Electrical Conductivity of Melts Containing Rare-Earth Halides. II. MCl-$PrCl_3$ (M = Li, Rb, Cs)

Alexei M. Potapov[a], Leszek Rycerz[b], Evgeniy S. Filatov[a], and Marcelle Gaune-Escard[c]

[a] Institute of High Temperature Electrochemistry, 22, S. Kovalevskaya Str., 620219 Ekaterinburg, Russia

[b] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wrocław, Poland

[c] École Polytechnique, Département Mécanique Energétique, IUSTI-CNRS UMR 7343, Technopôle de Château Gombert, 5 rue Enrico Fermi, F-13453 Marseille Cedex 13, France

Reprint requests to M. G.-E.; Fax: +33 491 117439;
E-mail: marcelle.gaune-escard@polytech.univ-mrs.fr

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The specific conductivity of molten LiCl-$PrCl_3$, RbCl-$PrCl_3$, and CsCl-$PrCl_3$ was measured from the liquidus temperature up to ∼1180 K by a conventional ac technique. The molar conductivity Λ was calculated by using literature data on the densities of the binary systems. In all cases, it was found that the plot $\ln\Lambda$ vs. $1/T$ is not a straight line. Thereby 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 observed with maxima in a range 35 – 45 mol. % $PrCl_3$. The results conform to the idea of dominating octahedral local coordination of Pr^{3+} ions over the entire concentration range.

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

1. Introduction

In our first paper of this series, the conductivity of the molten MCl-$NdCl_3$ (M = Li–Cs) mixtures was considered [1]. In the present paper, we extend our investigations on the MCl-$PrCl_3$ systems (M = Li, Rb, Cs). Among the $LnCl_3$-containing systems, the majority of publications on conductivity and density is devoted to the molten systems containing $PrCl_3$ (and $LaCl_3$) [2 – 13]. However, researches of these systems still remain actual as there are essential discrepancies even among the last data.

The purpose of the present paper is to obtain reliable and systematic data on the electrical conductivity of the molten MCl-$PrCl_3$ mixtures.

2. Experimental

2.1. Chemicals

The chemicals LiCl, RbCl, and CsCl were purchased from ALPHA (99.5%). Prior to use, they were dehydrated by progressive heating up to fusion in the flow of gaseous hydrogen chloride. LiCl was treated for more than 6 h, while RbCl and CsCl for about 2 h. Excess HCl was removed from the melt by purging with argon (water content less than 2 ppm). The hygroscopic chemical $PrCl_3$ (minimum 99.9%) was synthesized from Pr_4O_{11} produced by Hydromet Co (Kowary, Poland). The synthesis of anhydrous $PrCl_3$ was similar to the synthesis of anhydrous $NdCl_3$ as described in detail in [14]. The fact that Pr_4O_{11} was a mixed valence oxide had no influence on the effectiveness of the chlorination process. The final step of this synthesis was the double distillation under reduced pressure (about 0.1 Pa). Storage and all handlings were performed under dry argon.

2.2. Apparatus and Procedure

The U-shaped conductivity cells made of transparent fused silica with platinum electrodes were used to measure the electrical conductivity. The cell was heated in a furnace controlled by a EUROTHERM

regulator. The melt temperature was measured by means of a Pt-Rh10%Pt thermocouple with an accuracy ±1 K. The cell resistance was measured using a radiometer CDM230 conductivity meter, its accuracy is ±0.2%. The temperature and conductivity values were simultaneously recorded on a computer.

The detailed description of the used cell and the measurement procedure is given in [1].

3. Results and Discussion

3.1. Molten Praseodymium Chloride

The specific electrical conductivity of molten $PrCl_3$ was measured by several authors [2 – 13]. All these results are juxtaposed in Figure 1, and a noticeable difference among these data is observed. Our experimental data (see Table 1 and Figure 1) agree well with those, which appear to be the most reliable [3, 4, 7, 8, 11]. The maximum departure of our values from [3, 8, 11], which practically coincide, is +1.0%; from [7] +4.5%. There are several tens of percent difference compared with other results (up to 26%). The newest data [12] and [13] presents an essentially different slope of polytherms, and distinctions in conductivity reach 11% (at 1170 K).

