THE ION-EXCHANGE BEHAVIOUR OF NIOBATE AND TANTALATE IN ALKALINE SOLUTION

by

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P R E F A C E

I developed an interest in the chemistry of niobium and tantalum while employed as Chemist in the Geological Survey Department, Entebbe, Uganda. Niobium and Tantalum, the "earth acid" elements, occur naturally in Uganda, especially in the Columbite-Tantalite mineral series.

The research described in this thesis was carried out during the years 1960 to 1966, mostly in Entebbe. It has been during these years that most of the reliable work, upon which our present day knowledge of niobate and tantalate chemistry is based, has appeared in the literature.

The work reported herein is original and has not been submitted to any other University. The charge determinations described in chapter III and the chromatographic separation reported in chapter V have already been published in the chemical literature. (References 95, 96).

I wish to express my gratitude to three successive heads of the Geological Survey Department, Uganda, Mr. J. Cawley, Dr. C. F. Williams, and Mr. C. E. Tamale-Ssali, for permission to carry out this research.

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C O N T E N T S

CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

It has long been known that fusion of niobium and tantalum pentoxides with alkali hydroxide or carbonate, followed by aqueous extraction of the melts, results in the formation of soluble niobate and tantalate ions. The ion-exchange behaviour of these ions has not been studied before, and it seemed to the author that such an investigation would be of considerable interest, with a view to (1) developing a means of separating the ions, and (2) obtaining some information on the nature of the ions themselves.

The results reported in the chemical literature by various workers present a confused picture of the nature of the products formed in alkaline fusions of niobium or tantalum pentoxides; there are apparent contradictions. Since no review of the field has appeared in the literature, this thesis is prefaced by a comprehensive survey of all published work relating to the formation and structure of niobate and tantalate ions, in order to present a coherent picture of our present knowledge of the subject.

The distribution coefficients of niobate and tantalate on a strongly basic ion exchange resin have been determined under various conditions, with a view to finding the optimum conditions for a chromatographic separation. During this investigation, which is reported in Chapter III of this thesis, unusual kinetic effects were observed, which at first appeared to be related to a change in the structure of the ions. This effect was further investigated and the results are reported in Chapter IV. The development of a chromatographic separation is described in Chapter V.

Very little is known about the behaviour of the peroxy complexes of niobium and tantalum in alkaline solution. The ion-exchange behaviour of these complexes has therefore been briefly investigated as a possible basis for a method of separating the two elements. This is discussed in Chapter VI.

A new absorptiometric procedure for analysis of trace concentrations of tantalum was developed by the author, to facilitate this investigation; the method is described in Chapter II.

LITERATURE SURVEY

This survey covers first niobate and then tantalate; where results for both are included in the same paper, the information relating to each has been reported separately below.

Niobate.

In a series of papers (1 - 4) P. Sue reported on his studies of the reaction of niobium pentoxide and sodium carbonate: with the molar ratio $\frac{Nb_2O_5}{Na_2CO_3} = \frac{1}{3}$, and temperatures above 700°C, he obtained the orthoniobate Na_3NbO_4, and the metaniobate $NaNbO_3$; the orthoniobate was slightly soluble in water. He explained his results in terms of a slow irreversible reaction:

$$Nb_2O_5 + Na_2CO_3 \rightarrow 2NaNbO_3 + CO_2$$

and a rapid irreversible reaction:

$$2NaNbO_3 + 2Na_2CO_3 \rightarrow 2Na_3NbO_4 + 2CO_2$$

Guiter (5) and Carriere (15) studied the fusions of sodium, potassium and lithium carbonates with niobium pentoxide and reported that compounds corresponding to $5Me_2O.Nb_2O_5$ (where Me = alkali metal) were formed; all were soluble in water.

Britten & Robinson (9) prepared potassium niobates by crystallization of the aqueous extract of niobium pentoxide - potassium hydroxide melts (1:3 weight ratio). The $K_2O:Nb_2O_5$ ratio of the products varied from 1.33 to 1.41; they assumed that the "correct" salt was also obtained by reaction of calcined niobium pentoxide with sodium hydroxide solution (12).

Windmaisser (14) postulated the hydrolysis scheme:

7/5 salt → 4/3 salt → 7/6 salt → 1/1 salt → acid niobate → niobic acid.

The same paper contained information on the compounds which were isolated from solutions of the 7/6 and 4/3 salts by addition of alcohol. From 3-6% solutions two hydrated niobates were obtained,

$K_2O.Nb_2O_5.2H_2O$ and $K_2O.Nb_2O_5.4H_2O$

from more dilute solutions acid salts were formed, while in more concentrated solutions the 7/6 salt and metaniobates were formed.

Spitsyn and Lapitski (16) observed the loss of carbon dioxide from melts of sodium carbonate and niobium pentoxide with molar ratio Na:Nb = 3:1, 5:1. They postulated the formation of the compounds Na_5NbO_5 and $Na_4Nb_2O_7$ ("pyroniobate"), as well as the ortho- and meta-niobates. The corresponding potassium pyroniobate was reported by Guerchais (34), together with other acid salts detected by thermal analysis of the system K_2CO_3- Nb_2O_5. By similar thermal analysis studies of this system Reisman and Holtzberg (19) detected five definite compounds with $\frac{K}{Nb} = \frac{3}{1}, \frac{1}{1}, \frac{2}{3}, \frac{1}{3}$ and $\frac{3}{22}$.

In the system $Na_2O/Na_2CO_3 + Nb_2O_5$ four definite compounds were detected with $\frac{Na}{Nb} = \frac{1}{14}, \frac{1}{4}, \frac{1}{1}$ and $\frac{3}{1}$ (25).

The reaction of $K_2O + Nb_2O_5$ in equimolar proportions was studied by Reisman, Holtzberg and Berkenblit (28). Reaction of the product with water gave an insoluble fraction - $6K_2O.7Nb_2O_5$, but no formation of the meta-niobate. The soluble fractions were crystallized to give $K_7Nb_6O_{19}.27H_2O$.

Lapitski (29) formulated the aqueous extraction of alkaline melts of niobium and tantalum pentoxides as follows:-

(Me = Na or K, Nb can be replaced by Ta).

$$Me_5NbO_5 + H_2O \rightarrow Me_3NbO_4 + 2\ MeOH$$

$$6Me_3NbO_4 + 5H_2O \rightarrow Me_8Nb_6O_{19} + 10MeOH$$

$$2Me_8Nb_6O_{19} + H_2O \rightarrow Me_{14}Nb_{12}O_{37} + 2MeOH$$

Details of the solubility, pH and conductivity of various niobates have been published (21, 27).

It has been reported that the reactions of $K_{14}Nb_{12}O_{37}.27H_2O$ and $KNbO_3.2H_2O$ with various reagents are identical (23).

The existence of the hexameric niobate ion in the crystal was indicated by an X-ray study of the compound $Na_{14}Nb_{12}O_{37}.32H_2O$ by Lindquist (13).

Jander and Ertel (54) prepared potassium and sodium niobates by fusion of niobium pentoxide with from 7 to 60 times its weight of potassium hydroxide, extraction with water and crystallization from potassium hydroxide solution.

Sodium niobates were also obtained by addition of sodium hydroxide to solutions of the potassium compounds. In all cases the analyses corresponded to the 4/3 or 7/6 salts. By fusion of equimolar quantities of niobium pentoxide and alkali hydroxide these authors obtained the meta-niobate. The melt obtained by fusion of niobium pentoxide with excess sodium hydroxide was extracted with absolute ethanol to give the ortho-niobate.

On the basis of these results Jander and Ertel postulated that when niobium pentoxide is fused with excess alkali hydroxide, the following reaction occurs:-

$$18MeOH + 3Nb_2O_5 \rightarrow 6Me_3NbO_4 + 9H_2O$$

while leaching the melt with water gives the reaction:-

$$6[NbO_4]^{3-} + 10H^+ \rightarrow [Nb_6O_{19}aq]^{8-} + 5H_2O \quad \text{(irreversible reaction).}$$

Rohmer and Guerchais (47) proved the existence of ten different crystalline phases in the system K_2O - Nb_2O_5 - H_2O.

The various compounds were characterized by X-ray powder diagrams due to the inadequacy of chemical analyses. On the basis of thermogravimetry and differential thermal analysis these authors identified the following compounds:

(a) $4K_2O.3Nb_2O_5.9H_2O$.

(b) $7K_2O.6Nb_2O_5.25H_2O$.

(c) $7K_2O.5Nb_2O_5.32H_2O$.

(d) $13K_2O.10Nb_2O_5.40H_2O$.

(e) $K_2O.Nb_2O_5.xH_2O$.

as well as undefined acid potassium niobates and niobium pentoxide hydrates. All these compounds could be formulated as variations of the fundamental hexaniobate structure, as follows:-

(a) $K_8[Nb_6O_{18}(OH)_2].8H_2O$.

(b) $K_7[Nb_6O_{18}(OH)_2H].11H_2O$.

(c) $K_7[Nb_6O_{18}(OH)_{2(1-x)}H_{2x}].15H_2O$.

(d) $K_{8-x}[Nb_6O_{18}(OH)_2H_x].11H_2O$.

(e) $K_6[Nb_6O_{17}(OH)_2].xH_2O$.

or

$K_6[Nb_6O_{18}].(x+1)H_2O$.

As an alternative structure for the 7/5 compound (c - previous page), they gave

$K_7[Nb(NbO_4)_4].16H_2O$.

This latter structure was possibly suggested as a result of cryoscopic studies by Lehne, Goetz and Rohmer (31,59) in the same laboratories at this time, which indicated the existence of the pentaniobate ion. These authors studied the system Nb_2O_5 - KOH - H_2O by cryoscopy. For $\frac{OH}{Nb}$ > 2.5 they reported the ions $(NbO_4)^{3-}$, $(H_2Nb_2O_7)^{2-}$, and $(HNb_2O_7)^{3-}$ and at lower alkali concentrations the pentanuclear and hexanuclear species.

Later, however, these authors reported (61) that their analysis for potassium in the earlier paper had been in error, due to adsorption of excess acid by the precipitated niobic acid. Repetition of the experiments with a better analytical technique gave the degree of condensation as 6 at the lower alkali concentrations. Attempts to precipitate the 7/5 barium salt were unsuccessful and it was concluded that, unless this salt has a much higher solubility than the corresponding hexamer, the pentameric ion does not, in fact, exist.

These authors studied the variation of pH and conductivity caused by addition of a solution of barium chloride to solutions of the 4/3, 7/6 and 1/1 salts; their results are explained by assuming that all three are salts of one acid, $H_8Nb_6O_{19}$, and that the following ions exist in solution:

$[Nb_6O_{19}]^{8-}$, $[Nb_6O_{19}H]^{7-}$, $[Nb_6O_{19}H_2]^{6-}$, $[Nb_{12}O_{38}H_4]^{12-}$, $[Nb_{12}O_{38}H_6]^{10-}$.

The protonation and condensation reactions occur in weakly alkaline solutions.

Bouillard (62) heated Nb_2O_3 + Na_2CO_3(1:1) or Nb_2O_5 + $NaNO_3$(1:2) to obtain insoluble sodium metaniobate. With more alkali further reactions occurred but in each case the metaniobate was formed first. At 600-900° two water-soluble modifications of sodium orthoniobate were formed. Above 1000° the water-soluble pyroniobate ($Na_4Nb_2O_7$) was obtained. A more alkaline salt was also reported.

It has been reported by Lapitski (29) that niobium pentoxide dissolves in cold N sodium hydroxide to form the orthoniobate and Na_5NbO_5, and in boiling N sodium hydroxide to form the hexaniobate.

Mambetov (30) reported the formation of the definite compound: $NaNbO_3.5.35H_2O$. He also identified (33) a gel which was precipitated at pH 8.5 from niobate solutions, as $Nb_2O_5.7H_2O$. This was dehydrated over calcium chloride to $Nb_2O_5.5H_2O$, which was represented as H_5NbO_5, or $H_3NbO_4.H_2O$; boiled under water, it became $HNbO_3.xH_2O$.

It has been suggested (41) that in the alkaline range, up to pH12, the following equilibrium exists:

$$Nb(OH)_5 + OH^- \rightleftharpoons NbO_3^- + 3H_2O$$

On the basis of thermal dehydration studies and Debye diffraction patterns, the crystalline salts of the 7/6 and 4/3 series have been represented by Lapitski <u>et al</u> (32) as follows:-

$$M_x[(HNb_6O_{19})_2nH_2O]mH_2O.$$

where x = 14, 16 (16 possible if H not present in anion)

n = 1-5

m varies

Jander and Ertel (54) studied the ultraviolet absorption spectra of solutions of the 4/3 and 7/6 salts over the range pH 5 - 14. Beer's Law was obeyed at niobate concentrations below 10^{-2}M. Pure aqueous niobate gives an alkaline reaction due to hydrolysis; the pH was varied by addition of potassium hydroxide or by passing carbon dioxide through the solutions. Stable reproducible spectra were obtained and three distinct patterns were observed. Identical results were obtained for sodium and potassium niobates. Over the range of pH from 9.9 to 14, a series of isosbestic curves were obtained; this is characteristic of a binary equilibrium. These authors therefore interpret this as representing the following equilibrium:-

$$[Nb_6O_{19}aq]^{8-} + H_2O \underset{}{\overset{pH13}{\rightleftharpoons}} [HNb_6O_{19}aq]^{7-} + OH^-$$

Below pH 9 the absorption spectrum changes and over the range of pH 4.7 - 5.4 the shape of the spectrum is constant. This they interpret as reflecting the equilibrium:-

$$[HNb_6O_{19}aq]^{7-} + H^+ \rightleftharpoons [Nb_6O_{18}aq]^{6-} + H_2O$$

In a third paper (54) Jander and Ertel published the results of conductometric titrations of the salts, the analyses of which corresponded to the formulae:-

Na_3NbO_4, $Na_8[Nb_6O_{19}]$, $Na_7[HNb_6O_{19}]$ and $K_6[Nb_6O_{18}]$.

Breakpoints in the titration curves indicated the occurrence of the following reactions:-

$$6NbO_4{}^{3-} + 10H^+ \rightarrow [Nb_6O_{19}aq]^{8-} + 5H_2O$$

$$[Nb_6O_{19}aq]^{8-} + H^+ \overset{pH13}{\rightleftharpoons} [HNb_6O_{19}aq]^{7-}$$

$$[HNb_6O_{19}aq]^{7-} + H^+ \overset{pH9}{\rightleftharpoons} [Nb_6O_{18}aq]^{6-} + H_2O$$

$$[Nb_6O_{18}aq]^{6-} + 6H^+ \rightarrow H_6[Nb_6O_{18}aq] \rightarrow 3Nb_2O_5.aq + 3H_2O.$$

In the same study Jander and Ertel attempted to estimate the anionic weight by determining the rate of diffusion of niobate ions in these solutions over the same range, pH 5 - 14. The concentrations of the solutions used in the diffusion experiments are not given. Molecular weights were estimated from a graph showing the experimentally determined diffusion coefficients of various tungstate and molybdate ions as a function of their calculated molecular weights. According to this graph the diffusion coefficient of niobate at high pH corresponds to a molecular weight of approximately 1000. This is in agreement with the structures suggested on the basis of the optical measurements. Over the pH range 11 - 9 the diffusion coefficient drops to a value which corresponds to a molecular weight of about 3000. This indicates the formation of a polymeric species,

$$[(Nb_6O_{18})^{6-}]_n$$

Various early authors (1, 8, 9) studied conductometric and potentiometric titrations of alkali niobates; the results indicated the following hydrolysis scheme:-

$NbO_4^{3-} \rightarrow Nb_6O_{19}^{8-} \rightarrow HNb_6O_{19}^{7-} \rightarrow NbO_3^{-} \rightarrow Nb_2O_5$

This hydrolysis scheme has been confirmed in a recent reinvestigation of the conductometric titrations of alkali niobates (67), whereas the conclusions of Jander and Ertel were not confirmed. The new results for potassium niobate solutions could be explained in terms of equilibria between the ions:-

$[Nb_6O_{19}]^{8-}$, $[HNb_6O_{19}]^{7-}$, $[H_2Nb_6O_{19}]^{6-}$ and $[H_xNb_6O_{19}]^{8-x}$

All these are derived from the hypothetical acid $H_8Nb_6O_{19}$.

Neumann (55) studied solutions of the compound $K_8Nb_6O_{19}.16H_2O$ and also the 7/6 compound, prepared by addition of alcohol to a solution of the 4/3 compound in 0.1 M potassium hydroxide. E.M.F. titrations were performed at Nb concentrations of 50 x 10^{-3}M. At this concentration he observed some unexplained precipitation above pH 12.5. The experimental results were subject to some uncertainty but were considered to confirm the general conclusions of Jander and Ertel, and to support the existence of a hexameric niobate ion in solution.

The importance of the concentration of niobium in solution was first shown by Gridchina (65). Solutions were prepared by fusion of niobium pentoxide with potassium hydroxide, (1:1.5 weight ratio), extraction with water and dilution to give a Nb concentration of 0.36M in N potassium hydroxide. This author studied the dialysis of niobate ions in alkaline solution through a cellophane membrane and determined the dialysis coefficients relative to the reference ion, which in this case was chromate. In his paper the relative dialysis coefficient, D_x, of niobate is presented as a function of the niobate concentration and the concentration of potassium hydroxide. The following is a summary of the main findings:-

(1) At a constant potassium hydroxide concentration of 0.3 N, D_x decreases as the Nb concentration in the solution is increased from 0 - 0.0025 M. At Nb concentrations from 0.0025 - 0.025 M D_x is approximately constant.

(2) At a constant niobate concentration of 2.5×10^{-3} M, D_x increases as the potassium hydroxide concentration is increased from 0.007 - 1 N (the graph is a straight line from 0.1 N to 1.0 N and indicates that in more alkaline solutions D_x would continue to increase).

The varying values of D_x presumably reflect varying degrees of polymerisation of the "niobate" ion. Interpreting these results, Gridchina assumes arbitrarily that at the maximum dilution (2.5×10^{-5}M Nb), the "monomer" is formed, i.e. that the polymerisation factor is 1. On this basis the polymerisation factor, p, at higher concentration is calculated from the relation,

$$p = \left(\frac{D_{max}}{D_x}\right)^2$$

A value of 6 is obtained for p at niobate concentrations higher than 2.5×10^{-3} M (in 0.3 N KOH).

