Electrical Conductivity of Molten $LaBr_3$ and $LaBr_3$–MBr Binary Mixtures

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The electrical conductivity of liquid binary $LaBr_3$-alkali metal bromide mixtures was measured as function of the temperature over the whole composition range. Prior to these measurements, $LaBr_3$ was reinvestigated because of the discrepancies in the literature values. The classical Arrhenius equation did not stand for any individual mixture. These results were discussed in terms of complex formation in the melts.

Key words: Lanthanum(III) Bromide; Alkali Metal Bromides; Electrical Conductivity; Activation Energy; Complex Formation.

1. Introduction

We have previously measured and reported the thermodynamic properties (temperatures and enthalpies of phase transitions, heat capacity) of lanthanide(III) bromides and of compounds formed in $LnBr_3$-MBr binary systems (M = K, Rb, Cs; Ln = La [1, 2], Nd [3 – 6] and Tb [7]). The mixing enthalpy was also measured over the whole composition range of all above $LnBr_3$-MBr systems, including also M = Li and Na [8 – 10]. As transport properties of molten salts are sensitive to their liquid structure, analysis of the electrical conductivity is a useful tool to attain structural information. The present paper follows previous electrical conductivity investigations on liquid $NdBr_3$ and $NdBr_3$-MBr mixtures [11] and deals with $LaBr_3$ and $LaBr_3$-MBr systems.

2. Experimental

2.1. Chemicals

The preparation of the chemicals was analogous to the one described in [11] for $NdBr_3$-alkali bromide mixtures. The chemical analysis of $LaBr_3$ is given in Table 1.

Table 1. Chemical analysis of $LaBr_3$.

Compound	mass %			
	$Br_{experimental}$	$Br_{theoretical}$	$La_{experimental}$	$La_{theoretical}$
$LaBr_3$	63.30	63.31	36.70	36.69

2.2. Measurements

Electrical conductivity measurements were carried out in a capillary quartz cell with the conductivity meter Tacussel CDM 230. The procedure is described in details in [6, 7]. The cell, filled with the substance under investigation, was placed into a furnace in a stainless steel block, used to achieve a uniform temperature. The conductivity of the melt was measured during increasing and decreasing temperature runs by platinum electrodes with the conductivity meter Tacussel CDM 230. The mean of these two conductivities was used in the calculations. Experimental runs were performed at heating and cooling rates ranged from 1 to 2 $K\,min^{-1}$. Temperature and conductivity data acquisition was made with a PC computer, interfaced to the conductivity meter. The temperature was measured with a Pt/Pt-Rh thermocouple with 1 K accuracy. The experimental cell was calibrated with a pure NaCl melt [7]. All measurements were carried out under static argon atmosphere. The accuracy of the measurements was about ±2%.

3. Results

Several authors [12 – 14] have investigated the electrical conductivity of liquid $LaBr_3$. The critically evaluated data reported by Janz et al. [15] were based on the early experimental work of Yaffe and van Artsdalen [12]. Although the latter evaluation and also Janz [16], confirmed these previous recommended data, no other more recent data sources [13] have been examined for this purpose. It should be noted however that about 25% uncertainty was assessed to these recommended data. Therefore it seemed appropriate to perform new measurements, and at the same time to assess the reliability of all existing conductance data on $LaBr_3$. Our experimental conductivity data were plotted against temperature (Fig. 1) together with literature data [12 – 14] for comparison.

The electrical conductivity was also measured for all $LaBr_3$-MBr mixtures. Experimental determinations were conducted over the entire composition range in steps of about 10 mol%. For all systems, κ of every individual mixture was plotted against temperature as $\ln(\kappa) = f(1/T)$. All plots deviate from linearity (see example in Figure 2).

