Electrical Conductivity of Melts Containing Rare-Earth Halides. I. MCl-$NdCl_3$ (M = Li, Na, K, Rb, Cs)

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The electrical conductivity of molten MCl-$NdCl_3$ (M = Li, Na, Rb and Cs) has been measured from the liquidus temperature up to ~ 1180 K. The measurements were performed in usual U-shaped capillary quartz cells with platinum electrodes. The molar conductivity (Λ) has been computed by using literature data on the densities of the binary systems. In all cases, when the temperature range exceeds about 100 K, the plot $\ln\Lambda$ vs. $1/T$ is not a straight line. The activation energy of the conductivity does not remain constant but reduces with increasing temperature. In the specific and molar conductivity isotherms strong deviations from additivity are noted. The results are discussed in terms of octahedral local coordination of Nd^{3+} over the entire concentration range.

Key words: Rare Earth; Electrical Conductivity; Neodymium; Alkali Chloride.

1. Introduction

The electrical conductivity of molten lanthanide chlorides with alkali chlorides plays an important role in the production of lanthanide metals by molten salt electrolysis. The present work is part of our general research program on the thermodynamic properties and electrical conductivity of rare-earth chlorides ($LnCl_3$) and their mixtures with alkali metal halides (see for example [1 – 7]). In this work the electrical conductivities of molten $NdCl_3$ and MCl-$NdCl_3$ (M = Li, Na, Rb, Cs) have been determined. $NdCl_3$ has been the subject of a number of investigations, but the conductivity data are rather contradictory [7 – 13]. As for the MCl-$NdCl_3$ systems, only the NaCl and KCl mixtures have been investigated [10, 11].

2. Experimental

2.1. Chemicals

The lithium, sodium, rubidium and caesium chlorides were purchased from ALPHA (99.5%). Prior to use, they were dehydrated by progressive heating up to fusion under gaseous HCl. LiCl was treated for more than 6 h, while NaCl, RbCl and CsCl for about 2 h. Excess HCl was removed from the melt by purging with argon.

High grade $NdCl_3$ (minimum 99.9%) was prepared from Nd_2O_3 produced by the Chemical Department of the University of Lublin, Poland. The synthesis of anhydrous $NdCl_3$ is described in detail in [14]. The last step of this synthesis was double distillation under reduced pressure (about 0.1 Pa). Storage and all handlings were performed under dry Ar (water content less than 2 ppm).

2.2. Apparatus

Capillary quartz cells with platinum electrodes were used to measure the electrical conductivity. They consist of two quartz tubes connected by a capillary of approximately 1 mm inner diameter (Fig. 1). The tubes were hermetically closed with rubber plugs. A special sluice was welded to the cell for loading sam-

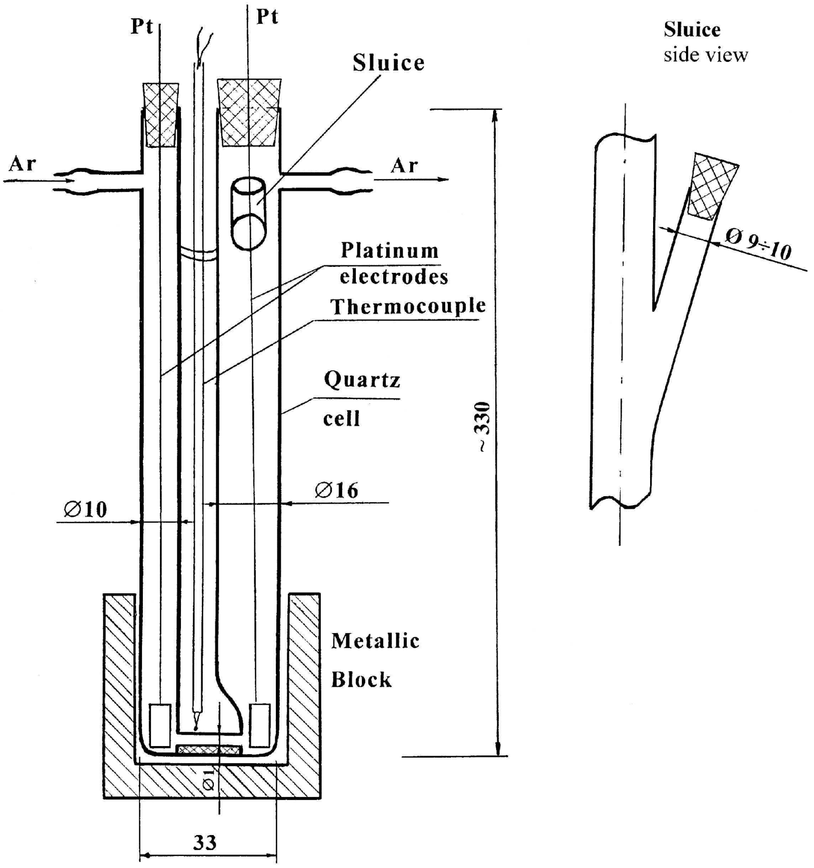

Fig. 1. Scheme of the cell for the electrical conductivity measurements.

ples before and during experiments. The cylindrical electrodes were made from platinum foils (~ 4 cm^2) welded to 1 mm diameter platinum wire. The melt volume required for investigation did not exceed 1.0–1.2 ml. The cell was placed into a furnace which contained a stainless steel block in order to achieve a uniform temperature. The temperature was controlled by a EUROTHERM regulator with a stability better than 1 K. The temperature was measured by means of a Pt-Rh10%Pt thermocouple with an accuracy ±1 K. The hot junction of the thermocouple was snagged against the cell capillary. A radiometer CDM230 conductivity meter was used for the conductivity measurements. In the cell resistance range corresponding to our investigations, the accuracy of this conductometer was ±0.2%. The temperature and conductivity values were simultaneously recorded on a computer.