In the same paper Gridchina reports a very interesting study of the ultraviolet absorption spectra of potassium niobate solutions (from 220 - 300 mμ) as a function of the potassium hydroxide concentration and the total niobate concentration. His main findings were:-

(1) At a constant potassium hydroxide concentration of 0.3 M, the extinction coefficient (at 245 mμ) decreases as the niobate concentration in the solutions is decreased from 2.5×10^{-2} M to 2.5×10^{-5} M.*

(2) The shape of the absorption curves changes with changing pH (12.5-14) at constant Nb concentration; this was observed at the different niobate concentrations 2.5×10^{-4} M and 2.5×10^{-3} M.

The data suggest that at definite concentrations of alkali and niobate a compound with an absorption maximum at 240 mμ is formed; Gridchina identifies this compound as the hexaniobate. This author attributes the decrease in light absorption with dilution to decomposition of the large niobate anion to form simpler ions.

It is of interest to note that the absorption peak at 240 mμ has been suggested as the basis of a possible spectrophotometric procedure for analysis of niobium solutions (74).

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* It can be seen that Gridchina's results contradict those of Jander and Ertel, who claimed that Beer's Law is obeyed at niobate concentrations below 10^{-2} M.

Nelson and Tobias studied the structure of the niobate ion by light scattering and ultra-centrifugation (56). They prepared potassium niobate by recrystallising from potassium hydroxide solution; precipitation with ethanol gave crystals of $K_{14}Nb_{12}O_{37}.27H_2O$. Their light scattering data covered the range 0.03 - 0.3 M Nb in 1M KCl (the concentration of potassium hydroxide was not given, but was very small.) The ultracentrifugation data were obtained for the range 0.01 - 0.35 M Nb in 1M KCl, without added alkali. These authors concluded that the solutions were monodisperse, the degree of polymerisation was 5 - 6, and that the effective charge in solution was no greater than -2. The light scattering results were indicative of the existence of a species with high symmetry.

Tantalate.

Marignac (6) prepared potassium tantalate by fusion of potassium hydroxide and tantalum pentoxide. Chemical analysis of the products obtained by crystallization from solutions gave $\frac{K_2O}{Ta_2O_5}$ ratios equal to 1 and 1.33. The latter corresponds to the hexatantalate - $K_8[Ta_6O_{19}]$. In 1925 Jander and Schulz (7) prepared potassium tantalate with $\frac{K_2O}{Ta_2O_5}$ equal to 1.40, corresponding to the pentatantalate. They used measurements of diffusion to calculate the molecular weight of the ion in solution, which they considered to confirm the formulation as a pentatantalate.

Windmaisser (10) prepared potassium tantalate by fusion of tantalum pentoxide with excess potassium hydroxide; the melt was extracted with water, filtered and concentrated. Analysis of the product showed that the ratio $\frac{K_2O}{Ta_2O_5}$ varied between 1.30 - 1.44, corresponding approximately to variation between the compounds $4K_2O \cdot 3Ta_2O_5 \cdot 16H_2O$ and $7K_2O.5Ta_2O_5.H_2O$. He could detect no differences in chemical properties or crystal structure among the various compounds, and concluded that they represent one compound in which exchange between K-O-H and H-O-H could occur.

Halla, Neth and Windmaisser (11) later examined the various tantalates (4/3 and 7/5) by X-ray powder photographs and suggested the structure $K_{16}[Ta_{12}O_{36}](OH)_4.30H_2O$, in which there could be variation by loss of water, addition of K^+ and replacement of OH^- by O^{2-}.

Lindquist and Aronsson (18) considered that their X-ray powder photographs of $K[Ta_6O_{19}]16H_2O$ proved the existence of the $[Ta_6O_{19}]^{8-}$ ion in the crystal. They doubted the results of Jander and Schulz supporting the pentameric structure.

Lapitski and Simanov (2) studied the dehydration of tantalic acid and suggested that it could be represented by the reaction

$$H_{13}Ta(TaO_4)_6 . 7.5H_2O \rightarrow H_7Ta(TaO_4)_4.$$

The structure on the right corresponds to the pentanuclear acid suggested by Jander and Schulz. However, later studies (32) of thermal dehydration led to the formulation of alkali niobates and tantalates as

$$M_x[(H(Nb)(Ta)_6O_{19})_2 . nH_2O]mH_2O$$

where x = 14, 16; n = 1-5 ("anionic water") and m ("cationic water") varies. (See comment on page 10).

Lapitski (29) investigated the solubility of tantalum pentoxide in sodium hydroxide solution. Solubility is very low in concentrated sodium hydroxide solution; with low alkali concentration the compounds $Na_8Ta_6O_{19} . 16H_2O$ and $Na_7Ta_5O_{16} . 11H_2O$ are obtained. He claimed that boiling freshly precipitated tantalum pentoxide with 1.8 N sodium hydroxide produced only the pentatantalate; in 3.1 N sodium hydroxide the pentatantalate and orthotantalate were obtained. Aqueous extraction of alkali-tantalum pentoxide melts gave only the hexatantalate.

Jander and Ertel (53) prepared potassium tantalate by fusion of tantalum pentoxide with excess potassium hydroxide (mole ratio 1:25), extraction with either hot or ice-cold water, and crystallization from solution. The crystals were filtered off, washed with water, ethanol and acetone and finally dried over calcium oxide. Other alkali tantalates were prepared by addition of excess sodium, lithium, rubidium or caesium salts to solutions of the potassium compound. Three crystalline forms of potassium tantalate, two forms of sodium tantalate and one form of lithium tantalate were obtained. In all cases the analyses of the compounds gave $\frac{Me_2O}{Ta_2O_5} = 1.39 - 1.40$. Analysis of the rubidium and caesium compounds gave $\frac{Me_2O}{Ta_2O_5} = 1.37, 1.36$. The low values were attributed to adsorption of rubidium and caesium ions by the tantalic acid precipitated in the analyses so that low values for alkali metal were obtained. The analyses may therefore be regarded as corresponding to the structure $Me_7Ta_5O_{16}.H_2O$ in all cases. The amount of water of crystallization varied. Jander and Ertel doubted Windmaisser's results.

These authors measured the ultraviolet absorption spectra of their compounds, varying pH by addition of potassium hydroxide or perchloric acid, and published a spectrum which they reported to be constant and independent of the pH or the particular alkali metal present. They do not give the concentrations or actual pH-values of their solutions.

Jander and Ertel attempted to determine the molecular weight of the tantalate ion by measurements of diffusion coefficients. Solutions 0.1 "equivalent normal" were prepared, and allowed to equilibrate for a few days after adjustment of the pH. The diffusion coefficient was found to be constant in potassium hydroxide solution up to 3N; the molecular weight of the ion was then calculated by comparison with similar diffusion measurements in acid solution on the ion $[I(MoO_4)_6]^{5-}$ the structure of which is considered to be well established. The value obtained was 1172; the theoretical value for the ion $[Ta_5O_{16}]^{7-}$ is 1160.

Jander and Ertel also studied the system potassium tantalate-ice-potassium nitrate by salt cryoscopy, from which a value of 4.88 was obtained for the polymerization factor in tantalate.

On the basis of these results the tantalate ion was pictured by these authors as a derivative of orthotantalic acid, H_3TaO_4:

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                O
                |
            O - Ta - O
                |
                O
                |
O - Ta - O - Ta - O - Ta - O     [Ta5O16]7-
                |
                O
                |
            O - Ta - O
                |
                O
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About the same time Spitsyn and Shavrova (98) showed conclusively that the reaction of socium hydroxide with tantalum pentoxide gives two definite crystalline compounds. Tantalum pentoxide was fused with sodium hydroxide (1:5 weight ratio), and the cold melt was ground in a mortar and treated with a little cold water to remove excess alkali. The crude product was then dissolved in warm water.

(1) Evaporation at 50° gave hexagonal plates; the analysis corresponded closely to $8Na_2O.6Ta_2O_5.33H_2O$.

(2) Addition of 0.1N sodium hydroxide solution in the cold gave needle-like crystals, the analysis of which corresponded to:- $7Na_2O.5Ta_2O_5.22H_2O$.

(3) Evaporation of the solution at a temperature above 85° also gave prismatic crystals of the pentatantalate.

All three compounds dissolved in water to give a solution of pH 8.5 (the concentration is not given).

In a second paper (99) the same authors considered the mechanism of the reaction of tantalum pentoxide with sodium hydroxide. They prepared sodium metatantalate by ignition of the 4/3 and 7/5 hydrates, followed by treatment with distilled water to remove completely any free alkali. The analysis of the dried product corresponded to $NaTaO_3$. Solubility of this compound in water and in sodium hydroxide solution was very slight, from which it was concluded that some compound other than the metatantalate is present in the melts of tantalum pentoxide with caustic alkalis.

In order to try to establish the identity of the initial fusion product, these authors leached the tantalum pentoxide - sodium hydroxide melt (1:5 weight ratio) with hot anhydrous alcohol till alkali-free. Analyses of the product for tantalum corresponded fairly well to Na_5TaO_5, but not to Na_3TaO_4 or $NaTaO_3$. The fusion reaction is therefore represented:-

$$10NaOH + Ta_2O_5 \rightarrow 2Na_5TaO_5 + 5H_2O.$$

Crystals of the pentatantalate separate from solutions of this compound in water; this could be represented as:-

$$5Na_5TaO_5 + 20H_2O \rightarrow Na_7Ta_5O_{16}.11H_2O + 18NaOH.$$

Nishanov and Lapitski (27) have published some details of the pH and conductivity of solutions of sodium pentatantalate and sodium hexatantalate. Because of hydrolysis however no conclusion about the nature of the ions in solution can be drawn from such data.

Lapitski (29) extracted alkaline melts of tantalum pentoxide with water; the solutions were in equilibrium with

$Na_8Ta_6O_{19}.12.5H_2O$ and $K_8Ta_6O_{19}.16H_2O$.

More recently, the existence of eight crystalline forms of potassium tantalate was shown by Dehand (49) as a result of a study of the system $Ta_2O_5 - K_2O - H_2O$. The $\frac{K_2O}{Ta_2O_5}$ ratio varied from 1.26 to 1.40. The analyses of the various phases corresponded to the compounds:-

(1) $2K_2O.1Ta_2O_5.8$ or $9H_2O$.

(2) $4K_2O.3Ta_2O_5.16H_2O$.

(3) $4K_2O.3Ta_2O_5.14H_2O$.

(4) $4K_2O.3Ta_2O_5.12H_2O$.

(5) $4K_2O.3Ta_2O_5.9H_2O$.

(6) $K_{8-x}H_xTa_6O_{19}.13H_2O$.

(7) $K_{8-x}H_xTa_6O_{19}.12H_2O$.

(8) $K_2O.Ta_2O_5$ (meta-tantalate)

(9) $2K_2O.3Ta_2O_5$.

X-ray diffraction, thermal and spectral data conclusively identified eight different crystalline compounds. The same series of salts could be obtained (50) from the product of the fusion of tantalum pentoxide with excess potassium hydroxide. Evaporation of the aqueous extract of the melt to various levels gave the above compounds. In this same paper the various compounds which can be precipitated by alcohol from solutions of potassium tantalate have been described.

Nelson and Tobias (45) prepared potassium tantalate by fusion of tantalum pentoxide with excess potassium hydroxide, extraction with a minimum of hot water, precipitation with ethanol and recrystallization of the crude product from potassium hydroxide solution. Analysis of the crystals gave $K_8Ta_6O_{19}.16H_2O$. Solutions of the compound were analysed by infra-red and ultra-violet spectrophotometry, measurements of e.m.f. and light-scattering.

The UV spectrum remained constant over the range 1.2 - 60 x 10^{-4} M Ta and 6 - 380 x 10^{-4} M hydroxide. The spectrum published by the author is in general agreement with that of Jander and Ertel; the absorption peak is below 2000 Angstroms and cannot be measured. From the constancy of the spectrum Nelson and Tobias inferred that the structure of the species is unchanged by changes in concentration. E.M.F. measurements showed that the number of protons bound per tantalum atom was constant at 0.12 over the range pH 10-13, and at Ta concentrations between 0.60 M and 0.24 M.

A light-scattering study was carried out in order to estimate the size of the tantalate species; it was concluded that the degree of polymerisation appeared to be in the range 6.0-6.5. The effective charge of the anions in the potassium chloride solution used was reduced to a value of about three as a result of binding of potassion ions.

In a later paper (46) the same authors described the results of equilibrium ultracentrifugation studies of the same solutions. Results indicated that in M potassium chloride only a single polyanion is present. The calculated degree of polymerisation, and effective charge, agreed with the results reported in the earlier paper. It was concluded that the tantalate ion in solution has the same structure as in the crystal, viz., $Ta_6O_{19}^{8-}$, but that the effective charge in solution is reduced to a value no greater than -2 by protonation and binding of potassium ions. The pH of the solutions used by these authors is not given, but would be the equilibrium values resulting from hydrolysis of the potassium tantalate in solution.

Aveston and Johnson (57) recrystallized potassium tantalate from water under a nitrogen atmosphere. The analyses of two samples prepared by them corresponded to

$4.1K_2O.3Ta_2O_5.16H_2O$ and $3.9K_2O.3Ta_2O_5.16H_2O$.

Ultracentrifugation data obtained by these authors could best be explained by assuming that the degree of polymerisation was about 6 or a little less. From the results obtained in potassium chloride and potassium hydroxide solution it was concluded that the effective charge in solution appeared to be reduced to about 0.5. These results refer to Ta concentrations of 0.008-0.1 M in M KCl and 1 M potassium hydroxide solution. At a Ta concentration of 0.008 M with 1 M potassium chloride as supporting electrolyte, anomalous results were obtained; these were interpreted as indicating that the tantalate ion is unstable at the low pH of this dilution.

In a very original experiment Aveston and Johnson compared the Raman spectrum of the crystalline potassium tantalate with that of its saturated solution. The spectra are very similar, adding further evidence that the tantalate ion existing in the crystal is the same as that which exists in solution. The simplicity of the spectra was considered to provide qualitative evidence for the very symmetrical octahedral arrangement of Ta atoms proposed by Lindquist (13).

Peroxy Compounds.

The peroxy compounds of niobium and tantalum in neutral and acid solution have been studied by many workers. The peroxy complexes of both elements in sulphuric acid have been used in spectrophotometric analysis (81, 82), but very little is known about the nature and behaviour of these complexes in alkaline solution.

Recently (87-90) studies have been made of the compound obtained by addition of ethanol to an alkaline solution of niobium or tantalum pentoxides in the presence of hydrogen peroxide. It has been shown that the white crystalline solids obtained contain the anion:

$$MO_8^{3-} \quad \text{where } M = Nb \text{ or } Ta.$$

These salts dissolve in water without decomposition.

There is evidence that cationic peroxy complexes exist below pH 3, whereas above pH 5 anionic peroxide complexes exist (91).

Discussion of Dialysis and Diffusion Methods.

It is worth considering the dialysis method used by Gridchina. The use of reference ions avoids experimental errors due to vibration, variation in pore size due to membrane swelling, etc. However there remains the problem of differing degrees of hydration of the ions and therefore absolute dialysis coefficients cannot be measured. The method should be valid, however, for determination of relative dialysis coefficients of different forms of the same ions, if the degree of hydration can be considered constant. The variation of the relative dialysis coefficient should therefore reflect, qualitatively at least, the degree of polymerisation of the ions.

The equation:polymerisation factor, p, = $\left(\frac{D_{max}}{D_x}\right)^2$, was checked in an earlier paper by Babko and Gridchina (42) by determining the dependence of the relative dialysis coefficients of aluminium and thorium on the concentration of the ions and on acidity. These elements do not form polyions in an acid medium, and these authors found that the relative dialysis coefficient was almost constant for aluminium and thorium concentrations between 0.001 - 0.1 M in N hydrochloric acid, and 0.01 M in 1-0.001 N hydrochloric acid. These results justified the application of the above equation to the interpretation of dialysis data for zirconium ions in acid solution. In the later paper (4) Gridchina applied this equation to dialysis coefficient results for acid solutions of niobium, and also for alkali niobate solutions.

The assumption that the maximum dialysis coefficient corresponds to the unpolymerised ionic form is a reasonable one; further the data on aluminium show that a variation of dialysis coefficient in acid solution does imply polymerisation or depolymerisation of the ions. However there is no experimental evidence to support the suggested quantitative relation between dialysis coefficient and degree of polymerisation. Any variation in retardation due to varying particle size is, of course, completely unknown. Further the variation in the degree of hydration of the various ions is unknown; in the case of polymerisation to form chains such as occur with zirconium ions, the degree of hydration is probably roughly proportional to the degree of polymerisation. However, in the case of decomposition of the compact, octahedrally constructed niobate ion to form monomeric units this factor would be considerable. (The number of water molecules attached to 6 monomeric niobate ions would probably be much more than 6 times the number attached to one hexaniobate ion).

Despite its drawbacks, dialysis is a useful technique for investigations such as this in that it is less likely to affect any equilibrium which may exist in solution between various ion forms than are ion-exchange techniques or methods involving precipitation of ions from solution.

The diffusion method employed in the studies of Jander and Ertel has been much criticised. There is no theoretical basis for the assumed relation between molecular weight and diffusion. Further these authors have included in their graph of molecular weight as a function of diffusion coefficient a point for the tantalate ion, which they considered to be $[Ta_5O_{16}]^{7-}$. However, as has been shown, the evidence is now very strongly in favour of the formula $[Ta_6O_{19}]^{8-}$ for the tantalate ion. Further, tantalate probably exists in solution as an ion corresponding approximately to the formula.

$$[K_6Ta_6O_{19}]^{2-} \quad (M.W. = 1590).$$

If the water sheath is allowed for, therefore, the effective anionic weight is probably greater than 1600, whereas the point for the tantalate ion, which falls exactly on the graph published by

Jander and Ertel, corresponds to an assumed ionic weight of 1160. This casts serious doubt on the whole method. Baker and Pope (48) have concluded that the diffusion method is worthless for determination of molecular weights.

Summary.

It is evident from the above literature survey that the results of the various investigations which have been carried out do not yet present a complete picture of the various niobate-tantalate compounds which can be prepared by alkaline fusions of niobium and tantalum pentoxides. There are a number of reasons for this:-

(1) The chemical composition of compounds such as $4K_2O.3Ta_2O_5.16H_2O$ and $7K_2O.5Ta_2O_5.28H_2O$ is very similar; precise analyses are required to distinguish between them.

(2) Apparent discrepancies in the formulae of various compounds may be due to incomplete washing of the crystals. An interesting example of this effect is given by Kennedy (Ref. 93 page 44). Alkali niobates were prepared and washed with cold water, to give a K:Nb ratio of 1.5; further washing with boiling alcohol however decreased the ratio to 1.31. It is, of course, possible that some chemical change took place during the washing.

