		0.0
6b	2.400	265	0.181	-	-	-	-	0.028	0.057	0.029	1.20×10^3	1.20×10^3	0.0
7b	2.690	265	0.128	-	-	-	-	0.045	0.076	0.031	1.19×10^3		−0.8
8b	3.780	265	0.138	-	-	-	-	0.058	0.092	0.034	1.20×10^3		0.0
9	1.106	295	0.212	0.010	0.068	0.058	-	-	-	-	1.04×10^3		−0.9
10	1.232	295	0.196	0.012	0.122	0.011	-	-	-	-	1.05×10^3	1.05×10^3	0.0
11	0.977	295	0.122	0.015	0.247	0.232	-	-	-	-	1.06×10^3		+0.9
12	1.190	295	0.126	0.018	0.361	0.343	-	-	-	-	1.05×10^3		0.0

2.1. Analysis of glass for vanadium

2.1.1. Calibration curve for pentavalent vanadium

Standard solution containing 100 μg V^{5+} ion/ml was prepared by dissolving 0.023 gram of AnalaR grade ammonium metavanadate (NH_4VO_3) with double distilled water in presence of few drops of concentrated H_2SO_4 and liquid ammonia in a 100 ml volumetric flask and the volume was made up to the mark with water. Different volumes of this solutions containing 5.0–15.0 $\times$ 10^2 μg V^{5+} ion were taken into 100 ml volumetric flask. One ml of 1 : 2 phosphoric acid and 5.0 ml of 0.5 M sodium tungstate solutions were added to each V^{5+} ion solutions contained in the flasks and the volume was made up to mark by double distilled water. An yellow colour of phosphotungstovanadic acid was developed in the flasks and the absorbances of which were measured on a SICOSPEC-200GL spectrophotometer at the wavelength maximum at 400 nm against a reagent blank solution. The colour of the solution was stable up to several hours. All the reagents used were of Analytical Reagent grade. A calibration curve was prepared by plotting the absorbance against concentration of V^{5+} ion and Beer's law was found to obey within the concentrations range studied as shown in Fig. 1.

2.1.2. Estimation of total vanadium as pentavalent in silicate glass

One gram of finely powdered and dried glass sample was taken in a 35 ml platinum dish and 5 ml 40% HF and few drops of concentrated H_2SO_4 were added in the dish. The platinum dish containing silicate glass sample was kept on a sand bath and the glass was hydrofluorized for one hour to remove silica. An another portion of 3 ml HF was further added to the dish along with few drops of concentrated H_2SO_4 and it was kept for an another half an hour on the sand bath to ensure complete hydrofluorisation of silica. The whole content was transferred from the dish to a 100 ml volumetric flask with distilled water and its volume was maintained up to the mark. An aliquot portion of this solution was taken in an another 100 ml volumetric flask and 3 drops of N/20 $KMnO_4$ solution was added to oxidise the lower valency state of vanadium into its pentavalent state by boiling the solution for 10 minutes. The content was cooled and the pink colour of $KMnO_4$ solution was discharged by addition of required millilitres of 10% hydrochloric acid solution. After this the yellow colour of phosphotungstovanadic acid in the solution was developed by adding one ml 1 : 2 phosphoric acid and 5.0 ml 0.5 M sodium tungstate solutions as per procedure described above. The absorbance of the yellow coloured solution was measured on the SICOSPEC-200 GL spectrophotometer at 400 nm against a reagent blank. The concentration of total vanadium in the glass was calculated as pentavalent with the help of calibration curve as shown in Fig. 1.

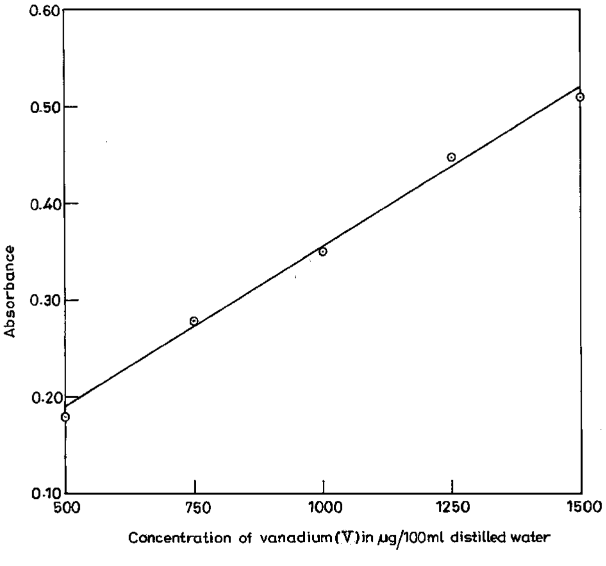


Figure 1 Calibration curve for pentavalent vanadium by sodium tungstate method.