2.3. Procedure

All preparations of experimental samples and cell fillings were carried out in a dry glove-box with water content less than 2 ppm. Sample loading into the cell was made only through the sluice to prevent any modifications of electrode positions. Measurements were performed in an atmosphere of pure argon (water content less than 2 ppm) from the melting temperature up to 1170–1200 K (1073 K for systems containing LiCl). At each concentration the temperature was automatically increased and decreased with a rate of 60–90 K/h. Separate experiments showed that non-reproducible conductivity values were obtained after two successive thermal runs only at rates larger than 120 K/h. The temperature and conductivity values were registered usually every 20 s.

The conductivity cells were calibrated with molten NaCl or KCl [15] and controlled every 4–6 experiments. In addition, secondary calibration was performed with two aqueous KCl standard solutions (0.1 and 1 M). It was repeated before every experiment in order to check for any change of the cell constant, which ranged from 40 to 80 cm^{-1}. Further controls were made while investigating the NaCl-NdCl$_3$

Composition, temperature range	Deviations of experimental points from the fit lines	Fit line		
		1st order	2nd order	exponential
CsCl-19.69 mol% NdCl$_3$,	Average	0.0818	0.0253	0.0768
$T = (1084 - 1167)$ K, $\Delta T = 83$ K	Maximum	0.28	0.125	0.278
CsCl-89.95 mol% NdCl$_3$,	Average	0.253	0.0799	0.886
$T = (990 - 1182)$ K, $\Delta T = 192$ K	Maximum	0.563	0.313	0.311
CsCl-44.96 mol% NdCl$_3$,	Average	1.5	0.281	1.88
$T = (839 - 1182)$ K, $\Delta T = 343$ K	Maximum	6.45	0.951	6.91

Table 1. Average and maximum deviations of experimental points from calculated line.

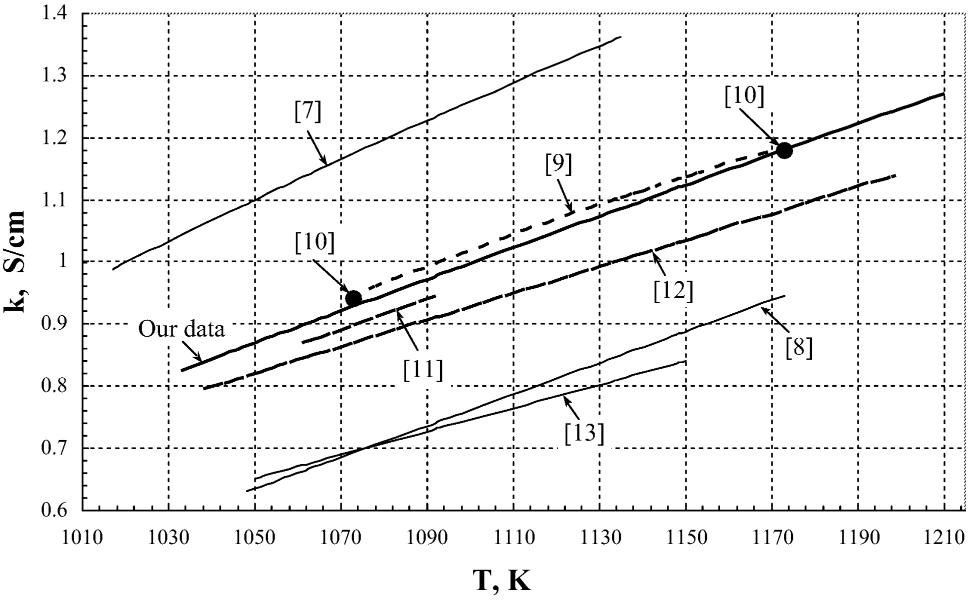

Fig. 2. Specific conductivity (k) of the individual molten NdCl$_3$.

or KCl-NdCl$_3$ systems: indeed, prior to any addition of NdCl$_3$, electrical conductivity measurements were performed on NaCl (KCl) ("autocalibration"). The working frequency of the conductivity meter was automatically selected as 23.4 kHz, i. e. far beyond the frequency range where the resistance is frequency-dependent [7, 16].

Although the accuracy of the CDM230 conductivity meter is 0.2%, by taking into account all other possible errors (concentration, temperature, etc.), the accuracy of the specific conductivity data is estimated to be ±2%.

