CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Mixing Enthalpy Estimation for CsX–PbX₂ Melts (X = Cl, Br) by Differential Scanning Calorimetry

D. S. Tsvetkov^{a,*}, D. A. Malyshkin^a, M. O. Mazurin^a, V. V. Sereda^a, and A. Yu. Zuev^a

^aUral Federal University, Yekaterinburg, 620002 Russia *e-mail: Dmitry. Tsvetkov@urfu.ru Received June 25, 2024; revised June 25, 2024; accepted July 7, 2024

Abstract—A comparatively simple method for estimating the mixing enthalpy of melts by differential scanning calorimetry using standard equipment is proposed. The enthalpies of mixing of CsX—PbX₂ (X = Cl, Br) melts are determined by this method. The measured values of mixing enthalpy in the CsCl—PbCl₂ system are in good agreement with those obtained by means of independent measurements. For the CsBr—PbBr₂ system, the enthalpy of mixing was measured for the first time. The similar values of mixing enthalpy were found for both studied systems.

Keywords: enthalpy of mixing, halides, melts, DSC

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The mixing enthalpy of melts is an important thermodynamic value that directly characterizes the interaction of components in the melt. Its study allows drawing conclusions about the structure of the melt, the nature of the liquid state in a specific system, and serves as a source of information for development of theoretical models of the molten state, as well as for thermodynamic analysis and modeling of phase equilibria involving liquid phase. In addition, various molten media are widespread in industry, what determines the practical necessity to study their properties.

Various methods for determining the enthalpy of melts mixing are described in literature. The most frequently used techniques include direct calorimetric measurements and calculations from the temperature dependence of the Gibbs free energy of mixing [1-3]. The latter, in turn, is often determined by EMF or vapor pressure method [3, 4]. It should be noted that both direct calorimetric measurements and determination of the enthalpy of mixing from measurements of EMF of galvanic cells or vapor pressure above the melt require the availability of the appropriate equipment, usually non-standard, manufactured by the researchers themselves and, therefore, not very widespread. This imposes certain restrictions on the range of objects that can be studied accordingly and leads to a certain lack of experimental data on the thermodynamic properties of melts. At the same time, as the authors [5] have shown, the relatively widely available method of differential scanning calorimetry (DSC) can be successfully used, among other things, to estimate the mixing enthalpy of melts along with determining the heat capacities and enthalpies of phase transitions.

Regarding the method proposed in [5], it should be noted that, firstly, it involves measurements in nonstandard hermetic steel crucibles equipped with a BN insert to prevent chemical interaction with the sample. Such experimental technique has undeniable advantages when working with chemically active samples with high vapor pressure, as was the case in [5]. Nevertheless, the individual manufacture of crucibles and ceramic inserts presents certain difficulties and, when working with less aggressive substances with low vapor pressure, seems to be inappropriate. Secondly, the method [5] allows determining the enthalpies of mixing only in mixtures with close melting points of components or in mixtures rich in a low-melting component. With a significant difference in the melting points of the components, the concentration dependence of the enthalpy of mixing cannot be obtained in the entire range of compositions, in particular, because part of the more refractory component until its melting point does not dissolve in the melt. For example, in the LiF-KF system with close melting temperatures of the components (their difference is around 10 K), measurements of the enthalpy of mixing were carried out in almost the entire range of compositions [5], while in the LiF–ThF₄ system (melting temperature difference more than 250 K), measurements were only possible in the range of mole fractions of refractory ThF_4 from 0 to 0.44. Simplifying the measurement procedure compared to [5] and extending it to a wider concentration range thus seems to be highly relevant.

The aim of this work, therefore, was to develop a technique for DSC measurements of the enthalpy of mixing using the example of C_sX-PbX_2 (X = Cl, Br) melts, which are of considerable interest due to a need in the thermodynamic description of phase equilibria involving perovskite-like halides C_sPbX_3 (X = Cl, Br, I) and solid solutions based on them, which are promising materials for solar cells, LEDs and X-ray detectors [6].

