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Infrared spectra and composition dependence investigations of the vitreous V_2O_5/P_2O_5 system

A. H. KHAFAGY, M. A. EWAIDA, A. A. HIGAZY, M. M. S. GHONEIM, I. Z. HAGER, R. EL-BAHNASAWY*
*Physics Department, and *Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Koom, Egypt*

A series of glasses in the V_2O_5–P_2O_5 system was prepared and their compositions analysed. The glass densities and molar volumes were determined. The results obtained revealed three compositional regions. In addition, the infrared absorption spectra of these glasses were measured at room temperature in the frequency range 1600–200 cm^{-1}. The compositional dependence of the bands present, attributed to a given band and mode of vibration, was investigated. However, the infrared data confirmed the results obtained from the density and molar volume measurements.

1. Introduction

Many phosphate glasses have been investigated by several authors [1–6] using chemical analysis techniques. It has been found that, in almost all cases, when glasses have been prepared by melting their constituents in air, some of the oxygen and phosphorus are lost; so that the composition of the final product may differ from that of the starting composition. Also, some reduction of the valencies of the cations may have taken place; therefore, the chemical analysis of the V_2O_5–P_2O_5 glasses in the present work was clearly necessary if the compositions were to be reliably known.

Infrared spectroscopy is a useful technique because it provides valuable information about atomic configurations in the glasses, i.e. the extent to which added cations either enter the network of the basic glass or reside interstitially, and the extent to which the double bond in the phosphate network is broken, can be qualitatively assessed.

Earlier infrared studies [7–9] for some vitreous solids have dealt with the experimental and theoretical investigations of the vibrational infrared spectra. However, recent attempts using infrared techniques have been made to study the structure of glassy materials. Quantitatively, vibrational spectra of various glassy systems including silicate [10], borate [11], and phosphate glasses [12, 13] were analysed, based on either the "localized model" or the "lattice model". These models are summarized by Borrelli and Su [14].

It is known [13] that when different cations are added to the P_2O_5 network, either, the phosphorus atoms are replaced by atoms of the new cation, or, the cation atoms enter the P_2O_5 network interstitially. In the first case, the infrared spectrum should remain the same as that of the phosphate, but with gradual shifts in its characteristic band group frequencies. In the second case, the cation atom enters the network as an ion. Then the network is gradually broken down and new spectral bands may appear corresponding to the vibrational character of those freely charged structural units. Types of ionic groups which might exist in sodium phosphate and cobalt phosphate have been previously described [13, 15]. The aim of the present study was to determine to what extent the addition of vanadium (in V_2O_5) to P_2O_5 follows either the former or the latter behaviour, as the added cation concentration increases and predominates in the phosphate network.

2. Experimental procedure

2.1. Glass preparation

Vanadium phosphate glasses of starting compositions expressed in mole per cent, were prepared from laboratory reagent grades of Analar P_2O_5 and Analar V_2O_5. Amounts of these oxides were weighed and mixed in an open alumina crucible which was then inserted into an electric furnace held at 250 °C for 1 h. After this treatment, each mixture was transferred to another electric furnace, open to the atmosphere, with its temperature pre-adjusted to that of the melt. It was observed that different temperatures were required to suite different preparations and the melting temperature lay in the range 700–950 °C, with the highest being that applied to the mixture of rich P_2O_5. The molten mixture was then occasionally stirred with an alumina rod to ensure homogeneity, and retained in the furnace for 15–30 min. Then the melt was poured into a mild steel mould to form glass rods 1.5 cm long and 1.2 cm diameter. After casting each glass, it was immediately transferred to an electric furnace held at 250 °C for 1 h. Then the furnace was switched off with the specimens inside it to be annealed and cooled slowly to room temperature. The amorphous nature

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of the prepared samples was confirmed by X-ray diffraction. The densities of the glasses were measured by Archimedes' method using toluene as the immersion liquid and, for comparison of the different glasses only, they are accurate to ± 0.001 g cm^{-3}.

