Mixing Enthalpies of $TbBr_3$-MBr Liquid Mixtures (M = Li, Na, K, Rb, Cs)

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Z. Naturforsch. **56 a**, 859–864 (2001); received November 14, 2001

The molar enthalpies of mixing, $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ in the binary liquid systems $TbBr_3$-MBr (M = Li, Na, K, Rb, Cs) have been measured with a Calvet-type high-temperature microcalorimeter over the entire composition range with an accuracy of about 6%. Mixing of the two liquid components was achieved by using the "break-off ampoule" technique. All the investigated systems show negative enthalpies of mixing with a minimum value of approximately –1.25, –8.3, –17.0, –20.0 and –22.5 kJ mol^{-1}, for M = Li, Na, K, Rb and Cs, respectively. The mixing enthalpy in the $TbBr_3$-LiBr system is positive in the $TbBr_3$-rich region. For all the systems, the enthalpy minimum occurs at mole fraction $x_{\mathrm{TbBr_3}} \approx 0.3$ - 0.4. The molar enthalpies of formation $\Delta_{\mathrm{form}}H_{\mathrm{m}}$ (3MBr, $TbBr_3$, l) for M = Li, Na, K, Rb and Cs at 1113 K (arising from the reaction $3\mathrm{MBr}_{(\mathrm{l})} + \mathrm{TbBr}_{3\,(\mathrm{l})} = (3\mathrm{MBr}, \mathrm{TbBr}_3)_{(\mathrm{l})}$) are found to be –4.8, –31.3, –63.3, –70.3 and –81.2 kJ mol^{-1}, respectively. The least-squares coefficients A, B, C, D and E in the equation λ (kJ mol^{-1}) $= A + Bx + Cx^2 + Dx^3 + Ex^4$, where λ is an interaction parameter and $x = x_{\mathrm{TbBr_3}}$, are also reported.

Key words: Terbium Bromide; Alkali Bromides; Mixing Enthalpy; Formation Enthalpy.

Introduction

Rare earths are extracted and processed into metals, magnet alloys, oxides and other forms. Lanthanide's extraction and processing is largely based on molten salt technologies. Many processes are still under development; particularly those dealing with reprocessing of spent nuclear fuel or nuclear waste processing [1, 2]. Data on lanthanide compounds, however, are scarce and not easily accessible in literature. As a consequence, intensive efforts are being made at an international level both on the research and development aspects and also on data bank development.

The present work is part of a research performed on LnX_3-MX systems (where Ln is lanthanide, M is alkali metal and X is halide) [3 - 12]. It reports the experimental enthalpies of mixing of the $TbBr_3$-MBr liquid systems, which were measured by direct calorimetry. A comparison with the analogous $TbCl_3$-MCl liquid mixtures [13] is also presented. The current data are discussed in terms of "relative ionic potentials" [14].

Experimental

Chemicals

$TbBr_3$ was prepared by sintering bromination of Tb_2O_3 with NH_4Br (POCh Gliwice, Poland). The Tb_2O_3-NH_4Br mixture (molar ratio = 1:14) was heated slowly up to 570 K. After 3 hours reaction at 570 K, the temperature was increased up to 650 K and NH_4Br was sublimated. Finally the salt was melted at 1150 K and an ampoule with $TbBr_3$ was transferred to the glove box. Further purification of crude terbium bromide was obtained by distillation under reduced pressure ($\sim$ 0.1 Pa) at 1170 K.

MBr, alkali metal bromides were Merck Suprapur reagents (min. 99.9%). Before their use, they were treated by progressive heating up to fusion under gaseous HBr atmosphere. Excess HBr was removed from the melt by argon.

All the chemicals were handled in an argon glove box with a measured volume fraction of water of about 2×10^{-6} and continuous gas purification by forced recirculation through external molecular sieves.

