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Dipole Moments of Alkyl Orthotitanates

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Dipole moments of tetraethyl orthotitanate, tetra-*n*-propyl orthotitanate, and tetra-*n*-butyl orthotitanate have been determined in *n*-heptane at 0, 25, and 50°. The dipole moment of tetra-*t*-butyl orthotitanate was determined at 25°. The values obtained for the ethyl, *n*-propyl, and *n*-butyl orthoesters are probably for the trimers, but are for the monomer of tetra-*t*-butyl orthotitanate. Variations of the dipole moments of these compounds with temperature are probably due to (1) decrease in restriction of rotation of the alkoxy groups; (2) decrease in the degree of association. A change in solvent effect may also be involved.

In previous papers[1,2] the electric moments of several alkyl orthotitanates in benzene and hexane solutions have been reported and compared to the theoretical moment of $Ti(OC_2H_5)_4$, assuming complete freedom of rotation of the ethoxy groups. The measured electric moments were all considerably less than the theoretical moment of 2.11 D., indicating restriction of rotation in the molecules.

In the present work dielectric measurements have been extended to *n*-heptane solutions of the ethyl, *n*-propyl, *n*-butyl, and *t*-butyl orthotitanates. For the ethyl, *n*-propyl, and *n*-butyl compounds these measurements were made over a temperature range (0 to 50°) in an attempt to obtain information concerning the potential energy barrier to rotation of the alkoxy groups.

Experimental

The tetraethyl and tetra-*n*-propyl titanates were prepared by the sodium alkoxide method.[3,4] Tetra-*t*-butyl titanate was prepared by the pyridine–ammonia method.[5,6] In the preparation of the *t*-butyl titanate, the *t*-butyl alcohol was carefully purified by fractionation of pure *t*-butyl alcohol in a column of 30 theoretical plates. No chemical analyses were performed on these materials; however, the physical properties were compared with previously analyzed compounds[1,2] in order to ascertain that they were the same material. Furthermore, infrared spectra were taken to assure identity of the compounds. The physical constants used are given in Table I. In the case of *t*-butyl titanate, for which we had no previous analysis, the boiling points and other constants were checked against those of Bradley, *et al.*,[5] and Cullinane, *et al.*,[6] since the same method of preparation was used.

The *n*-heptane used as the solvent in the measurements was obtained from Phillips Petroleum Co. (99 mole % purest grade), carefully purified by distillation in a fractionating column, and dried by distillation from sodium.

The apparatus used for the dielectric measurements has been described before.[1] However, the dielectric cell was modified slightly by placing a thermostated reservoir on top of the cell. This facilitated mixing of the solution in the cell after direct addition of solute. It also enabled a thermistor to be placed directly in the dielectric cell for accurate temperature measurement. A ground-glass stopper on the reservoir permitted introduction of solute from a weighing pipet, and the contents of the cell were completely sealed off from atmospheric moisture except during the brief periods of solute addition.

Densities of the solutions at 25 and 50° were obtained with a very sensitive Westphal balance. At the lower temperature of 0°, rapid absorption of water took place, hydrolyzing the solutions. Densities at 0° were obtained with a pycnometer.

The calibrations of the pycnometer and of the dielectric cell were made using *n*-heptane as a standard. The dielectric constants of heptane which were used at these temperatures are those reported by Dornte and Smyth[7]; densities used are those given by Smyth and Stoops.[8] The dielectric cell constant was slightly different for the three temperatures, having the values of 24.595, 24.625, and 24.692 $\mu\mu$f., respectively, for 0, 25, and 50°. However, small variations in the value occurred at any given temperature and accordingly the cell constant was determined preceding each set of measurements and used for that set. Measurements were made on solutions over a range of mole fraction from 0.002 to 0.01 for dielectric constants and from 0.001 to 0.02 for densities. From ten to seventeen different concentrations were measured for each compound at each temperature.