2.2. Infrared measurements

For infrared investigations, glass samples were ground in a clean mortar to a fine powder. A few milligrams of glass powder were mixed and ground with KBr. Then, reasonably transparent pellets were formed by pressing the mixture at 6 ton for a few minutes under vacuum. Infrared absorption spectra of our glass samples were determined by using a Perkin–Elmer 598 infrared spectrophotometer. All measurements were conducted at room temperature over the range of wave number from 200–1600 cm^{-1}.

2.3. Chemical analysis of prepared glasses

2.3.1. Determination of phosphorus content

The determination of the phosphorus concentration in the present glass system by atomic absorption spectroscopy was not possible because of the lack of suitable absorption lines. Therefore, the gravimetric chemical technique was employed. In the present investigations, the determination of phosphorus as magnesium ammonium phosphate $Mg(NH_4)PO_4 \cdot 6H_2O$, or as magnesium pyrophosphate $Mg_2P_2O_7$, [16] was not possible because of the interference of vanadium; therefore, the phosphate was precipitated as ferric phosphate, then ignited and determined as ferric oxide, Fe_2O_3. Portions of powdered glass, weighing about 0.1 g, were dissolved in hot concentrated hydrochloric acid. Then 20 ml 0.05 M $FeCl_3$ solution were added, followed by a sufficient quantity of ammonia solution until a brown precipitate of composition $FePO_4 \cdot xH_2O$ is formed. The precipitate was then carefully filtered using Whatmann Ashless filter paper number 44. Then the precipitate was washed using dilute ammonia solution. After this treatment, the precipitate and the filter paper were transferred into a preweighed porcelain crucible which was ignited on a bunsen flame and then transferred to an electric muffle furnace for 1 h at 850 °C and then cooled slowly to room temperature in a vacuum desiccator. After ignition to constant weight, the precipitate was weighed as Fe_2O_3 and then the phosphorus content was calculated from

$$\%\ P_2O_5 = \frac{\text{Weight of } Fe_2O_3}{\text{Weight of sample}} \times \frac{\text{Molecular weight of } P_2O_5}{\text{Molecular weight of } Fe_2O_3} \times 100 \quad (1)$$

2.3.2. Determination of vanadium content

Glass samples weighing 0.01–0.1 g were ground in a mortar then completely dissolved in hot concentrated hydrochloric acid, when the following reaction occurred

$$(P_2O_5, V_2O_5)\text{glass} + \text{conc.HCl} \xrightarrow{\text{Heat}} PO_4^{3-} + VO_4^{3-} \quad (2)$$

In an atmosphere of CO_2, the vanadate ion, VO_4^{3-}, is reduced by the iodide ion in strongly concentrated hydrochloric acid to the vanadyle ion, VO^{2+} [16]

$$2VO_4^{3-} + 2I^- + 12H = 2VO^{2+} + I_2 + 6H_2O \quad (3)$$

The liberated iodine and the excess iodide were determined by titration with standard potassium iodate solution according to Andrews method [17, 18]. The solution was placed in a 250 cm^3 stoppered reagent bottle and a rapid current of CO_2 was passed for 2–3 min into the bottle but not through the solution. Then a sufficient quantity of concentrated hydrochloric acid was added through a separating funnel to make the solution 6–8 M during the titration. A known volume (excess) of approximately 0.5 M potassium iodide was introduced, which has been titrated against the standard iodate solution. The contents of the bottle were mixed and left for about 2 min. Then 5 cm^3 carbon tetrachloride were added and the titration was carried out as rapidly as possible with standard 0.25 M potassium iodate until no more iodine colour could be detected in the organic layer

$$4VO_4^{3-} + 4I^- + IO_3^- + 5\,Cl^- + 30H^+ = 4VO^{2+} + 5ICl + 15H_2 \quad (4)$$

Concentrated hydrochloric acid solution was added as required during the titration to prevent it falling below 7 M. This method is applicable in the presence of phosphate, because

$$IO_3^- + 6H^+ + Cl^- + 4e = ICl + 3H_2O \quad (5)$$

The number of electrons transferred in Equation 5 is four, so

$$\text{Wt \% } V_2O_5 = \frac{\text{Volume of } KIO_3 \times \text{Molarity of } KIO_3}{4 \times \text{Weight of sample}} \times 100 \quad (6)$$

4. Results and discussion

4.1. Density and molar volume of V_2O_5–P_2O_5 glasses

The density and molar volume data of the prepared glasses are given in Table I. Each sample is specified by its chemically analysed composition (mol %), density and molar volume.

