Refractive Index Measurements on Fused $LiNO_3$, $RbNO_3$ and $CsNO_3$ with a Modified Thermooptic Technique

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A modified method for measuring absolute values of the refractive index and its temperature dependence is presented. A direct comparison is made between the refractive index of a liquid sample and ambient air. Values for $LiNO_3$, $RbNO_3$, and $CsNO_3$ within a temperature interval of about 80 K above the melting point for several different wavelengths are presented as well as the calculated values of the molar refractivity and the absorption lines of the NO_3^- ion.

Introduction

During recent years methods have been developed in this laboratory for measuring the refractive index of liquids covering a temperature range up to 700 °C with an accuracy comparable to that obtainable with precision methods at room temperature. These methods have so far been applied to the study of ionic liquids and in particular to molten alkali nitrates [1], making use of a reference plate normally made of fused quartz. However, it is quite obvious that the experimental procedure would be much simpler and less tedious if a liquid sample in the form of a rectangular prism could be directly compared with ambient air. There are also certain instances when it appears almost impossible to rotate a quartz plate in a sample, for instance in glass-forming liquids at lower temperatures. In order to avoid this difficulty and speed up the measurements a new measuring cell has been designed as shown in Figure 1.By using the same quartz windows both for the liquid and the reference medium it is possible to neglect the influence of the windows when comparing the optical paths of the light beams through the liquid sample and the air. In this way it is also ensured that we have the same geometrical paths at normal incidence through the two samples to be compared. The comparison is very easily achieved by increasing the shear of the interferometer so it becomes conveniently larger than the horizontal dividing plate between the samples.

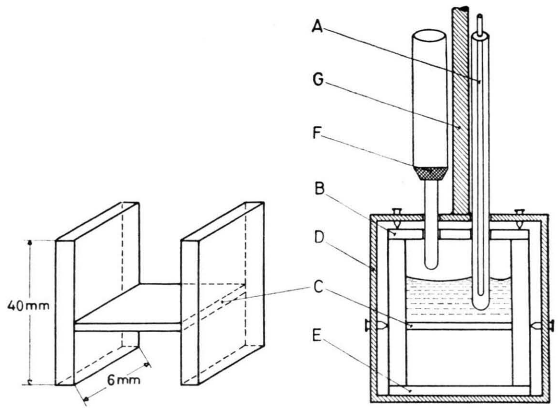

Fig. 1. *Left:* The frame of the cell to which two optical windows are to be fixed at the front and rear side to form two compartments, the upper one for the liquid, and the lower one for air as reference. — *Right:* The cell is here shown fixed inside the metal frame (D) directly connected to the goniometer via the axis G. A is the thermocouple with protecting glass tube. B, C, and E are covering plate, divding plate and bottom plate, respectively. F is an arrangement for passing the fused salt through a millipore filter.

Theory

Assuming that the front and rear windows are plane and of equal thickness, they do not contribute to the optical path difference between the light beams traversing the upper and lower parts of the cell (see Figure 1). Thus it is possibe to use the expressions for the optical path difference introduced by a tilted plane parallel plate accordingly

$$\frac{\lambda}{n_a\, d} = \frac{1}{\Delta m_i}\left[\,(n^2 - \sin^2 \alpha_i)^{1/2} - \cos \alpha_i - n + 1\right] \qquad (1)$$

where λ is the wave-length, d the thickness of the liquid (and air) container, measured between the inner surfaces of the optical windows.

$$n = n_s/n_a\,, \quad n_s \text{ and } n_a$$

are the refractive indices of the sample and the ambient air, respectively, α_i is the angle of incidence,

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and Δm_i is the change in the order of interference on rotating the cell from a position of normal incidence to a position with an angle of incidence equal to α_i. It is here assumed that the measurements are being performed under isothermal conditions, which means that d, n_a, and n can be considered constants.