The experimental conductivity data were well represented by the following equation:

$$\ln(\kappa) = A_0 + A_1 \cdot 10^3 \cdot \left(\frac{1}{T}\right) + A_2 \cdot 10^6 \cdot \left(\frac{1}{T}\right)^2, \quad (1)$$

where A_0, A_1 and A_2 are coefficients determined by the least-squares method. The activation energy, evaluated by analogy to the Arrhenius equation as

$$E_A(T) = -R\frac{d\ln(\kappa)}{d\left(\frac{1}{T}\right)}, \quad (2)$$

where R is the gas constant, becomes

$$E_A(T) = -R\left[A_1 + 2A_2\left(\frac{1}{T}\right)\right]. \quad (3)$$

All A_i coefficients are listed in Table 2, together with the E_A values determined at 1060 K for all the $LaBr_3$-MBr systems. Figure 3 reports, as an example, the evolution of the activation energy E_A for the $LaBr_3$-CsBr system, $x(LaBr_3) = 0.504$.

The electrical conductivity of all the alkali bromides was measured and discussed by us previously [11]. These data are also included in Table 2.

4. Discussion

The recommended conductivity values of liquid $LaBr_3$ (Fig. 1), reported by Janz [15], deviate significantly from those of all other investigators [12 – 14]. When compared to our results this difference ranges from 22% at 1060 K to 35% at 1130 K. Our results agree with the data of Dworkin et al. [13] within 3.5% in the temperature range examined by Dworkin, namely 1082 – 1162 K. They are by about 8% larger than those reported for 1090 – 1115 K by Fukushima and Iwadate [14].

In Fig. 4, for all systems, the experimental conductivity isotherms at 1060 K, covering the whole composition range, were plotted against the mole fraction of $LaBr_3$. The electrical conductivity decreases with increasing radius of the alkali metal cation, i. e. from lithium to caesium. In all systems the relative conductivity changes are significantly larger in the alkali bromide-rich region. In the lanthanum(III) bromide-rich region, the behaviour of the conductivity is somewhat more complicated. As shown in the insert of Fig. 4, an addition of alkali bromide to $LaBr_3$ results in a smooth conductivity increase in the systems with LiBr and NaBr which becomes smaller in the KBr system, and transforms into a broad, not clearly marked minimum in the systems with RbBr and CsBr. As discussed earlier [11], the dependence of the specific conductivity of binary mixtures on composition can be described by the Kuroda [17] equation

$$\kappa = {x_1}^2\kappa_1 + {x_2}^2\kappa_2 + 2x_1x_2\kappa_1, \quad (4)$$

where x_1, x_2 are the mole fractions of pure salts, and κ_1, κ_2 are the specific conductivity of $LaBr_3$ and MBr, respectively, with $\kappa_1 < \kappa_2$. Experimental electrical conductivity data deviate significantly from (4), as illustrated in Figure 5. These relative deviations were calculated from the equation

$$\Delta = (\kappa_{\text{exp.}} - \kappa_{\text{Kuroda}}) \cdot 100\%/\kappa_{\text{Kuroda}}. \quad (5)$$

For the systems $LaBr_3$–CsBr and $LaBr_3$–RbBr they are negative over the whole composition range. In the LiBr, NaBr and KBr systems, negative deviations occured in the MBr-rich composition range, followed by positive deviations starting at increasing $LaBr_3$ content in the sequence Li > Na > K. Biggest deviations, both in the positive and negative regime, are observed for the LiBr system, suggesting a mechanism different from that in the two other NaBr and KBr mixtures.

