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Polyanions of the Transition Metals. II. Ultracentrifugation of Alkaline Tantalum(V) Solutions; Comparison with Light Scattering[1,2]

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Alkaline aqueous tantalum(V) solutions prepared by dissolving the salt $K_8Ta_6O_{19}\cdot 16H_2O$ have been studied by means of equilibrium ultracentrifugation using both schlieren and interference optics. The sedimentation data for solutions 1 *M* in KCl indicate that the solutions contain only a single polyanion. The calculated values of the degree of polymerization and the effective charge of the polycondensed species are in good agreement with each other and with an earlier light scattering study. They indicate that the single isopolyanion in the solutions is essentially the same as that found in the crystalline tantalate, *i.e.*, $[Ta_6O_{19}]^{-8}$. Ion-exchange studies indicate a slight degree of protonation, and the charge is also reduced from the maximum of -8 by the binding of potassium counterions from the 1 *M* KCl medium used in the measurements to a value of no greater than about -2. The procedures were checked by centrifuging solutions of potassium 12-tungstosilicate as a known solute. Unexpectedly the results from the centrifugations of these systems with schlieren optics proved to be more accurate than the values obtained with interference optics. Possible causes of this are discussed. The assumptions inherent in the interpretation of centrifugation data are compared with those involved in the analysis of light scattering experiments on these low weight inorganic polymers.

In a recent report, we described studies on alkaline tantalum(V) solutions by spectrophotometric, e.m.f., and light scattering techniques and discussed the probable structure of the tantalate anion present in the solutions.[3] These measurements showed that the salt $K_8Ta_6O_{19}\cdot 16H_2O$ dissolves without appreciable hydrolysis, and the light scattering data indicated that the solutions contained polyanions with essentially the formula $[Ta_6O_{19}]^{-8}$. It appeared that this polyion was slightly protonated to give $[HTa_6O_{19}]^{-7}$. Since X-ray studies on the compound $K_8Ta_6O_{19}\cdot 16H_2O$ have indicated that the crystals contain discrete $[Ta_6O_{19}]^{-8}$ anions,[4] it seemed likely that the solutions contained the same anions that were found in the crystals.

The polyanions formed by the transition metals have weights, *e.g.*, in the range 1000–3000, which are rather too large to be determined conveniently by cryoscopic methods and smaller than ideal for study by procedures used for large polyelectrolytes like proteins. In order to obtain an independent determination of the size and effective charge of the isopolytantalate anion, it was decided to undertake measurements of the sedimentation equilibrium of the tantalate in an ultracentrifuge. These experiments should also allow a comparison of the accuracy of the light scattering and centrifugation methods for the study of inorganic polycondensed species. Finally, these measurements should permit a verification of the postulate that the solutions are monodisperse, *i.e.*, that they contain a single kind of polyanion.

In order to check the experimental procedures, solutions of neutralized 12-tungstosilicic acid were used as a "known" as was done in the light scattering study. They were centrifuged under conditions comparable to those used for the tantalate. X-Ray studies on concentrated solutions of the 12-tungstosilicic acid have shown that the same anion present in the crystals is also present in the solutions.[5]

Experimental

Solutions.—The solutions of potassium tantalate were prepared by dissolving crystalline $K_8Ta_6O_{19}\cdot 16H_2O$ synthesized as described earlier[3] in distilled water. Potassium 12-tungstosilicate solutions were also prepared using the procedure described earlier[3] from the acid, which was neutralized to the stoichiometry $K_{3.9}[H_{0.1}SiW_{12}O_{40}]$.

Sedimentation Equilibrium in the Ultracentrifuge.—The general experimental procedure was similar to that employed by Johnson and co-workers.[6,7] All centrifugations were carried out with a Spinco Model E ultracentrifuge using an Analytical "D" rotor. The optical systems standard with the instrument were used. Only one solution in a 12-mm. cell was centrifuged at a time. The temperature was controlled to 25 ± 0.1° in most of the experiments and the rotor speed to ±15 r.p.m. with accessories available for the centrifuge. All plates were read with a Bausch and Lomb sliding scale comparator. The 5461 Å. mercury line isolated with a Wratten 77A filter was used for all measurements. Solution densities were determined with a 2-ml. pycnometer.

Schlieren Measurements.—Schlieren patterns were taken at various bar angles between 60 and 85° and were recorded on Eastman Kodak 1-N spectroscopic plates. Values of Z, the vertical displacement of the bar image caused by the refractive index gradient in the cell, were tabulated as a function of x, the radius from the center of rotation. Attainment of equilibrium was assured by observing images from day to day and noting the time at which no further change took place. Centrifugations were then continued for an equal period of time before the final photographs were taken. In addition to the centrifugations of the polymeric solute in KCl, a background centrifugation was also run on the KCl solution alone. The difference between Z for the solution containing polymer plus KCl and the Z for KCl

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[1] This report is based on portions of a dissertation submitted by W. H. Nelson to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] The work has been supported by Grant NSF-G14173 from the National Science Foundation and by the Graduate School of the University of Minnesota.

