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Refractive indexes and electronic polarizabilities of molten $HoCl_3$–NaCl and $HoCl_3$–KCl mixtures

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Abstract

The refractive indexes of molten $HoCl_3$–NaCl and $HoCl_3$–KCl mixtures were measured by goniometry using visible light at eight wavelengths and expressed as functions of both temperature and wavelength into empirical formulas by a least-squares method. The electronic polarizabilities of ions in the mixture melts were obtained from the data of refractive indexes and molar volumes, and the polarizability of a Ho^{3+} ion was evaluated to be about 0.98×10^{-30} m^3 according to the Clausius–Mossotti equation. The isotherms of these properties show little deviation from their additivity line. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Refractive index; Electronic polarizability; Molar volume; Ionic melt; $HoCl_3$ mixtures

1. Introduction

Refractive index is one of the useful optical properties reflecting ionic or molecular behaviors in the melts. Furthermore, the index data are necessary for the measurement of hypersonic velocity in melt by Brillouin scattering [1] to characterize the high temperature relaxation process, in particular, having been indispensable for the estimation of thermal conductivity by wave-front shearing interferometry [2,3]. Comparison of the molar volume data between crystal and melt is capable of a simple evaluation for structural change on melting, in particular being of a potential use in well understanding the nearest neighbour coordination of unlike ionic pair. The electronic polarizabilities of ions or molecules in molten salts are generally estimated from the refractive indexes extrapolated to infinite wavelength and the molar volumes on the basis of evaluation of the effective local field around the species. It has been so far considered for molten salt system that refractivity should give information concerning the structure of these ionic melts, but strictly speaking, the polarizability data are fundamental parameters describing the dispersion force term in pair potentials as was used in the analysis of structure in condensed matter such as molten salts by computer simulation [4].

The electronic polarizabilities of the lanthanide ions, alkali ions and halide ions have already been reported [5–10] and well known to be closely related to the effective volumes of ions [8,11,12]. The main purpose of the present work is to obtain the refractive index and the electronic polarizabilities for molten salt mixtures and ions in order to acquire the information concerning the mutual influence of ions in the mixture on structure and the other physicochemical properties.

2. Experimental

2.1. Chemicals and melt preparation

The chemicals NaCl and KCl were of analytical reagent grade, which separately dehydrated under reduced pressure of about 6.7×10^{-2} Pa for 8 h just below the respective melting points, melted and rapidly quenched.

The hygroscopic chemical $HoCl_3$ was synthesized according to the reaction [13,14] at 623K for 2.5 h,

$$Ho_2O_3 + 6NH_4Cl \rightarrow 2HoCl_3 + 6NH_3 + 3H_2O \tag{1}$$

The obtained crude $HoCl_3$ was purified by sublimation at 1273 K for 8 h under reduced pressure in order to remove impurities such as unreacted oxides, excess NH_4Cl, oxychloride by-products and water. The sublimation apparatus has been fully described elsewhere [15]. The mole ratio of the mixtures was determined by accurately weighing out

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each component in a glove box filled with dry N_2 gas, melted for well mixing, rapidly quenched, and stored in ampoules.

2.2. Method

A hollow prismatic cell made of fused silica was used for the goniometric measurement of refractive index and experiments were made in the temperature range of 1073–1173 K using visible light at eight wavelengths, namely 440, 470, 500, 530, 560, 590, 620 and 650 nm. The angle of minimum deviation θ_λ was practically measured with a goniometer. The relation between refractive index n_λ and the angle θ_λ is expressed by the following formula,

$$n_\lambda = \sin\{(\theta_\lambda + A)/2\}/\sin(A/2) \qquad (2)$$

where A is the apex angle of the prismatic cell, which was calibrated beforehand with the aid of a reference material KNO_3 [16]. The molar volumes of the melts were measured by dilatometry, the data of which were employed in calculation of the electronic polarizabilities of ions. The apparatus and procedures were described in detail elsewhere [6,7].

