Refractive Index of Molten $PrCl_3$-NaCl and $PrCl_3$-KCl Mixtures

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The refractive indices of molten $PrCl_3$-NaCl and $PrCl_3$-KCl mixtures are measured by goniometry at seven wavelengths and expressed as functions of temperature and wavelength by a least squares method. With these data and published density data the molar refractivities and electronic polarizabilities are evaluated. The isotherms of these properties show little deviation from additivity.

Introduction

The refractive index serves to estimate the molar refractivity and the electronic polarizability using the Lorentz-Lorenz equation and the Clausius-Mossotti equation based on the evaluation of the effective local field around the species. It had been so far considered that the refractivity of molten salts should give information concerning the structure of these ionic melts. The molar refractivity at a particular wavelength has been thought to be constant characterizing an individual substance, and not to change with temperature.

From the measurement of the refractive indices of molten nitrate mixtures, Bloom and Rhodes [1] concluded that little or no additional ionic interaction occurred in these mixtures since the obtained molar refractivity isotherms showed no deviation from additivity beyond the experimental errors. At the same time, the molar refractivity of molten salts has been reported to increase slightly with rising temperature [1–7]. The electronic polarizability of an ion or a molecule has been so far evaluated from the refractive index of alkali halide crystals [8], liquid crystals [9], aqueous electrolyte solution [10], and organic liquids [11]. The values for pure melts have been summarized in the previous paper [12]. Refractive indices of molten rare earth chloride mixtures have not yet been published except for the systems $DyCl_3(YCl_3)$-NaCl [6], $DyCl_3(YCl_3)$-KCl [6], and $GdCl_3$-NaCl(KCl) [13].

Here we report the refractive indices of molten $PrCl_3$-NaCl and $PrCl_3$-KCl mixtures measured by goniometry. Our study aims at obtaining the molar refractivities and the electronic polarizabilities for these mixtures in order to obtain information concerning the mutual influence of the ions in the mixture and to make clear whether the electronic polarizability is really related to the structure of a molten salt or not.

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Experimental

Chemicals and Melt Preparation

The chemicals NaCl and KCl were of analytical reagent quality. The salts were dried under vacuum for 7 hours just below the respective melting points and then melted. The melts were purified by bubbling dried argon for 30 minutes, which was purified beforehand by passing it through a titanium sponge layer heated up to 1000 °C.

The hygroscopic chemical $PrCl_3$ was synthesized according to the reaction [14].

$$Pr_6O_{11} + 18\,NH_4Cl \rightarrow 6\,PrCl_3 + 18\,NH_3 + 9\,H_2O + O_2\,.$$

The crude $PrCl_3$ was purified by sublimation at reduced pressure for separating impurities such as oxides, NH_4Cl, and water. The sublimation apparatus has been fully described elsewhere [5]. The above pretreatments are indispensable since the reaction of $PrCl_3$ with water produces oxychloride at high temperature. The purified salts were stored in ampoules after solidification. The mole ratio of the mixture was determined by accurately weighing out each component which was also checked by chelate titration.

Method

In the goniometric measurements a hollow prismatic cell made of fused silica was used. The apparatus has been described in detail previously

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[5, 6]. The volume of melt needed for a run was 2 cm^3, and it took 1.5 hours to perform one run.

In order to evaluate the refractive index, the angle of minimum deviation was measured with a precision of 1 minute. The relation between the refractive index, n_λ, and the angle of minimum deviation, σ_λ, is

$$n_\lambda = \sin[(\sigma_\lambda + A)/2]/\sin(A/2), \quad (1)$$

where A is the apex angle of the prismatic cell. The apex angle A was calibrated beforehand by use of reference material whose refractive indices have been accurately measured by Gustafsson and Karawacki [15]. The temperature of the melt was automatically controlled and measured by directly inserting a sheathed chromel-alumel thermocouple into the melt and recorded with a precision of 0.1 °C during the experiment. The wavelengths used were 434.1, 510, 530, 560, 589.3, 620, and 656.3 nm. The accuracy of the data was the same as that previously reported [8].

Results and Discussion

Refractive Index

Highly accurate measurements of the refractive indices of molten salts with wave-front shearing interferometry have recently been carried out by Gustafsson and Karawacki [15]. In the low temperature range (<400 °C), our data are in good agreement with theirs as shown before. However, we estimated that the accuracy of the wave-front shearing interferometry in the high temperature range [16] (>800 °C) is nearly equal to that of goniometry. The refractive indices of pure $PrCl_3$, NaCl, and KCl melts measured at 589.3 nm wavelength are listed in Table 1 along with the published results [5, 6, 17]. As to the estimation of the molar refractivity and the electronic polarizability it is to be noted that the density has been measured up to four significant figures only.