EXPERIMENTAL

The experiments were carried out using an MHTC 96 evo calorimeter (Setaram, France) equipped with a DSC sensor. The measurements were performed in the heating mode at a rate of 2 K min⁻¹ in a dynamic atmosphere of dry nitrogen ($p_{\rm H_{2O}} < 10^{-4}$ atm, $p_{\rm O_2} < 10^{-4}$ atm) in the temperature range of 298–983 K at a total pressure of (100 ± 3) kPa. The calorimeter was calibrated for sensitivity and temperature using high-purity metals: Ga, In, Sn, Pb and Al.

The following halides were used to prepare the studied mixtures: CsCl (purity is not less than 99.99 wt %, Lankhit), PbCl₂ (purity is not less than 99.5 wt %, Vecton), CsBr (purity is not less than 99.99 wt %, Vecton) and PbBr₂. The latter was obtained by precipitation from an aqueous solution according to the following scheme:

$$Pb(CH_{3}COOH)_{2} \cdot 3H_{2}O + 2HBr$$

=
$$PbBr_{2}\downarrow + 2CH_{3}COOH + 3H_{2}O.$$
 (1)

A weighed portion of $Pb(CH_3COOH)_2 \cdot 3H_2O$ (purity is not less than 99.5 wt %, Vecton) was dissolved in distilled water with heating at around 80°C and stirring. The resulting solution with a concentration of 1.4 mol L^{-1} was filtered on a paper filter, heated again to around 80°C and a small excess (relative to the stoichiometric amount) of a solution of concentrated HBr (>46 wt %, ORT "Chemical Reactants") was added. The solution with the precipitated PbBr₂ crystals was then cooled to room temperature, afterwards the crystals were filtered on a glass filter under vacuum and abundantly washed with ethanol (>95 vol %, Samaramedprom) in small portions. The solvent and washing liquid residues were removed by drying in a vacuum oven at 70°C for 30 min. During all the described procedures, we tried to minimize the exposure of the PbBr₂ powder to light to avoid photolysis. The phase composition of the obtained product was controlled by X-ray phase analysis. The data were obtained in CuK_{α} radiation on an XRD 7000S diffractometer (Shimadzu, Japan).

The necessary powder components were weighed in the required quantities and placed in standard platinum-rhodium DSC crucibles with a working volume of 0.45 cm³. The masses of the mixtures were not less than 0.42 g. Weighing was performed on a Secura 225D microbalance (Sartorius, Germany).

During heating, the components of the mixture melted and mixed to form a homogeneous melt. The corresponding thermal effects were determined by integrating the measured DSC signal taking into account the baseline. The enthalpies of melting of pure initial salts were determined in the same way. All measurements were performed three times, each time using a freshly prepared sample. The obtained molar enthalpies values were then averaged. The expanded uncertainty of the result was estimated as twice the standard deviation (confidence interval $\approx 95\%$).

The melting point of pure components was determined as the extrapolated melting onset temperature at the intersection of the tangent drawn to the frontal part of the melting peak at the inflection point and the extrapolated baseline. Since the transition to the liquid state of mixtures, unlike pure components, occurs in a wide temperature range, and the corresponding effects on the DSC curves, as will be shown below, have a complex shape and cannot be separated into individual contributions, the total thermal effects were related to the average temperature of the transition interval.

Experimentally determined temperatures, T_{fus} , along with the enthalpies of melting of mixtures or pure components, related to these temperatures, $\Delta_{\text{fus}}H_{x,T}$, were used in further calculations of the mixing enthalpy of melts.

RESULTS AND DISCUSSION

Typical DSC curves of $CsCl-PbCl_2$ mixtures of different compositions is shown in Fig. 1, as an example. Similar results were obtained for $CsBr-PbBr_2$ mixtures. As seen, the obtained curves are complex in shape, with several peaks, the last one of which is related to melting, while the others are caused by various physical and chemical transformations occurring in the solid mixture upon heating.

In particular, CsCl undergoes a phase transition in the temperature range studied. For this reason, the thermodynamic characteristics of this transition in CsCl must be taken into account in further calculations. The peak on the DSC curve corresponding to this transition from the low-temperature (b.c.c, $Pm\overline{3}m$) to the high-temperature (f.c.c, $Fm\overline{3}m$) modification of CsCl is clearly seen in Fig. 1 ($\xi = 0$) to the left of the melting peak of CsCl.



Fig. 1. DSC melting curves of mixtures $(1 - \xi)CsCl-\xiPbCl_2$ of different compositions. The phase transition in CsCl is marked with an asterisk (*).

