

THERMODYNAMIC EXPLOITATION OF THE LIQUIDUS CURVES IN THE $M^I\text{PO}_3\text{-Pb}(\text{PO}_3)_2$, $M^I\text{PO}_3\text{-Cu}(\text{PO}_3)_2$ AND $M^I\text{PO}_3\text{-Ce}(\text{PO}_3)_3$ SYSTEMS ($M^I=\text{Li, Na, K, Rb, Cs, Ag, Tl}$)

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The thermodynamic exploitation of the solid–liquid equilibria in the $M^I\text{PO}_3\text{-Pb}(\text{PO}_3)_2$, $M^I\text{PO}_3\text{-Cu}(\text{PO}_3)_2$ and $M^I\text{PO}_3\text{-Ce}(\text{PO}_3)_3$ systems (with $M^I=\text{Li, Na, K, Rb, Cs, Ag, Tl}$) is carried out using a semi-empirical equation of the liquidus curves already used with success for similar binary systems.

The enthalpy of fusion is calculated for each pure polyphosphate on the assumption that the liquid solution is ideal and only formed by $M^I\text{PO}_3$ and $M(\text{PO}_3)_q$ entities ($q=2$ for Pb and Cu, $q=3$ for $M=\text{Ce}$). In the most binary systems, a wide difference between the calculated values of the melting enthalpies of these polyphosphates and the measured ones determined from the DTA curves, was observed. This difference is probably due to the existence of some molecular associations in the liquid phase.

The enthalpy of fusion of each terminal phase was then recalculated on the assumption that the liquid contains a molecular association of the type of $M_{pn}^I\text{Mn}(\text{PO}_3)_{n(q+p)}$ in the region of the diagram rich in $M^I\text{PO}_3$ or a molecular association of the type of $M_n^I\text{M}_{np}(\text{PO}_3)_{n(qp+1)}$ in the region rich in $M(\text{PO}_3)_q$ ($q=2$ for Pb and Cu, $q=3$ for $M=\text{Ce}$). In this case, the obtained values are in good agreement with experimental determinations.

Keywords: binary system, enthalpy, molecular association, polyphosphates, thermodynamic exploitation

Introduction

The phase diagrams of the $M^I\text{PO}_3\text{-Pb}(\text{PO}_3)_2$ systems (with $M^I=\text{Li, Na, K}$) have been established previously [1–3]. These studies showed the existence of only one intermediate compound in each binary system: $\text{LiPb}_2(\text{PO}_3)_5$, $\text{Na}_4\text{Pb}(\text{PO}_3)_6$ and $\text{K}_2\text{Pb}(\text{PO}_3)_4$. All of these compounds has a congruent melting point.

The phase diagrams of the $M^I\text{PO}_3\text{-Cu}(\text{PO}_3)_2$ systems (with $M^I=\text{Li, Na, K, Rb, Cs, Ag, Tl}$) have been established previously [4–9]. These studies showed the existence of only one intermediate compound:

- $M^I\text{Cu}(\text{PO}_3)_3$ with $M^I=\text{Li, Rb, Ag, Tl}$
- $M^I_2\text{Cu}(\text{PO}_3)_4$ with $M^I=\text{Na, K}$

in the exception of the $\text{CsPO}_3\text{-Cu}(\text{PO}_3)_2$ system which shows three intermediate compounds: $\text{Cs}_4\text{Cu}(\text{PO}_3)_6$, $\text{Cs}_2\text{Cu}(\text{PO}_3)_4$ and $\text{Cs}_2\text{Cu}_3(\text{PO}_3)_8$.

Only the $M^I\text{Cu}(\text{PO}_3)_3$, $\text{Cs}_2\text{Cu}(\text{PO}_3)_4$ and $\text{Cs}_2\text{Cu}_3(\text{PO}_3)_8$ compounds decompose peritectically on heating. The others present a congruent melting point.

The phase diagrams of the $M^I\text{PO}_3\text{-Ce}(\text{PO}_3)_3$ systems (with $M^I=\text{Li, Na, K, Rb, Cs, Ag, Tl}$) have been established previously [10]. This study showed the existence of two intermediate compounds : $M^I\text{Ce}(\text{PO}_3)_4$, $M^I_2\text{Ce}(\text{PO}_3)_5$ with $M^I=\text{K, Rb, Cs, Tl}$ and only one compound $M^I\text{Ce}(\text{PO}_3)_4$ with $M^I=\text{Li, Na, Ag}$. All compounds decompose peritectically on heating.

