formation in dichloromethane is not very accurate. If we assumed a value of $-\Delta H^\circ = 11.5$ kcal./mole, which is within the experimental uncertainty, it would account for the high formation constant and give relative magnitudes for the entropies of formation which are reasonable.

When an electron pair is involved in charge-transfer bonding, one should expect a lowering of the nonbonding orbital energy, giving rise to a blue shift for the $n-\pi^x$ transition, in analogy with observations in hydrogen-bonded systems. Experimental conditions, however, usually make it difficult to observe the influence of the acceptor on the donor absorption bands. In the complex between pyridine N-oxide and iodine in dichloromethane, Kubota[21] observed that the donor band at 284 mμ was shifted to 275 mμ in the complex. Strong evidence is given for assigning the 248 mμ band in triphenylarsine as a transition involving the arsenic lone-pair electrons. The apparent lack of perturbation of this band, therefore, is surprising.

It is found that a paramagnetic complex is formed when triphenylamine interacts with iodine, both in the solid and the liquid states.[31] The donor positive radical ion was identified. As triphenylamine undoubtedly is a very weak base toward iodine,[5] these observations seem surprising. Because triphenylarsine is a much stronger donor toward iodine, one might expect a definite paramagnetic behavior in this system. Although no quantitative data were obtained from the weak signal in concentrated acetonitrile solution, it is obvious that the present system shows a negligible e.p.r. resonance compared to the triphenylamine–iodine compound. The connection between e.p.r. behavior and the strength of charge-transfer complexes is not clear. More work undoubtedly has to be done before the mechanisms involved can be elucidated.

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Contribution from the Department of Chemistry,
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The Nature of Vanadate(V) Solute Species in Alkaline Solution

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Light-scattering measurements have been made on two series of sodium vanadate solutions, the total vanadium concentration being varied from 0.01 to 0.20 *M*. The first series was made up with a sodium to vanadium molar ratio of 1:1, corresponding to what is referred to commonly as sodium metavanadate, and is found to be tetrameric, in agreement with most previous findings. The second series contained a sodium to vanadium molar ratio of 2:1, corresponding to sodium pyrovanadate, and is found to be dimeric.

Introduction

The nature of solute vanadate species in aqueous solutions above pH 7 has been reviewed adequately as of 1964 by Ingri and co-workers.[1,2] For salts which we shall call sodium vanadate (2:1), commonly known as sodium pyrovanadate, there is general agreement that the vanadate species is a dimer in all but very dilute solutions.

For solutions of sodium vanadate (1:1), commonly known as sodium metavanadate, there is somewhat less agreement. The most recent work of Ingri and co-workers[2] proposes that both tetrameric and trimeric solute species are present, the former predominating at ordinary concentrations, and the latter becoming important in the 10^{-3} *M* total vanadium range. Very recently Naumann and Hallada[3] confirmed earlier work that the metavanadate behaves as though it is tetrameric in molten Glauber's salt.

We wish to report the results of light scattering measurements on the two series of vanadate solutions.

Experimental

Stock Solutions.—G. F. Smith Chemical Co. sodium perchlorate was recrystallized twice from water, dissolved, and brought to a pH of 2 with dilute $HClO_4$. The resulting solution was evaporated to the desired concentration under an atmosphere of N_2 gas. The final pH was adjusted to 6 with microdrops of concentrated aqueous NaOH. Stock solutions prepared in the foregoing manner were stored in polyethylene bottles and showed no turbidity when treated with $BaCl_2$ or $AgNO_3$.

Stock solutions of NaOH were prepared by dissolving J. T. Baker Chemical Co. pellets in carbonate-free distilled water. Stock $HClO_4$ solutions were made by simple dilution of J. T. Baker 70–72% $HClO_4$.

