Miscibility Gaps in Fused Salts

Note II. Systems of TlBr with two Alkali Nitrates and of two Thallous Halides with $NaNO_3$ *

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The miscibility gaps in the liquid state have been measured in sixteen systems of the type $TlBr + (Me_I, Me_{II})NO_3$, where Me_I, Me_{II} are alkali metals, and in eight systems of the type Tl(Cl, Br) or Tl(Cl, J) $+ NaNO_3$. For the systems of the first type, deviations from additivity of the demixing t_{max} have been put in connection with proper functions of ionic radii.

Moreover deductions have been drawn about miscibility gaps which were not directly measurable, owing either to the thermal instability of one component, or because the gaps were "submerged" under the corresponding SL curves.

In Note I [1] $TlX + MeNO_3$ binary systems (where X = Cl, Br, J, and Me = alkali metal), which are diagonal sections of the reciprocal systems Tl, Me/X, NO_3, have been studied. The systems containing TlBr show a mutual limited solubility in the liquid state, except for $TlBr + CsNO_3$, where, however, a branch of the SL (solid-liquid) curve is "S"-shaped, with an almost isothermal portion, thus showing a sharp tendency to split in the liquid phase.

Moreover it has not been possible to measure the temperature t_{max} (corresponding to the maximum of the demixing curve) in the $TlBr + LiNO_3$ system, owing to the thermal instability of the nitrate.

We have now studied demixing in mixtures of TlBr with pairs of alkali nitrates, in order to obtain on one hand more detailed data on the two above mentioned gaps, and on the other hand information on the interactions between the nitrates of each couple, inferred from the deviations of t_{max} from additivity.

To complete the picture, some mixtures of couples of thallous halides with $NaNO_3$ have also been studied.

Results and Discussion

a) Mixtures of TlBr with couples of alkali nitrates

The miscibility gaps in the systems of TlBr with: Li, Na (1:1, 1:3); Li, K (1:1, 1:3); Na, K (3:1, 1:1, 1:3), Na, Rb (3:1, 1:1, 1:3); Na, Cs (3:1, 1:1, 1:3); K, Rb (1:1); K, Cs (1:1); and Rb, Cs (1:1) nitrates have been measured.

The results are shown in Fig. 1 – 3, where circles are experimental data. In Table 1 are tabulated the temperatures t °C at which, by cooling and shaking, demixing takes place, the compositions (as molecular fractions x_{TlBr}) and the t_{max} values.

From Fig. 1 – 3 it can be seen that, in each system, the extent of the gap is increasing as the percentage of the nitrate with the smaller cation increases, in conformity with the tendencies to demix pointed out in Note I [1]. The primary crystallization from one of the two liquid phases in equilibrium

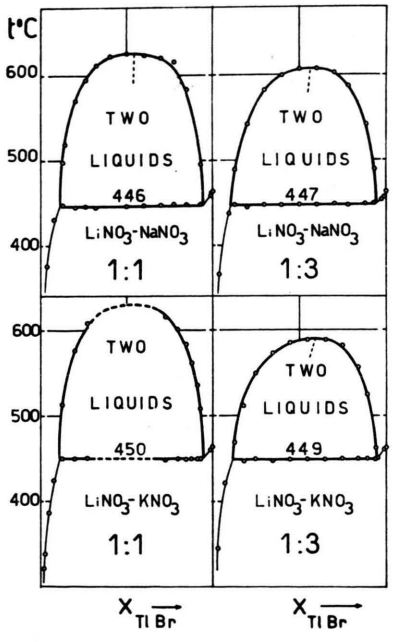


Fig. 1. Systems: $TlBr + (Li, Na)NO_3$ and $TlBr + (Li, K)NO_3$.

* Work carried out with the aid of the Consiglio Nazionale delle Ricerche (Rome).

[1] C. Sinistri, P. Franzosini, A. Timidei, and M. Rolla, Z. Naturforschg. **20 a**, 561 [1965].