2.1.3. Determination of V^{5+} ion in glass

One gram portion of the powdered and dried glass sample was hydrofluorized at room temperature in presence of few drops of concentrated H_2SO_4 for one hour. An excess of 40% HF was neutralised by the addition of desired volumes of 50% ammonia solution in presence of 1-2 drops of methyl red indicator. The whole content was transferred in a 100 ml measuring flask and the volume was made up to mark with the help of distilled water. An aliquot portion of this solution was taken in an another 100 ml measuring flask and the yellow colour of phosphotungstovanadic acid was developed in the solution with the help of 1 : 2 phosphoric acid and 0.5 M sodium tungstate solutions according to the procedure described earlier. The absorbance of the yellow coloured solution was measured on the spectrophotometer at 400 nm against a reagent blank. The decomposition of glass by 40% HF in presence of concentrated H_2SO_4 does not disturb the ratio of higher valence state to lower valence state of vanadium in the glass which is evident from the constant value of molar extinction coefficient of V^{5+} ion within ±5% experimental error. The concentration of V^{5+} ion was calculated in the glass with the help of calibration curve (Fig. 1).

2.2. Analysis of glass for titanium

Since the absorption spectra for a sodium silicate glass containing TiO_2 prepared under normal melting conditions do not produce any absorption band in the visible region it clearly shows that Ti^{3+} ion is not present in the glass [18, 20, 21]. Therefore, the glass was analysed for total titanium only as tetravalent spectrocolorimetrically [22]. However, Morinaga *et al.* [18] have established the presence of Ti^{3+} ion in alkali silicate glasses melted with small concentration of Ti_2O_3 under strongly reducing argon atmosphere at 1500°C.

2.2.1. Calibration curve for Ti^{4+} ion

A 100 ml standard solution containing 1.0 mg Ti^{4+} ion/ml was prepared by dissolving 0.740 gm

AnalaR grade potassium titanyl oxalate dihydrate ($K_2TiO(C_2O_4)_2 \cdot 2H_2O$) in double distilled water along with 0.08 gm ammonium sulphate and 1.0 ml concentrated H_2SO_4 in a 250 ml beaker. The whole content was boiled for 5–10 minutes and cooled to room temperature to get a clear solution. The solution was transferred in a 100 ml volumetric flask and the volume was made up to the mark with distilled water. 10 ml of this stock solution was diluted to 100 ml with distilled water in a 100 ml volumetric flask to get a solution containing 100 μg Ti^{4+} ion/ml. Different volumes of this solution containing 100–700 μg Ti^{4+} ion were taken in 50 ml volumetric flasks followed by the additions of 10 ml 6N-H_2SO_4 and 2.0 ml 3% H_2O_2 in each of these flasks. An yellow colour due to $[Ti(H_2O_2)]^{4+}$ ion in the solution was developed and the volume of the same was made up to the mark in the flask with water. The absorbance of the yellow coloured solution was measured on a SICOSPEC-200GL spectrophotometer at the wavelength maximum at 410 nm against a reagent blank. The colour was stable up to several hours. A calibration curve was prepared by plotting the absorbance of the coloured solution against concentrations of Ti^{4+} ion and Beer's law was found to obey within the concentrations range selected as shown in Fig. 2.