It is well known that any impurities actually reduce the electrical conductivity. We believe that a such wide spread of results is a consequence of insufficient purity of the salts used and primarily of $PrCl_3$. Oxychlo-

Table 1. Specific conductivity κ [S/cm] of molten MCl-$PrCl_3$ (M = Li, Rb, Cs); n-number points in polytherm.

$PrCl_3$, [mol.%]	A [S/cm]	$\kappa = A + B \cdot T + C \cdot T^2$ $B \cdot 10^3$ [S/(cm K)]	$C \cdot 10^6$ [S/(cm K^2)]	n	κ (1073 K)	κ (1173 K)	ΔT [K]
			LiCl-$PrCl_3$				
0[a]	−2.0647	12.127	−3.7641		6.615[b]	6.981[b]	917 – 1056
4.985	−6.0508	19.504	−8.0302	433	5.632	5.779[b]	862 – 1076
10.01	−4.8662	15.647	−5.9365	624	5.088	5.319[b]	844 – 1076
19.90	−6.0854	15.945	−6.3271	640	3.739	3.912[b]	780 – 1076
25.04	−7.0518	17.067	−6.8017	647	3.431	3.610[b]	760 – 1076
31.03	−6.1847	14.433	−5.4409	577	3.037	3.258[b]	736 – 1076
39.70	−4.3461	9.5338	−2.7546	683	2.713	3.047[b]	770 – 1075
49.82	−5.1677	10.405	−3.3135	510	2.182	2.478[b]	889 – 1076
59.81	−4.9311	9.4434	−2.9112	609	1.850	2.140[b]	945 – 1104
69.76	−4.3631	7.8719	−2.2443	505	1.500	1.783[b]	962 – 1098
79.94	−3.7191	6.3006	−1.5497	405	1.258	1.539[b]	1029 – 1111
89.76	−3.2209	5.2112	−1.1110	443	1.082	1.351[b]	1029 – 1120
100	−2.9026	4.4894	−0.7767		1.021	1.295	1102 – 1178
			RbCl-$PrCl_3$				
0	−2.9964	6.6146	−2.0957	1501	1.689	1.879	999 – 1203
12.18	−2.5599	5.3382	−1.6412	526	1.279	1.444	919 – 1174
24.94	−2.0810	3.9851	−1.0476	618	0.989	1.152	1034 – 1173
37.44	−1.7571	3.3424	−0.8321	787	0.872	1.019	924 – 1174
50.03	−2.3422	4.2352	−1.1520	3356	0.876	1.041	763 – 1174
62.43	−2.8364	4.8310	−1.2663	1813	0.899	1.099	863 – 1176
74.86	−2.7586	4.3159	−0.8284	613	0.919	1.164	946 – 1140
87.24	−3.3198	5.2424	−1.1757	220	0.952	1.212	1101 – 1178
			CsCl-$PrCl_3$				
0	−2.3816	5.1480	−1.4544		1.468	1.655	918 – 1248
5.040	−2.4227	5.1412	−1.5311	832	1.331	1.501	892 – 1185
10.09	−2.4447	5.0100	−1.5317	1155	1.168	1.325	862 – 1185
19.94	−1.7034	3.1477	−0.7093	274	0.858	1.013	1065 – 1171
25.03	−1.9301	3.4760	−0.8814	311	0.785	0.9345	1089 – 1185
29.52	−2.0232	3.5493	−0.9280	269	0.717	0.8633	1083 – 1166
46.00	−1.6736	3.0025	−0.7482	2605	0.687	0.8189	822 – 1181
59.95	−2.4142	4.1672	−1.1372	2771	0.748	0.9092	875 – 1191
73.23	−2.9580	4.8345	−1.2282	1060	0.816	1.023	909 – 1183
84.79	−4.6458	7.9122	−2.5932	594	0.859	1.067	1001 – 1185

[b] Extrapolation

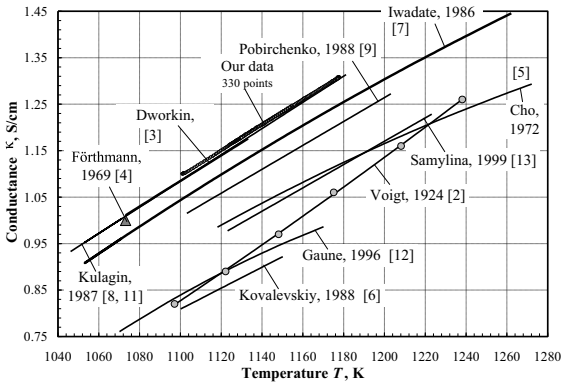

Fig. 1. Specific conductivity κ of individual molten $PrCl_3$.