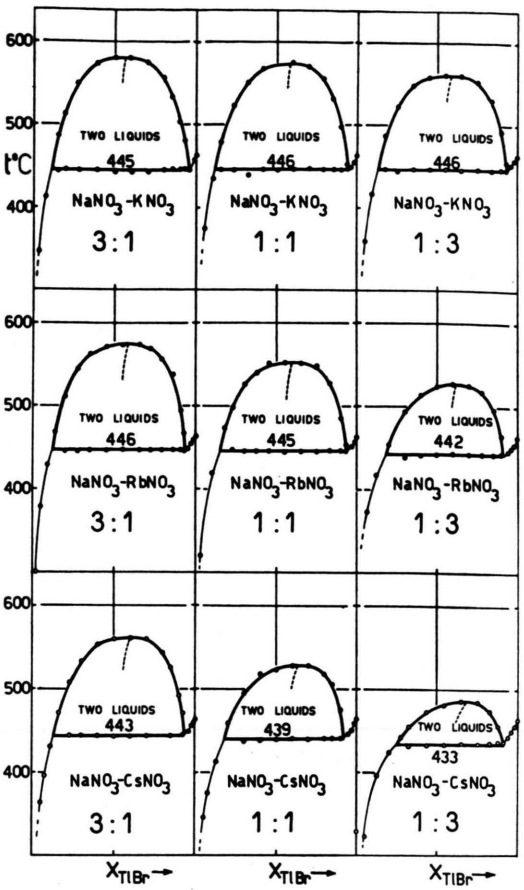


Fig. 2. Systems: $TlBr + (Na, K)NO_3$; $TlBr + (Na, Rb)NO_3$; and $TlBr + (Na, Cs)NO_3$.

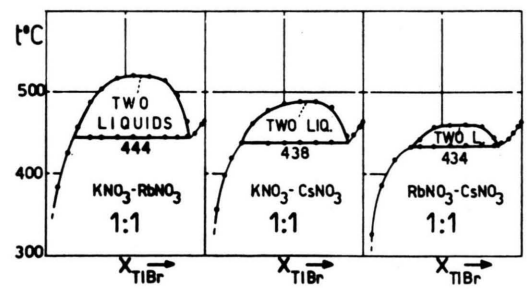


Fig. 3. Systems: $TlBr + (K, Rb)NO_3$; $TlBr + (K, Cs)NO_3$; and $TlBr + (Rb, Cs)NO_3$.

generally takes place at temperatures constant within the experimental fluctuations, except for mixtures containing $(Na, Cs)NO_3$ (1:3) where, however, the temperature variations with TlBr molecular fraction are not great. The average values of the primary crystallization temperatures are always reported in the figures.

In the $TlBr + (Li, K)NO_3$ (1:1) system the liquid-liquid (LL) curve could not be completely traced owing to the thermal instability of the melt, and so the temperature $t_{max} = 630\ ^\circ C$ could be evaluated only approximatively.

Availing ourselves of the data of Table 1 and Note I, it has been possible to describe the miscibility gaps in the systems $TlBr + NaNO_3 + (Li, K, Rb, Cs)NO_3$: a few LL isotherms are shown in Fig. 4.

Let us now consider the $TlBr + (K, Rb)NO_3$, $(Na, K)NO_3$ and $(Na, Rb)NO_3$ mixtures. Curves t_{max} *vs* (concentration ratio of the two nitrates) indicate deviation from additivity for the quantities $\Delta t \equiv t_{calc} - t_{obs}$, which are negative and which we think we may ascribe simply to the nonideality of the two nitrate mixtures. The parallelism between these $\Delta t < 0$ and the negative enthalpies of mixing in the corresponding binary nitrate mixtures is quite clear [2] (Fig. 5).

In order to extend similar remarks to the systems containing $CsNO_3$, it must be observed that the SL curve of the $TlBr + CsNO_3$ system shows an "S"-shaped branch with a large portion (for $0.40 < x_{TlBr} < 0.85$) practically isothermal at 429 °C. The flatness and extent of this portion suggest the occurrence of a metastable "submerged" miscibility gap [3], the t_{max} of which must lie so close to 429 °C, that, as a first approximation, this very temperature may be assumed as t_{max}. An evaluation, which is perhaps more careful, can be done by considering for the $TlBr + (Rb, Cs)NO_3$ mixtures Δt as negligible, which is justified by the fact that for the two nitrates the enthalpy of mixing is ≈ 0 [2]. A value $t_{max} = 426\ ^\circ C$ is drawn, which is used in the following calculations.

Δt values shown in Table 2 refer to the mixtures with a 1:1 ratio of the molecular fractions of the two nitrates, and are believed to be correct within $\pm 1\ ^\circ C$.

Previous authors [4] have related, in a semiempirical way, a number of properties of mixing with parameters (as Tobolsky's or Reiss, Katz, and

[2] O. J. Kleppa and L. S. Hersh, J. Chem. Phys. **34**, 351 [1961].

[3] J. E. Ricci, The Phase Rule, Van Nostrand Co., New York 1951, p. 175.

[4] See, e. g.; a) ref. [2]; b) H. Reiss, J. L. Katz, and O. J. Kleppa, J. Chem. Phys. **36**, 144 [1962]; c) B. DeNooijer and J. A. A. Ketelaar, Rec. Trav. Chim. Pays-Bas **83**, 573 [1964]; d) G. Bertozzi and G. Sternheim, J. Phys. Chem. **68**, 2908 [1964].