Table 1. Molar enthalpies of mixing $\Delta_{mix} H_m$ and interaction parameter λ of the $TbBr_3$-LiBr liquid system at 1113 K.

x_{TbBr_3}	$\Delta_{mix}H_m$/ kJ mol^{-1}	λ/ kJ mol^{-1}	x_{TbBr_3}	$\Delta_{mix}H_m$/ kJ mol^{-1}	λ/ kJ mol^{-1}
0.0899	–0.542	–6.624	0.5458	–0.140	–0.565
0.1434	–0.439	–3.574	0.5958	–0.542	–2.251
0.2043	–1.482	–9.116	0.6972	0.547	2.591
0.3011	–1.284	–6.101	0.8077	0.441	2.839
0.3559	–1.125	–4.908	0.8972	0.432	4.684
0.4124	–1.045	–4.312	0.8984	0.551	6.036

Table 2. Molar enthalpies of mixing $\Delta_{mix} H_m$ and interaction parameter λ of the $TbBr_3$-NaBr liquid system at 1113 K.

x_{TbBr_3}	$\Delta_{mix}H_m$/ kJ mol^{-1}	λ/ kJ mol^{-1}	x_{TbBr_3}	$\Delta_{mix}H_m$/ kJ mol^{-1}	λ/ kJ mol^{-1}
0.0512	–1.770	–36.436	0.3928	–7.768	–32.569
0.1011	–4.122	–45.357	0.5056	–6.891	–27.567
0.1465	–5.306	–42.435	0.5921	–5.349	–22.147
0.2008	–7.229	–45.046	0.6526	–3.989	–17.595
0.2257	–8.009	–45.829	0.6955	–3.017	–14.246
0.2960	–8.180	–39.254	0.7989	–1.872	–11.652
0.3465	–8.300	–36.655	0.8960	–0.787	–8.446

Procedure

The mixing experiments were all of the simple liquid-liquid type, performed under argon at atmospheric pressure. The calorimetric apparatus, Calvet-type high-temperature microcalorimeter, mixing devices used and experimental methods have been described in [15]. For every system under investigation, the terbium bromide was weighed in the glove box within $\pm 10^{-5}$ g and placed in the "break-off" quartz ampoule. The alkali metal bromide, weighed in the same way, was placed in a quartz crucible. The break-off ampoule was evacuated under controlled argon pressure in order to obtain the proper pressure at the temperature of the experiment. It was then welded to a quartz tube, which could be moved up and down through a special gas-tight ring. After attainment of thermal equilibrium the "break-off ampoule" was crushed and the thermal effect resulting from mixing was recorded. Calibration of the calorimeter was performed with NIST α-alumina; known amounts of alumina were dropped directly into the melt. The area of the thermograms was obtained automatically by a computer. The calibration of the calorimeter had an accuracy of about 3%. Therefore the molar enthalpies of mixing were obtained with an accuracy of about 6%, because they were measured during separate experimental runs.

Table 3. Molar enthalpies of mixing $\Delta_{mix} H_m$ and interaction parameter λ of the $TbBr_3$-KBr liquid system at 1113 K.

x_{TbBr_3}	$\Delta_{mix}H_m$/ kJ mol^{-1}	λ/ kJ mol^{-1}	x_{TbBr_3}	$\Delta_{mix}H_m$/ kJ mol^{-1}	λ/ kJ mol^{-1}
0.0462	–2.995	–67.967	0.5565	–12.715	–51.518
0.0996	–6.862	–76.517	0.5770	–13.526	–55.418
0.1521	–10.655	–82.619	0.6025	–10.829	–45.216
0.1993	–13.610	–85.287	0.6072	–10.897	–45.688
0.2218	–14.255	–82.587	0.6369	–10.204	–44.124
0.2273	–16.413	–93.450	0.6579	–8.430	–37.455
0.2449	–15.921	–86.095	0.6923	–8.600	–40.372
0.2694	–17.127	–87.017	0.7460	–7.345	–38.763
0.3008	–17.245	–81.994	0.781	–7.447	–43.540
0.3483	–17.156	–75.581	0.7986	–5.906	–36.720
0.4059	–15.927	–66.047	0.8499	–4.586	–35.949
0.4448	–16.233	–65.733	0.9004	–3.001	–33.463
0.5027	–13.586	–54.345	0.9384	–2.178	–37.678
0.5369	–13.943	–56.077	0.9585	–1.291	–32.455

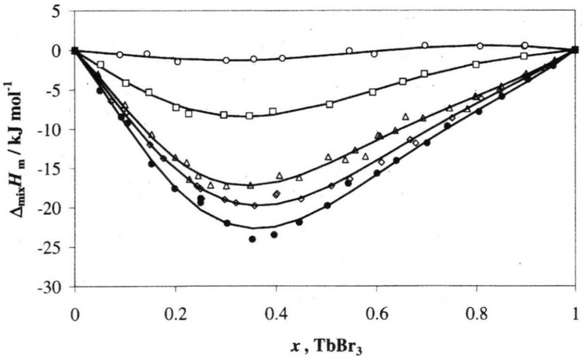

Fig. 1. Experimental mixing enthalpies $\Delta_{mix}H_m$ in $TbBr_3$-MBr liquid systems at 1113 K. Open circles: $TbBr_3$-LiBr, squares: $TbBr_3$-NaBr, triangles: $TbBr_3$-KBr, diamonds: $TbBr_3$-RbBr, full circles: $TbBr_3$-CsBr.