Results

Molar polarizations at infinite dilution were calculated by the method of Halverstadt and Kumler.[9] The slopes and intercepts of the dielectric constant *vs.* mole fraction and specific volume *vs.* mole fraction curves were obtained by the method of least squares. For each curve the standard deviation of the points from the curve was calculated. Molar refractions were calculated from the refractive indices of the pure solutes as reported by Speer.[4] In the calculation of the permanent polarizations, and subsequently the dipole moments, it was assumed that the distortion polarization is equal to the molar refraction. A program for the IBM 650 computer was written to perform these calculations. Table II lists for these compounds in heptane solution the intercepts ϵ_1 and V_1 and the slopes A and B for the dielectric constant and specific volume curves as a function of mole fraction; the standard deviations; the total polarizations P_∞; and the dipole moments, μ_M assuming monomer and μ_T assuming trimer, calculated from the Debye equation.

Discussion

Table II shows an increase of dipole moment with temperature for both the trimer and the monomer. For the monomer this increases toward the theoretical

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(1) R. W. Crowe and C. N. Caughlan, *J. Am. Chem. Soc.*, **72**, 1694 (1950).

(2) C. N. Caughlan, W. Katz, and W. Hodgson, *ibid.*, **73**, 5654 (1951).

(3) F. Bischoff and H. Adkins, *ibid.*, **46**, 256 (1924).

(4) R. J. Speer, *J. Org. Chem.*, **14**, 655 (1949).

(5) D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 4204 (1952).

(6) N. M. Cullinane, S. J. Chard, G. F. Price, and B. B. Millward, *J. Soc. Chem. Ind.* (London), **69**, Suppl. k, S38 (1950).

(7) R. W. Dornte and C. P. Smyth, *J. Am. Chem. Soc.*, **52**, 3546 (1930).

(8) C. P. Smyth and W. N. Stoops, *ibid.*, **50**, 1883 (1928).

(9) I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

TABLE I

Compound	B.p., °C. (mm.)	$n^{25}\mathrm{D}$	$d_{25}°$, g./ml.
Ethyl titanate	132–135 (5)	1.5052	1.1066
n-Propyl titanate	158 (9)		1.0353
n-Butyl titanate	180–182 (15) 155–157 (1–2)		0.9941
t-Butyl titanate	109 (11)	1.4430	0.8885

value of 2.11 D., calculated assuming complete freedom of rotation of the alkoxy groups in the monomeric species. These results suggest that rotation is less hindered at the higher temperatures and that the potential energy barrier to rotation is of the same order of magnitude as the thermal energy, kT, although other interpretations may be possible.

TABLE II
RESULTS OF DIELECTRIC STUDIES[a]

Compound	Temp., °C.	A	B	ϵ_1	$\sigma_1 \times 10^4$	V_1, cc./g.	$\sigma_2 \times 10^5$	P_∞, cc.	μ_M, D.	μ_T, D.
$Ti(OC_2H_5)_4$	50	2.0129	−1.3286	1.8816	4.8	1.5204	6.8	109.60	1.60	2.77
	25	2.0763	−1.2336	1.9181	7.4	1.4713	4.1	109.51	1.54	2.67
	0	2.1371	−1.1972	1.9537	2.6	1.4278	8.5	108.32	1.45	2.51
$Ti(O\text{-}n\text{-}C_3H_7)_4$	50	2.1635	−1.5141	1.8811	4.4	1.5203	1.5	129.30	1.60	2.77
	25	2.1389	−1.4599	1.9188	3.7	1.4712	8.7	125.34	1.47	2.55
	0	2.2053	−1.3469	1.9548	4.9	1.4278	5.8	125.92	1.42	2.46
$Ti(O\text{-}n\text{-}C_4H_9)_4$	50	2.1677	−1.7145	1.8818	5.4	1.5206	6.6	144.29	1.56	2.70
	25	2.2695	−1.5559	1.9187	4.4	1.4712	1.0	146.20	1.53	2.65
	0	2.3274	−1.4910	1.9547	4.7	1.4278	5.5	145.11	1.45	2.51
$Ti(O\text{-}t\text{-}C_4H_9)_4$	25	2.8316	−1.1348	1.9177	2.1	1.4714	5.9	172.27	1.85	

[a] The slopes and intercepts of the dielectric constant–mole fraction curves are A and ϵ_1, respectively. The standard deviations of the measured points from this line are given by σ_1. The slopes and intercepts of the specific volume–mole fraction curves are given by B and V_1, respectively. The standard deviations of the measured points from these lines are given by σ_2. The total molar polarization at infinite dilution is given by P_∞. The dipole moments calculated assuming monomer are μ_M. The dipole moments assuming trimers are μ_T.

