JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Calorimetric Investigation of $PrBr_3$-MBr Liquid Mixtures (M = Na, K, Rb, Cs)

L. Rycerz*[†] and M. Gaune-Escard[‡]

[†]Faculty of Chemistry, Department of Chemical Metallurgy, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

[‡]Ecole Polytechnique, Mecanique Energetique, Technopôle de Chateau-Gombert, 5 rue Enrico Fermi, 13453 Marseille Cedex 13, France

ABSTRACT: The molar enthalpies of mixing ($\Delta_{mix}H_m$) in liquid alkali bromide-praseodymium(III) bromide mixtures have been measured with a Calvet-type high temperature microcalorimeter over the entire composition range at 1070 K. All of the melts are characterized by negative enthalpies of mixing with a minimum value shifted toward the alkali bromide-rich compositions that are located in the vicinity of $x(PrBr_3) \sim 0.4$. The magnitude of the mixing enthalpy depends on the ionic radius of the alkali metal, radius of the common halide ion, and the ionic radius of the lanthanide(III) cation.

1. INTRODUCTION

The present work is a continuation of our systematic research performed on $PrBr_3$-based systems. Recently the phase diagrams of $PrBr_3$-MBr (M = Li, Na, K, Rb, Cs) binary systems as well as thermodynamic functions of congruently melting M_3PrBr_6 compounds were determined.[1−5] This work reports the results of mixing enthalpy measurements performed on $PrBr_3$-MBr (M = Na, K, Rb, Cs) liquid systems over the whole composition range. All gathered experimental data were subsequently optimized by computer coupling of phase diagrams and thermochemistry (CALPHAD) method, as was done for analogous $CeBr_3$-MBr binary systems.[6]

2. EXPERIMENTAL SECTION

2.1. Chemicals. Praseodymium(III) bromide was synthesized from the praseodymium oxide, Pr_6O_{11}, by a method analogous to that used for $CeBr_3$ synthesis.[7] The main steps of the synthesis involve: dissolution of praseodymium oxide in hot concentrated hydrobromic acid, crystallization of $PrBr_3 \cdot xH_2O$ hydrates, their dehydration in the presence of ammonium bromide, melting of anhydrous praseodymium bromide, and its distillation under reduced pressure (~0.1 Pa) in a quartz ampule at 1150 K. $PrBr_3$ prepared in this way was of a high purity—min. 99.9 %. Chemical analysis was performed by mercurimetric (bromine) and complexometric (praseodymium) methods. The results were as follows: Pr, (36.96 ± 0.15) % (37.02 % theoretical); Br, (63.04 ± 0.11) % (62.98 % theoretical).

Sodium, potassium, rubidium, and cesium bromides were Merck Suprapur reagents (min. 99.9 %). Prior to use, they were progressively heated up to fusion under a gaseous HBr atmosphere. HBr in excess was then removed from the melt by argon bubbling.

All chemicals were handled in an argon glovebox with a measured fraction of water of about 2 $mg \cdot kg^{-1}$ and continuous gas purification by forced recirculation through external molecular sieves.

Table 1. Molar Enthalpies of Mixing $\Delta_{mix}H_m$ and Interaction Parameters λ of the $PrBr_3$−NaBr Liquid System at T = 1070 K

	$\Delta_{mix}H_m$	λ		$\Delta_{mix}H_m$	λ
$x(PrBr_3)$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$x(PrBr_3)$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
0.026	−0.825	−32.578	0.477	−5.054	−20.259
0.044	−1.113	−26.459	0.528	−4.751	−19.063
0.099	−2.543	−28.509	0.590	−4.522	−18.693
0.152	−3.406	−26.424	0.649	−4.071	−17.871
0.199	−4.214	−26.437	0.704	−3.421	−16.417
0.249	−4.906	−26.235	0.750	−2.858	−15.243
0.284	−5.017	−24.672	0.792	−2.476	−15.030
0.324	−5.423	−24.759	0.823	−2.146	−14.732
0.375	−5.435	−23.189	0.884	−1.537	−14.989
0.430	−5.452	−22.243	0.923	−1.017	−14.310

2.2. Measurements. The mixing experiments were all of the simple liquid−liquid type, performed under pure argon at atmospheric pressure. The Calvet-type high-temperature microcalorimeter, the mixing device, and the "break-off bubble" experimental method have all been described in detail elsewhere.[7,8] Calibration of the calorimeter was performed with α-Al_2O_3 (National Institute of Standards and Technology, NIST). A detailed description of the calorimeter constant determination, calibration of the thermocouple used to measure the experimental temperature, and discussion of errors that influence the results of the mixing enthalpy measurements was presented in our previous paper.[7] The relative error of mixing enthalpy determination was estimated as ± (6 to 8) %.

