Refractive Indexes of TiCl_4 Liquid Measured by Goniometry

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1 INTRODUCTION

Throughout the experimental and theoretical studies on the refractive indexes of various materials such as gases, liquids, and crystals, the refractive index measurement is known to be the useful and convenient approaches for the estimation of the molar refractivities and the electronic polarizabilities for ions or molecules in media. Furthermore, the index data are indispensable for the measurement of hypersonic velocity in melt by Brillouin scattering¹⁾ which characterizes the high temperature relaxation process and for the evaluation of thermal conductivity by wave-front shearing interferometry²⁾ which requires temperature derivatives of the indexes.

In this work, the refractive indexes of TiCl_4 liquid were measured with visible light at 8 wavelengths by the goniometer method, from which the electronic polarizabilities of TiCl_4 molecule were calculated by combining the index data with the empirical

equation of molar volume.

2 EXPERIMENTAL

The chemical of TiCl_4 used was supplied from Toho Titanium Co. Ltd., which was purified twice by distillation. The impurities in sample are listed in Table 1³⁾. Since the pure TiCl_4 reacts easily with water or moisture and produces white fumes, the sample liquid was packed into the hollow prismatic cell in the glove box filled with dry N_2 gas. The refractive indexes were measured with visible light at 8 wavelengths over the temperature range of 295.6 to 318.1K.

Table 1 Impurities in TiCl_4 liquid (ppm).

Element	As	Sn	P	Si
Concentration	0.6	2	<10	2

The apparatus and the estimation procedure of refractive indexes were described in some detail elsewhere⁴⁾. In order to estimate the refractive indexes, the angles of minimum deviations were measured with a goniometer. The relation between the refractive index and the angle of minimum deviation is expressed by the formula,

$$n_\lambda = \sin\{(\theta_\lambda + A)/2\} / \sin(A/2)$$

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where n_λ , θ_λ , and A are the refractive index at wavelength λ , the angle of minimum deviation, and the apex angle of the prism, respectively. The angle A was calibrated beforehand by use of distilled H_2O whose refractive indexes have been accurately measured⁵⁾.

3 RESULTS AND DISCUSSION

The relations among refractive indexes of $TiCl_4$ liquid, wavelength, and temperature are shown in Fig. 1. The refractive indexes n_λ 's measured with light at a given wavelength λ decreased linearly with increasing temperature. A curvilinear decrease of n_λ 's was also observed against wavelength. These phenomena were well fitted by a unique equation called the modified Cauchy equation⁶⁾,

$$n(\lambda, T) = \sum_{i=0}^2 (P_i \cdot \lambda^{-2i}) + \left[\sum_{i=0}^2 (Q_i \cdot \lambda^{-2i}) \right] \cdot T$$

where P_i and Q_i are the constants determined by a least-squares method, and T the absolute temperature. The values of P_i and Q_i are given in Table 2.

Table 2 Least squares fitted parameters in the modified Cauchy equation.

P_0	P_1	P_2
1.90767	-1.57057×10^5	2.86471×10^{10}
Q_0	Q_1	Q_2
-1.18746×10^{-3}	5.84071×10^2	-9.52089×10^7

Molar Refractivity R_λ of $TiCl_4$ liquid was calculated at particular temperature and wavelength using the Lorentz-Lorenz equation,

$$R_\lambda = \left\{ (n_\lambda^2 - 1) / (n_\lambda^2 + 2) \right\} V_m$$

where V_m is the molar volume in $m^3 mol^{-1}$ given as the least-squares fitted equation³⁾,

Fig. 1 Variation of n with T and λ .

$$V_m = 75.40 \times 10^{-6} + 0.1176 \times 10^{-6} T$$

A slight increase in the molar refractivity with increasing temperature was observed and estimated to be $2.233 \times 10^{-8} \text{ m}^3 \text{ K}^{-1}$ for the visible light at wavelength 650 nm.

The electronic polarizability α_∞ was calculated from the semiclassical Clausius-Mossotti equation,

$$\alpha_\infty = (3\pi N_A/4) \{ (n_\infty^2 - 1)/(n_\infty^2 + 2) \} V_m$$

where the subscript ∞ refers to infinite wavelength, N_A Avogadro's number, n_∞ the refractive index at infinite wavelength evaluated with the aid of the modified Cauchy equation. The value of α_∞ calculated at 298.1 K was $14.0239 \times 10^{-30} \text{ m}^3$.

As shown in Fig. 2, the temperature dependence of α_∞ was found to be quite small and estimated to be $-1.071 \times 10^{-32} \text{ m}^3 \text{ K}^{-1}$.

Fig. 2 Temperature dependence of electronic polarizabilities of TiCl_4 liquid.

In an error estimation approach one can write

$$d \ln \alpha_\infty = d \ln (n_\infty^2 - 1) - d \ln (n_\infty^2 + 2) + d \ln V_m$$

The relative error in α_∞ is

$$| \Delta \alpha_\infty | = \alpha_\infty \{ 6 n_\infty / (n_\infty^2 - 1) / (n_\infty^2 + 2) \} | \Delta n_\infty | + (\alpha_\infty / V_m) | \Delta V_m |$$

As an example, we selected 318.1 K at which $n_\infty = 1.530$, $\Delta n_\infty = -0.11874 \times 10^{-2}$, $\alpha_\infty = 13.8096 \times 10^{-30} \text{ m}^3$, $\Delta V_m = 0.12 \times 10^{-6} \text{ m}^3$, and $V_m = 112.7958 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. Consequently, the relative error in α_∞ was computed to be $4.02 \times 10^{-32} \text{ m}^3$.

The electronic polarizabilities of TiCl_4 molecule determined accurately were found to be governed by contribution of four Cl^- ions whose electronic polarizability is close to $3.53 \times 10^{-30} \text{ m}^3$ in aqueous solution⁷⁾.

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