[3] W. H. Nelson and R. S. Tobias, *Inorg. Chem.*, **2**, 985 (1963).

[4] I. Lindqvist and B. Aronsson, *Arkiv Kemi*, **7**, 49 (1954).

[5] H. A. Levy, P. A. Argon, and M. D. Danford, *J. Chem. Phys.*, **30**, 1486 (1959).

[6] J. S. Johnson, K. A. Kraus, and T. F. Young, *J. Am. Chem. Soc.*, **76**, 1436 (1954).

[7] J. S. Johnson and K. A. Kraus, *ibid.*, **81**, 1569 (1959).

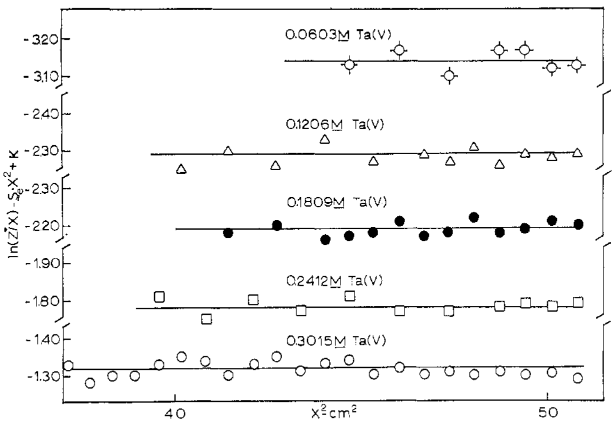

Fig. 1.—Test of constancy of S_0 for the tantalate schlieren centrifugations.

alone gave Z^*, from which the distribution of the polymeric solute could be calculated.

Interference Optics.—The Rayleigh interference fringe patterns were recorded on Eastman Kodak II-G spectroscopic plates with high green sensitivity. The plates were read by lining up the fringes using the air reference fringes, and the distances between "vertical" fringes from the meniscus to the cell bottom were measured. From these data, the differences in refractive index between the solution and background compartments at different values of x can be calculated. In some cases, a series of photographs of the fringe pattern was taken throughout the run so that the position of a given fringe could be followed. From these data, the absolute values of the refractive index differences at the various x values, n^*, could be obtained in the following way. From the movement of the fringes with time, the point where a given fringe at equilibrium would intersect the "reference fringe," *i.e.*, the position of the fringe before sedimentation, could be noted. At this point the difference between the refractive indices of solution and background compartments is equal to the initial and known difference before sedimentation took place. Since the difference in refractive index between fringes is known, n^* values can be tabulated for the points corresponding to a fringe intersection with the "reference fringe." In most of the experiments, the values of n^* were obtained by an integrative procedure which only required values of the difference between the refractive index at the meniscus and at various values of x. The x values corresponded to points of intersection of the curved solution fringes with a reference fringe picked arbitrarily to pass through the meniscus and to intersect a curved fringe. Cell distortions for the interference cell were determined by centrifugations with both compartments filled with water, and fringe deviations from the horizontal were noted as a function of angular velocity. The distortions were found to be very small with our cell, and at speeds under 20,000 r.p.m. they never exceeded 0.1 fringe interval.

Since the solutions were alkaline, Kel-F single sector and charcoal filled Epon double-sector centerpieces were used rather than the usual aluminum filled Epon. The difference in refractive index between compartments corresponding to one fringe interval was determined using a capillary type synthetic boundary cell and found to equal the value predicted from the instrument constants. Solution column thicknesses were determined by measuring the distance between the outer faces of the quartz windows with a micrometer and subtracting the known thicknesses of the windows.

Refractive Index Measurements.—The refractive index increments for tantalate and 12-tungstosilicate at 5461 Å. were determined with a Brice-Phoenix differential refractometer which was calibrated with sucrose solutions.

Anion-Exchange Measurements.—Initial attempts to bind the anionic tantalum(V) species to the hydroxide form of Dowex 2-X8 were unsuccessful, apparently because of the high degree of cross linking of the resin. It was possible to bind the tantalate quantitatively to the less highly cross-linked Dowex 2-X4. The column was washed with distilled water, and the hydroxide ion in the eluate was titrated with standard acid. The equilibrium pH of the original tantalate solution was measured with a Beckman H pH meter calibrated with KOH solutions.

