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Electronic polarizability of a Sm³⁺ ion estimated from refractive indexes and molar volumes of molten SmCl₃

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Abstract

The refractive indexes and the molar volumes of molten SmCl_3 were measured by goniometry and dilatometry, respectively. The electronic polarizability of a Sm^{3+} ion was estimated from these data to be $1.14 \times 10^{-30} \text{m}^3$ according to the Clausius–Mossotti equation. The correlation between the electronic polarizability of an ion and the ionic radius was also discussed. © 1999 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

The electronic polarizability of an ion is one of the most fundamental and physicochemical pieces of data in analysing the structure of condensed matter such as molten salts by computer simulation [1]. The refractive indexes of are needed for molten salts estimation of the polarizabilities of constituent ions, and especially the values extrapolated to infinite wavelength are directly related to the electronic polarizabilities of molecules or ions in the melts. Furthermore, the index data is indispensable for the measurement of hypersonic velocity in a melt by Brillouin scattering, [2] to characterize the high temperature relaxation process, and also for the evaluation of thermal conductivity of the melt by wave-front shearing interferometry [3,4] in which the temperature derivatives of the indexes are required. The polarizability of a molecule, an atom or an ion in a condensed state has been well known to be closely related to its volume [5,6]. In this work, the electronic polarizability of a Sm³⁺ ion in molten SmCl₃ was determined from the data of the refractive index and molar volume for molten SmCl₃. The results are discussed in comparison with those of the other lanthanide ions which have so far been reported in [6-10].

2. Experimental

The chemical SmCl₃ was synthesized by the reaction of

 Sm_2O_3 and NH₄Cl at 623 K for 2 h [11], and the obtained crude chloride was purified by sublimation at 1273 K for 8 h under reduced pressure in order to remove impurities such as unreacted oxides, excess NH₄Cl, oxychloride byproducts and water. The refractive index measurements were made in the temperature range of 973 to 1093 K using visible light at eight wavelengths, namely λ =470, 500, 530, 560, 590, 620, 650 and 680 nm, in which the angle of minimum deviation θ_{λ} was practically measured with a goniometer. The relation between the refractive index n_{λ} and the angle θ_{λ} is expressed in the form,

$$n_{\lambda} = \sin\{(\theta + A)/2\}/\sin(A/2) \tag{1}$$

where A is the apex angle of a hollow prismatic cell made of fused silica, which was calibrated beforehand by use of a reference material KNO_3 [12]. The molar volume of the melt was measured by dilatometry. The apparatus and procedure were described in detail elsewhere [13].

3. Results and discussion

The molar volume, $V_{\rm m}$, of molten SmCl₃ was measured in the temperature range of 947 to 1073 K, and represented as a linear function of temperature, $V_{\rm m} = 55.54 + 1.946 \times 10^{-3} T$ by the least-squares method, where $V_{\rm m}$ is in 10^{-6} m³mol⁻¹ and T in K. The standard error in this regression was estimated at 5.76×10^{-8} m³mol⁻¹.

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The refractive indexes of molten SmCl_3 measured with visible light at fixed wavelengths decreased linearly with increasing temperature. Since the refraction phenomenon is due to light scattering on and around the atom or ion, that is, the electron clouds, the magnitude of refractive index should be proportional to the number density of the species in the melt. Thus, the refractive indexes decreased linearly with increasing temperature. On the other hand, the refractive indexes decreased curvilinearly with increasing wavelengths at a given temperature, that is, the normal dispersion of refractive indexes was observed for molten SmCl_3 (see Fig. 1) as was also the case reported previously [14]. This phenomenon was well expressed by an equation called the modified Cauthy's relation [10,15,16] as shown below,

$$n(\lambda,T) = \sum_{i=0}^{2} (P_i \cdot \lambda^{-2i}) + \left\{ \sum_{i=0}^{2} (Q_i \cdot \lambda^{-2i}) \right\} \cdot T$$
(2)

where P_i and Q_i are the constants determined by the nonlinear least-squares method as follows, $P_0 = 1.9373$, $P_1 = -4.5538 \times 10^4$ nm², $P_2 = 8.7113 \times 10^9$ nm⁴, $Q_0 = -3.0997 \times 10^{-4}$ K⁻¹, $Q_1 = 7.6683 \times 10$ nm²K⁻¹ and $Q_2 = -1.1624 \times 10^7$ nm⁴K⁻¹. The standard error was quite small, being evaluated to be about 8×10^{-4} in the temperature range of 973 to 1073 K. The refractive indexes of molten SmCl₃ at 1013 K for the light at wavelength 560 nm was calculated to be 1.7448 with Eq. (2) and the above parameters. This value was very close to the experimental one, 1.7448 at the same temperature and wavelength. It proved from this finding that Eq. (2) was a very good empirical equation of refractive index.



