Refractivity of Molten Nitrates and Chlorides: Binary Mixtures Containing Cesium Ions

Yohji Uchiyama * and Ernest Karawacki
Department of Physics, Chalmers University of Technology, Göteborg, Sweden

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By using an interferometric technique, the refractive index of some molten salt mixtures containing Cs^+ ions was measured with high accuracy: (Li-Cs)NO_3, (Na-Cs)NO_3, (Ag-Cs)NO_3, (Li-Cs)Cl, and also pure RbCl. The isotherms of molar refractivity show a small negative deviation from additivity in the (Li-Cs)NO_3 and (Li-Cs)Cl systems and a positive deviation in the (Ag-Cs)NO_3 mixture. A tentative attempt was made to relate the excess molar refractivities with the absorption bands of the ions.

Introduction

In principle the refractivity of molten salts should give information about the structure of these melts. The refractive index, n, leads to the molar refractivity, R, by using the Lorentz-Lorenz equation based on the evaluation of the internal field from electromagnetic wave theory:

$$R = [(n^2 - 1)/(n^2 + 1)](M/d), \qquad (1)$$

where M is the molecular weight and d the density. In this simple model, R is constant for a given substance for a particular wave length of light, and its value does neither change with temperature, nor at phase transitions.

Bloom and Rhodes [1] determined the molar refractivities of (Na-Ag)NO_3 and (K-Ag)NO_3 mixtures. They obtained molar refractivity isotherms which showed no deviation from additivity beyond the experimental errors and concluded that little or no additional ionic interaction occurred in the systems. Murgulescu and Volanshi [2] have measured the refractive index of (Li-Na)NO_3 and (Li-K)NO_3 mixtures and obtained molar refractivities at 673 K which appear to indicate that the deformation action of the Li^+ ion has little effect on the refractometric behaviour of the mixtures. However, some investigators [1], [3], [4] reported that the value of R for all salts did increase slightly with rise in temperature.

The present research deals with the measurement of refractive index of molten mixtures of nitrates and chlorides with the cesium salt as one component. Cesium is the alkali ion which has the weakest interaction with anions. Our study aims to obtaining the molar refractivities in order to get information about the mutual influence of ions in a mixture. The refractive index was measured by the interferometry technique which is capable of giving the most accurate results obtainable on the present technical level. For the determination of the molar refractivity, the density has to be known. If the density data of an investigated system are inaccurate, it is of little value to measure the refractive index with high accuracy. The densities of the investigated mixtures of nitrates and chlorides are available with high accuracy from references [5], [6] and [7].

Experimental

Materials Used

All chemicals, analytical reagent quality $LiNO_3$, $NaNO_3$, $AgNO_3$, $CsNO_3$, LiCl, RbCl and CsCl (MERCK Chem. Ltd.) gave colourless clear melts. All substances were dried in a vacuum oven at about 500 K for one day. After being heated to 20 ∼ 30 K above the melting point, the melt was bubbled with dried argon gas for 20 minutes under vacuum. The chloride melts were further purified with HCl gas for 30 minutes. After purification, the salt was stored in a vacuum-desiccator. Silver nitrate was kept in darkness to prevent photolysis.

Method

The refractive indeces were measured with the interferometric technique developed and described in detail by Gustafsson and Karawacki [4], [8].

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* On leave from Tokyo Institute of Technology, Tokyo, Japan.

Reprint requests to Dr. E. Karawacki, Department of Physics, Chalmers University of Technology, Göteborg, Schweden.

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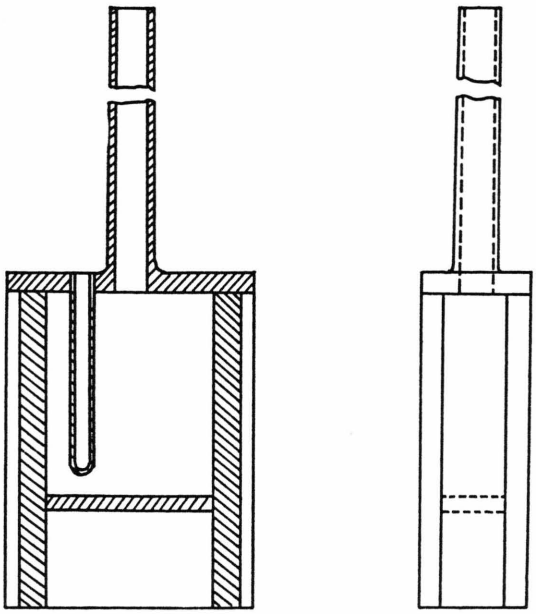

Fig. 1. Sketch of the cell which consists of two compartments, lower one containing air as reference.