Results

Calorimetric experiments were conducted at 1113 K for all the $TbBr_3$-MBr liquid systems (M = Li, Na, K, Rb, Cs). At this temperature, liquid mixtures are formed in the whole composition range.

The experimental enthalpies of the investigated systems are presented in Tables 1 - 5 and plotted vs. composition in Figure 1.

The interaction parameter

$$\lambda = \Delta_{mix}H_m/(x_{MBr}x_{TbBr_3}),$$

which represents the energetic asymmetry in a melt, has been calculated for all the systems. The limiting interaction parameter $\lambda_{(0)}$, i. e. λ at infinite di-

Table 4. Molar enthalpies of mixing $\Delta_{\mathrm{mix}} H_{\mathrm{m}}$ and interaction parameter λ of the TbBr$_3$-RbBr liquid system at 1113 K.

$x_{\mathrm{TbBr_3}}$	$\Delta_{\mathrm{mix}} H_{\mathrm{m}}$/ kJ mol^{-1}	λ/ kJ mol^{-1}	$x_{\mathrm{TbBr_3}}$	$\Delta_{\mathrm{mix}} H_{\mathrm{m}}$/ kJ mol^{-1}	λ/ kJ mol^{-1}
0.0463	−3.333	−75.482	0.4482	−18.935	−76.562
0.0720	−6.421	−96.099	0.5087	−17.296	−69.205
0.1023	−7.856	−85.545	0.5462	−16.414	−66.221
0.1486	−11.988	−94.753	0.6094	−14.277	−59.979
0.1752	−13.732	−95.028	0.6668	−11.382	−51.229
0.2425	−17.231	−93.803	0.6778	−11.817	−54.110
0.2497	−17.596	−93.920	0.7513	−8.591	−45.978
0.2516	−18.856	−100.139	0.7645	−10.382	−57.665
0.2974	−19.009	−90.972	0.8098	−6.193	−40.208
0.3202	−19.428	−89.254	0.8473	−5.126	−39.619
0.3565	−19.783	−86.235	0.8974	−3.319	−36.047
0.3989	−18.435	−76.883	0.9237	−1.968	−27.923
0.4009	−18.236	−75.927	0.9552	−1.692	−39.539

Table 5. Molar enthalpies of mixing $\Delta_{\mathrm{mix}} H_{\mathrm{m}}$ and interaction parameter λ of the TbBr$_3$-CsBr liquid system at 1113 K.

$x_{\mathrm{TbBr_3}}$	$\Delta_{\mathrm{mix}} H_{\mathrm{m}}$/ kJ mol^{-1}	λ/ kJ mol^{-1}	$x_{\mathrm{TbBr_3}}$	$\Delta_{\mathrm{mix}} H_{\mathrm{m}}$/ kJ mol^{-1}	λ/ kJ mol^{-1}
0.0503	−5.105	−106.866	0.5015	−19.811	−79.245
0.0926	−8.475	−100.862	0.5436	−16.984	−68.456
0.1045	−9.245	−98.793	0.6011	−15.706	−65.502
0.1523	−14.457	−111.979	0.6400	−14.072	−61.076
0.1983	−17.618	−110.821	0.7015	−11.811	−56.405
0.2500	−19.391	−103.419	0.7420	−9.683	−50.581
0.3029	−22.024	−104.304	0.8053	−7.847	−50.047
0.3523	−24.092	−105.581	0.8514	−5.921	−46.800
0.3956	−23.498	−98.277	0.9044	−3.754	−43.419
0.4451	−21.919	−88.746	0.9557	−2.011	−47.499