Three kinds of equations are generally used to represent the dependence of the electrical conductivity on temperature:

$$k = a + bT, \tag{1}$$

$$k = a + bT + cT^2, \tag{2}$$

$$k = \exp(-E_A/RT). \tag{3}$$

It is obvious that (1) is only valid if the temperature range is limited (less than 100 K) or experimental data have poor precision.

The Arrhenius-type exponential function (3) has been widely used, mostly because it provides, for simple liquids, a conventional way of estimating the activation energy E_A. However, when the experimental data are numerous and obtained for different compositions of a mixture, a more accurate representation, i. e. a smaller standard deviation, is achieved by the polynomial equation (2). In Table 1 typical examples are shown to demonstrate the fitting capability of equations (1) – (3). Both average and maximum deviations of experimental points from calculated lines increase with the widening of the temperature range. Equation (2) provides the closest fit.

An important advantage of (1) should be pointed out. In many cases some extrapolation of experimental data is required. Using the linear equation is more ap-

Table 2. Specific conductivity *k* (S/cm) of MCl-NdCl$_3$ (M = Li, Na, Rb, Cs) melts.

[NdCl$_3$], mol%		$k = a + b \cdot T + c \cdot T^2$		k (1073 K)	k (1173 K)	T K
	a, S/cm	$b \cdot 10^3$, S/(cm · K)	$c \cdot 10^6$, S/(cm · K^2)			
LiCl-NdCl$_3$ system						
0	−2.8445	13.670	−4.5260	6.613	6.963[a]	883–1073
5.09	−5.8895	19.254	−6.1513	5.821	6.001[a]	874–1078
10.14	−5.7459	17.511	−6.9121	5.085	5.284[a]	864–1078
15.02	−4.7940	13.883	−5.2038	4.111	4.331[a]	812–1078
19.96	−4.3424	12.291	−4.4416	3.733	3.964[a]	811–1077
24.92	−6.5094	16.225	−6.3436	3.597	3.794[a]	776–1078
29.98	−6.0916	14.473	−5.3671	3.259	3.501[a]	730–1078
39.93	−5.6150	12.342	−4.4219	2.537	2.778[a]	846–1078
49.98	−5.3320	10.910	−3.7323	2.077	2.330[a]	860–1078
60.41	−4.7650	9.183	−2.9137	1.733	1.997[a]	926–1077
69.225	−4.6227	8.575	−2.6833	1.489	1.744[a]	942–1078
79.43	−2.9954	5.033	−1.0196	1.232	1.506[a]	1009–1078
89.72	−1.6196	2.240	0.2128	1.029	1.301[a]	1020–1088
100	−2.3342	3.5216	−0.44775	0.929	1.181	1033–1210
NaCl-NdCl$_3$ system						
3.05	−10.644	22.432	−8.8363	3.253	3.511	1064–1201
7.04	−4.4962	11.088	−3.7261	3.111	3.383	1048–1203
10.16	−3.2373	8.8145	−2.9520	2.822	3.040	1021–1220
14.09	−3.5846	9.0734	−3.0491	2.641	2.863	999–1220
54.97	−4.1692	7.8490	−2.3977	1.492	1.739	815–1220
59.65	−4.0995	7.5567	−2.2707	1.395	1.640	854–1212
65.06	−4.0488	7.2410	−2.0780	1.328	1.586	887–1220
69.99	−3.8893	6.8249	−1.9030	1.243	1.498	915–1220
74.83	−3.7992	6.5347	−1.7458	1.203	1.464	944–1221
79.86	−3.7374	6.2566	−1.6089	1.123	1.388	963–1223
89.90	−3.4193	5.5433	−1.3008	1.031	1.293	992–1211
RbCl-NdCl$_3$ system						
0	−1.9823	4.7803	−1.2166	1.746	1.951	995–1193
4.06	−1.4533	3.5543	−0.6866	1.570	1.771	979–1174
7.56	−0.1864	1.0124	0.4466	1.414	1.616	960–1175
12.67	−0.4640	1.2832	0.2540	1.205	1.391	978–1182
15.88	−1.6631	3.3927	−0.6995	1.172	1.354	946–1175
25.17	−3.8773	6.8635	−2.2177	0.934	1.122	1054–1172
37.42	−0.9108	1.7017	0.0641	0.989	1.173	964–1173
48.59	−1.8627	3.2707	−0.6987	0.842	1.012	783–1173
53.48	−2.3206	3.9751	−0.9478	0.854	1.038	949–1178
59.12	−2.4248	4.1228	−0.9912	0.858	1.047	862–1180
62.50	−2.6519	4.5750	−1.2525	0.815	0.991	1016–1170
68.98	−2.6858	4.3509	−0.9746	0.861	1.077	873–1180
74.91	−4.1503	7.0063	−2.1953	0.840	1.048	1030–1184
87.38	−4.3143	7.0768	−2.0941	0.868	1.105	1028–1182
CsCl-NdCl$_3$ system						
0	−2.3816	5.1480	−1.4544	1.465	1.655	918–1248
5.21	−2.1382	4.6229	−1.2914	1.335	1.508	894–1177
10.00	−2.1585	4.3680	−1.1839	1.165	1.336	879–1177
19.69	−2.8091	5.0972	−1.5516	0.874	1.035	1084–1167
25.03	−0.8797	1.6212	−0.0378	0.816	0.970	1108–1183
35.01	−1.5715	2.8489	−0.6686	0.716	0.850	1041–1184
44.96	−1.8996	3.5520	−1.0499	0.703	0.822	839–1182
49.77	−1.6695	2.9596	−0.7062	0.693	0.830	800–1180
59.96	−2.3383	4.0685	−1.1311	0.725	0.878	865–1182
69.91	−2.3608	3.8368	−0.8616	0.764	0.954	894–1182
79.94	−2.7888	4.4189	−0.9953	0.807	1.025	936–1182
89.95	−2.8929	4.4971	−0.9238	0.869	1.111	990–1182

[a] Extrapolation.

