Electrical Conductivity of Molten Binary $NdBr_3$ – Alkali Bromide Mixtures

S. Gadzuric, E. Ingier-Stocka[a], L. Rycerz[a], and M. Gaune-Escard[b]

Faculty of Natural Science, Department of Chemistry, University of Novi Sad, Trg D. Obradovica 3,
21000 Novi Sad, Serbia & Montenegro
[a] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, University of Technology,
Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
[b] Ecole Polytechnique, Mecanique Energetique, Technopole de Chateau Gombert,
5 rue Enrico Fermi, 13453 Marseille Cedex 13, France

Reprint requests to M. G.-E., Fax: +33(0)4 91 11 74 39

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Electrical conductivity of liquid binary $NdBr_3$ – alkali metal bromide mixtures was measured as a function of temperature over the whole composition range. Prior to these measurements, $NdBr_3$ and alkali bromides were reinvestigated: a new assessment of literature data was made because of the discrepancy with reference values on $NdBr_3$, LiBr and CsBr. The classical Arrhenius equation describes well our electrical conductivity data for mixtures. These results are discussed in terms of complex formation in the melts.

Key words: Electrical Conductivity; Neodymium Bromide; $NdBr_3$; Alkali Bromide.

1. Introduction

We have previously measured and reported the thermodynamic properties (enthalpies and entropies of phase transitions, heat capacity) of neodymium(III) bromide and of compounds formed in $NdBr_3$-MBr binary systems (M=K, Rb, Cs) [1 – 4]. Mixing enthalpy was also measured over the whole composition range for all $NdBr_3$-MBr systems (M=Li, Na, K, Rb, Cs) [5]. This work continues our research program on above systems. It presents electrical conductivity of pure $NdBr_3$ and its mixtures with alkali metal bromides.

2. Experimental

2.1. Chemicals

Neodymium(III) bromide was prepared from Nd_2O_3 (99.9%) produced by the Chemistry Department of the University of Lublin (Poland). The synthesis included the following steps: dissolution of the oxide in hot concentrated hydrobromic acid, crystallisation of the $NdBr_3 \cdot 6\ H_2O$ hydrates, their dehydration and final purification of $NdBr_3$ by distillation under reduced pressure. The details of this synthesis have been described in [1, 5]. No insoluble matter was found on dissolving the synthesised $NdBr_3$ in water. Chemical analysis was performed by titration methods for bromide (mercurimetric) and lanthanide (complexometric). These results are presented in Table 1.

Table 1. Chemical analysis of $NdBr_3$.

Compound	$Br_{experimental}$ Mass %	$Br_{theoretical}$ Mass %	$Nd_{experimental}$ mass %	$Nd_{theoretical}$ mass %
$NdBr_3$	62.47	62.44	37.53	37.56

Alkali metal bromides were Merck Suprapur reagents, (min. 99.9%). Before use, they were progressively heated up to fusion under gaseous HBr atmosphere. HBr in excess was then removed from the melt by argon bubbling.

All chemicals were handled inside a high purity atmosphere argon glove box with a water content less than $2 \cdot 10^{-6}$ ppm. Continuous gas purification was ensured by forced recirculation through external molecular sieves.

2.2. Measurements

Electrical conductivity measurements were carried out in a capillary quartz cell with cylindrical platinum electrodes as described in [6]. The cell filled with the compounds under investigation was placed into a furnace with a stainless steel block, used to

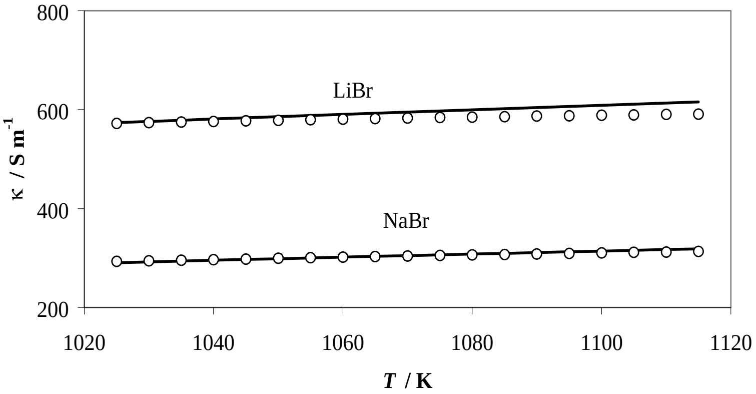

Fig. 1. Specific electrical conductivity of LiBr and NaBr *vs.* temperature: Circles: our experimental results, solid lines: literature data [7].