(3) Recent studies have indicated the existence of a number of different alkali niobate-tantalate compounds, with only slightly different stoichiometry, as well as some non-stoichiometric compounds. As regards the tantalates, the controversy between the 7/5 and

4/3 formulae, based on chemical analyses, was definitely resolved by Spitsyn and Shavrova (98), who described conditions for the preparation of both compounds from the same solution. This emphasises the fact that chemical data cannot provide conclusive proof regarding the nature of the ions present in solution.

The early results of Windmaisser (10) still hold great interest, indicating as they do that the 7/5 and 4/3 series may be variations of the same basic crystalline structure. This early interpretation has been supported and enlarged by the more recent work of Rohmer and Guerchais (47) who have formulated all the niobate compounds, including the metaniobate, as variations of the basic hexanuclear structure.

An interesting project for the future would be a physical study of the 7/5 series, with a view to establishing the structure of the ions in the crystal.

As regards the nature of niobate and tantalate ions in solution, the picture is somewhat clearer. Unambiguous data regarding the structure of the ions in solution are not easy to obtain. Normal methods for the determination of molecular weight cannot be used in this case; the anions hydrolyse to varying degrees and the exact amount of free acid or base present is not known. It has been shown that cryosopic methods tend to be unreliable when the degree of condensation is as high as six (52).

Comparison of the conductometric titrations of solutions of the 7/5 niobate compound, by Britton and Robinson (9) with those of solutions of the 4/3 compound by Dartiguenave et al (67) indicates very strongly that these solutions do in fact contain the same ions. Further, the similarity between the UV absorption spectra published by Jander and Ertel (53) and Nelson and Tobias (45) for the 7/5 and 4/3 tantalate compounds respectively indicates that the same tantalate ion is present in both solutions.

If the diffusion and cryoscopic results of Jander and Ertel are discounted, therefore, the combined evidence from light-scattering, ultracentrifugation, e.m.f. titrations and Raman spectra all indicates that the hexameric structure which exists in the crystal persists in solution, as $[H_xNb_6O_{19}]^{8-x}$ where Nb can be replaced by Ta.

It is likely that protonation-condensation reactions lead to the formation of larger polyanions in solutions of lower pH. The effective charge of the ions in solution is reduced by binding of cations.

A new dimension has been introduced into the picture by the dialysis experiments of Gridchina (40), showing the effect of concentration on the structure of the niobate ion. He obtained evidence for decomposition of the niobate ion at concentrations below 2.5×10^{-3}M Nb in 0.3 M potassium hydroxide. Other workers have not always given sufficient details about the concentrations of niobate and hydroxide in their solutions; however it appears that in all cases the concentration of niobate was greater than this value.

The extreme similarity of the niobate and tantalate anions is not surprising in view of the fact that the outer electronic configuration of Nb(V) and Ta(V) is identical. The most obvious difference in chemical properties between alkali niobate and tantalate solutions is the greater tendency of tantalate to hydrolyse. Tantalate undergoes hydrolytic precipitation at about pH 10, whereas niobate ions may remain in solution down to about pH 5; Jander and Ertel (54) recorded stable reproducible absorption spectra for niobate solutions in this pH range. This probably reflects a difference in the stability of the protonated forms of niobate and tantalate, rather than in the degree of protonation, of the two ions.

CHAPTER II

MATERIALS AND ANALYTICAL METHODS

Resin.

The resin used in this work was Deacidite FF, produced by the Permutit Co. This is a polystyrene-divinyl benzene resin containing quaternary ammonium groups. Resin of cross-linking 7-9% DVB (divinyl benzene) was chosen for this work, this being the highest cross-linking available. High cross-linking was considered desirable because high selectivity was required; selectivity is enhanced by increased cross-linking.

Resin of 14-52 mesh was used for the experiments on niobate/tantalate distribution. The larger particle size material was chosen for ease of filtration and handling after the equilibration experiments. This mesh size was also used for the kinetic investigations; with smaller particle size the reaction proceeded too rapidly to be followed by the experimental technique used. In this case the resin, prepared as described below, was further sieved through a 30 mesh sieve to decrease the particle size range. The prepared resin was therefore 14-30 mesh, corresponding approximately to bead diameters of 0.6 mm to 0.3 mm.

Resin of 100-200 mesh was used for the column investigations as rapid exchange is necessary in this case. This finer material was also used for one kinetic experiment in order to illustrate the effect of bead diameter on the reaction rate.

The resins were conditioned before use by cycling with hydrochloric acid and sodium hydroxide and finally washing with water till chloride-free. The fines were removed by stirring in water, allowing to settle and decanting. The slurry was filtered, sucked dry and allowed to dry in air. After coming to equilibrium with the atmosphere the resin beads were free flowing.

Preparation of Hydroxide Form of the Resin.

The hydroxide ion is very weakly adsorbed by strongly basic ion-exchangers; a large excess of hydroxide solution is therefore required to convert the resin to the hydroxide form. Column operation and a low flow rate are essential in order to remove the last traces of the preferred chloride ion.

The conversion of the resin to the hydroxide form was carried out in a small column, diameter 11 mm. The conversion of two grams of resin by means of 1.5 N sodium hydroxide solution is shown in figure 2.1. After 240 ml of the alkali solution had been passed, the chloride remaining on the resin was determined by passing 50 ml of 0.25 M sodium sulphate solution through the column and analysing the effluent for chloride. The effluent contained 0.021 mequiv. of chloride. From the known resin capacity (3.1 mequiv. per g of air-dried resin) the % conversion is

$$\frac{(6.2 - 0.021) \times 100}{6.2} = 99.5\%.$$

On the basis of this result the conditions chosen for conversion of the resin from the chloride form to the hydroxide form were: 200 ml of 2N sodium or potassium hydroxide solution for two grams of resin.

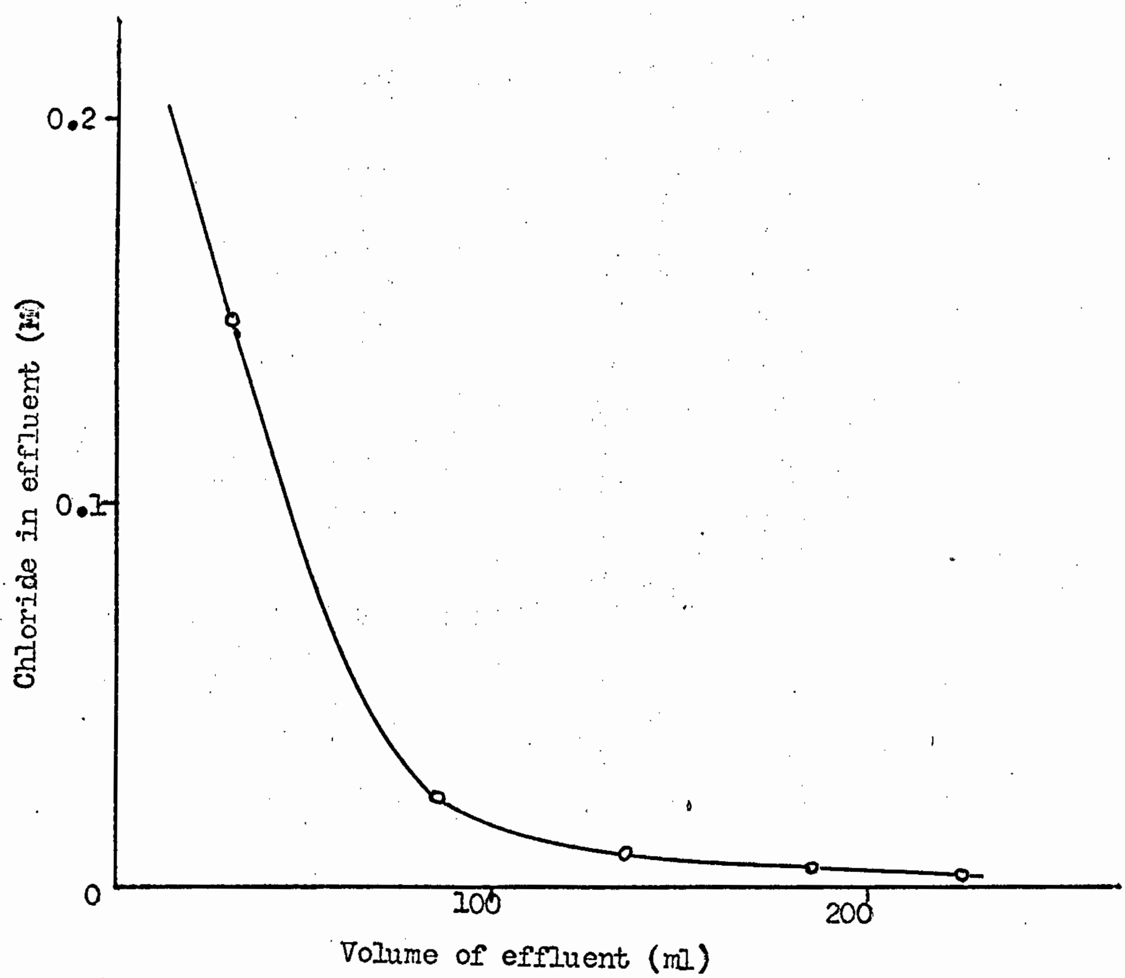

FIGURE 2.1 Conversion of 2 g of Deacidite FF resin (14-52 mesh) to hydroxide form by 1.5 N KOH solution.

Chemicals.

Niobium pentoxide: Hopkin and Williams reagent 6097. "Typical Analysis" (75): 99.8% Nb_2O_5, max 0.05% Ta, Si 800 p.p.m., Sn 400 p.p.m., Fe 300 p.p.m., Ti 220 p.p.m.

Tantalum pentoxide: Hopkin and Williams reagent 8405. "Typical Analysis" (75): 99.7% Ta_2O_5; Nb 60 p.p.m., Si 0.2%, K 500 p.p.m., Fe 500 p.p.m.

Carbonate-free potassium hydroxide was prepared by passing potassium chloride solution over a strongly basic anion exchange resin in the hydroxide form.

Zerolit N-IP strongly basic resin was used to prepare a column 42 cm long and 3.3 cm diameter. The resin was converted to the hydroxide form by passing 4 litres of 10% sodium hydroxide solution from which carbonate had been removed by addition of excess barium hydroxide solution and decanting. After this solution had been passed through the column the effluent was found to be chloride-free when tested with silver nitrate-nitric acid solution. Deionized water was then passed through the column to remove the alkali and potassium chloride solution passed through to prepare carbonate-free potassium hydroxide. When chloride began to appear in the effluent the column was regenerated as described above.

Carbonate-free Ammonia.

To 200 ml of concentrated (s.g.0.910) ammonia solution was added 50 ml of a saturated solution of barium hydroxide. The mixture was heated at atmospheric pressure, the ammonia being absorbed by deionized water.

Liquid Ion-Exchangers.

Preliminary experiments were carried out with cetyl trimethyl ammonium bromide, since this was the only quaternary ammonium compound available. Tests with a M/10 solution of this compound in iso-amyl alcohol showed that the ion-exchange of niobate/tantalate in alkaline solution proceeded in a manner analogous to the reactions with solid ion-exchange resin. However, with this liquid exchanger difficulty was experienced with formation of emulsions at the liquid interface. Later a sample of General Mills' Aliquat 336 was obtained and this was used for the experiments with hydrogen peroxide reported in Chapter VI. Aliquat 336 is methyl tricaprilyl ammonium chloride. This exchanger showed little tendency to emulsion formation in a variety of solvents. This difference in behaviour is presumably attributable to the higher proportion of long aliphatic chains present.

A solvent denser than water was required for the simple experimental procedure adopted Chloroform and carbon tetrachloride, having low solubilities in water, were investigated. Chloroform was rejected because of a slow decomposition which occurred on contact with the alkaline solutions. For the final determinations a M/10 solution of Aliquat in carbon tetrachloride was used. The solution was standardised by titration for chloride as follows:-

5 ml of the approximately M/10 exchanger solution was added to 5 ml of saturated sodium nitrate solution. The mixture was titrated

with N/10 silver nitrate solution using potassium chromate as indicator; a rapid and sharp end-point was obtained. In the absence of the high concentration of nitrate ions attainment of equilibrium was slow as the end-point was approached, and the titre was not reproducible.

Preparation of Niobate/Tantalate Solutions.

Approximately ten grams of potassium hydroxide pellets were fused over a bunsen burner at a low heat until the melt was quiet. Approximately 1 g of niobium pentoxide (or 2 g of tantalum pentoxide) was then added, a little at a time. After each addition the fusion was continued until the melt became clear before further additions were made. After all the pentoxide had been added the temperature was raised to a dull red heat for a few minutes. The crucible was then set aside to cool. The cooled melt was then extracted with 50 - 100 ml of water, with efficient stirring. The solution was filtered through Whatman 542 paper and diluted to 1000 ml.

These solutions were stable for years, apart from a slight deposit which appeared on long standing. The solutions were filtered and standardised by the PAR method (see page 43) before use.

Determination of exchange capacity of resin.

A common procedure for determining anion-exchange capacities involves leaching the resin sample in the chloride form first with ammonia and then with sodium sulphate solution, to displace chloride. Determination of chloride in the effluents provides a measure of the weak base groups in the first case, and strong base groups in the second.

However, the following points should be noted in this method:

(1) The ammonia must be carbonate-free. (2) Even carbonate-free ammonia does have some effect on quaternary ammonium groups, and the amount of strongly basic groups that are regenerated by ammonia varies with the total volume and concentration of ammonia used (78).

Therefore, a modified method of analysis was used in this work, based on information from Permutit Co., London. This procedure involves passing sodium sulphate solution through the resin sample and determining chloride in the effluent as a measure of the total ion exchange groups. Carbonate-free ammonia is then passed through the resin in order to convert all the weak base groups to the unionized form. (Some of the strongly basic groups are also affected). A 10% sodium chloride solution is then passed through the resin in order to convert strong base groups to the chloride form. Finally, the sample is leached with 4% sodium sulphate; determination of chloride in the effluent then provides a measure of the strongly basic groups only.

Method: 5.00 g of air-dried resin was placed in a short-stemmed 60° filter funnel containing Whatman 540 paper. The resin was treated with N hydrochloric acid and then washed with alcohol till acid-free. 1 litre of 4% sodium sulphate solution was then passed through the resin and collected in a 1 litre volumetric flask. After 1 litre of ammonia and 1 litre of 10% sodium chloride solution had been passed the resin and paper were washed with water till chloride-free. The resin was again leached with 4% sodium sulphate solution, which was collected in a 1 litre volumetric flask. The sodium sulphate leachates were analysed for chloride by titration with silver nitrate in order to determine the total ion-exchange capacity and the strong base capacity, respectively. *

At the same time the moisture content of the resin was determined by drying 5 g samples of resin overnight at 115°, cooling in a dessicator and weighing to determine the loss in weight.

Results obtained for the 14-52 mesh resin used in this work:

Strong base capacity = 3.06 mequivalents per g of air-dried resin

Weak base capacity = 0.11 " " " " " "

The moisture content of the resin was found to be 18% in this case. (The moisture content of the air-dried resin varies, depending on atmospheric conditions.)

<u>Direct determination of Niobate/Tantalate adsorbed on the resin.</u>

The following method was used for the determination of the distribution coefficients of niobate and tantalate on the resin. The various resin-solution mixtures, after equilibration overnight as described in Chapter III, were filtered through a coarse sintered glass filter funnel under suction.*+

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* Potassium chromate was used as the indicator. Due to the coagulating effect of the high concentration of sodium sulphate present, 2% dextrin solution was added in order to facilitate detection of the endpoint of the titration.

*+ This gives a rapid and complete separation of the two phases with their equilibrium concentrations of niobate/tantalate. With filtration through paper an appreciable volume of solution remains in the paper; this remaining solution is diluted by the wash liquid and there is a possibility of redistribution of niobate/tantalate during the slower process of filtration through filter-paper.

The resin beads on the sintered glass were washed with water; there is no possibility of niobate/tantalate loss at this stage as the ions are very strongly adsorbed from dilute solutions. The resin and filter were then washed once with alcohol and once with ether and finally sucked dry. The beads were no longer sticky and could be easily transferred to silica crucibles for ashing. The crucibles were ignited to constant weight at 800°. Blank determinations were carried out by equilibrating resin and solution in the absence of niobate/tantalate, filtering, washing and igniting as before. The blank values were subtracted from the residue of niobate/tantalate plus resin, in order to determine the Nb_2O_5, Ta_2O_5.

Absorptiometric Analysis for Niobium and Tantalum.

For the column work reported in Chapter V, the positions of the peaks in the eluates were determined by means of established colorimetric procedures based on the yellow niobium-thiocyanate complex (79) and the yellow pyrogallol tantalum complex in acid solution (80). Sensitivity of the pyrogallol method for tantalum is poor and it was therefore decided to seek a more sensitive method for tantalum for the later investigation of resin kinetics and the experiments with liquid ion-exchangers.

In recent years many new analytical procedures for both niobium and tantalum have appeared in the literature; these have been well summarized in two good reviews (72, 73). All methods have been developed for acid solutions; no published method is directly applicable to alkaline tantalate/niobate solutions. Further, one aspect of the present work was the investigation of the behaviour of niobate and tantalate in the presence of hydrogen peroxide in alkaline solutions, and the extent to which peroxide would interfere in any of the published spectrophotometric procedures was unknown.*

For these reasons it seemed that an analytical method based on the peroxy complexes of niobium and tantalum in concentrated sulphuric acid would be suitable for the purpose of this research. Analysis of niobium by means of the yellow complex formed with peroxide in concentrated sulphuric acid is a well-established method (81). More recently a method involving measurement of the absorption at 285 mμ of the pertantalic complex in concentrated sulphuric acid was outlined (82). Freshly fumed sulphuric acid is required, as absorption by the complex is affected by the presence of water in the acid. Further, the concentration of hydrogen peroxide must be precisely controlled as this reagent itself in sulphuric acid absorbs strongly below 300 mμ. Further, in the author's experience, pure tantalic acid tends to precipitate from concentrated sulphuric acid (see below). The method for tantalum is insentitive. For these reasons, as well as the inconvenience of working in concentrated sulphuric acid, this method was abandoned in favour of the procedure outlined below.

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* Babko and Shtokalo list peroxide as forming niobium complexes stronger than tartaric acid and second only to oxalic acid (44). The peroxide complexes of tantalum are known to be even more stable than those with niobium.