Received: August 2, 2010
Accepted: June 14, 2011
Published: June 30, 2011

dx.doi.org/10.1021/je200419x | J. Chem. Eng. Data 2011, 56, 3273–3276

Table 2. Molar Enthalpies of Mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ and Interaction Parameters λ of the $PrBr_3$−KBr Liquid System at T = 1070 K

$x(PrBr_3)$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ $\mathrm{kJ\cdot mol^{-1}}$	λ $\mathrm{kJ\cdot mol^{-1}}$	$x(PrBr_3)$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ $\mathrm{kJ\cdot mol^{-1}}$	λ $\mathrm{kJ\cdot mol^{-1}}$
0.052	−2.811	−56.611	0.542	−11.713	−47.194
0.100	−5.957	−66.188	0.611	−10.645	−44.799
0.155	−9.077	−69.413	0.659	−10.063	−44.805
0.187	−10.128	−66.700	0.692	−9.174	−43.042
0.240	−11.825	−64.793	0.744	−7.349	−38.584
0.297	−12.830	−61.497	0.789	−5.452	−32.749
0.343	−13.004	−57.697	0.843	−4.124	−31.159
0.399	−13.312	−55.513	0.898	−2.925	−31.933
0.454	−12.704	−51.249	0.947	−1.725	−34.368
0.490	−13.278	−53.131			

Table 3. Molar Enthalpies of Mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ and Interaction Parameters λ of the $PrBr_3$−RbBr Liquid System at T = 1070 K

$x(PrBr_3)$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ $\mathrm{kJ\cdot mol^{-1}}$	λ $\mathrm{kJ\cdot mol^{-1}}$	$x(PrBr_3)$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ $\mathrm{kJ\cdot mol^{-1}}$	λ $\mathrm{kJ\cdot mol^{-1}}$
0.032	−2.379	−76.801	0.514	−15.628	−62.561
0.054	−4.196	−82.139	0.554	−14.002	−56.660
0.073	−5.691	−84.098	0.606	−13.158	−55.109
0.101	−7.273	−80.101	0.653	−11.543	−50.942
0.121	−9.314	−87.571	0.682	−10.746	−49.549
0.152	−11.384	−88.319	0.725	−8.518	−42.723
0.181	−13.147	−88.687	0.757	−7.765	−42.212
0.200	−14.368	−89.803	0.791	−6.619	−40.038
0.251	−15.783	−83.952	0.837	−4.775	−34.999
0.301	−16.809	−79.891	0.875	−4.747	−43.401
0.353	−17.118	−74.950	0.915	−2.660	−34.201
0.404	−16.976	−70.503	0.956	−1.758	−41.793
0.467	−16.031	−64.404			

Table 4. Molar Enthalpies of Mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ and Interaction Parameters λ of the $PrBr_3$−CsBr Liquid System at T = 1070 K

$x(PrBr_3)$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ $\mathrm{kJ\cdot mol^{-1}}$	λ $\mathrm{kJ\cdot mol^{-1}}$	$x(PrBr_3)$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ $\mathrm{kJ\cdot mol^{-1}}$	λ $\mathrm{kJ\cdot mol^{-1}}$
0.032	−2.828	−91.296	0.471	−18.369	−73.724
0.051	−4.689	−96.882	0.526	−18.517	−74.268
0.096	−8.712	−100.387	0.576	−16.582	−67.897
0.151	−13.097	−102.161	0.650	−14.595	−64.153
0.199	−15.888	−99.674	0.696	−13.480	−63.710
0.241	−17.945	−98.103	0.758	−11.260	−61.384
0.301	−18.942	−90.028	0.806	−9.558	−61.127
0.357	−19.302	−84.085	0.849	−6.925	−54.017
0.400	−18.835	−78.479	0.894	−5.424	−57.236
0.434	−19.022	−77.437	0.948	−2.960	−60.054

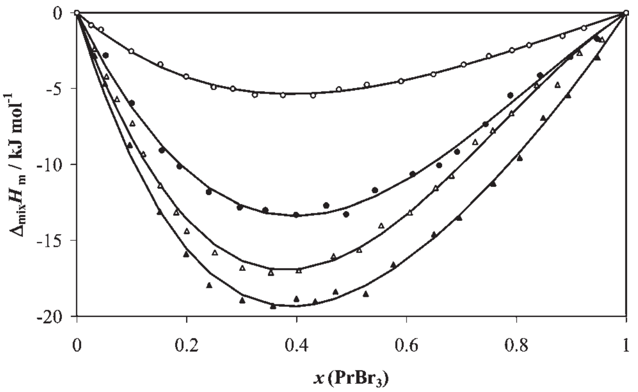

Figure 1. Molar enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ of the $PrBr_3$-MBr liquid systems: ○, NaBr; ●, KBr; △, RbBr; ▲, CsBr.