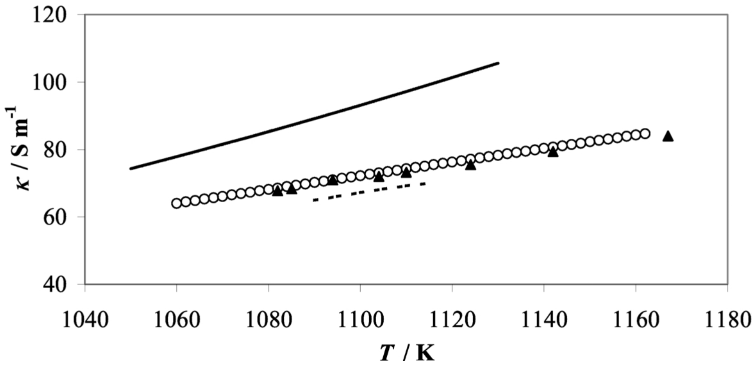

Fig. 1. Electrical conductivity of molten $LaBr_3$ vs. temperature: open circles: this work, solid line: literature data [12], black triangles: literature data [13], broken line: literature data [14].

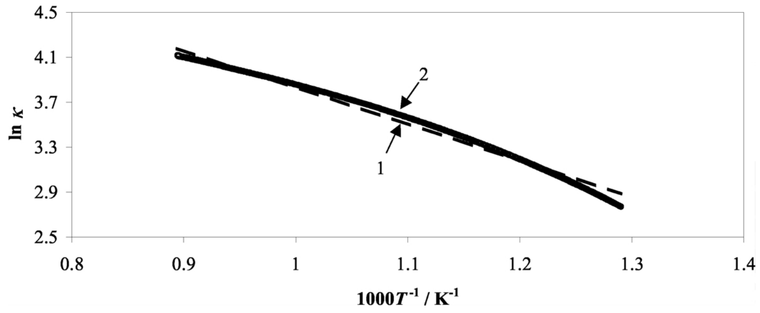

Fig. 2. ln κ vs. $1000/T$ of molten $LaBr_3$-CsBr ($x = 0.504$): x: mole fraction of $LaBr_3$; 1) - - - Arrhenius equation 2) — this work.

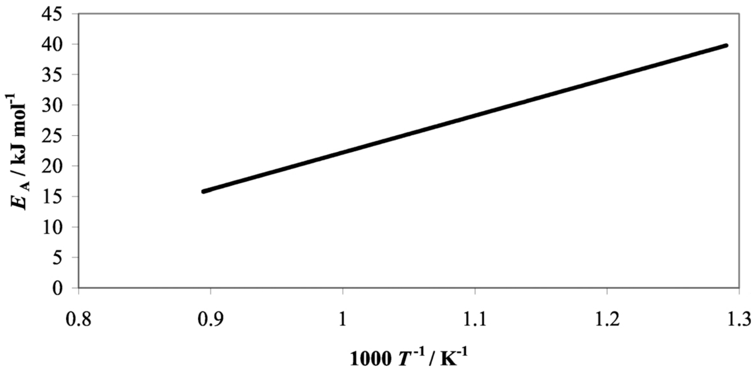

Fig. 3. Dependence of E_A vs. $1000/T$ for $LaBr_3$-CsBr, $x(LaBr_3) = 0.504$.

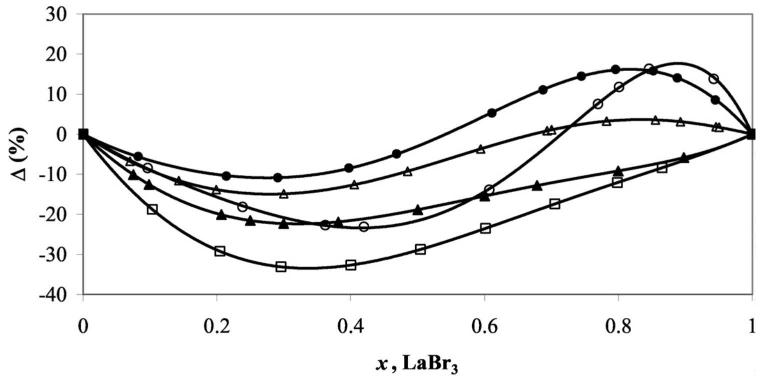

Fig. 5. Relative deviations of the electrical conductivity from the Kuroda equation (4) for $LaBr_3$-MBr liquid mixtures: open circles: M = Li, black circles: M = Na, open triangles: M = K, black triangles: M = Rb, open squares: M = Cs.