The formation of coloured niobium and tantalum complexes with 4 (2 pyridyl - azo -) resorcinol (PAR) was reported in 1962 (83). At about the same time this reagent was used for semi-quantitative determination of niobium and tantalum by means of the mixed hydrogen peroxide - PAR complexes (84). A quantitative method for determination of niobium in acid solutions, by means of the mixed peroxide-PAR complex was reported in 1963 (85). Applicability of the method to alkaline niobate solutions was not discussed. I } a later paper a method for determination of tantalum in acid solutions by means of the PAR-oxalate complex was described (86). In the same paper some data for the peroxide-PAR complex of tantalum were reported. On the basis of this preliminary information, the author has developed the following simple, rapid analytical method for analysis of alkaline tantalate solutions.

The red colour of the tantalum-peroxy-PAR complex was developed in the presence of sodium acetate-acetic acid buffer solutions of various pH values. In this way it was established that the optical density of the solutions was a maximum at pH 5, using the Hilger and Watts Spekker photometer and the Kodak green filters (No.5). It was further established that at this pH the maximum optical density of solutions containing up to 200 μg of tantalum pentoxide in 100 ml is achieved in the presence of 0.15% hydrogen peroxide and 0.002%PAR.

PAR solutions: The PAR used was prepared by R. Light & Co., Colnbrook, U.K. A 0.04% solution in ethanol was prepared and filtered.

Peroxide solution: An approximately 3% solution was prepared by dilution of AR "100 volumes" hydrogen peroxide; the concentration was checked by titration with permanganate.

Buffer solution: The pH of an approximately 2M solution of sodium acetate was adjusted to 5 by addition of glacial acetic acid; the solution was diluted until the sodium acetate was approximately 1M.

Preparation of standard Ta solution.

Attempts to prepare solutions of tantalum pentoxide in sulphuric acid - HF mixtures showed that there is a tendency for tantalum to precipitate from solutions on evaporation of the HF. Prolonged heating does not redissolve the precipitate. However it was accidentally discovered that the presence of niobium has a remarkable catalytic effect on the solubility of tantalum. Only traces are required. In one test, treatment of 100 mg of Ta_2O_5 with 2 ml HF and 10 ml sulphuric acid in a platinum crucible did not produce a clear solution, even after strong fuming for four hours. A speck of Nb_2O_5 was added and within minutes the solution became completely clear. This is undoubtedly the reason for the incorrect statements in the older literature that tantalum pentoxide dissolves in concentrated sulphuric acid.

Method for preparation of standard tantalum solution.

50 mg of Ta_2O_5 (an d a speck of Nb_2O_5) were warmed in a platinum crucible with 10 ml of 40% hydrogen fluoride solution and 10 ml of 1:1

sulphuric acid on a sand bath. The heat was slowly increased and the mixture was finally taken to strong white fumes to remove the last traces of fluoride. After cooling the mixture was poured into about 70 ml of solution containing 10 ml of 30% hydrogen peroxide in a 250 ml beaker. The contents of the crucible were washed into the peroxide solution and diluted to 100 ml in a standard flask, to obtain a solution containing 500 μg of tantalum pentoxide per ml. This solution was diluted ten times to obtain a 50 μg per ml standard solution, suitable for preparation of the calibration curve.

Method of analysis of tantalate solutions.

An aliquot of tantalate solution, containing up to 200 μg of tantalum pentoxide, was pipetted into a 100 ml flask. To this was added

5 ml of 3% hydrogen peroxide solution
50 ml of pH 5 buffer solution
5 ml of 0.04% PAR solution.

The flask was well shaken after each addition. The mixture was diluted to 100 ml and well mixed. After 30 minutes the optical density was measured in a Hilger and Watts Spekker photometer, using the Kodak green filter (No.5), and 2 cm cells, against a blank solution containing all the reagents except the tantalum solution. The concentration of the solution was then read from the calibration curve, a typical example of which is shown in figure 2.2.

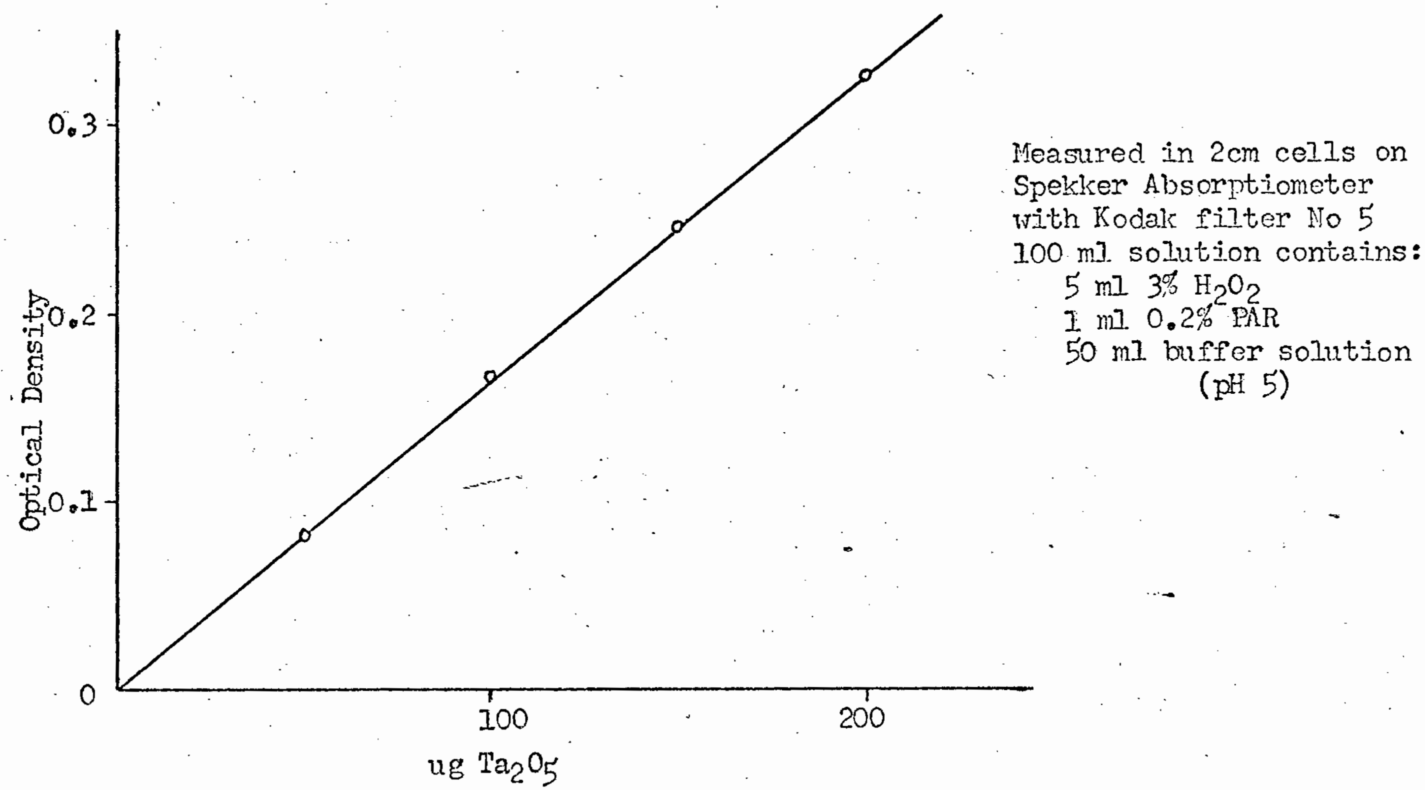

FIGURE 2.2 Standard graph for PAR method

Analysis of niobate solutions.

Niobate solutions were analysed by measurement of the analogous violet-coloured niobium-peroxy-PAR complex. The instructions given by Elinson and Pobedino (85) were modified so as to give a method similar to that described above for tantalate. See Appendix II.

Both photometric methods are characterized by a mean square error of 2-5%, over the range 20-200 μg pentoxide.

NOTE:

Some erratic results in the spectrophotometric work were traced to contamination by tantalum adhering to the surface of the glassware. The tantalum complex tends to precipitate from the solutions on standing and it was necessary to wash all flasks and cells immediately after use. Flasks suspected of contamination can be cleaned by filling with the "blank" reagents and allowing to stand overnight.

In the rest of this research work glassware stained by niobium or tantalum was cleaned by allowing to stand for about a half-hour filled with dilute 1% hydrofluoric acid.

CHAPTER III

DISTRIBUTION COEFFICIENTS

The distribution of a solute species between an ion-exchange resin and the solution with which it is in contact may be defined in terms of the distribution coefficient, K_d, as follows:

$$K_d = \frac{\text{mg of solute on resin}}{\text{mg of solute in solution}} \times \frac{\text{ml of solution}}{\text{g of resin}} \quad \ldots\ldots\ldots \quad 3.1$$

The distribution coefficient is determined by equilibrating a known mass of resin in a suitable ionic form with a solution containing the ionic species under investigation, and analysing the solution or the resin phase to determine the concentration of the solute.

The distribution of trace amounts of niobate and tantalate between resin and solution was determined in potassium chloride solution and in potassium hydroxide solution. The solution concentrations were varied so as to cover the range from 100% adsorption to 100% desorption of niobate/tantalate. In addition the distribution coefficients were determined at a single potassium chloride concentration, at 55°C, in order to observe the effect of temperature on the separation factor. (The separation factor is defined in chapter V). The distribution coefficients were also determined in 0.2 M solutions of potassium chloride in mixed aqueous-organic solvents, and at elevated temperature, in order to observe the effect of these variables on the separation factor.

EXPERIMENTAL

Distribution coefficients in potassium chloride solutions.

One-gram portions of resin in the chloride form were weighed into 200 ml glass bottles with well-fitting screw-top lids. At the same time two one-gram portions were weighed into glass weighing bottles for the moisture determination. To each bottle was added 100 ml of a potassium niobate solution* (0.75×10^{-3} M Nb) or potassium tantalate solution (0.45×10^{-3} M Ta) containing potassium hydroxide (pH 12.2) and varying amounts of solid potassium chloride (0.15-0.275M). Chloride ion is much more strongly adsorbed by Deacidite FF resin than hydroxide ion, so that under the experimental conditions used the resin remains in the chloride form. The ion-exchange process studied is thus simple exchange between chloride ions and niobate/tantalate ions.

The well-closed bottles were shaken gently overnight at a temperature varying between 24° and 26°C. Rate determinations (see Chapter IV) showed that this time was sufficient to allow equilibrium to be reached.

The mixtures were filtered through sintered glass and analysed as described in Chapter II.

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* In all the experiments described in this chapter the concentration of the potassium niobate solutions was 0.75×10^{-3} M Nb, and the concentration of potassium tantalate was 0.45×10^{-3} M Ta.

Effect of Temperature: Distribution Coefficients in 0.25M Potassium Chloride Solution at 55°C.

One-gram portions of resin (100-200 mesh) in the chloride form were weighed into the reaction bottles. 100 ml aliquots of the slightly alkaline niobate or tantalate solutions, which were 0.25 M with respect to potassium chloride, were warmed to 55° and then added. The bottles were immersed in a water bath at $55^{\circ} \pm 1^{\circ}$ and shaken every ten minutes for four hours. It is shown in the chapter on kinetics that this is sufficient time for equilibrium to be reached with 100-200 mesh resin. The mixtures were then filtered and analysed as described above.

Effect of Solvent: Distribution Coefficients in 0.2M Potassium Chloride Solution containing 10% of Acetone or Alcohol.

One-gram portions of resin (100-200 mesh, chloride form) were equilibrated overnight with 100 ml of niobate/tantalate solution which was 0.2M with respect to potassium chloride and contained 10% ethanol or acetone. The mixtures were separated and analysed as described above.

Distribution Coefficients in Potassium Hydroxide Solution.

One-gram portions of resin (14-52 mesh, chloride form) were weighed out as described above. To each bottle was added 100 ml of potassium niobate solution or potassium tantalate solution containing varying amounts of potassium hydroxide (0.3-1N). The mixtures were shaken overnight at a temperature varying between 24° and 26°C, filtered and analysed as before.

RESULTS

From the equilibrium distribution data the distribution coefficients were calculated according to equation 3.1.

The distribution coefficients in 0.15 - 0.3M potassium chloride are shown as a function of the concentration of chloride in solution in figure 3.1. (96).

The distribution coefficients in 0.25 M potassium chloride at 55° are shown in table 3.1 and the results obtained in 0.2 M potassium chloride in the presence of ethanol or acetone are shown in table 3.2. The data in potassium hydroxide solution are shown in figure 3.2. Thes results are discussed in Chapter V.

DISCUSSION

Distribution Coefficients in Potassium Chloride Solution:

The resin coverage in these experiments can be calculated as follows:

The average charge on the niobate and tantalate species under the experimental conditions is shown below to be 7. This corresponds to the structures $[HNb_6O_{19}]^{7-}$ and $[HTa_6O_{19}]^{7-}$. The equivalent weight of niobium and tantalum in these ion-exchange reactions is therefore $\frac{6Nb}{7}$ and $\frac{6Ta}{7}$. Each bottle contained 100 ml of either 0.75×10^{-3} M Nb solution, or 0.45×10^{-3} M Ta solution.

This corresponds to $0.75 \times 10^{-3} \times 100$ millimoles Nb

$$= \frac{6 \times 0.75 \times 10^{-1}}{7} \text{ milli-equivs Nb}$$

$$= \underline{0.064 \text{ milli-equivs Nb}}$$

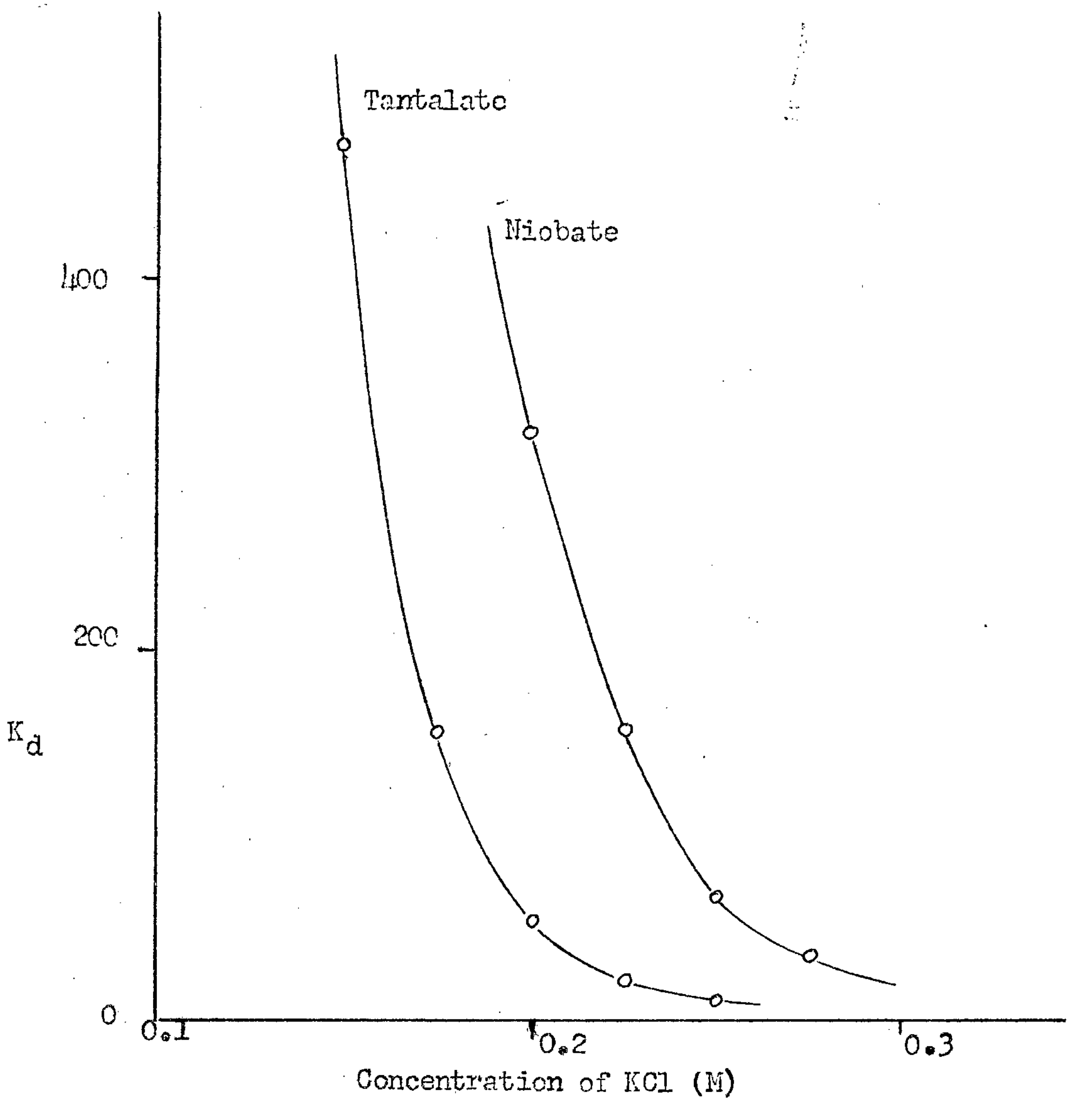

FIGURE 3.1 Distribution Coefficients in KCl Solution

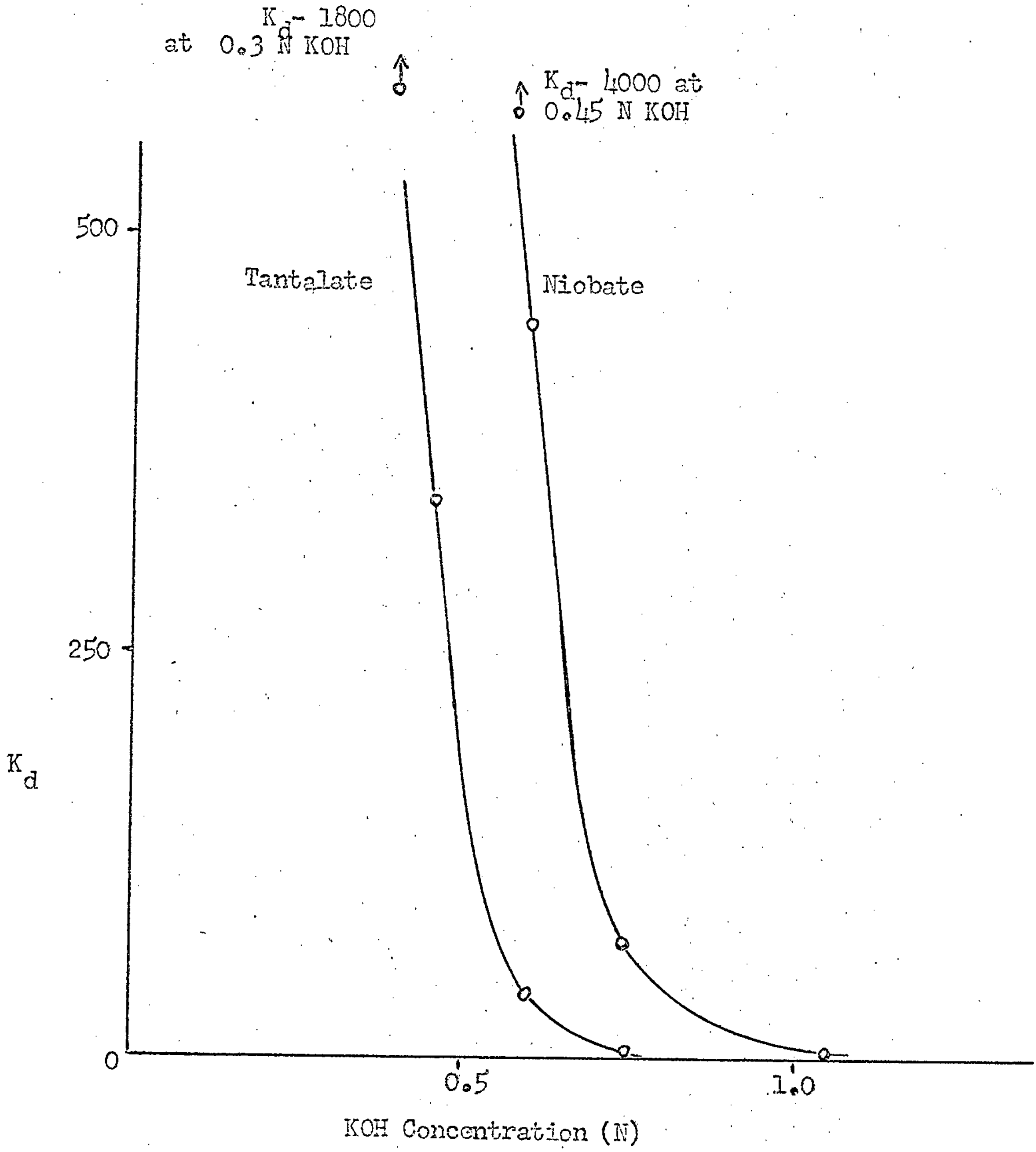

FIGURE 3.2 Distribution Coefficients in KOH solution

K_d Niobate	K_d Tantalate	Separation Factor
306	43	7.2

Table 3.1 Distribution coefficients in 0.25 M potassium chloride solution at 55°C.

