Refractive Index and Molar Refractivity of Molten $AgNO_3$

Robert Aronsson and Ernest Karawacki
Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

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The refractive index of molten $AgNO_3$ has been measured for four wavelengths (6832 Å, 5145 Å, 4880 Å and 4579 Å) at temperatures up to about 80° C above the melting point. It is shown that the molar refractivity (R) of molten $AgNO_3$ calculated according to the Lorentz-Lorenz equation is temperature (t) and hence density (ϱ) dependent. The estimated dR/dt and $dR/d\varrho$ values for visible light are $1.06 \cdot 10^{-9}$ (m^3/mole K) and $-0.984 \cdot 10^{-9}$ (m^6/kg mole), respectively.

Introduction

During recent years a number of accurate investigations of the refractive index of molten alkali nitrates have been reported (Ref. [1–9]). This paper presents refractive index data for molten $AgNO_3$ in the temperature range up to about 80 °C above the melting point for four wavelengths: 6328 Å, 5134 Å, 4880 Å and 4579 Å. It is shown that, as for the alkali nitrates, the molar refractivity and polarizability of molten $AgNO_3$, when calculated by means of the Lorents-Lorenz equation, is temperature (density) dependent.

Experimental

The measurements have been done with the modified thermo-optic technique (Ref. [7]). As sources of light the Spectra Physics lasers No. 132 (6328 Å) and No. 164 (5145 Å, 4880 Å and 4579 Å) have been used, while the interference fringes have been produced with a Variable Shearing Interferometer (Ref. [10]). All refractive index data were determined on the same sample. The molten salt was kept in a quartz cell with optically flat windows. First the weak laser intensity wavelengths (6328 Å and 4579 Å) were applied, and then the stronger ones (4880 Å and 5145 Å).

During the experiments the chemical stability of salt was controlled visually. Above 280 °C the salt showed a strong tendency to escape from the cell.

The refractive index n was determined by comparing the optical path difference between the salt and a calibrated 5 mm thick quartz plate. When the temperature is constant, the optical path difference and corresponding order of interference can be altered by rotating the plate. The relation between the change of the order of interference Δm_i and the angle of rotation α_i from the position of normal incidence allows to calculate the refractive index n_s from the equation

$$\lambda \Delta m_i/d = [n_p^2 - n_s^2 \sin^2 \alpha_i]^{1/2} - n_p + n_s(1 - \cos \alpha_i), \quad (1)$$

where d and n_p are the thickness and the refractive index of the plate, respectively, while λ is the wavelength of the light. In the next step the plate is placed perpendicularly to the incident light and the temperature is changed from t_0 to t (the so-called thermo-optical run). Using the known thermal and optical properties of the plate and the variation of the order of the interference Δm with temperature, the refractive index dependence on temperature is obtained from

$$n_s(t) = n_p(t) - \frac{n_p(t_0) - n_s(t_0)}{1 + \alpha(t - t_0)} - \frac{\Delta m \lambda}{d(t)}, \quad (2)$$

where α denotes the thermal linear expansion of the plate (for more details, see Ref. [7]).

During the thermo-optical procedure the temperature was changed continuously at a rate of 0.5 °C per minute. About 100 refractive index data, each calculated for a successive complete change in the interference order during a particular thermo-optical run, have been obtained for every wavelength. The experimental errors were estimated to be of the order of $\pm 1 \cdot 10^{-5}$.

Results and Discussion

Linear functions $n = n_0 + (dn/dt)(t - 485\,K)$ and $n = n_0 + (dn/d\varrho)(\varrho - 3959.3)$ have been least

Reprint requests to Dr. E. Karawacki, Department of Physics, Chalmers University of Technology, S-41296 Gothenburg, Schweden.

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squares fitted to the experimental results. t is temperature in K and ϱ is density in (kg/m^3). The coefficients n_0, dn/dt and $dn/d\varrho$ are presented in Table 1, in the columns 3, 4 and 5, respectively.

If the refractive index and density are known, the molar refractivity R and atomic polarizability α can be calculated according to the Lorentz-Lorenz theory from the relation (Ref. [11])

$$R = \frac{(n^2-1)}{(n^2+2)} \cdot \frac{M}{\varrho} = \frac{N_A \alpha}{3\varepsilon_0}, \qquad (3)$$

where N_A is Avogadro's number, $\varepsilon_0 = 1/4\pi$ the dielectric constant in vacuum and M the molecular weight. According to the general theory R should be a constant. However, our results show definitely that the molar refractivity of molten $AgNO_3$ when calculated from (3) is temperature- and, hence, density-dependent. The obtained molar refractivity data are presented in Table 2 in the form of a linear function of temperature $R = R_0 + (dR/dt)\,(t-485)$ and density $R = R_0 + (dR/d\varrho)\,(\varrho - 3959.3)$. As an average for visible light we have found $dR/dt = 1.06 \cdot 10^{-9}$ m^3/mole K and $dR/d\varrho = -0.984 \cdot 10^{-9}$ m^6/kg mole.

A similar dependence of the molar refractivity on density has been observed for molten alkali nitrates. The $dR/d\varrho$ values of molten alkali nitrates and $AgNO_3$ are given in Table 3.