achieve uniform temperature. The conductivity of the melt was measured with the conductivity meter Tacussel CDM 230. Experimental runs conducted upon heating and cooling at a rate of 1 $K\,min^{-1}$ showed reproducibility within 1%. An average value was used in further calculations. Temperature and conductivity data acquisition was made with a PC interfaced to the conductivity meter. The accuracy of the electrical conductivity measurements was estimated to be ±2%. Temperature was measured by means of a Pt/Pt-Rh thermocouple with an accuracy of 1 K. The experimental cells were calibrated with pure KCl melt by the same experimental procedure [7]. The resulting cell constants amounted to 8000 – 18200 m^{-1}. The cell constants were checked from time to time in order to control any possible evolution. All measurements were carried out under static argon atmosphere.

3. Results and Discussion

Prior to the measurement on $NdBr_3$-MBr based mixtures the experimental method was checked by remeasuring the electrical conductivity of all liquid alkali bromides. The results of these measurements are presented in Figs. 1 and 2, together with literature data (for the sake of clarity, only a few experimental points at selected temperatures are displayed). Excellent agreement with published data is observed. The electrical conductivity results of the present work agree within 1 – 2% with the results reported by Janz on NaBr, KBr, and RbBr [7]. For LiBr, the results agree very well with [7] at temperatures just above the melting point, and are slightly smaller at higher temperatures (about 4% at 1115 K). More deviation was observed for CsBr. The reference value given in [7] was based on experimental data of Van Artsdalen and Yaffe [8]. However, while just above the melting point, our results agree very well with [7], they are at 1100 K by about 10% smaller. In view of this deviation, we reexamined all existing data on CsBr and found other references [9 – 11] that agree closely with our results (Figure 2).

Our experimental data on Neodymium bromide are also displayed in Figure 2. While Yaffe's original data [12] had been selected by Janz [7] as reference, Fig. 2 clearly shows that other authors agree better altogether (Dworkin [13] and Vogel [14]), with our measurements. The maximum deviation with the previously quoted authors [13 – 14] is 5% at 1045 K and 10% at 1095 K, respectively, while it ranges between 10 and 45%, depending on the temperature, with the previous "reference" value [12].

For all $NdBr_3$-MBr mixtures the electrical conductivity was measured over the entire composition range in steps of about 10 mol%. In all these systems, the classical Arrhenius equation

$$\kappa = \kappa_0 \exp(-E_A/RT) \tag{1}$$

with κ the specific electrical conductivity and κ_0 and E_A are constants, describes very well our experimental data. Figure 3 displays as an example the results of ten $NdBr_3$-NaBr liquid mixtures of different composition. The $\ln(\kappa_0)$ and E_A values of (1) were calculated by a least-squares treatment of the experimental data. These values, together with the number of experimental data points (***n***) and the standard deviation of estimate (***s***), are listed in Table 2.

The composition dependence of most molar properties is indicative of chemical interaction changes upon mixing. With no marked chemical interaction between the components, the properties do not deviate significantly from additivity. Conversely, large deviations

Table 2. Electrical conductivity of $NdBr_3$-MBr liquid mixtures: κ (in $\mathrm{S\,m^{-1}}$) $= \kappa_0 e^{-E_A/RT}$. ***n*** is the number of data points and ***s*** the standard deviation.