	K_d Niobate	K_d Tantalate	Separation Factor
10% Ethanol	167	17.5	9.5
10% Acetone	212	30.3	7.0

Table 3.2 Distribution coefficients in 0.2M potassium chloride solution containing 10% ethanol or acetone. Temperature 29-32°C.

and for tantalum, $0.45 \times 10^{-3} \times 100$ millimoles Ta

$$= \frac{6 \times 0.45 \times 10^{-1}}{7} \text{ milli-equivs Ta}$$

$$= \underline{0.039 \quad \text{milli-equivs Ta}}$$

Further, each jar contained one gram of air-dried resin, which corresponds to 3.1 milli-equivs of exchangeable sites (see Chapter II).

Therefore, complete adsorption of niobate corresponds to

$$\frac{0.064 \times 100}{3.1} = 2.1\% \text{ resin coverage,}$$

and complete adsorption of tantalate corresponds to

$$\frac{0.039 \times 100}{3.1} = 1.3\% \text{ resin coverage.}$$

Under these trace conditions the theory of ion-exchange can be greatly simplified. The resin is largely in the same ionic form throughout. Further, the concentration of potassium chloride in solution is low, and varies only slightly over the range of the determinations, from 0.15 - 0.25 M in the tantalate determinations, and from 0.2 - 0.275 for the determinations of niobate distribution.

The amount of electrolyte penetration into the resin over this range can be calculated as follows:-

On the basis of the simple Donnan theory,

$$[\overline{K^+}] \times [\overline{Cl^-}] = [K^+] \times [Cl^-] \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

where $[\overline{K^+}]$, $[\overline{Cl^-}]$, represent the concentrations inside the ion-exchang resin, and $[K^+]$, $[Cl^-]$, represent the concentrations in the solution.

The concentration of chloride ions associated with the exchange sites inside the resin beads can be calculated approximately as follows The capacity of Deacidite FF resin is given as 1.6 milli-equivalents of ionogenic groups per ml of packed resin bed. In a packed bed the spherical resin beads would occupy about 60% of the total volume, so that the above figure corresponds to

$$1.6 \times \frac{100}{60} = 2.7 \text{ milli-equivalents per ml.}$$

The chloride form of the exchanger is therefore 2.7 M with respect to chloride, internally.

Suppose penetration of potassium chloride into the resin from the solution corresponds to x milli-equivalents of potassium chloride per ml of the bead volume. The chloride concentration inside the resin is therefore (2.7 + x) g equiv. per litre; the potassium concentration would be x g equiv. per litre.

If the equilibrium solution concentration is 0.2 M potassium chloride, equation 3.2 becomes

$$x \times 2.7 + x = 0.2 \times 0.2$$

$$\text{whence} \quad x = 0.01$$

This means that as the external solution concentration increases from 0 to 0.2 M, the chloride concentration inside the resin changes only from 2.70 to 2.71 M.

Therefore over the limited concentration range of the experiments, electrolyte penetration into the resin can be ignored, and the chloride concentration inside the ion-exchanger can be considered constant.

For these reasons swelling of the resin can be considered constant over the range of the results shown in figure 3.1. On the basis of the same considerations, the activity coefficients in the resin phase can also be considered constant.

Simple niobate-chloride exchange can be represented as follows:

$$\overline{\text{Niobate}^{y-}} + y\ Cl^- \rightleftharpoons \text{Niobate}^{y-} + y\ \overline{Cl^-} \quad ...... \quad 3.3$$

If non-ionic adsorption, for example by van der Waals forces, is ignored, the Law of Mass Action can be applied. The thermodynamic equilibrium constant would then be written:

$$K = \frac{\gamma_{\overline{Nb}}[\overline{\text{Niobate}^{y-}}] \times \gamma_{Cl}[Cl^-]^y}{\gamma_{Nb}[\text{Niobate}^{y-}] \quad \gamma_{\overline{Cl}}[\overline{Cl^-}]^y} \quad ...... \quad 3.4$$

where $\gamma_{\overline{Nb}}$, etc., refer to the activity coefficients.

Coverage of the resin with chloride ion varied from 98-100%. Therefore, to a first approximation, $[\overline{Cl^-}]^y$ can be considered constant

The maximum concentration of niobate in solution in the distribution experiments was 0.75×10^{-3} M Nb, that of tantalate was 0.45×10^{-3} M Ta. In these circumstances the ionic strength of the solution is determined mainly by the much higher concentrations of potassium chloride. Data for the activity coefficients of potassium chloride solutions are shown in the figure 3.3. The relevant concentration range for tantalate is 0.15 - 0.25 M potassium chloride, and for niobate, 0.2 - 0.275 M potassium chloride. From figure 3.3 the approximate activity coefficients are 0.86 - 0.83, and 0.85 - 0.83. As a further approximation, therefore, it can be assumed that the activity coefficients in the solution phase are also constant over the range covered by the determinations for each species.

Equation 3.4 now reduces to

$$K^* = \frac{[\overline{\text{Niobate}}]}{[\text{Niobate}]} \times [Cl^-]^y \quad ....3.5$$

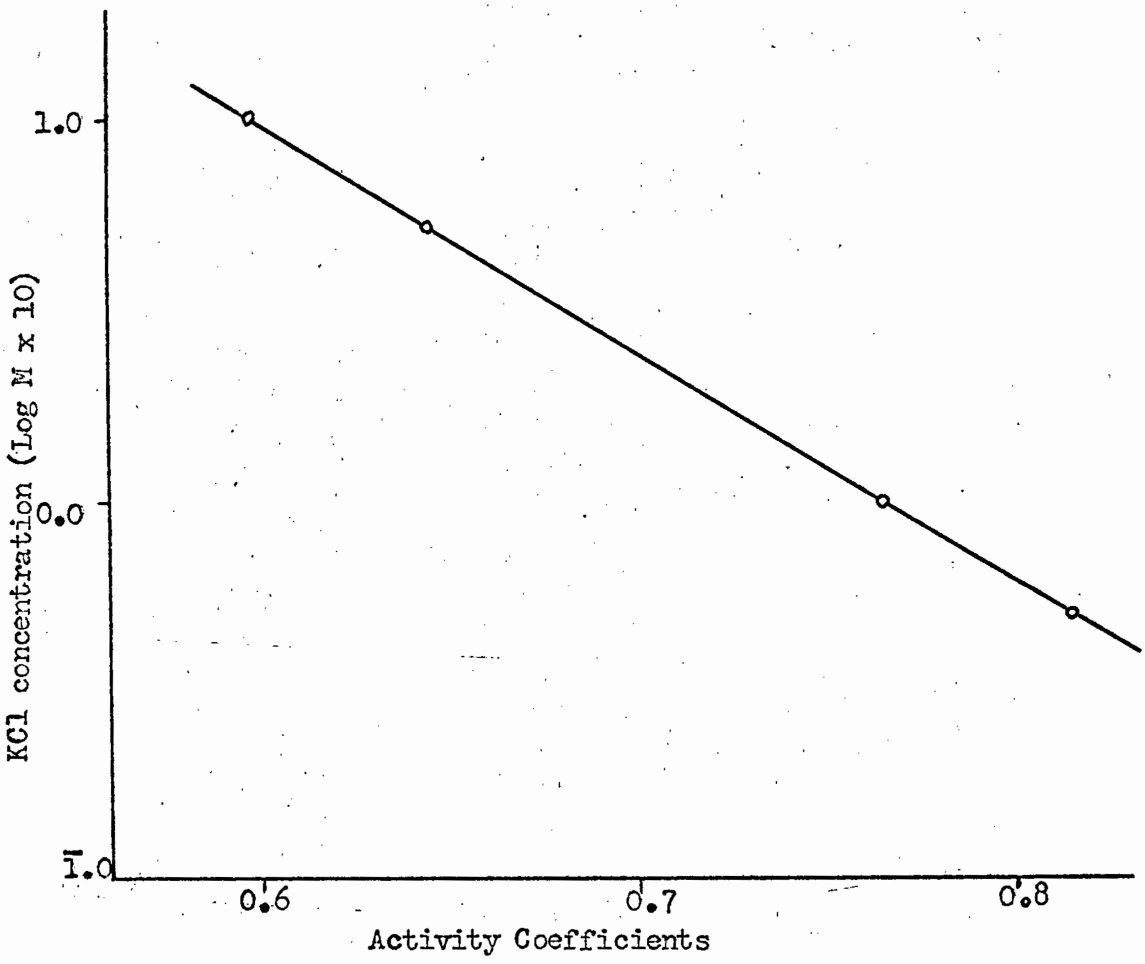

FIGURE 3.3 Activity coefficients of Potassium Chloride solutions. From EMF measurements. (97)

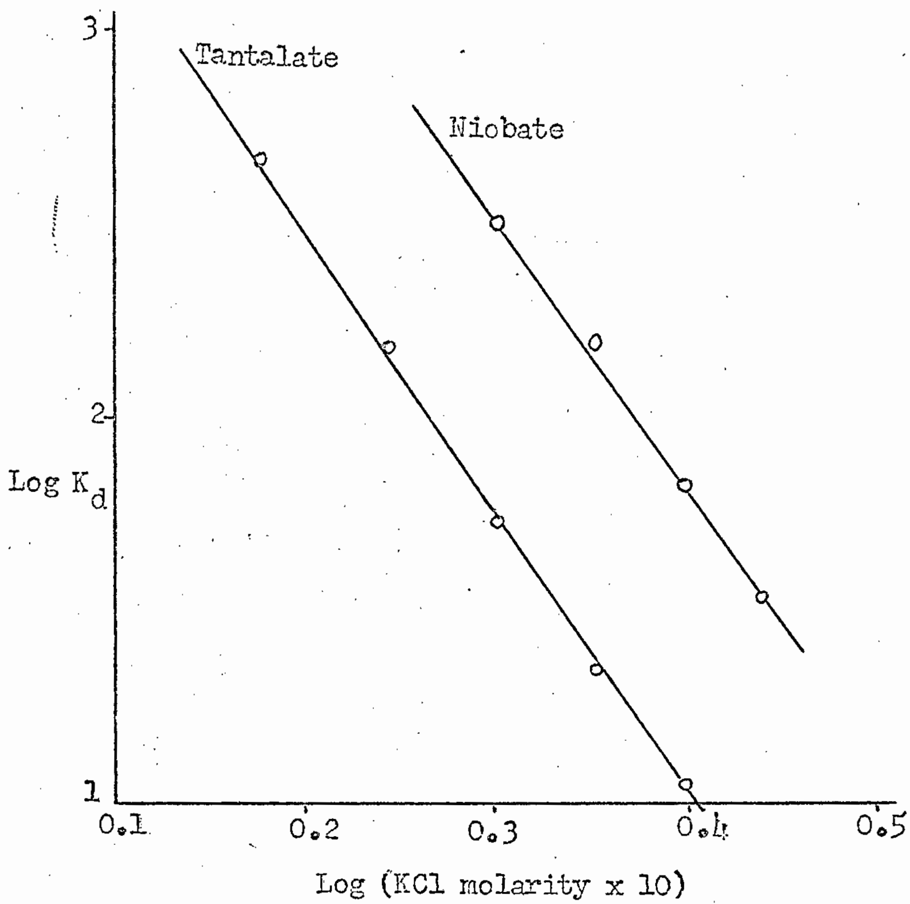

FIGURE 3.4 Distribution Coefficients in Potassium Chloride solution

Using suitable units $\frac{[\overline{\text{Niobate}}]}{[\text{Niobate}]}$ becomes the distribution coefficient K_d defined in equation 3.1,

therefore,

$$K^* = K_d \times [Cl^-]^y \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.6$$

$$\log K^* = \log K_d + y \log [Cl^-] \quad \ldots\ldots\ldots\ldots \quad 3.7$$

$$\log K_d = \text{Constant} - y \log [Cl^-] \quad \ldots\ldots\ldots\ldots \quad 3.8$$

This means that the plot of log K_d versus log $[Cl^-]$ should be linear. The results of the present work have been plotted in figure 3.4 and it can be seen that the graphs are linear.

<u>Charge on Niobate and Tantalate Ions</u>.

The slope of the graphs in figure 3.4 is 7.1 for both niobate and tantalate. According to equation 3.8 this figure represents the charge carried by both the niobate and tantalate ions under the experimental conditions. The data in figure 3.4 refer to a solution pH of 12.2. Since the exchanger is in the chloride form the pH inside the exchanger would be approximately the same as that of the external solution.

Neumann (55) used e.m.f. titrations to study niobate solutions which were acidified by addition of ammonium chloride; the ammonia formed was removed by passing nitrogen gas through the solutions. He represented the acidification process as follows:-

$$[Nb_6O_{19}]^{8-} + H^+ \underset{}{\overset{\text{pH } 13.8}{\rightleftharpoons}} [HNb_6O_{19}]^{7-}$$

$$[HNb_6O_{19}]^{7-} + H^+ \underset{}{\overset{\text{pH } 10.9}{\rightleftharpoons}} [H_2Nb_6O_{19}]^{6-}$$

From the e.m.f. measurements Neumann determined the average negative charge per niobium as a function of log $[OH^-]$ up to about pH 13. From his published results the charge per niobium atom is found to be approximately 1.16 at pH 12.2.

Nelson and Tobias (56) determined the charge per niobium in potassium niobate solutions from ion-exchange measurements. Niobate was adsorbed on a column of Dowex 2-X-4 resin in the hydroxide form * and the hydroxide displaced was determined by titration with acid. They calculated the charge per niobium atom, and obtained the average value of 1.12. They do not report the pH of their solutions.

Thus it can be seen that the species charge of 7.1 calculated from the slope of the graphs in figure 3.4 is in good agreement with the findings of Neumann. His value of 1.16 per niobium atom would correspond to a charge of 7.0 for the protonated hexanuclear niobate ion at pH 12.2.

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* Nelson and Tobias (Ref. 56 page 734) report that they failed to adsorb niobate on Dowex 2-X-8 (8% DVB) whereas they succeeded with the same resin containing 4% DVB. They attribute this to steric hindrance of the large niobate anion in the more highly cross-linked resin. However Dowex 2 has the same resin structure as Deacidite FF, the resin used in the present work; this resin, cross-linked with 7-9% DVB has been found to adsorb niobate very strongly. Nelson and Tobias used the resin in the hydroxide form, under which conditions niobate is most strongly adsorbed by the resin. Therefore, whatever the reason may be for their failure to adsorb niobate, it is unlikely to be due to the physical size of the niobate ion.

As far as the tantalate ion is concerned, Nelson and Tobias (46) determined the average charge per tantalum atom as 1.12, using an ion-exchange method similar to that described above for niobate. They also used e.m.f. measurements (45) to calculate n, the number of protons bound per tantalum atom, as a function of the hydroxide concentration over the pH range 13 - 11.7. Solution concentrations were 24 and 60 x 10^{-4} M Ta. They found a constant value of n of 0.12 over the pH range studied, and suggest that this value may have been due to traces of potassium hydroxide in the crystals of tantalate. However, if the value of 0.12 is correct, it would correspond to an average of 0.6 protons per hexatantalate ion, so that their published data would presumably reflect the equilibrium:

$$[Ta_6O_{19}]^{8-} + H^+ \rightleftharpoons [H\,Ta_6O_{19}]^{7-}$$

In the pH range of their data the average structure is therefore

$$[H_{0.6}Ta_6O_{19}]^{7.4-}$$

This is in fair agreement with the charge of 7.1 for this pH range which is reported in the present work.

The value of 7.1 for the charge of the niobate ion is also in agreement with the conclusions of Gridchina. In his study of the dialysis of niobate solutions, Gridchina found evidence for the decomposition of the hexameric niobate ion in solutions which were more dilute than 2.5 x 10^{-3} M Nb, and which were 0.3 M with respect to potassium hydroxide. His results also indicated that in more dilute potassium hydroxide solutions, the hexaniobate ion was stable at concentrations below 2.5 x 10^{-3} M Nb.

In the present work the concentration of niobate in the distribution experiments was 0.75 x 10^{-3} M Nb and the concentration of potassium hydroxide was 0.016N. The stability of the hexaniobate ion under the experimental conditions is therefore in harmony with the general trend of Gridchina's dialysis data, assuming his interpretation of these data to be correct.

It should be noted that in the results reported by other workers the ionic charge of the niobate and tantalate ions has been calculated on the basis of an assumed hexanuclear structure. The results presented here are particularly interesting as they represent a direct measurement of species charge without any assumption as to the structure of the ion.

