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# Formation enthalpies of the MBr–$LaBr_3$ liquid mixtures (M = Li, Na, K, Rb, Cs)

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**Abstract**

Molar enthalpies of mixing of the LiBr–$LaBr_3$, NaBr–$LaBr_3$, KBr–$LaBr_3$, RbBr–$LaBr_3$ and CsBr–$LaBr_3$ systems have been measured with a Calvet-type high-temperature microcalorimeter. The enthalpies decrease gradually from $-0.67$ kJ mol$^{-1}$ for the lithium system through $-4.32$, $-10.73$ and $-14.97$ kJ mol$^{-1}$ for the sodium, potassium, and rubidium systems to $-16.81$ kJ mol$^{-1}$ for that of cesium at the composition of the 3 MBr·$LaBr_3$ compound. The results have been discussed in terms of the conformal solution theory of Davis as well as in terms of relative ionic potentials.

*Keywords:* Alkali bromides; Enthalpy of mixing; High temperature calorimetry; Lanthanum bromide; Molten bromides; Molten salt mixture

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## 1. Introduction

The work presented here is a part of a general research program focused on halide melts which contain rare-earth halides [1–7]. This paper presents the results of measurements of the molar mixing enthalpy $\Delta_{mix}H_m^0$ of the liquid systems MBr–$LaBr_3$ (with M = Li, Na, K, Rb, and Cs). Systematization of the thermodynamic behavior of unsymmetrical ionic melts and examination of the possibilities of complexing in these

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mixtures are the main purposes of this work. New data are compared with enthalpy measurements of the MBr–$NdBr_3$ liquid systems [8] and are discussed in terms of the conformal solution theory of Davis [9] as well as in terms of relative ionic potentials [10].

## 2. Experimental

### 2.1. Chemicals

Lanthanum (III) bromide was prepared from lanthanum oxide supplied by "Hydro-Met" Kowary Inc. (Poland). $La_2O_3$ was dissolved in concentrated HBr solution and $NH_4Br$ was added to the solution in the molar ratio $LaBr_3 : NH_4Br = 1:4$. The solution was gradually evaporated to remove excess water. This wet mixture of hydrated $LaBr_3$ and ammonium bromide was first heated to 570 K in a quartz ampoule under vacuum (to remove the rest of the water) and then heated to 650 K for sublimation of $NH_4Br$. Finally the salt was melted at 1100 K and the quartz ampoule containing $LaBr_3$ was opened in a dry-box. Crude lanthanum bromide was purified by distillation [2] under reduced pressure ($\sim$ 0.1 Pa) in another quartz ampoule at 1150 K. $LaBr_3$ prepared this way was of a high grade — min. 99.9%.

MBr alkali bromides (where M = Li, Na, K, Rb, Cs) were Merck Suprapur reagents (min. 99.9%). Before the use, they were treated by progressive heating up to fusion under an atmosphere of gaseous HBr. Excess HBr was removed from the melt by argon.

All handling of dry chemicals was performed in a glove-box under argon which was continuously purified by recirculation through molecular sieves.

### 2.2. Experimental procedure

The mixing experiments were of the simple liquid–liquid type. They were performed under argon at atmospheric pressure. The Calvet-type high temperature microcalorimeter, the specially designed quartz cells, and the experimental procedures have been described in detail elsewhere [2, 11]. For any investigated system the more volatile component was weighed with precision of $10^{-5}$ g and placed in the break-off quartz ampoule. The second component weighed with the same precision was placed in a quartz crucible. The break-off ampoule was filled with argon at an appropriate pressure in order to keep the pressure inside and outside the ampoule constant at the temperature of experiment. Then it was welded to the quartz tube which could be moved up and down along the calorimetric cell through a tight-ring. Argon entered the calorimetric cell by the same quartz tube. The ampoule was broken after thermal equilibrium had been achieved and the thermal effect resulting from mixing process was recorded. Calibration of the calorimeter was performed with NIST $\alpha$-alumina (30–100 mg) by dropping it to the calorimetric cell with the melt and registering the thermal effect of its heating from ambient temperature to that of the experiment [12]. Integration of thermograms was computerized.