Table 1. Comparison of refractive indexes of pure $PrCl_3$, NaCl, and KCl melts at 900 °C*.

Melt	References			
	[5]	[6]	[17]	this work
$PrCl_3$	1.7185	—	—	1.7266 (+ 0.47%)
NaCl	—	1.4103	1.398 (− 0.87%)	1.4135 (+ 0.23%)
KCl	—	1.3779	1.373 (− 0.36%)	1.3800 (+ 0.15%)

* The percent deviations from the values in Refs. [5] and [6] are denoted in parantheses.

It is well-known that the refractive index changes drastically near absorption bands (abnormal dispersion) [18]. Since a Pr^{3+} ion possesses three absorption bands in the visible wavelength region (440 – 490 nm) [19], the refractive indices of molten $PrCl_3$-NaCl and $PrCl_3$-KCl mixtures were measured outside this region.

The refractive indices of the mixtures decreased linearly with rising temperature in the same manner as described previously [12]. As pointed out by Gustafsson et al. [3, 15, 20], in the low temperature range the refractive indices can be better fitted by quadratic functions of temperature. On the other hand, in the high temperature range the index data were represented by linear functions because of experimental uncertainties [16]. It was also found in the present work that the refractive index decreases curvilinearly with increasing wavelength at fixed temperature. This phenomenon of normal dispersion [18] is usually represented by the Cauchy dispersion formula

$$n_\lambda = A + B/\lambda^2 + C/\lambda^4, \quad (2)$$

which is derived by expanding the dispersion formula

$$\frac{n^2-1}{n^2+2} = \frac{e^2}{3\pi^2 m} \sum_{i,j} \frac{N f_{ij}}{\nu_{ij}^2 - \nu^2} \quad (3)$$

to order $1/\lambda^4$, where m and e are the elctron mass and the charge, ν and N are the frequency of the incident light and the number of electrons per unit volume, ν_{ij} is the frequency of the transition $i \rightarrow j$, and f_{ij} is the corresponding transition probability. Other expressions have been proposed as dispersion formulas, but we have ascertained experimentally that (2) is best applicable to the refractive index of ionic melts [8, 12]. Since the refractive index is dependent on both temperature and wavelength, the following empirical equation has already been used [7]:

$$n(\lambda, t) = (P + Q/\lambda^2 + R/\lambda^4) + (P_t + Q_t/\lambda^2 + R_t/\lambda^4)\, t, \quad (4)$$

where the constants P to R_t are determined by a least squares method. The results for molten $PrCl_3$-NaCl and $PrCl_3$-KCl mixtures are tabulated in

Table 2. Refractive index equation $n(\lambda, t) = (P + Q/\lambda^2 + R/\lambda^4) + (P_t + Q_t/\lambda^2 + R_t/\lambda^4)t$; ($\lambda$/nm and t/°C).

Content (mol%)					
$PrCl_3$	100.0	0.0	9.5	26.8	42.4
NaCl	0.0	100.0	90.5	73.2	57.6
KCl	0.0	0.0	0.0	0.0	0.0
P	1.7910	1.5053	1.6072	1.6158	1.7225
$10^{-4}\,Q$	3.7546	0.3172	0.2123	2.9883	0.8845
$10^{-8}\,R$	− 31.8985	6.2150	5.8505	− 15.7229	4.7467
$10^{4}\,P_t$	− 1.0867	− 1.2155	− 1.9264	− 1.2856	− 1.8490
Q_t	− 30.3830	2.7264	4.6797	− 28.1671	− 1.3614
$10^{-6}\,R_t$	4.0768	− 0.4931	− 4.5649	2.2963	− 0.1855
$10^{3}\,\varepsilon$	0.43	0.47	1.30	1.01	0.50
temp	811	841	846	798	744
	—	—	—	—	—
range	941	941	921	900	893

Content (mol%)					
$PrCl_3$	56.1	66.8	84.1	0.0	10.2
NaCl	43.9	33.2	15.9	0.0	0.0
KCl	0.0	0.0	0.0	100.0	89.8
P	1.7684	1.7272	1.8006	1.5376	1.5253
$10^{-4}\,Q$	1.3673	3.3180	2.2690	− 2.9830	0.4896
$10^{-8}\,R$	3.4684	− 23.0135	− 11.7280	52.0603	2.8694
$10^{4}\,P_t$	− 1.8828	− 1.1752	− 1.6183	− 1.9250	− 1.3655
Q_t	− 8.9185	− 29.6223	− 12.6262	38.7629	1.0685
$10^{-6}\,R_t$	0.3460	3.2720	1.5071	− 5.6508	− 0.2192
$10^{3}\,\varepsilon$	1.11	0.80	0.35	0.45	0.31
temp	719	758	773	858	776
	—	—	—	—	—
range	886	896	894	946	909