Consider first the monomer. As would be expected, for each temperature at which measurements were made, the dipole moments determined for the ethyl, the *n*-propyl, and the *n*-butyl titanates are very nearly the same. It should be noted that in proceeding from the ethyl to the *n*-butyl titanates the dipole moments decrease somewhat, indicating an increase in the restriction of rotation of these groups. This is to be expected from steric effects. However, the value for *t*-butyl titanate is considerably higher than for the other three esters at the same temperature (at 25°, 1.86 D. for the *t*-butyl and 1.54 D. for the ethyl). One would expect less freedom of rotation of the alkoxy groups in the *t*-butyl titanate than in the others, due to greater steric hindrance. However, this effect would tend to cause the *t*-butyl titanate to have a lower, not higher, dipole moment than the others. A different explanation for this difference must then be found.

Although most of the alkyl orthotitanates have been shown to be trimers in solution,[10,11] the calculations for the dipole moments in the previous papers and in the next to last column of Table II were made assuming the compounds to be monomers. Since molar polarizations were obtained by extrapolating the concentration curves to infinite dilution, it had been assumed that values for monomers were being obtained. However, very careful molecular weight measurements by Bradley and Holloway[12] show that these compounds remain in the trimeric form even in very dilute solutions. This then might indicate that the dielectric measurements are for trimers, not monomers. Furthermore, the dielectric constant and specific volume *vs.* concentration curves were linear,[1,2] indicating the degree of association of these compounds remained constant.

Since *t*-butyl titanate is monomeric in solution,[5] the differences between its dipole moment and those of the other titanates are probably due to differences in the degree of association of these compounds. The last column of Table II lists the dipole moments calculated assuming trimeric species of the ethyl, *n*-propyl, and *n*-butyl titanates.

The possible effects of the solvent should be considered. Here we have assumed the associated species to be trimeric in heptane solutions. The existence of trimeric titanium alkoxides has been confirmed only in benzene solution, even though it seems reasonable to assume the same degree of association in benzene and heptane. However, Ibers[13] has shown that the tetraethyl titanate is a tetramer in the solid state, and this suggests that it may exist as the tetrameric species in solution as well. No reference was made as to how the crystals were grown. We have determined that in the solid state monomethyltriethyl titanate is also tetrameric.[14] Crystals of this compound used for the structure determination were obtained from benzene solution, in which the compound presumably exists in the trimeric form. At present we can say that the assumption that the compounds studied are trimeric in heptane solutions seems reasonable, although the possibility does exist that they may be associated to a greater or less degree.

It would be desirable to calculate a theoretical moment for the trimer. This requires knowledge of

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[10] C. N. Caughlan, H. S. Smith, W. Katz, W. Hodgson, and R. W. Crowe, *J. Am. Chem. Soc.*, **73**, 5652 (1951).

[11] R. L. Martin and G. Winter, *Nature*, **197**, 687 (1963).

[12] D. C. Bradley and C. E. Holloway, *Inorg. Chem.*, **3**, 1163 (1964).

[13] J. A. Ibers, *Nature*, **197**, 686 (1963).

[14] R. W. Witters and C. N. Caughlan, Abstracts, Bozeman Meeting, American Crystallographic Association, Summer 1964, p. 90.

the structure and this was one of the reasons for attempting solution of the crystal structures of these compounds. Since the crystal structures have shown the solid state to be a tetramer, we do not feel that an estimation of a theoretical moment for a trimer of unknown structure would be meaningful.

Thus, for these three compounds there seem to be at least two factors affecting the dipole moments with increasing temperature: (1) the decrease in the degree of restriction of rotation of the alkoxy groups; (2) a decrease in molecular complexity. A change in solvent effect is also possible.