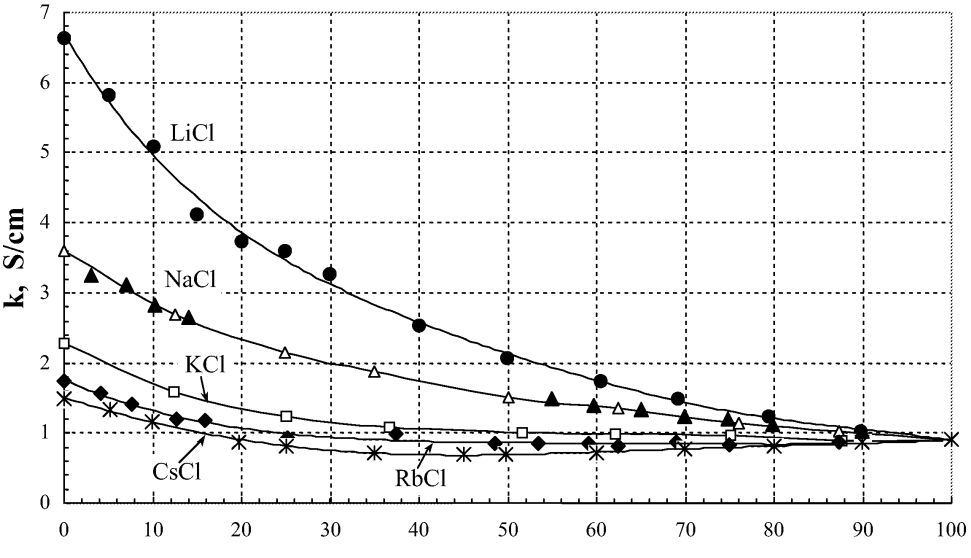

Fig. 3. Specific conductivity (k) of molten MCl-NdCl$_3$ systems (M = Li, Na, K, Rb, Cs) at 1073 K. Open symbols, data from [11]; closed symbols, our data.

propriate for this purpose. Other equations frequently lead to absurd results even at short extrapolation (for instance see second footnote in Table 3).

3. Results and Discussion

3.1. Molten Lithium, Rubidium and Caesium Chlorides

Because the specific electrical conductivity of molten NaCl and KCl [15] was used for the cell constant determination, the conductivity of all other salts directly depends on the accuracy of these data. The conductivity measured for fused LiCl is nearly the same as in [15]. Thus the conductivity of pure LiCl used in this work was adopted from [15]. However, preliminary experiments did not confirm the conductivity values of RbCl and CsCl cited in [15]. Since it is important that in a mixture the properties of the pure components are determined accurately, careful measurements of the conductivities of molten RbCl and CsCl were undertaken. Cells with high constants ($\sim$ 200 cm^{-1}) were used for this purpose. For these experiments special samples were prepared each time just before the measurements. In addition to the usual treatment by gaseous HCl, the samples of RbCl and CsCl (99.9% purity) were purified by sublimation. The results are shown in Table 1. For RbCl, the maximum deviation of our data from the selected critical values in Janz's compilation [15] is -3.7%, i. e. within the accuracy reported by the authors of [16], quoted in this book as $\pm 4\%$. For CsCl, the maximum deviation observed with the values of [16] also reported by Janz [15] is larger (11% at 1173 K). However, it should be noted that our data on CsCl agree within 2% with those published by Smirnov and Khokhlov [17, 18].

3.2. Molten Neodymium Chloride

The specific electrical conductivity of molten NdCl$_3$ was measured by several authors [7 – 13]. All these results are juxtaposed in Fig. 2, and a noticeable difference among these data is observed. Our experimental data (see Table 2 and Fig. 2) agree well with those which appear as the most reliable ones [9 – 12]. The maximum departure of our values from [9] is -2.1%; from [10] -1.2%, from [11] $+3.2\%$, and from [12] $+8\%$. It is well known that any impurities actually reduce the electrical conductivity. We believe that this is responsible for the low values published in [8] and possibly in [13] in spite of the lack of experimental details.