## 3. Results

All calorimetric experiments were performed at 1081 K. Molar mixing enthalpies of the $LiBr–LaBr_3$, $NaBr–LaBr_3$, $KBr–LaBr_3$, $RbBr–LaBr_3$ and $CsBr–LaBr_3$ liquid systems were determined over the whole composition range. Experimental values of $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$ are given in Tables 1–5 and are plotted against $X_{\mathrm{LaBr_3}}$ in Fig. 1. Formal

Table 1
Molar mixing enthalpies and $\lambda$ parameters for the $LiBr–LaBr_3$ system at 1081 K

| $X_{\mathrm{LaBr_3}}$ | $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) | $X_{\mathrm{LaBr_3}}$ | $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.1203 | −0.33 | −3.14 | 0.6061 | −0.70 | −2.92 |
| 0.201 | −0.59 | −3.68 | 0.6962 | −0.48 | −2.27 |
| 0.2979 | −0.69 | −3.30 | 0.8020 | −0.24 | −1.50 |
| 0.4141 | −0.96 | −3.97 | 0.9031 | −0.12 | −1.37 |
| 0.4999 | −0.70 | −2.82 | 0.9511 | −0.04 | −0.86 |

Table 2
Molar mixing enthalpies and $\lambda$ parameters for the $NaBr–LaBr_3$ system at 1081 K

| $X_{\mathrm{LaBr_3}}$ | $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) | $X_{\mathrm{LaBr_3}}$ | $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.0497 | −1.09 | −23.16 | 0.4816 | −4.67 | −18.72 |
| 0.0999 | −2.20 | −24.47 | 0.5475 | −4.53 | −18.30 |
| 0.1204 | −2.73 | −25.81 | 0.6014 | −4.06 | −16.95 |
| 0.1469 | −3.29 | −26.23 | 0.6523 | −3.85 | −16.97 |
| 0.2314 | −4.14 | −23.27 | 0.7567 | −2.79 | −15.15 |
| 0.2540 | −4.38 | −23.12 | 0.790 | −2.48 | −14.92 |
| 0.3055 | −4.80 | −22.64 | 0.8594 | −1.86 | −15.37 |
| 0.3478 | −4.90 | −21.60 | 0.895 | −1.22 | −13.00 |
| 0.4111 | −4.71 | −19.46 | | | |

Table 3
Molar mixing enthalpies and $\lambda$ parameters for the $KBr–LaBr_3$ system at 1081 K

| $X_{\mathrm{LaBr_3}}$ | $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) | $X_{\mathrm{LaBr_3}}$ | $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.0241 | −1.34 | −56.97 | 0.4921 | −11.27 | −45.11 |
| 0.0497 | −2.74 | −57.99 | 0.5495 | −12.39 | −50.07 |
| 0.0992 | −5.28 | −59.13 | 0.5863 | −11.52 | −47.48 |
| 0.1497 | −7.83 | −61.55 | 0.6495 | −9.45 | −41.49 |
| 0.2037 | −9.27 | −57.17 | 0.7035 | −9.57 | −45.88 |
| 0.2485 | −11.30 | −60.51 | 0.7542 | −6.30 | −34.00 |
| 0.3005 | −11.85 | −56.39 | 0.8022 | −6.34 | −39.96 |
| 0.3418 | −12.41 | −55.14 | 0.8484 | −5.28 | −41.03 |
| 0.3471 | −12.03 | −53.07 | 0.8997 | −3.79 | −41.96 |
| 0.4005 | −12.33 | −51.35 | 0.9010 | −2.28 | −25.53 |
| 0.4521 | −12.64 | −51.04 | 0.9492 | −1.82 | −37.85 |

Table 4
Molar mixing enthalpies and $\lambda$ parameters for the RbBr–$LaBr_3$ system at 1081 K

| $X_{LaBr_3}$ | $\Delta_{mix}H^0_m$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) | $X_{LaBr_3}$ | $\Delta_{mix}H^0_m$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.0489 | −3.36 | −72.22 | 0.4514 | −17.23 | −69.56 |
| 0.0749 | −5.03 | −72.64 | 0.5017 | −15.73 | −62.94 |
| 0.098 | −7.51 | −84.95 | 0.5378 | −15.00 | −60.34 |
| 0.1467 | −11.09 | −88.58 | 0.5925 | −14.36 | −59.49 |
| 0.2004 | −11.96 | −74.67 | 0.6501 | −13.07 | −57.48 |
| 0.2496 | −15.32 | −81.82 | 0.7391 | −9.87 | −51.17 |
| 0.2517 | −16.99 | −90.21 | 0.8012 | −7.09 | −44.53 |
| 0.3009 | −17.38 | −82.60 | 0.8449 | −4.93 | −37.59 |
| 0.3513 | −17.45 | −76.57 | 0.8952 | −3.16 | −33.70 |

