The (Tl, Na, Li)NO_3, (Tl, Na, Rb)NO_3, (Tl, Na, Cs)NO_3 Ternary Systems *

A. CINGOLANI, M. A. BERCHIESI, G. PIANTONI, and D. LEONESI

Istituto Chimico della Università, Camerino (Italia)

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Solid-liquid equilibria were studied by a visual method in order to draw the polythermal projections of the (Tl, Na, Li) NO_3, (Tl, Na, Rb) NO_3, and (Tl, Na, Cs) NO_3 ternary systems. The seven pertinent binaries are also discussed and data concerning the invariant points and crystallization regions are given.

Among the ternaries formed with $TlNO_3$, $NaNO_3$, and an another alkali nitrate, only (Tl, Na, K) NO_3 was so far investigated [1].

We now report on the topology of (Tl, Na, Li)NO_3, (Tl, Na, Rb)NO_3, and (Tl, Na, Cs)NO_3.

Experimental

The solid-liquid equilibrium temperatures were mostly taken by a visual method, the details of which were described elsewhere [2]. Whenever necessary to get more complete information, a Perkin-Elmer Differential Scanning Calorimeter (DSC-1B) was also used.

C. Erba RP $NaNO_3$ (m. p. 306.5 °C), and Schuchardt $TlNO_3$ (209.0 °C), $LiNO_3$ (253.0 °C), $RbNO_3$ (312.5 °C), and $CsNO_3$ (406.5 °C), whose purity was never less than 99.5%, were employed. In order to obtain water clear melts, a re-crystallization of $TlNO_3$ from water was needed. All salts were anyway carefully dried before use.

Pertinent Binaries

a) **(Tl, Na)NO_3:** As for this system, which exhibits a eutectic at 164 °C ($X_{NaNO_3} = 0.225$) and constitutes the common side of the three ternaries taken into account, we adopted recent literature data [3].

b) **(Na, Li)NO_3:** The solid-liquid equilibrium temperatures newly taken by us are in excellent agreement with previous SINISTRI's data [4]: the coordinates of the eutectic are 193.0 °C and $X_{LiNO_3} = 0.540$.

c) **(Li, Tl)NO_3:** As for this system, some discrepancies exist among previous author's data. BRISCOE et al. [5] and PROTSENKO et al. [6] found a simple eutectic (at 136.5 °C and 132.0 °C, respectively), while SINISTRI et al. [4] postulated the formation of the congruently melting (at 138 °C) intermediate compound $LiNO_3 \cdot 2\,TlNO_3$. Since the latter (whose existence field ought anyhow to be extremely narrow) could not be put into evidence through our visual measurements, we assumed the system as having a simple eutectic at 135 °C ($X_{LiNO_3} = 0.318$).

d) **(Na, Rb)NO_3:** The re-investigation of the liquidus curve allowed us to confirm DIOGENOV's results [7], inasmuch as we too found the congruently melting (at 176.5 °C) compound $NaNO_3 \cdot 2\,RbNO_3$, and two eutectics at 175.0 °C ($X_{NaNO_3} = 0.306$), and at 171.0 °C ($X_{NaNO_3} = 0.446$), respectively. Earlier data by PUSHIN [8] and by BLIDIN [9] are probably to be rejected.

e) **(Rb, Tl)NO_3:** This system was studied by one of us and fully discussed in another paper [10]. The solid-liquid equilibrium temperatures are progressively increasing as the molar fraction of $RbNO_3$ increases, with a remarkable slope variation at ~260 °C ($X_{TlNO_3} = 0.180$).

f) **(Na, Cs)NO_3:** For this system we found a simple eutectic at 193.0 °C ($X_{CsNO_3} = 0.452$), in good agreement with recent literature data [11].

Table 1. Liquidus curve of the (Tl, Cs) NO_3 binary system.

X_{CsNO_3} (mole fraction)	t(°C)	X_{CsNO_3} (mole fraction)	t(°)
0,000	209.0	0.250	224.6
0.008	208.6	0.261	227.1
0.017	208.5	0.269	228.3
0.022	208.4	0.281	231.2
0.027	208.6	0.289	232.2
0.038	208.8	0.305	235.9
0.042	208.8	0.306	236.2
0.048	208.8	0.349	246.5
0.056	209.0	0.416	263.5
0.070	209.0	0.482	280.4
0.083	209.4	0.525	291.5
0.109	210.7	0.554	300.2
0.150	210.9	0.630	319.1
0.174	213.3	0.700	335.9
0.207	217.4	0.749	347.8
0.224	219.8	0.801	359.8

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g) **$(Cs, Tl)NO_3$:** This mixtures form a continuous series of solid solutions: at about $X_{TlNO_3} = 0.980$ the freezing temperature passes through a minimum, a few tenths of a degree lower than the melting point of pure $TlNO_3$ (see Table 1).