In this critical evaluation of the electrical conductivity it seems that previous results obtained in our laboratory [7] and all other previous data [9 – 12] are larger than those obtained in the present work. Since the ex-

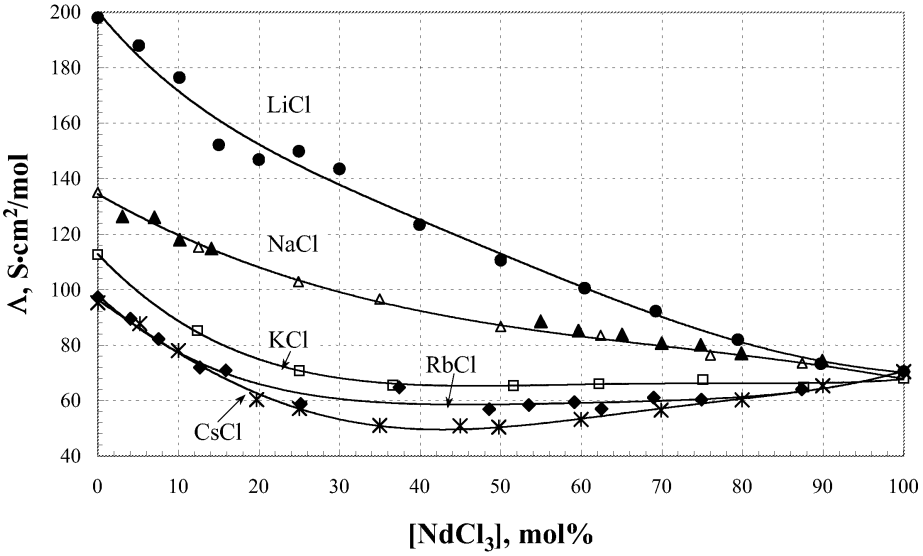

Fig. 4. Molar conductance (Λ) of molten MCl-NdCl$_3$ systems (M = Li, Na, K, Rb, Cs) at 1073 K. Open symbols, data from [11]; closed symbols, our data.

perimental procedure for the salt preparation was the same, the difference cannot be ascribed to impurities. The experimental technique for conductivity measurements was similar but the cell design is different in many respects. Actually, when we became aware of this difference, we double checked all possible causes for it. While the cell constant used in our previous work [7] was smaller than in the present work, the main reason was the electrical conductivity value of NaCl used for calibration, values were given by the same author in two different equations [15, 19].

3.3. Binary Mixtures

The electrical conductivity of three binary mixtures, LiCl-NdCl$_3$, RbCl-NdCl$_3$ and CsCl-NdCl$_3$, was studied over the entire composition range with an increment of $\sim$ 10 mol% each time. These data were parameterized using (2) and are listed in Table 2. The specific conductivity dependence on composition at 1073 K is shown in Fig. 3 for each system. The NaCl-NdCl$_3$ and KCl-NdCl$_3$ systems have been investigated in [15], and the corresponding data are also plotted in Fig. 3 for comparison. To make sure the mutual agreements of our results with data of [11], the measurements for the NaCl-NdCl$_3$ mixture were repeated for some compositions. In all cases very good agreement (better than 2%) with data of Mochinaga et al. [11] was found (see Table 2).

Thus our results, together with [11], form a self-consistent system of conductivity data on MCl-NdCl$_3$ systems (M = Li, Na, K, Rb, Cs). In these systems the conductivity reduces from LiCl to CsCl. In the systems LiCl-NdCl$_3$, NaCl-NdCl$_3$, KCl-NdCl$_3$ the conductivity smoothly reduces with increase of the NdCl$_3$ content. In the RbCl-NdCl$_3$ and CsCl-NdCl$_3$ mixtures the conductivity reduces up to 30 – 35% NdCl$_3$, and then a wide minimum is observed around 40 mol% NdCl$_3$.

3.4. Molar Conductivity

The molar conductivity (Λ) of a molten salt is related to the specific electrical conductivity (k) by the equation

$$\Lambda = kV_\mathrm{m} = k \cdot M/d, \qquad (4)$$

where V_m is molar volume of the salt, M the molar mass, and d the density. The same equation is applied to the mixtures. In MCl-LnCl$_3$ mixtures the maximum excess volumes (V_ex) are relatively small ranging from 1.5% in LiCl systems to 6.0% in CsCl systems. The empirical equations for computing molar volumes of such binary mixtures based on known molar volumes of end-members of mixtures were recently proposed [20, 21]. The equations were developed based on the analysis of all available excess volume data on these melts. It was shown that V_ex mainly depends on the nature of the alkali metal cation. In the present work this

