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Molar volume variation and ionic conduction in molten $ErCl_3$–NaCl and $ErCl_3$–KCl systems

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Abstract

Molar conductivities (Λ) of molten $ErCl_3$–NaCl and $ErCl_3$–KCl systems were evaluated using the data of molar volume, V_m, and conductivity, κ, which were measured as a function of the mole fraction of $ErCl_3$ and temperature, by dilatometry and a conventional a.c. technique, respectively. The Λ values of molten $ErCl_3$ were smaller than those of molten YCl_3, in which a loose disordered network of edge-sharing octahedral units has been reported to exist. The Λ values of $ErCl_3$–NaCl and $ErCl_3$–KCl systems increased with decreasing $ErCl_3$ concentration, x, and in the range $x > 0.25$ the increment in Λ with x was much smaller than that in the range of $x < 0.25$. In a series of molten rare earth chlorides, Λ values have been found to be affected qualitatively by cationic radii and the types of linkage, that is, corner- or edge-sharing of octahedral units.

Keywords: Erbium chloride; Alkali chloride; Melt; Molar conductivity

1. Introduction

Several reports have so far been published on the structures of rare earth chlorides (RCl_3) by X-ray diffraction [1,2], neutron diffraction [3] and Raman spectroscopy [1,4–6], revealing that there existed in melt the octahedral complex anion RCl_6^{3-} and a loose disorderd network of corner- or edge-sharing octahedral units. Moreover, the measurements of conductivities are of much use in studying the dynamics of molten salts, reflecting the average dynamic structure. The molar conductivities of several rare earth chlorides were reported [7–10] and the results suggested that the existence of dimeric or more polymeric complex anions may be presumed in these melts. The structures of molten $ErCl_3$, $ErCl_3$–3NaCl and $ErCl_3$–3KCl were investigated [2,11] and the existence of octahedral complex ions, $ErCl_6^{3-}$, was confirmed. Also expected is some clustering of distorted octahedra with edge-sharing. It may be of interest to investigate the physical properties of molten $ErCl_3$ and discuss the results in comparison with the other molten rare earth chlorides. In this work the molar volumes and the conductivities of molten $ErCl_3$–NaCl and $ErCl_3$–KCl systems were measured individually, and the molar conductivities were estimated.

2. Experimental

The chemicals NaCl, KCl and KNO_3 of analytical reagent grade were dried under reduced pressure for 8 h at temperatures just below the respective melting points, melted, quenched, and stored in ampoules. The hygroscopic chemical $ErCl_3$ was synthesized by the reaction of Er_2O_3 and NH_4Cl, and purified by sublimation at 1273 K under reduced pressure to remove impurities such as oxides, NH_4Cl, and water. The sublimation apparatus employed has fully been described in Ref. [8]. The mole ratio of the mixture was determined by accurately weighing out each component in a glove-box filled with dry N_2 gas. The molar volumes of molten $ErCl_3$–NaCl and $ErCl_3$–KCl systems were measured as the functions of the mole fraction of $ErCl_3$ by dilatometry, as reported in Ref. [12]. A conventional a.c. technique was applied to attain the polarization-free resistance of the melt by varying the input frequency from 1.0 to 10 kHz and

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extrapolating the obtained impedance to infinite frequency. The disk-like electrodes were made of platinum. The inner surface of the furnace tube was coated by a very thin gold film in order to reflect the infrared light and thus achieve a uniform temperature distribution. The U-shaped conductivity cell made of transparent fused silica was calibrated before each experimental run with pure dried KNO_3 melt [13]. The values of the real resistance were corrected by subtracting the resistance in the leads (0.8 S^{-1}) from the apparent resistance.

The V_m and κ values were measured over the temperature ranges of 765 to 1213 K and 752 to 1178 K, respectively, which were chosen in view of the phase diagram [14,15].

