[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MONTANA STATE COLLEGE]

Electric Moments of VCl_4 and $VOCl_3$

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The electric moments of $VOCl_3$ and VCl_4 have been estimated from solution measurements in CCl_4 at 25°. VCl_4 appears to have zero moment and $VOCl_3$ a small moment, calculated to be about 0.3 debye unit. At 25° the dielectric constant of VCl_4 is 3.11 and the dielectric constant of $VOCl_3$ is 2.90. The index of refraction of $VOCl_3$ at 27°, for the sodium-D line, is 1.630.

Introduction

The low boiling points and high solubilities of $VOCl_3$ and VCl_4 in non-polar solvents indicate molecules of low electric moment. Since it appears that no data are available in the literature concerning the electric moments of these compounds, this study was undertaken to supply the missing moments and to obtain information on the structure of the molecules in the liquid state. Vanadium oxytrichloride, $VOCl_3$, is a mobile, yellow liquid, boiling at 127°. Its vapor pressure,[1] viscosity,[2,3] electronic spectra,[4] Raman and infrared spectra,[5,6] melting point and heat of fusion[7] and dielectric constant[8] have been studied.

Vanadium tetrachloride, VCl_4, is an opaque, red-black liquid which disproportionates slowly to VCl_3 and Cl_2. Its dielectric constant,[8] vapor pressure,[9] b.p., f.p.,[10] density and magnetic susceptibility[11] have been studied.

Both substances react avidly with minute traces of moisture. For this reason the methods used for measuring density, dielectric constant and index of refraction were picked to give minimum error from this source.

Experimental

Carbon Tetrachloride.—Reagent grade CCl_4 was distilled and a center cut retained. The distillate was dried with either P_2O_5 or CaH_2. It was freshly distilled from the drying agent as needed.

Vanadium Oxytrichloride.—This was prepared by the method of Prandtl and Bleyer.[12] V_2O_5 was reduced with H_2 to form V_2O_3 which was then chlorinated to $VOCl_3$. For the majority of the measurements the $VOCl_3$ was distilled and a center cut taken, portions of which were distilled into the weight pipet just before use. This cut boiled at 120.7° at a pressure of 645 mm.

Vanadium Tetrachloride.—VCl_4 was prepared by the chlorination of ferrovanadium.[13] The product was stored as a CCl_4 solution to prevent rapid disproportionation and, when needed, the CCl_4 was removed by distillation and a center cut of the VCl_4 distilled directly into the weight pipet. All material used for the measurements boiled above 140° at the usual pressure of about 630 mm. Material prepared in this manner gave these values for vanadium: 26.36, 26.62, 26.31%; theoretical 26.43%.

Dielectric Constant Measurements.—Dielectric constants of the solutions and the pure liquids were measured at 4.6 mc. with an apparatus similar to that of Caughlan and Crowe.[14] The cell condenser was three concentric platinum cylinders with a capacity of about 25 $\mu\mu$fds. It was jacketed and provided with a jacketed reservoir of about 100-ml. capacity. Water from a thermostat was circulated through both jackets for temperature control.

Approximately one mole of CCl_4 was weighed into the cell and successive dielectric constant measurements and weighed additions of the vanadium halide were made. A small weight pipet, provided with a standard taper joint matching the top of the reservoir, was used to dispense the halides.

Refractive Index Measurements.—The refractive index of the solutions was measured with a modified Bausch and Lomb dipping refractometer. The proper prism was cemented into the mouth of a 125-ml. round bottomed flask to which an additional 12 mm. tube had been sealed. Dry CCl_4 was weighed into the flask, which then was attached to the dipping refractometer, and the entire assembly was immersed into the thermostat to the level of the upper part of the prism. Weighed additions of the halide were made to the CCl_4 through the 12 mm. tube, the refractive index being measured after each addition. A 60 watt incandescent bulb outside the thermostat provided illumination.

The refractive index measurements of pure $VOCl_3$ were made with an Abbe refractometer. The temperature was kept at 27° by circulating water from a thermostat. The $VOCl_3$ was introduced between the prisms with a fine tipped micropipet; some hydrolysis of the halide undoubtedly occurred. This method cannot be recommended since the instrument required disassembly for cleaning after this use.

Density Measurements.—Solution density measurements were made with a magnetically controlled float. The apparatus was similar in principle to that of Hall and Jones.[15] The electromagnet was contained in an aluminum box suspended in a 0.002° thermostat at 25°. A cylindrical glass cell, which contained a weighed amount of CCl_4 and a magnet-bearing float was placed in a fixed position in the thermostat directly above the electromagnet. The minimum current needed to hold the totally immersed float in a reproducible position (in this case, the cell bottom) is a linear function of the density. The electromagnet was a 170 ohm coil from the junk box. Magnet current was provided by a 5K helical potentiometer in series with 4 "D" flashlight cells. The current was measured with a precision multirange ammeter (0–10 ma. range). The floats used had volumes of 11.22 and 7.69 ml. and constants of 2.46 and $0.833 \times 10^{-3}\ \Delta d$/ma.