2.2.2. Determination of tetravalent titanium in glass

1.0 gm of finely powdered and dried silicate glass sample was hydrofluorized and decomposed in a platinum dish kept on a sand bath with the help of 5.0 ml 40% HF in presence of a few drops concentrated H_2SO_4. In order to ensure complete hydrofluorisation of the glass 3.0 ml of HF was added to the content of the platinum dish along with the addition of 4-5 drops of concentrated H_2SO_4 and the dish was heated on a sand bath till dryness. The content of the dish was dissolved in distilled water and it was transferred to a 100 ml volumetric flask. The platinum dish was washed with the distilled water and the wash solution was also added to the flask. The volume of the solution was maintained upto the mark of the flask with distilled water. An aliquot portion of this solution was taken in a 50 ml measuring flask and 10 ml of 6N-H_2SO_4 followed by the addition of 2.0 ml 3% hydrogen peroxide was added. An yellow coloured, $[Ti(H_2O_2)]^{4+}$ ion complex was developed in the solution after 48 hours. The volume of the coloured solution was made upto the mark with distilled water. The absorbance of the yellow coloured solution was measured at 410 nm on the spectrophotometer against a reagent blank. The concentration of total titanium as Ti^{4+} ion was calculated with the help of the calibration curve prepared earlier as shown in Fig. 2 as Ti^{3+} ion was not present in the glass.

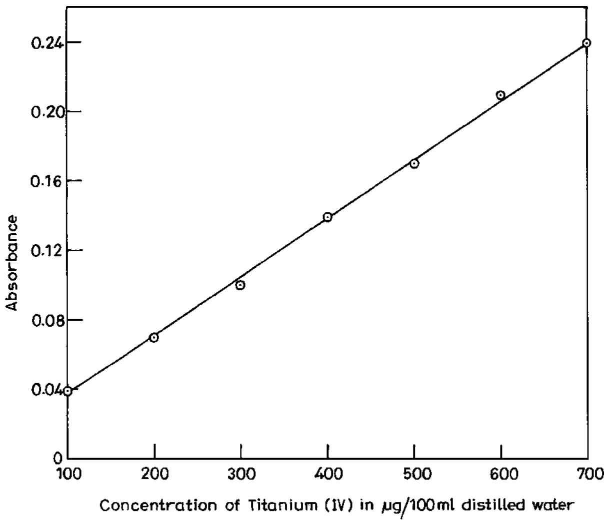


Figure 2 Calibration curve for tetravalent titanium by hydrogen peroxide method.

2.3. Analysis of glass for copper

2.3.1. Calibration curve for Cu^+ ion

Since cuprous copper is very sensitive to air oxidation in aqueous solution even at room temperature, the preparation of a standard and stable solution of cuprous ion is difficult. Therefore, iodine monochloride method for spectrocolorimetric determination of cuprous copper in the glass was adopted [22] and to overcome the difficulty in preparing a stable solution of cuprous ion an approximate N/10 solution of iodine in Guaranteed Reagent grade carbon tetrachloride was prepared in stead. An approximate N/10 aqueous solution of iodine was prepared by dissolving 2.0 gm iodate free KI and 1.27 gm resublimed I_2 with 30–40 ml distilled water in a 100 ml volumetric flask. The volume of the solution was made up to the mark. This approximate N/10 solution of iodine was standardised against a previously titrated approximate N/10 aqueous sodium thiosulphate solution with standard N/10 aqueous potassium iodate solution. Accordingly, the exact concentration of I_2/ml in CCl_4 solution was calculated and different volumes of this solution containing 2–10 mg I_2 in carbon tetrachloride were taken in 50 ml volumetric flasks and the volumes of the solution were maintained up to the mark with carbon tetrachloride. The absorbances of the pink I_2-CCl_4 solutions were measured on a SICOSPEC-200 GL digital spectrophotometer at 520 nm against a reagent blank. A calibration curve for the determination of equivalent amount of Cu^+ ion was prepared by plotting absorbance versus concentration of I_2/50 ml CCl_4 solution as shown in Fig. 3. The curve was found to obey Beer's law in the concentration range of iodine dissolved in carbon tetrachloride. The pink color of iodine in carbon tetrachloride was stable up to several hours.