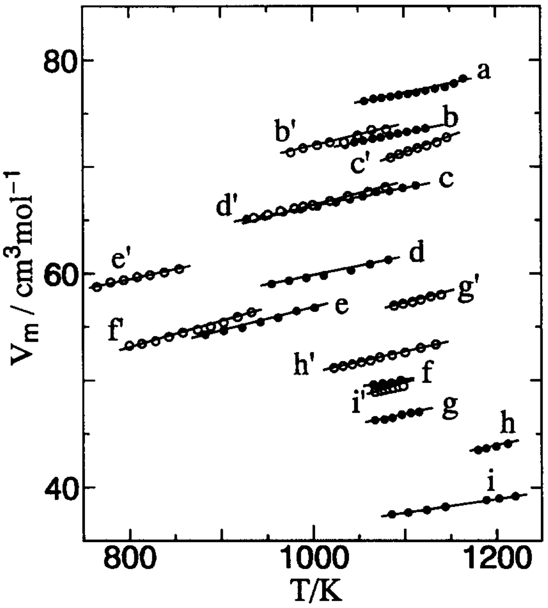

Fig 1. Molar volume of molten $ErCl_3$-NaCl and $ErCl_3$-KCl systems. ●, $ErCl_3$-NaCl system: ($ErCl_3$ mol%) a,100.00; b, 87.30; c, 74.87; d, 62.41; e, 49.97; f, 37.59; g, 24.97; h, 12.50; i, 0.00. ○, $ErCl_3$-KCl system: ($ErCl_3$ mol%) b′, 87.37; c′, 75.02; d′, 62.75; e′, 49.79; f′, 37.44; g′, 25.06; h′, 12.46, i′, 0.00.

3. Results and discussion

The molar volumes could be well fitted as linear functions of temperature for fixed mole fractions only if the temperature ranges were not too large (see Fig. 1). The results were similar to those of the other rare earth chlorides described in Refs. [12,16,17]. As for the molten $ErCl_3$ the equation was given as follows: $V_m = 57.71 + 0.01738\ T$, with T being the absolute temperature.

The volume change of monoclinic $ErCl_3$ on melting (1049 K) was calculated in the way described in Ref. [2] to be 5.30%, using the crystallographical data [18]. This value, when compared with those of the other rare earth chlorides [19] (see Table 1), suggests that the short range arrangement in molten $ErCl_3$ is not so different from that in solid. In fact the coordination number of Cl^- around Er^{3+} was estimated to be 5.8 by X-ray diffraction of molten $ErCl_3$ [2], which is close to 6 in crystal [18].

For the molar volumes of molten binary mixtures the following empirical equation has been reported [16],

Table 1
Molar conductivity Λ at 1.1 T_m at T_{1150} for pure molten salt

Salt	Symmetry and structure-type of crystal	T_m (K)	1.1 T_m (K)	Λ (10^{-4} S m^2 mol^{-1})		V_m (10^{-6} m^3 mol^{-1})		ΔV[a] (%)	Molecular weight	Cationic radius [22] (Å)
				1.1 T_m	T_{1150}	1.1 T_m	T_{1150}			
$LaCl_3$	Hexagonal UCl_3	1150 [19]	1265	42.52 [9]	33.44	78.27 [17]	76.31	19.1	245.26	1.03
$PrCl_3$	Hexagonal UCl_3	1059 [19]	1165	32.10 [7]	30.93	76.81 [16]	76.43	21.0	247.27	0.99
$NdCl_3$	Hexagonal UCl_3	1041 [23]	1145	27.48 [8]	27.85	76.16 [16]	76.26	21.8	250.60	0.98
YCl_3	Monoclinic $AlCl_3$	987 [19]	1086	15.60 [10]	18.90	76.50 [16]	77.50	0.5	195.26	0.90
$ErCl_3$	Monoclinic $AlCl_3$	1049 [23]	1154	12.80	12.62	77.75	77.68	5.3	273.56	0.89
NaCl	Cubic NaCl	1073 [24]	1180	152.9	147.6	38.85 [12]	38.40	38.0	58.45	0.99
KCl	Cubic NaCl	1043 [24]	1147	121.7	122.3	50.42 [17]	50.48	28.5	74.56	1.37
$CaCl_2$	Orthorhombic $CaCl_2$	1055 [24]	1161	62.51 [9]	61.27	52.95 [16]	52.82	0.4	110.98	1.00
$ZnCl_2$	Tetragonal	591 [25]	650	0.537 [26]	–	54.00 [25]	–	18.5[b]	136.29	0.60