In the present work, two gas lasers served as light sources: a He-Ne laser (6326 Å) Spectra-Physics model 132 and an Ar-Kr ion laser Spectra-Physics model 165. As sample container, a specially designed all quartz cell [4] was used. For lithium chloride, the cell has been slightly rearranged, since the cell must be sealed completely in order to avoid reactions with moisture, see Figure 1. The cell worked quite satisfactory up to 973 K for molten LiCl.

Results

The refractive indices of the nitrate mixtures were measured over a temperature range of about 100 K above the melting point. The experimental data are given in Table 1 in terms of two alternative equations. δ gives the standard deviation of the experimental values from the adjusted functions. The deviations from the quadratic functions are smaller than those from the linear ones.

Table 2 presents the results for the system (Li-Cs)Cl in terms of the same equations as used for the nitrate systems and the result for pure RbCl. Also for the chloride system the fit of the data to quadratic functions of the temperature is better than that to linear ones.

Table 1. Refractive index of molten (Li-Cs)NO_3, (Na-Cs)NO_3 and (Ag-Cs)NO_3 mixtures expressed by the equations $n_s(t) = a + bt$ and $n_s(t) = a_0 + a_1 t + a_2 t^2$, where t is in °C.

$LiNO_3$ mol%	λ (Å)	a	$-b \times 10^4$	$\delta \times 10^5$	a_0	$-a_1 \times 10^4$	$a_2 \times 10^8$	$\delta \times 10^5$	Temper. range (°C)
					(Li-Cs)NO_3				
75	4880	1.514100	1.6369	7.8	1.518752	1.9637	5.635	0.7	222—358
	4965	1.513197	1.6411	6.0	1.515961	1.8371	3.397	1.7	213—364
50	4765	1.516502	1.7950	3.6	1.518439	1.9399	2.656	0.9	205—339
	4880	1.514947	1.7909	4.3	1.518128	2.0339	4.572	0.7	210—322
	4965	1.514325	1.8104	5.1	1.518185	2.1106	5.754	0.8	207—319
40	4880	1.515168	1.8154	6.2	1.519195	2.0984	4.891	0.7	224—335
	4965	1.514620	1.8240	5.8	1.518249	2.0868	4.677	0.7	216—346
20	4880	1.511968	1.7661	3.3	1.519090	2.1108	4.150	0.7	364—467
	4965	1.511308	1.7726	1.3	1.514041	1.9064	1.632	0.7	364—456
$NaNO_3$ mol%					(Na-Cs)NO_3				
50	4765	1.502238	1.7368	9.2	1.508769	2.1531	6.531	0.5	250—388
	4880	1.500560	1.7282	8.2	1.506466	2.1056	5.935	0.3	250—386
	5145	1.498037	1.7308	8.4	1.503406	2.0719	5.330	2.4	249—392
$AgNO_3$ mol%					(Ag-Cs)NO_3				
50	4579	1.608241	1.9731	5.7	1.612151	2.2699	5.543	1.0	210—326
	4880	1.602729	1.9751	9.0	1.607960	2.3833	7.813	1.4	199—324
	5145	1.598321	1.9646	10.4	1.604077	2.4016	8.127	0.9	203—335

Table 2. Refractive index of molten (Li-Cs)Cl mixtures and pure RbCl expressed by the equations $n_S(t) = a + bt$ and $n_S(t) = a_0 + a_1 t + a_2 t^2$, where t is in °C.