2.3.2. Determination of Cu^+ ion in glass

0.5 gm of finely powdered and dried glass sample was weighed and transferred to a polythene separatory funnel with 7.5 ml distilled water. 7.5 ml of 40% HF + 7.5 ml of concentrated HCl along with 2 ml iodine monochloride was added to the funnel. Further addition of 20 ml CCl_4 was done immediately. The mouth of the funnel was tightened with the cap. The entire content was shaken vigorously for 1 hour to dissolve the sodium silicate glass sample. The cuprous copper was oxidised to cupric state resulting in simultaneous

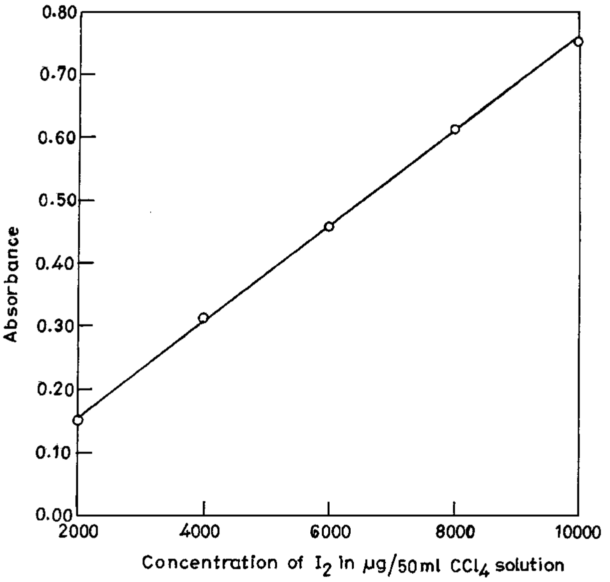


Figure 3 Calibration curve using iodine for determination of equivalent amount of Cu^+ ion.

liberation of equivalent amount of iodine in CCl_4. The pink coloured CCl_4 phase containing I_2 was separated in a 50 ml volumetric flask. The volume of the coloured I_2-CCl_4 solution was maintained up to 50 ml with carbon tetrachloride and its absorbance was measured at 520 nm on a spectrophotometer. The concentration of cuprous copper was determined with the help of calibration curve (Fig. 3). The constant value of ε^+_{Cu} at its λ_{max} shows that $Cu^+ : Cu^{2+}$ ratio is not disturbed during decomposition of the silicate glass.

2.3.3. Determination of total copper in the glass as Cu^{2+} ion

After hydrofluorisation of silicate glass by 40% HF in presence of concentrated H_2SO_4 in a 35 ml platinum dish kept on the sand bath, the content of the dish was brought into aqueous solution. An aliquot portion of this solution was boiled in presence of 4-5 drops of concentrated HNO_3 to oxidise all the cuprous ion into cupric form till the fumes of nitric acid. The total copper in the glass as cupric was determined spectrocolorimetrically by sodium diethyldithiocarbamate method according to procedure described by earlier workers [22, 23]. Earlier it has been pointed out that the determination of Cu^{2+} ion in the silicate glass does not disturb the cuprous : cupric ratio in the glass [11, 13].

3. Results and discussion

The molar extinction coefficients of V^{5+}, Ti^{4+} and Cu^+ ions were calculated in a $30Na_2O{\cdot}70SiO_2$ glass at their wavelength maxima at around 295, 250, 290 nm as well as at 240 and 265 nm, respectively using the following Beer's and Bouger's equation No. 2 and comparative results are presented in Table I and Fig. 4 along with their values for Cr^{6+}, Fe^{3+} and Ce^{4+} ions in the same glass. The stabilities of colours due to phosphotungstovanadic acid, $[Ti(H_2O_2)]^{4+}$ ion and iodine in their respective solutions are shown in Fig. 5 for several hours

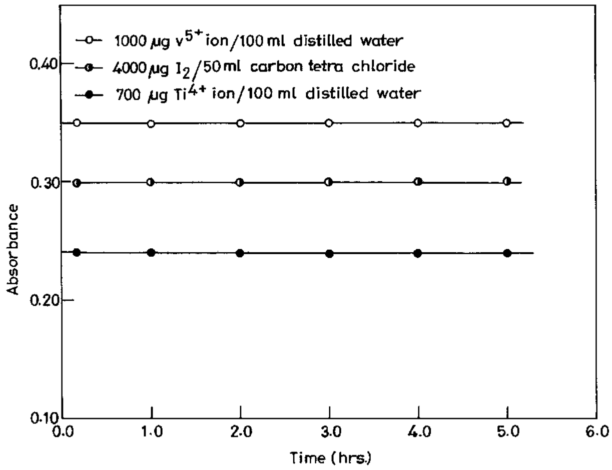


Figure 5 Stabilities of yellow and pink colors due to phosphotungstovanadic acid, $[Ti(H_2O_2)_4]^{4+}$ ion complex and iodine in respective solutions.