The solution densities were obtained by measuring the magnet current at which a float just broke free before and after each weighed addition of the halide. The floats were calibrated by determining the change in minimum magnet current caused by hanging small platinum weights on the floats in liquids of known density. The results of the dielectric constant and refractive index measurements on the pure liquids are

$$\epsilon_{VOCl_3} = 2.898 \pm 0.007 \text{ at } 25°$$

$$\epsilon_{VCl_4} = 3.107 \pm 0.007 \text{ at } 25°$$

$$n_D\,(VOCl_3) = 1.6298,\ 1.6302 \text{ av.} = 1.6300 \text{ at } 27°$$

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TABLE I[a]

Compound	T (°C.)	ϵ_{CCl_4}	$\Delta d/\Delta N$	$\Delta\epsilon/\Delta N$	$\Delta(n_D^2)/\Delta N$	P (cc.)	R_D (cc.)
$VOCl_3$	25	2.2283	0.226	0.660	0.524	38.5 ± 0.5	35.0 ± 0.5
$VOCl_3$	35	2.2077	.229	.624	...	38.0 ± .5	....
VCl_4	25	2.2275	.246	.878	0.642	45.2 ± .5	40.0 ± 0.5
VCl_4	35	2.2078	.250	.908	...	45.9 ± .5	....

[a] Solvent was CCl_4, $d^{25}{}_4$ 1.5858, $d^{35}{}_4$ 1.5666, $n^{25}{}_D$ 1.4587.

Discussion and Results

On the basis of cryoscopic measurements in CCl_4, VCl_4 has been postulated to form a dimer.[10] This is probably erroneous due to the formation of a solid solution between CCl_4 and VCl_4.[11] Infrared and Raman studies of liquid $VOCl_3$ indicate the molecule to have a C_{3v} symmetry, which is in agreement with the structure of the vapor as determined by electron diffraction.[16] It seems probable that both compounds are monomeric in dilute solutions, and monomeric molecular weights were used in calculations. Total polarizations and molar refractions were calculated using the extrapolation formula of Hedestrand.[17] The results of the calculations are summarized in Table I.

Because of the tetrahedral structure and general covalent properties, the small difference between P and R_D for VCl_4 probably is due only to atomic polarization. Therefore, as expected the electric moment is zero.

The uncertainty in the total polarization (P) and molar refraction (R_D) is estimated to be about 0.5 cc. A crude estimate of the atomic polarization of $VOCl_3$ can be made from Smyth's data.[18] P_a for $VOCl_3$ (estimated) is 2 cc. Using this value for the atomic polarization (P_a) the electric moment of $VOCl_3$ is calculated to be 0.31 debye unit. Since the difference between the total polarization and the sum of electronic and atomic polarization, *i.e.*, the orientation polarization, is then only 2.5 cc., and the uncertainty is possibly 1 cc., the uncertainty in the electric moment must be ± 0.1–0.2 debye unit. Therefore, the electric moment of $VOCl_3$ is small, being probably between 0.1 and 0.4 debye unit.

This is a low value compared with the large (2.4 debyes) moment of $POCl_3$. However a similar compound, CrO_2Cl_2, has been shown to have a similar small value.[19] It is tempting to postulate a dimer to account for this value, and our cryoscopic data taken in CCl_4 support this. However, our inability to show the absence of a solid solution, and the infrared and Raman studies make a dimer unlikely. We conclude that the V–Cl and the V–O bond moments are similar and that the approximate tetrahedral structure accounts for the low moment.

In order to provide an independent check, the dielectric constant and refractive index of $VOCl_3$ were measured and used in Onsager's equation.[20] This gave a moment of 0.39 debye unit, which is in agreement with our value. Our measured value for the dielectric constant of $VOCl_3$ differed from the previous value of Loomis and Schlundt[8] by −0.5 unit. We are unable to explain the discrepancy, since the work of Loomis and Schlundt appeared to have been carefully done.

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[20] See ref. 19, p. 226.

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[CONTRIBUTION FROM THE PIGMENTS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Preparation of the Ferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ in Transparent Form[1]

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The ferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ have been prepared by the interaction of ferric oxide and the corresponding alkaline earth fluoride or chloride under oxygen. The crystals obtained by this technique are small transparent platelets, up to 1 mm. in diameter and approximately 50 μ thick, which are essentially free of strain, thus permitting directly the observation and study of the internal magnetic domain structure by transmitted polarized light without delicate grinding and polishing procedures. X-Ray diffraction patterns taken on of single crystals gave these parameters: $a_0 \approx 5.88$ Å., $c_0 = 23.20$ Å. for $BaFe_{12}O_{19}$; and $a_0 = 5.86$ Å., $c_0 = 23.00$ Å. for $SrFe_{12}O_{19}$. Pycnometric and X-ray densities are in excellent agreement. Other compounds prepared in transparent form by this technique were: $CaFe_2O_4$, $Ca_2Fe_{10}O_{17}$, $LiFe_5O_8$ and α-Fe_2O_3.

Introduction

Adelsköld[2] first characterized $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ by their corresponding X-ray powder patterns as belonging to a group of compounds which crystallize in the hexagonal magnetoplumbite structure with the space group $D^4{}_{6h}$ (P 6_3/mmc). Went, *et al.*,[3] investigated the magnetic properties

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[1] Part of this paper was presented at the American Chemical Society Meeting, September 12, 1958.

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