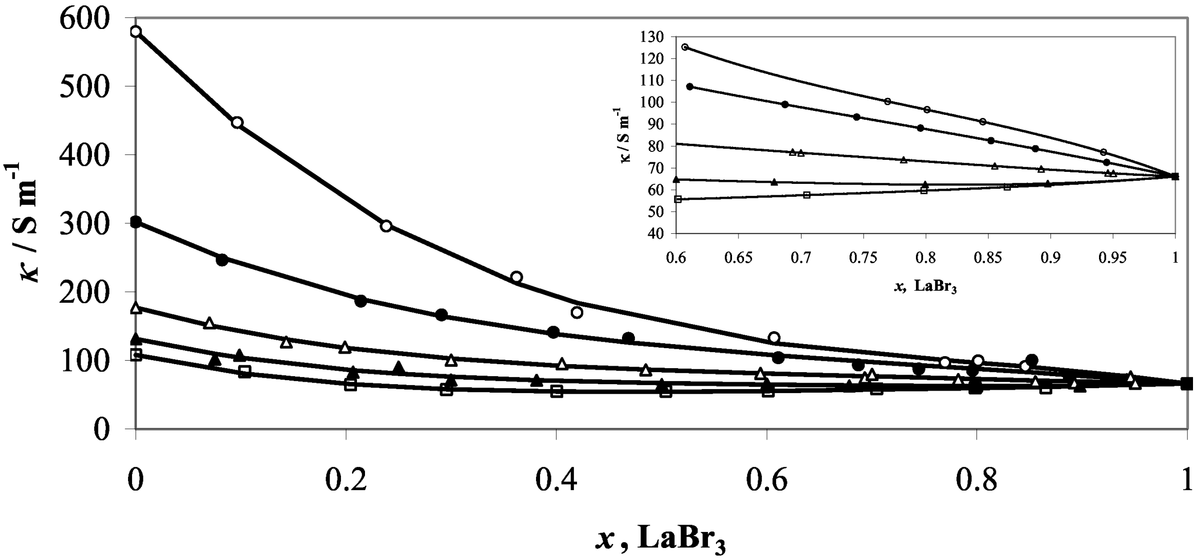

Fig. 4. Electrical conductivity isotherms of $LaBr_3$-MBr liquid mixtures at 1060 K: open circles: M = Li, black circles: M = Na, open triangles: M = K, black triangles: M = Rb, open squares: M = Cs.