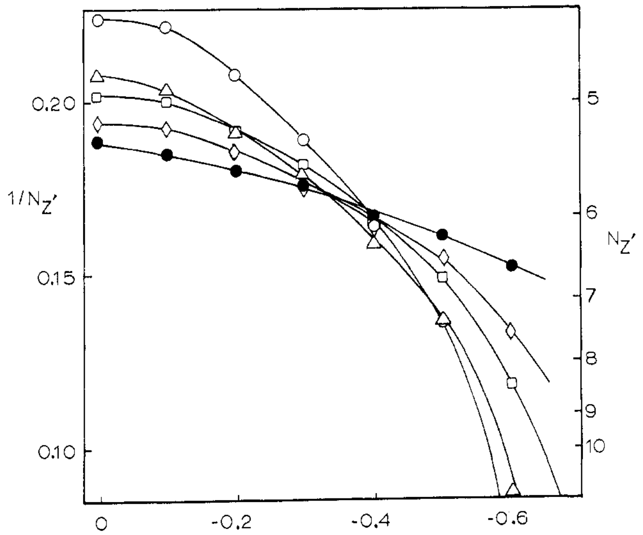

Fig. 2.—Schlieren optics determination of $1/N_{Z'}$ as a function of Z' with concentration as a parameter for the tantalate: ●, 0.0603 *M;* ◇, 0.1206 *M;* □, 0.1809 *M;* △, 0.2412 *M;* ○, 0.3015 *M* Ta(V).

Results

Schlieren Ultracentrifugation.—Since the e.m.f. measurements of the average charge per tantalum atom indicated that the crystals of $K_8Ta_6O_{19}\cdot 16H_2O$ dissolve in water with little change in stoichiometry, the hypothetical monomer unit $\{K_{1.34-\bar{p}}\,K_{\bar{p}}TaO_{3.17}\}$ was used in the earlier light scattering calculations.[3] The e.m.f. data had indicated that there was a small, constant amount of proton binding by the tantalate in the pH range 11.5–13, and a value of 0.12 was obtained for the average number of protons bound per tantalum. This corresponds to an average maximum charge per tantalum atom of 1.22. Ion-exchange studies were carried out to determine the average charge per tantalum in solutions prepared by dissolving $K_8Ta_6O_{19}\cdot 16H_2O$ in distilled water. Duplicate determinations gave values of 1.12 and 1.14.

In the centrifugation measurements, it is necessary to assign a formula weight to the monomer unit; while in the light scattering studies it was necessary only to know the molarity of the monomer, *i.e.*, of Ta(V). In the calculations, it was assumed that the polytantalate was built up of oxo rather than hydroxo groups, since structural studies have generally shown this to be the case for iso- and heteropolyanions.[8] The slight degree of protonation indicated above has a negligible effect and was ignored. If the structure were assumed to be completely hydrated, *i.e.*, that the monomer unit were, unreasonably, $K_{1.34-\bar{p}}[K_{\bar{p}}Ta(OH)_{6.34}]$, this would increase the monomer weight by about 20%. This change in monomer weight, however, has no significant

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(8) A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford, 1962, p. 446.

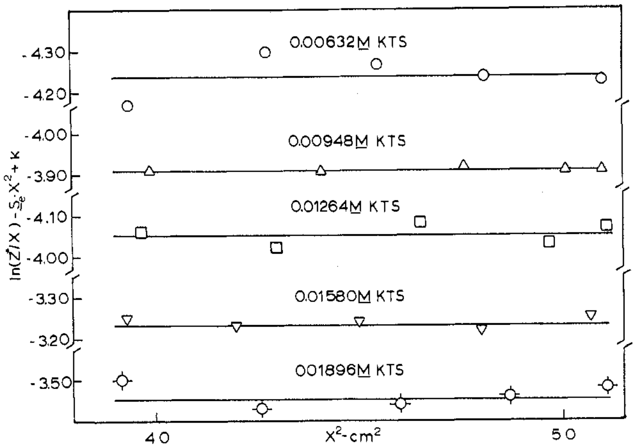

Fig. 3.—Test of constancy of $\mathbf{S}_e$ for the 12-tungstosilicate schlieren centrifugations.

effect on the calculated degree of polymerization, N; for the increase in the partial specific volume of the monomer leaves the quantity $M'(1 - \rho\bar{v}')$ unchanged within the experimental error. As in the case of the light scattering measurements, it is necessary to determine the degree of polymerization N, *i.e.*, the number of the monomer units which are contained in the polyanion, and the effective charge per monomer unit Z' simultaneously. The schlieren data were treated in the usual manner.[9] The values of $\ln Z^*/x$ were plotted as a function of (x^2) in order to determine graphically the value of $\mathbf{S}_e = \mathrm{d} \ln (Z^*/x)/\mathrm{d}(x^2)$. Straight lines were obtained, indicating that only one polyanion was present. The schlieren data are shown in Fig. 1, where the measurements are presented as the deviation functions ($\ln Z^*/x - \mathbf{S}_e x^2 + K$). The constant K had the value of 2.303 and was only used to normalize the deviations to the range of -1 to -2.