$NdBr_3$ (mol %)	Temp.range (K)	$\ln(\kappa_0)$ ($\mathrm{S\,m^{-1}}$)	E_A $\mathrm{kJ\,mol^{-1}}$	$\ln(\boldsymbol{s})$ ($\mathrm{S\,m^{-1}}$)	***n***
$NdBr_3$-LiBr					
0.00	828 – 1115	6.8468	4.298	0.0102	3158
10.04	800 – 1106	6.7836	6.453	0.0076	1338
20.26	756 – 1117	6.9841	10.853	0.0129	811
29.86	700 – 1097	6.5296	8.556	0.0165	1158
40.63	786 – 1149	6.2757	11.758	0.0123	2721
47.50	807 – 1022	6.2677	12.690	0.0102	1885
59.38	904 – 1053	6.5611	14.997	0.0158	2064
69.67	847 – 971	6.8413	17.832	0.0309	677
80.98	958 – 1054	6.5997	22.246	0.0115	495
89.67	975 – 1054	6.8097	25.152	0.0147	619
100	956 – 1107	7.3961	29.270	0.0160	399
$NdBr_3$-NaBr					
0.00	1026 – 1117	6.4969	6.941	0.0068	245
10.51	970 – 1065	6.4295	8.862	0.0011	415
20.65	868 – 1068	6.4124	10.743	0.0033	750
30.34	823 – 1065	6.5503	13.212	0.0088	1002
39.06	682 – 1055	7.0201	17.620	0.0242	661
50.69	750 – 864	7.7745	24.361	0.0031	235
58.56	816 – 869	7.3052	22.616	0.0048	174
72.37	875 – 990	7.2406	24.008	0.0063	341
89.37	944 – 1068	7.1051	25.532	0.0029	210
$NdBr_3$-KBr					
0.00	1020 – 1122	6.4336	11.073	0.0010	238
10.27	953 – 1110	6.1398	15.404	0.0134	430
19.65	885 – 1110	6.4631	15.403	0.0059	771
24.88	923 – 1120	6.3705	15.770	0.0038	427
30.00	912 – 1132	6.3669	15.846	0.0069	646
44.69	870 – 1130	6.3478	17.131	0.0069	526
56.36	850 – 1123	6.7692	21.543	0.0170	575
69.44	952 – 1120	6.7083	21.477	0.0068	420
79.45	971 – 1125	7.2006	26.422	0.0183	332
85.78	918 – 1110	7.2550	26.992	0.0096	426
$NdBr_3$-RbBr					
0.00	993 – 1124	6.1344	11.076	0.0028	287
10.18	967 – 1112	6.2374	14.381	0.0023	373
20.10	946 – 1126	6.2108	16.594	0.0101	380
30.10	1000 – 1113	6.1616	17.093	0.0014	168
40.31	916 – 1128	6.2020	17.752	0.0041	440
49.46	794 – 1113	6.4779	20.636	0.0192	746
59.25	916 – 1146	6.3215	18.981	0.0086	603
68.75	996 – 1113	6.4799	20.640	0.0037	323
79.55	997 – 1126	6.7026	22.513	0.0030	372
89.14	948 – 1114	7.1356	26.852	0.0055	792
$NdBr_3$-CsBr					
0.00	936 – 1137	6.0325	11.966	0.0027	1072
8.51	981 – 1140	6.1577	14.271	0.0040	460
16.28	1000 – 1096	6.3304	18.244	0.0143	237
29.94	1040 – 1145	6.1474	19.043	0.0018	587
38.54	903 – 1111	6.1858	20.011	0.0068	477
49.57	847 – 1146	6.2598	20.494	0.0110	616
59.30	887 – 1111	6.3612	21.176	0.0092	536
67.45	1065 – 1164	6.1979	20.605	0.0021	201
79.16	1040 – 1109	6.6620	23.180	0.0017	256
89.24	930 – 1112	7.2626	28.383	0.0119	468

from additivity may indicate strong chemical interaction resulting in complex formation in the melt, and thus decrease of the ionic electrical conductivity.

Experimental conductivity isotherms covering the whole composition range are presented in Figs. 4 and 5 for all systems. The electrical conductivity decreases with increasing alkali metal cation radius, *i.e.* from lithium to caesium. For all the systems, the relative changes of conductivity are significantly larger in the alkali bromide-rich region. In the neodymium bromide-rich region the conductivity behaviour is somewhat more complicated. Its smooth decrease in the systems with LiBr and NaBr becomes smaller in the KBr system, and transforms in a broad minimum, not clearly marked, in systems with RbBr and CsBr.

In early investigations, the conductivity of mixed molten salts was compared with values computed from a simple additivity law [15]. It was assumed that, if the components of the melt did not react chemically, the conductivity of the mixture should be the sum of the individual conductivities, and thus the conductivity isotherms would depend linearly on composition. Since conductivity is a kinetic property, Markov [15] showed that the simple additivity law for conductivity is not applicable to molten salt mixtures even in the case of the simplest melts (without chemical interaction). Instead, for the equivalent electrical conductivity of these mixtures he introduced equation:

$$\Lambda = {x_1}^2 \Lambda_1 + {x_2}^2 \Lambda_2 + 2 x_1 x_2 \Lambda_1, \tag{2}$$

where x_1, x_2, Λ_1 and Λ_2 are the mole fractions and the equivalent conductivities of the pure salts, respectively, with $\Lambda_1 < \Lambda_2$.