LiCl mol%	λ (Å)	a	$-b \times 10^4$	$\delta \times 10^5$	a_0	$-a_1 \times 10^4$	$a_2 \times 10^8$	$\delta \times 10^5$	Temp. range (°C)
100	4880	1.586082	1.2284	1.8	1.591875	1.4034	1.317	1.3	611–716
	5145	1.582632	1.2270	2.6	1.571457	0.8893	– 2.545	1.3	609–717
75	6328	1.562905	1.6468	4.1	1.587517	2.6502	10.200	1.7	456–528
50	4579	1.582562	1.5551	3.5	1.582273	1.5424	– 0.137	3.5	375–552
	4765	1.571241	1.5873	4.0	1.568209	1.4555	– 1.417	1.7	373–557
	4880	1.570009	1.5849	2.8	1.568461	1.5157	– 0.765	2.4	374–531
	5145	1.566459	1.5758	3.3	1.564212	1.4786	– 1.038	2.1	377–570
	5682	1.564153	1.5895	3.4	1.562510	1.5160	– 0.815	3.1	379–523
	6328	1.558268	1.5437	4.9	1.552925	1.2813	– 3.211	4.6	367–451
25	4579	1.575970	1.6682	1.8	1.570233	1.4712	– 1.688	1.6	541–625
	4880	1.575118	1.7277	3.2	1.563419	1.3250	– 3.461	3.0	548–615
	5145	1.573190	1.7465	5.6	1.553338	1.0666	– 5.808	3.7	536–635
	5682	1.568813	1.7544	7.3	1.545202	0.9412	– 6.982	3.9	528–637
	6328	1.565326	1.7636	3.1	1.596540	2.8595	9.612	1.3	536–689
0	4579	1.574432	1.6692	1.0	1.574451	1.6697	0.004	1.0	671–758
	4765	1.573404	1.6914	2.6	1.589902	2.1723	3.502	2.5	651–723
	4880	1.571327	1.6799	5.0	1.574569	1.7749	0.696	5.0	649–718
	4965	1.568400	1.6569	1.9	1.568280	1.6535	– 0.024	1.9	662–741
	5145	1.566310	1.6499	2.0	1.565737	1.6333	– 0.121	2.0	654–724
	6328	1.556291	1.6838	2.1	1.572522	2.1553	3.420	1.2	652–727
RbCl	6328	1.513187	1.5647	8.6	1.569740	3.0158	9.293	1.8	727–835

Table 3. Effect of temperature on the molar refractivity R (cm^3/mol) of molten nitrate mixtures.

$LiNO_3$-$CsNO_3$ system					
$LiNO_3$ mol%	Wave-length (Å)	260 °C	290 °C	320 °C	350 °C
75	4880	12.6980	12.7241	12.7615	12.8290
	4965	12.6746	12.7006	12.7370	12.8023
		230 °C	260 °C	290 °C	320 °C
50	4765	14.4905	14.5143	14.5381	14.5663
	4880	14.4523	14.4755	14.4997	14.5291
	4965	14.4240	14.4453	14.4681	14.4966
40	4880	15.1437	15.1668	15.1923	15.2204
	4965	15.1220	15.1448	15.1699	15.1975
		370 °C	400 °C	430 °C	460 °C
20	4880	16.6997	16.7303	16.7641	16.7997
	4965	16.6695	16.7006	16.7334	16.7665
$NaNO_3$-$CsNO_3$					
		260 °C	290 °C	320 °C	350 °C
50	4765	14.8608	14.8834	14.9202	14.9602
	4880	14.8395	14.8427	14.8798	14.9198
	5145	14.7367	14.7687	14.8043	14.8425
$AgNO_3$-$CsNO_3$					
		230 °C	260 °C	290 °C	320 °C
50	4579	17.4813	17.5204	17.5629	17.6079
	4880	17.3377	17.3745	17.4156	17.4602
	5145	17.2313	17.2661	17.3054	17.3486

The experimental results presented in Tables 1 and 2 show that;

i) the refractive index decreases with increasing temperature, and

ii) the refractive index increases with decreasing wavelength.

Discussion

(1) Effect of Temperature on the Molar Refractivity

Molar refractivities for the investigated mixtures were calculated at four representative temperatures by using (1). The calculated molar refractivities for the three nitrate mixtures are shown in Table 3. The densities of the mixtures were taken for (Li-Cs)NO_3 from James et al. [5], for (Na-Cs)NO_3 from Murgulescu et al. [6] and for (Ag-Cs)NO_3 from Zuca et al. [7]. The molar refractivities of the (Li-Cs)Cl mixtures were calculated from our refractive indices and the densities given by Smirnov et al. [9]. The results are shown in Table 4. In all cases a slight increase in molar refractivity with increasing temperature is observed.

(2) Molar Refractivity Isotherms

Table 5 lists the excess molar refractivity ΔR of the investigated mixtures, i.e. the deviation of the

Table 4. Effect of temperature on the molar refractivity R (cm^3/mol) of molten (Li-Cs)Cl.