The temperature, $T_{\rm tr} = (748.6 \pm 0.8)$ K, and enthalpy, $\Delta_{\rm tr} H^{\circ}_{\rm CsCl} = (3.09 \pm 0.04)$ kJ mol⁻¹, of this phase transition determined in present work are in good agreement with the literature data [7–10].

In a view of the complex nature of the various transformations occurring during heating and melting of CsX and PbX₂ mixtures and observed on the DSC curves (see Fig. 1), one can determine the total heat of the overall process of a transition from the initial mechanical mixture of binary halides to a homogeneous melt. This process can be written as

$$(1 - \xi)CsX(s,T) + \xiPbX_2(s,T)$$

= $(1 - \xi)CsX(melt,T) + \xiPbX_2(melt,T),$ (2)

where "s" corresponds to the most stable (only) polymorphic modification in the solid state for all halides except CsCl, and for CsCl—to its low-temperature modification ($Pm\bar{3}m$), and "melt" corresponds to the state of the halide in a mixed melt of composition ξ . The enthalpy of process Eq. (2), $\Delta_{fus}H_{x,T}$, was determined as the sum of the integrals of all the heat effects observed on the DSC curves in certain temperature ranges ΔT_{fus} . The values of $\Delta_{fus}H_{x,T}$ and ΔT_{fus} obtained in this way are given in Table 1. It should also be noted that the standard enthalpies and melting temperatures of pure salts determined in present work are in good agreement with the values given in the literature [8–10].

The enthalpy of process Eq. (2), $\Delta_{\text{fus}}H_{x,T}$, is related to the molar mixing enthalpy of melts at temperature T, $\Delta_{\text{mix}}H_T$, as follows:

$$\Delta_{\rm mix} H_T = \Delta_{\rm fus} H_{x,T} - \xi \Delta_{\rm fus} H_{\rm PbX_2,T}^{\circ}$$

$$- (1 - \xi) \Delta_{\rm fus} H_{\rm CsX,T}^{\circ},$$
(3)



Fig. 2. Mixing enthalpy of $CsX-PbX_2$ melts (X = Cl, Br) at 938.15 K: symbols are the experimental results of the present work and [11], dotted line is the calculation using the Eq. (8).

where ξ , $\Delta_{\text{fus}} H^{\circ}_{\text{PbX}_2,T}$ and $\Delta_{\text{fus}} H^{\circ}_{\text{CsX},T}$ —the molar fraction of halide PbX₂ (X = Cl, Br) in the melt and the molar enthalpies of melting of the initial components at temperature *T*, respectively.

In order to obtain the dependence $\Delta_{mix} H_T(\xi)$ at one specific temperature as a result of calculations using Eq. (3), the enthalpies of transition of components and mixtures to the liquid state were also recalculated to the same temperature, and 938.15 K was chosen as such one. This choice is due to the convenience of comparison with the results of direct measurements for CsCl–PbCl₂ melts, performed by McCarthy and Kleppa [11] using the mixing calorimetry method. When recalculating the heat capacity of the initial mechanical mixture of solid salts as well as that of the melt was estimated as the sum of the heat capacities of the components (taking into account their molar fraction) in the solid or liquid state, respectively. Thus,

$$\Delta_{\rm fus} H_{938.15} = \Delta_{\rm fus} H_{x,T} + \Delta_{\rm corr} H, \tag{4}$$

where $\Delta_{\text{corr}} H$ is the value of the enthalpy increment for recalculating $\Delta_{\text{fus}} H_{x,T}$ to a temperature of 938.15 K, which is equal to

$$\Delta_{\rm corr} H = \int_{T}^{938.15} \Delta C_p(2) dT.$$
 (5)

The heat capacities of the corresponding salts were taken from the data given in [10]. The obtained values of enthalpies $\Delta_{fus} H_{938.15}$ and the enthalpies of mixing at 938.15 K calculated using the equation Eq. (3) are given in Table 2.

