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THERMODYNAMIC STUDY OF THE SOLID–LIQUID EQUILIBRIA IN THE M^IPO_3–$Cu(PO_3)_2$ SYSTEMS

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Abstract

Thermodynamic exploration of solid–liquid equilibria of the M^IPO_3–$Cu(PO_3)_2$ (with M^I=Li, Na, K, Rb, Cs, Ag, Tl) systems is carried out with a semi-empirical equation of the liquidus curves. The enthalpies of fusion of pure polyphosphates and some intermediate compounds were determined from DTA curves.

The temperature, enthalpy and entropy of fusion are calculated for each solid phase with the exception of silver polyphosphate and the intermediate compound $Cs_4Cu(PO_3)_6$ which have very limited crystallization fields.

The calculated values of the melting enthalpies are approximately equal to the measured ones. The melting enthalpy of $Cu(PO_3)_2$ calculated from different binary systems shows a wide variation in the obtained values, 35–54 kJ mol^{-1}. The experimental value is 33.65 kJ mol^{-1}.

The calculated temperatures and compositions in most binary systems are in good agreement with experimental determinations.

Keywords: binary system, enthalpy, phase diagram, polyphosphates, thermodynamic exploration

Introduction

Phase diagrams of M^IPO_3–$Cu(PO_3)_2$ (with M^I=Li, Na, K, Rb, Cs, Ag, Tl) systems have been established previously [1–8]. These studies showed the existence of only one intermediate compound:

$$M^ICu(PO_3)_3 \text{ with } M^I\text{=Li, Rb, Tl}$$

$$M^I{}_2Cu(PO_3)_4 \text{ with } M^I\text{=Na, K, Ag}$$

With the exception of $CsPO_3$–$Cu(PO_3)_2$ system which shows three intermediate compounds: $Cs_4Cu(PO_3)_6$, $Cs_2Cu(PO_3)_4$ and $Cs_2Cu_3(PO_3)_8$.

Only $M^ICu(PO_3)_3$, $Cs_2Cu(PO_3)_4$ and $Cs_2Cu_3(PO_3)_8$ compounds decompose peritectically upon heating. The others have a congruent melting point.

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Analysis, processing and thermodynamic exploration of solid–liquid equilibria curves of corresponding systems are presented in this paper.

To refine and interpret the experimental data given in the literature [1–8] we have applied a semi-empirical equation [9–11. This formula was used with success in previous papers [12, 13] for similar binary systems of $M^{I}PO_3$–$M^{III}(PO_3)_3$ (M^{III}=Ce, Pr).

A complementary study using calorimetry is undertaken to compare thermodynamic values of monovalent metal polyphosphates [11] and copper polyphosphate to those determined by liquidus curve computation.

Experimental

The melting enthalpies of monovalent metal polyphosphates and copper polyphosphate were determined using a Setaram DTA 92 apparatus coupled to a calculator allowing, through an appropriate program, integration of area of the thermal effects. The melting enthalpies of K_2SO_4 and CaF_2 [14] (0.02 g in a platinum crucible) were used to calibrate the apparatus. The heating rate was 5 K min^{-1}. This apparatus was also used to measure melting points, i. e. the onset temperature in the DTA curve. A Pt/Platinel thermocouple was used to measure temperature.

Results

Thermal analysis and calorimetry

The experimental values of melting points and melting enthalpies of $M^{I}PO_3$ and $Cu(PO_3)_2$ determined by DTA are presented in Table 1. The values of melting enthalpies of monovalent cation polyphosphate were given in the previous paper [12]. They are reported again in this paper in order to be compared to the calculated ones. The melting enthalpy of copper polyphosphate is measured for the first time. No value is found in the literature.

