astable systems in the interaction K_2O–Nb_2O_5 and represent an extension of the ternary, aqueous, into the binary anhydrous diagram.

Further experiments were conducted with the

4:3·16 hydrate which also exhibited a non-reversible exotherm at *ca.* 510° resulting in the formation of the stable anhydrous system.

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Constitution of Aqueous Oxyanions: Perrhenate, Tellurate and Silicate Ions

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Evidence is presented which indicates that the predominant form of the perrhenate ion in aqueous solution is tetrahedral, but that forms of higher coördination number are possible under extreme conditions of acidity and basicity. From Raman spectral data, the silicate ion is shown to be $SiO_2(OH)_2^=$. Equilibrium constants for the first two ionizations of telluric acid have been measured by potentiometric and spectrophotometric techniques and have been found to be $K_1 = 2.0 \times 10^{-8}$ and $K_2 = 9.2 \times 10^{-12}$. Spectrophotometric evidence has been found for a third ionization; the value $K_3 = 3 \times 10^{-15}$ has been estimated. The ultraviolet absorption spectra of telluric acid and its mono- and di-negative ions have been measured. The stability constant of the peroxytellurate ion has been found to have the value $K_s = 0.68$. Potentiometric evidence for the existence of polytellurate ions is given. The coördination number of tellurium in tellurate species is shown to be six in aqueous solutions.

Introduction

It has been realized for some time that the central atoms of oxyanions in aqueous solution may not have the same coördination number (hereafter c.n.) at all pH values. For example, tetravalent carbon can be in either c.n. two or c.n. three and heptavalent iodine can be in c.n. four or c.n. six. In this study, perrhenate, tellurate and silicate ions have been investigated by various experimental methods to see if any change in c.n. could be detected.

Experimental

Equipment.—The Raman spectra were taken on a Photo-electric Recording Raman Monochromator. Infrared spectra were taken using the pellet technique. The ultraviolet spectra were taken with a Beckman DU Spectrophoto and quartz cells. pH data were obtained with the Beckman models G and GS meters. All equilibrium measurements were made at 25°. The limits of error for measurements are indicated in appropriate sections.

Materials.—For the perrhenate studies, Re_2O_7 samples from A. D. Mackay, Inc., and The University of Tennessee were used. In the silicate studies, B. & A. sodium metasilicate, $Na_2SiO_3·9H_2O$, and ACS reagent sodium hydroxide were the compounds mostly used; other silicate samples gave similar results. Na_2PO_3F was obtained from Ozark–Mahoning Co. Reagent grade salts were used wherever available; other salts were recrystallized. Telluric acid was prepared by oxidizing impure metal with nitric acid to TeO_2 and then oxidizing the dioxide with permanganate.[1] Purification was effected by one recrystallization from nitric acid, followed by from seven to nine recrystallizations from water. Some telluric acid samples were prepared by alternative methods[2] or were purchased. All of the telluric acid samples were recrystallized from water. Solutions of the acid were standarized by pH titration in the presence of glycols.[4] The well-known colloid-forming property of hexavalent tellurium was often encountered. Solutions containing more than 0.04 M of KH_5TeO_6 were observed to form opalescent suspensions on standing; therefore the highest concentration used was 0.03 M.

Hydrogen peroxide solutions were made from 90% reagent material donated by·BECCO. Other solutions were made from reagent materials and were analyzed by standard procedures.

Procedures.—Measurements of optical absorbancy as a function of pH were made as follows: Two hundred ml. of telluric acid solution of the desired concentration and ionic strength was placed in a beaker in a water-bath. The pH of this solution was repeatedly adjusted by the addition of very small quantities of 2.5 M base from a microburet. After each addition, the pH of the solution was measured and a 5-ml. sample withdrawn and placed in a closed container. When samples covering the desired pH range had been withdrawn, the absorbancy of each sample was measured and the entire procedure then repeated. For pH values greater than 12, samples were made up individually with concentrated KOH; H_0 values were calculated from the hydroxyl ion concentrations.

Optical density measurements at 275 mm. (mμ) were corrected for absorption due to hydroxyl ion using 0.017 as the appropriate molar extinction coefficient. Tellurate buffer solutions were prepared by adding the calculated amount of base to acid solutions and then diluting to the desired volume.

The effect of μ (ionic strength) on the pH of these buffers was studied as follows. Two equal portions of the buffer were diluted, one with stock electrolyte ($NaClO_4$ or NaCl) and the other with water; both were thermostated and one portion titrated into the other with the pH being measured after each addition. The effect of concentration of buffer was studied in a similar manner, isotonic salt solutions being mixed with the buffer and the pH measured after each mixing.

Extinction coefficients for the tellurate ions were measured on solutions prepared by diluting telluric acid stock solutions with buffers (borate and phosphate) of the appropriate pH. Polymerization experiments were performed by measuring the pH of solutions prepared by diluting concentrated telluric acid solutions. Peroxide systems were made up using tellurate buffers as previously described and 3.0 M hydrogen peroxide.

Results

Perrhenate Ion.—The majority of the perrhenate salts found suggest an anion of tetrahedral symmetry; however, there is a hint that the rhenium atom can take on a higher c.n. Raman and infrared data in solution are consistent with the tetrahedral structure,[5–7] although the results at

(1) F. C. Mathers, C. M. Ric, H. Broderick and R. Forney, in "Inorganic Syntheses," Vol. II, L. F. Audrieth, Ed., McGraw–Hill Book Co., New York, N. Y., 1950, p. 145.