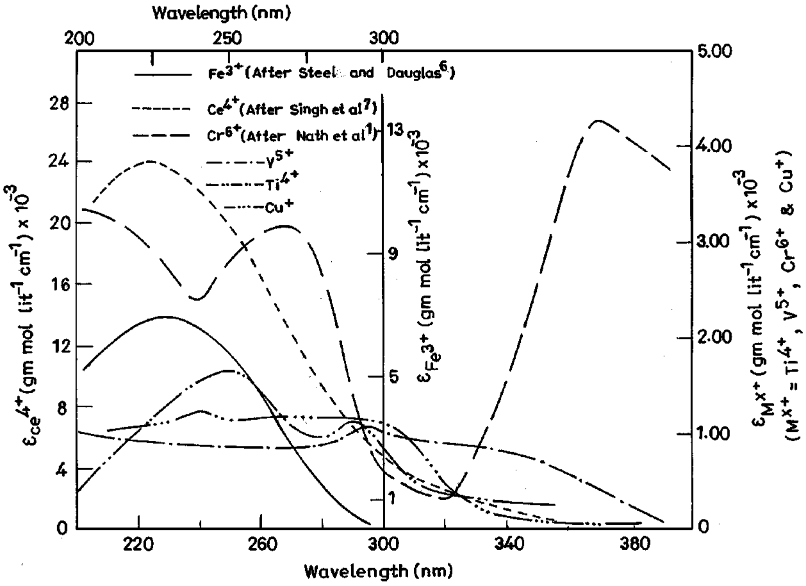


Figure 4 UV-Absorption characteristics of d-state ions in a $30Na_2O{\cdot}70SiO_2$ glass.

TABLE II Comparative data on molar extinction coefficients of d^0, d^5 and d^{10} ions in $30Na_2O{\cdot}70SiO_2$ glass

Glass Sample No.	Metal Ions	Electronic Configuration	Wavelength maxima (nm)	Molar extinction coefficient (gm mol lit^{-1} cm^{-1})
1a	Ti^{4+}	$3d^0$	250	1.65×10^3
1b	Ti^{4+}	$3d^0$	290	1.13×10^3
2	V^{5+}	$3d^0$	295	1.05×10^3
3	Cr^{6+}	$3d^0$	370	4.2×10^3
4	Ce^{4+}	$5d^0$	225	24.0×10^3
5	Fe^{3+}	$3d^5$	230	7.0×10^3
6a	Cu^{+}	$3d^{10}$	240	1.25×10^3
6b	Cu^{+}	$3d^{10}$	265	1.20×10^3

as such the measurements of absorbances were satisfactory.

$$\varepsilon = \frac{[2\log(1-R)+A] \times \text{ Atomic weight of the element}}{C_\mathrm{w} \times t \times d \times 10} \qquad (2)$$

where, C_w = Concentration of the metal ion (wt%)
t = thickness of the glass sample (cm)
d = density of glass at room temperature (gm/cc)
A = absorbance of the glass sample at λ_max
R = Reflactance factor.

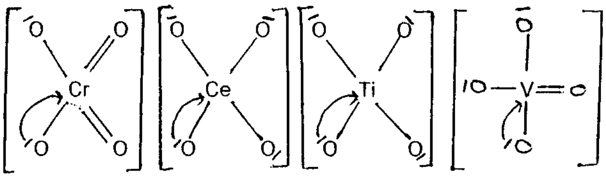
The nature of absorption behaviour of the sodium silicate glass containing V^{5+} ($3d^\circ$), Ti^{4+} ($3d^\circ$) and Cu^+ ($3d^{10}$) ions in UV-region were presented in Table II and Fig. 4 in order to compare with those of Cr^{6+} ($3d^0$), Ce^{4+} ($5d^0$) and Fe^{3+} ($3d^5$) ions reported by earlier workers [1, 6, 7] in the same glass composition and wavelength region.