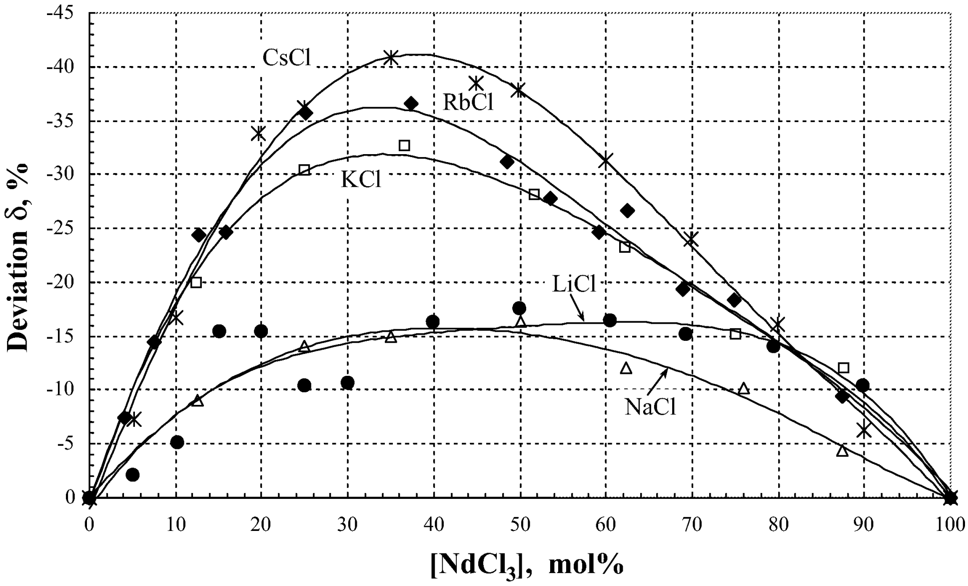

Fig. 5. Molar conductivity deviations from additivity in molten MCl-NdCl$_3$ systems (M = LiNa, K, Rb, Cs) at 1073 K. Open symbols, data from [11]; closed symbols, our data.

Table 3. Molar conductivity Λ (S · cm^2/mol) of molten RbCl, CsCl and NdCl$_3$.

	Λ (1073 K)	Λ (1173 K)	Ref.
RbCl	93.93	108.97	This work
" "	95.73	114.14	[22]
CsCl	94.08	110.63	This work
" "	100.32	123.06	[22]
" "	94.40	112.21	[17]
NdCl$_3$	70.39	91.86	This work
" "	74.1	–	[10]
" "	67.26	–	[11]

procedure was used for computing molar volumes of the systems under investigation. For the calculation of the density of molten NdCl$_3$ the following relation was used:

$$d = 4.238 - 8.6745 \cdot 10^{-4} \cdot T,\ \text{g/cm}^3. \tag{5}$$

This formula is an average of two sets of data published [22, 23]. The density of molten alkali chlorides was taken from [15].

The molar conductivities of molten RbCl, CsCl and NdCl$_3$ at two temperatures are listed in Table 3, together with some literature data. In the case of RbCl, the discrepancy with data in [24] reaches 4.7%. Our results on the CsCl molar conductivity agree very well with [17]. The difference is smaller than 1.4% (1173 K). Our $\Lambda(\text{NdCl}_3)$ value is by 5.3% lower than the value published in [10] and 4.7% higher than in [11].

For binary mixtures the results Λ vs. [NdCl$_3$] at 800 °C are depicted in Figure 4. The molar conductivity shows a similar trend with the composition as the specific conductivity. However, the minimum at $\sim$ 40% NdCl$_3$ in the RbCl-NdCl$_3$ and CsCl-NdCl$_3$ systems is observed more clearly in this plot. All these curves have essential deviations from additive behaviour. In Fig. 5 the relative deviations from additivity of the molar conductivity $[\delta = ((\Lambda_{\text{addit}} - \Lambda)/\Lambda_{\text{addit}}) \cdot 100\%]$ are shown. The maximum deviation in the LiCl-NdCl$_3$ system is about 17%, whereas in the RbCl-NdCl$_3$ and CsCl-NdCl$_3$ systems, it reaches 37 and 41%, respectively. The maximum deviations occur in the range 35 – 45 mol% NdCl$_3$.

Such strong deviations from additivity are clearly indicative of complex formation in the melts. Indeed, a structural study by Raman spectroscopy [25] showed that the predominant species in these melts are [NdCl$_6$]$^{3-}$ octahedra in dilute solutions ([NdCl$_3$] $<$ 25 mol%). At compositions rich in NdCl$_3$ ([NdCl$_3$] $>$ 25 mol%) these species still exist, but there are gradual distortions of the [NdCl$_6$]$^{3-}$ octahedra resulting from the sharing of common chloride ions between the octahedra, with a loose network structure consisting of octahedra sharing edges, as pure NdCl$_3$.

As a consequence of these structural features, the position of maximum deviations from additivity will

Table 4. Molar conductivity Λ ($\mathrm{S \cdot cm^2/mol}$) of MCl-NdCl$_3$ (M = Li, Na, K, Rb, Cs) melts.

