Electrical Conductivity of Molten $LaCl_3-NaCl$, $LaCl_3-KCl$, and $LaCl_3-CaCl_2$

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The electrical conductivities ($\varkappa$'s) of molten $LaCl_3-NaCl$, $LaCl_3-KCl$, and $LaCl_3-CaCl_2$ were measured at 893–1168 K, by a conventional ac technique and fitted by quadratic functions of temperature. They increase with increasing temperature and decrease with increasing mole fraction of $LaCl_3$. The equivalent conductivities (Λ's) follow a linear relationship of $\ln \Lambda$ vs. $1/T$. The Λ's of $LaCl_3-NaCl$ and $LaCl_3-KCl$ decrease drastically with increasing $LaCl_3$ concentration. Λ of molten $LaCl_3$ is smaller than that of molten $CaCl_2$, in which the octahedral complex anion $CaCl_6^{4-}$ is known to exist. It seems reasonable to assume that complex ions or cluster species such as $LaCl_6^{3-}$ and $La_2Cl_{11}^{5-}$ exist in molten $LaCl_3$ and its mixture melts. Similar results, reported in a previous paper, were obtained for $PrCl_3-NaCl$, $PrCl_3-KCl$, and $PrCl_3-CaCl_2$.

Introduction

There exist some data on the electrical conductivity of molten mixtures containing trivalent ions, e.g. $AlCl_3-NaCl$ [1], $AlCl_3-KCl$ [2, 3] and their fluoride analogues [4]. It is well known that complex ions such as $AlCl_4^-$, $Al_2Cl_7^-$, and AlF_6^{3-} exist in these mixture melts. As for $LaCl_3-KCl$, Papatheodorou reported that highly symmetrical $LaCl_6^{3-}$ octahedra are predominant in mixtures rich in alkali chloride [5]. Our X-ray diffraction data also suggested the existence of $LaCl_6^{3-}$ octahedra in molten $LaCl_3$ and $LaCl_3$ mixtures [6]. We have reported the electrical conductivities of molten $PrCl_3-KCl$, $PrCl_3-NaCl$, and $PrCl_3-CaCl_2$ systems in a previous paper [7].

In this work, the electrical conductivities of $LaCl_3-NaCl$, $LaCl_3-KCl$, and $LaCl_3-CaCl_2$ melts were measured, and the equivalent conductivities were evaluated using the molar volumes reported in [8].

Experimental

Analytical grade NaCl, KCl, and $CaCl_2$ were dried under vacuum for 8 h at temperatures just below the respective melting points and then melted, solidified and stored in ampoules. The hygroscopic $LaCl_3$ was synthesized according to the reaction

$$La_2O_3 + 6\,NH_4Cl \rightarrow 2\,LaCl_3 + 6\,NH_3 + 3\,H_2O$$

and purified by sublimation at 1273 K under reduced pressure to remove impurities such as oxides, NH_4Cl, and water. The above pretreatments are indispensable, since the reaction of $LaCl_3$ with water produces oxychloride at elevated temperature. The sublimation apparatus is fully described in [9]. The mole ratios of the mixtures were determined by accurately weighing their components. A conventional ac technique was applied to attain the polarization-free resistance of the melt by varying the input frequency from 0.5 to 10 kHz. The measurements covered the temperature range 893 to 1168 K, which was chosen in view of the phase diagram [10, 11]. A variable capacitance was introdced in the Wheatstone bridge arrangement to correct for the capacity of the electrical double layer in the vicinity of the electrode surface. A block diagram of the conductivity acquisition system is reported in [12]. 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 run with pure NaCl melt [13]. Two conductivity cells were used with cell constants of about 141 and 231 cm^{-1}. The subtracted resistance of the leads amounted to 0.8 S^{-1} from the apparent resistance.

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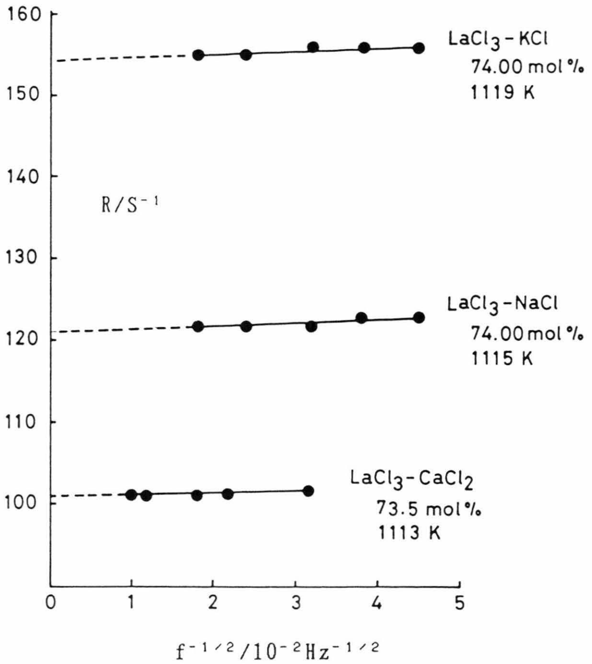

Fig. 1. Resistance variation with frequency.