The degree of polymerization was calculated as a function of charge from eq. 1 and 2.

$$\mathrm{d} \ln m'/\mathrm{d}(x^2) = S = \mathbf{S}_e + \frac{\dfrac{Z'^2 m'}{2A'm_3}(S - \sigma)^2}{1 + \dfrac{Z'^2 m' \sigma}{2A'm_3}} \qquad (1)$$

$$N_{Z'} = \frac{S}{A' - \dfrac{Z'^2 m'}{2m_3}(S - \sigma)} \qquad (2)$$

Here $A' = M'(1 - \bar{v}'\rho)\omega^2/2RT$ where ρ is the solution density, ω is the angular velocity, and $\bar{v}'$, the monomer component partial specific volume, is given by $(M_{\mathrm{Ta}}\bar{v}_{\mathrm{Ta}} - Z'M_{\mathrm{KCl}}\bar{v}_{\mathrm{KCl}}/2)/M'$. The formula weight of the monomer unit $\mathrm{K}_{1.34-\bar{\nu}}[\mathrm{K}_{\bar{\nu}}\mathrm{TaO}_{3.17}]$ is M_{Ta}, and the formula weight of the monomer component $\{\mathrm{K}_{1.34-\bar{\nu}}\mathrm{K}_{\bar{\nu}}\text{-}\mathrm{TaO}_{3.17} - Z'\mathrm{KCl}/2\}$ is M'. The quantities $\bar{v}_{\mathrm{Ta}}$ and $\bar{v}_{\mathrm{KCl}}$ are the partial specific volumes for the tantalate monomer unit and KCl, respectively. The apparent molal volume for the tantalate monomer unit was found to be essentially independent of concentration and has the value 28.4 ml. mole^{-1}, and $\Phi_{\mathrm{Ta}}/M_{\mathrm{Ta}} = \bar{v}_{\mathrm{Ta}}$. The value of $\sigma = \mathrm{d} \ln m_3/\mathrm{d}(x)^2$ was calculated from the relation $\sigma \simeq M_{\mathrm{KCl}}(1 - \bar{v}_{\mathrm{KCl}}\rho_{\mathrm{KCl}})\omega^2/4RT$. The centrifugation data are tabulated in Table I. Figure 2 shows the calculated values of $1/N_{Z'}$ as a function of Z' with concentration as the parameter for the tantalate. This figure may be compared with the light scattering data for the same system presented earlier,[3] and it is seen that the two cases are very similar. In both, the degree of polymerization is found to be ~6 and the charge per monomer unit is about -0.4. The higher precision obtained with the centrifugation data allows a somewhat more accurate determination of N and Z'.

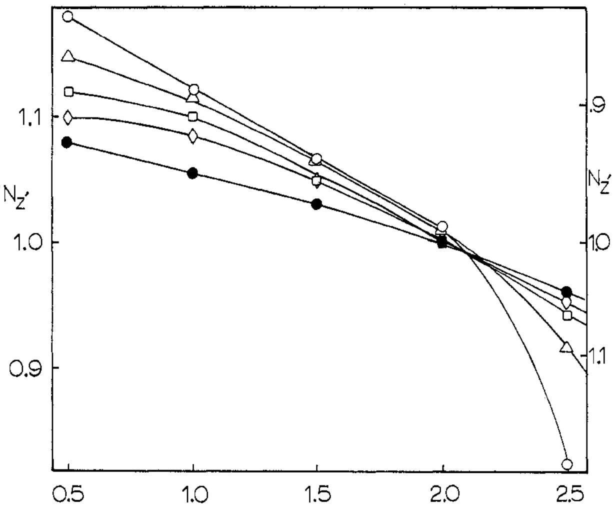

Fig. 4.—Schlieren optics determination of $1/N_{Z'}$ as a function of Z' with concentration as a parameter for the 12-tungstosilicate: ●, 0.00632 *M*; ◇, 0.00948 *M*; □, 0.01264 *M*; △, 0.01580 *M*; ○, 0.01896 *M* tungstosilicate.