The analysis, the processing and the thermodynamic exploitation of the solid–liquid equilibrium curves of the corresponding systems on the assumption that the solution is ideal and that the liquid phase is only formed by $M^I\text{PO}_3$ and $M(\text{PO}_3)_q$ ($q=2$ for Pb and Cu, $q=3$ for $M=\text{Ce}$) were presented in previous papers [11–13].

In that work, a wide difference between the calculated values of the melting enthalpies of these polyphosphates obtained in the three types of systems and the measured ones determined from the DTA curves, was shown. This difference is probably due to the existence of some molecular associations in the liquid phases.

The thermodynamic exploitation of the solid–liquid equilibrium curves of the corresponding systems is now given on the assumption that the solution contains a molecular association. Such a model [14–16] was already applied to systems presenting an associated liquid phase. In that examples, the obtained values of the melting enthalpies of each terminal phase were in good agreement with the experimental determinations.

Experimental

The long chain polyphosphates were prepared by classical thermal methods [17] using di-ammonium

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hydrogenophosphate $(\text{NH}_4)_2\text{HPO}_4$ and the considered metal carbonate (>99% mass percent purity). The temperature and time of heating are mainly dependent on the nature of the metallic cation.

The melting enthalpies of the monovalent metal polyphosphates, lead polyphosphate, copper polyphosphate and cerium polyphosphate were determined with an estimated error of $\sim 2 \text{ kJ mol}^{-1}$ using a Setaram DTA 92 apparatus coupled to a calculator allowing, through an appropriate program, the integration of the area of the different thermal effects. The melting enthalpies of K_2SO_4 and CaF_2 [18] were used to calibrate the apparatus. Samples of 0.02 g, in a platinum crucible, were analysed and the heating rate of the furnace was 5 K mn^{-1} . Pt/Pt–Rh 10 % thermocouple was used at temperature higher than 1273 K, below this temperature a Pt/Platinel thermocouple was more convenient.

Results and discussion

Thermodynamic exploitation of the liquidus curves in the ideal solution model

The previous thermodynamic exploitation of the liquidus curves [11–13] in the different equilibrium phase diagrams corresponding to the binary systems of M^IPO_3 – $\text{Pb}(\text{PO}_3)_2$, M^IPO_3 – $\text{Cu}(\text{PO}_3)_2$ and M^IPO_3 – $\text{Ce}(\text{PO}_3)_3$ (with $M^I=\text{Li, Na, K, Rb, Cs, Ag, Tl}$) allows in particular an evaluation of the melting enthalpies of each pure polyphosphate with the exception of AgPO_3 whose experimental liquidus curve was not sufficiently well defined.

The different values of the melting enthalpies of each terminal phase, calculated on the assumption that the liquid solution is ideal and only formed with M^IPO_3 and $\text{M}(\text{PO}_3)_q$ ($q=2$ for Pb and Cu, $q=3$ for $M=\text{Ce}$). The experimental values are reported in Figs 1 and 2. These two representations show in most systems a wide difference ($\geq 10 \text{ kJ mol}^{-1}$) between the calculated values of the melting enthalpies and the experimental determinations.

The results of the calculation of the relative error

$$\frac{\Delta_{\text{fus}} H_{\text{m}}^{0_{\text{exp}}} - \Delta_{\text{fus}} H_{\text{m}}^{0_{\text{cal}}}}{\Delta_{\text{fus}} H_{\text{m}}^{0_{\text{exp}}}}$$

for the considered pure polyphosphates in each system are presented in Tables 1–6. In most cases, the obtained values are higher than 5%. Otherwise, relative error lower than 5% (shown by * in Tables 1–6 would be acceptable if it is considered that 5% is the experimental one.