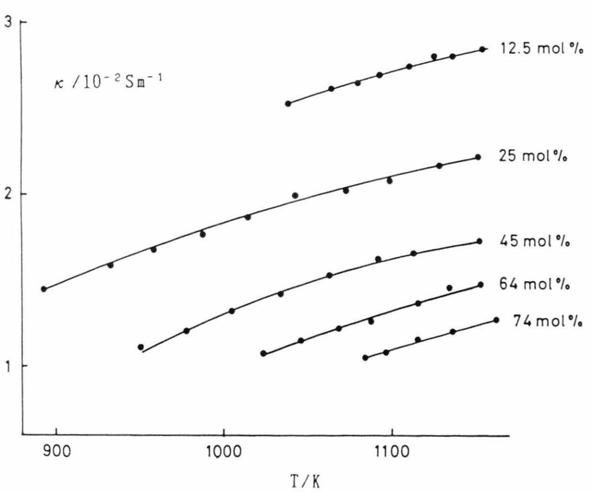

Fig. 2. Dependence of the conductivity of molten $LaCl_3$–NaCl on temperature and $LaCl_3$ content. The solid lines correspond to values evaluated from Table 1.

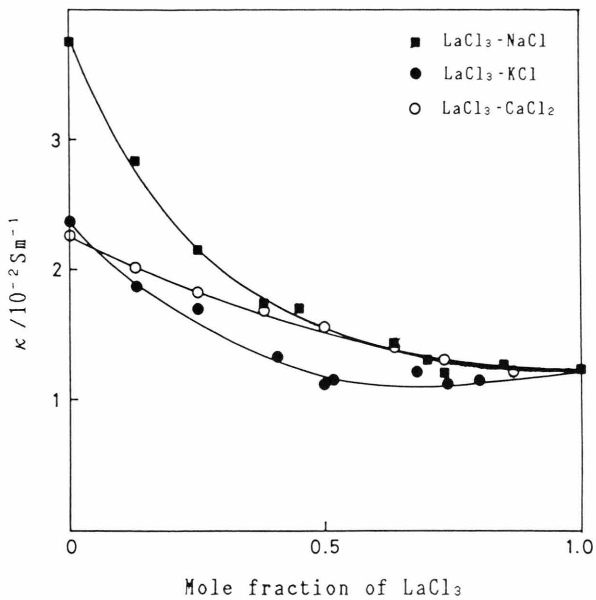

Fig. 3. Electrical conductivity isotherms at 1133 K.

Results and Discussion

The variation of the resistance with frequency is known to be well expressed in the form,

$$R_{meas} = R_{inf} + C \cdot f^{-1/2},$$

where R_{meas} and R_{inf} are the measured resistance at the frequency f and the polarization-free resistance at infinite frequency, respectively, and C is a fitting parameter. R_{inf} is estimated by linear extrapolation of R_{meas} against $f^{-1/2}$. It should be noted that the best extrapolation technique is dependent on factors such as the cell constant, concentration, and range of frequencies, as indicated by Tomkins et al. [14]. For molten $LaCl_3$–NaCl, $LaCl_3$–KCl, and $LaCl_3$–$CaCl_2$, the relationship between the resistance and the applied frequency is shown in Figure 1. The temperature dependence of the conductivity $\varkappa$ of $LaCl_3$–NaCl for various $LaCl_3$ contents is shown in Figure 2. $\varkappa$ of the investigated systems was fitted by quadratic functions of temperature [15], see Table 1. Conductivity isotherms of the three systems are shown in Figure 3. They have the same shape as for $PrCl_3$–NaCl, $PrCl_3$–KCl, and $PrCl_3$–$CaCl_2$ [7]. A comparison of the electrical conductivity of molten $LaCl_3$ with previous data [16–19] is given in Table 2.