Table 1 Experimental melting points and melting enthalpies of $Cu(PO_3)_2$ and $M^{I}PO_3$ (M^{I}=Li, Na, K, Rb, Cs, Ag, Tl)

Components	$T_{fus}^{0\,(exp)}$/K	$\Delta_{fus}H_m^{0(exp)}$/kJ mol^{-1}
$Cu(PO_3)_2$	1199	33.65
$LiPO_3$	936	24.20
$NaPO_3$	909	23.73
KPO_3	1084	13.61
$RbPO_3$	1079	9.89
$CsPO_3$	1006	11.52
$AgPO_3$	767	11.84
$TlPO_3$	711	14.45[a]

[a] the value given is the melting enthalpy of the α-phase

Choice of a model for calculation of solid-liquid equilibria in the M^IPO_3-$Cu(PO_3)_2$ systems

Equation for liquidus curves

Several models have been proposed in the literature [13, 15, 16] for the description of phase diagram.

As already stated in a previous publication concerning the critical evaluation of binary systems [11], the models used for description of polyphosphates systems must comply with several constraints:

- the solid phases (M^IPO_3, $Cu(PO_3)_2$, $M^ICu(PO_3)_3$, $M^I_2Cu(PO_3)_4$, $M^I_4Cu(PO_3)_6$, $M^I_2Cu_3(PO_3)_8$) are stoichiometric
- the fitting equations of liquidus curves must never be in contradiction with thermodynamic laws
- the model can be extended to systems presenting an associated liquid phase.

The model presented in a previous paper [11] and re-examined in [14] was applied successfully to the binary systems M^IPO_3–$Ce(PO_3)_3$ [10]. This same model is used here for M^IPO_3–$Cu(PO_3)_2$ systems. The analytical expression which describes the liquidus curves is:

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

where ν_{i0} is the stoichiometry of the species *i* in the solid, x_{i0} and x_i are the mole fractions of species *i* in the solid and the liquid phases, respectively. *A*, *B* and *C* are constants and can be calculated by a least squares method. The liquid phase, in all systems, is considered as ideal.

Fitting equation

The first member of Eq. (1) can be easily expressed as a function of the composition of liquid phase. If we assume that the species of the liquid phase are only M^IPO_3 and $Cu(PO_3)_2$, the values of the left side of Eq. (1) for the solid phases of the M^IPO_3-$Cu(PO_3)_2$ systems are given in Table 2, where *x* is the mole fraction of $Cu(PO_3)_2$ in the liquid phase.

Discussion

Analysis of the liquidus curves

The phase equilibrium diagrams of the binary M^IPO_3–$Cu(PO_3)_2$ (with M^I=Li, Na, K, Rb, Cs, Ag, Tl) systems given by the literature [1–8] and those calculated (this work) are described in Figs 1–7. The parameters *A*, *B* and *C* of the liquidus equation of $Cu(PO_3)_2$ were calculated for each system. They are given in Table 3.

Table 2 $M^{I}PO_3$-$Cu(PO_3)_2$ systems: values of $\sum_i \nu_{i0} \ln\left(\frac{x_i}{x_{i0}}\right)$

Solid phase	$\sum_i \nu_{i0} \ln\left(\frac{x_i}{x_{i0}}\right)$
$M^{I}PO_3$	$\ln(1-x)$
$M^{I}_pCu_q(PO_3)_{2q+p}$ (p=1, 2 ; q=1, 3)	$\ln[(1-x)^p x^q (p+q)^{(p+q)}/(p^p q^q)]$
$Cu(PO_3)_2$	$\ln x$

x – mole fraction of $Cu(PO_3)_2$

The calculated temperatures and compositions of eutectic and peritectic points in systems $M^{I}PO_3$–$Cu(PO_3)_2$ with (M^{I}=Li, Na, Rb, Tl) are in good agreement with experimental determinations. In the other systems (M^{I}=K, Cs, Ag), there is a remarkable difference between experimental and calculated results of the transformation characteristics especially in the region rich in $Cu(PO_3)_2$.

In general, the liquidus curves of $M^{I}PO_3$ were defined by a small number of experimental values. Because the melting point T^0_{fus} of pure solids is more precisely known than the determined solubility values, the liquidus curves must pass through these points. The parameters A, B and C of the different $M^{I}PO_3$ liquidus equations are presented in Table 4.