This method of determining ionic charge has been applied successfully before. Lederer and Jakovac (94) determined the distribution coefficients of the protoactinate ion in potassium hydroxide solutions of various concentration. The log-log plots were linear with a slope of -3.1, indicating that a trivalent protoactinate ion exists in alkaline solution.

CHAPTER IV

KINETICS

The rates of adsorption and desorption of the niobate ion by Deacidite FF resin in the hydroxide form have been studied as a function of the concentration of hydroxide in solution.

EXPERIMENTAL

The resin used in most of the experiments was 14-30 mesh (particle diameters of 0.6 to 0.3 mm). 100-200 mesh resin (particle diameters from 0.075 to 0.037 mm) was used in one run, in order to determine the effect of particle size on the exchange rate. Two gram samples of resin (chloride form) were weighed out and converted to the hydroxide form before use, as described in Chapter III.

The reaction vessel was a 500 ml two-necked flask. Owing to the tendency of alkaline solutions to absorb carbon dioxide it was necessary to exclude air. The vessel was therefore closed and a magnetic stirrer was employed. Initial tests with the simple magnetic stirrer were unsuccessful, as a considerable amount of grinding of the resin beads occurred. This was overcome by supporting the stirrer in a special holder, as illustrated in figure 4.1. The stirrer could not pass through the neck and had to be assembled inside the flask. The polythene pointed base was drilled to provide a press fit for the stirring magnet. This magnet, gripped in tweezers, was inserted through the side arm of the reaction flask and fitted into the hole in

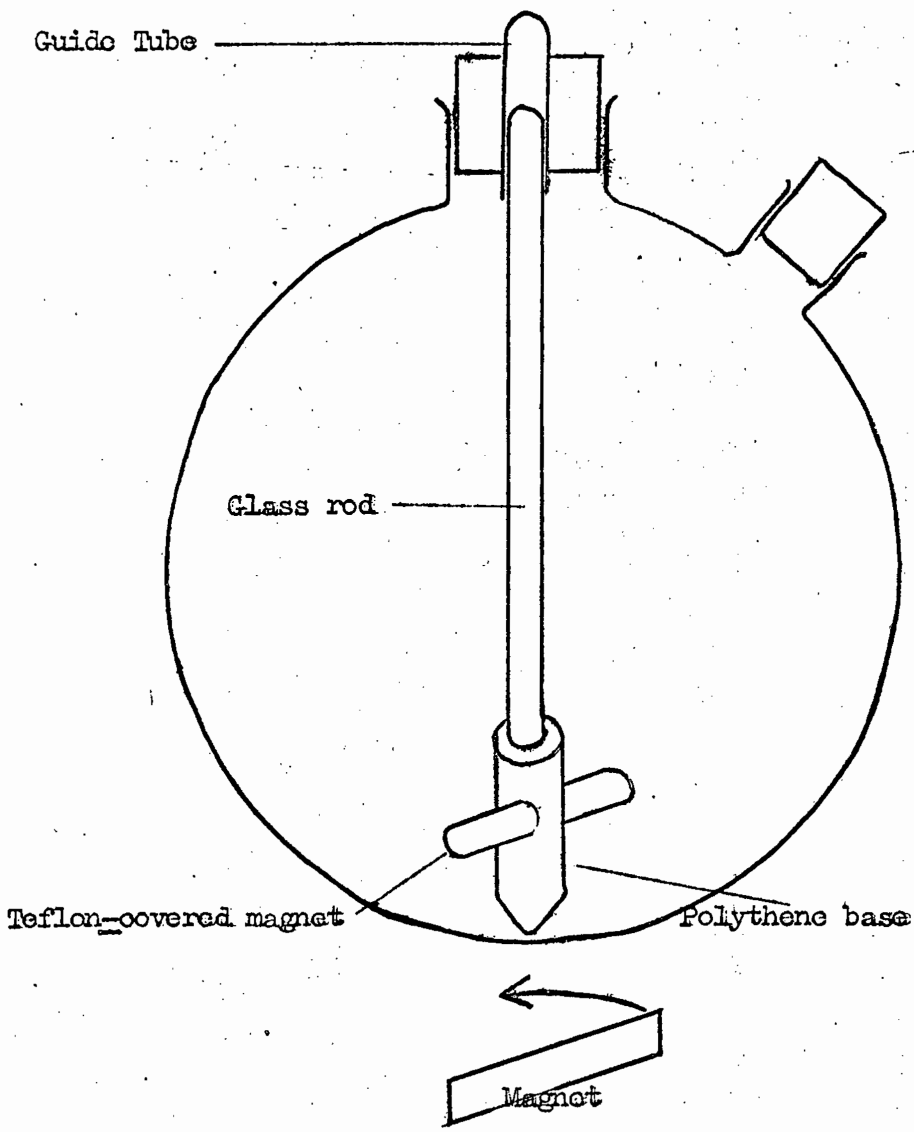

Figure 4.1. Illustration of reaction vessel used for kinetic investigations.

the base of the stirring arm. This technique worked very successfully.

The reaction vessel was immersed in a thermostatically controlled water bath, maintained at 24-26°C.

For determination of adsorption rates the resin in the required form was placed in the flask, and 200 ml of the appropriate niobate solution (0.75×10^{-3} M Nb)* was added and the stirrer started. The exact time of the start of the reaction was noted, and at known intervals of time aliquots of solution were withdrawn for analysis.

For the experiments on rates of desorption, the niobate was adsorbed on to the resin first. The resin, in the hydroxide form, was stirred with a dilute niobate solution containing the required amount of niobate. Under these conditions the niobate is rapidly and completely adsorbed from solution by the resin. The mixture was then filtered through a porous sintered glass filter and sucked dry; in this way a rapid separation was obtained. The resin was then transferred to a funnel placed in the neck of the reaction flask and washed into the flask with 100 ml of water. 100 ml of the appropriate solution (twice the required concentration of hydroxide) was then added to start the desorption reaction, the exact time being noted.

The technique used for sampling was as follows:-

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* By comparison with the calculations on page 52, it can be seen that the maximum resin coverage in these tests was approximately 2%.

One minute before sampling the stirrer was stopped to allow the resin to settle. A pipette was inserted through the side-arm of the vessel to take the sample from the upper layer of clear solution. The pipette contained a small wad of cotton wool in the tip, in order to exclude the resin particles. Immediately after sampling, the stirrer was started again. Sampling was carried out as quickly as possible in order to minimize exposure of the solution to the atmosphere and interruption of stirring. The samples were analysed colorimetrically by the PAR method.

In most of the experiments five or six 1.0 ml samples were taken during the course of the reaction. In one experiment (adsorption in 0.53N KOH) four 2.0 ml samples were taken. The original volume in each case was 200 ml, therefore the decrease in solution volume was 2-3% in most experiments and in no case more than 4%. The data have been used for qualitative interpretation only and therefore in calculating the "% approach to equilibrium" the volume of solution has been considered constant and equal to the final volume.

In the early stages of this work the exchange rates were observed at potassium hydroxide concentrations up to 2N. The generally slow rates of desorption observed suggested that the resin might be changing its nature somehow in concentrated alkali solution, making fast reactions impossible. This was checked by observing the desorption of dichromate ions from Deacidite FF resin in 4N potassium hydorxide solution, as follows:-

A sample (0.8 g) of air dried resin, 14-30 mesh, was converted to the hydroxide form. The resin was then transferred to a beaker containing 4N potassium hydroxide solution in order to allow swelling to proceed to equilibrium in this solution. The swollen resin was then filtered off, washed twice with distilled water and stirred for 15 minutes with 200 ml of 5% potassium dichromate solution. The resin was filtered off, washed with distilled water and then transferred to a 4 cm absorption cell used in the Spekker photoelectric colorimeter. The absorption cell was placed in position in the colorimeter with another cell containing a blank solution of 4N KOH, and the green filters were inserted in the light path.

At time zero 20 ml of 4N KOH was added to the reaction cell and the mixture gently stirred with a glass rod. At intervals stirring was stopped, and as soon as the resin had settled the optical density of the solution was determined against the blank solution. In this way the increasing concentration of dichromate in solution could be followed directly in the reaction cell.

The reaction was 98% complete within three minutes. This confirmed the fact that fast ion-exchange reactions are possible with this resin in alkaline solutions as concentrated as 4N KOH.

RESULTS AND DISCUSSION

The results of the rate experiments have been calculated in terms of the percentage approach to equilibrium, i.e. 100% corresponds to the equilibrium solution concentration attained for each run. The actual concentration of niobate in solution at equilibrium, of course, is different for each run. These results are shown in figures (4.2, 4.3). Further, all the kinetic data are summarized in figure 4.4 which shows the times for "80% approach to equilibrium" as a function of the potassium hydroxide concentration.

The rate of an ion-exchange reaction between a solution and an ionogenic group attached to the resin chain is generally transport-controlled and governed by the rate at which the exchanging ions can diffuse through the Nernst film* and through the pores of the resin. The rate may be "particle-diffusion controlled" or "film diffusion controlled" depending on which of the two processes is the slower.

The reason for the pattern of variation of reaction rates in the present work is not immediately obvious. A possible explanation may be sought in terms of changes in ionic size. If the size of the niobate ion varies with solution pH, for example by polymerization, then the rates of transport of the ions inside the solid exchanger framework may be expected to vary.

As shown in Chapter II, there is apparently some experimental evidence for a change of ionic size with changing concentration of potassium hydroxide. Gridchina (see page 14) interprets his experimental data on rates of dialysis of niobate ions through cellophane membranes by suggesting that the polymeric size of the niobate ion

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* Mixing of the solution does not take place right up to the surface of the resin beads. The beads are therefore surrounded by a thin film of unmixed solution, through which the exchanging ions must diffuse.

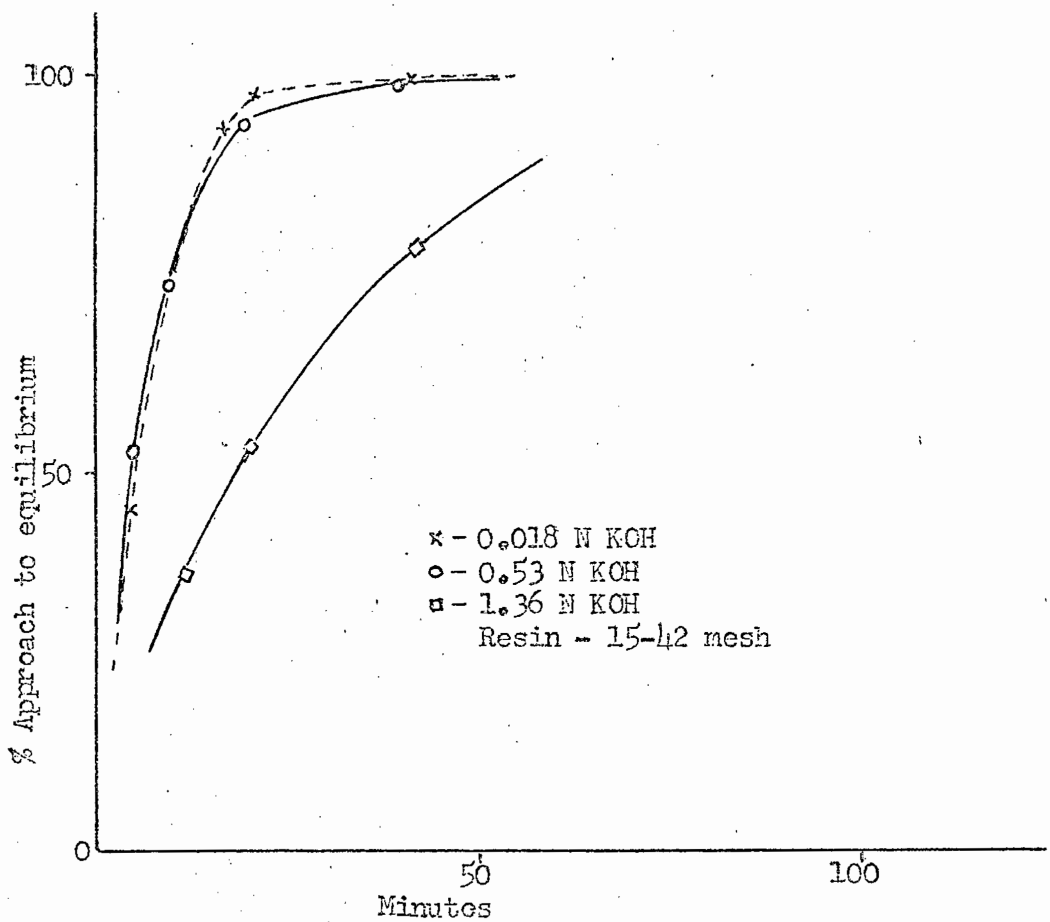

FIGURE 4.2 Rate of adsorption of niobate

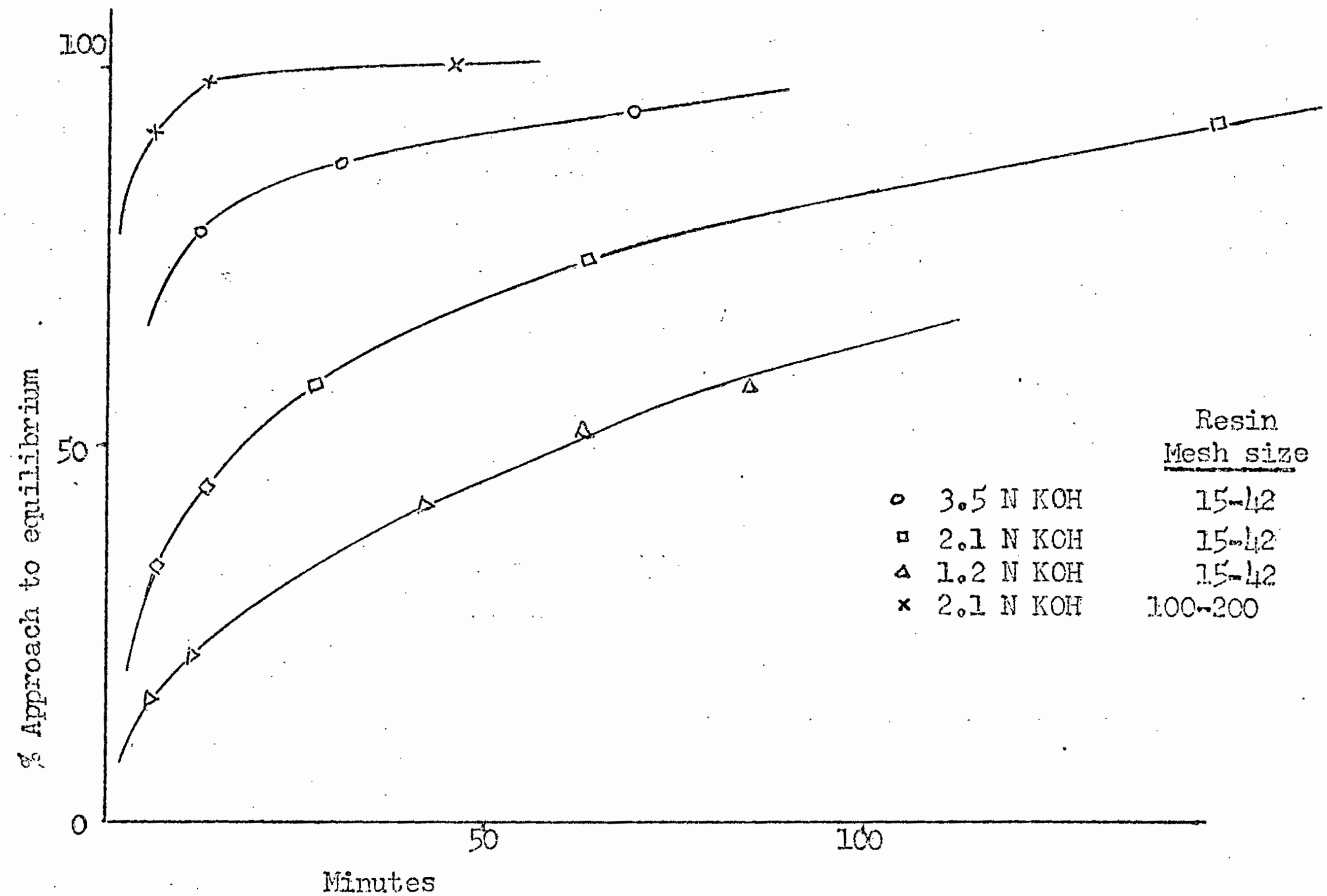

FIGURE 4.3 Rate of desorption of niobate

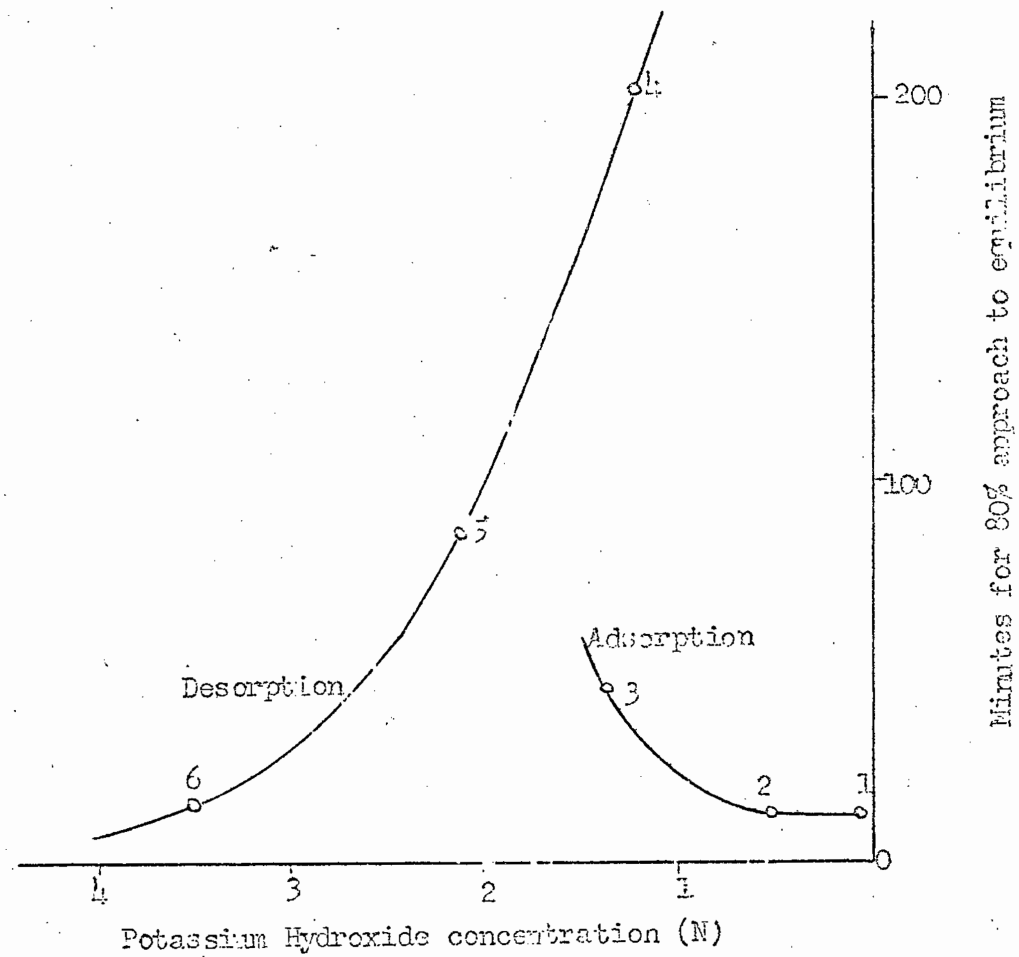

FIGURE L.4 Rate of niobate exchange

decreases with increasing potassium hydroxide concentrations. His published results refer to potassium hydroxide concentrations in the range 0-1 N, and extrapolation of the graph shown in his paper would suggest that the effect continues at concentrations above 1 N. However it can be seen from figure 4.4 that the adsorption rate of niobate is constant at potassium hydroxide concentrations ranging from 0.02-0.53 N over which range the ionic size is supposed to be decreasing. At potassium hydroxide concentrations above 0.6 N the adsorption rate decreases; depolymerization should lead to an increase in rate. In the case of desorption, the rate does increase with increasing concentration of potassium hydroxide; however the exchange rates observed are slower than the rates of adsorption at low potassium hydroxide concentration. It is clear, therefore, that the suggested changes in ionic structure do not explain the observed kinetic effects.