Equivalent conductivities (Λ's) were evaluated by the equation [20]

$$\Lambda = \varkappa V_m \Big/ \sum_i X_i n_i,$$

where V_m, X_i, and n_i are the molar volume of the mixture in cm^3/mol, the mole fraction of the salt i and the valence of the cation of salt i, respectively. The V_m's

Table 1. Least squares fitted equations of electrical conductivity $\varkappa = A + BT \cdot 10^{-3} + CT^2 \cdot 10^{-6}$ ($\varkappa$: 10^{-2} Sm^{-1}, T: K)

$LaCl_3$ (mol%)	Temp. range (K)	A (Sm^{-1})	B ($Sm^{-1} \cdot K^{-1}$)	C ($Sm^{-1} \cdot K^{-2}$)	Standard error (Sm^{-1})
$LaCl_3$–NaCl					
100.0	1134–1143	−51.823	90.590	−38.598	0.001
84.5	1121–1159	−23.789	41.030	−16.711	0.012
74.2	1084–1162	−11.802	20.196	−7.688	0.010
69.7	1082–1161	−27.540	47.997	−19.880	0.022
63.7	1024–1152	−3.238	5.030	−0.793	0.018
44.9	951–1152	−9.616	17.887	−6.959	0.013
38.0	897–1153	−9.320	18.486	−7.662	0.040
25.0	893–1151	−5.052	10.518	−3.636	0.019
12.5	1038–1154	−8.405	17.458	−6.661	0.010
$LaCl_3$–KCl					
100.0	1134–1143	−51.823	90.590	−38.598	0.001
80.0	1116–1143	−82.435	144.860	−62.720	0.011
74.0	1076–1133	−4.829	7.446	−1.909	0.006
67.7	984–1142	−8.998	15.749	−5.935	0.010
50.8	948–1131	−4.454	8.215	−2.859	0.011
50.0	922–1145	−3.240	5.562	−1.485	0.011
41.0	925–1148	−1.625	2.651	−0.018	0.007
24.6	965–1148	−1.302	2.705	−0.056	0.023
12.7	1039–1135	−0.503	2.116	−0.023	0.005
0.0	1093–1168	−2.447	6.080	−1.605	0.003
$LaCl_3$–$CaCl_2$					
100.0	1134–1143	−51.823	90.590	−38.598	0.001
87.4	1113–1153	−10.030	17.323	−6.522	0.003
73.5	1082–1138	−19.661	34.749	−14.301	0.004
62.6	1073–1114	−5.125	8.865	−2.710	0.003
49.6	1051–1129	−6.084	10.279	−3.104	0.003
37.5	1045–1114	−7.708	13.451	−4.540	0.001
25.2	1018–1063	−10.052	18.356	−6.945	0.002
12.5	1072–1113	−6.384	11.349	−3.440	0.075
0.0	1087–1126	−14.451	26.122	−10.036	0.002

Table 3. Least squares fitted equations of equivalent conductivity $\Lambda = A\,e^{-E_a/RT}$ (Λ: 10^{-4} Sm^2 equiv.$^{-1}$); (T: K); (R: gas constant, 8.314 J K mol^{-1}).

$LaCl_3$ (mol%)	Temp. range (K)	A (Sm^2 equiv.$^{-1}$)	E_a (J mol^{-1})
$LaCl_3$–NaCl			
100.0	1134–1143	469.5	25260
84.5	1121–1159	624.2	27890
74.2	1084–1162	717.6	29260
69.7	1082–1161	942.1	30960
63.7	1024–1152	795.8	28260
44.9	951–1152	659.9	24080
38.0	897–1153	440.4	19500
25.0	893–1151	457.0	17460
12.5	1038–1154	439.5	14100
$LaCl_3$–KCl			
100.0	1134–1143	469.5	25260
80.0	1116–1143	961.9	32020
74.0	1076–1133	1183.6	33840
67.7	984–1142	1120.7	32370
50.8	948–1131	498.8	24170
50.0	922–1145	731.1	27960
41.0	925–1148	632.3	24630
24.6	965–1148	532.5	19730
12.7	1039–1135	417.2	15480
0.0	1093–1168	620.4	15530
$LaCl_3$–$CaCl_2$			
100.0	1134–1143	469.5	25260
87.4	1113–1153	507.0	24270
73.5	1082–1138	648.9	26340
62.6	1073–1114	543.4	24490
49.6	1051–1129	750.9	27040
37.5	1045–1114	719.1	26050
25.2	1018–1063	747.7	25530
12.5	1072–1113	586.7	22370
0.0	1087–1126	509.9	20260

Table 2. Electrical conductivities of molten $LaCl_3$ at 1143 K.