In order to obscure the UV-bands for Ti^{4+}, Cu^+ and V^{5+} having high intensities of the order of around 10^3 gm mole/lit/cm of the glass in ultra-violet region, the concentration of these absorbing ions introduced in the glass was kept very small which essentially required the micro determination of these species by spectrocolorimetric methods for reliable results on their molar extinction coefficients. The values of the molar extinction coefficients of pentavalent vanadium, tetravalent titanium and monovalent copper as shown in Table I and Fig. 4 lie in the order of around 10^3 gm mol lit^{-1} cm^{-1} of the glass at their wavelength maxima which clearly correspond to the intensities of the charge transfer bands occurring as a result of absorption of high energy ultra-violet radiations. The present glass samples containing vanadium, titanium and copper were melted in normal melting conditions of temperature and partial pressure of oxygen as such copper and vanadium were found to be mostly present in their oxidised and reduced states both in the present sodium silicate glass while Ti^{4+} ion was the only valency state of titanium present in the glass under these melting conditions (Table I). The mechanism of charge transfer in case of copper redox as an exchange of electron can be given as $M \rightarrow L \rightarrow M$ cooperative charge transfer in the glass as Cu^+—O—Cu^{2+} which is analogous to Fe^{2+}—O—Fe^{3+} and Ce^{3+}—O—Ti^{4+} cooperative charge transfer processes occurring in yttrium iron garnet and sodium boroalumino silicate glass, respectively [4, 5].

Whenever an equilibrium between a lower and the higher valence states of a multivalent element is established in a molten glass it may be true in some cases that the redox ratio at equilibrium would depend upon the total concentration of an element if it is present into its lower concentration in the molten glass. Such data on redox ratios are used in studying the activity of the redox ions equilibrated in glasses at high temperature. It is further mentioned herewith that many systematic investigations have been carried out in the past on oxidation-reduction phenomena in glasses with different redox pairs to study the effect of temperature, partial pressure of oxygen, base glass composition and oxygen ion activity on their equilibrium [8–10, 12, 14, 24–40]. In order to ensure the applicability of redox ratios, Singh *et al.* [12, 32, 33, 39] have also conducted the studies on kinetics and thermodynamics of redox reactions in glasses containing Cu^+/Cu^{2+}, V^{3+}/V^{5+}, As^{3+}/As^{5+} and Cr^{3+}/Cr^{6+} pairs at different temperatures in air atmosphere. However, the molar extinction coefficient of a particular absorbing ion is always independent of the concentration of the ion as well as the total concentration of the element introduced in a glass of constant composition irrespective of its redox equilibrium conditions. Therefore, any variation in redox ratio with total concentration of an element in the present investigation would not affect the value of MEC of an ion in the glass even in its non-equilibrium condition.

While melting sodium silicate glasses in Pt/Rh crucible, no flake of rhodium was observed on the surface of the glass. Earlier workers [25–27, 29] had also reported that alumina did not interfere with the ferrous-ferric, cerous-ceric and chromic-chromate equilibria in binary alkali silicate glasses melted in alumina crucibles in air as furnace atmosphere. The present glass was also not found to contaminate with alumina during its melting.

Since the glasses melted with the compounds of titanium and vanadium contain tetravalent titanium and pentavalent vanadium as the only ultra-violet absorbing species, therefore, the probable mechanism of charge transfer is suggested herewith as the transfer of an electron from oxygen (O^{2-}) ligands to fill up the vacant d°-orbitals of these metal ions present in the glass in form of titanates $[TiO_4]^{4-}$ and vanadates $[VO_4]^{3-}$ like chromates $[CrO_4]^{2-}$ and cerates $[CeO_4]^{4-}$ ions. The mechanism of L → M charge transfer in these complex metal ions having an identical tetrahedral structures in glasses as suggested by previous workers [1, 7] for chromates and cerates is given as below.



In acid borosilicate and phosphate glasses Ti^{3+} ion can be obtained [20] more readily but it was not present in the silicate glass melted in air. However, the trivalent state of vanadium is present as V^{3+} ion in the glass as reported by Kumar [19] in alkali silicate glass which has a strong absorption band in the near infrared region at around 1120 nm. Since V^{3+} ion does not absorb in UV-region nor the intensity of its I.R. band was calculated as such the cooperative charge transfer in the case of titanium and vanadium systems is not probable.