3. Results and discussion

3.1. Molar volume

The molar volumes V_m values of molten $HoCl_3$–NaCl and $HoCl_3$–KCl mixtures were illustrated in Fig. 1. The molar volumes increased linearly with increasing temperature in the whole compositions. By simply comparing molten $HoCl_3$ with solid state $HoCl_3$, the volume expansion on melting V_m was estimated to be 1.3%, which was quite small in comparison with 19–26% for light lanthanide chlorides (see Table 1). The V_m values are expressed as functions of mole fraction of $HoCl_3$, X, and temperature, T, by the least-squares fitted empirical equation,

$$V_m(X,T) = \sum_{i=0}^{3} (a_i \cdot X^i) + \left\{ \sum_{i=0}^{3} (b_i \cdot X^i) \right\} \cdot T \qquad (3)$$

where a_i and b_i are the constants, V_m in 10^{-6} m^3 mol^{-1} and T in K. The values of a_i and b_i for molten $HoCl_3$–NaCl and $HoCl_3$–KCl systems are given in Table 2. Fig. 2 shows the molar volume variations with composition in molten $HoCl_3$–NaCl and $HoCl_3$–KCl mixtures at 1113 K. A straight line in Fig. 2 indicates the additivity,

$$V_{mix} = X_1 V_1 + X_2 V_2 \qquad (4)$$

where V_{mix} is the molar volume of the mixture melt, and X_i and V_i refer to the molar fraction and molar volume of the i-th component, respectively. It was demonstrated that the deviations from additivity were within the range of 5%.

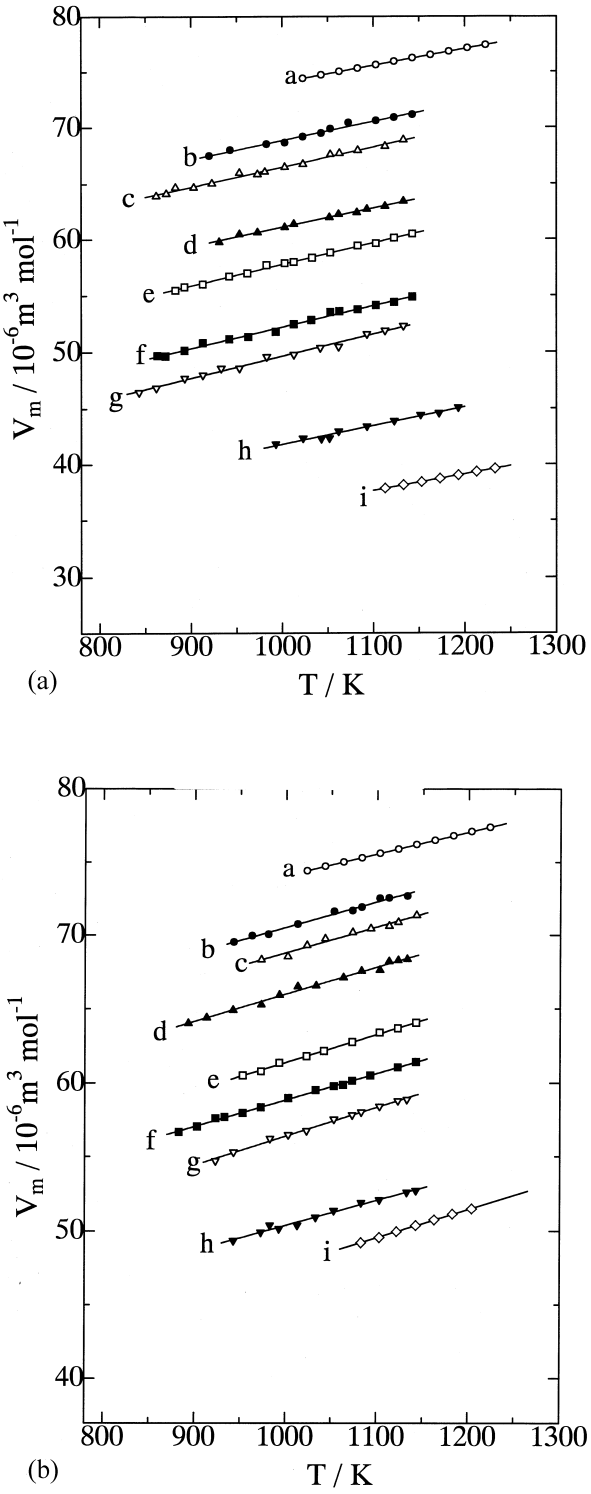

Fig. 1. (a) Molar volume of molten $HoCl_3$–NaCl system. $HoCl_3$ (mol%): (a) 100; (b) 87.5; (c) 75.0; (d) 62.5; (e) 50.0; (f) 37.5; (g) 25.0; (h) 12.5; (i) 0.0%: (b) Molar volume of molten $HoCl_3$–KCl system. $HoCl_3$ (mol%): (a) 100; (b) 87.5; (c) 75.0; (d) 62.5; (e) 50.0; (f) 37.5; (g) 25.0; (h) 12.5; (i) 0.0.