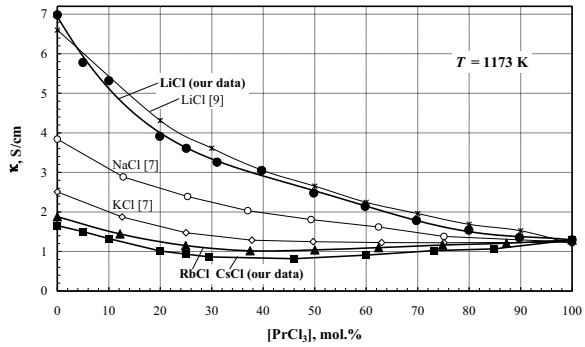

Fig. 2. Specific conductivity κ of molten MCl-$PrCl_3$ systems.

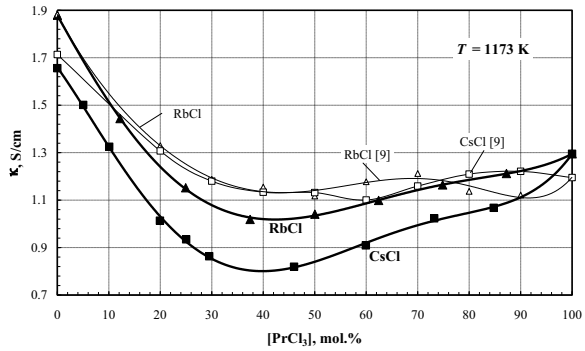

Fig. 3. Specific conductivity κ of molten RbCl-$PrCl_3$ and CsCl-$PrCl_3$ system. Our and [9] data together.

rides can be a part of the initial praseodymium chloride or may be formed during the experiments as the result of the interaction with atmosphere or constructional materials.

3.2. Binary Mixtures

The electrical conductivity of three binary mixtures, LiCl-$PrCl_3$, RbCl-$PrCl_3$, and CsCl-$PrCl_3$, was studied over the entire composition range with an increment of ~10 mol. % each time. These data were approximated by a parabolic function whose coefficients are listed in Table 1. The specific conductivity dependence on the composition at 1173 K is shown in Figure 2 for each system. The NaCl-$PrCl_3$ and KCl-$PrCl_3$ systems were investigated in [7], and the corresponding data are also plotted in Figure 2 for comparison.

The electrical conductivity of all five molten mixtures MCl-$PrCl_3$ (M = Li, Na, K, Rb, Cs) was measured in the dissertation [9]. For the system LiCl-$PrCl_3$, the average disagreement with our data is about 5.7%, maximum one 13% at 1173 K, see Figure 2.

For RbCl-$PrCl_3$ and CsCl-$PrCl_3$ systems, the maximum difference reaches 11.3 and 42% (1173 K), respectively. Furthermore, even the tendency of conductivity is not clear enough when going from the rubidium to the cesium system, see Figure 3. Presumably $PrCl_3$, used in work [9], contained an appreciable quantity of oxychlorides, various in different samples. Therefore, we excluded work [9] from any further consideration.

As was found in [1] the data of [15] on the conductivity of fused individual $NdCl_3$ and fused systems NaCl-$NdCl_3$ and KCl-$NdCl_3$ are in good agreement with our results on the MCl-$NdCl_3$ (M = alkaline metals) systems. Close coincidence of the fused $PrCl_3$ conductivity, received by the authors of the present work and in work of the same group [7], is the evidence of the adequate preparation of anhydrous $PrCl_3$ and the consequent reliability of other data on the conductivity of the fused NaCl-$PrCl_3$ and KCl-$PrCl_3$ systems [7]. Our data together with the data of work [7] seem to form a self-consistent system of data on the conductivity of the molten MCl-$PrCl_3$ (M = Li, Na, K, Rb, Cs) mixtures. In these systems, the conductivity reduces from LiCl to CsCl. In the systems LiCl-$PrCl_3$, NaCl-$PrCl_3$, KCl-$PrCl_3$ the conductivity smoothly reduces with increase of the $NdCl_3$ content. In the KCl-$PrCl_3$ system, conductivity is actually constant in the concentration range 40 – 100 mol. % $PrCl_3$. In the RbCl-$PrCl_3$ and CsCl-$NdCl_3$ mixtures, the conductivity reduces up to 30 – 30 mol. % $PrCl_3$, and then a wide minimum is observed around 40 mol. % $PrCl_3$.