The wide difference between the calculated values of the melting enthalpies and the experimental

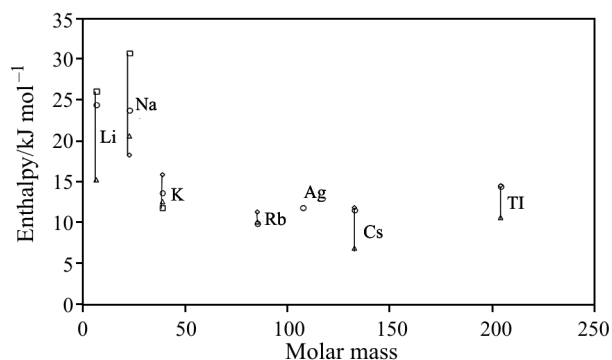


Fig. 1 Melting enthalpies of M^IPO_3 polyphosphates obtained from thermodynamic exploitation of the different binary phase diagrams (ideal model); \circ – exp, \diamond – Li, \blacksquare – Na, \blacktriangle – K, \bullet – Rb, $+$ – Cs, \triangle – Ag and \square – Tl

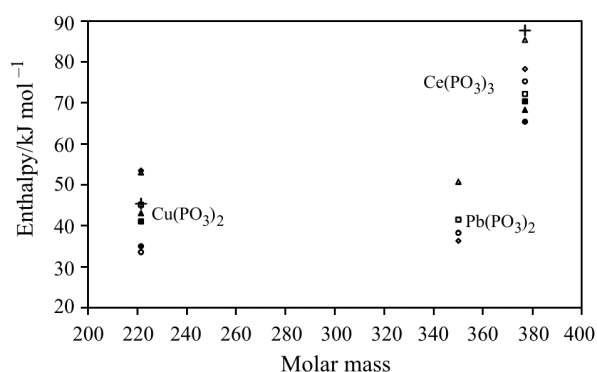


Fig. 2 Melting enthalpies of $\text{M}(\text{PO}_3)_q$ polyphosphates ($q=2$ for $M=\text{Pb}$ and Cu , $q=3$ for $M=\text{Ce}$) obtained from thermodynamic exploitation of the different binary phase diagrams (ideal model); \circ – exp, \square – Pb, \triangle – Cu, \diamond – Ce

determinations is probably due to the existence of some molecular associations in the liquid phase.

Thermodynamic exploitation of the liquidus curves in the molecular association model for liquid phase

Model of associated liquid phase

The thermodynamic exploitation of the liquidus curves in the ideal model of the terminal phases applied to the considered systems, suggests the existence of molecular associations in the liquid phase. On the assumption of associated liquid phases, a new thermodynamic exploitation of the liquidus curves in each binary system is applied. The considered molecular associations are of the types:

- $[(\text{M}^I\text{PO}_3)_p\text{M}(\text{PO}_3)_q]_n$ or $\text{M}_{\text{pn}}^I\text{M}_n(\text{PO}_3)_{n(q+p)}$ – $q=2$ for Pb and Cu, $q=3$ for $M=\text{Ce}$ in the regions of the diagrams rich in M^IPO_3 .
- $[\text{M}^I\text{PO}_3(\text{M}(\text{PO}_3)_q)_p]_n$ or $\text{M}_{\text{pn}}^I\text{M}_{np}(\text{PO}_3)_{n(qp+1)}$ – $q=2$ for Pb and Cu, $q=3$ for $M=\text{Ce}$ in the regions of the diagrams rich in $\text{M}(\text{PO}_3)_q$.

The same method for the thermodynamic exploitation as applied in the ideal model is used. However, the first member of the analytical expression of the liquidus curve which has the general formula for the ideal solution:

$$\sum_i v_{i0} \ln \frac{x_i}{x_{i0}} = \frac{A}{T} + B \ln T + C \quad (1)$$

will be expressed differently as shown in Table 7. v_{i0} is the stoichiometry of the species i in the solid, x_{i0} and x_i are the mole fractions of the i species in the solid and in the liquid phases, respectively. A , B and C are constants.

Results

The different values of the parameters p and n corresponding to the considered association formula, have been calculated through an appropriate program [19]

using Eq. (1). The obtained values which give a perfect agreement between the calculated values of the melting enthalpies and the experimental determinations are presented in Tables 8–11.

Discussion

From this study, some remarks can be deduced:

- The molecular association in the liquid phase for a large number of the considered binary systems, are of the type of $[M^I_2M(PO_3)_{(2+q)}]$, a formula corresponding to $p=2$ and $n=1$; $q=2$ for Pb and Cu; $q=3$ for Ce; $M^I=Li, Na, K, Rb, Cs, Ag$ and Tl.
- The liquid in the binary system LiPO₃-Pb(PO₃)₂ shows an association of type LiPb₂(PO₃)₅. However, in the previous work [20], it is shown that the same binary system was athermal and the liquid phase has an ideal behaviour.