The variations of the density and molar volume of vanadium phosphate glasses with composition are illustrated in Fig. 1a and b, respectively. This figure shows three regions of glass density dependence on composition, Fig. 1a. The first region indicates a rapid increase in the glass density with an increase in the V_2O_5 content from O up to ~ 22 V_2O_5 mol %. In the second region (22–53 V_2O_5 mol %), the density is almost stable. Above 53 V_2O_5 mol %, the density shows considerable increases with increasing V_2O_5

TABLE I Density and molar volume data of V_2O_5/P_2O_5 glasses and their chemical compositions

Sample number	Analysed composition (mol %)		Density, ρ (g cm^{-3})	Molar volume, M/ρ (cm^3)
	V_2O_5	P_2O_5		
Pure P_2O_5[a]	–	100	2.5200	56.327
1	9.33	90.67	2.5988	56.053
2	17.67	82.33	2.7044	55.096
3	18.00	82.00	2.7082	55.067
4	22.06	77.94	2.7472	54.876
5	24.00	76.00	2.7559	54.985
6	26.00	74.00	2.7610	55.172
7	29.69	70.31	2.7694	55.536
8	51.63	48.37	2.7799	58.478
9	54.25	45.75	2.8006	58.419
10	55.45	44.55	2.8276	58.031
11	56.50	43.50	2.8345	58.038
12	58.05	41.95	2.8399	58.146
13	60.55	39.45	2.8619	58.047
14	62.75	37.55	2.8820	58.095
15	64.54	35.46	2.8916	58.209
16	67.67	32.33	2.9202	57.863
17	68.67	31.33	2.9032	58.339
18	78.07	21.93	3.0195	57.335
19	78.50	21.50	3.0210	57.363
20	83.75	16.75	3.0601	57.547
21	84.50	15.50	3.776	57.087
22	87.85	12.15	3.0870	57.346
23	89.52	10.48	3.1249	56.864

[a] Data obtained from Reference 13.

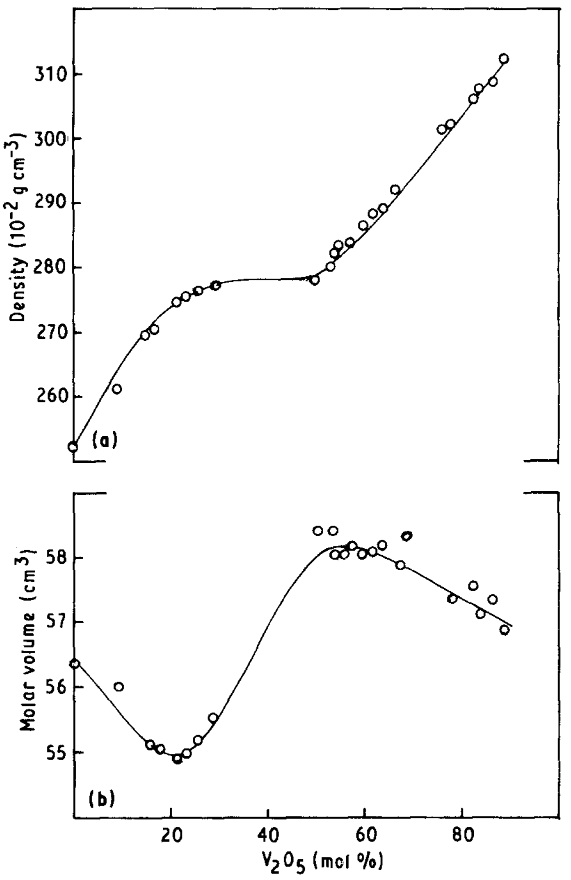

Figure 1 Compositional dependence of (a) the glass densities and (b) the molar volume for V_2O_5/P_2O_5 glasses.

content. On the other hand, Fig. 1b reveals three regions of molar volume variations with composition corresponding to the above three density regions but with a converse behaviour to that shown in Fig. 1a. The anomalous behaviour observed in Fig. 1a and b for both the glass density and molar volume may be attributed to structural changes in the present glass system. This anomalous behaviour has been observed previously [19–22] in vanadium phosphate glasses.