(2) In this Laboratory, Mr. H. A. Chopoorian found it difficult to obtain good results with the method of Horner and Leonard.[3]

(3) H. J. Horner and G. W. Leonard, Jr., This Journal, **74**, 3694 (1952).

(4) J. O. Edwards and A. L. Laferriere, *Chemist-Analyst*, **45**, 12 (1956).

(5) L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 615 (1956).

(6) R. Fonteyn, *Naturw. Tijdschr. (Belg.)*, **20**, 20 (1938).

(7) H. H. Claasen and A. J. Zielen, *J. Chem. Phys.*, **22**, 707 (1954).

one point were felt to indicate that the ion was ReO_6^{-5}.[6]

In order to check the number and strength of replaceable protons in perrhenic acid, a potentiometric titration of a 0.01 M solution was made. The initial pH of 2.06 indicates that the acid is completely ionized. The titration curve shows a sharp end-point from pH 5 to 9 at the correct position for one ionizable proton. Up to pH 11, there is no sign of a second ionization. Although oxyacids of the transition metals do not seem to follow exactly the rules for ionization constants of the non-metal oxyacids,[8] it seems probable that their behavior should be generally similar. Thus one can conclude that perrhenic acid is $HReO_4$ and not H_3ReO_5 or H_5ReO_6 and that ReO_4^- is the predominant species in the pH range from two to eleven.

The Raman spectra in acidic and neutral media has been reinvestigated, and the results agree also with those of Claasen and Zielsen.[7] We also investigated the spectrum in alkaline solutions and again found the same lines. (Because of the insolubility of sodium perrhenate, it was not possible to go higher than 3 M in base concentration while maintaining a measurable perrhenate concentration.) Thus the spectral data are in agreement with the pH data in indicating no equilibrium involving perrhenate ion in dilute aqueous solutions; further, the Raman results extend the range of presence of ReO_4^- out to highly acidic and basic solutions. In Table I, the spectra of $WO_4^=$, ReO_4^- and OsO_4 are presented for comparison. The evidence for ReO_4^- as the structure of the aqueous perrhenate ion appears to be convincing.

TABLE I

RAMAN LINES FOR THREE RELATED SPECIES[a]

Type of line	WO_4^-	ReO_4^-	OsO_4
Broad, strong, depol.	324	332	335
Diffuse, weak, depol.	833	916	954
Sharp, vy. strong, polar.	931	972	965

[a] See discussion in reference 5 concerning the similarities in these spectra.

In view of the lack of evidence for a higher c.n. in aqueous solution, it was felt that the report[9] of the isolation of the compound known as barium mesoperrhenate should be checked. This compound which precipitates from hot alkaline solutions was said to have the formula $Ba_3(ReO_5)_2$. The procedure was repeated here several times and an 85% yield (based on rhenium) of a greenish-yellow solid was obtained. The material was analyzed for barium by sulfate precipitation and for rhenium by precipitation of the nitron salt. Our results are presented in Table II and may be compared with Ba:Re ratios reported earlier,[9] 3.05:2 by Noddack and Noddack and 3.3:2 reported by Scharnow. The analytical results for percentage of barium which have been obtained are somewhat high, yet the over-all results leave little doubt that the formula $Ba_3(ReO_5)_2$ is near to the correct one. Since none of the species, $Ba(ReO_4)_2$, $BaCO_3$, BaO or $Ba(OH)_2$, have colors, nor do any

(8) J. Y. P. Tong and E. L. King, THIS JOURNAL, 75, 6180 (1953).

(9) I. Noddack and W. Noddack. Z. anorg. allgem. Chem., 215, 146 (1933); (b) B. Scharnow, ibid., 215, 185 (1933).

related sodium salts, it does not seem possible to explain the main product of this preparation as a mixture of known compounds.

TABLE II

ANALYSES OF BARIUM PERRHENATE

Sample wt., g.	Ba wt., g.	Re wt., g.	Molar ratio Ba:Re
1.475	0.703	0.540	3.54:2
1.616	0.775	0.587	3.56:2

Infrared spectra of barium mesoperrhenate and the normal barium salt have been taken; although analysis of the spectrum of the former compound cannot be done at present, there are differences between the spectra. For example $Ba(ReO_4)_2$ shows a symmetrical absorption peak at 850 cm.$^{-1}$,[10] whereas the mesoperrhenate had a broad absorption band in the same spectral region with distinctly separated peaks at 857, 880 and 917 cm.$^{-1}$.

The most striking thing about the barium mesoperrhenate is its color, as the normal perrhenate ion absorbs only in the far ultraviolet. We do not know of any other perrhenate salt that has color (other than those with colored cations, of course). On the other hand, Re_2O_7 is a yellowish-green as are very concentrated solutions of perrhenic acid.[7] The occurrence of and similarities in color for these three cases suggest that some common, fundamental change in the c.n. of rhenium is taking place.

While heptavalent rhenium seems to prefer a c.n. of four, the existence, composition and peculiar properties of barium mesoperrhenate, etc., lead us to conclude that rhenium can expand its coördination shell to either five or six. An increase in c.n. in both acid and base is possible; such has been observed in periodate solutions.[11] One possible check on this hypothesis would be to evaluate the c.n. of the rhenium atoms in Re_2O_7, perhaps by X-ray.