Table 5
Molar mixing enthalpies and $\lambda$ parameters for the CsBr–$LaBr_3$ system at 1081 K

| $X_{LaBr_3}$ | $\Delta_{mix}H^0_m$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) | $X_{LaBr_3}$ | $\Delta_{mix}H^0_m$/(kJ mol$^{-1}$) | $\lambda$/(kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.0249 | −2.23 | −91.76 | 0.4609 | −19.60 | −78.91 |
| 0.0495 | −3.91 | −83.19 | 0.5028 | −18.64 | −74.56 |
| 0.0778 | −6.02 | −83.95 | 0.5445 | −17.89 | −72.12 |
| 0.1176 | −9.74 | −93.88 | 0.5634 | −16.24 | −66.01 |
| 0.1257 | −10.86 | −98.86 | 0.6016 | −16.67 | −69.57 |
| 0.1495 | −13.05 | −102.65 | 0.6558 | −15.18 | −67.25 |
| 0.1965 | −15.28 | −96.76 | 0.7001 | −13.93 | −66.33 |
| 0.2233 | −16.42 | −94.66 | 0.7225 | −12.20 | −60.85 |
| 0.2357 | −14.87 | −82.54 | 0.7861 | −10.45 | −62.16 |
| 0.2514 | −17.99 | −95.57 | 0.8129 | −8.23 | −54.12 |
| 0.2996 | −18.19 | −86.67 | 0.8594 | −7.03 | −58.21 |
| 0.3254 | −19.07 | −86.85 | 0.9047 | −4.73 | −54.81 |
| 0.3416 | −19.61 | −87.19 | 0.9499 | −2.62 | −54.97 |
| 0.3983 | −19.53 | −81.51 | | | |

accuracy of the single measurement depended on the value of $\Delta_{mix}H^0_m$ and was estimated as 3–6% of the measured value on the basis of calibration experiments. Moreover, single points were disregarded from some sets of experimental data when incomplete mixing (due to too thick walls of the break-off ampoule) was observed.

## 4. Discussion

The investigated melts are characterized by negative values of $\Delta_{mix}H^0_m$ which decrease with increasing ionic radius of the alkali metal cation. This feature is very similar to that observed for MBr–$NdBr_3$ systems [8]. The minimum of the molar enthalpy of mixing is shifted towards the alkali bromide-rich part and is located in the

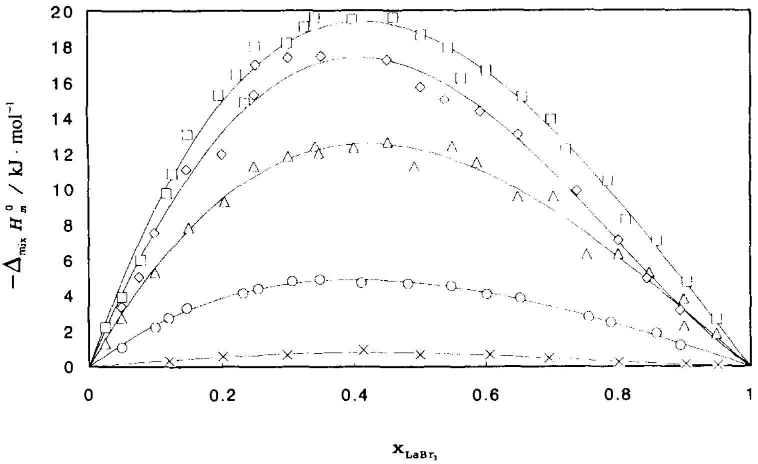

Fig. 1. Molar mixing enthalpy of the systems: ×, LiBr–LaBr$_3$; ○, NaBr–LaBr$_3$; △, KBr–LaBr$_3$; ◇, RbBr–LaBr$_3$, □, CsBr–LaBr$_3$ at 1081 K.

vicinity of $X_{LaBr_3} = 0.4$ for all investigated systems. Corresponding values of $\Delta_{mix}H^0_m$ are also very similar.