As a check on our experimental procedure, we employed the same known used in testing the light

TABLE I

ULTRACENTRIFUGATION CONDITIONS

Molarity of component 2	Speed of rotation, r.p.m.	Optical system[a]	$\mathbf{S}_e$[b] or $\mathbf{S}$	N computed for Z'	
		Tantalate in 1 *M* KCl			
0.0603	17980	S	0.096	6.0	−0.4
0.1206	17980	S	0.092	6.1	−0.4
0.1809	17980	S	0.087	6.1	−0.4
0.2412	17980	S	0.085	6.3	−0.4
0.3015	17980	S	0.079	6.1	−0.4
0.0272	17980	I	0.09440	6.0	−0.4
0.0302	15171	I	0.06769	5.9	−0.4
0.0446	15220	I	0.06811	6.1	−0.4
0.0584	12590	I	0.04580	5.9	−0.4
0.0758	12590	I	0.04580	5.9	−0.4
0.1156	12590	I	0.02540	6.0	−0.4
0.1526	9330	I	0.02479	6.1	−0.4
		12-Tungstosilicate in 0.5 *M* KCl			
0.00632	15220	S	0.120	1.00	−2.0
0.00948	15220	S	0.116	0.99	−2.0
0.01264	15220	S	0.114	1.00	−2.0
0.01580	15220	S	0.111	0.99	−2.0
0.01896	15220	S	0.108	0.99	−2.0
0.001463	17980	I	0.1765	1.011	−2.0
0.003018	15220	I	0.1269	1.000	−2.0
0.004495	14290	I	0.1100	1.004	−2.0
0.004495	14290	I	0.1099	1.000	−2.0
0.006011	12590	I	0.08421	1.011	−2.0

[a] I, interference; S, schlieren. [b] Average of values at different bar angles.

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[9] J. S. Johnson, K. A. Kraus, and R. W. Holmberg, *J. Am. Chem. Soc.*, **78**, 26 (1956).

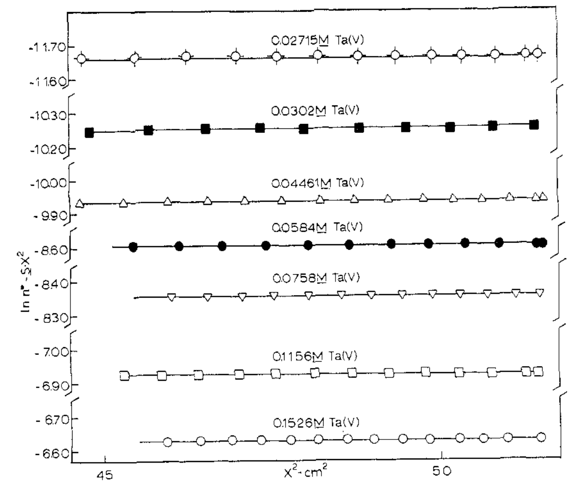

Fig. 5.—Test of constancy of **S** for the tantalate interference centrifugations.

scattering measurements,[3] the 12-tungstosilicate in the presence of 0.5 *M* KCl. The apparent molal volume of this solute was also approximately concentration independent, and the value of 441 ml./mole was obtained. This is, as expected, slightly larger than the value for $Na_{3.8}[H_{0.2}SiW_{12}O_{40}]$ of 406 ml./mole found by Johnson, Kraus, and Scatchard.[10] The deviation functions for the centrifugations of the potassium 12-tungstosilicate with schlieren optics are given in Fig. 3, and Fig. 4 shows the plot of $1/N_{Z'}$ *vs.* Z' with concentration as the parameter. This latter figure is very similar to the one presented earlier on the basis of light scattering measurements.[3] Since the monomer component used in the calculations was $\{K_{3.9}[H_{0.1}SiW_{12}O_{40}] - Z'KCl/2\}$, the calculated degree of polymerization should be 1, and this was found to be the case. The charge Z' was *ca.* 2.2, again in good agreement with the light scattering value.

The interference optics data were treated as suggested by Johnson, Scatchard, and Kraus,[11] and these centrifugations are also summarized in Table I. The values of the differences in refractive index between the solution and background compartments, n^*, as a function of the radius, x, were calculated by a numerical integration procedure using eq. 3 to compute the equilibrium value of n^* at the meniscus, n^*_α.

$$(\psi_{Ta}m'_0 + \psi_3 m_{30} - \psi_3 m_{bg0})(x_\omega^2 - x_\alpha^2) = n^*_\alpha(x_\omega^2 - x_\alpha^2) + \int_\alpha^\omega (n^* - n^*_\alpha)\, d(x^2) \quad (3)$$

Since the differences $(n^* - n^*_\alpha)$ were determined from the Rayleigh patterns, the values of n^* at the different points in the cell could be calculated. Here m_{30} is the initial concentration of KCl in the solution compartment, m^*_{bg0} is the initial concentration in the background compartment (taking into account the unsymmetrical location of the slits in the Spinco optical system and different meniscus positions), and m'_0 is the initial tantalate concentration. The refractive index increment for KCl, ψ_3, at 5461 Å. was taken from the literature,[12] and the value for the tantalate monomer unit, ψ_{Ta}, was independent of concentration and determined to be 0.0290 l./monomole. The value determined earlier at 4358 Å. was 0.0300 l./monomole.[3] The measurements were made in the presence of the supporting KCl and the small amount of KOH found previously.[3] Corrections were applied for the contributions of these latter species to the refractive index. The value for the $K_{3.9}H_{0.1}SiW_{12}O_{40}$ solutions in 0.5 *M* KCl was essentially concentration independent and found to be 0.291 M^{-1}, which may be compared to the value of 0.310 M^{-1} obtained at 4358 Å.