Table 1 Relative error of the melting enthalpy of M^IPO₃ determined in the M^IPO₃-Pb(PO₃)₂ systems (ideal model)

M ^I PO ₃	$\Delta_{\text{fus}}H_m^{0,\text{cal}}/\text{kJ mol}^{-1}$	$\Delta_{\text{fus}}H_m^{0,\text{exp}}/\text{kJ mol}^{-1}$	$(\Delta_{\text{fus}}H_m^{0,\text{exp}} - \Delta_{\text{fus}}H_m^{0,\text{cal}}) / \Delta_{\text{fus}}H_m^{0,\text{exp}}/\%$
LiPO ₃	26.08	24.2	-7.7
NaPO ₃	30.73	23.73	-29
KPO ₃	11.79	13.61	13.3

Table 2 Relative error of the melting enthalpy of M^IPO₃ determined in the M^IPO₃-Cu(PO₃)₂ systems (ideal model)

M ^I PO ₃	$\Delta_{\text{fus}}H_m^{0,\text{cal}}/\text{kJ mol}^{-1}$	$\Delta_{\text{fus}}H_m^{0,\text{exp}}/\text{kJ mol}^{-1}$	$(\Delta_{\text{fus}}H_m^{0,\text{exp}} - \Delta_{\text{fus}}H_m^{0,\text{cal}}) / \Delta_{\text{fus}}H_m^{0,\text{exp}}/\%$
LiPO ₃	15.22	24.2	37.1
NaPO ₃	20.57	23.73	13.3
KPO ₃	12.57	13.61	7.6
RbPO ₃	10.05	9.89	-1.6*
CsPO ₃	6.86	11.52	40.4
TlPO ₃	10.65	14.45	26.2

Table 3 Relative error of the melting enthalpy of M^IPO₃ determined in the M^IPO₃-Ce(PO₃)₃ systems (ideal model)

M ^I PO ₃	$\Delta_{\text{fus}}H_m^{0,\text{cal}}/\text{kJ mol}^{-1}$	$\Delta_{\text{fus}}H_m^{0,\text{exp}}/\text{kJ mol}^{-1}$	$(\Delta_{\text{fus}}H_m^{0,\text{exp}} - \Delta_{\text{fus}}H_m^{0,\text{cal}}) / \Delta_{\text{fus}}H_m^{0,\text{exp}}/\%$
NaPO ₃	18.24	23.73	23.1
KPO ₃	15.81	13.61	-16.1
RbPO ₃	11.26	9.89	-13.8
CsPO ₃	11.84	11.52	-2.7*
TlPO ₃	14.52	14.45	-0.4*

Table 4 Relative error of the melting enthalpy of Pb(PO₃)₂ determined in the M^IPO₃-Pb(PO₃)₂ systems (ideal model)

M ^I PO ₃	$\Delta_{\text{fus}}H_m^{0,\text{cal}}/\text{kJ mol}^{-1}$	$\Delta_{\text{fus}}H_m^{0,\text{exp}}/\text{kJ mol}^{-1}$	$(\Delta_{\text{fus}}H_m^{0,\text{exp}} - \Delta_{\text{fus}}H_m^{0,\text{cal}}) / \Delta_{\text{fus}}H_m^{0,\text{exp}}/\%$
LiPO ₃	36.31	38.26	5*
NaPO ₃	41.47	38.26	-8.3
KPO ₃	50.72	38.26	-32.5

Table 5 Relative error of the melting enthalpy of $\text{Cu}(\text{PO}_3)_2$ determined in the $\text{M}^1\text{PO}_3\text{-Cu}(\text{PO}_3)_2$ systems (ideal model)