LiCl mol%	Wave-length (Å)	620 °C	650 °C	680 °C	710 °C
100	4880	7.8245	7.8412	7.8583	7.8760
	5145	7.7806	7.7977	7.8144	7.8306
		450 °C	480 °C	510 °C	540 °C
75	6328	9.2236	9.2313	9.2378	9.2411
50	4579	11.3748	11.4051	11.4344	11.4546
	4765	11.1354	11.1605	11.1841	11.1982
	4880	11.1140	11.1388	11.1623	11.1766
	5145	11.0547	11.0794	11.1027	11.1167
	5682	10.9991	11.0221	11.0437	11.0560
	6328	10.9255	10.9481	10.9685	10.9789
		540 °C	570 °C	600 °C	630 °C
25	4579	13.1481	13.1620	13.1750	13.1872
	4880	13.0536	13.0627	13.0700	13.0755
	5145	12.9848	12.9928	12.9980	13.0003
	5682	12.8736	12.8797	12.8825	12.8818
	6328	12.7831	12.7845	12.7862	12.7931
		660 °C	690 °C	720 °C	750 °C
0	4579	15.0455	15.0578	15.0708	15.0836
	4765	14.9752	14.9850	14.9962	15.0089
	4880	14.9381	14.9489	14.9598	14.9707
	4965	14.8987	14.9111	14.9231	14.9349
	5145	14.8528	14.8652	14.8771	14.8887
	6328	14.5083	14.5121	14.5171	14.5235

experimental value from that given by the relation of additivity

$$R' = C_1 R_1 + C_2 R_2 , \tag{2}$$

with C_1, C_2 the mole fractions and R_1, R_2 the molar refractivities of the pure components respectively. R_1 and R_2 for the nitrates were calculated from the data in references [10], [11]. In the calculation of the molar refractivities, in cases the equations of Table 1 and 2 were used slightly beyond the experimental temperature range.

The maximum error involved in the measurement of the refractive index was below ±0.01%. The composition of a mixture has been determined by weighing appropriate amounts of the purified salts with a balance. The errors in weighing were of the order of a fraction of a miligram, and that could not affect the mole percentage of the components in the first decimal place, i.e., the influence on the value of molar refractivity is estimated to be below ±0.1%. In the determination of the molar refractivity, there is a more serious error, i.e. that associated with density. The standard deviation for density measurements reported by different investigators may be as much as ±0.3% for nitrates and ±0.7% for chlorides. Thus, the possible error in molar refractivity due to density errors is estimated to be of the order of ±0.3% for nitrates and ±0.7% for chlorides. This is to be compared with the systematic deviations of the molar refractivity as shown in Table 5. Thus, small deviations from additivity are evident for all the investigated systems except (Na-Cs)NO$_3$, for which the deviation is within experimental errors.

The molar refractivity is related to the high-energy absorption frequencies by

$$R = \frac{N e^2}{3\,\varepsilon_0 \mu} \sum_k \frac{f_{ka}}{\omega_{ka}^2 - \omega^2} , \tag{3}$$

where e and μ are the charge and mass of the electron, ε_0 is the dielectric constant, N is Avogadro's number, ω_{ka} and f_{ka} are the resonance angular frequency and the oscillation strength of the $k \to a$

Table 5. Excess molar refractivity of molten (Li-Cs)NO$_3$, (Na-Cs)NO$_3$, (Ag-Cs)NO$_3$ and (Li-Cs)Cl mixtures.

(Li-Cs)NO$_3$ (693 K)			
LiNO$_3$ mol%	Wave-length λ Å	R cm^3/mol	ΔR %
20	4880	16.7514	− 0.58
	4965	16.7212	− 0.59
40	4880	15.3327	− 0.51
	4965	15.3074	− 0.50
50	4765	14.6480	− 0.58
	4880	14.6227	− 0.48
	4965	14.5916	− 0.51
75	4880	12.8327	− 0.48
	4965	12.7971	− 0.59
(Na-Cs)NO$_3$ (693 K)			
50	4765	15.0691	− 0.03
	4880	15.0276	− 0.06
	5145	14.9444	− 0.02
(Ag-Cs)NO$_3$ (693 K)			
50	4579	17.7794	+ 0.80
	4880	17.6392	+ 0.63
	5145	17.5228	+ 0.43

(Li-Cs)Cl (923 K)			
LiCl mol%	Wave-length λ Å	R cm^3/mol	ΔR %
25	4880	13.0774	− 0.64
	5145	12.9995	− 0.66
50	4880	11.2347	− 1.34
	5145	11.1790	− 1.29

transition, respectively and ω is the angular frequency of the light used for the measurements. ω_{ka} is related to the ultraviolet absorption energy of the ion according to $E_{ka} = \hbar\omega_{ka}$. Compared to the anions, the contribution of the cations to the total molar refractivity can be neglected in a first approximation because of the rather large difference in resonance energies between cations and anions [12], [13].