[NdCl$_3$],	$\ln \Lambda = L_0 + L_1/T + L_2/T^2$			E_A (1073 K),	E_A (1173 K),	T
mol%	L_0	L_1, K	$L_2 \cdot 10^{-5}$, K^2	kJ/mol	kJ/mol	K
LiCl-NdCl$_3$ system						
0	6.29897	−1137.33	0.53473	8.63	8.70[a]	883 – 1073
5.09	5.60126	95.8660	−5.22645	7.30	6.61[a]	874 – 1078
10.14	5.61580	19.1318	−5.29953	8.05	7.35[a]	864 – 1078
15.02	5.70721	−345.079	−4.14746	9.30	8.75[a]	812 – 1078
19.96	5.78338	−505.886	−3.70936	9.95	9.46[a]	811 – 1077
24.92	5.32016	531.216	−9.26676	9.94	8.72[a]	776 – 1078
29.98	5.36240	514.342	−10.0837	11.35	10.0[a]	730 – 1078
39.93	5.15573	868.782	−13.2460	13.3	11.6[a]	846 – 1078
49.98	4.90820	1451.91	−17.9172	15.7	13.3[a]	860 – 1078
60.41	4.96680	1464.28	−19.8215	18.5	15.9[a]	926 – 1077
69.225	4.66065	2168.01	−24.8306	20.5	17.2[a]	942 – 1078
79.43	5.67192	240.830	−17.1572	24.6	22.3[a]	1009 – 1078
89.72	6.64350	−1722.59	−8.56993	27.6	26.5[a]	1020 – 1088
100	6.19587	−689.389	−14.9644	28.9	27.0	1033 – 1210
NaCl-NdCl$_3$ system (this work)						
0	5.36815	428.329	−9.99426	11.9	10.6	1080 – 1250
3.05	3.68317	4122.95	−30.9324	13.5	9.59	1064 – 1201
7.04	5.71232	−349.852	−6.32426	12.7	11.9	1048 – 1203
10.16	5.68773	−578.588	−4.34687	11.5	11.0	1021 – 1220
14.09	5.63889	−456.189	−5.42471	12.2	11.4	999 – 1220
54.97	4.57459	2196.41	−24.5690	20.0	17.9	815 – 1220
59.65	4.61943	2166.57	−25.2270	21.1	18.8	854 – 1212
65.06	4.75932	2038.61	−25.6673	22.7	20.3	887 – 1220
69.99	4.85389	1886.06	−25.5689	23.7	21.2	915 – 1220
74.83	4.99044	1710.59	−25.3348	24.8	22.2	944 – 1221
79.86	4.98978	1828.39	−27.0684	26.5	23.6	963 – 1223
89.90	5.20622	1479.20	−26.2100	28.1	25.2	992 – 1211
NaCl-NdCl$_3$ system (calculated from data [11])						
0	5.91700	585.322	−9.84612	10.1	9.13	1115 – 1258
12.5	6.80346	−2877.60	7.21277	12.4[b]	12.8[b]	1042 – 1081
24.9	6.25351	−1742.44	0.046513	14.4[b]	14.4[b]	973 – 1072
35	5.70327	−503.937	−7.63236	18.0[b]	16.1[b]	928 – 1074
50	4.01079	3034.72	−27.4862	29.7[b]	21.4[b]	843 – 991
62.4	4.37965	2657.23	−28.0002	28.2[b]	21.3[b]	933 – 1082
76	−18.8594	51552.5	−286.1075	51.3[b]	18.3[b]	993 – 1067
87.4	−2.98555	18761.9	−117.473	35.8[b]	26.4[b]	1019 – 1072
100	5.89413	−82.6875	−18.3777	29.5[b]	28.7[b]	1061 – 1092
KCl-NdCl$_3$ system (calculated from data [11])						
0	5.77827	−509.473	−6.68079	14.5	13.7	1095 – 1260
12.4	5.75291	−777.911	−6.71136	18.0[b]	16.9[b]	973 – 1073
25	6.43246	−2418.52	0.926453	18.6[b]	18.7[b]	987 – 1064
36.6	4.99305	531.158	−15.0398	21.9[b]	19.4[b]	952 – 1052
51.6	4.77839	1183.79	−19.6187	27.0[b]	21.5[b]	896 – 1053
62.2	4.37550	2643.43	−30.5472	36.0[b]	27.3[b]	892 – 1047
75.1	5.13190	1429.30	−25.9209	32.9[b]	28.6[b]	969 – 1071
87.6	−2.48764	17121.9	−107.052	34.3[b]	24.5[b]	1008 – 1068

[a] Extrapolation. [b] Calculated in end-values of temperature range, because extrapolation to 1073 and 1173 K leads to absurd results in some cases.

be shifted from 25 mol% to higher contents of neodymium chloride. Similarly, the enthalpies of mixing of the MCl-NdCl$_3$ systems (M = Na, K, Rb, Cs) [1, 14] exhibit strongly exothermic minima in similar composition ranges (35 – 45 mol% NdCl$_3$). It should be noted that Mochinaga et al. [11] also inferred six-coordinated complexe forming from their electrical conductivity measurements and prior to structural determinations [25]. In the alkali chloride-rich range the electrical conductivity drastically decreases with increasing NdCl$_3$ content because Cl$^-$ anions are bound in stiff complexes, and the content of mobile alkali cations decreases too. In the concentration range 40 – 100 mol% NdCl$_3$, the deviations decrease, probably due to a new mechanism of electricity transport by “anion jump”. Isolated mononuclear and polynuclear

Table 4 (continued).