Tellurate Ion.—The structure of solid telluric acid as determined by X-rays[12] is $Te(OH)_6$. Raman spectra indicate that this structure is maintained, at least to a large degree, in solution.[13]

Large differences between the ultraviolet spectra of tellurates in media of various pH have been found.[14,15] It was suggested that the change in spectrum was to be explained by a dehydration reaction occurring in aqueous solution. If such a dehydration reaction were significant in the tellurate case, there should be certain observable effects on the ultraviolet spectra and on the ionization constants. We have searched for such effects without success.

The variation in optical density with pH was measured at 275 mm. for solutions 0.0199 M in

(10) The tetrahedral ion has one line in this region corresponding to the Raman line at 916 cm.$^{-1}$, but the difference of 66 cm.$^{-1}$ seems quite large and may be an indication of some structural distortion.

(11) (a) C. E. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, THIS JOURNAL, 71, 3031 (1949); (b) C. E. Crouthamel, A. M. Hayes and D. S. Martin, ibid., 73, 82 (1951).

(12) (a) L. M. Kirkpatrick and L. Pauling, Z. Krist., 63, 302 (1926); (b) L. Passerini and M. A. Rollier, Atti. accad. Lincei., 21, 364 (1935).

(13) (a) C. S. Venkateswaran, Proc. Indian Acad. Sci., 7A, 144 (1938); (b) J. Gupta, Indian J. Phys., 12, 223 (1938).
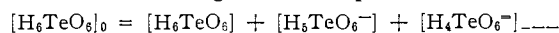
(14) C. Stuber, A. Braida and G. Jander, Z. physik. Chem., A171, 320 (1934).

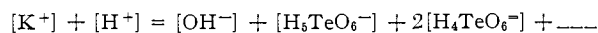(15) H. Ley and E. König, ibid., B41, 365 (1938).

telluric acid and 0.1 M in potassium perchlorate. The curves obtained by these measurements are shown in Fig. 1. Each curve has an initial flat portion at low pH corresponding to the low absorption of the undissociated acid. There are then two sharp increases in absorbancy, each followed by a plateau. These result from the first and second ionizations of telluric acid. A further rise in optical density at high pH can best be explained as resulting from a third ionization. The equilibrium constants for these ionizations under particular conditions of μ can be estimated from data such as is presented in Fig. 1. For the first two ionizations, however, potentiometric techniques provide a more convenient method of determining thermodynamic values of the constants.

For solutions containing equal amounts of H_6TeO_6 and KH_5TeO_6, the pH at constant μ should be independent of the concentration of KH_5TeO_6 since activity coefficients should not depend on the nature of the electrolyte at these low values. It was found that the pH of the tellurate buffer slightly increases as its concentration increases even at constant μ; this effect can be attributed to polymerization (vide infra). The dependence of buffer pH on μ seemed normal for the plots of pH against $\sqrt{\mu}$ were linear. Buffers with various concentrations of hexavalent tellurium had roughly the same dependence on μ and the pH displacements for the same μ which result from the concentration effect were observed to be the same as those found in experiments designed to show the effect of buffer concentration. Extrapolating to zero μ and zero buffer concentration, we obtain for the first ionization constant the thermodynamic values $pK_1 = 7.70 \pm 0.01$ and $K_1 = 2.00 \pm 0.05 \times 10^{-8}$.

For a solution of telluric acid to which an equivalent amount of potassium hydroxide has been added, the following relationships hold

$$[H_6TeO_6]_0 = [H_6TeO_6] + [H_5TeO_6^-] + [H_4TeO_6^=]\ldots$$

and

$$[K^+] + [H^+] = [OH^-] + [H_5TeO_6^-] + 2[H_4TeO_6^=] +\ldots$$

where brackets denote concentrations and the subscript zero denotes the initial amount before addition of base. Since hydrogen ions and ions of greater negative charge than $H_4TeO_6^=$ only exist in negligible amounts at this pH, the relationships above can be reduced to

$$[H_6TeO_6] = [OH^-] + [H_4TeO_6^=]$$

If this equation is multiplied by $[H^+]^2$, divided through by $[H_6TeO_6]$ and treated by the introduction of K_w, K_1 and K_2, one obtains

$$[H^+]^2 = \frac{K_1K_w}{[H_5TeO_6^-]} + K_1K_2$$

A plot of pH against $[H_5TeO_6^-]_0$ for solutions containing KH_5TeO_6 at ionic strength 0.15 and at 25° showed that the pH value levels off in the region above $[H_5TeO_6^-] = 0.01\ M$. Thus in this region

$$K_1K_2 > \frac{K_1K_w}{[H_5TeO_6^-]}$$

and

$$[H^+]^2 = K_1K_2$$

It was found that a plot of pH against $T\mu$ for solu-
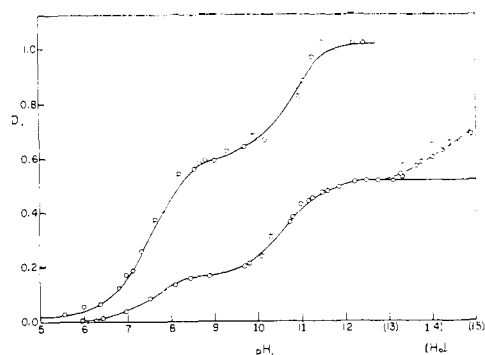