The Topology of the Liquidus Areas

In order to give a picture of the simultaneous crystallization and isothermal curves, solid-liquid equilibria were measured along eight internal sections of the $(Tl, Na, Rb)NO_3$ system, and along ten sections of both the $(Tl, Na, Li)NO_3$ and $(Tl, Na, Cs)NO_3$ ternaries.

The results are summarized in Tables 2 – 4, while in the Figs. 1 – 3 the pertinent polythermal projections are shown.

Three crystallization regions are apparent both in the $(Tl, Na, Li)NO_3$ and $(Tl, Na, Rb)NO_3$ ternaries. Those of the first one are to be referred to $LiNO_3$, $TlNO_3$, and $NaNO_3$; those of the second to continuous $(Rb, Tl)NO_3$ solid solutions, to $NaNO_3$, and to the compound $NaNO_3 \cdot 2\,RbNO_3$, respectively.

Table 2. Sections in the $(Tl, Na, Li)NO_3$ system.

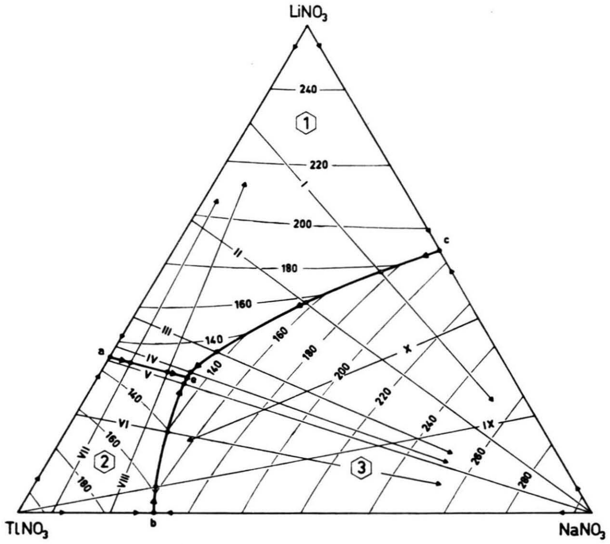
Section	Composition of the starting mixture (in mole)		Added component (ac)	Characteristic points x_{ac}	t(°C)
1	$LiNO_3 + TlNO_3$	4.00 : 1	$NaNO_3$	0.380	182.0
2	$LiNO_3 + TlNO_3$	1.50 : 1	$NaNO_3$	0.282	164.5
3	$LiNO_3 + TlNO_3$	0.66 : 1	$NaNO_3$	0.178	136.0
4	$LiNO_3 + TlNO_3$	0.52 : 1	$NaNO_3$	0.152	124.0
5	$LiNO_3 + TlNO_3$	0.45 : 1	$NaNO_3$	0.154	124.0
6	$LiNO_3 + TlNO_3$	0.25 : 1	$NaNO_3$	0.176	140.0
7	$TlNO_3 + NaNO_3$	15.66 : 1	$LiNO_3$	0.306	131.0
8	$TlNO_3 + NaNO_3$	4.00 : 1	$LiNO_3$	0.292	125.0
9	$NaNO_3 + LiNO_3$	4.00 : 1	$TlNO_3$	0.734	158.0
10	$NaNO_3 + LiNO_3$	1.50 : 1	$TlNO_3$		

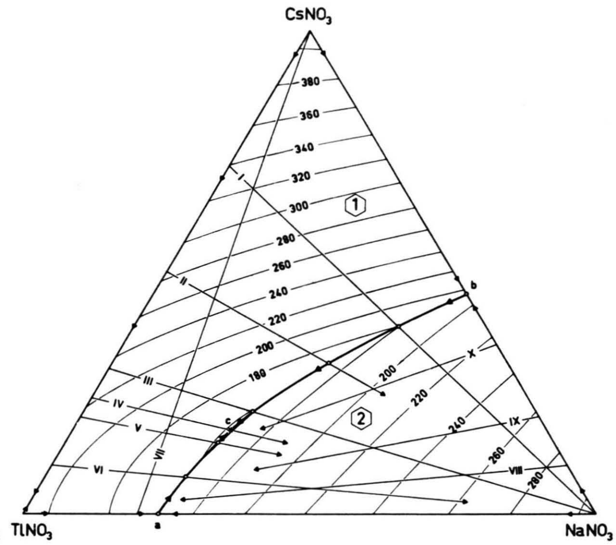
Table 3. Sections in the $(Tl, Na, Rb)NO_3$ system.