[a] 100 $(V_m - V_s)V_s^{-1}$ (%): V_m, the molar volumes of melts at melting points; V_s, the molar volumes of crystals.
[b] In the case of monoclinic crystal: $\Delta V = 17.4$.

$$V_{\mathrm{m}} = \sum_{0}^{n} a_n x^n + \left(\sum_{0}^{n} b_n x^n\right) T \qquad (1)$$

where V_{m} is the molar volume in cm^3 mol^{-1} and x is the mole fraction of the cationic species with the higher valency. The parametes a_{n} and b_{n}, which are determined by least squares fitting of the experimental data, are listed in Table 2. Fig. 2 shows the molar volume isotherms for the two molten systems at 1073 K. The solid lines evaluated from Eq. (1) agreed with the values obtained by linear functions in Fig. 1. In each system a little deviation from the additivity was found.

The relationship between the impedance and the applied frequency is shown Fig. 3. The polarization-free resistance component (R_{inf}) of the melt was estimated by a linear extrapolation of the measured impedance (R_{meas}) to infinite frequency on the basis of the equation,

$$R_{\mathrm{meas}} = R_{\mathrm{inf}} + Cf^{-1/2} \qquad (2)$$

where f and C are the frequency and a fitting parameter in this regression, respectively. κ values of the $ErCl_3$–NaCl system increased with an increase in temperature, as was also the case with $ErCl_3$–KCl system. κ values of the investigated systems were well fitted by quadratic functions of temperature [20], as seen in Table 3.

Λ values were evaluated by the following equation (see for example Ref. [21]),

$$\Lambda = \kappa V_{\mathrm{m}} / \sum_{i} x_i n_i \qquad (3)$$

where V_{m}, x_i and n_i are the molar volume of the mixture in cm^3 mol^{-1}, the mole fraction of the salt i, and the valence of the cation of salt i, respectively. The V_{m} values were calculated from the empirical equations listed in Table 2. Since the lnΛ vs. $1/T$ plots for molten $ErCl_3$–NaCl and $ErCl_3$–KCl systems were almost linear, the Λ values were parameterized into the conventional Arrhenius-type equation,

$$\Lambda = A \cdot \exp(-E_{\mathrm{a}}/RT) \qquad (4)$$

The results for the frequency factor A and the

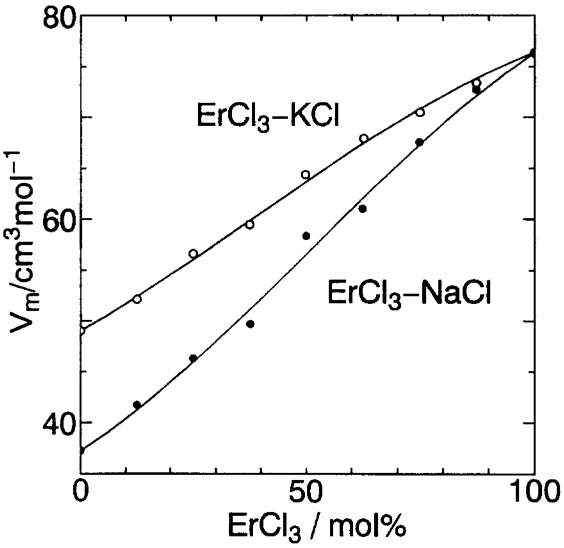

Fig 2. Molar volume variation with composition at 1073 K. The solid lines correspond to the values evaluated from the equations in Table 2.