Fig. 1.—Variation of optical density with pH of aqueous telluric acid solutions at 25°. Upper curve: 0.00127 M H_6TeO_6, 0.1 M KClO$_4$, 240 mm.; lower curve, 0.0199 M H_6TeO_6, no added salt, 275 mm. The points are experimental data and the curves are calculated using the equation given in text.

tions whose $[H_5TeO_6^-] = 0.027\ M$ was linear. Extrapolating to zero μ

$$pH = \tfrac{1}{2}(pK_1 + pK_2) = 9.37 \pm 0.02$$

was obtained which when combined with the thermodynamic value found for pK_1 gives the thermodynamic value $pK_2 = 11.04 \pm 0.05$ and $K_2 = 9.2 \pm 0.5 \times 10^{-12}$.

A value for K_3 cannot be obtained from potentiometric data since this ionization does not begin until the pH is nearly 13. From data obtained on the spectrophotometer, it is estimated that K_3 has a value of 3×10^{-15} in terms of concentration.

The plateaux in Fig. 1 correspond to the optical absorbancies of the individual species H_6TeO_6, $H_5TeO_6^-$ and $H_4TeO_6^=$. The extinction coefficient of the acid was measured in solutions brought to pH 2 to 3 by the addition of hydrochloric, sulfuric and perchloric acids; identical values were obtained in the presence of all three acids, indicating that little complexing with the corresponding anions occurs at this pH. The coefficient of the mononegative ion was measured in borate buffers of pH 9.2. For the dinegative ion the measurement was made in phosphate buffer at pH 12.0. The results obtained are presented in Fig. 2; no deviations from Beer's law were observed. In all cases the buffer was used as the reference liquid for these measurements, but the phosphate buffer is the only one that has significant absorption in the regions studied.

Extinction coefficients for the undissociated acid agree with those reported previously[1,2]; however, the values obtained for the coefficients of the dissociated forms are considerably different from those of the earlier investigators who did not realize the critical nature of the pH of the solution.

Using the extinction coefficients thus measured and the ionization constants calculated from potentiometric data, it is possible to compute a curve of absorbancy against pH. The results of such computations are the solid curves of Fig. 1.

Evidence for polytellurate ions in tellurate buffers has already been presented. In solutions which contain only telluric acid plus polytelluric acids (represented by HTe_x), the hydrogen ion concentration is given by the relation
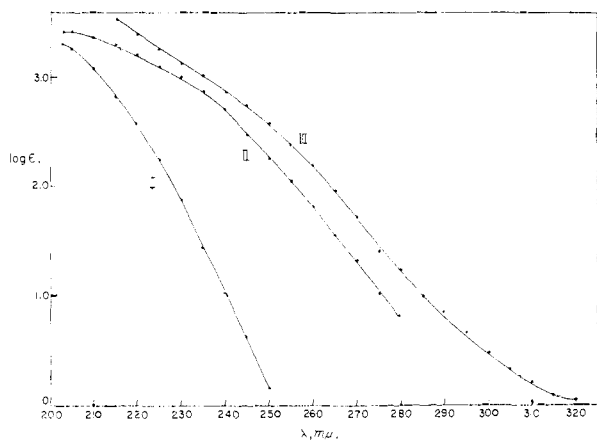
$$[H^+] = [H_5TeO_6^-] + \Sigma_x\{[Te_x^-]\}$$

Fig. 2.—Molar extinction coefficients of tellurate species as a function of wave length: I, H_6TeO_6; II, $H_5TeO_6^-$; III, $H_4TeO_6^=$. Aqueous solution at 25°.

The assumption that the polytellurate ions are of mononegative charge seems quite reasonable, in view of the results found for the similar boric acid system.[16] Upon substitution into the above equation of K_1 and of a polymer equilibrium constant

$$K_x = \frac{[H^+][Te_x^-]}{[H_6TeO_6]^x}$$

and upon simplification, one obtains

$$\frac{[H^+]^2}{[H_6TeO_6]} = k_1 + \Sigma_x \{K_x[H_6TeO_6]^{x-1}\}$$

The data in Table III show the variation of $[H^+]^2/[H_6TeO]_0$ with $[H_6TeO_6]_0$; there should be no varia-

TABLE III

pH EVIDENCE FOR POLYTELLURATES IN SOLUTIONS OF TELLURIC ACID

$[H_5TeO_6^-]_0$ M	pH	$[H^+]^2/[H_6TeO_6]_0 \times 10^7$
0.0724	4.399	0.226
.0828	4.328	.268
.1035	4.210	.378
.166	4.057	.454
.207	3.929	.671
.259	3.806	.751
.311	3.712	1.211
.362	3.642	1.44
.414	3.552	1.91
.518	3.432	2.65
.621	3.351	3.20
.724	3.234	4.71
.828	3.161	5.75
.931	3.054	8.40
1.035	2.981	10.53

tion if only monomeric telluric acid were present. A reasonable fit of the data is obtained using the equation

$$\frac{[H^+]^2}{[H_6TeO_6]_0} = 2 \times 10^{-8} + 8.3 \times 10^{-7} [H_6TeO_6]_0^2$$

This expression, which corresponds to the presence of a trimer as the only polymer, fits the experimental points well in the region of concentration between 0.4 and 1.1 M. In the region below 0.4 M

(16) (a) J. O. Edwards, THIS JOURNAL, 75, 6151 (1953); (b) P. J. Antikainen, Suomen Kemistilehti, B30, 74 (1957), and prior publications.

where dimers would be more important and in the region above 1.0 M where higher polymers could form, deviations from this expression are found. Other experiments with varying amounts of telluric acid have been carried out with similar, but not identical, results. We do not feel that our data are sufficiently precise or accurate to permit more rigorous treatment, although there can be little doubt that polytellurate ions are present in such solutions.