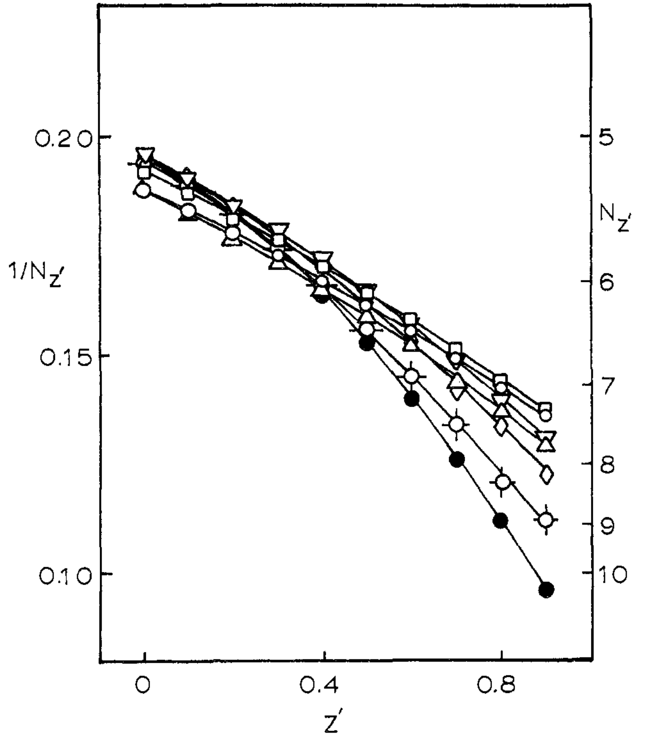

Fig. 6.—Interference optics determination of $1/N_{Z'}$ as a function of Z' with concentration as a parameter for the tantalate: O, 0.0272 *M*; □, 0.0302 *M*; △, 0.0446 *M*; ▽, 0.0584 *M*; ◇, 0.0758 *M*; O, 0.1156 *M*; ●, 0.1526 *M* Ta(V).

The refractive index data were used to calculate values of $\eta = Z'm'/2m_3$ for assumed values of Z' by solving the quadratic equation (4) derived by Johnson, *et al.*[11]

$$(1 - \eta^2)(1 - \eta_0 + \Delta)^2(n^* + \psi_3 m_{bg}^*)^2 = m_{bg}^2(1 - \eta_0^2)[2\psi'\eta/Z' + \psi_3]^2 \quad (4)$$

Here η_0 is the initial value of η, m_{bg}^* is the corrected background concentration taking into account the unsymmetrical location of the slits in the Spinco optical system, $\Delta = (m_{bg0} - m_{BX0})/m_{30}$, and $\psi' = \psi_T - Z'\psi_{KCl}/2$. The distribution of the solutes is then obtained from eq. 5 and 6. The data ln m' and ln $(1 + \eta)/(1 - \eta)$ as functions of x^2 were fitted by a least-squares procedure using equal weights to determine the

$$m_3 = \frac{n^* + \psi_3 m_{bg}^*}{2(\psi'\eta/Z') + \psi_3} \quad (5)$$

$$m' = 2m_3\eta/Z' \quad (6)$$

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(10) J. S. Johnson, K. A. Kraus, and G. Scatchard, *J. Phys. Chem.*, **64**, 1867 (1960).

(11) J. S. Johnson, G. Scatchard, and K. A. Kraus, *ibid.*, **63**, 787 (1959).

(12) A. Kruis, *Z. physik. Chem.*, **34B**, 13 (1936).

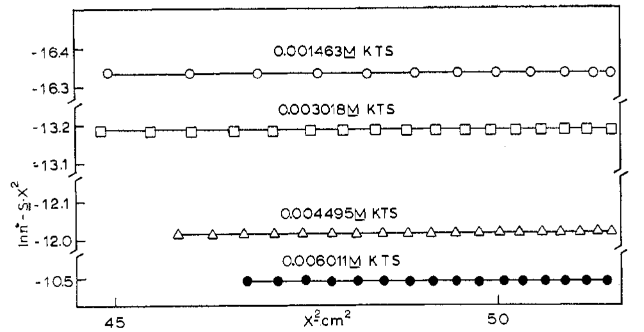

Fig. 7.—Test of constancy of S for the 12-tungstosilicate interference centrifugations.