Table 2. Molar conductance Λ [S cm^2/mol] and their activation energy E_A of molten MCl-PrCl$_3$ mixtures (M = Li, Rb, Cs); ($R = 8.31441$ kJ/(mol K)).

$PrCl_3$ [mol.%]	$\ln\Lambda = L_0 + L_1/(RT) + L_2/(RT)^2$ L_0	$L_1 \cdot 10^{-3}$	$L_2 \cdot 10^{-6}$	Λ (1073 K) [S cm^2/mol]	E_A (1073 K) [kJ/mol]	Λ (1173 K) [S cm^2/mol]	E_A (1173 K) [kJ/mol]
				LiCl-PrCl$_3$			
0*	6.45195	−12.0236	14.4424	197.5	8.76	215.0	9.02
4.985	5.46690	2.25060	−41.1992	181.6	6.99	193.4	6.20
10.01	5.81467	−3.05019	−24.0327	176.1	8.44	190.4	7.98
19.90	5.31909	3.26878	−55.4289	146.8	9.16	159.4	8.10
25.04	5.04957	8.33270	−81.3144	142.9	9.90	155.9	8.34
31.03	5.11678	7.48328	−83.7585	134.7	11.3	148.9	9.69
39.70	5.86354	−2.66683	−54.8788	131.0	15.0	150.4	13.9
49.82	5.29778	7.02643	−106.346	115.5	16.8	134.3	14.8
59.81	5.23024	8.91392	−124.440	106.3	19.0	126.0	16.6
69.76	5.03688	12.8737	−155.138	92.8	21.9	112.8	18.9
79.94	5.34207	8.75812	−151.120	83.5	25.1	104.7	22.2
89.76	5.33826	9.48041	−164.198	76.5	27.3	97.91	24.2
100	5.944	0.188345	−129.172	76.9	28.8	100.0	26.3
				RbCl -PrCl$_3$			
0*	5.85914	−7.59403	−37.0366	93.93	15.9	110.0	15.2
12.18	5.54184	−4.49935	−56.2763	75.99	17.1	89.02	16.0
24.94	5.73139	−8.60791	−50.9531	61.95	20.0	74.67	19.1
37.44	5.53275	−6.45299	−61.1463	56.89	20.2	68.60	19.0
50.03	3.37836	33.3337	−240.798	59.70	21.9	71.14	19.7
62.43	3.93850	28.8449	−241.294	62.81	25.2	78.20	20.6
74.86	4.65843	20.6981	−222.284	65.74	29.1	85.09	24.9
87.24	5.45827	7.94503	−167.310	69.87	29.6	91.28	26.4
				CsCl-PrCl$_3$			
0*	6.20341	−12.4750	−20.7611	94.09	17.1	110.6	16.7
5.040	5.85383	−7.62790	−42.0784	87.37	17.1	102.4	16.3
10.09	5.47817	−2.29873	−68.5342	78.21	17.7	92.01	16.4
19.94	6.06119	−13.9351	−33.3336	59.17	21.4	72.38	20.8
25.03	5.68138	−7.50466	−66.5476	54.82	22.4	67.51	21.2
29.52	5.35637	−1.75340	−98.4994	50.51	23.8	62.87	22.0
46.00	4.45659	12.2592	−153.102	49.75	22.3	60.58	19.8
59.95	3.95598	25.8097	−226.354	54.87	24.9	68.21	20.6
73.23	3.63972	36.9494	−292.914	60.41	28.7	77.39	23.1
84.79	2.9088	51.2475	−357.801	63.92	29.0	81.59	22.1

3.3. Molar Conductivity

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

$$\Lambda = \kappa V_m = \kappa M/d\,, \tag{1}$$

where V_m is the molar volume of the salt, M the molar mass, and d the density. The same equation is applied to the mixtures.