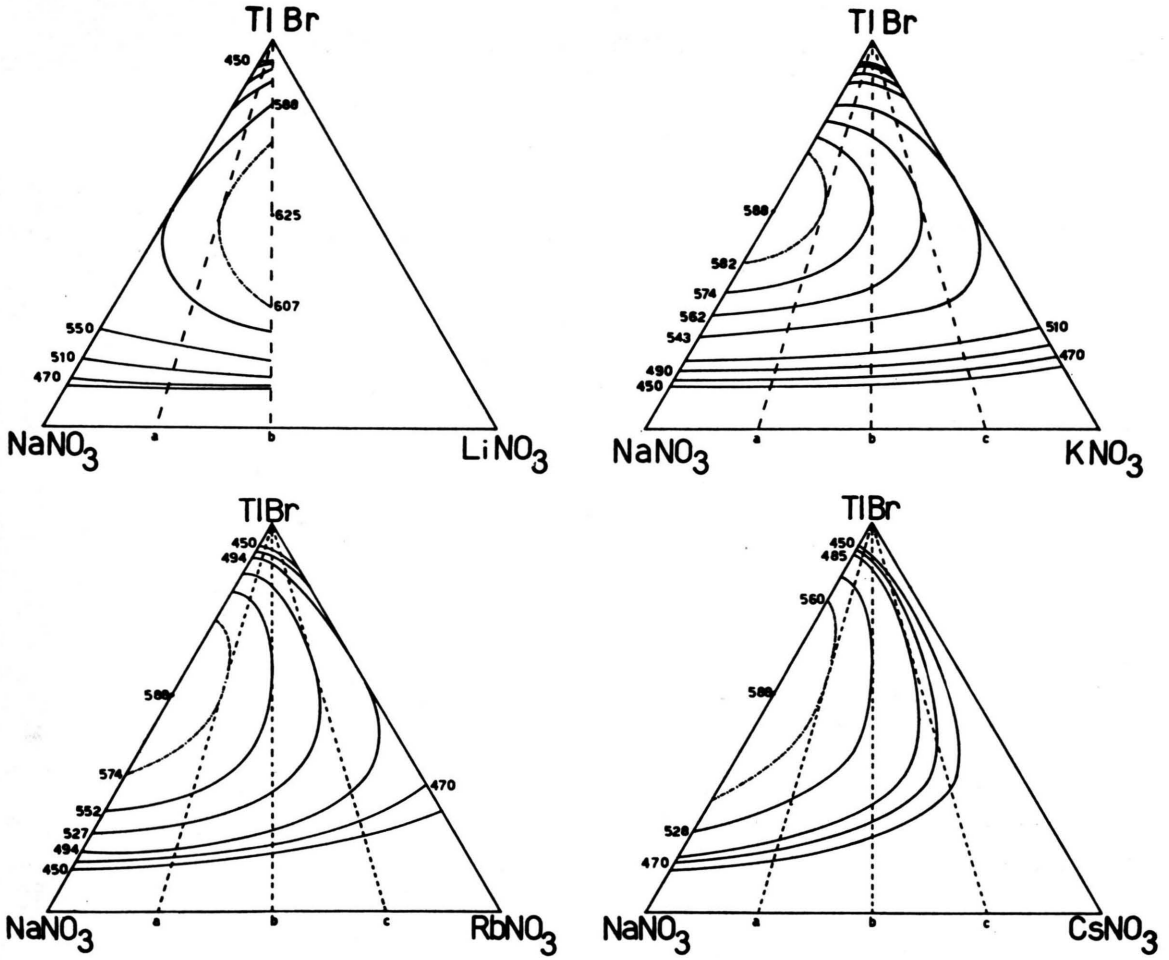
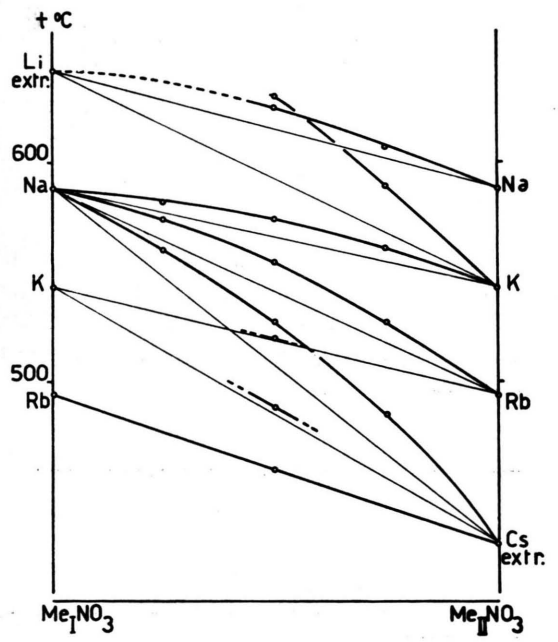


Fig. 4. LL isotherms for the systems: $TlBr + NaNO_3 + (Li, K, Rb, Cs)NO_3$.