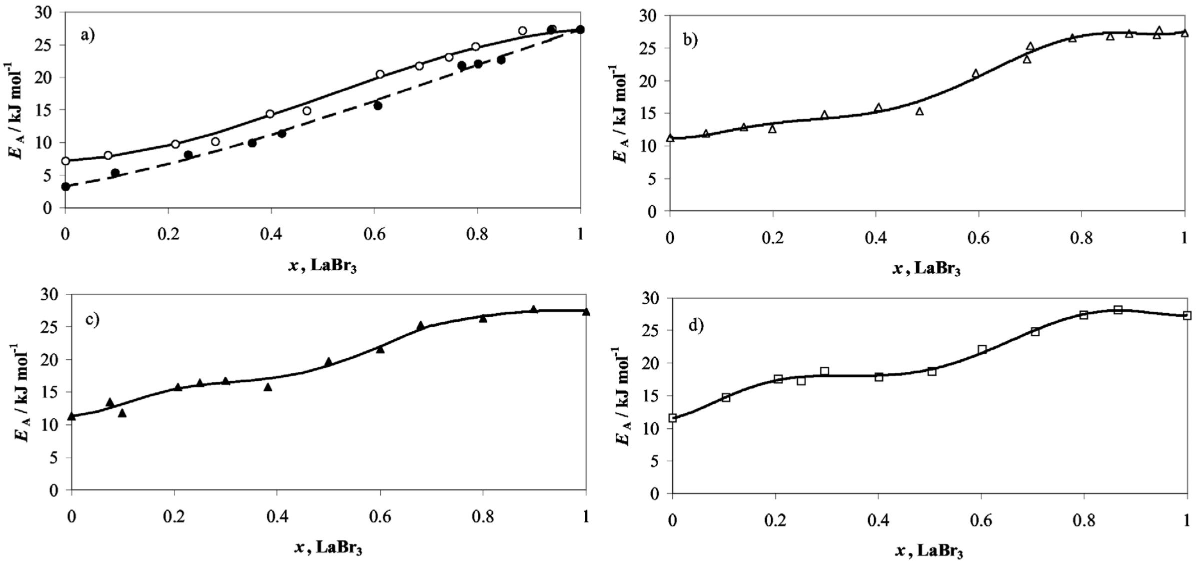

Fig. 6. Activation energy at 1060 K of $LaBr_3$-MBr liquid mixtures: a) open circles: M = Li, black circles: M = Na, b) M = K, c) M = Rb, d) M = Cs.

According to [18–20], marked negative electrical conductivity deviations from additivity are strongly indicative of complex formation. If only one complex species exists in the melt, the deviation is maximal at the composition corresponding to the stoichiometry of this complex. If several complex species exist, the location of the minimum may slightly deviate from the exact stoichometry of the predominant species.

Raman spectroscopic investigations [21] showed that octahedral $LnBr_6^{3-}$ ions are formed in $LnBr_3$-MBr liquid mixtures. These ions constitute the predominant species in the MBr-rich liquid mixtures. As the $LnBr_3$ concentration increases, distorted octahedra occurs, which are bridged by bromide anions. The formation of these $LaBr_6^{3-}$ complexes should influence the electrical conductivity vs. composition plot

Table 2. Coefficients of the equation: $\ln\kappa = A_0 + A_1(1T) + A_2(1T)^2$ and the activation energy of the electrical conductivity (E_A) of liquid LaBr$_3$-MBr binary mixtures at 1060 K: κ in S m^{-1}, $\ln(s)$ – standard deviation of $\ln\kappa$, n= number of experimental data points.