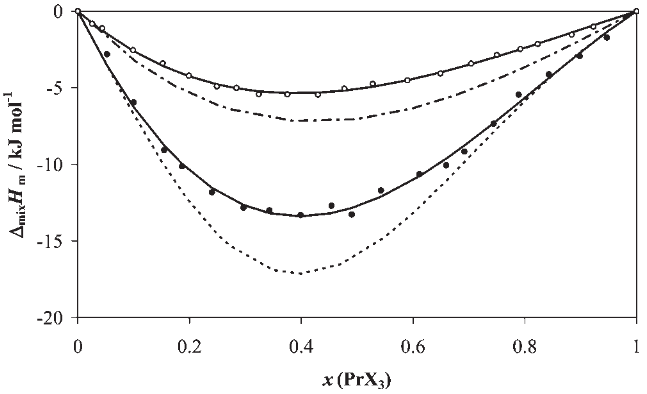

Figure 2. Molar enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ of the $PrBr_3$-MBr (M = Na, K) and $PrCl_3$-MCl (M = Na, K) liquid systems: ○, $PrBr_3$−NaBr; dotted line, $PrCl_3$−NaCl; ●, $PrBr_3$−KBr; dashed line, $PrCl_3$−KCl.

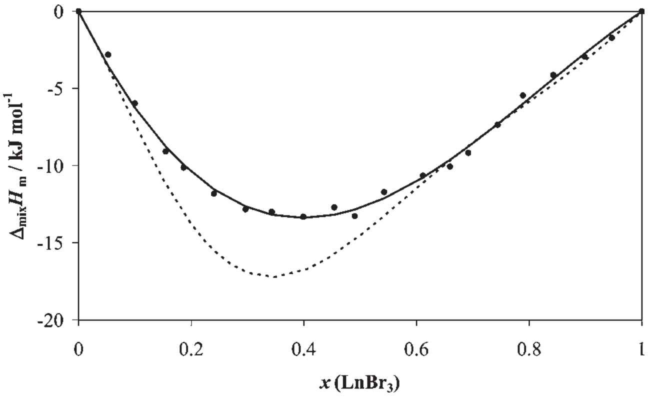

Figure 3. Molar enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ of the $PrBr_3$−KBr (●, solid line) and $TbBr_3$−KBr [15] (dashed line) liquid systems.

3. RESULTS AND DISCUSSION

The calorimetric experiments were performed at 1070 K over the entire composition range for the systems with NaBr, KBr, RbBr, and CsBr. The results obtained are presented in Tables 1 to 4 and are plotted against composition in Figure 1. Three decimals (without physical meaning), in the presentation of thermodynamic values, are in accordance with the recommendation of the CODATA Task Group on Chemical Thermodynamic Tables.[9]

All of the melts are characterized by negative enthalpies of mixing with a minimum value of approximately (−5.4, −13.4,

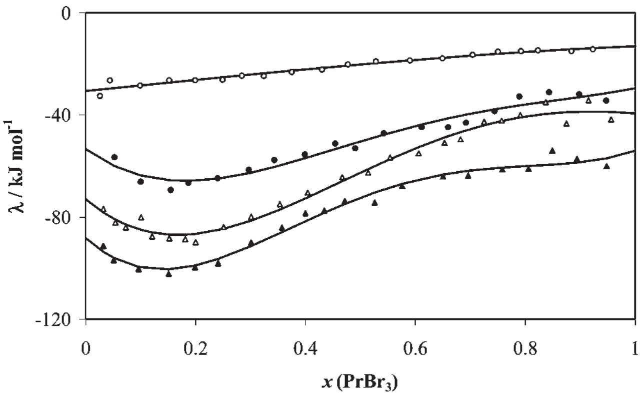

Figure 4. Variation of the interaction parameter λ with composition for the $PrBr_3$-MBr liquid systems: ○, NaBr; ●, KBr; △, RbBr; ▲, CsBr.