This equation could not be tested by our experimental results, because data of the molar volumes were lacking. Therefore it was assumed that specific conductivity would obey a similar law as exemplified in [16 – 17] for the $CoCl_2$-KCl and some binary fluoride systems:

$$\kappa = {x_1}^2 \kappa_1 + {x_2}^2 \kappa_2 + 2 x_1 x_2 \kappa_1, \tag{3}$$

where x_1, x_2, κ_1 and κ_2 are the mole fractions and specific conductivities of pure salts, respectively, with $\kappa_1 < \kappa_2$.

The relative conductivity deviations from (3) of the $NdBr_3$-MBr mixtures are presented in Figure 6: in all systems, a negative deviation is observed in the alkali bromide-rich range. This deviation increases with the size of the alkali cationic up to about 40% for the $NdBr_3$-CsBr system. In all systems (with exception of $NdBr_3$-LiBr), the maximal deviation occurs at about 25 – 35 mol % $NdBr_3$. In the $NdBr_3$-LiBr system this deviation is shifted to the LiBr-richer composition (about 20 mol % $NdBr_3$).

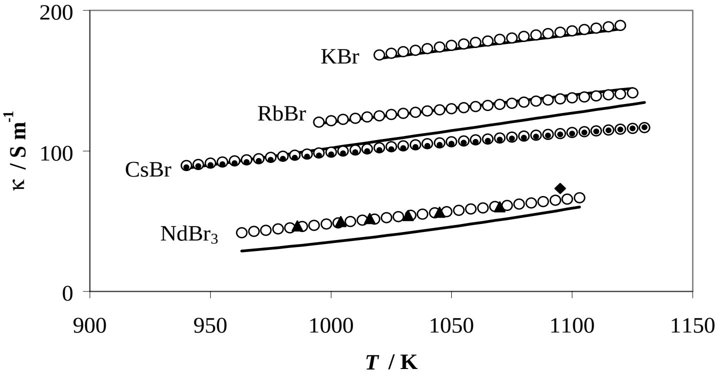

Fig. 2. Specific electrical conductivity of KBr, RbBr, CsBr and $NdBr_3$ *vs.* temperature: Circles: our experimental results, solid lines: [7], points: [9 – 11], triangles: [8], rhombus: [9].

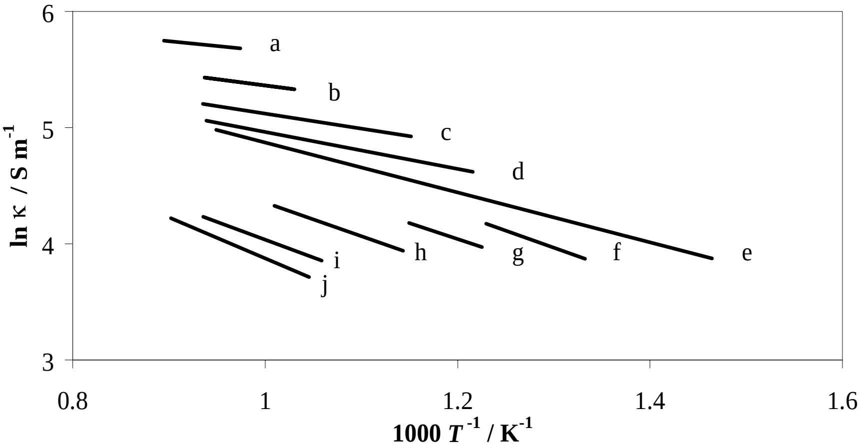

Fig. 3. lnκ *vs.* 1/T of $NdBr_3$-NaBr liquid mixtures. $x =$ mole fraction of $NdBr_3$ a: $x = 0.00$, b: 0.1051, c: 0.2065, d: 0.3034, e: 0.3906, f: 0.5096, g: 0.5856, h: 0.7237, i: 0.893, j: 1.00.

A positive electrical conductivity deviation from (3) is also observed in all systems in the neodymium bromide-rich compositions, with exception of $NdBr_3$-CsBr. This deviation decreases with increasing radius of the alkali ion (from lithium to rubidium).