Table 1
Classification of pure Lanthanide trichloride melts on the basis of structural information

Salt	Symmetry and structure type of crystal	m.p (K)	ΔV^a (%)	Molecular weight	Cationic radius (nm)
$LaCl_3$	Hexagonal UCl_3	1150	19.1	245.26	0.103
$PrCl_3$	Hexagonal UCl_3	1059	21.0	247.27	0.099
$NdCl_3$	Hexagonal UCl_3	1041	21.8	250.60	0.098
$SmCl_3$	Hexagonal UCl_3	935	24.5	256.72	0.096
$GdCl_3$	Hexagonal UCl_3	875	26.4	263.63	0.094
YCl_3	Monoclinic $AlCl_3$	987	0.5	195.26	0.090
$HoCl_3$	Monoclinic $AlCl_3$	993	1.3	271.29	0.090
$ErCl_3$	Monoclinic $AlCl_3$	1049	5.3	273.56	0.089
NaCl	Cubic NaCl	1073	38.0	58.45	0.099
KCl	Cubic NaCl	1043	28.5	74.56	0.137
$CaCl_2$	Orthorhombic $CaCl_2$	1055	0.4	110.99	0.100
$ZnCl_2$	Tetragonal	591	18.5^b	136.30	0.060

[a] $\Delta V = 100(V_l^{Tm} - V_s)/V_s$, where V_l^{Tm} is the molar volume of liquid at melting point, V_s the molar volume of solid (crystal).
[b] $\Delta V = 17.4\%$ in case of monoclinic crystal.

3.2. Refractive index

The refractive indexes of molten $HoCl_3$–NaCl and $HoCl_3$–KCl measured with visible light at fixed wavelengths decreased linearly with increasing temperature in the same manner previously reported [8,10,16]. Since the refraction phenomenon occurred by light scattering on and around the atom or ion, namely, the electron clouds, the magnitude of refractive index should originally be proportional to the number density of the species in the melt, and in consequence the refractive indexes decreased linearly with increasing temperature (see Figs. 3 and 4). The same tendency was recognized in the molten $HoCl_3$–KCl system. On the other hand, the refractive indexes decreased curvilinearly with increasing wavelengths at a given temperature (see Fig. 4), and this phenomenon was found to correspond to normal dispersion of refraction [8,17], which could be expressed by the Cauchy's dispersion formula,

$$n(\lambda) = p + q/\lambda^2 + r/\lambda^4 \tag{5}$$

Furthermore, a series of phenomena were well reproduced by the so-called modified Cauchy's relation [7,12,18],

$$n(\lambda,T) = \sum_{i=0}^{2} (P_i \cdot \lambda^{-2i}) + \left\{ \sum_{i=o}^{2} (Q_i \cdot \lambda^{-2i}) \right\} \cdot T \tag{6}$$

where P_i and Q_i were the constants determined by the nonlinear least-squares method and λ is the wavelength. The results for molten $HoCl_3$–NaCl and $HoCl_3$–KCl mixtures are tabulated in Table 3, where δ is the standard error on fitting.

Table 2
Parameters in empirical equations of molar volumes for molten $HoCl_3$–NaCl and $HoCl_3$–KCl systems

	System	
	$HoCl_3$–NaCl	$HoCl_3$–KCl
$10^{-1}\ a_0$	1.991	2.797
$10^{-1}\ a_1$	−8.797	4.391
$10^{-1}\ a_2$	1.060	−3.275
$10^{-1}\ a_3$	−6.601	1.985
$10^{2}\ b_0$	1.602	1.956
$10^{2}\ b_1$	4.207	−1.097
$10^{2}\ b_2$	−1.062	2.534
$10^{2}\ b_3$	6.317	−1.886
δ	0.861	0.742

δ, standard error ($\times 10^{-6}$ m^3 mol^{-1}).