lution of TbBr$_3$ in alkali metal bromides, was determined in separate experiments. For each system, with the exception of TbBr$_3$-LiBr, an average value was taken from at least 5 measurements. The corresponding $\lambda_{(0)}$ values are −40.52, −59.32, −72.45 and −80.34 kJ mol^{-1} for the NaBr, KBr, RbBr and CsBr systems, respectively. This limiting parameter for the TbBr$_3$-LiBr system was calculated from the general dependence of λ on concentration. The dependence of the interaction parameter on the mixture composition is shown in Figure 2. The values of λ for the five measured liquid systems are also included in Tables 1 - 5. For each system, the values of λ were fitted by the method of least squares to a polynomial of the form

$$\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4,$$

where x is the mole fraction of TbBr$_3$. The polynomial coefficients are presented in Table 6.

Table 6. Least-squares coefficients for the equation of λ for the liquid alkali bromide - terbium bromide mixtures: $\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4$, in kJ mol^{-1} ($x$ = mole fraction of TbBr$_3$).

System	A kJ mol^{-1}	B kJ mol^{-1}	C kJ mol^{-1}	D kJ mol^{-1}	E kJ mol^{-1}
LiBr-TbBr$_3$	−3.9727	−27.476	82.102	−44.75	–
NaBr-TbBr$_3$	−40.525	−58.80	268.56	−217.27	39.50
KBr-TbBr$_3$	−59.320	−328.27	1277.96	−1391.78	517.51
RbBr-TbBr$_3$	−72.540	−258.21	889.70	−853.64	255.16
CsBr-TbBr$_3$	−80.344	−334.48	1153.79	−1138.92	352.46

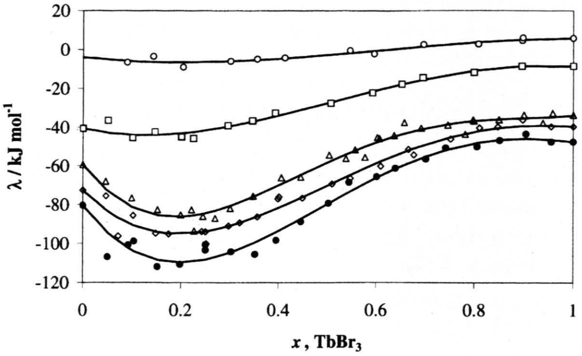

Fig. 2. Variation of the interaction parameter λ with concentration in TbBr$_3$-MBr liquid systems at 1113 K. Open circles: TbBr$_3$-LiBr, squares: TbBr$_3$-NaBr, triangles: TbBr$_3$-KBr, diamonds: TbBr$_3$-RbBr, full circles: TbBr$_3$-CsBr.

Discussion

In all bromide systems the enthalpies of mixing are negative and the minimum is situated similarly as in the chloride systems at $x_{\mathrm{TbBr_3}} \approx 0.3$ - 0.4 [13]. The absolute values of the enthalpies of mixing for the bromide systems are smaller than those of the chloride systems [14]. The TbBr$_3$-LiBr system is an interesting exception: The enthalpy of mixing is positive for high concentrations of TbBr$_2$ (higher than 60 mol.%).

Evidently the ionic radius of the alkali metal cation influences the magnitude of the mixing enthalpy and the position of the minimum. The smaller the ionic radius, the smaller is the absolute value of the mixing enthalpy and the more is the minimum shifted towards alkali bromide rich composition.

Figure 2 shows the dependence of the interaction parameter λ on the mole fraction of TbBr$_3$. This dependence is very close to linear for the LiBr-TbBr$_3$ system. But for the systems with NaBr, KBr, RbBr, and CsBr this dependence is somewhat more complicated: A broad minimum appears at $x_{\mathrm{TbBr_3}}$ of about

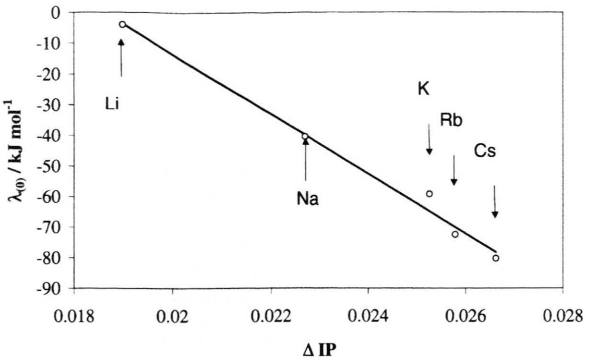

Fig. 3. Dependence of the limiting interaction parameter $\lambda_{(x\to 0)}$ on the "relative ionic potential" ΔIP in $TbBr_3$-MBr liquid systems.