Content (mol%)					
$PrCl_3$	25.8	40.1	55.6	70.3	85.2
NaCl	0.0	0.0	0.0	0.0	0.0
KCl	74.2	59.9	44.4	29.7	14.8
P	1.5934	1.6587	1.7523	1.7903	1.7968
$10^{-4}\,Q$	0.8931	0.2598	− 0.4051	1.0494	2.2686
$10^{-8}\,R$	− 1.0237	8.3465	18.1294	6.6216	− 13.2463
$10^{4}\,P_t$	− 1.4194	− 1.7426	− 2.2817	− 2.0366	− 1.6346
Q_t	− 2.0476	5.3133	16.4633	0.1778	− 12.9756
$10^{-6}\,R_t$	0.2443	− 0.7366	− 2.1088	− 0.6616	1.7075
$10^{3}\,\varepsilon$	0.38	0.40	0.37	0.62	0.39
temp	742	747	731	747	759
	—	—	—	—	—
range	898	895	888	894	895

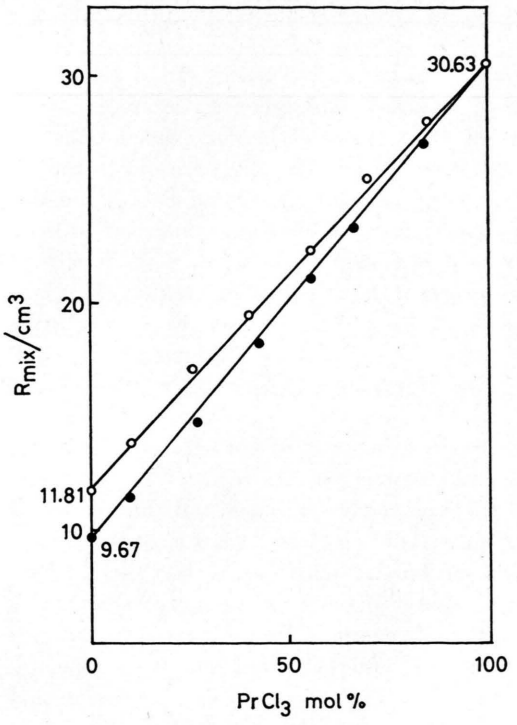
Table 2, where ε is the standard error on fitting. Equation (4) has proved of great value since the refractive index extrapolated to infinite wavelength is reduced to $P + P_t t$, which is needed to evaluate the electronic polarizability.

Molar Refractivity

The molar refractivities of the investigated mixtures were calculated using the data in Table 2 and the Lorentz-Lorenz equation

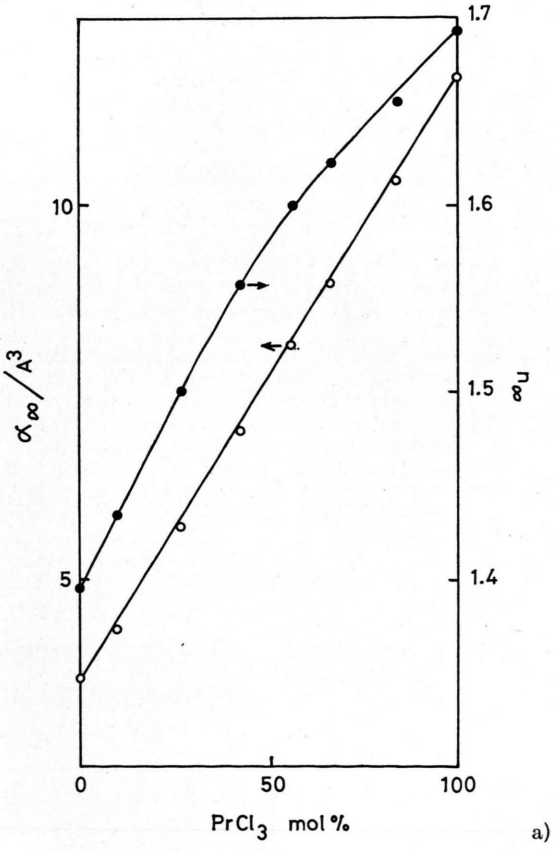
$$R_\lambda = \frac{n_\lambda^2 - 1}{n_\lambda^2 + 2}(M/d), \tag{5}$$

where M and d are the molecular weight and the density. The densities of the mixtures were taken from the literature [21]. A slight increase of R_λ with increasing temperature is observed except for $PrCl_3$-NaCl with 26.75 and 56.12 mol% $PrCl_3$,