The pH of buffers containing equimolar telluric acid and tellurate ion is raised when acetone, methanol, ethanol or dioxane is added. On the other hand, it is significantly lowered by the addition of hydrogen peroxide as may be seen in Fig. 3. The
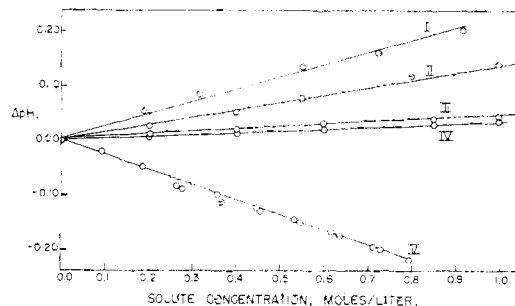

Fig. 3.—Variation of pH of tellurate buffers as a result of addition of solutes: I, dioxane; II, acetone; III, ethanol; IV, methanol; V, hydrogen peroxide. The quantity Δ pH is given by the pH of the solution with solute less the pH of the solution without solute.

effect of the organic solvents probably results from the change in dielectric constant of the medium. In the case of hydrogen peroxide, the apparent increase in K_a can be attributed at least in part to a reaction of the type

$$H_5TeO_6^- + H_2O_2 \rightleftharpoons H_5TeO_7^- + H_2O$$
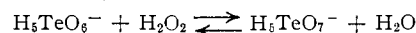
Under the conditions of our experiments, the relation

$$K_c = \frac{1}{[H_2O_2]} \left\{ \frac{[H^+]}{[H^+]_0} - 1 \right\}$$

where K_c is the mass action expression for peroxytellurate formation, has been derived. Employing data of the type presented in Fig. 3, values of K_c have been obtained.

A slight variation in the value of K_c was observed as the concentration of hydrogen peroxide was changed. A plot of K_c against concentration of peroxide was found to be linear with an intercept value of 0.68 ± 0.02 and a slope of only 0.15. The intercept is believed to be the best value for K_c. The slight positive slope of the line might indicate a diperoxide complex; in view, however, of the dielectric effect mentioned earlier, no great significance is to be attributed to this secondary effect.

Data on extinction coefficients, ionization constants, peroxides and polymers of the aqueous tellurate system have been presented. Certain features of these results are worthy of discussion. Concerning the ultraviolet absorption, there is no evidence for a maximum in any of the curves; such a maximum was found with IO_4^- but not with the periodates of c.n. six.[11] The intensities of absorption by tellurates increase as the charge increases;

again this agrees with the data for H_5IO_6 and $H_3IO_6^-$ which are the species for which there are comparable results.[11] In all probability the tellurate species, like other anions, absorb ultraviolet radiation by a charge transfer mechanism. No general theory for this type of absorption has been developed as yet, but it is generally agreed[17] that the transfer of an electron between the absorbing substance and the surroundings is involved. The data on periodates indicate that the process is more easily achieved in the case of IO_4^- than in the cases of H_5IO_6, $H_4IO_6^-$ and $H_3IO_6^=$. One would expect a similar situation to prevail in the cases of the isoelectronic tellurates; that is to say, it would be expected that a dehydrated form would absorb much more strongly than a hydrated form at some wave lengths. The fact that the absorbancies of the tellurate ions increase in the same order as the charges on the ions is an indication that no change in the c.n. of tellurium is occurring.

The agreement of the observed values of the ionization constants with the values predicted by semiempirical relationships[18,19] also indicates that the c.n. of six is maintained. The equation of Ricci[18] predicts $pK_1 = 8.0$ and $pK_2 = 12.0$ for telluric acid. The observed values are $pK_1 = 7.7$ and $pK_2 = 11.0$ which are in as good agreement as one can reasonably expect. The predicted and observed values, 16.0 and 14.5, for pK_3 are also in fair agreement considering the high ionic strength involved. If dehydration were significant, the spacings between pK_a values would be less regular; the equation of Hill[19] predicts for pK_3 a value of 14.2, which is to be compared with our observed value of 14.5.

As neither the ultraviolet spectra nor the ionization constants showed any abnormalities which could be attributed to a dehydration equilibrium, we conclude that there can be little if any dehydration occurring in the various tellurate ions so that the predominant c.n. is six throughout.