The stoichiometry of the intermediate binary compounds found in the different systems correspond to the formula $M^{I}_pCu_q(PO_3)_{2q+p}$ with p=1, 2 or 4 and q=1 or 3.

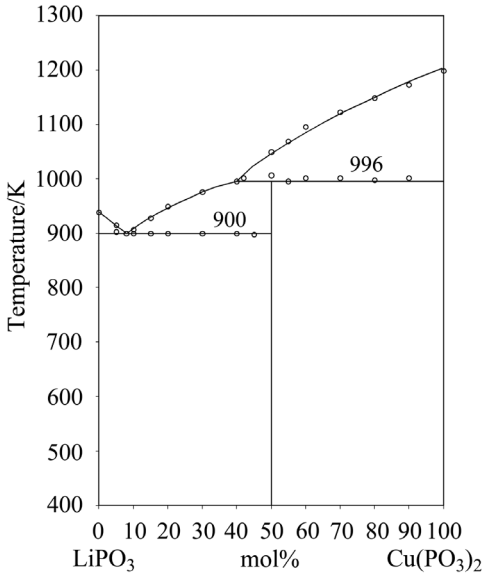

Fig. 1 Equilibrium diagram of the $LiPO_3$–$Cu(PO_3)_2$: — – calculated liquidus curve [our work], o – experimental points [1]

Table 3 $M^{I}PO_3$–$Cu(PO_3)_2$ systems: liquidus of $Cu(PO_3)_2$

Systems	A/K	B	C	$\Delta_{fus}H^0_m$/kJ mol^{-1}	$\Delta C^0_{p,m}$/J K^{-1} mol^{-1}	$\Delta_{fus}S^0_m$/J K^{-1} mol^{-1}	T^0_{fus}/K
$LiPO_3$–$Cu(PO_3)_2$	5066.335	9.571	–72.091	53.46	79.579	44.513	1199
$NaPO_3$–$Cu(PO_3)_2$	3733.561	7.230	–54.370	41.03	60.111	34.222	1199
KPO_3–$Cu(PO_3)_2$	14405.66	16.33	–127.82	43.07	135.81	35.925	1199
$RbPO_3$–$Cu(PO_3)_2$	4482.56	7.252	–55.153	35.03	60.297	29.218	1199
$CsPO_3$–$Cu(PO_3)_2$	16083.17	17.96	–140.79	45.39	149.38	37.864	1199
$AgPO_3$–$Cu(PO_3)_2$	3260.23	8.038	–59.703	53.02	66.829	44.222	1199
$TlPO_3$–$Cu(PO_3)_2$	10993.59	13.69	–106.29	45.18	113.90	37.678	1199

Table 4 $M^{I}PO_3$–$Cu(PO_3)_2$ systems: liquidus of $M^{I}PO_3$ (M^{I}=Li, Na, K, Rb, Cs, Tl)

Compound	A/K	B	C	$\Delta_{fus}H^0_m$/kJ mol^{-1}	$\Delta C^0_{p,m}$/J K^{-1} mol^{-1}	$\Delta_{fus}S^0_m$/J K^{-1} mol^{-1}	T^0_{fus}/K
$LiPO_3$	–818.579	1.07775	–6.5057	15.22	8.96	16.206	939
$NaPO_3$	–2157.04	0.35364	–0.0901	20.57	2.94	22.865	900
KPO_3	4550.26	5.629	–43.528	12.57	46.802	11.676	1077
$RbPO_3$	966.3123	2.01475	–14.967	10.05	16.75	9.312	1080
$CsPO_3$	322.5033	1.13001	–8.141	6.86	9.394	6.755	1016
$TlPO_3$	–4912.26	–5.0833	40.281	10.65	–42.263	14.924	714

Table 5 $M^{I}PO_3$–$Cu(PO_3)_2$ systems: liquidus of $M^{I}_{p}Cu_q(PO_3)_{2q+p}$ (p=1, 2 and q=1, 3)