Table 5. Least-Squares Coefficients for the λ Equation for Liquid Praseodymium(III) Bromide-Alkali Bromide Mixtures: λ ($kJ \cdot mol^{-1}$) = $A + Bx + Cx^2 + Dx^3 + Ex^4$ and Standard Deviation (SE, in $kJ \cdot mol^{-1}$)

system	A	B	C	D	E	SE
Pr−Na	−30.659	21.855	−2.298	−1.988		1.040
Pr−K	−53.386	−156.759	597.673	−672.154	255.050	2.354
Pr−Rb	−73.081	−182.913	713.030	−725.284	228.826	2.435
Pr−Cs	−88.247	−197.148	945.412	−1237.810	523.766	2.112

−17.1, and −19.3) $kJ \cdot mol^{-1}$, for M = Na, K, Rb, and Cs, respectively. Similarly, like in the case of $CeBr_3$-MBr liquid mixtures,[7] the minimum of the enthalpy of mixing is shifted toward the alkali bromide-rich compositions and is located in the vicinity of $x(PrBr_3) \sim 0.4$. The magnitude of the mixing enthalpy depends on the ionic radius of the alkali metal (Figure 1). The smaller the ionic radius, the smaller the absolute value of mixing enthalpy and the enthalpy minimum location shifted more toward the alkali bromide-rich compositions. Accordingly, the absolute value of the mixing enthalpy is the largest for the system with CsBr and decreases in the sequence from CsBr to NaBr (as does ionic radius of M^+).

The mixing enthalpy also depends on the ionic radius of the common halide ion. As displayed in Figure 2, when this radius increases [from chloride to bromide, (181 and 196) pm, respectively[10]], a significant decrease of the mixing enthalpy is observed. For example, the minimum of the molar mixing enthalpy is of about −7.3 $kJ \cdot mol^{-1}$ and −17.1 $kJ \cdot mol^{-1}$ for the systems $PrCl_3$−NaCl and $PrCl_3$−KCl,[11] whereas in analogous $PrBr_3$-based bromide systems these values are (−5.4 and −13.4) $kJ \cdot mol^{-1}$, respectively.

Finally, the mixing enthalpy in LnX_3-MX liquid systems is dependent on the ionic radius of lanthanide(III) cation. In Figure 3 the mixing enthalpy was plotted against molar fraction of the lanthanide halide for $PrBr_3$−KBr and $TbBr_3$−KBr.[12] The decrease of the Ln^{3+} ionic radius from 101.3 pm (Pr^{3+}) to 92.3 pm (Tb^{3+})[10] results both in an increase of the absolute value of the mixing enthalpy, when compared to analogous alkali metal systems, and shifting of the mixing enthalpy minimum toward alkali halide-rich compositions.

Figure 4 shows the composition dependence of the interaction parameter λ

$$\lambda = \Delta_{mix}H_m/(x(PrBr_3) \cdot (1 - x(PrBr_3)))$$

which is representative of the energetic asymmetry in these melts. The values of λ for the liquid systems under investigation are also included in Tables 1 to 4. 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 $PrBr_3$. The coefficients A, B, C, D, and E as well as the standard deviation (SE) are collected in Table 5. Figure 4 shows the dependence of the enthalpy interaction parameter λ on the mole fraction of $PrBr_3$. All of the systems have negative interaction parameters λ, whose absolute values increase sharply with an increase of the ionic radius of the alkali metal cation. All systems show more negative values of the interaction parameter in the alkali bromide-rich than in the praseodymium bromide-rich range.

The composition dependence of the interaction parameter λ for $PrBr_3$-MBr systems is identical to the dependence observed for $CeBr_3$-MBr systems[7] and can be attributed to the formation of $PrBr_6^{3-}$ complexes in the melts. The possibility of octahedral LnX_6^{3-} complex formation in LnX_3-MX liquid mixtures was confirmed by Raman structural studies.[13]

4. SUMMARY

The molar mixing enthalpies in the liquid praseodymium(III) bromide-alkali metal bromide systems have been measured over the whole composition range. All of the melts are characterized by negative enthalpies of mixing. The minimum of the enthalpy of mixing is shifted toward the alkali bromide-rich compositions and located in the vicinity of $x(PrBr_3) \sim 0.4$. The magnitude of the mixing enthalpy depends on the ionic radius of the alkali metal (the bigger radius the more negative the mixing enthalpy), the radius of the common halide ion (a significant decrease of the mixing enthalpy with an increase of this radius) and the ionic radius of the lanthanide(III) cation (a decrease of the Ln^{3+} ionic radius results both in an increase of the absolute value of the mixing enthalpy, when compared to analogous alkali metal systems and a shifting of the mixing enthalpy minimum toward alkali halide-rich compositions).