After the determination of the refractive index (n), and the thickness of the liquid sample (d) at a temperature t_0, the temperature is slowly raised and the change in the order of interference (Δm) is continuously recorded. The refractive index $[n_s(t)]$ is then obtained as a function of temperature according to the following equation:

$$n_s(t) = n_a(t) + \frac{n_s(t_0) - n_a(t_0)}{1 + a(t - t_0)} + \frac{\Delta m \, \lambda}{d\,(t_0)\,[1 + a(t - t_0)]} \qquad (2)$$

where a is the coefficient of thermal expansion of the container. If this coefficient is not known a second "isothermal" measurement can be made at a temperature different from t_0 and from the two thickness and temperature measurements a value of a can be readily determined.

The particular way in which the Eqs. (1) and (2) are used, with respect to the rather large collection of data normally obtained, is discussed in detail elsewhere[1].

The particular difficulties encountered when the parallelepipedian sample, which is being rotated, does not have perfectly parallel front and back surfaces can be corrected for by choosing a proper position of the axis of rotation and by focusing the interferometer so that the final image plane is conjugate to the plane containing the axis of rotation[2].

Experimental

The most crucial component of the equipment is the specially designed container for the liquid (Figure 1). It is made of fused quartz and consists of a H-formed frame to which the front and rear windows are fused permanently. The fixing of the windows was done with a special vacuum technique by the manufacturer (Hellma, W. Germany). The inside dimensions of the compartment for the liquid are as follows: 6 mm long (in the direction of the optical axis of normal incidence) and 35 mm wide. With these dimensions of the cell it is possible to rotate the cell approximately 60 degrees from normal incidence when it is filled with a typical liquid. The thickness of the cell walls is about 4 mm and that of the dividing plate between the two compartments, as well as that of the covering plates, is about 2 mm.

The optical quality of the container was tested carefully prior to use with the interferometer, particularly because the optical windows had been fused to the frame after polishing. It turned out that the optical flats are still of high interferometric quality above and below a region of approximately 1.5 mm on either side of the dividing horizontal plate. By using a shear in the interferometer that is larger than 5 mm in the test plane it is possible to completely avoid the non-perfect region of the container. The cell was placed inside a metal frame, firmly fixed to the vertical axis that supports the goniometer. The frame, with the cell, was enclosed in a metal housing directly connected to the evacuated light ports leading through the walls of the high temperature thermostat. The metal housing served to keep the temperature homogeneous around the cell and to minimize the air convection between the cell and the lightport windows. Both the bottom and the top of the cell were closed by two quartz plates, the upper one having two holes: one for the thermocouple and the other for the salt container with the millipore filter. Both the salt container and the thermocouple rotate during the experiment together with the cell-metal frame combination.

When recording the change in refractive index as a function of temperature, slight temperature gradients are inevitably set up in the liquid sample. However, it is very easy to record them with the interferometer and in all these measurements the optical path differences due to these temperature gradients were kept below the limit of resolution of the shearing interferometer, in this case the Variable Shearing Interferometer[3, 4]. The way to suppress these unwanted temperature gradients is simply to change the temperature of the thermostat very slowly.

Results and Discussion

The results of the measurements of the refractive index of molten $LiNO_3$, $RbNO_3$, and $CsNO_3$ are given in Table 1. The experimental values were fitted to both linear and quadratic functions by least squares methods. The errors in the refractive indices are generally well below $1 \cdot 10^{-5}$, which means that the measurements are now more precise, mainly because it has been possible to avoid the previously necessary calibration of the test plate. The number of experimental points during an isothermal mea-

Table 1. Refractive index of molten $LiNO_3$, $RbNO_3$, and $CsNO_3$ expressed by the two equations $n_S(t) = a + b\,t$ and $n_S(t) = a_0 + a_1\,t + a_2\,t^2$, where t is in °C *.

