REFRACTIVE INDICES AND ELECTRONIC POLARIZABILITIES OF ALKALI HALIDE SINGLE AND BINARY MELTS

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ABSTRACT

The refractive indices of alkali halide single and LiCl-CsCl, LiBr-CsBr, NaCl-CsCl, NaCl-Nal, KCl-KI and CsCl-CsI binary melts have been measured with high accuracy at the wave length of 470 to 670nm. The electronic polarizabilities of the melts have been determined from the measured refractive indices by the Lorentz-Lorenz equation. The relation between the electronic polarizability and the structure of the salts has been examined. The electronic polarizabilities of the melts have the positive temperature dependence and those of the binary melts deviate slightly from the additive rule. Factors which affect the electronic polarizabilities of the melts have been investigated.

NOMENCLATURE

A apex angle of prism
δ_min minimum deviation angle
n refractive index
α electronic polarizability
V molar volume
N Avogadro's number
r_s first neighboring distance of the crystal at m.p.
r_l first neighboring distance of the melt
V_s molar volume of the crystal at m.p.
V_l molar volume of the melt
C_N_s coordination number of the crystal at m.p.
C_N_l coordination number of the melt
INTRODUCTION

The refractive index is indispensable for the optical measurements such as the Brillouin scattering. Furthermore, the electronic polarizability derived from the wavelength dependence of the refractive index gives us the information about the extent of the electronic polarization of ions under applied electric field.

The alkali halide melts are comprised completely spherically symmetric halide anions and alkali cations. Therefore, the alkali halide melt has been considered as a simple ionic liquid. But, it should be noted that electronic polarization of the ions exists even in such a typically ionic melt as alkali halide melts, and may influence the transport and thermodynamic properties of the ionic melts. Therefore, it is interesting to determine the electronic polarizability of the melts and to clarify the effect of the electronic polarization on physicochemical properties.

This paper reports the results of the measurements of the refractive index at the wavelength of 470 to 670 nm for the single melts and the binary LiCl-CsCl, LiBr-CsBr, NaCl-CsCl, NaCl-NaI, KCl-KI and CsCl-CsI systems. The electronic polarizabilities of the melts have been derived from the refractive indices observed, and the relative importance of the factors which control the electronic polarization has been investigated.

EXPERIMENTAL

The refractive index was measured at the wavelength of 470 to 670 nm and at the temperatures ranging from the m.p. up to 1200 K. The schematic diagram of the experimental apparatus is shown in Fig.1. It consists of a halogen lamp, a monochromator, an oven, a collimator, a prism cell and a telescope. The prism cell was constructed of the optical parallel plates of transparent quartz. The purified salts were sealed under vacuum into the cell.

The refractive index was determined by the minimum deviation angle method. The deviation angle takes minimum value when the incident beam and the refracted beam are symmetrical about the axis of the prism cell. The refracted beam was observed by the telescope. The prism cell was turned so as to minimize the deviation angle. The refractive index is
calculated by eq.1 from the minimum deviation angle, δmin, observed.
\[ n = \frac{\sin\left(\frac{A + \delta_{\text{min}}}{2}\right)}{\sin\left(\frac{A}{2}\right)} \]  
(1)
The apex angle, A was measured by means of an autocollimation method. Therefore, this measurement is an absolute method without a calibration process.

RESULT AND DISCUSSION

I. Error Sources of The Measurement

The factors of the error involved in the measurement of the refractive index and their contribution to the results have been evaluated. Three factors being important as the error sources are as follows:
1. The error involved in the measurement of the apex angle and the minimum deviation angle.
2. Deviation of the incident angle from right angle.
3. Parallel of the outside and inside of the windows of the optical cell.

Taking account of the error sources discussed above, the total error involved in the determination of the refractive index is estimated to be less than 0.08%.

II. Refractive Index

The refractive indices of CsCl-CsI binary melts decrease linearly with increasing temperature. The same temperature dependence has been observed for all the melts measured. According to the Lorentz-Lorenz eq.2, refractive index depends on the number density and the electronic polarizability of the constituent ions of the melts.

\[ \frac{n^2 - 1}{n^2 + 3} = \frac{4\pi N\alpha}{3V} \]  
(2)

We consider that the negative temperature dependence of the refractive index of the melts is mainly due to the decrease in the number density of the melts with an increase in temperature.

The isotherm curves of the refractive indices for the binary melts are shown in Fig.3. There are curve-linear relations between the refractive index and composition. As mentioned
above, refractive index is a function of electronic polarizability and number density. Assuming the additive rule for electronic polarizability of salts, refractive index of the mixture can be reproduced within a few percent.

The dispersion curves of the refractive index for CsCl-CsI binary melts are shown in Fig.4. The refractive indices of the melts decrease monotonically with increasing wave length at the wave length range of 470 to 670nm. These dispersion curves are typical of normal dispersion. The same normal dispersion curves have been observed for the other melts. The dispersion observed is considered to be due to the electronic polarization of the constituent ions of the melts.

III. Electronic Polarizability

The electronic polarizabilities of the melts have been determined from the refractive index and the molar volume by the Lorentz-Lorenz eq.2. The molar volumes of the single melts and the binary melts except LiBr-CsBr system are quoted from Janz (1). The molar volume of LiBr-CsBr binary melts is quoted from Smirnov et al (2).