The composition dependence of the interaction parameter λ for the $PrBr_3$-MBr systems is indicative of $PrBr_6^{3-}$ octahedral complex formation.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +48 71 320 33 89. E-mail: leszek.rycerz@pwr.wroc.pl.

Funding Sources

Financial support by the Polish Ministry of Science and Higher Education from budget on science in 2007−2010 under Grant No. N204 4098 33 is gratefully acknowledged.

■ ACKNOWLEDGMENT

L.R. wishes to thank the Ecole Polytechnique de Marseille for hospitality and support during this work.

■ REFERENCES

(1) Ingier-Stocka, E.; Rycerz, L.; Berkani, M.; Gaune-Escard, M. Thermodynamic and transport properties of the $PrBr_3$−MBr Binary Systems (M = Li, Na). *J. Mol. Liq.* **2009**, *148*, 40–44.

(2) Rejek, J.; Rycerz, L.; Ingier-Stocka, E.; Gaune-Escard, M. Thermodynamic and Transport Properties of the $PrBr_3$−KBr Binary System. *J. Chem. Eng. Data* **2010**, *55*, 1871–1875.

(3) Rycerz, L.; Ingier-Stocka, E.; Berkani, M.; Gaune-Escard, M. Thermodynamic and transport properties of the $PrBr_3$-RbBr binary system. *J. Alloys Compd.* **2010**, *501*, 269–274.

(4) Rycerz, L.; Ingier-Stocka, E.; Berkani, M.; Gaune-Escard, M. Phase Diagram and Electrical Conductivity of the $PrBr_3$-CsBr Binary System. *Z. Naturforsch.* **2010**, *65a*, 859–864.

(5) Rycerz, L.; Chojnacka, I.; Berkani, M.; Gaune-Escard, M. Thermodynamic Functions of $PrBr_3$ and Congruently Melting M_3PrBr_6 compounds (M = K, Rb, Cs). *J. Chem. Eng. Data* **2011**, *56*, 1293–1298.

(6) Kapala, J.; Rutkowska, I.; Chojnacka, I.; Gaune-Escard, M. Modelling of the thermodynamic properties of the ABr-$CeBr_3$ (A = Li-Cs) systems. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2010**, *34*, 15–19.

(7) Rycerz, L.; Gaune-Escard, M. Calorimetric investigation of the $CeBr_3$-MBr liquid mixtures (M = Na, K, Rb, Cs). *J. Chem. Eng. Data* **2009**, *54*, 2622–2625.

(8) Gaune-Escard, M. Thermochemical methods. In *Molten Salts: From Fundamentals to Applications, NATO Science Series*; Gaune-Escard, M., Ed.; Kluwer Academic Publishers: Norwell, MA, 2002; Vol. 52, p 375.

(9) *CODATA Thermodynamic Tables, Selection for Some Compounds of Calcium and Related Mixtures: A Prototype Set of Tables*; Garvin, D., Parker, V. B., White, H. J., Eds.; Hempshire Publishing Corporation: Bristol, PA, 1987.

(10) Sharpe, A. G. *Inorganic Chemistry*; Longman: New York, 1986.

(11) Gaune-Escard, M.; Rycerz, L.; Szczepaniak, W.; Bogacz, A. Calorimetric investigation of $PrCl_3$-NaCl and $PrCl_3$-KCl liquid mixtures. *Thermochim. Acta* **1994**, *236*, 59–66.

(12) Rycerz, L.; Gaune-Escard, M. Mixing enthalpies of $TbBr_3$-MBr liquid mixtures (M = Li, Na, K, Rb, Cs). *Z. Naturforsch.* **2001**, *56a*, 859–864.

(13) Photiadis, G. M.; Borresen, B.; Papatheodorou, G. N. Vibrational modes and structures of lanthanide halide-alkali halide binary melts: $LnBr_3$-KBr (Ln = La, Nd, Gd) and $NdCl_3$-ACl (A = Li, Na, K, Cs). *J. Chem. Soc., Faraday Trans.* **1998**, *94* (17), 2605–2613.