3.3. Electronic polarizability

The electronic polarizability α_∞ of an 'apparent' molecule in a melt is defined by the semiclassical Clausius–

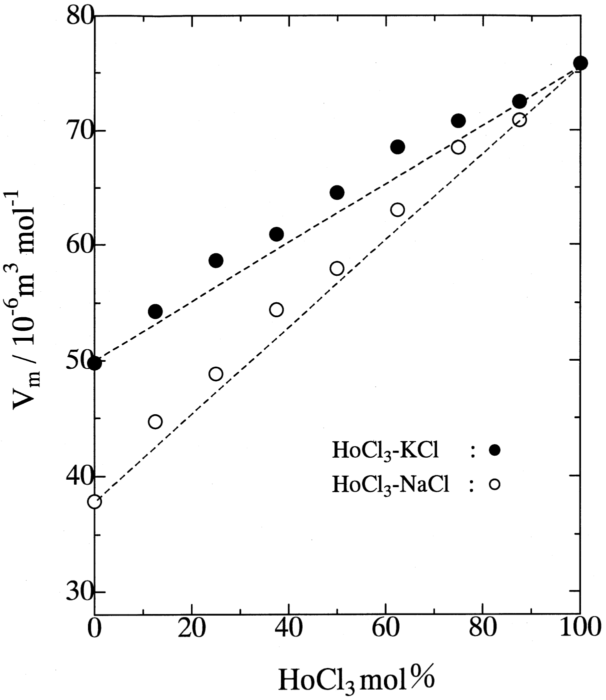

Fig. 2. Molar volume variation with composition in molten $HoCl_3$–NaCl and $HoCl_3$–KCl systems at 1113 K.

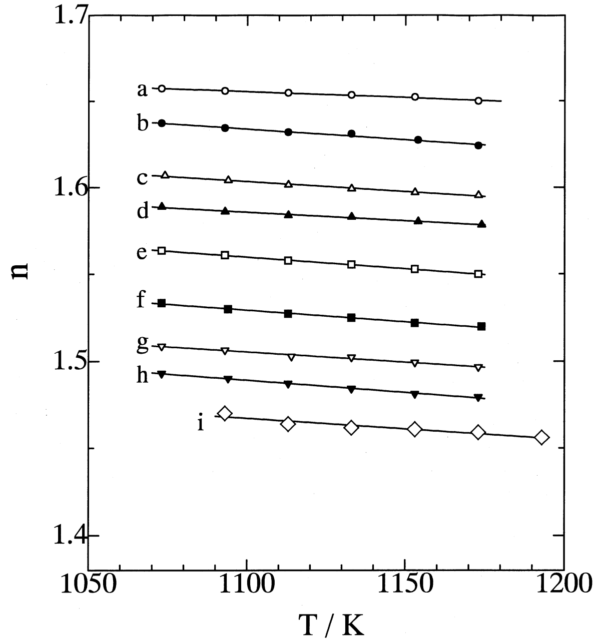

Fig. 3. Refractive indexes of molten $HoCl_3$–NaCl system at 560 nm. $HoCl_3$ (mol%): (a) 100; (b) 87.5; (c) 75.0; (d) 62.5; (e) 50.0; (f) 37.5; (g) 25.0; (h) 12.5; (i) 0.0.

Mossotti equation (similar to the Lorentz–Lorentz equation),

$$\alpha_\infty = \{3/(4\pi N_A)\}\{(n_\infty^2 - 1)/(n_\infty^2 + 2)\} \cdot V_m \tag{7}$$

where the subscript ∞ refers to infinite wavelength, N_A is Avogadro constant and n_∞ the value of n_λ at $\lambda = \infty$. With the aid of Eq. (6), n_∞ can be quite easily evaluated to be $P_0 + Q_0 T$. The temperature dependence of α_∞ obtained for a $HoCl_3$–NaCl stoichiometric unit in melt and the isotherms of α_∞ for the mixtures are shown in Figs. 5 and 6, respectively. According to the Clausius–Mossotti equation, the electronic polarizability should be independent of temperature because of cancellation between the dispersion term of $(n_\infty^2 - 1)/(n_\infty^2 + 2)$ and the molar volume V_m in Eq. (7), but α_∞ slightly decreased or increased linearly with increasing temperature in the present work. This phenomenon may be caused by the fact that experimental error in V_m was larger than that in n_∞, that is, being much larger than that in $(n_\infty^2 - 1)/(n_\infty^2 + 2)$. If additivity is assumed to apply to α_∞ as well as Eq. (4), the following relation holds good,

$$\alpha_{mix} = X_1 \alpha_1 + X_2 \alpha_2 \tag{8}$$

where α_i refers to the electronic polarizability of the i-th component. The deviations from additivity are turned out to be within a few percent (see Fig. 6).