Components	A/K	B	C	$\Delta_{fus}H^0_m$/kJ mol^{-1}	$\Delta C^0_{p,m}$/J K^{-1} mol^{-1}	$\Delta_{fus}S^0_m$/J K^{-1} mol^{-1}	T^0_{fus}/K
$LiCu(PO_3)_3$	–131826.50	–128.080	1016.575	14.05	1064.9	13.833	1016
$RbCu(PO_3)_3$	–7331.26	–3.923	34.880	31.90	–32.619	35.831	980.8
$AgCu(PO_3)_3$	–13171.72	–6.337	57.757	62.33	–52.658	69.575	895.9
$TlCu(PO_3)_3$	2575.656	7.0452	–50.551	10.65	–42.263	14.924	714
$Na_2Cu(PO_3)_4$	–5116.845	2.1264	–9.43101	59.88	17.678	61.049	935.85
$K_2Cu(PO_3)_4$	–4942.789	0.029	5.082765	41.32	0.2416	44.153	1080
$Cs_2Cu(PO_3)_4$	–17770.119	0.238	0.509999	16.37	1.9820	19.561	837
$Cs_2Cu_3(PO_3)_8$	8802.383	12.100	–92.3575	26.49	100.60	26.735	984

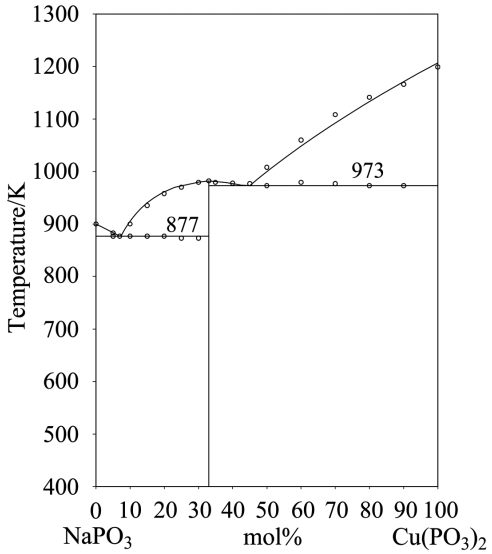

Fig. 2 Equilibrium diagram of the $NaPO_3$–$Cu(PO_3)_2$: — – calculated liquidus curve [our work], o – experimental points [3]

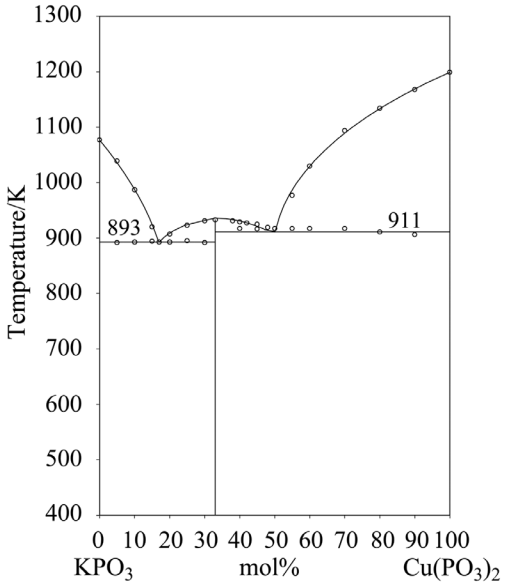

Fig. 3 Equilibrium diagram of the KPO_3–$Cu(PO_3)_2$: — – calculated liquidus curve [our work], o – experimental points [4]

Some intermediate compounds have a congruent melting point and the others undergo a peritectic decomposition. Their stable or metastable melting points were calculated respectively and are presented in Table 5 with the parameters *A*, *B* and *C*.