One may define the interaction parameter $\lambda$ which describes the energetic asymmetry of the melts:

$$\lambda = \frac{\Delta_{mix}H^0_m}{X_{LaBr_3} \times (1 - X_{LaBr_3})} \tag{1}$$

Fig. 2 shows how this parameter depends on $X_{LaBr_3}$. For each system the experimental values of $\lambda$ were fitted by the method of the least squares to appropriate polynomials.

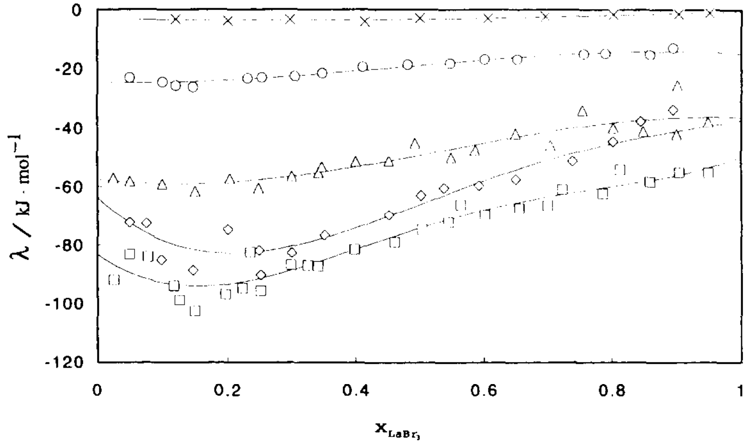

Fig. 2. Dependence of the $\lambda$ parameter on $X_{LaBr_3}$ at 1081 K. ×, LiBr–LaBr$_3$; ○, NaBr–LaBr$_3$; △, KBr–LaBr$_3$; ◇, RbBr–LaBr$_3$; □, CsBr–LaBr$_3$.

Table 6
Least-square coefficients of the $\lambda$ dependence on composition for liquid MBr–LaBr$_3$ mixtures, $\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4$, in kJ mol$^{-1}$; $X = X_{LaBr_3}$

| System | $A$ | $B$ | $C$ | $D$ | $E$ | S.E. |
|---|---|---|---|---|---|---|
| LiBr–LaBr$_3$ | −3.07 | −3.05 | 5.74 | – | – | 0.34 |
| NaBr–LaBr$_3$ | −24.60 | −5.50 | 51.93 | −36.77 | – | 0.99 |
| KBr–LaBr$_3$ | −57.44 | −27.25 | 127.02 | −78.63 | – | 3.95 |
| RbBr–LaBr$_3$ | −63.66 | −211.52 | 715.75 | −729.74 | 251.83 | 5.15 |
| CsBr–LaBr$_3$ | −83.19 | −158.59 | 699.12 | −874.34 | 367.34 | 4.63 |

Their coefficients and standard errors are given in Table 6. It may be noticed from Fig. 2 that dependence of the $\lambda$ parameter on composition is very close to linear for the LiBr–LaBr$_3$ and NaBr–LaBr$_3$ systems. But for the systems with KBr, RbBr, and CsBr this dependence is somewhat more complicated — a broad minimum appears at $X_{LaBr_3} \sim 0.2$. Similar variations of $\lambda$ were observed for MCl–LnCl$_3$ liquid systems [2,3,13,14] (where Ln = La, Ce, Pr, or Nd). They were attributed to the formation of LnCl$_6^{3-}$ complexes. The minimum of the dependence of the interaction parameter $\lambda$ on concentration cannot be explicitly deduced from the conformal solution theory. However, using the simple model of formation of complexes introduced by Papatheodorou and Østvold [13] for the MCl–LaCl$_3$ systems it is possible to give a semiquantitative explanation of this minimum as a result of LaBr$_6^{3-}$ complex formation. A detailed discussion of possible complexing in chloride melts has been presented in a previous paper [2]. Existence of the LnCl$_6^{3-}$ complexes was confirmed by Raman structural studies of lanthanum chloride [15], yttrium chloride [16] and neodymium chloride [17] in the liquid alkali chlorides. Also a report of Fukushima et al. [18] gives information on the existence of octahedral complexes in molten LaBr$_3$. Therefore, it may be assumed that LaBr$_6^{3-}$ octahedral complexes may be formed in the investigated systems and that this results in specific dependence of $\lambda$ on composition.