In case of molten salts which are composed of several different chemical particles, additivity is expressed as follows,

$$(n_\infty^2 - 1)/(n_\infty^2 + 2) = (4\pi/3)\sum N_j \alpha_j \tag{9}$$

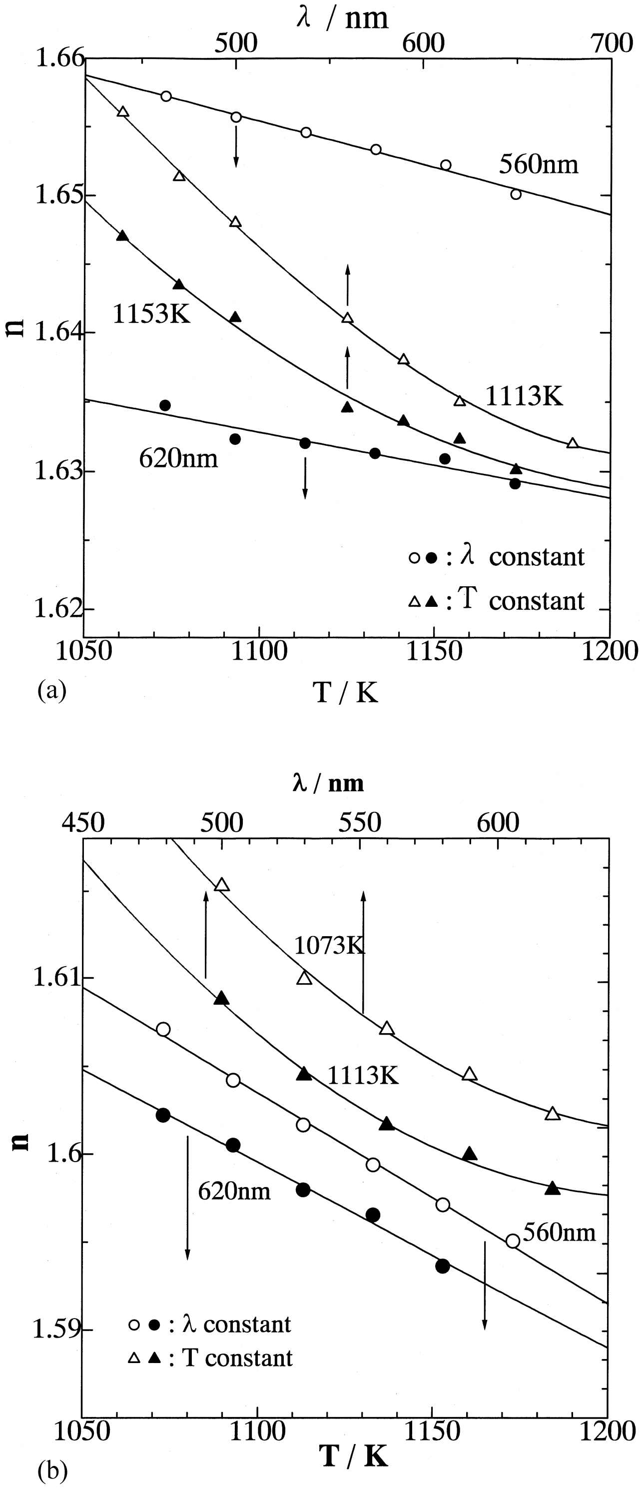

Fig. 4. Refractive index variation of molten $HoCl_3$–NaCl with temperature and wavelength. (a) $HoCl_3$:NaCl = 100:0 (mol%); (b) $HoCl_3$:NaCl = 75:25 (mol%).

where N_j and α_j are the number of j-th particles (ions) per unit volume and the electronic polarizability of the j-th particles, respectively. For example, in the fully ionic description of the molten salt with a stoichiometry CA_3,

Table 3
Parameters in empirical equations of refractive index for molten $HoCl_3$–NaCl and $HoCl_3$–KCl systems