0.2. The absolute value of λ increases sharply with increase of the ionic radius of the alkali metal ion. All the systems show more negative values of the interaction parameter at the alkali bromide-rich than at the terbium bromide-rich compositions. The behaviour of λ follows a pattern similar to that found in the lanthanide chloride - alkali chloride mixtures [5 - 6, 13, 16]. One can thus assume that $TbBr_6^{3-}$ octahedral complexes are formed in the investigated systems. Their formation results in a specific dependence of λ on the melt composition. X-ray diffraction, Raman spectroscopy and molecular dynamics simulation [17 - 24] confirmed the existence of such complexes in lanthanide chloride - alkali metal chloride systems.

Table 7. Molar enthalpies of formation $\Delta_{\mathrm{form}}H_{\mathrm{m}}$ ((3MX, TbX_3), l, T) / kJ mol^{-1} of the liquid mixtures according to the reaction $3MX_{(l)} + TbX_{3\,(l)} = (3MX, TbX_3)_{(l)}$, where M = Li, Na, K, Rb, Cs,; X = Cl, Br.

	$\Delta_{\mathrm{form}}H_{\mathrm{m}}(3MCl,TbCl_3)$ kJ mol^{-1} [14]	$\Delta_{\mathrm{form}}H_{\mathrm{m}}(3MBr,TbBr_3)$ kJ mol^{-1}	r_{M^+}/pm [29]
Li	−9.6 (1109 K)	−4.8 (1113 K)	74
Na	−36.1 (1109 K)	−31.3(1113 K)	102
K	−72.6 (1109 K)	−63.3 (1113 K)	138
Rb	−87.4 (1175 K)	−70.3 (1113 K)	149
Cs	−97.6 (1175 K)	−81.2 (1113 K)	170

$r_{Tb^{3+}}$ = 92.3 pm, r_{Cl^-} = 181 pm, r_{Br^-} = 196 pm [29].

In a system with charge-unsymmetrical cations and common anions the enthalpy of mixing is determined primarily by the charge and size of the two cations and only to a lesser extent by the nature of the common anion. It depends on the "relative ionic potential" of the two cations [14], which is defined as

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

where z_1, z_2 and r_1, r_2 are the valency and the ionic radius of Tb^{3+} and M^+, respectively. While the magnitude of the "relative ionic potential" will mainly reflect the change in coulombic interaction on mixing, it is also related to the magnitude of the polarisation of the common anion by its neighbouring cations. The larger the "relative ionic potential", the more negative is the enthalpy of mixing. Hong and Kleppa [14] showed for many kinds of molten salt mixtures involving ions of different valency, that a linear relation exists between the corresponding "relative ionic potentials" and the limiting interaction parameter:

$$\lambda_{(x\to 0)} = \alpha + \beta \cdot \Delta IP.$$

In Fig. 3 we give a plot of the enthalpy interaction parameter $\lambda_{(x\to 0)}$ vs. ΔIP for the family of $TbBr_3$-MBr liquid mixtures. A least-squares treatment of the experimental data yields

$$\lambda_{(x\to 0)} = 182.22 - 9784 \cdot (3/r_{Tb^{3+}} - 1/r_{M^+}) \pm 3.7\,\mathrm{kJmol}^{-1}.$$

According to Kleppa [25] the term α, which is positive, can be ascribed, in part, to London - van der Waals dispersion interaction between second nearest neighbour cations and in part to the steric effect associated with the mixing of two cations of different size and charge. The negative term $\beta \cdot \Delta IP$ arises mainly from contributions to the mixing enthalpy from the coulombic and polarisation energy terms. For systems with a quite small negative $\beta \cdot \Delta IP$ term the positive α term yields a positive mixing enthalpy. Such an effect was observed previously by us for the $DyCl_3$-$PrCl_3$ liquid system, where the mixing enthalpy is positive in the whole composition range [9]. For the $TbBr_3$-MBr systems under investigation, the large negative term $\beta \cdot \Delta IP$ dominates and gives rise to a negative mixing enthalpy.

The melting temperature T_{fus} of M_3TbBr_6 compounds increases from potassium to caesium [26]. The enthalpy of mixing increases in the same order and has the largest absolute value for the $TbBr_3$-CsBr system.