M^1PO_3	$\Delta_{\text{fus}}H_{\text{m}}^{0,\text{cal}}/\text{kJ mol}^{-1}$	$\Delta_{\text{fus}}H_{\text{m}}^{0,\text{exp}}/\text{kJ mol}^{-1}$	$(\Delta_{\text{fus}}H_{\text{m}}^{0,\text{exp}} - \Delta_{\text{fus}}H_{\text{m}}^{0,\text{cal}}) / \Delta_{\text{fus}}H_{\text{m}}^{0,\text{exp}}/\%$
LiPO ₃	53.46	33.58	-58.8
NaPO ₃	41.03	33.58	-21.9
KPO ₃	43.07	33.58	-27.9
RbPO ₃	35.03	33.58	-4.1*
CsPO ₃	45.39	33.58	-34.8
AgPO ₃	53.02	33.58	-57.5
TlPO ₃	45.18	33.58	-34.26

Table 6 Relative error of the melting enthalpy of $\text{Ce}(\text{PO}_3)_3$ determined in the $\text{M}^1\text{PO}_3\text{-Ce}(\text{PO}_3)_3$ systems (ideal model)

M^1PO_3	$\Delta_{\text{fus}}H_{\text{m}}^{0,\text{cal}}/\text{kJ mol}^{-1}$	$\Delta_{\text{fus}}H_{\text{m}}^{0,\text{exp}}/\text{kJ mol}^{-1}$	$(\Delta_{\text{fus}}H_{\text{m}}^{0,\text{exp}} - \Delta_{\text{fus}}H_{\text{m}}^{0,\text{cal}}) / \Delta_{\text{fus}}H_{\text{m}}^{0,\text{exp}}/\%$
LiPO ₃	78.22	75.22	-3.9*
NaPO ₃	70.34	75.22	6.4
KPO ₃	68.28	75.22	9.2
RbPO ₃	65.37	75.22	13
CsPO ₃	87.63	75.22	-16
AgPO ₃	85.35	75.22	-13.4
TlPO ₃	72.16	75.22	4*

Table 7 Values of $\sum_i v_{i0} \ln \frac{x_i}{x_{i0}}$ on the assumption of a molecular association in the liquid phase; X is the mole fraction of $\text{M}(\text{PO}_3)_q$

Solid phase	$\sum_i v_{i0} \ln \frac{x_i}{x_{i0}}$
M^1PO_3 $M^1 = \text{Li, Na, K, Rb, Cs, Tl, Ag}$	$\ln\{[1-x(1+p)]/[1-x(1+p-1/n)]\}$
$\text{M}(\text{PO}_3)_q$ $q=2$ for $M=\text{Pb, Cu}$; $q=3$ for $M=\text{Ce}$	$\ln\{[1-(1-x)(1+p)]/[1-(1-x)(1+p-1/n)]\}$

- The liquid in the binary system $\text{LiPO}_3\text{-Cu}(\text{PO}_3)_2$ shows an association of type $\text{Li}_4\text{Cu}(\text{PO}_3)_6$.
- The liquid in the binary system $\text{NaPO}_3\text{-Pb}(\text{PO}_3)_2$ shows an association of type $\text{Na}_4\text{Pb}(\text{PO}_3)_6$.

The most important remark is that the stoichiometry of most of the molecular associations in the liquid phase for all systems are similar to the stoichiometry of the intermediate compounds formed as solid compounds.

Table 8 Melting enthalpy of M^1PO_3 , ($M^1 = \text{Li, Na, K, Rb, Cs, Tl}$), calculated on the assumption of a molecular association in the binary liquid $\text{M}^1\text{PO}_3\text{-M}(\text{PO}_3)_q$ rich in M^1PO_3 ($M = \text{Pb, Cu, Ce}$; $q=2, 3$)