X	P_0	$10^{-5}\ P_1$	$10^{-9}\ P_2$	$10^4\ Q_0$	$10^{-2}\ Q_1$	$10^{-7}\ Q_2$	δ
$HoCl_3$-NaCl							
100.0	1.686	2.096	−1.606	−5.385	−9.674	1.476	0.390
87.5	1.946	−1.213	1.707	−4.335	1.709	−2.285	0.620
75.0	1.746	−4.339	1.095	−1.911	5.536	−1.245	0.592
62.5	1.824	−9.735	1.585	−3.073	1.391	−2.105	0.497
50.0	1.712	7.820	−6.348	−2.193	−7.750	6.657	0.950
37.5	1.683	−4.008	9.837	−2.292	6.405	−1.232	0.815
25.0	1.635	−2.640	5.057	−2.030	5.115	−7.720	0.543
12.5	1.520	3.060	−1.312	−8.948	−1.455	−4.078	0.620
0.0	1.786	−1.801	2.750	−3.900	2.089	−3.071	0.520
$HoCl_3$−KCl							
100.0	1.686	2.096	−1.606	−5.385	−9.674	1.476	0.390
87.5	1.883	−1.230	2.606	−3.088	1.600	−3.184	0.435
75.0	1.628	0.786	−0.666	−1.013	−0.896	0.866	0.494
62.5	1.565	4.793	−2.080	−0.716	−4.326	1.474	0.697
50.0	1.641	2.720	−3.357	−1.567	−2.589	3.936	0.822
37.5	1.713	−5.313	9.162	−2.668	7.018	−1.090	0.815
25.0	1.622	−3.504	6.507	−1.994	5.219	−8.159	0.256
12.5	1.890	2.091	2.091	−4.659	2.023	−2.595	1.520
0.0	1.752	1.463	−1.593	−3.665	−1.713	1.871	1.359

X, $HoCl_3$ (mol%); δ, standard error ($\times 10^{-3}$); temperature range, 1073–1173 K.

the α_∞ is divided into the two contributions of cation, α_C, and anion, α_A, in the following manner,

$$\alpha_\infty = \alpha_C + 3\alpha_A \tag{10}$$

As for molten $HoCl_3$, α_C and α_A correspond to the electronic polarizabilities of a Ho^{3+} ion and a Cl^- ion, respectively. The electronic polarizability of a Ho^{3+} ion, $\alpha_\infty(Ho^{3+})$, was estimated by subtracting the contributions of three Cl^- ions from the value of α_∞ for a $HoCl_3$ unit. However, the electronic polarizability of the individual ions cannot be calculated from α_∞ until the specific hypothesis [12,19,20] was introduced for the ion with less electron such as Li^+ ion. The value of $\alpha_\infty(Li^+)$ has already been calculated in Ref. [21] to be 0.029×10^{-30} m^3. According to the calculation process and the assumption for α_∞ as mentioned above, the electronic polarizability of the Cl^- ion, $\alpha_\infty(Cl^-)$, was computed from α_∞ of LiCl [7,12] unit to be 3.17×10^{-30} m^3, therefore, the α_∞ values of Na^+, K^+ and Ho^{3+} were equal to 0.33, 1.10 and 0.98×10^{-30} m^3, respectively.

The electronic polarizabilities of alkali, alkaline earth

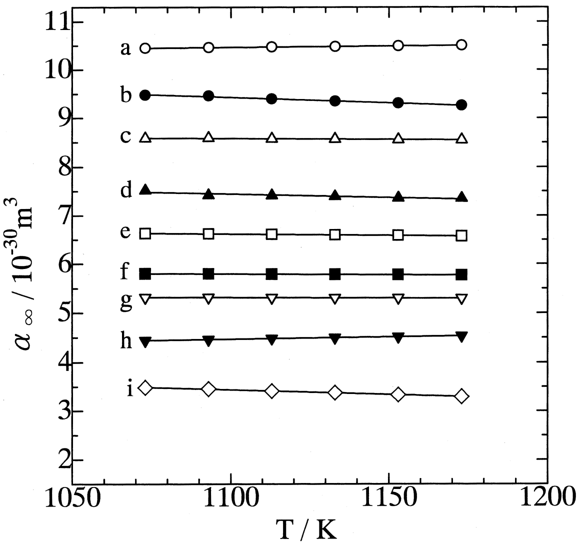

Fig. 5. Temperature dependence of electronic polarizability for molten $HoCl_3$–NaCl system. $HoCl_3$ (mol%): (a) 100; (b) 87.5; (c) 75.0; (d) 62.5; (e) 50.0; (f) 37.5; (g) 25.0; (h) 12.5; (i) 0.0.