The literature data on the density of the molten MCl-LnCl$_3$ mixtures do not correlate well to each other. The data on the densities of the LiCl-PrCl$_3$, RbCl-PrCl$_3$, and CsCl-PrCl$_3$ melts are absent with the only exception of data [9] that we consider to be doubtful. The procedure suggested in works [16, 17] was used to calculate the densities of these systems. In these works, empirical equations for computing molar volumes of such binary mixtures based on known molar volumes of end-members of mixtures were proposed. The equations were developed based on the analysis of all available excess volume data on these melts.

For calculations, the densities of LiCl, RbC,l and CsCl were adopted from [18] and for the density of molten PrCl$_3$ the following relation was used [19]:

$$d = 4.123 - 7.86 \cdot 10^{-4} T, \ \ [\mathrm{g/cm^3}]. \tag{2}$$

In a large number of publications, authors assume that the $\ln(\Lambda)$ (or $\ln(\lambda)$) vs. $1/T$ plot is a straight line (λ is the equivalent conductivity) [7, 9, 13, 20–23].

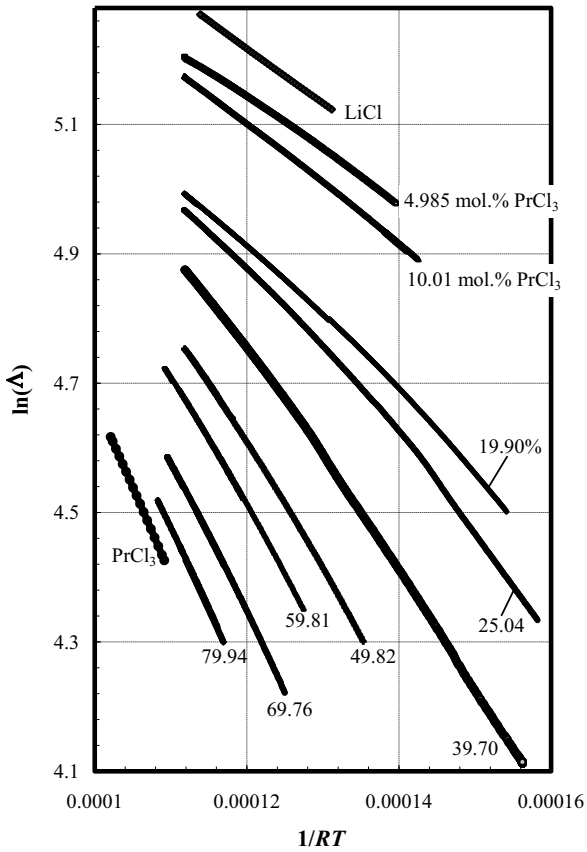

Fig. 4. The dependence $\ln(\Lambda)$ vs. $1/RT$ for molten LiCl-$PrCl_3$ systems. Some coalesced curves are not shown.

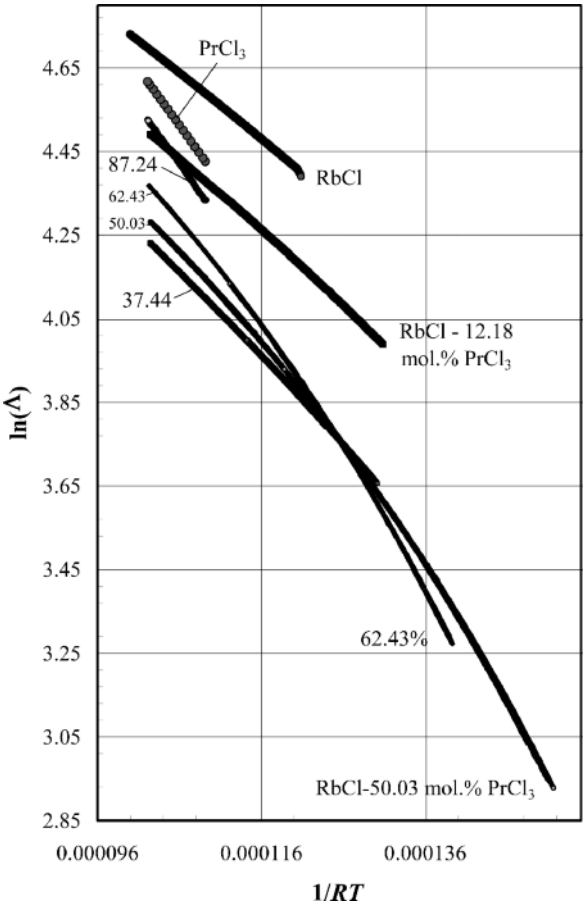

Fig. 5. The dependence $\ln(\Lambda)$ vs. $1/RT$ for molten RbCl-$PrCl_3$ systems. Some coalesced curves are not shown.