Temperature Dependence of Electronic Polarizability

The temperature dependence of the electronic polarizabilities of CsCl-CsI binary melts is shown in Fig.5. The electronic polarizabilities of the melts increase slightly but more than the limits of the experimental errors with increasing temperature. The same positive temperature dependence of the electronic polarizability has been observed for the other melts investigated. The electronic polarizability is a parameter expressing the extent of the polarization of ions under the applied electric field, and is proportional to the ionic volume if the electronic structure is the same. According to the quantum mechanical calculations and the calculations of the atomic scattering factor for X-ray of crystalline alkali halides (3-6), the electronic polarizability of the anion decreases, on the contrary, that of the cation increases somewhat in passing from the free ionic state into the condensed state (7). The extent of the variation accompanying the change in state is larger for the anion than the cation (3-8). Wilson (8) pointed out the correlation between the electronic polarizability of ions and the inter-ionic distance of crystalline alkali halide. On the other hand, in molten state, the volume expansion induced by
the temperature increase is mainly due to the decrease in coordination number, and the first neighboring ionic-distance is almost kept constant upon an increase in temperature. Therefore, the positive temperature dependence of the electronic polarizability observed in the present investigation are considered to be due to the decrease in coordination number upon temperature increase. The contribution of the coordination number to the electronic polarizability has not yet been examined for the case of crystalline state. So, the relative importances of the inter-ionic distance and coordination number in molten and solid station have been investigated taking the cesium halide as a sample substance, because cesium halides show a structural transformation from CsCl type, whose coordination number is 8, to NaCl type, whose coordination number is 6.

The electronic polarizabilities of the cesium halides are plotted against inter-ionic distance and shown in Fig.6. The electronic polarizabilities of the CsCl type and NaCl type crystals are quoted from Tessman et al. (9) and Jaswal et al. (10), respectively. The coordination numbers are cited in parentheses for the reference. As shown in Fig.6, the correlation between the electronic polarizability and the inter-ionic distance of each salt at constant coordination number can be examined only for the case of coordination number, 8. In this case, the electronic polarizability increases with increasing inter-ionic distance. However, if the electronic polarizabilities of different coordination number of each salt are compared, there is no systematic correlation between the electronic polarizability and the inter-ionic distance. The electronic polarizabilities of cesium halide melts and crystals are plotted against coordination number and shown in Fig.7. The coordination number of the melts are determined by the Furukawa's eq.3 (11).

\[
\text{CN}_1 = \text{CN}_8 \left( \frac{r_1}{r_8} \right)^3
\]

(3)

As shown in Fig.7, the electronic polarizability of each salt decreases with increasing coordination number. Two plots of each salt at the coordination number 8 represent the values measured at different temperatures. The same coordination number dependence of the electronic polarizabilities are observed for the other salts investigated.
Composition Dependence of Electronic Polarizability

The electronic polarizabilities of the binary melts observed are plotted against composition and shown in Fig. 8. The electronic polarizabilities of the binary melts, except LiBr-CsBr binary melts, agree well with the additive values. But the electronic polarizability of LiBr-CsBr binary melts deviates from the additive values by 1% at 50 mol% CsBr exceeding the limits of experimental error. As discussed above, the coordination number and the inter-ionic distance are the important factors for the electronic polarizability of the melts. In case of the binary melts of LiBr-CsBr, the molar volume deviates significantly from additive rule by maximally 3% at 10~40 mol% CsBr. This may be because of the difference of the ionic sizes of LiBr-CsBr binary melts, Li⁺, Cs⁺ or Br⁻, is the largest of the binary melts investigated. Composition dependence of electronic polarizability will be discussed in detail in the following. It seems that the volume expansion is due to the decrease in the mean coordination number or the increase in the inter ionic distance. So it is considered that the positive deviation of the electronic polarizability of LiBr-CsBr binary melts is due to the decrease in the mean coordination number, because the electronic polarizabilities of the salts are mainly influenced by the change in the coordination number.

CONCLUSION

The refractive index of the single and the LiCl-CsCl, LiBr-CsBr, NaCl-CsCl, NaCl-NaI, KCl-KI and CsCl-CsI binary melts have been measured with high accuracy at the wave length range of 470 to 670 nm. The electronic polarizabilities of the melts have been determined from the measured refractive indices by the Lorentz-Lorenz equation. The factors which affect the electronic polarizabilities of the salts have been investigated. The conclusion to be drawn from these results is as follows:
1. The electronic polarizability varies with the change in coordination number and inter-ionic distance.
2. The coordination number is the most important factor of the electronic polarizabilities of the salts.
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Figure 1. Schematic Diagram of Apparatus.

- LiBr–CsBr at 873K
- NaCl–KCl at 1073K
- CsI–CsCl at 973K

Figure 3. Isotherms of Refractive Index for Alkali Halide Binary Melts.

- CsI at 920.8 K
- 25.0 mol% CsCl at 859.0 K
- 50.0 mol% CsCl at 824.5 K
- 76.9 mol% CsCl at 868.5 K
- 90.9 mol% CsCl at 901.4 K

Figure 4. Dispersion in Refractive Index for CsCl-CsI Binary Melts.
Figure 5. Temperature Dependence of Electronic Polarizability for CsCl-CaI Binary Melts.

Figure 6. Correlation Between Electronic Polarizability and Inter-ionic Distance for Cesium Halides.

Figure 7. Correlation Between Electronic Polarizability and Coordination Number for Cesium Halides.

Figure 8. Isotherms of Electronic Polarizability for Alkali Halide Binary Melts.