Fisher Scientific Co. sodium metavanadate was found to have other than a 1:1 molar ratio of Na to V. Even so, stock solutions were prepared of "metavanadate" by dissolving the commercial sample in enough water to give *ca.* 0.5 *M* vanadium. Sodium vanadate (1:1) stock solution was prepared by adding calculated amounts of molar NaOH to Fisher Scientific Co. vanadium pentoxide. The solution was stirred for 48 hr. at 60°.

Analyses.—Stock NaOH solutions were standardized with

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[1] N. Ingri and F. Brito, *Acta Chem. Scand.*, **13**, 1971 (1959).
[2] F. Brito, N. Ingri, and L. G. Sillén, *ibid.*, **18**, 1557 (1964).
[3] A. W. Naumann and C. J. Hallada, *Inorg. Chem.*, **3**, 70 (1964).

Merck and Co. potassium hydrogen phthalate. Stock $HClO_4$ solutions were standardized with a stock NaOH solution. Aliquots (5-ml.) of the $NaClO_4$ stock solution were pipetted into tared flasks, evaporated to dryness, and heated to 110°. The weights of dry $NaClO_4$ were used to calculate the concentration of the $NaClO_4$ stock solution.

The vanadium content of the V_2O_5 was determined by dissolving a weighed sample in excess NaOH and diluting to a known volume. Aliquots of the resulting solution were dissolved in 100 ml. of 2% H_2SO_4, reduced by means of a Jones reductor, caught in excess Fe(III) solution, and titrated with standard Ce(IV).

The sodium content of the commercial "metavanadate" solution was determined by passing aliquots through a Dowex 1-X8 ion-exchange column in the OH^- form and titrating the eluent with standard $HClO_4$. The vanadium content of the same solution was determined in the manner described above for the analysis of V_2O_5. The molar ratio of Na to V in the commercial "metavanadate" was 1.215:1.00.

Experimental Solutions.—Each solution under investigation was prepared by measuring calculated amounts of the several stock solutions into a 100-ml. volumetric flask, diluting to the mark, mixing thoroughly, and storing at 25° for 48 hr. Sufficient $NaClO_4$ was added in preparation to give a final concentration of 1 *M* in each case.

Solutions of sodium vanadate (1:1) were prepared ranging in total vanadium concentration from 0.01 to 0.19 *M*. One solution was prepared for measurement with this series from the commercial "metavanadate" without adjusting the Na/V ratio.

Solutions of sodium vanadate (2:1) were prepared by measuring calculated amounts of commercial "metavanadate" stock into the flasks, then adding amounts of standard NaOH sufficient to bring the sodium/vanadium ratio to 2:1. Lastly the $NaClO_4$ supporting electrolyte was added. One solution was prepared for measurement with this series from the sodium vanadate (1:1) stock.

Density, pH, and Refractive Index Measurements.—Densities were determined pycnometrically at 25°. The pH of each solution was measured at 25° using a Leeds and Northrup pH meter standardized with solutions of NaOH in 1 *M* $NaClO_4$. Refractive index increments were determined at 4358 Å. and at 25° using a Brice-Phoenix differential refractometer calibrated with sucrose solutions.

Light-Scattering Measurements.—Turbidities were measured as described previously.[4] Thiophene-free benzene was used as the secondary standard, and we continue to use 7.71×10^{-4} cm.$^{-1}$ as the value for its turbidity.[5] The gross turbidity of a solution, τ, is the sum of the turbidity due to the vanadate species, τ^*, and the background turbidity of the $NaClO_4$ and solvent. The latter was taken as the extrapolated value at zero vanadium concentration of the τ *vs.* molarity of vanadium plot. Subtraction of the background turbidity from τ gives τ^* values. All measurements were made at 4358 Å. on solutions which had been clarified by passage through 100-mμ Millipore filters under nitrogen gas pressure until turbidities were reproducible between filtrations.