The situation is further complicated by the fact that the pH inside the exchanger does not follow the pH of the solution.

From the argument presented in Chapter III (page 53) it is evident that the hydroxide form of the resin, even when in contact with water, has an internal hydroxide concentration of about 2.7 N. It can be shown from equation 3.2 that as the external potassium hydroxide concentration increases from 0 to 1 N, the internal concentration changes only from 2.7 N to 3.0 N hydroxide.

Even when the situation inside the exchanger is considered, therefore, it is evident that the depolymerization effects suggested by Gridchina cannot explain the observed changes in rate.

A possible explanation for the kinetic results is as follows. The equilibrium data for the various rate experiments have been calculated and are shown in figure 4.5, the abscissae have been drawn to the same scale in figures 4.4 and 4.5. Comparison of the two sets of results indicates very strongly that there is a relationship between the kinetic and equilibrium data.

The system involves exchange between a strongly adsorbed trace component (niobate) and a weakly adsorbed component (hydroxide) always present in excess, in both resin and solution. Under these conditions it is the transport of the trace component which determines the overall exchange rate (See F. Helfferich, "Ion-exchange" page 283). This would be especially true in this case; from the point of view of ionic size and electrostatic drag, the diffusion of the niobate ion would obviously be rate-controlling.

In these strongly alkaline solutions the niobate ion would not exist in the protonated structure - $[HNb_6O_{19}]^{7-}$, but as the most basic octavalent form - $[Nb_6O_{19}]^{8-}$. The overall charge carried by this ion would be decreased by attachment of potassium ions. Nelson and Tobias (56) report that in potassium niobate solutions in water the effective charge of the anion appears to be reduced to a value of no greater than -2. For the sake of argument therefore the mobile ion may be represented as $[K_6Nb_6O_{19}]^{2-}$. The charge determinations in Chapter III show that the potassium ions attached to the niobate ion are all displaced by the ionogenic groups of the resin.

The exchange reaction therefore is -

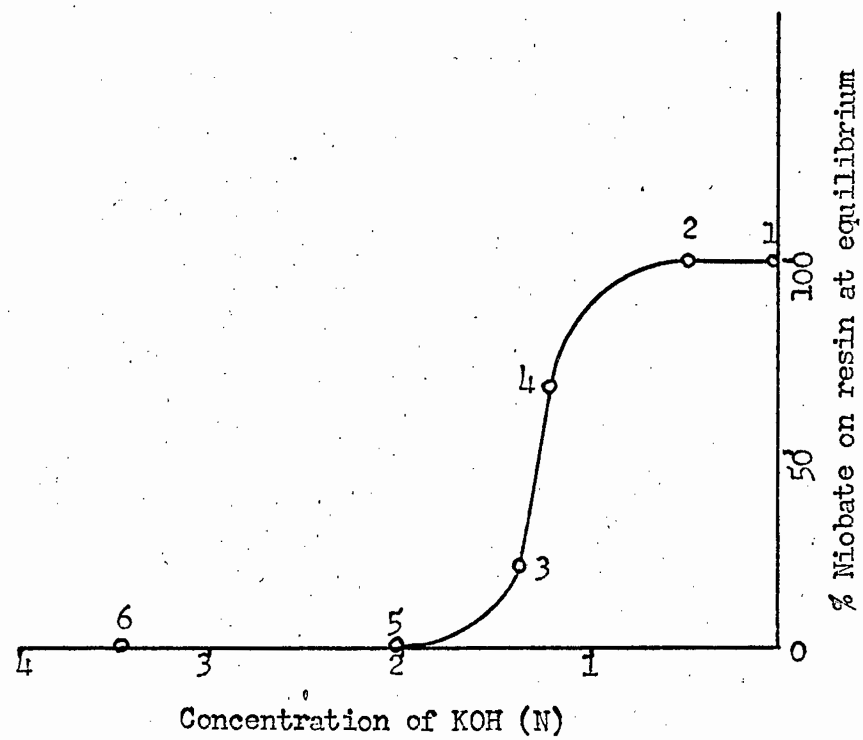

FIGURE 4.5 Distribution of niobate between resin and solution in kinetic experiments

$$[K_6Nb_6O_{19}]^{2-} + 8\overline{OH^-} = [\overline{Nb_6O_{19}}]^{8-} + 8OH^- + 6K^+ \quad \ldots\ldots\ldots 4.1$$

The overall exchange process can therefore be summarized as follows in the case of adsorption:-

1. Diffusion of $[K_6Nb_6O_{19}]^{2-}$ from the bulk solution through the Nernst film to the surface of the exchanger bead.
2. Diffusion of $[K_6Nb_6O_{19}]^{2-}$ inside the bead.
3. Exchange of $[K_6Nb_6O_{19}]^{2-}$, replacement of the six potassium ions by six exchange groups, and liberation of eight hydroxide ions from the resin.
4. Diffusion of the eight hydroxide ions to the surface of the bead.
5. Diffusion of the eight hydroxide ions across the Nernst film.

The bulk solution was stirred sufficiently to keep the beads in suspension, and transport through the bulk solution can therefore be ignored.

There are as yet few ion-exchange reactions in which chemical exchange is known to be the slow, rate-controlling step. However this is theoretically quite possible, especially in the case of reactions involving ions with a charge as high as that of the niobate ion. The reaction at the eight different exchange sites presumably proceeds in stages as the sheath of potassium ions surrounding the niobate ion is progressively displaced by quaternary ammonium groups. Therefore step 3 above cannot be ruled out, a priori, as the rate-determining step. For this reason the effect of resin particle size was determined in the case of 2N potassium hydroxide solution. The results are shown in figure 4.3. The great increase in reaction rate with decreased particle size of the resin proves that the over-all exchange rate is transport-controlled (92).

The explanation given below is based on the assumption that film diffusion of the niobate ions is the rate-controlling step. While this has not been proved experimentally, it seems to be the expected mechanism, for the following reasons:-

(1) It is well-known that very dilute solutions favour film diffusion control. The maximum concentration of niobate in these experiments was 0.75×10^{-3} M Nb.

(2) Under the experimental conditions 100% adsorption of niobate corresponds to 1-2% resin coverage. It is known that in the older grades of polystyrene-divinyl-benzene resins, such as that used in this work*, the crosslinks are not homogeneously distributed; sites of low cross-linking would be favoured under these trace conditions, so that diffusion of niobate inside the particles would not be hindered and therefore would not be expected to be rate-controlling.

The following picture of the transport process is based on a consideration of the changing concentration of niobate ions at the resin-film interface.

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* Permutit Company have now replaced Deacidite FF with a new product, Zerolit FF - IP ("Isoporous") in which it is claimed that the cross-links are more or less homogeneously distributed.

Adsorption of niobate will be considered first.

At low potassium hydroxide concentration the trace concentrations of niobate are 100% adsorbed, as shown in figure 4.5. Therefore the niobate ions are adsorbed by the resin as fast as they diffuse through the Nernst film, and the concentration of niobate on the resin side of the film is therefore virtually zero, so that the concentration gradient across the film is relatively steep.* Thus the rate of exchange is fast and is independent of the potassium hydroxide concentration in the solution. This would explain the fact that the reaction rate is independent of the potassium hydroxide concentration at concentrations below about $\frac{1}{2}$ N. (Points 1 and 2 in figure 4.4).

As the concentration of potassium hydroxide is increased, the equilibrium in equation 4.1 shifts to the left. Niobate ions diffusing from the solution through the film are then incompletely adsorbed by the exchanger so that there is a finite concentration of niobate ions at the resin side of the film.

The concentration gradient across the film thus decreases as the KOH concentration increases. The overall adsorption rate therefore decreases with increasing potassium hydroxide concentration at

---

* This refers of course to the initial concentration gradient. There is no quasi-stationary state under trace conditions such as this; the solution concentration falls rapidly from the initial concentration (0.005 mg/ml in this case) to zero.

concentrations above 0.5 N (points 2 and 3 in figure 4.4). As the potassium hydroxide concentration approaches 2 N the increasing competition by hydroxide ions inhibits adsorption of niobate to an increasing extent until finally the stage is reached where no adsorption of niobate takes place at all (points 5 and 6 in figure 4.5).

Let us now consider the desorption of niobate where the equilibrium is approached from the other side.

The concentration of niobate ions on the solution side of the film is always low, since these ions are mixed in the bulk solution as they diffuse through the film. As the concentration of potassium hydroxide is increased, the equilibrium in equation 4.1 shifts to the left. A greater proportion of niobate ions are desorbed and make their way to the surface of the resin beads, increasing the concentration gradient across the film. The flux across the film, and therefore the overall exchange rate, thus increases with increasing concentration of potassium hydroxide (points 4, 5 and 6 in figure 4.4).

This theory seems to present a satisfactory explanation for the observed trends.

CHAPTER V

COLUMN SEPARATION OF NIOBATE AND TANTALATE

The important parameter in chromatography of two chemical species is the "separation factor" which is defined as a function of the difference in adsorption potentials of the two species on the sorbent. In the case of ion-exchange chromatography involving development by elution, the practical separation factor α may be defined as follows:-

$$\alpha = \frac{K_1}{K_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.1$$

where K_1 and K_2 are the equilibrium distribution coefficients, which have been defined in Chapter III. In the present case, -

$$K_{Nb} = \frac{\text{mg } Nb_2O_5 \text{ on resin}}{\text{mg } Nb_2O_5 \text{ in solution}} \times \frac{\text{volume of solution}}{\text{mass of resin}} \quad \ldots \quad 5.2$$

$$K_{Ta} = \frac{\text{mg } Ta_2O_5 \text{ on resin}}{\text{mg } Ta_2O_5 \text{ in solution}} \times \frac{\text{volume of solution}}{\text{mass of resin}} \quad \ldots \quad 5.3$$

Equation 5.1 may therefore be written

$$\log \alpha = \log K_{Nb} - \log K_{Ta} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 5.4$$

It is evident from figure 3.4 that log α is a constant and independent of the concentration of the eluting ion, in this case chloride. This is to be expected since in the absence of special complexing agents it is evident that the ionic structures remain constant; therefore the separation factor in this system is a function only of the relative selectivities of the resin for the two ions.

The separation factors in the range 0.2 - 0.75 M KCl and 0.75 N KOH for the various conditions investigated are summarized below:-

	Separation Factor
0.25 M KCl	6.0
0.20 M KCl (55°C)	7.2
0.25 M KCl (10% acetone)	7.0
0.25 M KCl (10% ethanol)	9.5
0.75 M KOH	11.1

The main difference in chemical properties between the niobate and tantalate ions is the greater tendency of tantalate to hydrolyze. For this reason the effect of temperature and of added organic solvents was tried. Concentrations of 10% ethanol and acetone were used because at higher concentrations precipitation of niobate and tantalate tends to occur.

These separation factors are quite adequate for chromatographic separation. Even smaller separation factors have been successfully exploited for this purpose (68).

It is clear that no great improvement in separation factor is effected in all conditions examined. Therefore it was decided to attempt the column separation under the simplest conditions, viz., in potassium chloride solution at room temperature. Use of potassium hydroxide solution required special precautions to exclude carbon dioxide of the atmosphere and special preparation of carbonate-free KOH.

Choice of Column.

The minimum requirements for column size and operating conditions to separate niobate and tantalate can be calculated on the basis of the distribution coefficients.

A mathematical treatment of ion-exchange chromatography has been worked out, based on the "plate" theory. The basic parameter involved in the theoretical application is the Effective Height of a Theoretical Plate (EHTP), i.e., the length of the column in which equilibrium exists between the effluent solution and the resin at the entrance. Glueckauf has published theoretical curves describing the purity of two separated peaks as a function of the number of theoretical plates in the column, and the equilibrium distribution coefficients of the two solutes between resin and eluant (69).

In the present case, suppose that a 99.9% separation of equal quantities of niobate and tantalate was required. The distribution coefficients with chloride resin and M/4 potassium chloride solution are:-

K_d Niobate = 68

K_d Tantalate = 11

From the curves published in Glueckauf's paper the number of theoretical plates required is about 10.

The EHTP is a function of the size of the ion-exchange beads and the flow-rate through the column. Decreasing the bead size and decreasing the flow rate results in closer approach to equilibrium and therefore a shorter effective plate height. The theoretical relationship between the height equivalent to a theoretical plate and the various operating parameters in an ion-exchange column has been calculated (71). A very useful empirical graph showing the approximate relationship between the EHTP and resin particle size at various flow rates has been published by Cornish (70).

In the present case 100-200 mesh resin was used, and the chosen flow rate was approximately 1 ml per minute, which is equivalent to 0.32 ml per cm^2 per minute, for the column used.

Substituting in Cornish's published graph, the EHTP under these conditions is 0.3 - 0.6 mm. The minimum column length required is, therefore, 0.6 x 10 = 6 mm.

Calculations such as this are used as a guide only, and it is normal to overdesign the column by a factor of say 10-20 to ensure easy operation in a laboratory application. Further, in the present application there was some doubt about the chloride-hydroxide exchange which might occur on the column at various hydroxide concentration. Therefore it was decided to prepare a column longer than that required by these calculations. The column actually used was 28 cm long.

EXPERIMENTAL

Preparation of Column.

Deacidite FF resin, 7-9% cross-linking, 100-200 mesh, was used. About 60 g of damp resin was prepared by stirring in a large beaker of water, allowing to settle and decanting to remove the fines. This was repeated and the slurry then poured slowly into a glass column (internal diameter 2 cm), care being exercised to remove air bubbles and to obtain a uniform packing. The final length of the packed resin bed was 28 cm. The "aspect ratio" of the column is therefore described as

$$\frac{\text{length}}{\text{diameter}} = \frac{28}{2} = 14$$

The resin column was conditioned by cycling with potassium hydroxide solution and hydrochloric acid, being finally left in the chloride form and washed to remove the acid. The column and feed mechanism are shown diagrammatically in figure 5.1.

Notes on the apparatus:

1. The soda lime guard tube was used to prevent absorption of carbon dioxide by the alkaline solutions.
2. A plastic ball was floated on top of the solution in the column to prevent disturbance of the column by the incoming solution.
3. The fraction cutter was controlled by an automatic timing mechanism.
4. After use the column was always converted completely to the chloride form by passing strong potassium chloride solution and stored in contact with potassium chloride solution.

Determination of initial volume V_o

The following procedure was employed to determine the "initial volume" of the column, i.e. the volume of eluate collected between the introduction of a neutral solute at the top of the column and the first appearance of that solute in the eluate.

An ammoniacal solution of copper chloride (2% CuO) was prepared. This contains the bright blue cuprammonium cation, which is not adsorbed by the basic Deacidite FF resin. Using this solution it was easy to follow the passage of solution through the column visually. The volume of eluate collected between the introduction of the copper

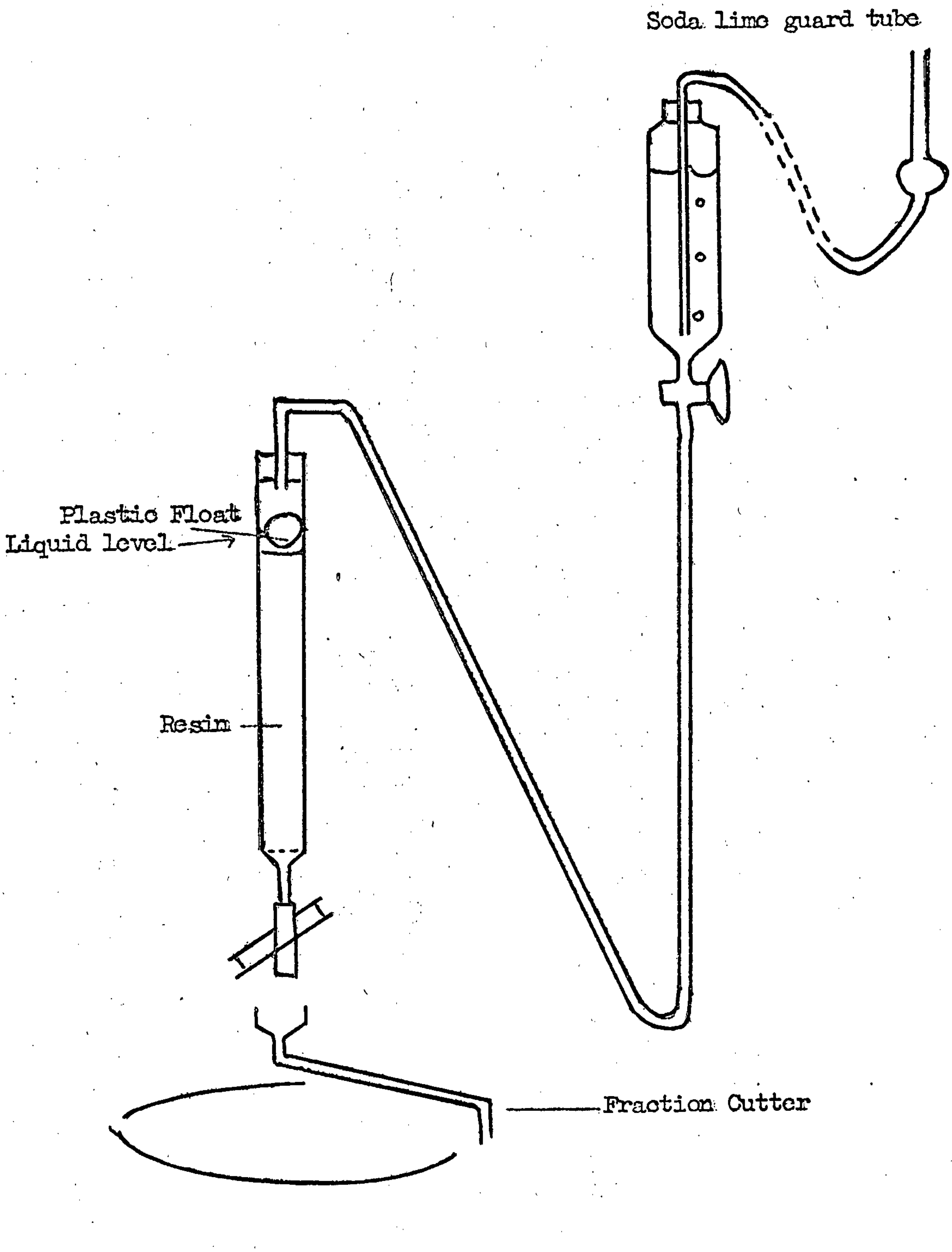


Figure 5.1. Ion-exchange column and Feed Mechanism

solution at the top of the column and the first appearance of the blue colour in the eluate was 35 ml.