The conformal solution theory of Davis [9] predicts that at fixed temperature, pressure, and composition the interaction parameter $\lambda$ should, to a second-order approximation, be a function of the size parameter $\delta_{12}$:

$$\lambda = a(T,p,x) + b(T,p,x) \times \delta_{12} + c(T,p,x) \times \delta_{12}^2 \quad (2)$$

where $a$, $b$ and $c$ are complicated integral functions of $T$, $p$ and $x$, and $\delta_{12} = \frac{d_1 - d_2}{d_1 \times d_2}$, where $d_1 = r_{M^+} + r_{X^-}$ and $d_2 = r_{Ln^{3+}} + r_{X^-}$; $r_{M^+}$ is the ionic radius of the alkali metal, $r_{Ln^{3+}}$ is the ionic radius of the lanthanide metal (Nd, La), and $r_{X^-}$ is the ionic radius of the halide (Br).

The dependence of interaction parameter $\lambda$ on the size parameter $\delta_{12}$ for the MBr–LaBr$_3$ liquid systems is tested in Fig. 3 by plotting $\lambda_{(x_{LaBr_3} \to 0)}$ and $\lambda_{(x_{LaBr_3} \to 1)}$ against $\delta_{12}$. These dependencies may be described by the following equa-

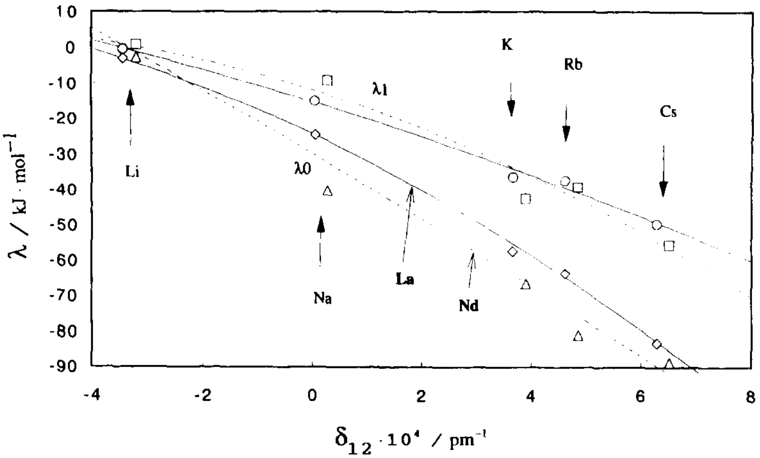

Fig. 3. Dependence of the interaction parameters $\lambda_{(x_{\mathrm{LnBr_3}} \to 0)}$ (λ0) and $\lambda_{(x_{\mathrm{LnBr_3}} \to 1)}$ (λ1) on the size parameter $\delta_{12}$ for MBr–LaBr$_3$ (solid line) and MBr–NdBr$_3$ [8] (dashed line) systems at 1081 K. ○, ◇, lanthanum compounds; □, △, neodymium compounds.

tions:

$$\lambda_{(x_{\mathrm{LaBr_3}} \to 0)} = -24.3 - 7.27 \times 10^4 \times \delta_{12} - 3.23 \times 10^7 \times \delta_{12}^2 \quad (3)$$

$$\lambda_{(x_{\mathrm{LaBr_3}} \to 1)} = -15.2 - 4.74 \times 10^4 \times \delta_{12} - 1.09 \times 10^7 \times \delta_{12}^2 \quad (4)$$

We have also included in this figure the corresponding values for the MBr–NdBr$_3$ systems [8] (measurements were carried out at 1063 K). The figure reveals that for each MBr–LnBr$_3$ series these theoretical equations may be well fitted to the data. It should be noticed that dependencies of $\lambda_{(x_{\mathrm{LaBr_3}} \to 0)}$ on $\delta_{12}$ MBr–LaBr$_3$ systems and $\lambda_{(x_{\mathrm{LaBr_3}} \to 0)}$ on $\delta_{12}$ for MBr–NdBr$_3$ systems are very similar. Such similarity may also be found for the dependencies of $\lambda_{(x_{\mathrm{LaBr_3}} \to 1)}$ on $\delta_{12}$ for the MBr–LaBr$_3$ system and $\lambda_{(x_{\mathrm{NdBr_3}} \to 1)}$ on $\delta_{12}$ for the MBr–NdBr$_3$ system.