x, LaBr$_3$	Temp. range (K)	A_0	A_1 (K)	A_2 (K^2)	$\ln(s)$	n	E_A at 1060 K (kJ/mol)
LaBr$_3$ – LiBr							
0.00	828 – 1115	6.1292	0.8843	−0.6784	0.0083	2589	3.290
0.097	915 – 1103	5.9604	0.9488	−0.8456	0.0021	539	5.376
0.238	748 – 1085	5.8180	0.7098	−0.8966	0.0052	642	8.163
0.362	800 – 1101	5.4561	1.0901	−1.2131	0.0142	647	9.967
0.420	860 – 1107	5.1347	1.6681	−1.6098	0.0095	906	11.384
0.607	995 – 1107	4.5385	2.6251	−2.3871	0.0047	792	15.621
0.769	1034 – 1176	5.1068	1.4915	−2.1820	0.0013	772	21.829
0.801	1038 – 1156	4.8995	2.0159	−2.4739	0.0028	661	22.048
0.846	1059 – 1163	6.0834	−0.6022	−1.1277	0.0027	502	22.697
0.942	1074 – 1181	4.8565	2.0411	−2.8193	0.0012	501	27.257
1.00	1052 – 1172	6.0867	−0.7326	−1.3538	0.0016	215	27.329
LaBr$_3$ – NaBr							
0.00	1026 – 1117	5.2807	1.7775	−1.4020	0.0003	220	7.215
0.082	980 – 1115	5.7331	0.4924	−0.7764	0.0008	410	8.085
0.214	880 – 1114	5.4452	0.7184	−1.0054	0.0006	520	9.799
0.291	808 – 1010	4.8904	1.6952	−1.5447	0.0016	516	10.138
0.397	793 – 1066	5.2010	1.1978	−1.5528	0.0026	738	14.400
0.469	836 – 1070	4.2686	3.0881	−2.5820	0.0089	418	14.829
0.611	937 – 1060	5.5714	0.5003	−1.5718	0.0085	277	20.498
0.687	955 – 1134	4.9249	1.7893	−2.3337	0.0067	386	21.733
0.745	1001 – 1173	4.3810	2.9658	−3.0436	0.0003	422	23.087
0.796	1030 – 1115	3.9140	4.0969	−3.7464	0.0006	182	24.708
0.852	1033 – 1156	6.3838	−0.7095	−1.5513	0.0040	232	30.235
0.888	1030 – 1168	4.8950	2.0552	−2.8183	0.0016	519	27.124
0.945	1055 – 1153	4.5204	2.7743	−3.2180	0.0169	592	27.415
LaBr$_3$ – KBr							
0.00	1020 – 1122	5.9635	−0.3176	−0.5468	0.0008	263	11.218
0.070	1016 – 1154	5.8687	−0.3079	−0.5975	0.0072	702	11.933
0.143	996 – 1136	5.7005	−0.2703	−0.6772	0.0017	827	12.871
0.199	876 – 1145	4.3337	2.4694	−2.1126	0.0143	1057	12.609
0.300	892 – 1067	5.1199	0.7033	−1.3200	0.0034	813	14.860
0.405	876 – 1143	4.7963	1.4124	−1.7660	0.0013	757	15.960
0.485	872 – 1067	1.8480	7.3764	−4.8871	0.0238	791	15.336
0.594	813 – 1064	2.8642	5.7935	−4.4203	0.0137	917	21.173
0.693	1027 – 1163	4.7877	1.8078	−2.4453	0.0054	712	23.330
0.700	997 – 1145	3.8209	4.2361	−3.8622	0.0044	884	25.367
0.782	1010 – 1116	6.0032	−0.4627	−1.4478	0.0127	524	26.559
0.855	1027 – 1162	5.8556	−0.2047	−1.6026	0.0021	718	26.842
0.892	1050 – 1120	6.0664	−0.6616	−1.3851	0.0009	829	27.229
0.946	1085 – 1145	6.1624	−0.6403	−1.3808	0.0008	190	26.985
0.950	1045 – 1166	4.4166	2.8949	−3.3069	0.0064	671	27.807
LaBr$_3$ – RbBr							
0.00	993 – 1124	5.7114	−0.4031	−0.5083	0.0009	386	11.325
0.075	970 – 1115	5.5853	−0.4112	−0.6443	0.0010	961	13.526
0.099	1063 – 1163	6.0130	−1.4058	−0.0090	0.0030	488	11.829
0.207	960 – 1118	5.5490	−0.4971	−0.7408	0.0011	964	15.754
0.249	950 – 1116	5.2436	0.04263	−1.0677	0.0015	895	16.395
0.250	959 – 1139	5.4381	−0.3585	−0.8390	0.0019	416	16.395
0.300	960 – 1115	5.4832	−0.5622	−0.7656	0.0007	952	16.684
0.381	846 – 1110	4.9542	0.4345	−1.2438	0.0032	900	15.758
0.500	870 – 1115	4.1467	2.4275	−2.5443	0.0042	576	19.702
0.600	823 – 1117	2.7896	5.5682	−4.3282	0.0075	1160	21.602
0.678	948 – 1115	3.7078	3.9569	−3.7076	0.0045	372	25.263
0.799	992 – 1136	5.1960	0.9239	−2.1649	0.0052	309	26.280
0.898	1038 – 1116	6.0581	−0.7256	−1.3816	0.0013	240	27.699
LaBr$_3$ – CsBr							
0.00	936 – 1137	4.9549	0.8146	−1.1708	0.0011	1073	11.594
0.104	869 – 1114	4.9661	0.6204	−1.2695	0.0012	778	14.757
0.205	1012 – 1119	5.3814	−0.4660	−0.8749	0.0021	227	17.599
0.250	1026 – 1191	6.0490	−2.0703	−0.0002	0.0025	327	17.216
0.296	1020 – 1118	5.3523	−0.5111	−0.9267	0.0022	276	18.787
0.400	1000 – 1138	5.2882	−0.5701	−0.8388	0.0023	315	17.898
0.504	775 – 1116	2.8911	4.6182	−3.6437	0.0063	775	18.763
0.601	872 – 1138	3.1442	4.4975	−3.7920	0.0034	775	22.093
0.705	933 – 1135	3.6018	3.9740	−3.6879	0.0024	525	24.812
0.798	1038 – 1134	5.9733	−0.6969	−1.3747	0.0012	228	27.360
0.865	1048 – 1119	6.0204	−0.6991	−1.4238	0.0017	186	28.148