M^1PO_3	System	p	n	Association type ($\text{M}_p^1\text{M}(\text{PO}_3)_{p+q})_n$ $q=2, 3$	$\Delta_{\text{fus}}H_{\text{m}}^{0,\text{exp}}/\text{kJ mol}^{-1}$
LiPO ₃	LiPO ₃ -Pb(PO ₃) ₂	0.5	1.2≈1	Li _{0.5} Pb(PO ₃) _{0.5+2} ≈LiPb ₂ (PO ₃) ₅	24.13
	LiPO ₃ -Cu(PO ₃) ₂	3.99≈4	0.92≈1	Li ₄ Cu(PO ₃) ₆	24.16
NaPO ₃	NaPO ₃ -Pb(PO ₃) ₂	4	1.99≈2	[Na ₄ Pb(PO ₃) ₆] ₂	23.73
	NaPO ₃ -Cu(PO ₃) ₂	2	1	Na ₂ Cu(PO ₃) ₄	23.83
	NaPO ₃ -Ce(PO ₃) ₃	2	1.4≈1	Na ₂ Ce(PO ₃) ₅	23.21
KPO ₃	KPO ₃ -Pb(PO ₃) ₂	2	0.7≈1	K ₂ Pb(PO ₃) ₄	13.07
	KPO ₃ -Cu(PO ₃) ₂	2	0.9≈1	K ₂ Cu(PO ₃) ₄	13.66
	KPO ₃ -Ce(PO ₃) ₃	2	1.2≈1	K ₂ Ce(PO ₃) ₅	13.57
RbPO ₃	RbPO ₃ -Ce(PO ₃) ₃	2	1.1≈1	Rb ₂ Ce(PO ₃) ₅	9.99
CsPO ₃	CsPO ₃ -Cu(PO ₃) ₂	2	0.7≈1	Cs ₂ Cu(PO ₃) ₄	11.63
TlPO ₃	TlPO ₃ -Cu(PO ₃) ₂	2	1.1≈1	Tl ₂ Cu(PO ₃) ₄	14.43

Table 9 Melting enthalpy of $\text{Pb}(\text{PO}_3)_2$ calculated on the assumption of a molecular association in the binary liquid $M^I\text{PO}_3\text{-Pb}(\text{PO}_3)_2$, ($M^I=\text{Na, K}$), rich in $\text{Pb}(\text{PO}_3)_2$

System	p	n	Association type ($M^I\text{Pb}_p(\text{PO}_3)_{2p+1})_n$	$\Delta_{\text{fus}}H_m^{\text{exp}}/\text{kJ mol}^{-1}$
$\text{NaPO}_3\text{-Pb}(\text{PO}_3)_2$	0.25	$1.2\approx 1$	$\text{NaPb}_{0.25}(\text{PO}_3)_{1.5}\approx\text{Na}_4\text{Pb}(\text{PO}_3)_6$	39.09
$\text{KPO}_3\text{-Pb}(\text{PO}_3)_2$	$0.45\approx 0.5$	1	$\text{KPb}_{0.5}(\text{PO}_3)_2\approx\text{K}_2\text{Pb}(\text{PO}_3)_4$	37.95

Table 10 Melting enthalpy of $\text{Cu}(\text{PO}_3)_2$, calculated on the assumption of a molecular association in the binary liquid $M^I\text{PO}_3\text{-Cu}(\text{PO}_3)_2$, ($M^I=\text{Li, Na, K, Cs, Ag, Tl}$), rich in $\text{Cu}(\text{PO}_3)_2$

System	p	n	Association type ($M^I\text{Cu}_p(\text{PO}_3)_{2p+1})_n$	$\Delta_{\text{fus}}H_m^{\text{exp}}/\text{kJ mol}^{-1}$
$\text{LiPO}_3\text{-Cu}(\text{PO}_3)_2$	0.25	2	$[\text{LiCu}_{0.25}(\text{PO}_3)_{1.5}]_2\approx[\text{Li}_4\text{Cu}(\text{PO}_3)_6]_2$	34.32
$\text{NaPO}_3\text{-Cu}(\text{PO}_3)_2$	$0.45\approx 0.5$	$1.3\approx 1$	$\text{NaCu}_{0.5}(\text{PO}_3)_2\approx\text{Na}_2\text{Cu}(\text{PO}_3)_4$	33.67
$\text{KPO}_3\text{-Cu}(\text{PO}_3)_2$	$0.45\approx 0.5$	$1.3\approx 1$	$\text{KCu}_{0.5}(\text{PO}_3)_2\approx\text{K}_2\text{Cu}(\text{PO}_3)_4$	33.87
$\text{CsPO}_3\text{-Cu}(\text{PO}_3)_2$	0.5	$1.2\approx 1$	$\text{CsCu}_{0.5}(\text{PO}_3)_2\approx\text{Cs}_2\text{Cu}(\text{PO}_3)_4$	34.52
$\text{AgPO}_3\text{-Cu}(\text{PO}_3)_2$	0.25	$2.1\approx 2$	$[\text{AgCu}_{0.25}(\text{PO}_3)_{1.5}]_2\approx\text{Ag}_2\text{Cu}(\text{PO}_3)_4$	34.68
$\text{TlPO}_3\text{-Cu}(\text{PO}_3)_2$	0.5	$2.2\approx 2$	$[\text{TlCu}_{0.5}(\text{PO}_3)_2]_2\approx[\text{Tl}_2\text{Cu}(\text{PO}_3)_4]_2$	35.07