Table 7
$\lambda_{(x_{\mathrm{LnBr_3}} \to 0)}$ and $\lambda_{(x_{\mathrm{LnBr_3}} \to 1)}$ for MBr–LaBr$_3$ and MBr–NdBr$_3$ systems; $r_{\mathrm{M^+}}$ is the alkali metal ionic radius

| | LaBr$_3$ | | NdBr$_3$ | | |
|---|---|---|---|---|---|
| System | $\lambda_{(x=0)}$/(kJ mol$^{-1}$) | $\lambda_{(x=1)}$/(kJ mol$^{-1}$) | $\lambda_{(x=0)}$/(kJ mol$^{-1}$) | $\lambda_{(x=1)}$/(kJ mol$^{-1}$) | $r_{\mathrm{M^+}}$/[21] pm[a] |
| LiBr–LnBr$_3$ | −3.07 | −0.38 | −2.700 | 0.88 | 74 |
| NaBr–LnBr$_3$ | −24.60 | −14.94 | −40.32 | −9.19 | 102 |
| KBr–LnBr$_3$ | −57.44 | −36.30 | −66.64 | −42.53 | 138 |
| RbBr–LnBr$_3$ | −63.66 | −37.34 | −80.98 | −39.18 | 149 |
| CsBr–LnBr$_3$ | −83.19 | −49.66 | −88.67 | −55.57 | 170 |

[a] $r_{\mathrm{La^{3+}}}$/pm = 101.6 [21] $r_{\mathrm{Nd^{3+}}}$/pm = 99.5 [21] $r_{\mathrm{Br^-}}$/pm = 196.0 [21]

In general, it is rather obvious that the enthalpy of mixing of a charged unsymmetrical system with different cations and a common anion should depend in a first place on the charge and size of the cations. In our previous paper [8] we analyzed the dependence of the $\lambda$ parameter on the ionic potential of the melt. Now we apply a similar, relative ionic potential introduced by Hong and Kleppa [19,20]. This potential is defined as:

$$\Delta IP = \frac{z_1}{r_1} - \frac{z_2}{r_2} \tag{5}$$

where $z_1, z_2$ and $r_1, r_2$ are the valences and ionic radii of cations 1 and 2, respectively. So the defined "relative ionic potential" reflects in the main the change in Coulombic interactions on mixing; however, it should also be related to the magnitude of the polarization of the common anion by its neighboring cations. Generally, the larger is the relative ionic potential the more negative is the enthalpy of mixing. Hong and Kleppa [19] proved that there is a linear relationship between the corresponding relative ionic potential and limiting interaction parameter for many molten salt mixtures with ions of different valences (M′X–M″$X_2$):

$$\lambda_{(x_{\mathrm{LaBr_3}} \to 0)} = \alpha + \beta \times \Delta IP \tag{6}$$

We give in Fig. 4 a plot of the enthalpy interaction parameter $\lambda_{(x_{\mathrm{LaBr_3}} \to 0)}$ against $\Delta IP$ for the MBr–$\mathrm{LaBr_3}$ and MBr–$\mathrm{NdBr_3}$ families [8]. These dependencies may be described by the simple equations ($r_{\mathrm{M^+}}$ and $r_{\mathrm{La^{3+}}}$ in pm):

$$\lambda_{(x_{\mathrm{LaBr_3}} \to 0)} = 163.1 - 1.001 \times 10^4\left(\frac{3}{r_{\mathrm{La^{3+}}}} - \frac{1}{r_{\mathrm{M^+}}}\right)[\pm 5], \mathrm{kJ\ mol^{-1}} \tag{7}$$