According to literature [15], large negative electrical conductivity deviations are undoubtedly due to complex formation upon mixing of salts in the liquid state. Theoretically, the maximum deviation should be observed at a concentration corresponding to the complex composition. In the present work, the deviation curves in all systems (Fig. 6) exhibit a rather broad minimum, and it is impossible to determine accurately the composition and thus to ascribe any complex stoichiometry. A similar trend has been observed on enthalpy of mixing determinations of the same systems [5]. This enthalpy, negative in all systems, was found to increase (in absolute value) with the size of the alkali cation. Similarly, as described above for the electrical conductivity deviations, the maximum mixing enthalpy (in absolute values) was situated at compositions of 30 – 40 mol % $NdBr_3$. This was ascribed to possible $NdBr_6{}^{3-}$ complex formation. We had assumed that $NdBr_6{}^{3-}$ anions dominate in melts of neodymium(III) bromide with alkali metal bromides (especially for systems with heavier alkali metal cations), although the existence of other complexes could not be excluded. These conclusions were confirmed by Raman spectroscopy investigations [18]. Octahedral $NdBr_6{}^{3-}$ complexes were found to be predominant in MBr-rich liquid mixtures. However, increase of the $NdBr_3$ concentration leads to distortion of these octahedra and to polymer formation (distorted octahedra which are bridged to each other through bromide anions).

When a complex forms in the melt, it is clear that a minimum electrical conductivity should be observed at the composition of that complex. However, if more than one complex is formed or if one form of complex transforms to an other one, this minimum will not be clearly marked. This can explain the shift

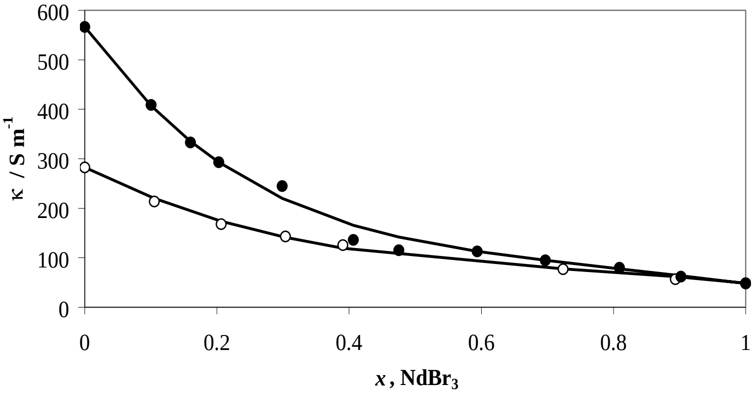

Fig. 4. Electrical conductivity isotherms at 1000 K: Black circles -$NdBr_3$-LiBr, open circles: $NdBr_3$-NaBr, solid lines: polynomial fitting of experimental results.

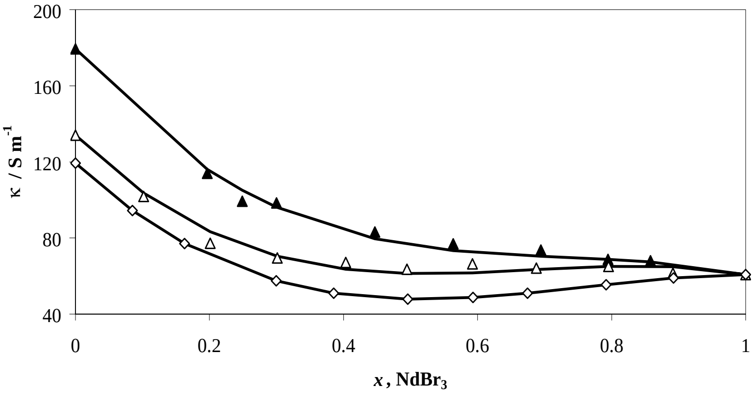

Fig. 5. Electrical conductivity isotherms at 1070 K: Black triangles: $NdBr_3$-KBr, open triangles: $NdBr_3$-RbBr, open rhombs: $NdBr_3$-CsBr, solid lines: polynomial fitting of experimental results.

of the conductivity minimum from 25 mol% $NdBr_3$ (composition that corresponds to pure $NdBr_6^{3-}$) to higher concentrations that correspond to polymer formation.

The positive deviations at $NdBr_3$-rich compositions are apparently caused by the disruption of associates in pure neodymium bromide, resulting in a new structure in which neodymium bromide contributes much to the transfer of electricity. It is evident that this disruption will be larger in the case of highly polarising cations. As the polarisability decreases from lithium to caesium cations, the positive deviation of the electrical conductivity decreases in the same order and does not exist in the system with caesium bromide.