However, if the data are smooth enough its nonlinearity is revealed in all cases. These lines are convex upwards even though they seem by eye to be straight, see Figures 4 – 6. For instance, for the system RbCl-50.04 mol. %$PrCl_3$, studied in the widest temperature range ($\Delta T = 411$ K), the activation energy E_A was lowered from 42.3 (763 K) to 19.7 kJ/mol (1174 K). For the LiCl-79.94 mol. % $PrCl_3$ system studied in the narrowest temperature range ($\Delta T = 82$ K) the activation energy E_A was lowered from 27.0 (1029 K) to 24.3 kJ/mol (1111 K).

These deviations are small for the individual salts and increase when transferred to the binary mixtures and with temperature decreasing.

For binary mixtures, the results Λ vs. [$PrCl_3$] at 1173 K are depicted in Figure 7. The molar conductivity shows a similar trend with the composition as the specific conductivity. However, the minimum at ~40% $PrCl_3$ in the KCl-$PrCl_3$, RbCl-$PrCl_3$, and CsCl-$PrCl_3$ systems is observed more clearly in this plot. All these curves have essential deviations from additive behaviour. In Figure 8, 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-$PrCl_3$ system is about 18%, whereas in the RbCl-$PrCl_3$ and CsCl-$PrCl_3$ systems, it reaches 35 and 43%, respectively. The maximum deviations occur in the range 35 – 45 mol. % $PrCl_3$, except for the LiCl-$PrCl_3$ system. Its maximum deviations lays around 50 mol. % $PrCl_3$.

Such strong deviations from additivity are clearly indicative of complex formation in the melts. We found only one work, where precisely the structure of molten $PrCl_3$ was studied. In this work [24], the structures of $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $GdCl_3$, $DyCl_3$, and

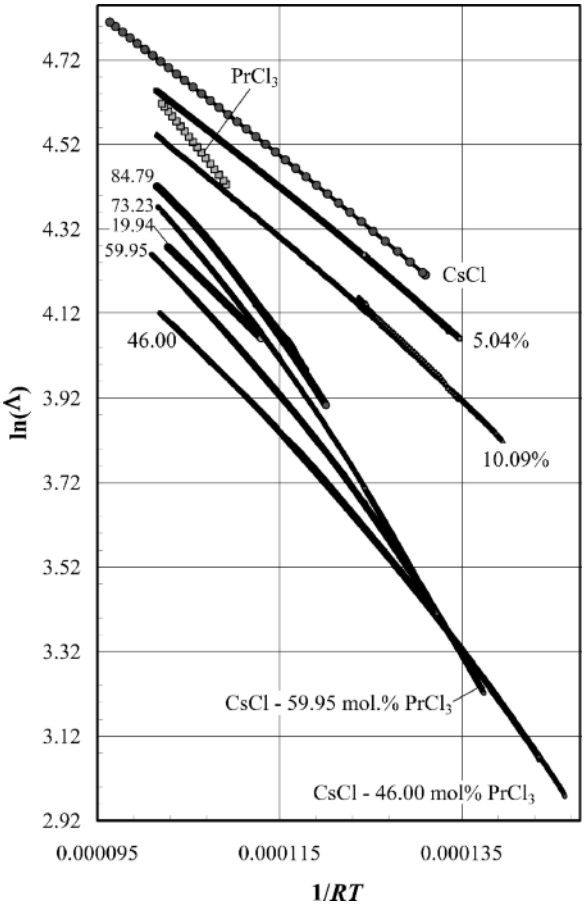

Fig. 6. The dependence $\ln(\Lambda)$ vs. $1/RT$ for molten CsCl-$PrCl_3$ systems. Some coalesced curves are not shown.