slopes $S = d \ln m'/d(x^2)$ and $d \ln [(1 + \eta)/(1 - \eta)]/d(x^2)$. The precision of the data for a given run was much better than in the schlieren measurements, as is shown by the deviation functions for the tantalate data, $\ln n^* - S(x^2)$, $S = d \ln n^*/d(x^2)$, in Fig. 5. Finally the degree of polymerization was calculated as a function of the charge per monomer unit with eq. 7, the analog of eq. 2. The entire calculation was programmed for the Control Data Corporation 1604 computer at the University of Minnesota.[13]

$$N_{Z'} = \frac{S}{A' - \frac{Z'}{2}\, d \ln \frac{(1+\eta)}{(1-\eta)}/d(x)^2} \qquad (7)$$

The results of the interference optics centrifugations of the tantalate solutions are shown in Fig. 6 again as $1/N_Z'$ *vs.* Z'. The results for N and Z' are similar to those obtained with schlieren optics although somewhat less precise. The same thing was observed when the 12-tungstosilicate solutions were centrifuged. The deviation functions $\ln n^* - S(x^2)$ for this latter solute are presented in Fig. 7, and the plot of $1/N_{Z'}$ as a function of Z' is given in Fig. 8.

Discussion

In summary, the following experimental information is available for determining the nature of the tantalate anion in the pH range 11.5–13. At lower pH values precipitation occurs, while the high hydroxide ion concentrations at pH values greater than 13 make measurements difficult. (a) E.m.f. and ultraviolet absorption measurements indicate that there are no labile equilibria involving the tantalate anion which are important in this pH range. (b) E.m.f. and ion-exchange measurements indicate that the compound $K_8Ta_6O_{19} \cdot 16H_2O$ dissolves in water with only a very slight change in the stoichiometry of the tantalate species. (c) The constancy of the centrifugation slope terms S_e and especially the more accurately determined S is very good evidence for the existence of only a single polyanion in the system. (d) The values obtained for the degree of polymerization, N, and effective charge, Z', by centrifugation with schlieren and interference optics are in good agreement with each other and with the values obtained earlier by light scattering.

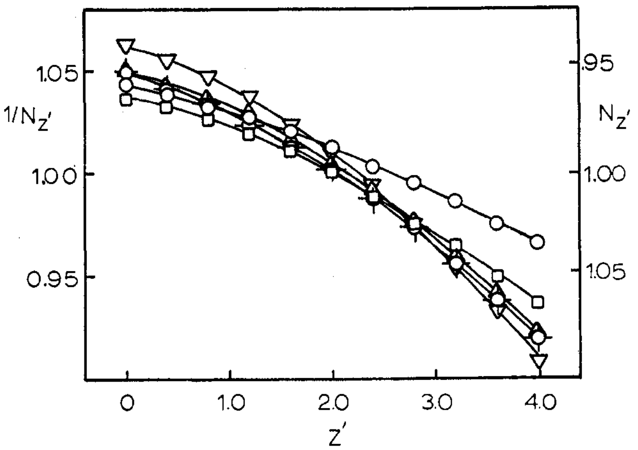

Fig. 8.—Interference optics determination of $1/N_{Z'}$ as a function of Z' with concentration as a parameter for the 12-tungstosilicate: O, 0.00146 *M;* □, 0.00302 *M;* △, 0.00450 *M;* -Ọ-, 0.00450 *M;* ▽, 0.00601 *M* tungstosilicate.

All three methods give $N = 6$ and $Z' = -0.3$ to -0.4. These data indicate that the single polyanion has essentially the formula $[HTa_6O_{19}]^{-7}$ and that it interacts strongly with the 1 *M* potassium ions from the medium. (e) The absence of depolarization in the light scattering measurements[3] tends to indicate a species with high symmetry.

Since, as has been discussed earlier,[3] the salt $K_8Ta_6O_{19} \cdot 16H_2O$ contains discrete anions with six tantalum atoms and cubic symmetry, it appears very likely that the same anions present in the crystals are present in the solutions. Indeed, considering the large amount of hydration water, the environment about the anions in the crystal lattice must be rather "wet."

Unexpectedly, the results from the centrifugations of the tantalate as well as of the "known" 12-tungstosilicate with schlieren optics proved to be more accurate than the values obtained with interference optics. This presents somewhat of a paradox in that the slopes S for a given run with interference optics could be determined much more accurately than the corresponding quantities S_e in the schlieren case. This is clearly shown by the deviation functions, Fig. 1, 3, 5, and 7. Some of the possible sources of error have recently been discussed with respect to centrifugations of alkaline niobium(V) solutions.[14] The most likely source would appear to be the wide variations in angular velocity which were necessary in order to resolve the fringes as the concentrations were varied.