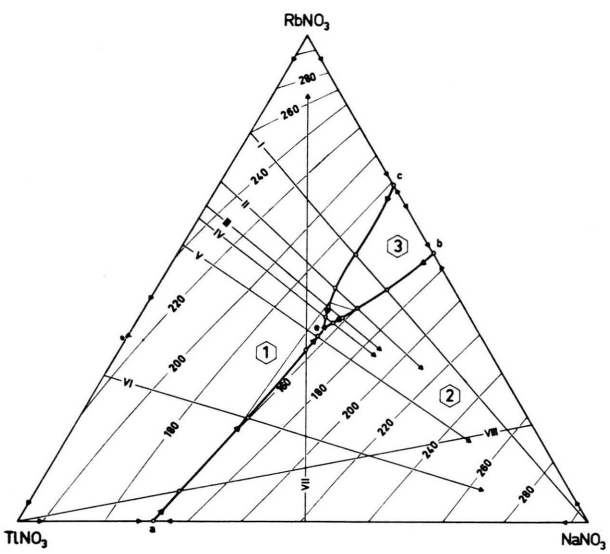
Section	Composition of the starting mixture (in mole)		Added component (ac)	Characteristic point x_{ac}	t(°C)	x_{ac}	t(°C)
1	$RbNO_3 + TlNO_3$	4.00 : 1	$NaNO_3$	0.312	167.0	0.403	164.0
2	$RbNO_3 + TlNO_3$	2.33 : 1	$NaNO_3$	0.312	162.5	0.370	160.5
3	$RbNO_3 + TlNO_3$	1.86 : 1	$NaNO_3$	0.317	159.0	0.353	158.5
4	$RbNO_3 + TlNO_3$	1.66 : 1	$NaNO_3$	0.323	157.5	0.344	156.5
5	$RbNO_3 + TlNO_3$	1.33 : 1	$NaNO_3$	0.329	155.0		
6	$RbNO_3 + TlNO_3$	0.43 : 1	$NaNO_3$	0.291	159.0		
7	$TlNO_3 + NaNO_3$	1.00 : 1	$RbNO_3$	0.354	154.5		
8	$NaNO_3 + RbNO_3$	4.00 : 1	$TlNO_3$	0.687	162.5		

Table 4. Sections in the $(Tl, Na, Cs)NO_3$ system.

Section	Composition of the starting mixtures (in mole)		Added component (ac)	Characteristic x_{ac}	t(°C)
1	$CsNO_3 + TlNO_3$	2.56 : 1	$NaNO_3$	0.462	180.0
2	$CsNO_3 + TlNO_3$	1.00 : 1	$NaNO_3$	0.376	169.0
3	$CsNO_3 + TlNO_3$	0.43 : 1	$NaNO_3$	0.294	160.0
4	$CsNO_3 + TlNO_3$	0.32 : 1	$NaNO_3$	0.274	158.5
5	$CsNO_3 + TlNO_3$	0.25 : 1	$NaNO_3$	0.266	159.0
6	$CsNO_3 + TlNO_3$	0.11 : 1	$NaNO_3$	0.247	161.0
7	$TlNO_3 + NaNO_3$	4.00 : 1	$CsNO_3$		
8	$NaNO_3 + CsNO_3$	9.00 : 1	$TlNO_3$		
9	$NaNO_3 + CsNO_3$	4.00 : 1	$TlNO_3$		
10	$NaNO_3 + CsNO_3$	1.86 : 1	$TlNO_3$		







System	point	Composition X_{NaNO_3} (mole fraction)	X_{TlNO_3} (mole fraction)	Temp. °C
(Tl, Na, Li)NO_3	e	0.153	0.569	121.5
(Tl, Na, Rb)NO_3	e	0.331	0.268	154.5

Table 5. Coordinates of the invariant points.

System	Crystallization region	% liquidus area
(Tl, Na, Li)NO_3	(1)	36.7
	(2)	11.0
	(3)	52.3
(Tl, Na, Rb)NO_3	(1)	50.6
	(2)	45.0
	(3)	4.4
(Tl, Na, Cs)NO_3	(1)	60.5
	(2)	39.5

Table 6. Areas of the crystallization region.

Regarding (Tl, Na, Cs)NO_3 the univariant curve a – b, which divides the crystallization region belonging to the continuous (Cs, Tl)NO_3 solid solutions from that belonging to $NaNO_3$, exhibits a minimum **c** at 158.5 °C ($X_{NaNO_3} = 0.274$; $X_{TlNO_3} = 0.551$).

(Tl, Na, Li)NO_3, and (Tl, Na, Rb)NO_3 are ternaries provided with a single eutectic **e**. The coordinates (see Table 5) of the latter were in both cases determined by projecting the co-crystallization curves a – e, b – e, and c – e onto two sides; the eutectic melting temperatures were then confirmed by measuring the melting points of samples of the detected compositions.

The areas of the different regions (expressed in percentages of each triangle total area) are reported in Table 6.

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