If the Lorentz-Lorenz equation is correct, then a temperature variation of the molar refractivity indicates shifts of the resonance energies (and, hence, of the oscillator strengths) with temperature (density). According to the quantum theory of dispersion (Ref. [12]).

$$\alpha = \frac{e^2}{m} \sum_k \frac{f_{ka}}{\omega_{ka}^2 - \omega^2} \qquad (4)$$

where e and m are the electronic charge and mass, ω_{ka} and f_{ka} are the resonance angular frequency and oscillator strength of the $k \rightarrow a$ transition (the subscript a refers to the ground state) and ω is the angular frequency of the incident light. The summation is performed over all resonance frequencies k and in the present case it must include a rather wide resonance band of NO_3^- ions (Ref. [13, 14]).

It has been shown (Ref. [13]) that in the case of molten $LiNO_3$ and $NaNO_3$ the bands shift to lower frequencies with increasing temperature i. e. decreasing density. This corresponds to a negative $dR/d\varrho$ which qualitatively agrees with the results given in Table 3. A more quantitative discussion requires, however, accurate spectroscopic studies of the behavior of absorption lines with temperature.

The molar refractivity and polarizability as calculated from (3) at the temperature $1.1\,T_m = 533$ K, 10% above the melting point, for four different wavelengths are given in Table 4.

In the case of colorless compounds the relation (Ref. [4]):

$$\frac{n^2+2}{n^2-1} = A - B\,\omega^2 \qquad (5)$$

is usually used for extrapolating the experimental results to infinite wavelength and for determining the constants A and B, which are then utilized for calculating the refractive index values for a given

Table 1. Refractive index of molten $AgNO_3$ as a function of temperature and density:
$n = n_0 + \frac{dn}{dt}(t - 485)$ and $n = n_0 + \frac{dn}{d\varrho}(\varrho - 3959.3)$.

λ(Å)	N	n_0	$-\frac{dn}{dt}\cdot$ ($\cdot 10^{-4}$ K^{-1})	$\frac{dn}{d\varrho}\cdot$ ($\cdot 10^{-3}$ m^{3}kg^{-1})
6328	95	1.671318	1.6776	0.1645
5145	139	1.689171	1.7659	0.1731
4880	150	1.695473	1.7253	0.1691
4579	145	1.704553	1.8244	0.1789

The temperature interval is 485 K to 563 K.
λ is the wavelength in (Å), N is the number of experimental points, ϱ (kg/m^3) has been calculated according to Ref. [17].

Table 2. Molar refractivity of molten $AgNO_3$ as a function of temperature and density:
$R = R_0 + dR/dt\,(t - 485)$, $R = R_0 + dR/d\varrho\,(\varrho - 3959.3)$.

λ(Å)	R_0 (10^{-6} m^3 mole^{-1})	dR/dt (10^{-10} m^3 K^{-1} mole^{-1})	$dR/d\varrho$ (10^{-9} m^6 kg^{-1} mole^{-1})
6328	16.051	9.98	− 0.978
5145	16.383	9.71	− 0.944
4880	16.499	10.90	− 1.066
4579	16.666	9.65	− 0.948

The temperature interval is 485 K to 563 K. λ is the wavelength in (Å) and t is in K, ϱ (kg/m^3) are taken from Ref. [17]

Table 3. $dR/d\varrho$ of molten alkali and silver nitrates for the visible light.

	$dR/d\varrho$ (10^{-9} m^6 kg^{-1} mole^{-1})
$LiNO_3$	− 1.4875
$NaNO_3$	− 1.4274
KNO_3	− 1.1562
$RbNO_3$	− 0.8926
$AgNO_3$	− 0.9839
$CsNO_3$	− 1.1034

The $dR/d\varrho$ (m^6/kg mole) values for molten alkali nitrates are calculated from Ref. [7] and Ref. [8] and ϱ given by Ref. [17].

Table 4. The molar refractivity and polariszability as calculated from Eq. (3) at the temperature 1.1 $T_m = 533$ K.

λ(Å)	R(10^{-6} m^3 mole^{-1})	α(10^{-33} m^3)
6328	16.10	6.39
5145	16.42	6.52
4880	16.50	6.55
4579	16.71	6.63

frequency ω, lying far away from the resonance frequencies ω_{ka}.

The extrapolation of our results to infinite wavelength gives the following temperature and density dependence of the refractive index and molar refractivity:

$$n_\infty = 1.63830 - 0.0001553\,(t - 485),$$
$$n_\infty = 1.63830 + 0.1522 \cdot 10^{-3}\,(\varrho - 3959.3),$$
$$R_\infty = 15.428 + 0.0010\,(t - 485),$$
$$R_\infty = 15.428 - 0.976 \cdot 10^{-3}\,(\varrho - 3959.3).$$

In order to calculate the phonon velocities in molten $AgNO_3$ from Brillouin scattering measurements the refractive index data of Batsanov and Vesnin [2] for the wavelengths 588 nm and 674 nm at the temperatures 210 °C, 250 °C and 300 °C (with an experimental accuracy of the order of $\pm 1 \cdot 10^{-3}$) had been extrapolated by means of (5) to the wavelengths 4579 Å (Ref. [15]) and 4880 Å (Ref. [16]). Our results at these wavelenths differ slightly from the extrapolated ones. Compare, for example, our value 1.676 at 4880 Å and 326.4 °C with the extrapolated one 1.668 (Ref. [16]). The phonon velocities should therefore be recalculated using our refractive index data.

The observed dependence of the refractivity on temperature could stimulate studies of the shift of the resonans lines and oscillator strengths with temperature.

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