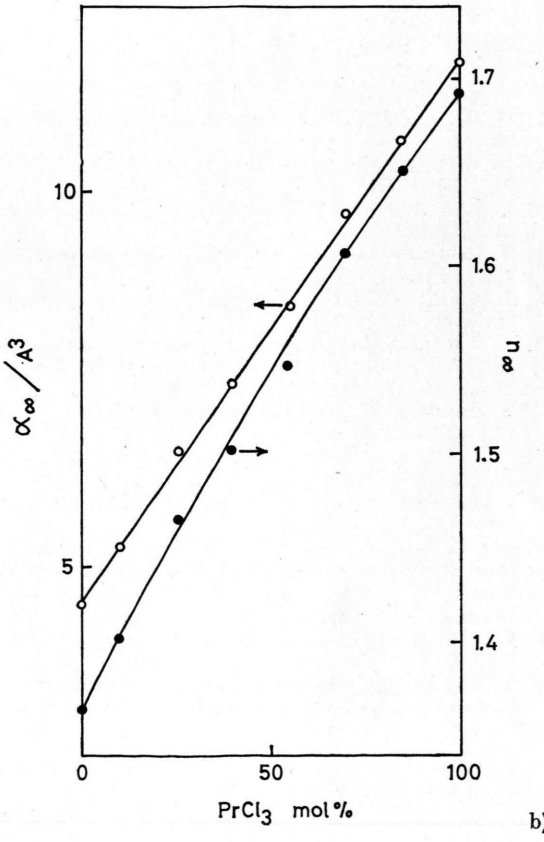


← Fig. 1. Molar refractivity of molten $PrCl_3$-NaCl and $PrCl_3$-KCl mixtures (900 °C, 589.3 nm). ●: $PrCl_3$-NaCl, ○: $PrCl_3$-KCl.

Fig. 2. Electronic polarizability and refractive index at infinite wavelength at 900 °C. a): $PrCl_3$-NaCl, b): $PrCl_3$-KCl.
↓



a)



b)

where the temperature gradient is estimated to be less than 6×10^{-3} cm^{33} °C^{-1}. An appreciable decrease of R_λ with increasing wavelength is also found. For pure $PrCl_3$ it amounts to more than 43% in the studied wavelength range.

Molar refractivity isotherms for molten $PrCl_3$-NaCl and $PrCl_3$-KCl mixtures are shown in Figure 1. The straight lines correspond to additivity:

$$R_{\text{mix}} = X_1 R_1 + X_2 R_2 , \qquad (6)$$

where X_1 and X_2 are the mole fractions of the salts. The minimum and maximum percent deviations from the additivity are -3.34% for $PrCl_3$-NaCl and 2.82% for $PrCl_3$-KCl, respectively.

Electronic Polarizability

The electronic polarizability (α_∞) we have to deal with [12] is defined by the semiclassical Clausius-Mossotti equation:

$$\alpha_\infty = (3/4\pi N)\,[(n_\infty^2 - 1)/(n_\infty^2 + 2)]\,(M/d), \quad (7)$$

where N is Avogadro's number and the subscript ∞ refers to infinite wavelength. The isotherms of α_∞ are shown in Fig. 2 together with those of n_∞ as calculated by means of (4).

The n_∞'s are skewed convexly from additivity, but the α_∞'s increase linearly with increasing mole fraction of $PrCl_3$ just in the same manner as the molar refractivities do. The structure of our molten mixtures surely changes on adding $PrCl_3$, but our results suggest that the electronic polarizabilities of the ions remain essentially constant, as is supported by the fact that the dispersion energy calculated from the ionization potential and the polarizability makes little contribution to the total potential energy as was estimated to be about 5% by Okada et al. [22].

The refractive index does not exactly express the polarization phenomenon. As reported by Tanemoto et al. [23], the refractive index and the density of molten $MnCl_2$-KCl mixtures deviate negatively from additivity in the KCl-rich range, but these effects cancel, so that the molar refractivity behaves additively, though complex formation is reported for molten $MnCl_2$-KCl mixtures by Laser-Raman spectroscopic study [24]. We come to the conclusion that not only the molar refractivity but also the electronic polarizability does not always afford a criterion for detecting the formation of complex ions in binary molten mixtures.

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