Separation of Niobate and Tantalate (95)

A series of trial runs were made in order to establish the approximate positions of the eluted niobate and tantalate peaks. The separation of a niobate-tantalate mixture was then demonstrated by the following experiment.

The column, described above, was conditioned by passing 300 ml of a solution of 0.7 M potassium chloride which was also 0.035 M with respect to KOH. The adsorption was performed by passing 50 ml of a solution containing 5 mg of niobium pentoxide and 4.9 mg of tantalum pentoxide in 0.035 M KOH, to which had been added 6.6 ml of 0.1 M potassium chloride solution. The KCl was added in order to maintain the resin largely in the chloride form throughout.

The tantalate was eluted by passing through the column 920 ml of 0.25 M potassium chloride solution, which was 0.01 M with respect to potassium hydroxide, at a flow rate of one ml per minute. The automatic fraction cutter was used to obtain fractions of approximately 40 ml each. A 0.5 M solution of potassium chloride, which was 0.01 M with respect to potassium hydroxide, was then passed through the column to elute the niobate. The fractions collected were analysed by the methods described on page 41, and the results obtained are as shown in figure 5.2.

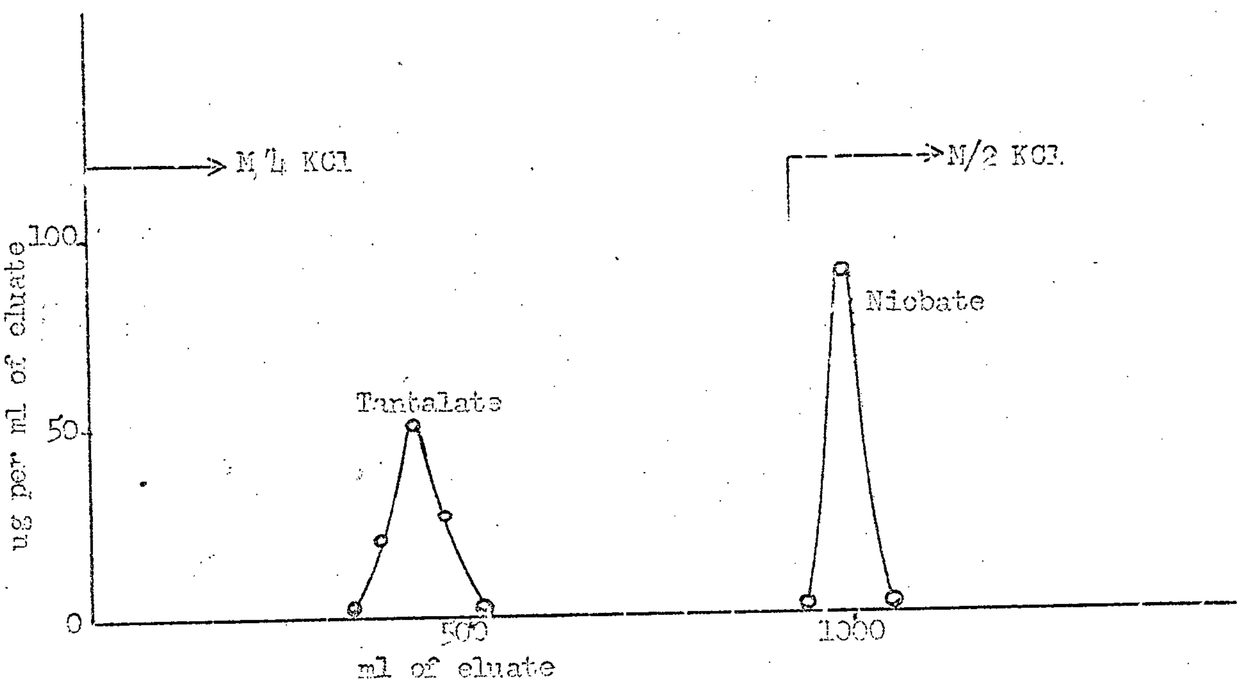


FIGURE 5.2 Elution of Niobate/Tantalate

DISCUSSION

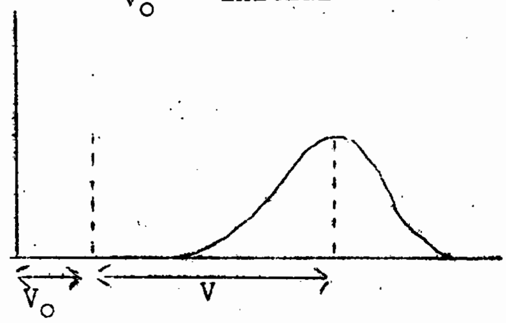
The column performance demonstrated experimentally in figure 5.3 could be predicted from the equilibrium distribution coefficients, as follows.

Theoretically, the volume of eluant required to elute an adsorbed species across a given mass of resin in a column is given in the following equation, where V, V_o have the significance shown.

Figure 5.3

V_o = "initial volume"

$$V = V_o + K_d \times \text{Mass of resin} \quad \text{---5.5}$$



For this relation to be valid, in practice, two important conditions must be met.

(1) The species must be adsorbed on a very small amount of resin at the top of the column. If this is not so the "mass of resin" factor in equation 5.5. is not a constant, as the ions to be eluted do not all start from the same point. For this requirement to be fulfilled, the species must be sorbed, prior to development, from a sample of very small size, or else if the volume is large the distribution coefficient must have a very high value so that no movement down the column occurs during the adsorption step.

In the present case, adsorption was performed from approximately 0.013 M potassium chloride solution; it can be seen in page 53).

The kinetics of ion-exchange are quite different in the two systems. In both cases the actual chemical exchange reactions are virtually instantaneous; however, as shown in the chapter on kinetics, the reaction time for solid exchangers is relatively slow, governed by the rate of transport of the ions, across the unmixed liquid film surrounding the exchanger beads, and through the pores of the resin itself. With liquid exchangers the transport process is extremely rapid, governed only by the kinetic energy of the solutes and the size of the liquid-liquid interface.

EXPERIMENTAL

The ion-exchanger used has been described in Chapter II. The following simple experimental technique was used.

The exchange reactions were performed in corked 20 ml test tubes. 7 ml each of the aqueous and organic layers were pipetted into the tubes and shaken. It was established that gentle rocking of the tubes in a horizontal position for one minute was sufficient for equilibrium to be attained. With this procedure any tendency to emulsification is completely eliminated. After the equilibration complete separation of the aqueous and organic phases occurred after only a few minutes. A pipette was then inserted directly into the upper aqueous layer to remove a sample for analysis.

Hydrogen peroxide concentration in the tests reported below was 0.13%. The adequacy of this concentration was established as follows.

To each of three tubes was added 7 ml of an alkaline (1.16 N potassium hydroxide) tantalate solution (0.32×10^{-3} M Ta); the concentration of hydrogen peroxide in the three solutions were 0.13%, 0.21% and 0.43% respectively. 7 ml of the Aliquat solution was added to each, and the tubes were gently rocked for one minute. A 1 ml sample was then withdrawn from the aqueous layer in each tube and analysed. The amount of tantalate extracted was found to be constant, irrespective of the concentration of peroxide. A concentration of 0.13% was thus deemed sufficient.

The hydrogen peroxide was added to the diluted solutions of niobate/tantalate at least one hour befere the ion-exchange reactions were carried out. Initial tests showed that allowance of a longer time for equilibration of peroxide-tantalate in 1.16 N KOH had no effect on the distribution results.

Determination of distribution ratios.

5 ml of a solution of niobate (0.75×10^{-3} M Nb) or tantalate (0.45×10^{-3} M Ta) was pipetted into each of the reaction tubes. 2 ml of potassium hydroxide solution of varying concentration, and containing enough hydrogen peroxide to give a final concentration of 0.13%, was added to each tube and the solutions mixed. After one hour, 7 ml of the Aliquat solution was added to each tube. The tubes were corked and rocked gently for one minute in a horizontal position. After the phases had separated the aqueous solution was analysed by the PAR method, and the concentration of niobate-tantalate in the organic phase was determined by difference. From these data the distribution ratio D was

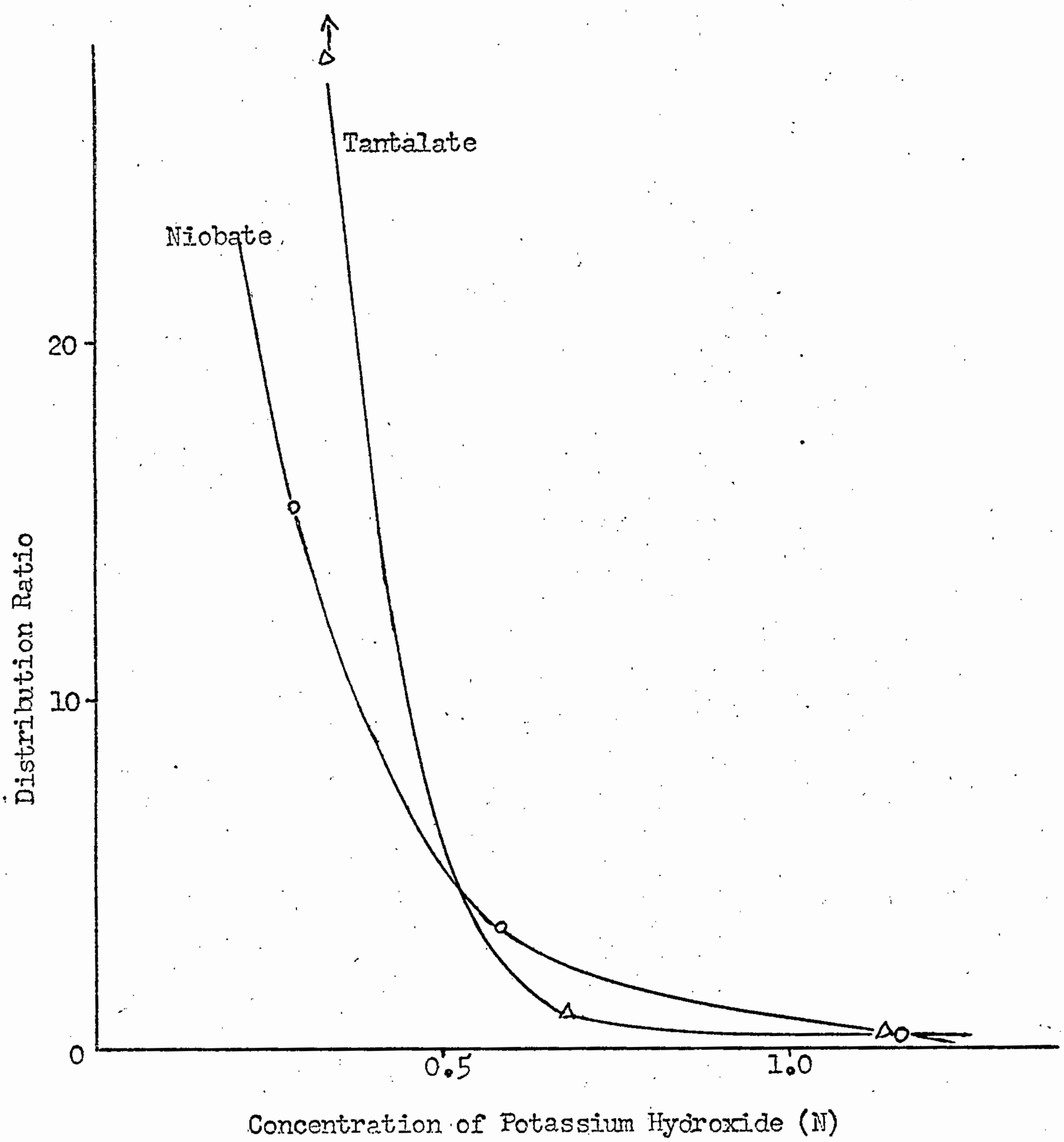


FIGURE 6.1 Distribution Ratios between Potassium Hydroxide solution and Aliquat 336

calculated:

$$D = \frac{\text{Concentration of niobate/tantalate in exchanger phase.}}{\text{" \quad " \quad " \quad aqueous phase.}}$$

The results are shown in Figure 6.1.

DISCUSSION

In these experiments, the coverage of the ionogenic groups in the exchanger phase at complete adsorption was approximately 0.5% for niobate and 0.3% for tantalate.

The general pattern of behaviour evident in Figure 6.1 resembles that observed for the reaction of niobate and tantalate alone with ion-exchange resins (see Figure 3.2). At low hydroxide concentrations in the aqueous phase the niobate and tantalate ions are completely adsorbed into the ion-exchanger phase. Increasing the concentration of hydroxide causes these ions to be transferred to the aqueous phase.

Figure 6.1 shows that the distribution pattern followed by the two ions under these conditions is very similar. It is unlikely, therefore, that the procedure used in these experiments could be used as a means of separating these ions.

CHAPTER VII

SUMMARY AND CONCLUSIONS

Both niobate and tantalate ions are very strongly adsorbed from aqueous solution by Deacidite FF resin (7-9% cross-linking) and Aliquat 336 liquid ion-exchanger. By suitable adjustment of the concentration of hydroxide or chloride ions in solution, the niobate/tantalate can be transferred quantitatively to either the exchanger phase or the aqueous phase.

The separation factor for niobate and tantalate in alkaline solution varies from 6 to 12 when the eluting agent is hydroxide ion or chloride ion in aqueous and in mixed aqueous-organic solvents. The well-separated elution peaks which were obtained in the column separation described in Chapter V are in accord with the expected performance based on the theory of ion-exchange chromatography.

The similarity of behaviour of niobate and tantalate ions is to be expected in view of the fact that both ions probably have the same structure. The value of about 7 obtained for the charge of niobate and tantalate indicates that both ions are protonated at pH 12, and that condensation reactions are unimportant at this pH. Under these experimental conditions there was no evidence of depolymerisation of niobate ions. This is in agreement with the general trend of the results of Gridchina (40); the hexameric niobate structure is maintained with increasing dilution of niobate, provided the concentration of potassium hydroxide also decreases.

Only two peaks were obtained when niobate and tantalate were separated on the resin column, indicating that both ions were present on the column in only one form. It should be noted, however, that this result does not entirely rule out the possibility that a mobile equilibrium of, say, two forms of niobate ion existed in the original solution, which equilibrium was displaced by preferential adsorption of one ionic form by the resin.

An interesting field for further application of the ion-exchange reactions discussed in this thesis would be an investigation of niobate exchange under conditions of high pH and decreasing concentration of niobate; in this way it may be possible to confirm the changing ion structure suggested by Gridchina. Disturbance of possible equilibria between different ions in solution could be minimised by use of a liquid exchanger, with which the exchange process is completed in less than a minute, rather than the slower-reacting resin.

The unusual variations observed in the rate of ion-exchange of niobate seem to be satisfactorily explained by the theory suggested in Chapter IV, based on the assumption that film diffusion is the rate-controlling step. It is certainly most unlikely that the rate variations are in any way due to changes in the structure of the niobate ion.

An interesting project for the future would be a careful investigation of the kinetics of niobate exchange in potassium hydroxide solutions containing small amounts of chloride ion. In this way the pH could be varied while the concentration of competing anions was still maintained within the range over which niobate is only partially adsorbed. It could then be observed whether the reaction rate is always slow in the region of partial exchange, irrespective of the pH of the solution. This would demonstrate unequivocally that the observed variations in rate are not due to any changes in the resin or the niobate ion occurring over the particular range of pH covered in the experiments described in this thesis, and would be strong evidence in favour of the theory suggested in Chapter IV.

APPENDIX I

During the course of this research it was observed that complete solution of the melt obtained by fusion of tantalum pentoxide with potassium hydroxide depends on the concentration of hydrogen peroxide. Conditions for obtaining a clear solution are as follows.

Heat 1 g of potassium hydroxide pellets in a nickel crucible over a gas flame until the melt becomes quiet. Add 100 mg of tantalum pentoxide, a little at a time, waiting for the melt to become clear before making further additions. After all the pentoxide has been added, raise the temperature to a dull red heat for five minutes, and set the crucible aside to cool. Extract the melt with 5 ml of 1.5% solution of hydrogen peroxide, and dilute to 100 ml. A clear solution is obtained.

Clear solutions of niobium pentoxide can be obtained in the same way.

APPENDIX II

METHOD FOR ANALYSIS OF NIOBATE SOLUTIONS

To an aliquot of niobate solution, (containing up to 100 µg of Nb_2O_5) in a 50 ml volumetric flask, add

5 ml of 3% hydrogen peroxide solution

50 ml of sodium acetate-acetic acid buffer solution (pH 5)

5 ml of 0.04% PAR solution in ethanol.

Mix well after each addition. Dilute to the mark and mix well. Measure the optical density against a reagent blank after 30 minutes using 2 cm cells and the Kodak No. 5 filter. A standard graph is constructed at the same time using a standard niobium solution.

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