The concentration dependences of the enthalpy of mixing in both studied systems in comparison with

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Table 1. Enthalpies, $\Delta_{\text{fus}}H_{x,T}$, and temperatures, T_{fus} , of a transition to the liquid state (see Eq. (2)) for the studied CsX–PbX₂ (X = Cl, Br) mixtures

ξ_{PbX_2}	$\Delta_{\text{fus}}H_{x,T},$ kJ mol ⁻¹	$ \underset{\text{mol}^{-1}}{\overset{}{}} \frac{U(\Delta_{\text{fus}}H_{x,T})^*}{\text{kJ mol}^{-1}}, $		$U(T_{\rm fus})$ or $\Delta T_{\rm fus}^{**}$, K				
X = Cl								
0.0	23.2***	0.1	917.3	0.4				
0.05	20.0	1.2	808	214				
0.1	19.7	1.4	795	189				
0.15	16.3	1.5	781	160				
0.2	13.3	1.3	769	136				
0.25	13.5	1.1	789	192				
0.3	12.0	0.7	794	188				
0.4	11.6	0.9	797	194				
0.5	11.1	0.7	799	198				
0.6	14.1	1.0	790	178				
0.7	16.1	1.9	764	125				
0.8	16.9	0.9	759	116				
0.85	19.2	1.9	740	80				
0.9	19.6	1.4	737	64				
0.95	21.3	2.1	742	82				
1.0	23.2	0.1	771.2	0.2				
X = Br								
0.0	22.1	0.1	910.3	0.2				
0.1	15.6	1.2	759	291				
0.2	11.8	1.2	719	233				
0.3	7.9	0.6	697	174				
0.4	7.3	0.6	719	234				
0.5	7.9	0.5	734	263				
0.6	9.5	0.5	718	232				
0.7	11.7	1.0	700	196				
0.8	11.3	0.4	642	77				
0.9	13.0	1.1	635	63				
0.95	14.1	1.0	634	61				
1.0	16.3	0.1	644.1	0.1				

* Expanded uncertainty of the enthalpy of transition to the liquid state (confidence level $\approx 95\%$).

** For pure components, the expanded uncertainty of the melting point $U(T_{\rm fus})$ is given (confidence level $\approx 95\%$), for mixtures—the width of the interval of transition to the liquid state, $\Delta T_{\rm fus}$.

*** One includes the enthalpy of the phase transition b.c.c. CsCl to f.c.c. CsCl (3.09 ± 0.04) kJ mol⁻¹ at (748.6 \pm 0.8) K and the enthalpy of melting of the high-temperature modification f.c.c. CsCl (20.1 ± 0.1) kJ mol⁻¹ at (917.3 \pm 0.4) K.

each other and with the data reported by McCarthy and Kleppa [11] are shown in Fig. 2. It is evident that the results obtained for the $CsCl-PbCl_2$ system in the present work are in good coincidence with those independently determined in [11]. In addition, the enthalpies of mixing in the bromide and chloride systems, as can be seen from Fig. 2, coincide within the error limits.

The similar nature of the interaction between the components of the studied chloride and bromide melts $CsX-PbX_2$ (X = Cl, Br) is also evidenced by the almost identical activities of the components. As an example, Fig. 3 shows the activities of lead halides according to the data of [12, 13]. Ibidem the activities are given calculated as follows:

$$a_{\rm PbX_2} = \xi \Delta \gamma_{\rm PbX_2} = \xi \exp\left(\frac{\Delta \overline{h}_{\rm E,PbX_2}}{RT} - \frac{\Delta \overline{s}_{\rm E,PbX_2}}{R}\right), \quad (6)$$

where $\Delta \overline{h}_{E, PbX_2}$ and $\Delta \overline{s}_{E, PbX_2}$ are the excess partial molar enthalpy and entropy of lead halide in the melt, respectively, and ξ is its mole fraction.

As a first approximation, in calculations using Eq. (6), the contribution of excess partial molar entropy was neglected, assuming that the main contribution was enthalpic, which was calculated from the concentration dependences of the enthalpy of mixing as follows:

$$\Delta \overline{h}_{\text{E, PbX}_2} = \Delta_{\text{mix}} H_{938.15} + (1 - \xi) \left(\frac{\partial \Delta_{\text{mix}} H_{938.15}}{\partial \xi} \right)_{P,T}.$$
 (7)

The enthalpy of mixing, in turn, was represented as:

$$\Delta_{\min} H_{938.15} = \xi (1 - \xi) [a + b(1 - \xi) + c(1 - \xi)^2 + d(1 - \xi)^3].$$
(8)

The coefficients in Eq. (8) were determined by the nonlinear regression using the Levenberg–Marquardt algorithm. Since, as noted above, the enthalpy of mixing in the chloride and bromide systems are the same within the error limits, the sum of squared deviations was minimized on the combined data array. The resulting calculated line with the coefficients: a = -27313.9; b = -24545.2; c = -32964.7; d = 46697.0 is shown in Fig. 2 by a dotted line. The determination coefficient, R^2 , was equal 0.987.