Results and Discussion

In each of the two series studied here, we shall consider that we have a three-component system, solvent (1), vanadate solute (2), and $NaClO_4$ (3) supporting electrolyte. The values of pH of the solutions justify the neglect of NaOH as a fourth component. Using Scatchard's[6] definition of component 2 we have the following in the two series: sodium vanadate (1:1)

$$\left[Na_\nu H_2VO_4^{(1-\nu)-} + (1-\nu)Na^+ - \frac{1-\nu}{2}(Na^+ClO_4^-)\right]_{N_{z'}}$$

sodium vanadate (2:1)

$$\left[Na_\nu HVO_4^{(2-\nu)} + (2-\nu)Na^+ - \frac{2-\nu}{2}(Na^+ClO_4^-)\right]_{N_{z'}}$$

The degree of aggregation, $N_{z'}$, of the vanadate species is related to the turbidity by[7]

$$\frac{1}{N_{z'}} = \frac{H''M'\Phi\psi'^2}{\tau^*} - \frac{z'^2M'}{2M_3}$$

where

$$H'' = \frac{32000\pi^3n^2}{3N\lambda^4}$$

and M' is the molarity of vanadium, Φ is the volume fraction of the solvent, N is Avogadro's number, n is the refractive index of the solution, λ is the wave length of light scattered, ψ' is the differential of refractive index with respect to "monomer" vanadate, and

$$\psi' = \frac{\partial n}{\partial M'} - \frac{z'}{2}\frac{\partial n}{\partial M_3}$$

where z' is $(1 - \nu)$ for sodium vanadate (1:1) and $(2 - \nu)$ for sodium vanadate (2:1)

$$M_3 = 1.00 - \frac{z'}{2}M$$

The values of $\partial n/\partial M_3$ were taken from Goehring's data.[8]

Since refractive index measurements were made using 1 *M* $NaClO_4$ as the reference, plots of Δn *vs.* M' gave zero intercepts, and the differential refractive indices were the slopes of the lines. For sodium vanadate (1:1), $\partial n/\partial M' = 3.086 \times 10^{-2}$ l. mole^{-1}. For sodium vanadate (2:1), $\partial n/\partial M' = 4.178 \times 10^{-2}$ l. mole^{-1}. Solvent volume fractions for each solution were calculated from the density data using the reported value of $\bar{V}_1$ in aqueous $NaClO_4$ solutions.[9]

The turbidities and refractive index increments for the vanadate species and the pH values and solvent volume fractions for the solutions are given in Table I.

Degrees of Aggregation and Estimated Charges on the Vanadate Species.—Figure 1 shows plots of $1/N_{z'}$ *vs.* M' for the two series, with z' as a parameter. The obvious limits of z' for the 1:1 series are 0 and -1. It is clear that the vanadate is tetrameric, with a charge of *ca.* -2 on the tetramer, in essential agreement with the tetramer school of thought.[2,3] However, it should be noted that the low limit of concentration is 0.01 *M*

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[5] D. K. Carpenter and W. R. Krigbaum, *J. Chem. Phys.*, **24**, 1041 (1956).

[6] G. Scatchard, *J. Am. Chem. Soc.*, **68**, 2315 (1946).

[7] R. S. Tobias and S. Y. Tyree, Jr., *ibid.*, **81**, 6385 (1959).

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[9] H. E. Wirth and F. N. Collier, *J. Am. Chem. Soc.*, **72**, 5292 (1950).

TABLE I
EXPERIMENTAL TURBIDITIES, REFRACTIVE INDEX INCREMENTS, SOLVENT VOLUME FRACTIONS, AND pH

M'	$10^5\tau$*	$10^3\Delta n$	Φ	pH
		1:1 Series		
0.19	15.60	5.842	0.947	7.20
0.17	14.12	5.261	0.949	7.20
0.15	12.07	4.592	0.950	7.20
0.13	10.57	3.968	0.950	7.20
0.11	9.17	3.408	0.951	7.14
0.09	7.76	2.776	0.952	7.10
0.07	5.66	2.153	0.952	7.03
0.05	3.99	1.486	0.952	6.96
0.03	2.33	0.871	0.953	6.84
0.01	0.77	0.286	0.953	6.68
		2:1 Series		
0.20	17.36	8.355	0.952	9.96
0.17	14.75	7.076	0.952	9.90
0.14	12.28	5.890	0.952	9.80
0.11	9.52	4.615	0.953	9.75
0.08	7.05	3.319	0.954	9.69

and the points in the concentration range below 0.08 M show a drift to higher values of $1/M_{z'}$. The one additional solution studied, in which Na/V = 1.215, showed a degree of aggregation of 4 also.