Fig. 1. Refractive index variation of molten SmCl_3 with temperature and wavelength.

The electronic polarizability α_{∞} of a molecule in a melt is given by the Clausius–Mossotti equation,

$$\alpha_{\infty} = \{3/(4\pi N_{\rm A})\}\{(n_{\infty}^2 - 1)/(n_{\infty}^2 + 2)\} \cdot V_{\rm m}$$
(3)

where the subscript ∞ refers to infinite wavelength, N_A Avogadro constant and n_{∞} the value of n_{λ} at $\lambda = \infty$. With the aid of Eq. (2), n_{∞} can be quite easily calculated to be $P_0 + Q_0 T$. Fig. 2 shows the temperature dependence of α_{∞} obtained for a stoichiometric unit SmCl₃ in melt, the average value of which was computed to be $10.59 \times$ 10^{-30} m³ in the temperature range of 973 to 1073 K. According to the Clausius-Mossotti equation, the electronic polarizability should be independent of temperature due to cancellation between the dispersion term of $(n_{\infty}^2 1)/(n_{\infty}^2+2)$ and the molar volume $V_{\rm m}$, but α_{∞} slightly decreased linearly with increasing temperature in this work. This phenomenon is not necessarily essential and may be caused by the fact that the experimental error in $V_{\rm m}$ is lager than that in n_{∞} , so to say, being much larger than that in $(n_{\infty}^2 - 1)/(n_{\infty}^2 + 2)$.

In the fully ionic description of the molten salt with a stoichiometry CA₃, the α_{∞} is separable into the two contributions from cation $\alpha_{\rm C}$ and anion $\alpha_{\rm A}$ in the following manner,

$$\alpha_{\infty} = \alpha_{\rm C} + 3\alpha_{\rm A} \tag{4}$$

Since $\alpha_{\rm C}$ and $\alpha_{\rm A}$ corresponded to the electronic polarizabilities of a Sm³⁺ ion and a Cl⁻ ion, respectively, in molten SmCl₃, the electronic polarizability of a Sm³⁺ ion, α_{∞} (Sm³⁺), was evaluated by subtracting the contributions of three Cl⁻ ions from the value of α_{∞} for a SmCl₃ unit. However, the electronic polarizability of the Cl⁻ ion, α_{∞} (Cl⁻), could not be estimated from α_{∞} until a unique hypothesis [17–19] for the ion with less electrons, that is, the $\alpha_{\rm C}$ of Li⁺ ion has been reported by Pauling [20] to be



Fig. 2. Temperature dependence of electronic polarizability of a stoichiometric unit of $SmCl_3$ in a melt.

 0.029×10^{-30} m³. According to the calculation process and the assumption for the electronic polarizability of a Li⁺ ion as mentioned above, the α_{∞} (Cl⁻) was calculated from α_{∞} of a LiCl [21,22] unit to be 3.15×10^{-30} m³ and thus the α_{∞} (Sm³⁺) was equal to 1.14×10^{-30} m³ in consequence.

The electronic polarizabilities of alkali ions, alkaline earth ions and halide ions have been well known to be closely related to the volumes of ions [6,10]. As shown in Fig. 3, α_{∞} 's were approximately proportional to the values r^3 , where r was the effective ionic radius recommended by Shannon [23], but the correlation between α_{∞} and r^3 in lanthanide ions shifted from that in alkali and halide ions. The electron shells of alkali and halide ions possess the same electron structure as the inert gases in which the inner orbitals are completely filled and the outer shells m consist of s- and p-orbital electrons having an electron configuration such as ns^2np^6 (n=principal quantum number). On the other hand, the peculiarity of the lanthanide



Fig. 3. Correlation between the electronic polarizability of an ion (α_{∞}) and the ionic radius $(r) \odot: Sm^{3+}$.

ions can be explained by their own special electronic configuration. Since the lanthanide ions possess antibonding electrons in 4f orbital which screen the electrostatic interaction between the nucleus and the outer electrons, their electronic polarizabilities are larger than otherwise expected. From this point of view, the ionic radius should be excluded from the factors which essentially govern the magnitude of the electronic polarizability of an ion. The nuclear charge of an ion should also be excluded in as much as it directly affects the ionic radius, since an ion with the larger nuclear charge has the smaller ionic radius. Importance in evaluation of the electronic polarizability of an ion consist in the number density and the electron configuration of constituent species.

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