4.2. Infrared absorption and structural investigations of V_2O_5–P_2O_5 glasses

Vibrational absorption peaks observed for some V_2O_5–P_2O_5 glasses as well as vanadium oxide powder are listed in Table II. Fig. 2 shows the vibrational absorption spectra for both the investigated glasses, which were annealed at 250 °C for 1 h, and V_2O_5 powder. Crystalline V_2O_5 powder exhibits sharp vibrational absorption peaks at 235, 260, 300, 380, 470, 620, 820, 970 and 1040 cm^{-1}. Also, from an inspection of the spectra of the investigated glasses in Fig. 2, it appears that they are almost always similar in their general shape. However, the observed peaks are quite broad and overlap, especially in the range 300–1600 cm^{-1}. As seen from Table II, analyses of the infrared spectra of the investigated glasses may be described as follows.

(i) Although, no peaks were observed up to 300 cm^{-1} as reported by Anderson and Compton [23], for 70 mol % V_2O_5–30 mol % P_2O_5 sample, there are some weak bands which appeared at about

TABLE II Infrared absorption midband position for V_2O_5/P_2O_5 glasses

V_2O_5 (mol %)	Unattributed bands		V^{4+}	Harmonic P–O–P	P–O–P stretching	P–O–P bending	PO_4^{3-}	V–O stretching	P–O
0				500	700–730	910–940	1015		1240–1270
22.06	230	260	370	500	680	830	950	1050	1250
24.00	240	265	340	440	625	825	950	1045	1250
26.00	230	250	390	430	600	815	940	1040	1225
29.69	225	245	410	460	595	790	930	1040	1195
51.63	220	240	375	480	600	790	930	1045	1195
56.50	245	290	390	520	630	770	920	1035	1170
58.05	235	280	400	570	640	770	940	1040	1170
64.54	240	255	405	600	660	770	–	1035	1140
67.67	230	260	280	–	630	–	850	1010	1160
V_2O_5 powder	235	260	300	380 470	620	820	970	1040	

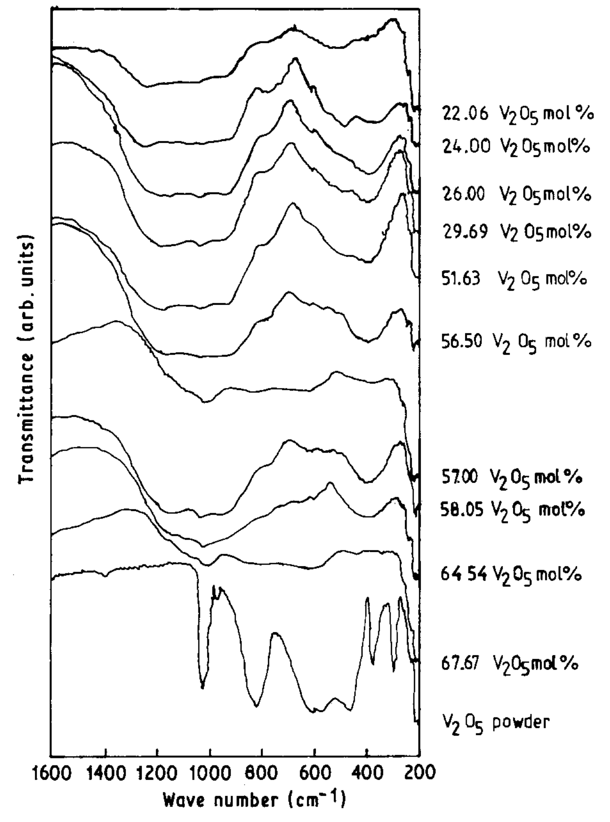

Figure 2 Infrared absorption spectra for V_2O_5/P_2O_5 glasses in a KBr matrix.