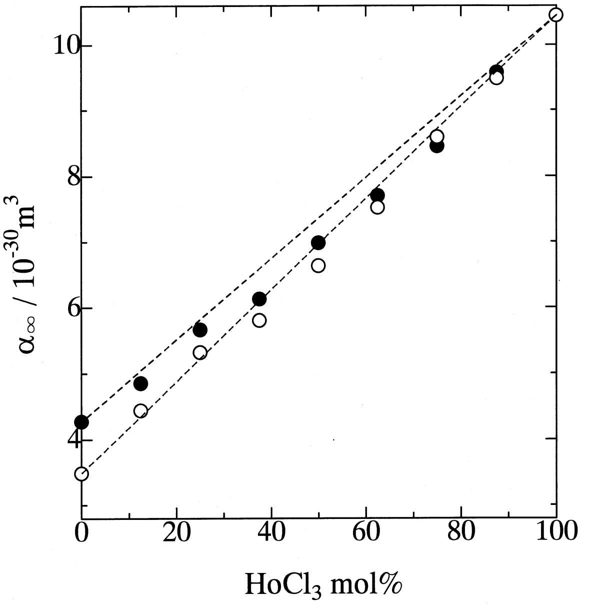

Fig. 6. The electronic polarizability variation with composition in molten $HoCl_3$–NaCl (○) and $HoCl_3$–KCl (●) systems at 1073 K.

ion and halide ions are well known to be closely related to the volumes of ions [22,23], as was also demonstrated in Fig. 7. α_∞ values were approximately proportional to the value r^3, where r was the effective ionic radius recommended by Shannon [24], but the correlation between α_∞ and r^3 in lanthanide ions shifted from that in alkali and halide ions, the reason of which has been described in detail elsewhere [12]. The $\alpha_\infty(\mathrm{Ho}^{3+})$ was well along the straight line which was best fitted for the other lanthanide ions having antibonding electron configuration in 4f orbitals. The correlation between α_∞ and r^3 for lanthanide ions can be expressed in the following form by the least-squares fitting,

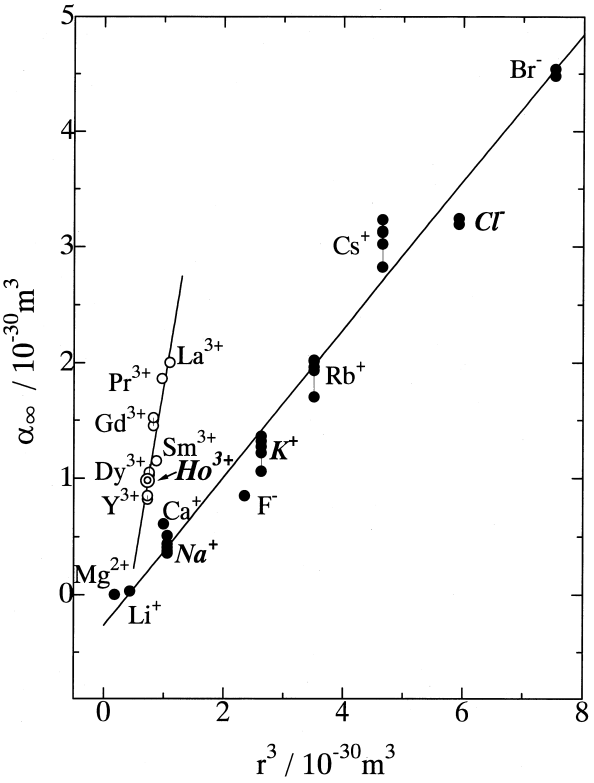

Fig. 7. Correlation between the electronic polarizability of an ion (α_∞) and the effective ionic radius (r). (⊚) Ho^{3+}.

$$\alpha_\infty = -1.375 + 3.176r^3 \tag{11}$$

where r refers to the effective ionic radius of trivalent lanthanide ions with six-fold coordination. Taking into account the trends in Eq. (11), behaviors similar to that observed in the lanthanide ions might appear at the ionization of the other inner transition elements.

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