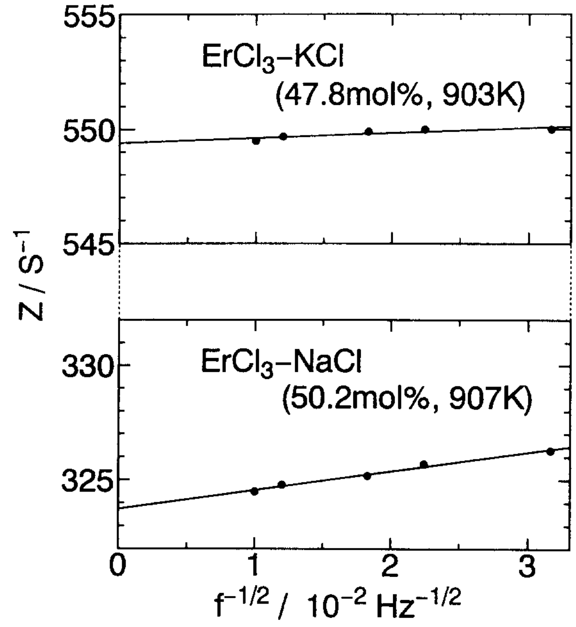

Fig. 3. Impedance variation with frequency.

Table 2
Polynomial parameters in empirical equations of molar volumes:

$$V_{\mathrm{m}} = \sum_{0}^{n} a_n x^n + \left(\sum_{0}^{n} b_n x^n\right) T$$

(V_m, cm^3 mol^{-1}; x, mole fraction of $ErCl_3$; T, K)

System	$10^{-1}a_0$	$10^{-1}a_1$	$10^{-1}a_2$	$10^{-1}a_3$	10^2b_0	10^2b_1	10^2b_2	10^2b_3	δ
$ErCl_3$–NaCl	2.312	1.508	6.205	−4.255	1.317	1.236	−2.926	2.110	0.737
$ErCl_3$–KCl	2.900	−5.886	27.00	−18.25	1.866	7.890	−24.00	16.00	0.534

δ, standard error in cm^3 mol^{-1}.

Table 3
Least squares fitted equations of conductivities
$\kappa = A + B \cdot T \cdot 10^{-3} + C \cdot T^2 \cdot 10^{-6}$ (κ, 10^{-2} S m^{-1}; T, K)

$ErCl_3$ (mol%)	Temp. range (K)	A (S m^{-1})	B (S m^{-1} K^{-1})	C (S m^{-1} K^{-2})	Standard error (S m^{-1})
(1) $ErCl_3$–NaCl system					
100.00	1069–1178	−1.801	2.505	−0.448	0.006
87.38	1058–1135	−6.839	11.918	−4.663	0.007
74.97	971–1092	−2.833	5.193	−1.708	0.010
62.41	869–988	−1.502	2.580	−0.182	0.002
50.21	752–928	−2.908	6.322	−2.364	0.017
37.59	867–986	−2.743	5.954	−1.840	0.002
24.97	1022–1105	−8.900	17.263	−6.645	0.003
12.49	1063–1158	−3.282	8.047	−2.442	0.002
0.00	1093–1141	−46.629	86.864	−37.379	0.003
(2) $ErCl_3$–KCl system					
100.00	1069–1178	−1.801	2.505	−0.448	0.006
87.37	1022–1108	−1.444	1.939	−0.076	0.003
75.02	1003–1128	−1.494	2.227	−0.245	0.001
62.75	869–988	−1.484	2.480	−0.378	0.006
49.79	791–910	−1.818	3.233	−0.720	0.004
37.44	1033–1111	−3.381	6.355	−2.173	0.002
25.06	1103–1134	−9.297	16.559	−6.388	0.001
12.46	1013–1095	−2.445	5.010	−1.177	0.002
0.00	1093–1168	−2.447	6.080	−1.605	0.003

activation energy E_a are listed in Table 4. Λ values increased with an increase in temperature (see Fig. 4). Fig. 5 shows the molar conductivity isotherms at 1073 K. Λ values of the molten $ErCl_3$–NaCl and $ErCl_3$–KCl systems increased steeply with decreasing $ErCl_3$ concentration in the range $x < 0.25$. These results suggest that in a low concentration of $ErCl_3$, the formation of dimeric or more polymeric complex anions composed of $ErCl_6^{3-}$-type octahedra as structural units might be restrained and discrete $ErCl_6^{3-}$ might increase, as described in the Raman spectroscopic study of $GdCl_3$–