Although polymerization does not seem to cause deviations from Beer's law in the ultraviolet spectral data, it is significant enough to be detected potentiometrically both in solutions of pure acid and in buffer solutions. As mentioned previously, polymerization is presumably the cause of the effects presented in Table III and discussed under pH data of buffers. Reactions such as

$$3H_6TeO_6 \rightleftarrows H^+ + Te_3^-$$
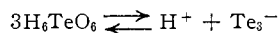
in pure acid can cause the lowering of pH as the amount of tellurium is increased. The magnitude of the effect is quite small and telluric acid is difficult to obtain in a pure state, thus a definitive interpretation of the polymerization data cannot be given at this time.[20] It is worth noting that autopolymerization occurs to a lesser extent in tellurates than it does in borates. It is also true that the stability constant of the peroxytellurate com-

(17) *Cf.* L. E. Orgel, *Quart. Rev.*, **8**, 422 (1954).

(18) J. E. Ricci, THIS JOURNAL, **70**, 109 (1948).

(19) T. L. Hill, *ibid.*, **65**, 1564 (1943).

(20) Reviews on work pertinent to the ionization constants and aqueous polymers of telluric acid may be found in the following article: (a) E. Norton, R. W. Stoenner and A. I. Medalia, *ibid.*, **75**, 1827 (1953); (b) P. J. Antikainen, *Suomen Kemistilehti*, **B28**, 135 (1955); (c) **B30**, 201 (1957); (d) D. A. Everest and W. J. Popiel, *J. Inorg. Nucl. Chem.*, **6**, 153 (1958).

plex is less than that of the peroxyborate. The instability of tellurate polymers and peroxides relative to the analogous borate complexes is somewhat surprising at first sight in view of the fact that tellurate ion complexes with simple polyhydric alcohols are more stable than the analogous borate complexes.

Silicate Ion.—Consideration of the chemistry of the aqueous silicates plus data from the literature indicates that a c.n. of four or six would be reasonable since examples of each are found for silicon in the solid state.

A portion of the experimental results for the Raman spectra of silicate ions in various solutions is presented in Table IV. A figure showing the silicate ion and related spectra may be found in reference 21. The influence of silicate ion and hydroxyl ion concentrations on the spectra may be noted in the data of Table IV; silicate was varied from 0.5 to 3.2 M and hydroxide from zero to 4.0 M. There appear to be five lines present in several but not all solutions; the average values for line wave lengths are 448 (50), 607 (65), 777 (55), 935 (70) and 1040 cm.$^{-1}$; the numbers in parentheses are the line widths at half height.

TABLE IV[a,b]

RAMAN SPECTRA OF SODIUM SILICATE SOLUTIONS

Concn., M		Raman lines in cm.$^{-1}$ 1 M NaOH solutions			
[Na$_2$SiO$_3$]					
0.50		616(0)?	782(2)b	929(1)b	
0.75			780(2)	933(1)b	1044(1)b
1.00			780(3)	936(2)wsh	
1.50			782(3)b	936(2)b	
2.00	447(1)	608(1)	782(3)	940(2)b	1050(1)b
		2.50 M Na$_2$SiO$_3$ solutions			
[NaOH]					
0.00	456(1)	614(2)b	779(4)b	937(3)b	1030(2)b
.025	448(1)	608(2)b	783(4)b	939(3)b	1039(2)b
.25	457(0)	608(2)b	785(4)b	938(3)b	1037(2)b
.50	451(1)	606(2)	780(5)wsh	937(3)b	1023(2)b
1.00	432	595(2)	777(5)	935(5)b	1031(1)b
2.00	442(1)	612(2)	775(6)	932(5)b	1063(0)b
4.00	454(2)	614(2)b	784(7)	932(7)	

[a] The numbers in parentheses denote the relative height of the line above the background; (0) indicates a barely discernible line (1) indicates the peak is higher than (0) but lower than (2), etc. [b] The letters indicate the line shape; b, broad, wsh, weak shoulder. The question mark indicates lines which were observed occasionally but not in every run.

The line at 1040 cm.$^{-1}$ is relatively intense in solutions to which little or no sodium hydroxide is added. In solutions containing large amounts of base (greater than 2 M), the lines at 777 and 935 cm.$^{-1}$ seem sharper while the 1040 cm.$^{-1}$ line is usually absent. Calculations based on estimated equilibrium constants[22] indicated that hydrolysis and polymerization would be significant up to about 2 M in base, therefore the evidence indicates that the line at 1040 cm.$^{-1}$ results from a species other than a monomeric ion of dinegative charge. As the constants[22] indicate that polymerized species are more likely than a hydrolyzed monomer, we

(21) D. Fortnum and J. O. Edwards, *J. Inorg. and Nuclear Chem.*, **2**, 264 (1956).

(22) (a) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell Univ. Press, Ithaca, New York, N. Y., 1955, p. 26; (b) P. S. Roller and G. Ervin, Jr., THIS JOURNAL, **62**, 461 (1940).

Table V[a,b,c]

RAMAN SPECTRA OF RELATED TETRAHEDRA

Substance	Ref.	Observed lines					
XO₄							
ClO_4^-	25	472m	641m	*947Ssp*	1131m		
SO_4^-	26	617m	617m	*986Ssp*	1090mb		
$PO_4^{\equiv}$	27	573mb	573mb	*936Sp*	1014wb		
XO₃(OH)							
$HClO_4$	25	425wsp	572Ssp	585wb	738Ssp	*1032Ssp*	
					1182–1312wb		
HSO_4^-	28	417m	590m	895mw	*1050S*	1195w	
$HPO_4^=$	27	537mb	865mb	*976msp*	1081mb		
XO₃F							
SO_3F^-	28				*1087*		
$PO_3F^=$	24	385vwb	538vsb	ca. 810vwb	*1010m*	1127vwb	
XO₂(OH)₂							
$SO_2(OH_2)$	28	391m	417m	562S	912S	976W	
					1125–96S	1377mw	
$PO_2(OH)_2^-$	27	383wb	511m	*886Ssp*	1062m		
$SiO_2(OH)_2^=$		448vw	607wb	777m	935mb		
XO₂F₂							
SO_2F_2	29	388mvb	547mvb	*847Ssp*	887vw	1263msp	1497
XO(OH)₃							
$PO(OH)_3$	27	366wb	508mb	*918Ssp*	1058mb		
XOF₃							
POF_3	30	377	476ms	875ms	*982vs*	1395ms	