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X-Ray Diffraction Evidence for Microphases in CeCd$_{\sim 4.5}$ Solid Solutions[1]

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If the actual composition of a compound differs from that associated with the crystallographically ideal structure, then defects have been created in the lattice. In the CeCd$_{4.3-4.7}$ region such defects may be randomly distributed throughout the lattice as was previously shown by vapor pressure measurements. In addition, the defects may order into many true phases which break up the random solution into ordered structures separated by two-phase regions. The ordered structures are called microphases and their existence is confirmed by the present X-ray diffraction results. All the superlattices observed may be classified by four characteristic key patterns which appear over wide areas between the reciprocal lattice spots of the parent structure. The superlattices appear to be orthorhombic, hexagonal, or monoclinic and may be correlated with vapor pressure measurements. All parent lattice distances are the same in the a axis direction. A hexagonal superlattice unit cell with a axis distance ~126 Å., c axis distance ~15.46 Å. has been identified. The c axis parent lattice distance is ~15.55 Å. at CeCd$_{4.35}$ but decreases by ~0.6% as the composition shifts to CeCd$_{4.65}$. The decrease in the c axis follows approximately the decrease of 0.64% in the electron/atom ratio, but the usual Brillouin zone argument seems inadequate to explain the shift for two reasons: first, the unchanging a axis distance is unusual and second, the apparently different superlattice symmetries would create different Brillouin zone shapes.

Introduction

The room temperature crystallographic structure of CeCe$_{\sim 4.5}$ previously heat treated at 640° is a hexagonal lattice in which cerium and cadmium atoms each occupy their specific lattice sites. Thermal vibrations in such a lattice will always cause partial dissociation of the lattice and will create a range of solid composition. Vapor pressure measurements at the higher temperature[2] have indicated several features of this solid solution behavior: First, they show that the principal dissociation forms random cadmium vacancies and cadmium atoms randomly misplaced in some particular type of less tightly bonded position. Second, if the crystal varies from CeCe$_{4.5}$ in composition, additional random cadmium vacancies are created or more cadmium atoms randomly enter the less tightly bonded positions. Third, there is some annihilation between the two types of sites, following mass action behavior.

The above conclusions were not surprising. However, certain additional vapor pressure measurements could only be explained by assuming that the defects could also arrange themselves to give a large number of more complicated, ordered structures (microphases) having small composition ranges with very narrow two-phase regions separating them. Because these findings were so unexpected, it seemed important to confirm them independently. The present X-ray diffraction work does confirm many and contradicts none of the earlier conclusions; it extends our understanding of the microphases, particularly with regard to their structures.

Experimental

The physical appearances and chemical purities of the cerium and cadmium alloy constituents and the additional purification procedures used have been described elsewhere.[3] Three alloys were prepared, by different techniques, in out-gassed tantalum containers encapsulated in quartz.

Alloy I.—A CeCd$_{4.35}$ gross composition alloy was prepared by allowing small pieces of cadmium, in contact with a larger piece of cerium, to melt and diffuse into the cerium. This alloy was then heat treated for 2 days at 650°. In this preparation the intention was to create an alloy which was nearly but not completely uniform in composition.

Alloy II.—A CeCd$_{4.5}$ gross composition alloy was prepared in the same manner as alloy I but was heat treated for 1 year at 650° in an attempt to assure its homogeneity.

Alloy III.—First, CeCd$_{\sim 6}$ was prepared in an isopiestic balance.[2,3] Then CdCd$_{\sim 4.5}$ was obtained from the CeCd$_{\sim 6}$ by allowing some of the cadmium to evaporate to the lower temperature reservoir. This alloy was used in a series of vapor

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(1) Sponsored by the U. S. Atomic Energy Commission. Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 10, 1964.

(2) G. R. B. Elliott and J. F. Lemons, Advances in Chemistry Series, No. 39, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1964, pp. 144-152, 153-169.

(3) G. R. B. Elliott and J. F. Lemons, *J. Phys. Chem.*, **64**, 137 (1960).