230–250 cm^{-1} and 250–280 cm^{-1} for all the investigated glasses and for each vanadium content less than 70 mol %.

(ii) There is an absorption band observed at about 380 cm^{-1}. This band is assumed not to be a feature of either pure V_2O_5 or P_2O_5. It can be attributed to the creation of V^{4+} sites in the glass, as suggested previously [24]. The intensity of this peak is shown to increase with P_2O_5 content.

(iii) The P–O–P ring frequency of P_2O_5 at 780 cm^{-1} [25] agrees with our results. The spectra also displayed strong bands at 1250, 1015 and 500 cm^{-1} which may be due to the P–O stretching vibration, a normal vibration mode (v_3 symmetric stretching) of the PO_4^{3-} ion and harmonics of the P–O–P bending vibrations, respectively [13].

(iv) A very strong and broad absorption band appeared within the 900–1250 cm^{-1} range. It has been reported [25, 26] that the peak is due to the vanadium–oxygen stretching vibration appearing at 1015 cm^{-1}. However, the broad band in the range 900–1250 cm^{-1} seems to be due to the combination of both V_2O_5 and P_2O_5 as PO_4^{3-}, V–O and P–O vibrational bands occur in this range of wave numbers.

4.3. The observed infrared vibrational bands and structure of V_2O_5–P_2O_5 glasses

For each band attributed to a given vibrational mode, Figs 3 and 4 show plots of midband wave number against glass composition. Those illustrated vibrational modes clarify the three composition regions. This is evidently noted from the observed dependence of the bands position on the V_2O_5 content as follows:

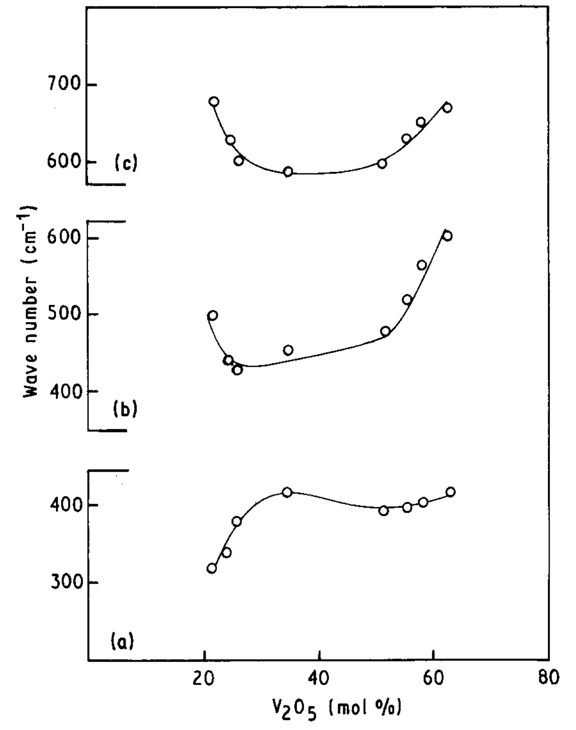

Figure 3 Compositional dependence of the wave numbers for (a) V^{4+}, (b) harmonic P–O–P bending and (c) P–O–P stretching absorption bands in the infrared spectra of V_2O_5/P_2O_5 glasses.