given in Fig. 4 for all systems. On the deviation curves (Fig. 5) these experimental results show a broad minimum located at lanthanum bromide mole fractions ranging 0.25 – 0.40.

For every system, the shift of the conductivity minimum from 25% LaBr$_3$ (composition that would correspond to LaBr$_6{}^{3-}$ being the only complex species) towards richer composition, as also its broadening is consistent with the structural conclusion [21] that LaBr$_6{}^{3-}$ octahedra generate and coexist with polymeric units of the same. A correlation can be made with previous calorimetric investigations of the same systems [8]. Negative for all, enthalpy of mixing exhibited a minimum beyond x(LaBr$_3$) = 0.25 and located around x(LaBr$_3$) = 0.3 – 0.4, again in agreement with the above description of the melt in terms of complexes.

LaBr$_3$-LiBr should proceed in another way, since complex formation fails to explain the very small enthalpy of mixing, thus suggesting a low probability of complex formation and, at the same time, large negative deviations of the electrical conductivity. A possible rationale may arise from the specific features of the small Li$^+$ cation in terms of polarisability [19]. When lanthanum bromide is added to the lithium bromide, the lithium ions coordinate an additional number of bromide ions at the expense of the lanthanum ions. This polarisation effect results in a large negative electrical conductivity departure from (4). Similarly, but to a lesser extent, polarisation interactions also take place in the sodium bromide system, in which the global negative deviation also accounts for an increased (in comparison with the LiBr system) possibility of complex formation. In the systems with heavier alkali metal bromides (KBr, RbBr and CsBr) negative electrical conductivity deviations mostly arise from complex formation.

The deviations of electrical conductivity from (4) become positive at increasing LaBr$_3$ composition for the LiBr, NaBr and KBr-LaBr$_3$ systems (Fig. 5). In those systems, as already indicated in the insert of

Fig. 4, a small addition of alkali bromide results in an electrical conductivity increase, indicating the disruption of associates in pure lanthanum(III) bromide. This effect is more marked for the most polarizing cations, i. e. from lithium to caesium, and the positive electrical conductivity deviations decrease in the same order from lithium to potassium, while the RbBr and CsBr systems only deviate negatively from (4).

As indicated above, the activation energy for conductivity changes with temperature in every individual mixture, validating the early statement made by Yaffe and van Artsdalen [22 – 23] of a correlation with structural changes in melts.

Figure 6 shows the activation energy at 1060 K as function of the composition of all systems. The LiBr and NaBr-$LaBr_3$ mixtures display a smooth concentration evolution, while in the KBr, RbBr and CsBr systems a stabilisation effect from about 25 mol% up to about 40 – 50 mol% respectively, is observed. This is consistent with the predominant ${LaBr_6}^{3-}$ octahedral complexes in melts rich in KBr, RbBr and CsBr with an increasing amount of polymeric species in the $LaBr_3$-rich melts. Figure 6 also clearly illustrates that the activation energy increases with the alkali cationic radius in MBr-rich melts.

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