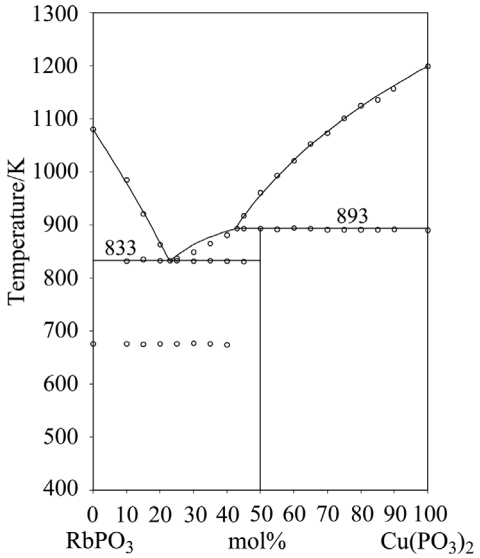

Fig. 4 Equilibrium diagram of the $RbPO_3$–$Cu(PO_3)_2$: — – calculated liquidus curve [our work], o – experimental points [2]

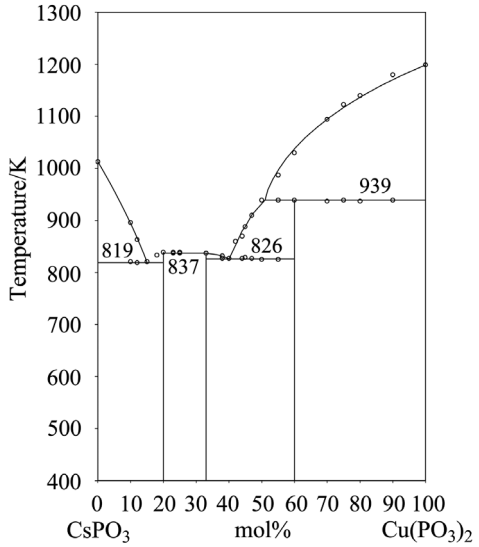

Fig. 5 Equilibrium diagram of the $CsPO_3$–$Cu(PO_3)_2$: — – calculated liquidus curve [our work], o – experimental points [6]

Thermodynamic exploration of liquidus curves

The values of the melting enthalpy of copper polyphosphate obtained in the different systems vary from 35 to 54 kJ mol^{-1} (Table 3). Among these values, the nearest one to

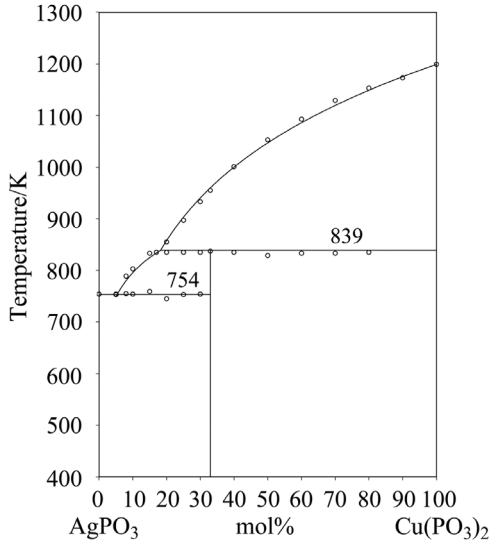

Fig. 6 Equilibrium diagram of the $AgPO_3$–$Cu(PO_3)_2$: — – calculated liquidus curve [our work], o – experimental points [5]

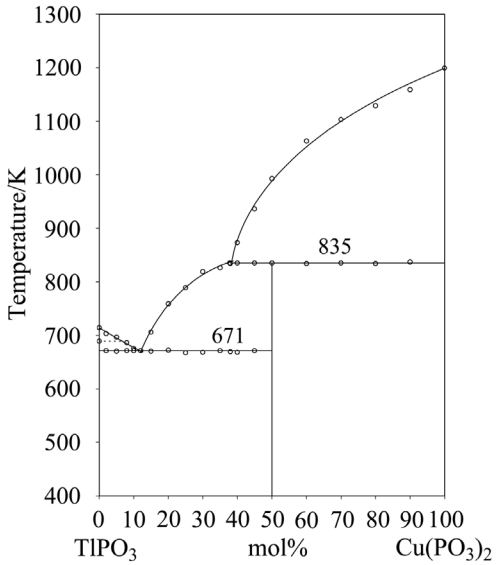

Fig. 7 Equilibrium diagram of the $TlPO_3$–$Cu(PO_3)_2$: — calculated liquidus curve [our work], o – experimental points [2]

the experimental melting enthalpy (33.65 kJ mol^{-1}) is obtained in $RbPO_3$–$Cu(PO_3)_2$ system (35.03 kJ mol^{-1}). This is due to:

- the great number of the experimental points used in liquidus calculation.