Ref.	$\varkappa$ (10^{-2} Sm^{-1})	Difference (%)
Van Artsdalen and Yaffe [15]	1.4949	+15.4
Dworkin et al. [16]	1.2907	− 0.34
Smirnov and Khokhov [17]	1.2559	− 3.03
Cho and Kuroda [18]	1.1006	−15.0
this work	1.2951	–

were calculated from the molar volume equations reported in [8]. As shown in Figure 4, the ln Λ vs. $1/T$ plot for $LaCl_3$–NaCl at 25.0 mol% $LaCl_3$ is a straight line. The same trends are observed for the other systems. Therefore, the Λ's were parameterized into the Arrhenius-type equation

$$\Lambda = A \exp(-E_a/RT).$$

The results for A and E_a are listed in Table 3, of which an interpolation to 1133 K gives the equivalent conductivity isotherms shown in Figure 5. The Λ's of the $LaCl_3$–NaCl and $LaCl_3$–KCl systems decrease steeply with increasing $LaCl_3$ concentration, while for the $LaCl_3$–$CaCl_2$ the decrease is not steep and corresponds to the slight variations of $\varkappa$ and V_m with $LaCl_3$ concentration. The equivalent conductivities at 1033 and 1133 K, designated as Λ_{1033} and Λ_{1133}, respectively, were calculated from the equations in Table 2. The Λ_{ratio}, defined as $\Lambda_{1133}/\Lambda_{1033}$, and the coefficient $\Delta\Lambda/\Delta T$, defined as $(\Lambda_{1133}-\Lambda_{1033})/100$, are listed in Table 4. An increase of temperature from 1033 and 1133 K corresponds to an increase of the kinetic energy, whose ratio is evaluated to be 1.097. The Λ ratios were always a little larger than the kinetic energy ratios, which shows that the equivalent conductivities are not only governed by the translational motion of the ions. The coefficient $\Delta\Lambda/\Delta T$ became smaller with addition of $LaCl_3$. We regard the decrease of $\Delta\Lambda/\Delta T$ as being due to the fact that free Cl^- ions make greater

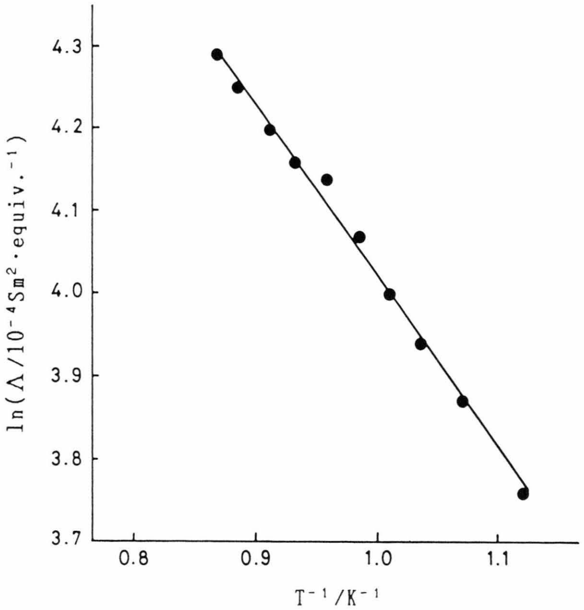

Fig. 4. Relation between ln Λ and $1/T$ for molten $LaCl_3$–NaCl with 25.0 mol% $LaCl_3$.

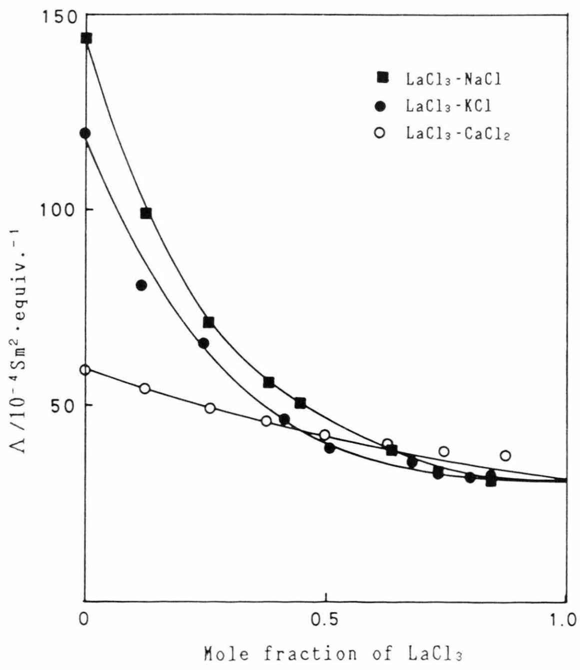

Fig. 5. Equivalent conductivity isotherms at 1133 K.