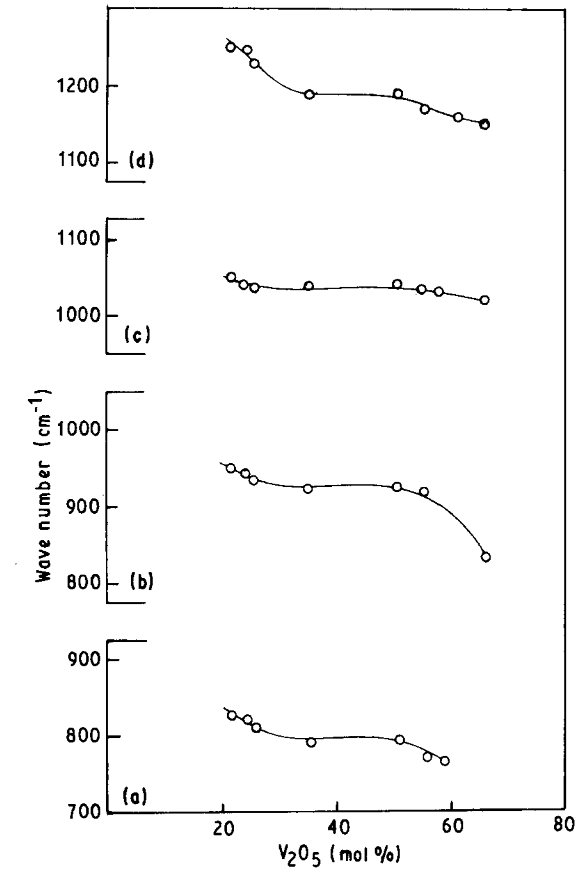

Figure 4 Compositional dependence of the wave number for (a) P–O–P bending, (b) PO_4^{3-}, (c) V–O stretching and (d) P–O absorption bands in the infrared spectra of V_2O_5/P_2O_5 glasses.

1. In the first region, as the concentration of V_2O_5 increases up to 22 mol %

(i) the V^{4+} band shifts rapidly to increasing wave number;

(ii) some modes are rapidly shifted to decreasing wave number, e.g. the harmonic P–O–P bending, P–O–P stretching and P–O bonds; and

(iii) the other modes, e.g. the V–O stretching, PO_4^{3-} and P–O–P bending are shifted to lower wave number.

2. In the second region where the V_2O_5 content is increased from about 22–53 mol %

(i) the V^{4+} shifts slowly to decreasing wave number;

(ii) the harmonic P–O–P bending shifts slowly to increasing wave number, and

(iii) the other modes, P–O–P stretching, P–O, V–O stretching, PO_4^{3-} and P–O–P bending show nearly constant band position with V_2O_5 content.

3. In the third region for V_2O_5 content greater than 53 mol %

(i) the V^{4+} band shifts slowly to increasing wave number;

(ii) the harmonic P–O–P bending and stretching modes are rapidly shifted to increasing wave numbers, and

(iii) the rest of the modes are slowly shifted to decreasing wave number.

Because the wave number is directly proportional to the energy which affects the amplitude of the vibrational motion of the band, i.e. movement of the band to higher wave number as the V_2O_5 content is increased, means that increasing the energy of the bond increases its amplitude, and vice versa. Therefore, the behaviour obtained here of the band wave number shifts with composition, as observed in Figs 3 and 4 for the V_2O_5–P_2O_5 glasses studied, confirms the suggestion of their anomalous character through the appearance of the three composition regions. These regions are, to a great extent, analogous to those obtained from the density and molar volume data investigated in Section 4.1 for these glasses and agree with previously reported results [13] for other vitreous phosphate systems. However, anomalous behaviour which has been observed in all binary phosphate glasses, investigated in previous works [13, 19–22] was attributed to the occurrence of some structural changes which result from the different properties of the added cations to the phosphate matrix, i.e. the way in which the added cation can enter the glass network, either interstitially or substitutionally.

5. Conclusion

The compositional dependence of the infrared spectra of the V_2O_5–P_2O_5 system investigated may be summarized as follows. As the vanadium cation (in V_2O_5) is added to the P_2O_5 content, the ability of this new cation either to enter into the phosphate network or reside interstitially in the diffuse matrix is possible. The evidence for the occurrence of the above behaviour is confirmed by the following observations.

1. the weakness of the P–O band with the bond which is ruptured by the network-forming vanadium cation. This is implied from the observed shift (over the three composition regions) to lower wave numbers as the V_2O_5 content increases;

2. the observation of some bands due to ionic bonds, such as the V^{4+} band and PO_4^{3-}. The results in Figs 3 and 4 show that the former band was strengthened (i.e. shifts to higher frequency) at the expense of the weakening (i.e. shift to lower frequency) of the other band, as the vanadium cation goes into the phosphate matrix.

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