Enthalpies of formation of liquid mixtures at x_{TbBr_3} = 0.25 for all the $TbBr_3$-MBr systems (M =

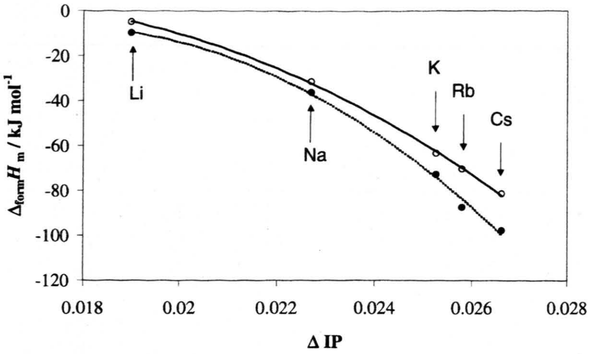

Fig. 4. Dependence of the formation enthalpy of (3MX, LnX_3) liquid mixtures on ΔIP. Solid line with open circles: bromide systems, dashed line with full circles: chloride systems.

Li, Na, K, Rb, Cs) are given in Table 7. These values correspond to the enthalpy variation related to the reaction

$$3\ MBr_{(l)} + TbBr_{3(l)} = (3MBr,\ TbBr_3)_{(l)}.$$

The enthalpies of formation for the $TbCl_3$-MCl systems are included in Table 7 for comparison. It is evident, that an increase in the radius of the alkali metal cation causes an increased stability of the ionic complexes LnX_6^{3-} both for chloride and bromide systems. This is reflected in the increased values of the exothermic enthalpies of formation of (3MX, TbX_3) liquid mixtures. Increase in the radius of the alkali metal ion results in an increase of the "relative ionic potential" ΔIP. The higher the "relative ionic potential" the higher the formation enthalpy, both in the chloride and bromide systems. Figure 4 presents the dependence of the formation enthalpy of (3MX, TbX_3) liquid mixtures on the "relative ionic potential" ΔIP. The same "relative ionic potential" causes different results for the chloride and bromide series. This phenomenon is due to the different ionic radii of the chloride and bromide ions. Such a difference is not taken into account in "relative ionic potential".

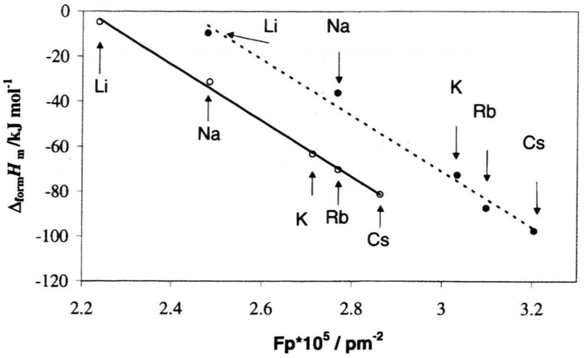

Fig. 5. Dependence of the formation enthalpy of (3MX, LnX_3) liquid mixtures on the polarising force. Dashed line with full circles: chloride systems, solid line with open circles: bromide systems.

The different coulombic interaction, due to the different size of halide anions, may be explained by polarisation force given by [27, 28]

$$F_p = \frac{z_2}{d_2^2} - \frac{z_1}{d_1^2},$$

where F_p is the polarisation force (coulombic force in which the ion charges are divided by the charge of the electron), $z_2 = 3$ (valency of terbium cation), $z_1 = 1$ (valency of alkali metal cation), $d_2 = r_{Tb^{3+}} + r_{Br^-}$ (or r_{Cl^-}), $d_1 = r_{M^+} + r_{Br^-}$ (or r_{Cl^-}). Ionic radii are given in Table 7. A simple linear variation was found for the dependence of the formation enthalpies on the polarisation force both for the liquid (3MBr, $TbBr_3$) and (3MCl, $TbCl_3$) mixtures (Figure 5). The enthalpies of formation are higher for the chloride melts than for the corresponding bromide melts with the same alkali cation.

Acknowledgements

One of us (LR) acknowledges support from the Polish Committee for Scientific Research under the Grant 3 T09A 091 18. LR also wishes to thank the Institut des Systemes Thermiques Industriels (IUSTI) for hospitality and support during this work.

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