[NdCl$_3$],	$\ln\Lambda = L_0 + L_1/T + L_2/T^2$			E_A (1073 K),	E_A (1173 K),	T
mol%	L_0	L_1, K	$L_2 \cdot 10^{-5}$, K^2	kJ/mol	kJ/mol	K
			RbCl-NdCl$_3$ system			
0	6.54034	−2314.39	2.22124	15.9	15.2	995 – 1193
4.06	6.75890	−2877.88	4.80557	16.4	17.2	979 – 1174
7.56	7.51350	−4609.85	13.7197	17.0	19.1	960 – 1175
12.67	7.33884	−4399.74	11.9296	18.0	19.8	978 – 1182
15.88	6.33708	−2176.83	−0.54102	18.9	19.1	946 – 1175
25.17	4.27240	2551.51	−29.6877	24.8	20.9	1054 – 1172
37.42	6.95991	−3470.54	5.11832	20.8	21.8	964 – 1173
48.59	4.49734	1731.61	−23.7478	23.1	21.7	783 – 1173
53.48	5.17425	610.424	−19.2970	24.6	22.8	949 – 1178
59.12	4.28803	2586.64	−30.0304	25.1	23.0	862 – 1180
62.5	4.93942	1085.82	−21.9855	25.0	22.2	873 – 1180
68.98	3.71756	4213.71	−40.6008	27.9	25.3	1016 – 1170
74.91	3.63373	4483.99	−42.7507	28.8	23.6	1030 – 1184
87.38	3.72333	4693.34	−45.3416	31.1	25.6	1028 – 1182
			CsCl-NdCl$_3$ system			
0	6.18730	−1465.30	−3.19351	17.1	16.7	918 – 1200
5.20	6.06908	−1378.76	−3.56486	17.0	16.5	894 – 1177
10.0	5.87845	−1028.32	−6.47612	18.6	17.7	879 – 1177
19.69	5.04670	688.523	−18.2894	22.6	20.2	1084 – 1167
25.03	7.01431	−3828.88	6.89748	21.1	22.1	1108 – 1183
35.00	5.72282	−1200.53	−7.73594	22.0	20.9	1041 – 1184
44.96	4.40509	1450.87	−21.0314	20.5	17.8	839 – 1182
49.77	4.39030	1693.75	−23.5369	22.4	19.3	800 – 1180
59.96	2.66926	5641.48	−45.3879	23.4	17.4	865 – 1182
69.91	4.15633	3089.79	−34.5084	27.8	23.2	894 – 1182
79.94	4.18512	3438.62	−37.8908	30.1	25.1	936 – 1182
89.95	4.97591	1965.24	−30.2620	30.6	26.6	990 – 1182

complexes are replaced by chain or net structures with high concentration and small distance between Cl$^-$ anions.

For all systems, the activation energy of the electrical conductivity, E_A, was calculated numerically as the derivative of $\ln\Lambda$ vs. $1/T$. Our electrical conductivity measurements were made in a wide temperature range typically exceeding 200 – 300 K, and a temperature dependence of the activation was evidenced. The results for 1073 and 1173 K are presented in Table 4. E_A significantly reduces with temperature even in the individual molten salts (very few exceptions are the result of some data scattering). This means that smooth structural changes leading to a reduction of energy barriers for electricity transport take place in the melts with increasing temperature.

This question was specially investigated in [25]. Unfortunately it turned out that Raman spectroscopy is not sensitive enough in this respect. For most systems studied the isotropic and anisotropic relative intensities and the overall shape of the spectra were found as temperature-independent. The same is true for LaBr$_3$, GdBr$_3$, YCl$_3$ and YBr$_3$ melts.

In the monograph [26], complex formation of Nd^{3+} in molten NaCl, KCl, RbCl, CsCl and (Li-K)Cl$_{\text{eut}}$ was studied by electronic spectroscopy. In principle, f-f transitions are of little sensitivity to surroundings like solvent or temperature. But for neodymium chloride, hypersensitive transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$ exist in the range 570 – 620 nm, which provide some information. Predominant octahedral local symmetry of Nd^{3+} was found over the entire composition range including pure molten NdCl$_3$. The part of octahedral configuration (or lifetime of [NdCl$_6$]$^{3-}$ complexes) increases in the row

$$\text{LiCl} < \text{NaCl} \approx (\text{Li}-\text{K})\text{Cl} < \text{KCl} < \text{RbCl} < \text{CsCl}.$$

This tendency also indicates that the Nd-Cl distance and average coordination number of Nd^{3+} increases from Cs$^+$ to Li$^+$. Thus in molten NaCl, and especially in LiCl, the average coordination number of neodymium cations somewhat exceeds six. This conclusion is in accordance with our results. The activation energy of the conductivity increases from LiCl to CsCl.

The fact that the intensity of hypersensitive transitions increases with temperature, while that of other transitions decreases, is indicative of a better organized octahedral coordination with more energetic Nd-Cl bonds (the Nd-Cl distance becomes shorter). In fact this slightly paradoxical conclusion corresponds to the strengthening of Nd-Cl bonds in complexes and weakening bonding in the second coordination sphere, with alkali metal cations and between complexes. Both alkali metal cations and complexes become more mobile, resulting in the reduction of the electrical conductivity activation energy.

4. Conclusion

The molar conductivity exhibits essential negative deviations from additivity in all MCl-NdCl$_3$ binary mixtures. Maximum deviations are situated at around 40 mol% NdCl$_3$. This is probably due to the existence of $[NdCl_6]^{3-}$ octahedral units and their linkage, as confirmed by Raman and electronic spectroscopy.

The reduction with temperature of the electrical conductivity activation energy is probably related to the weakening interaction in the second coordination sphere.

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