λ (Å)	a	$-b \times 10^4$	$\sigma \times 10^5$	a_0	$-a \times 10^4$	$a_2 \times 10^8$	$\sigma \times 10^5$
		$LiNO_3$					
6328	1.499921	1.2908	2.3	1.501619	1.3945	1.578	1.9
4965	1.511552	1.3043	1.9	1.512979	1.3927	1.353	0.8
4880	1.512475	1.3026	0.7	1.513226	1.3491	0.711	0.8
4765	1.514070	1.3060	2.1	1.516052	1.4290	1.890	1.5
		$RbNO_3$					
6328	1.473728	1.6328	2.0	1.479823	1.9864	5.112	0.7
5145	1.482018	1.6573	2.7	1.489832	2.1128	6.615	0.8
4965	1.483830	1.6592	2.4	1.491615	2.1131	6.592	0.8
4880	1.484928	1.6676	1.1	1.487619	1.8245	2.279	0.4
4765	1.486341	1.6670	1.8	1.492911	2.0529	5.561	0.6
4579	1.488670	1.6786	1.5	1.490749	1.7980	1.734	1.3
		$CsNO_3$					
6328	1.500612	1.7037	2.8	1.510372	2.1307	4.657	1.5
5145	1.507712	1.7252	2.4	1.512960	1.9543	2.492	1.4
4965	1.509906	1.7292	1.9	1.514812	1.9432	2.326	0.4
4880	1.510997	1.7322	1.8	1.515396	1.9239	2.080	1.3
4765	1.512646	1.7338	2.2	1.520997	2.0981	3.962	1.5
4579	1.515238	1.7466	1.8	1.520467	1.9748	2.481	0.7

* The temperature intervals are: for $LiNO_3$: 270 °C – 360 °C, for $RbNO_3$: 310 °C – 380 °C and for $CsNO_3$: 420 °C – 510 °C. σ is the standard error.

Table 2. The molar refractivity of molten $LiNO_3$, $RbNO_3$, and $CsNO_3$ calculated from the Lorentz-Lorenz equation for different wavelengths and temperatures.

T (°C)	4579 Å	4765 Å	4880 Å	4965 Å	5145 Å	6328 Å	∞
		$LiNO_3$					
270		11.032	11.002	10.983		10.760	10.425
300		11.056	11.026	11.007		10.782	10.443
330		11.081	11.051	11.031		10.804	10.463
360		11.107	11.077	11.057		10.827	10.483
		$RbNO_3$					
310	15.560	15.496	15.454	15.429	15.374	15.139	14.699
330	15.577	15.512	15.470	15.444	15.389	15.154	14.712
350	15.595	15.530	15.488	15.462	15.406	15.169	14.726
370	15.613	15.549	15.506	15.481	15.428	15.187	14.742
		$CsNO_3$					
420	18.333	18.259	18.201	18.166	18.093	17.869	17.374
450	18.370	18.296	18.239	18.204	18.130	17.903	17.404
480	18.410	18.337	18.279	18.243	18.168	17.940	17.438
510	18.452	18.380	18.319	18.284	18.208	17.981	17.477

Table 3. Calculated absorption lines for the NO_3^--ion in the fused alkali nitrates.

Salt	Temp. °C	Absorption lines (nm)	
$LiNO_3$	270	124	20
$NaNO_3$	310	128	21
KNO_3	340	130	27
$RbNO_3$	310	131	32
$CsNO_3$	410	133	39

surement was about 15 and during a thermooptical recording at least 150. The treatment of those data has been discussed elsewhere [1]. In this connection it should be noted that the time needed to carry out a particular experiment has been substantially reduced with this new direct method.

In Table 2 the molar refractivities are given as calculated from the Lorentz-Lorenz formula. The density values used in the calculations are those recommended by the National Bureau of Standards [5, 6]. From these data it is eminently obvious that the molar refractivity at zero frequency increases with temperature for all three liquids investigated here. This has earlier been observed using a less accurate method [7]. Consequently referring to a previous work on $NaNO_3$ and KNO_3 [1], it has been established that the molar refractivity at zero frequency of all the alkali nitrates increases with temperature.

In Table 3 we have given the calculated values of the absorption lines of the NO_3^- ion in the five different liquids. A systematic displacement of the lines towards lower frequencies can be observed as the anion is surrounded by cations of increasing radius. All the values are given for a temperature close to the melting point.

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