Although, the values of molar extinction coefficients of d^0, d^5 and d^{10} ions as presented in Table I and Fig. 4 do not seem to be merely dependent upon the number of electrons transferred from the surrounding oxygen ligands to the central metal ions or vice-versa but the intensities of the UV-bands are expected to depend upon

(a) the nature and symmetries of the ions
(b) electronic configurations and
(c) their wavelength maxima.

However, the role of the number of electrons transferred also appears to be of vital importance during the charge transfer processes taking place in solutions, crystals and glasses.

The applicability of Urbach's Rule as written in Equation 3 was tested for V^{5+}, Ti^{4+} and Cu^{+} ions in the present sodium silicate glass and compared with those of Cr^{6+}, Ce^{4+} and Fe^{3+} ions in the same glass as given in Fig. 6.

$$\varepsilon = K_o\, e^{-\sigma(h\nu_0 - h\nu)/KT} \tag{3}$$

where, K_o, σ and ν_o are the materials constants.

$$\log \varepsilon = A + B\nu \tag{4}$$

where, A and B are constants and ν is the frequency of UV-radiation. On plotting the logarithm of molar extinction coefficients of all the species such as V^{5+}, Ti^{4+}, Cu^{+}, Cr^{6+}, Ce^{4+} and Fe^{3+} ions against the frequency of UV-radiations, straight lines followed by curvatures were obtained as shown in Fig. 6. The low energy tails of the UV-bands due to V^{5+}, Ti^{4+} and Cu^{+} ions were found to obey the Urbach's Rule over the range 25,000–30,000 cm^{-1}, 26,700–34,500 cm^{-1} and 27,000–32,600 cm^{-1} respectively, which was also true in the cases of Cr^{6+}, Ce^{4+} and Fe^{3+} ions present in the silicate glass. The deviations of the curves from its rectilinear behaviour as shown in Fig. 6 indicate that absorption bands due to V^{5+}, Ti^{4+} and Cu^{+} ions are being approached in the glass similarly as it has happened with reference to Cr^{6+}, Ce^{4+} and Fe^{3+} ions in the same $30Na_2O{\cdot}70SiO_2$ glass. This suggests that only V^{5+}, Ti^{4+} and Cu^{+} ions have their absorption bands at 225, 250 and 290 as well as 240 and 265 nm in $30Na_2O{\cdot}70SiO_2$ glass. Similar results were also reported by Nath *et al.* [1], Steele and Douglas [6] as well as Singh *et al.* [7] in the sodium silicate glass with particular reference to Cr^{6+}, Ce^{4+} and Fe^{3+} ions, respectively.

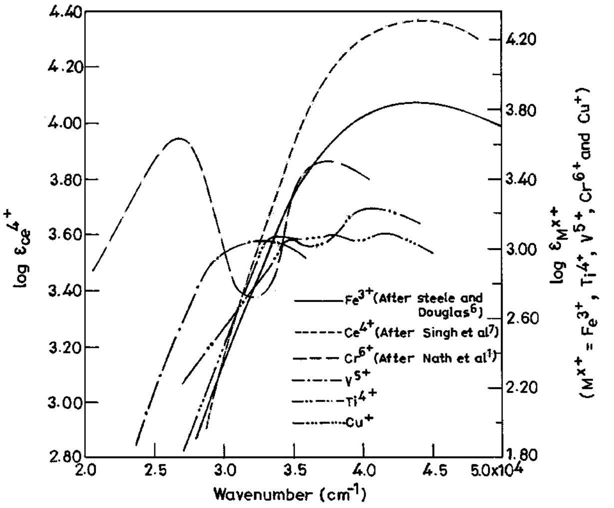


Figure 6 Varification of Urbach's Rule by relation between logarithm of molar extinction coefficient and frequency of UV-radiation.

The values of the molar extinction coefficients for these ions at their respective wavelength maxima can be used as a monitoring tool for calculating the concentrations of the present ions optically in silicate glasses under identical conditions. The present investigation is expected to throw light on the mechanism of charge transfer processes in glasses where very little work had been done earlier. Further work is also in progress to study the absorption behaviour of charge transfer bands due to such species in other glass systems.

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