[a] In each case, the line which seems to be the breathing mode is *italicized*. [b] Key to Table V: b, broad; m, medium; mb, medium, broad; msp, medium, sharp; mvb, medium, very broad; mw, moderately weak; s, strong; Sh, shoulder; Ssp, strong sharp; vs, very sharp; vw, very weak; vwb, very weak, broad; wb, weak, broad; wsh, weak, shoulder; wsp, weak, sharp. [c] Data on $PO_3F^=$ and $SiO_2(OH)_2^=$ are from this study.

conclude that the line at 1040 cm.$^{-1}$ can be assigned to a polymeric ion.

The other four lines have relatively constant intensity ratios, therefore these are attributed to the silicate ion.[23] It was assumed here that no oxygen–hydrogen lines appear in this region of the spectrum and that fluoroanions have Raman spectral patterns similar to their oxyanion counterparts; for example the spectra of TeF_6 and $Te(OH)_6$ are similar. These assumptions have been carefully examined and found to be valid under the conditions of this study.[24]

It is feasible on this basis to predict the number of Raman fundamentals to be expected for the two possible structures. The octahedral form $Si(OH)_6^=$ should have three lines, whereas the modified tetrahedron $SiO_2(OH)_2^=$ might show nine lines.

The octahedral form of the silicate ion can be eliminated for the following reasons. The number of lines observed for the silicate ion is greater than that predicted and observed for compounds having octahedral structures. If the 777 cm.$^{-1}$ line is assigned as the breathing mode because of its sharpness, it is noted that this is at a higher frequency than the breathing mode of $SiF_6^=$ which is at 646 cm.$^{-1}$; for all known cases oxyanions have their breathing modes at lower frequencies than the analogous fluoroanions.

(23) The positions of the lines, particularly the one at 448 cm.$^{-1}$, are somewhat uncertain due to the high background near the exciting line. A figure showing typical spectra may be found in reference 21.

(24) D. Fortnum, Ph.D. Thesis, Brown University, 1958.

Although it now seems quite conclusive that the silicate ion is not $Si(OH)_6^=$, it is still necessary to demonstrate that the Raman spectrum observed is consistent with the modified tetrahedral form, $SiO_2(OH)_2^=$. The spectral pattern is not unlike those found for related substances of tetrahedral symmetry. Many such spectra, both from the literature and from measurements made here are compiled in Table V. These tetrahedra have second row elements for central atoms; the outer atoms are oxygen (either as $O^=$ or as OH^-) and/or fluorine.

It is apparent that in many cases of modified tetrahedra of the above types, the observed number of Raman lines is less than the predicted number. Undoubtedly this divergence represents experimental circumstances rather than fundamental disagreement. In aqueous solutions, lines are broad-

(25) O. Redlich, E. K. Holt and J. Bigeleisen, This Journal, 66, 13 (1944).

(26) J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939, p. 397.

(27) (a) P. Hoffman and T. J. Hanwick, J. Chem. Phys., 16, 1163 (1948); (b) A. Simon and G. Schultz, Z. anorg. allgem. chem., 242, 333 (1939).

(28) (a) C. K. Ingold, D. J. Millen and H. G. Poole, J. Chem. Soc., 2576 (1950); (b) L. A. Woodward and R. G. Hovner, Proc. Roy. Soc. (London), A144, 129 (1934). Three lines at 590, 895 and 1050 cm. are found only in solutions where the predominant species is HSO₄⁻. Two lines, 417 and 1195 cm.⁻¹, are found throughout the range of H₂SO₄ concentration from 10 to 100%. It seems reasonable that these five lines represent the Raman spectrum of HSO₄⁻.

(29) P. Bender and J. Wood, Jr., J. Chem. Phys., 23, 1316 (1955).

(30) H. S. Gutowsky and A. D. Liehr, ibid., 20, 1652 (1952).

ened significantly by the polar solvent especially when hydrogen bonding can occur, thus two lines close together often appear as one. Weak lines are difficult to observe in water because of the well-known trouble in getting water free from colloidal matter and motes.

The spectral patterns for H_2SO_4, $H_2PO_4^-$ and silicate ion showed a marked resemblance that has already been pointed out.[21] As one goes from H_2SO_4 to $H_2PO_4^-$ and on to $H_2SiO_4^=$, there is a de-

crease in sharpness of the spectral lines, however. Since the observed silicate spectrum is consistent with that expected for the $H_2SiO_4^=$ form, the weight of evidence strongly favors this as the structure.