The limits of z' for the 2:1 series are 0 and -2, but we have not varied z' to the lower limit, since it was clear that the species has a low charge (magnitude). The degree of aggregation is 2 with a charge of about -0.5. The point for the solution prepared from stock sodium vanadate (1:1) falls on the curve also.

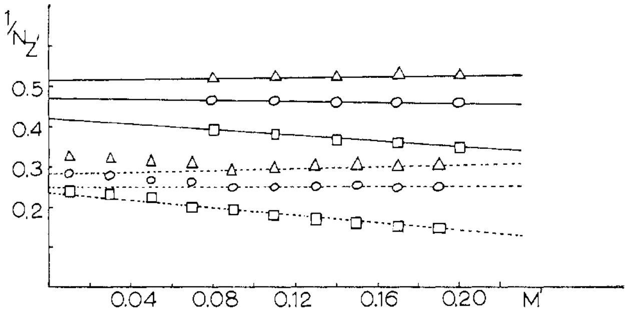

Figure 1.—$1/N_z'$ *vs.* M', solid lines for sodium vanadate (2:1) series, dashed lines for sodium vanadate (1:1) series: △, $z' = 0$; ○, $z' = 0.5$; □, $z' = 1.0$.

By comparison of our pH values with those of Hazel, McNabb, and Santini,[10] we conclude that our solutions are indeed at equilibrium, in sharp contrast to the slow approach to equilibrium we reported recently in the tungstate system.[11]

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
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Chemistry of Polynuclear Metal Halides. I. Preparation of the Polynuclear Tantalum Halides Ta_6X_{14}[1a]

BY PHYLLIS J. KUHN[1b] AND ROBERT E. MCCARLEY

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The anhydrous halides $(Ta_6X_{12})X_2$ (X = Br, I) have been produced in good yields by the reduction of the tantalum(V) halides with aluminum foil in a temperature gradient according to the reaction $18TaX_5(g,l) + 16Al(s) = 3(Ta_6X_{12})X_2(s) + 16AlX_3(g,l)$. Final products having atom ratios X/Ta smaller than the calculated 2.33 were shown to contain some tantalum metal. A lower tantalum chloride mixture was prepared by the same procedure, but evidence indicated the principal phase present was $TaCl_{2.5}$ (Ta_6Cl_{15}). However, good yields of the ion $Ta_6Cl_{12}^{2+}$ could be obtained in solution from the anhydrous solids. Reflectance spectra of the anhydrous solids and absorption spectra of aqueous solutions were determined. The spectra were found to exhibit bands very characteristic of the $Ta_6X_{12}^{2+}$ structure.

Introduction

Green aqueous solutions produced by the lower tantalum halides have been attributed by early workers to the presence of species of Ta(II)[2] and Ta(III),[3] Ta_3X_{10},[4] and the ions $Ta_6X_{12}^{2+}$.[5] More recently the existence and structure of the polynuclear ions $Ta_6X_{12}^{2+}$ (as well as $Nb_6X_{12}^{2+}$) in alcohol solutions were ascertained by diffuse scattering of X-rays.[6] However, much of the earlier uncertainty concerning the nature

(1) (a) Contribution No. 1662. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Presented in part before the Division of Inorganic Chemistry, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964. (b) A portion of a thesis presented by Miss P. J. Kuhn to Iowa State University in partial fulfillment of the requirements for the degree of Master of Science.

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