Table 4
Least squares fitted equations of molar conductivities
$\Lambda = A \cdot \exp(-E_a/RT)$
(Λ, 10^{-4} S m^2 mol^{-1}; T, K; E_a, J mol^{-1};
R, gas constant: 8.314 J mol^{-1} K^{-1})

$ErCl_3$ (mol%)	Temp. range (K)	A (S m^2 mol^{-1})	E_a (kJ mol^{-1})
(1) $ErCl_3$–NaCl system			
100.00	1069–1178	656.5	37.78
87.38	1058–1135	419.5	29.58
74.97	971–1092	277.2	23.10
62.41	869–988	421.2	23.68
50.21	752–928	392.4	21.05
37.59	867–986	321.0	17.45
24.97	1022–1105	467.3	18.27
12.49	1063–1158	343.9	12.50
0.00	1093–1141	564.2	12.82
(2) $ErCl_3$–KCl system			
100.00	1069–1178	656.5	37.78
87.37	1022–1108	590.0	32.93
75.02	1003–1128	406.0	28.10
62.75	869–988	509.3	27.61
49.79	791–910	743.4	27.15
37.44	1033–1111	368.0	21.00
25.06	1103–1134	528.8	22.49
12.46	1013–1095	605.2	19.75
0.00	1093–1168	620.4	15.53

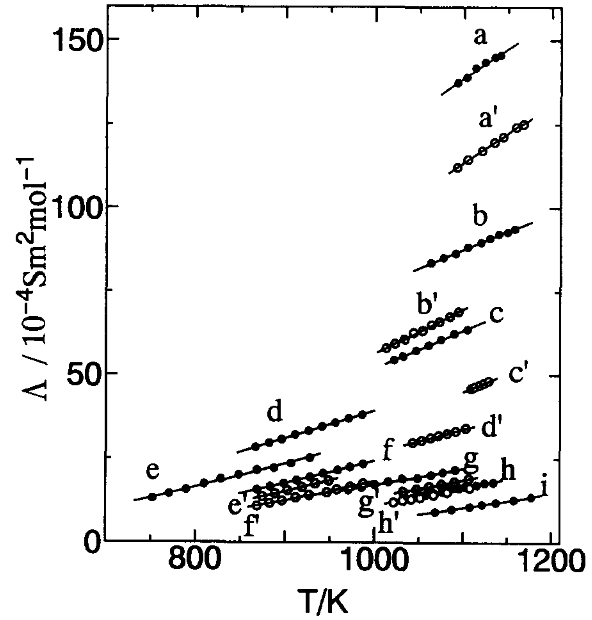

Fig. 4. Temperature dependence of the molar conductivity of molten $ErCl_3$–NaCl and $ErCl_3$–KCl systems. ●, $ErCl_3$–NaCl system: ($ErCl_3$mol%) a, 0.00; b, 12.49; c, 24.97; d, 37.59; e, 50.21; f, 62.41; g, 74.97; h, 87.38; i, 100.00. ○, $ErCl_3$–KCl system: ($ErCl_3$mol%) a', 0.00; b', 12.46; c', 25.06; d', 37.44; e', 49.79; f', 62.75; g', 75.02; h', 87.37. The solid lines correspond to the values evaluated from the equations in Table 4.