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The Conductance of Tetrabutylammonium Tetraphenylboride in Acetonitrile–Carbon Tetrachloride Mixtures at 25°

BY FILIPPO ACCASCINA, SERGIO PETRUCCI AND RAYMOND M. FUOSS[1]

The conductance of $Bu_4N \cdot BPh_4$ was measured in acetonitrile ($D = 36.0$) and in six mixtures of MeCN with CCl_4 with dielectric constants of 33.2, 28.8, 24.9, 15.35, 7.20 and 4.80. Association to ion pairs is slight ($K_A = 14.3$) in MeCN but steadily increases as the dielectric constant decreases; at $D = 4.80$, $K_A = 3.0 \times 10^6$. Triple ion clustering also occurs in the two mixtures of lowest dielectric constants. The system illustrates the transition from almost negligible association in MeCN, where the phoreogram lies above the Onsager tangent, to the case of marked association where $c\Lambda^2$ is approximately constant. Both ions are very large compared to the solvent molecules; nevertheless, the Walden product decreases with increasing CCl_4 content of the solvent. This variation shows that Stokes law must be corrected for the electrostatic interaction between the ions and the dipoles of the polar constituent of the solvent.

Introduction

Recent theoretical work[2] has shown that the conductance of ionophores can be described on the basis of a model in which the ions are represented as charged spheres in a continuum. In solvents of high dielectric constant, the conductance changes with concentration primarily because the long range electrostatic forces between the ions reduce the mobility as the concentration increases; with decreasing dielectric constant, the conductance decreases still more rapidly, because part of the solute is then present as non-conducting ion pairs. Tetrabutylammonium tetraphenylboride[3] is an electrolyte in which both ions are very large compared to ordinary solvent molecules and have centrally located charges. This salt, therefore, conforms quite well to the theoretical model. The purpose of this paper is to present conductance data on $Bu_4N \cdot BPh_4$ in acetonitrile ($D = 36.0$) and in a series of mixtures of this solvent with carbon tetrachloride, which cover the dielectric constant range down to 4.80 (95% CCl_4). A continuous transition is observed, from almost negligible association ($K_A = 14.3$) in acetonitrile to marked association ($K_A = 2.96 \times 10^6$) at $D = 4.80$. This system thus supplements work on the system tetraethylammonium picrate–methanol–water[4] which covered the range of moderate to completely negligible association. While the continuum model serves to describe the electrostatic effects, however, it is found to be inadequate for the hydrodynamic properties. Despite the fact that the ions of $Bu_4N \cdot BPh_4$ are both much

larger than the molecules of either acetonitrile or carbon tetrachloride, the Walden product $\Lambda_0 \eta$ is not constant but decreases with increasing carbon tetrachloride in the mixed solvent. A relaxation field between ions and solvent dipoles could account for the inconstancy of $\Lambda_0 \eta$.

Experimental

Materials.—Tetrabutylammonium bromide (Eastman, special order, unpurified raw product from tri-n-butylamine and n-butyl bromide) was dissolved in benzene at 80° (5 cc./g.) and precipitated by adding hot n-hexane (15 cc./g.) and allowing to cool. The hygroscopic precipitate was dried over phosphorus pentoxide in an evacuated desiccator for 24 hr. and then kept at 40° and 10^{-4} mm. for a week. This procedure was repeated twice; m.p. 116–117° (or on some batches, a metastable form[5] melting at 101–102° was obtained).

Tetrabutylammonium tetraphenylboride[3] was prepared by metathesis from purified tetrabutylammonium bromide and sodium tetraphenylboride.[6] The latter was dissolved in conductance water (2% solution); after filtration to remove a small amount of insoluble impurities, an equivalent amount of tetrabutylammonium bromide in 2% aqueous solution was slowly added. The bulky white precipitate was washed 5 times by decantation. After drying, the product was recrystallized 4 times from 1:3 water–acetone (200 cc./g. salt) and finally dried for several days at 40° and 10^{-4} mm.; m.p. 223–225°.

Acetonitrile was treated as recommended by Wawzonek and Runner[7]; b.p., 81.5° at 760 mm. For conductance work, the purified solvent was distilled from P_2O_5, using a conductance cell between the condenser and the receiver to monitor the product; distillate with conductance 5–9 × 10^{-8} mho was collected. Due to its hygroscopicity, acetonitrile was always transferred from one container to another by dry nitrogen pressure after the final distillation.

(1) On sabbatical leave from Yale University, second semester 1957–1958. Grateful acknowledgment is made for a Fulbright Grant.

(2) R. M. Fuoss, THIS JOURNAL, **80**, 3163 (1958).

(3) R. M. Fuoss, J. B. Berkowitz, E. Hirsch and S. Petrucci, *Proc. Nat. Acad. Sci.*, **44**, 27 (1958).

(4) F. Accascina, A. D'Aprano and R. M. Fuoss, THIS JOURNAL, **81**, 1058 (1959).

(5) H. M. Daggett, E. I. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

(6) G. Wittig and P. Raff, *Ann.*, **573**, 195 (1951); bibliography 1949–1955, A. J. Barnard, Jr., *Chem. Anal.*, **44**, 104 (1955).

(7) S. Wawzonek and M. E. Runner, *Trans. Electrochem. Soc.*, **99**, 457 (1952); see also P. Walden and E. I. Birr, *Z. physik. Chem.*, **144A**, 269 (1929); A. I. Popov and N. E. Skelly, THIS JOURNAL, **77**, 3722 (1955).