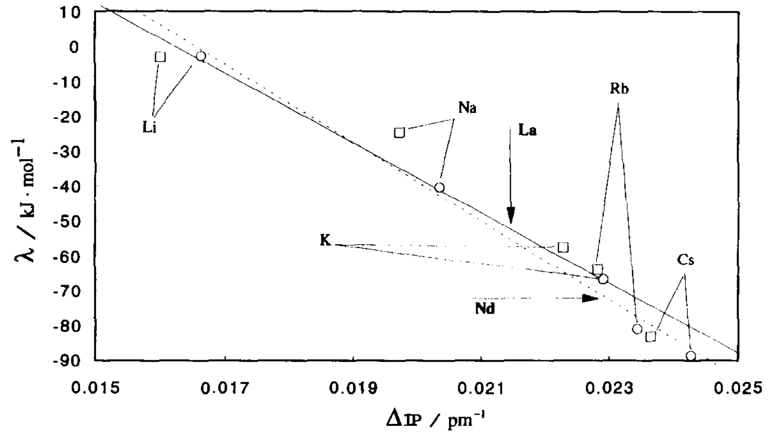

Fig. 4. Dependence of the interaction parameters $\lambda_{(x_{\mathrm{LnBr_3}} \to 0)}$ on the relative ionic potential $\Delta IP$ for the systems MBr–$\mathrm{LaBr_3}$ (solid line, ○ symbols) and MBr–$\mathrm{NdBr_3}$ [8] (dashed line, □ symbols) at 1081 K.

for MBr–LaBr$_3$ and,

$$\lambda_{(X_{\mathrm{NdBr_3}}\to 0)} = 186.1 - 1.124 \times 10^4\left(\frac{3}{r_{\mathrm{Nd^{3+}}}} - \frac{1}{r_{\mathrm{M^+}}}\right)[\pm 4], \mathrm{kJ\ mol^{-1}} \tag{8}$$

for MBr–NdBr$_3$ liquid systems.

According to Kleppa [10] the first positive term may be ascribed partially to London–van-der-Waals dispersion interactions between second-nearest-neighbor cations and partially to the steric effect associated with the mixing of two cations of different size and charge. Thus, one would expect to find very small positive values of the first term of Eq. (6) for binary symmetrical systems MX–M′X (M, M′ = Li, Na, K, Rb, Cs; X = F, Cl, Br) and its value increasing in the sequence MX–M′X < MX–Me″X$_2$ < MX–Me‴X$_3$. On the other hand, the second $\beta \times \Delta IP$ term is negative and involves in the first place contributions of the coulombic and polarization energies to the molar enthalpy of mixing. For systems with quite small values of the $\Delta IP$ this term may be too small in comparison with a value of $\alpha$ that will result in a net positive mixing enthalpy. We have observed this phenomenon for the DyCl$_3$–PrCl$_3$ [5] system which is the symmetrical one with a small value of $\alpha$ but, due also to a very small value of the $\beta \times \Delta IP$ term, $\lambda_{(X_{\mathrm{LaBr_3}}\to 0)}$ is positive and equal to 1.53 kJ mol$^{-1}$ [5].

## 5. Conclusions

Molar enthalpies of mixing of the LiBr–LaBr$_3$, NaBr–LaBr$_3$, KBr–LaBr$_3$, RbBr–LaBr$_3$, and CsBr–LaBr$_3$ systems decrease gradually with increasing alkali metal atomic numbers.

A broad minimum of the $\lambda$ interaction parameter appears in its dependence on lanthanum bromide molar fraction at $X_{\mathrm{LaBr_3}} \sim 0.2$ for the RbBr–LaBr$_3$ and CsBr–LaBr$_3$ systems. This minimum is very small for the system KBr–LaBr$_3$ and disappears for systems NaBr–LaBr$_3$ and LiBr–LaBr$_3$.

Dependence of the $\lambda$ interaction parameter on the size parameter $\delta_{12}$ satisfies predictions of the conformal solution theory of Davis and this dependence for the lanthanum bromide and neodymium bromide systems seems very similar.

Dependence of the $\lambda$ interaction parameter on $\Delta IP$ is linear both for LaBr$_3$ and NdBr$_3$ systems although its small curvature may be noticed.

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