As seen in Fig. 3, in general, the experimental and calculated values of the activities of PbX_2 (X = Cl, Br) halides are in good agreement, that also serves as an additional confirmation of the reliability of the obtained values of mixing enthalpies.

Summarizing the obtained results, one can conclude that the method proposed for determining the enthalpies of mixing of melts allows obtaining reliable data, while being methodologically simple and not requiring specific non-commercial equipment or spe-

MIXING ENTHALPY ESTIMATION

-	-		5					
ξ_{PbX_2}	$\Delta_{\rm corr} H^*$,	$\Delta_{\mathrm{fus}}H_{x,938},$	$U(\Delta_{\rm fus}H_{x,938})^{**},$	$\Delta_{\rm mix}H_{938},$	$U(\Delta_{\rm mix}H_{938})^{**},$			
	kJ mol ⁻¹							
X = Cl								
0.0	0.27	23.5***	0.1	0.0				
0.05	1.77	21.8	1.2	-1.8	1.2			
0.1	1.98	21.7	1.4	-2.1	1.4			
0.15	2.23	18.5	1.5	-5.4	1.5			
0.2	2.44	15.8	1.3	-8.3	1.3			
0.25	2.18	15.6	1.1	-8.5	1.1			
0.3	2.12	14.1	0.7	-10.2	0.7			
0.4	2.14	13.7	0.9	-10.9	0.9			
0.5	2.17	13.3	0.7	-11.6	0.7			
0.6	2.40	16.5	1.0	-8.6	1.0			
0.7	2.95	19.0	1.9	-6.4	1.9			
0.8	3.13	20.0	0.9	-5.7	0.9			
0.85	3.56	22.7	1.9	-3.1	1.9			
0.9	3.66	23.3	1.4	-2.7	1.4			
0.95	3.61	24.9	2.1	-1.2	2.1			
1.0	3.05	26.3	0.1	0.0				
X = Br								
0	0.48	22.6	0.1	0.0				
0.1	3.40	19.0	1.2	-3.4	1.2			
0.2	4.08	15.9	1.2	-6.3	1.2			
0.3	4.40	12.3	0.6	-9.7	0.6			
0.4	3.81	11.1	0.6	-10.8	0.6			
0.5	3.37	11.3	0.5	-10.4	0.5			
0.6	3.55	13.1	0.5	-8.4	0.5			
0.7	3.76	15.4	1.0	-5.9	1.0			
0.8	4.81	16.1	0.4	-5.0	0.4			
0.9	4.81	17.8	1.1	-3.1	1.1			
0.95	4.76	18.9	1.0	-2.0	1.0			
1	4.46	20.7	0.1	0.0				

Table 2. Enthalpies of transition to the liquid state, $\Delta_{fus}H_{x,938,15}$, of the studied mixtures CsX–PbX₂ (X = Cl, Br) at 938.15 K and the mixing enthalpies calculated using Eq. (3), $\Delta_{mix}H_{938,15}$

* Enthalpy increment calculated using Eq. (5) for conversion from the experimental temperature T_{fus} (see Table 1) to a temperature of 938.15 K.

** Expanded uncertainty (confidence level $\approx 95\%$).

*** One includes the phase transition enthalpy of (3.09 ± 0.04) kJ mol⁻¹ at (748.6 ± 0.8) K, which corresponds to the enthalpy of melting of the low-temperature CsCl (b.c.c, $Pm\overline{3}m$) modification.



Fig. 3. Activity of lead halides in melts $(1 - \xi) CsX - \xi PbX_2$ (X = Cl, Br). Points—experimental data [12, 13], solid lines—calculation according to Eq. (6).

cial experimental conditions. This method was used for the first time to determine the enthalpies of mixing in $CsBr-PbBr_2$ melts, and their closeness to those for $CsCl-PbCl_2$ melts was shown.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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