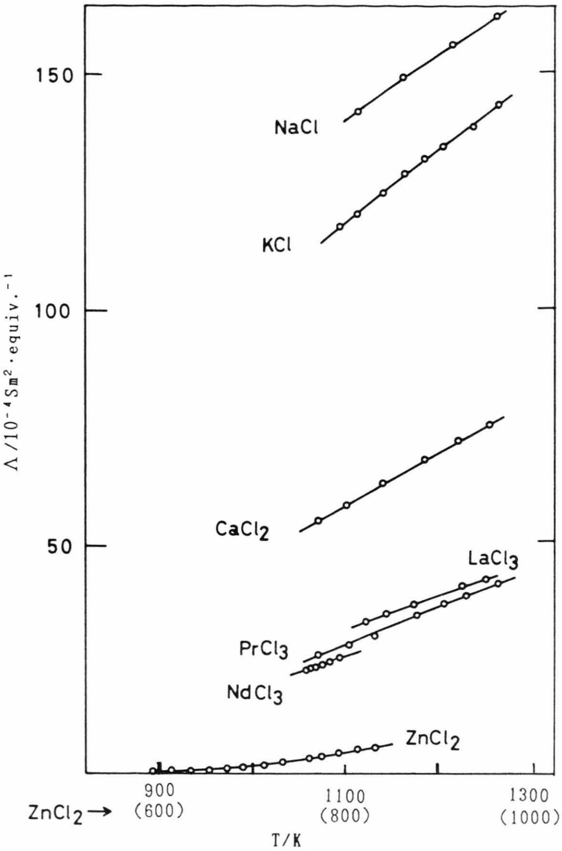

Fig. 6. Equivalent conductivity of several molten salts. The temperatures in the parentheses refer to $ZnCl_2$ melt.

contributions to the electrical conduction in the $LaCl_3$ poor range, Cl^- ions forming $LaCl_6^{3-}$ complexes and clusters. For comparison, Λ's of other metal chloride melts are shown in Fig. 6, in which the data on $ZnCl_2$ were taken from [21] and the others from [7, 20]. The equivalent conductivity of molten $LaCl_3$ is lower than that of molten $CaCl_2$ in which the existence of the octahedral complex anion $CaCl_6^{4-}$ has been confirmed [22]. It seems reasonable to assume that $LaCl_6^{3-}$, $La_2Cl_{11}^{5-}$ and polymer ions exist in molten $LaCl_3$ and its mixture melts, since the coordination number of Cl^- around the La^{3+} has been estimated to be six, and a La^{3+}–La^{3+} correlation has also been observed. The network-forming $ZnCl_2$ melt has a very small conductivity [21]. As Λ of molten $LaCl_3$ is larger than that of molten $ZnCl_2$, the ion-clustering or polymerization of ions in molten $LaCl_3$ seems to be not of long range in comparison with molten $ZnCl_2$.

Table 4. Λ ratio and $\Delta\Lambda/\Delta T$ (mol%).

(1) $LaCl_3$–NaCl

$LaCl_3$ (mol%)	Λ ratio*	$\frac{\Delta\Lambda}{\Delta T}$
100.0	1.296	0.074
84.5	1.332	0.081
74.2	1.351	0.083
69.7	1.374	0.096
63.7	1.336	0.098
44.9	1.281	0.112
38.0	1.222	0.101
25.0	1.197	0.118
12.5	1.156	0.133
0.0	1.112	0.151

(2) $LaCl_3$–KCl

$LaCl_3$ (mol%)	Λ ratio	$\frac{\Delta\Lambda}{\Delta T}$
100.0	1.296	0.074
80.0	1.390	0.090
74.0	1.416	0.096
67.7	1.395	0.102
50.8	1.282	0.084
50.0	1.333	0.094
41.0	1.288	0.104
24.6	1.225	0.120
12.7	1.172	0.119
0.0	1.174	0.177

(3) $LaCl_3$–$CaCl_2$

$LaCl_3$ (mol%)	Λ ratio	$\frac{\Delta\Lambda}{\Delta T}$
100.0	1.296	0.074
87.4	1.283	0.085
73.5	1.311	0.094
62.6	1.286	0.090
49.6	1.320	0.103
37.5	1.307	0.106
25.2	1.300	0.115
12.5	1.259	0.112
0.0	1.231	0.111

*: Defined as the ratio of the equivalent conductivity at 1133 K to that at 1033 K.

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