Table 6 gives the absorption energies of anions [13]—[15] and the molar refractivities for the investigated salts. As seen in the table, the values of R increase with decreasing absorption energy of the anion in both nitrates and chlorides. The increase of E is connected with the closeness of the cationic environment to the anion, i.e., the value of E increases with a decrease in the radius of the alkali cation. The anion is assumed to be situated in a deep, narrow potential box. The electrons of the anion are more strongly bound than, for example, in a free ion, and they have a smaller polarisability. Thus, the molar refractivity decreases as the system is tightened by the strong electric field of the charges.

From X-ray diffraction studies [16] of alkali nitrate, the coordination number of nearest neighbours for molten $LiNO_3$ and $AgNO_3$ salts is six, while that for molten $NaNO_3$, KNO_3 $RbNO_3$ and $CsNO_3$ salts is four. This would imply that Li^+ and Ag^+ ions possess a certain group structured character (like-ion groups) also in a mixture.

Among the alkali ions Li^+ has the strongest interaction with adjacent anions, while Cs^+ has the weakest. For a fluid mixture we can expect a Li^+ ion to be tightly surrounded by anions.

The replacement of a Cs^+ cation with coordination number four by a Li^+ cation with coordination number six will additionally initiate a minor shift of the energy levels towards higher absorption frequencies in two anions. As a result of this one can expect, therefore, that the molar refractivity of $(Li\text{-}Cs)NO_3$ will deviate negatively from additivity. The same explanation regarding Li^+ should hold also for (Li-Cs)Cl where there is a larger difference between the absorption energies E^- of the pure salts, see Table 6, for which we also find a larger deviation of the molar refractivity from additivity, see Table 5. In the case of $(Na\text{-}Cs)NO_3$, both cations have the coordination number four and rather small differences in the absorption frequencies of the anions. Therefore, the deviation of molar refractivity from additivity is expected to be nearly negligible.

Table 6. Absorption energies of the anion E^- and molar refractivities (* our results).

Sample	E^- (eV)	R (cm^3/mol) (4880 Å)
$LiNO_3$	4.32 [13]	11.1 (693 K) [10]
$NaNO_3$	4.15 [13]	11.8 (693 K) [10]
KNO_3	4.06 [13]	13.8 (693 K) [10]
$RbNO_3$	4.03 [13]	15.4 (693 K) [10]
$CsNO_3$	4.00 [13]	16.8 (693 K) [10]
$AgNO_3$	3.80 [14]	18.3 (693 K) [11]
LiCl	10.0 [15]	7.8 (923 K)*
RbCl	8.2 [15]	11.9 (1003 K)* (6328 Å)
CsCl	8.0 [15]	14.9 (923 K)*

A similar discussion as for Li^+ can be applied for Ag^+, which also has the coordination number six. However, since the absorption energy of NO_3^- for Ag^+ is less than that for Cs^+, the molar refractivity of $(Ag\text{-}Cs)NO_3$ should show a positive deviation from additivity as seen in Table 5.

Nissen [17] has pointed out that significant departures of the surface tension from that expected for the random mixture of a regular solution were seen for mixtures which contained $AgNO_3$, and that the deviations found are attributed to the presence of significant non-Coulomb interactions in the melt which invalidate the random mixing assumption implicit in the theoretical equations. It might be suggested that the deformation action of the Ag^+ ion due to the strong non-Coulomb interaction has some effect on the refractometric behaviour of $(Ag\text{-}Cs)NO_3$ mixtures.

From the point of view of absorption energies, the small increase of molar refractivity with increasing temperature might be explained by assuming a decrease of the absorption energy of an anion, i.e. the system is loosened by vigorous thermal motion of the ions with rise in temperature. For further discussion, the shift of the absorption peak in the mixture should be determined by measuring ultraviolet absorption spectra in these systems.

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