Table 11 Melting enthalpy of $\text{Ce}(\text{PO}_3)_3$, calculated on the assumption of a molecular association in the binary liquid $M^I\text{PO}_3\text{-Ce}(\text{PO}_3)_3$, ($M^I=\text{Na, K, Rb, Cs, Ag}$), rich in $\text{Ce}(\text{PO}_3)_3$

System	p	n	Association type ($M^I\text{Ce}_p(\text{PO}_3)_{3p+1})_n$	$\Delta_{\text{fus}}H_m^{\text{exp}}/\text{kJ mol}^{-1}$
$\text{NaPO}_3\text{-Ce}(\text{PO}_3)_3$	0.5	$1.2\approx 1$	$\text{NaCe}_{0.5}(\text{PO}_3)_{2.5}\approx\text{Na}_2\text{Ce}(\text{PO}_3)_5$	77.01
$\text{KPO}_3\text{-Ce}(\text{PO}_3)_3$	$0.45\approx 0.5$	$1.2\approx 1$	$\text{KCe}_{0.5}(\text{PO}_3)_{2.5}\approx\text{K}_2\text{Ce}(\text{PO}_3)_5$	76.08
$\text{RbPO}_3\text{-Ce}(\text{PO}_3)_3$	0.5	1	$\text{RbCe}_{0.5}(\text{PO}_3)_{2.5}\approx\text{Rb}_2\text{Ce}(\text{PO}_3)_5$	76.21
$\text{CsPO}_3\text{-Ce}(\text{PO}_3)_3$	$0.55\approx 0.5$	$1.8\approx 2$	$[\text{CsCe}_{0.5}(\text{PO}_3)_{2.5}]_2\approx[\text{Cs}_2\text{Ce}(\text{PO}_3)_5]_2$	74.93
$\text{AgPO}_3\text{-Ce}(\text{PO}_3)_3$	0.5	$1.2\approx 1$	$\text{AgCe}_{0.5}(\text{PO}_3)_{2.5}\approx\text{Ag}_2\text{Ce}(\text{PO}_3)_5$	74.99

Conclusions

A semi-empirical equation of the liquidus curve, already established in the water–salt binary systems is applied with success to salt–salt systems: $M^I\text{PO}_3\text{-Pb}(\text{PO}_3)_2$, $M^I\text{PO}_3\text{-Cu}(\text{PO}_3)_2$ and $M^I\text{PO}_3\text{-Ce}(\text{PO}_3)_3$ (with $M^I=\text{Li, Na, K, Rb, Cs, Ag, Tl}$).

The melting enthalpies were calculated for all the solid phases whose experimental liquidus curves have been determined on the assumption that the liquid solution is ideal and only formed by $M^I\text{PO}_3$ and $M(\text{PO}_3)_q$ ($q=2$ for Pb and Cu, $q=3$ for $M=\text{Ce}$). With these simplified hypothesis, the measured and calculated values of the melting enthalpies of the terminal phases can not considered to be in accordance. In most cases, a wide difference greater than 10 kJ mol^{-1} between the calculated melting enthalpies and the experimental determinations was shown.

The enthalpy of fusion of each terminal phase was then recalculated on the assumption that the liquid contains a molecular association of the type of $M_{pn}^I M_n(\text{PO}_3)_{n(q+p)}$ in the region of the diagram rich in $M^I\text{PO}_3$ or a molecular association of the type of $M_n^I M_{np}(\text{PO}_3)_{n(qp+1)}$ in the region rich in $M(\text{PO}_3)_q$ ($q=2$ for Pb and Cu, $q=3$ for $M=\text{Ce}$). In this case, the obtained values are in good agreement with experimental determinations.

The most important result is that the stoichiometry of the molecular associations in liquid phase for most of the systems are similar to the stoichiometry of the intermediate compounds formed as solid compounds.

In perspective, we wish to improve our model choice by others exits that are based on calorimetric measures such that the case of the binary system $\text{LiPO}_3\text{-Pb}(\text{PO}_3)_2$ [20].

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