The large reduction in charge from the maximum value of 1.1 to 1.2 indicated by the e.m.f.[3] and ion-exchange data points out the importance of a determination of the "effective" charge. Calculations of N based on the maximum charge give much larger degrees of polymerization. It is also encouraging that both the light scattering and ultracentrifugation measurements give the same values for the effective charge. It has been noted that the values obtained from light scattering data are often lower than those given by electrophoresis, and this has been attributed to inade-

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(13) The complete Fortran 60 deck listing, duplicate decks, and a flow sheet for this program may be obtained by writing to R. S. T.

(14) W. H. Nelson and R. S. Tobias, *Can. J. Chem.*, in press.

quacies in the theory used in interpreting light scattering data.[15] The assumptions inherent in the treatment of the light scattering and centrifugation data are somewhat different. Centrifugation requires that the partial specific volumes of KCl and the tantalate be constant, and the solution density is assumed to be constant to facilitate computation. Both methods assume a monodisperse polymeric solute, and they both require that the degree of complexing by medium ions be constant, that the appropriate species activity coefficient products be constant, and both light scattering and schlieren centrifugations require that $\eta = Z'm'/2m_3 << 1$. The latter condition would appear to be somewhat more critical for the light scattering case, for the cross term in the activities, $(\partial \ln a_2/\partial m_3)$, is proportional to $\eta/(1 - \eta^2)$.[16] At the highest concentrations in the light scattering and the schlieren centrifugations $\eta \simeq 0.06$, while the largest value in the interference optics centrifugations was *ca.* 0.03. Since charge effects were rather small, it was necessary to centrifuge with rather high concentrations to obtain an estimate of Z'. The assumption of constancy of activity coefficients or more specifically that the derivatives of the activity coefficients with concentration vanish should be valid for the polymer noncross term at the concentrations encountered here, *i.e.*, $(\partial \ln \gamma_2/\partial m_2) \simeq 0$. The other derivatives are not necessarily zero, and for KCl the change of activity coefficients with concentration does not generally reach a minimum until the molarity is *ca.* 2.5.[17]

When the studies of tantalate solutions were begun, it was thought that the light scattering measurements would provide the simplest means of determining the degree of polymerization. In practice, because of the difficulty in clarifying the solutions for light scattering, ultracentrifugation with interference optics proved to be the simplest method once a computer program was written to process the data.

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[16] R. S. Tobias and S. Y. Tyree, *J. Am. Chem. Soc.*, **81**, 6385 (1959).

[17] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth Scientific Publications, London, 1955, p. 479.

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Catalysis of Substitution Reactions of Rhodium(III) Complexes. The Reaction of Aquopentachlororhodate(III) Ion with Pyridine

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The observation of Delepine that alcohol facilitates the synthesis of certain rhodium(III) complexes was investigated. For the reaction between $K_2[Rh(H_2O)Cl_5]$ and pyridine (py) to yield *trans*-$[Rh(py)_4Cl_2]Cl$, it was found that the role of the alcohol is to generate catalytic amounts of a lower oxidation state of rhodium. It is assumed that this is Rh(I), and a two-electron bridged activated complex mechanism is proposed for the catalysis reaction.

Introduction

In 1929[1] and again in 1953,[2] Delepine reported a peculiar observation of a ligand exchange reaction for rhodium(III) which appeared to be catalyzed by alcohols. He had been synthesizing the chloropyridine complexes of rhodium(III) by the reaction of an aqueous solution of $Na_3[RhCl_6]$ with pyridine and isolating the products which were successively formed by the slow introduction of pyridine into the coordination sphere. Due to the insoluble nature of the tripyridine complex $[Rh(py)_3Cl_3]$, some difficulty was experienced in introducing a fourth molecule of pyridine. Delepine found that adding an excess of pyridine to a slurry of the insoluble complex and heating the mixture on a steam bath produced a considerable amount of the desired product in 10 hr. In order to increase the solubility of the nonionic intermediate, he added alcohol to a reaction mixture and was surprised to observe that the reaction went immediately and quantitatively from $[RhCl_6]^{3-}$ to $[Rh(py)_4Cl_2]Cl$ at room temperature.

Delepine found that the alcoholic hydroxyl group was responsible for the increase in reaction rate. All primary alcohols had about the same activity, secondary alcohols were significantly less active, and tertiary alcohols were inactive. Ether, dioxane, and acetone were likewise without activity.

On the basis of weight, methanol was the most active catalyst. Delepine stated, however, that the promotion of the reaction by trace amounts of it was an artifact based on the tenfold difference in molecular weight of methanol and $Na_3[RhCl_6]$. In fact, it appeared that about 1 mole of alcohol had to be present for each mole of rhodium in order for the reaction to take place. No suggestion was offered for the role of the alcohol in the catalysis mechanism. This paper reports observations on this system which suggest that the alcohol generates a lower oxidation state of rhodium which is the catalyst.

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[1] M. Delepine, *Bull. Soc. Chim. France*, **45**, 235 (1929).

[2] M. Delepine, *Compt. rend.*, **236**, 559 (1953).