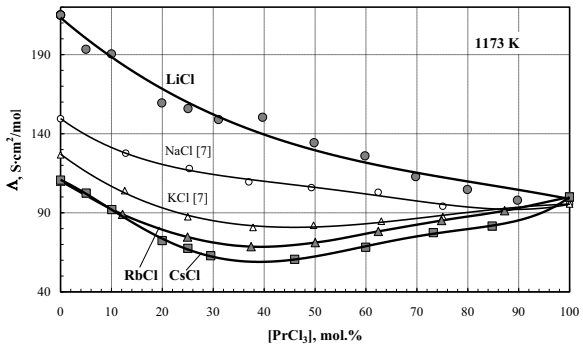

Fig. 7. Molar conductance Λ of molten MCl-$PrCl_3$ systems.

$SmCl_3$ melts were studied by X-ray diffraction analysis. It was inferred that in all cases the Ln^{3+} cation was surrounded by six Cl^- ions with the local octahedral symmetry. By the virtue of the fact that the Nd^{3+} ion is the closest Pr^{3+} analogue, the conclusion on the structure of the MCl-$NdCl_3$ melts are equally usable for the MCl-$PrCl_3$ melts. These references have been done before [1]. It will be relevant to repeat only one of the conclusions from work [25], that the six-fold coordination around the rare earth cation in the MCl-$LnCl_3$ melts is preserved at all mole fractions. Two basic facts including the fast decreasing of conductivity at $PrCl_3$ addition and the location of the maxima of the relative deviations in the range 33 – 40 mol. % $PrCl_3$ show agreement with this concept of the melt structure. For further information please refer to [1].

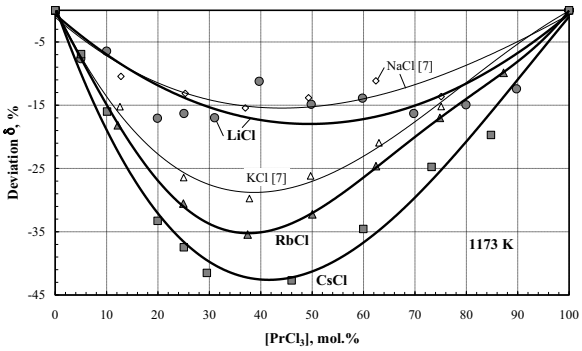

Fig. 8. Molar conductivity deviations from additivity in molten MCl-$PrCl_3$ systems.

The maximal relative deviations in the LiCl-$PrCl_3$ system were clearly shifted to the range 50 mol. % $PrCl_3$. This is not an experimental error, but the result of the Pr^{3+} and Li^+ ions interference. The lithium ion potential (charge-to-radius ratio) is the closest to the praseodymium ion potential among the alkali metals (($\varphi(Pr^{3+}) = 3/0.997 \approx 3.01$; $\varphi(Li^+) = 1/0.59 \approx 1.69$; $\varphi(Na^+) = 1/0.59 \approx 1.01$; $\varphi(K^+) \approx 0.73$; $\varphi(Rb^+) \approx 0.66$; $\varphi(Cs^+) \approx 0.60$).

The Li^+ ion is quite a strong complexing agent in itself. It forms the $LiCl_4^{3-}$complexes, and hence is competitive with the Pr^{3+} ion. Consequently, the praseodinium complexes have the smallest strength and the largest distortions. It resulted in the smallest deviations of the conductivity from the additivity and in the shift of the deviations maxima to 50 mol. % $PrCl_3$.

4. Conclusion

The conductivity of molten LiCl-$NdCl_3$, RbCl-$PrCl_3$, and CsCl-$PrCl_3$ was measured. Together with

data [7] on conductivity of NaCl-$PrCl_3$ and KCl-$PrCl_3$ molten mixtures, our new facts form a full and self-consistent data system on the electrical conductivity of MCl-$PrCl_3$ molten systems.

The $\ln \Lambda$ vs. $1/T$ dependence was found not to be a straight line. The deviations from the linearity were found to be larger in the mixtures than in the individual salts. In all cases, the activation energy reduces with temperature increase.

The results conform to the literature data on the structure of the investigated melts. Six Cl^- ions are the nearest neighbour ions of each Pr^{3+} ion over the entire concentration range.

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