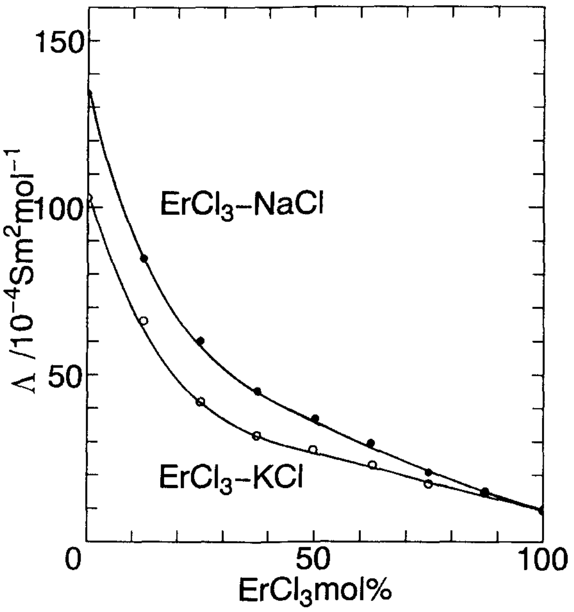

Fig. 5. Molar conductivity isotherms at 1073 K.

NaCl and $GdCl_3$-KCl systems [6]. Also the free Na^+, K^+ and Cl^-, which were not ligands of Er, relatively increased with decreasing $ErCl_3$ concentration and, consequently, the conductivities of the systems were increased.

For comparison, Λ values of other chloride melts are shown in Table 1 together with several physicochemical properties. Taking into account the magnitude of Λ values and the structure deduced from the other rare earth trichloride melts, the complex ion $ErCl_6^{3-}$ and its dimeric species $Er_2Cl_{11}^{5-}$ and $Er_2Cl_{10}^{4-}$ might exist in molten $ErCl_3$ and its mixture melts as well as other rare earth chloride melts. As shown in the first three rows of Table 1, $LaCl_3$, $PrCl_3$ and $NdCl_3$ in the solid state possess the UCl_3-type structure [18]. In contrast, YCl_3 and $ErCl_3$ crystals have the $AlCl_3$-type structure [18]. These five rare earth chloride melts are not so different from one another in view of the molar volume but the Λ values of the former group are apparently larger than those of the latter group, reflecting the order of cationic radious (see Fig. 6). It was reported that the dimers with corner-sharing of octahedral units exit in molten $LaCl_3$, $PrCl_3$ and $NdCl_3$ [1] and those with edge-sharing in molten YCl_3 [3] and $ErCl_3$ [2]. It might be thought that the melts with corner-sharing of octahedral units have larger Λ values than the melts with edge-sharing.

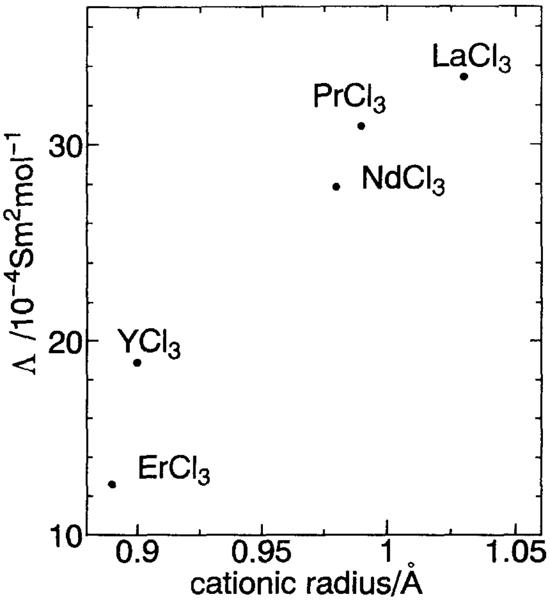

Fig. 6. Molar conductivity at 1150 K for pure molten salts.

4. Conclusions

The Λ of molten $ErCl_3$ is 12.62×10^{-4} S m^2 mol^{-1} at 1150 K. This value suggests in a series of molten rare earth chlorides that the Λ values are affected qualitatively by cationic radii and the types of linkage, that is, corner- or edge-sharing of octahedral units. In $ErCl_3$-NaCl and $ErCl_3$-KCl systems Λ values decreased steeply with increasing $ErCl_3$ concentration in the range $x < 0.25$, probably owing to the existence of $ErCl_6^{3-}$ and the linkage of octahedral units confirmed by X-ray diffraction.

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