Complex formation in the melt should also influence the activation energy for electrical conductivity, which should increase with increasing amount of complex formed. Such a behaviour was really observed in the systems under investigation (Table 2). However, some differences were found between $NdBr_3$-LiBr and $NdBr_3$-NaBr on the one hand, and other $NdBr_3$-MBr systems (M=K, Rb, Cs), on the other (Fig. 7). Whereas in the systems with LiBr and NaBr the activation energy increases with $NdBr_3$ concentration, in the other systems it increases rapidly up to about 20 mol% $NdBr_3$ and becomes almost stable up to about 70 mol% $NdBr_3$. In these potassium, rubidium and caesium systems, the activation energy increases slightly with the radius of the alkali ion (from potassium to caesium). It is likely that this is due to an increase in the complex concentration. This observation agrees with mixing enthalpy measurements [5], that also showed that the formation enthalpy, attributed to $NdBr_6^{3-}$ complex ions, increases with the ionic radius of the alkali metal cation. The alkali bromides provide additional bromide ions to enable Nd^{3+} to expand its coordination shell. But there is competition between M^+ and Nd^{3+} for Br^- in the ionic environment. The result of this competition depends on the relative attracting power of the alkali ion. The radius of the alkali metal will therefore govern the complex ion formation in $NdBr_3$-MBr binary systems. Thus the presence of CsBr in mixtures with $NdBr_3$ favours complex ion formation more than addition of RbBr and

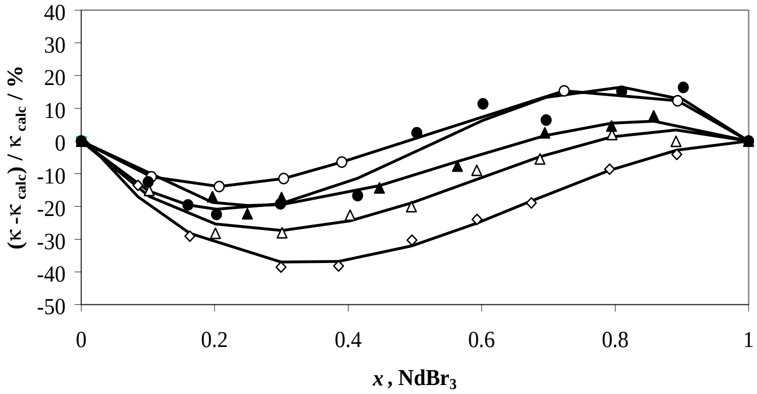

Fig. 6. Relative deviations of the specific conductivity from (3) Rhombus: $NdBr_3$-CsBr, open triangles: $NdBr_3$-RbBr, black triangles: $NdBr_3$-KBr, open circles: $NdBr_3$-NaBr, black circles: $NdBr_3$-LiBr, solid lines: polynomial fitting of experimental results.

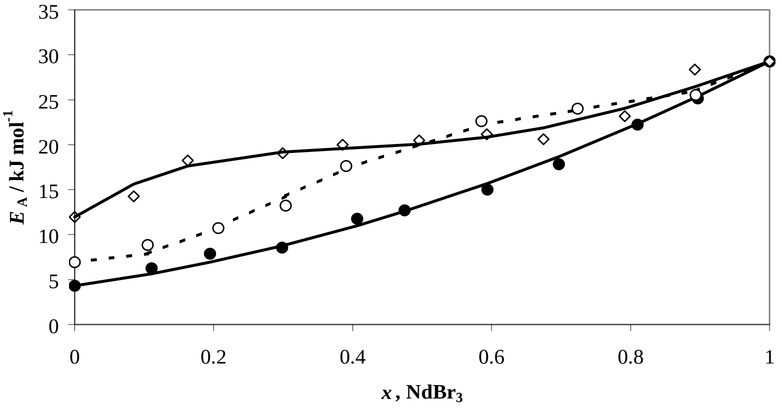

Fig. 7. Dependence of activation energy E_A of electrical conductivity on composition: Rhombs: $NdBr_3$-CsBr, open circles: $NdBr_3$-NaBr, black circles: $NdBr_3$-LiBr, solid and dashed lines: polynomial fitting of experimental results.

results in a larger enthalpy of formation, larger activation energy for conductivity, etc. The plateau in the activation energy plot *vs.* composition can be explained in terms of coexistence of different forms of complexes in the melt, as evidenced by Raman spectroscopy [18].

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