- the good coherence between the liquidus curve as calculated and the experimental points.

So we assume that the melting enthalpy of $Cu(PO_3)_2$ is equal to 34±1 kJ mol^{-1}.

The liquidus calculation of the M^IPO_3 polyphosphates, whose experimental liquidus curves were sufficiently well defined to allow a thermodynamic exploration, with the exception of silver polyphosphate, was done. Given the precision and the number of experimental determinations, the calculated values of the enthalpy of fusion (Table 6) are of the same order of magnitude as the experimental ones and those given by the previous thermodynamic study of M^IPO_3–$M^{III}(PO_3)_3$ systems [11–14] where M^{III} is a trivalent cation.

Table 6 Experimental and calculated melting enthalpies of monovalent cation polyphosphates

Components	$\Delta_{fus}H_m^{0\,(calculated)}$ [this work]/kJ mol^{-1}	$\Delta_{fus}H_m^{0\,(experimental)}$ /kJ mol^{-1}	$\Delta_{fus}H_m^{0\,(calculated)}$ [literature]/kJ mol^{-1}
$LiPO_3$	15.22	24.20	25.50[11]
$NaPO_3$	20.57	23.73	22.20[11]; 18.24[12]; 22.20[13]
KPO_3	12.57	13.61	10.9[11]; 15.81[12]
$RbPO_3$	10.05	9.89	11.1[11]; 11.26[12]; 11.1[13]
$CsPO_3$	6.86	11.52	10.1[11]; 11.84[12]; 10.1[13]
$TlPO_3$	10.65	14.45[a]	17.2[a][11]; 14.52[12]

[a]the value given is the melting enthalpy of the α-phase

The calculated thermodynamic functions of fusion of the intermediate compounds that have a congruent melting point are displayed in Table 5. In this case, the calculated melting enthalpies agree with the experimental values (Table 7).

Table 7 Experimental and calculated melting enthalpies of some intermediate compounds

Components	$\Delta_{fus}H_m^{0\,(exp)}$/kJ mol^{-1}	$\Delta_{fus}H_m^{0\,(calculated)}$/kJ mol^{-1}
$Na_2Cu(PO_3)_4$	53.66	59.88
$K_2Cu(PO_3)_4$	38.86	41.32

The fusion of the intermediate phases which decompose peritectically on heating was not studied further by calorimetry. The thermodynamic functions of fusion were calculated at the metastable melting point. The results are displayed in Table 5. These values are given only as an indication, since they are calculated on the assumption that the solution is ideal and the liquid phase is only formed by M^IPO_3 and $Cu(PO_3)_2$.

Conclusions

A semi-empirical equation of the liquidus curve, already established in the water-salt binary systems, was applied with success to salt-salt systems: $M^{I}PO_3$–$Cu(PO_3)_2$ (with M^{I}=Li, Na, K, Rb, Cs, Ag, Tl).

This equation is useful for an intermediate or limiting phase in the complete range of temperatures and compositions. The analytical expression obtained describes the experimental liquidus curves of all the solid phases in the $M^{I}PO_3$–$Cu(PO_3)_2$ systems. Moreover, the thermodynamic function characteristic of the fusion was calculated with a simplified hypothesis for all the solid phases whose experimental liquidus curves have been determined. Comparison of the measured and calculated values of enthalpies of fusion of $M^{I}PO_3$ and some intermediate compounds which have a congruent melting point can be considered to be in concordance. The melting enthalpy of $Cu(PO_3)_2$ was adjusted to 34 1 kJ mol^{-1}.

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