← Fig. 5. t_{max} *vs* $Me_INO_3/Me_{II}NO_3$ for the systems: TlBr + two alkali nitrates.

Kleppa's), which are functions of the interionic distances of the pure salts. As a matter of fact, when, for 1:1 nitrate ratio mixtures, quantities $-R\,\Delta t$ are plotted *vs* the RKK's parameter [4b]:

$$\delta^2 = [(d_1 - d_2)/(d_1\, d_2)]^2$$

(d_1 being the sum of the ionic radii of the first nitrate, and d_2 the same quantity for the second

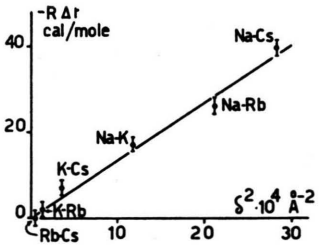


Fig. 6. Values of $-R\,\Delta t$ as a function of the Reiss, Katz, and Kleppa parameter.

System TlBr +	x_{TlBr}	t (°C)
$(Li,Na)NO_3$ 1 : 1 $t_{max} = 625$	0.125	497
	.138	518
	.200	570
	.259	594
	.320	611
	.403	622
	.500	625
	.600	623
	.700	620
	.775	616
	.850	582.5
	.926	494.5
$(Li,Na)NO_3$ 1 : 3 $t_{max} = 607$	0.125	488
	.200	542
	.300	582
	.400	599
	.500	606
	.600	607
	.700	602
	.780	587
	.875	541.5
	.925	489
$(Li,K)NO_3$ 1 : 1 $t_{max} \sim 630$	0.125	513
	.200	576
	.274	609
	.725	616.5
	.800	602
	.850	584
	.880	562
	.910	536
	.932	507.5
$(Li,K)NO_3$ 1 : 3 $t_{max} = 589$	0.125	469
	.180	512
	.250	550
	.350	574
	.450	586
	.550	589
	.650	589
	.750	583
	.840	557
	.892	525
	.940	463
$(Na,K)NO_3$ 3 : 1 $t_{max} = 581.5$	0.150	487
	.196	513
	.273	550
	.390	575
	.500	581
	.600	580.5
	.700	575.5
	.800	558
	.850	534
	.899	504
	.925	481
$(Na,K)NO_3$ 1 : 1 $t_{max} = 574$	0.150	479
	.230	523.5
	.321	552
	.410	567.5
	.600	574
	.700	571
	.790	556
	.850	532
	.899	498
	.940	452.5
$(Na,K)NO_3$ 1 : 3 $t_{max} = 561$	0.175	486
	.250	523
	.350	548
	.450	558
	.550	561
	.649	561
	.749	554.5
	.839	531
	.899	492
	.932	456
$(Na,Rb)NO_3$ 3 : 1 $t_{max} = 574$	0.135	468
	.200	510
	.275	544
	.350	561.5
	.450	571
	.550	573
	.650	572.5
	.720	569
	.790	556
	.860	528
	.905	493.5
	.925	466
$(Na,Rb)NO_3$ 1 : 1 $t_{max} = 554$	0.175	473
	.225	498
	.300	526
	.375	540
	.450	551
	.550	552
	.650	553.5
	.750	548
	.830	527
	.900	484
	.930	453
$(Na,Rb)NO_3$ 1 : 3 $t_{max} = 527$	0.200	453
	.300	493
	.403	513
	.500	524
	.600	527
	.700	525
	.780	517.5
	.849	496
	.900	465
$(Na,Cs)NO_3$ 3 : 1 $t_{max} = 560$	0.160	470.5
	.225	507
	.300	533
	.400	552
	.500	559
	.600	560
	.703	559
	.800	543
	.850	525
	.900	492
	.925	470
$(Na,Cs)NO_3$ 1 : 1	0.200	459
	.300	494
$t_{max} = 527$	.400	517
	.500	522
	.600	526.5
	.700	527
	.800	517
	.850	505
	.900	474
$(Na,Cs)NO_3$ 1 : 3 $t_{max} = 485$	0.275	441
	.325	454
	.440	472
	.546	480
	.650	485
	.750	484
	.825	473
	.875	455
$(K,Rb)NO_3$ 1 : 1 $t_{max} = 519.5$	0.200	457
	.280	487.5
	.350	504
	.450	517
	.550	519.5
	.650	519
	.750	514
	.826	495
	.890	464
$(K,Cs)NO_3$ 1 : 1 $t_{max} = 488$	0.300	460.5
	.400	477
	.500	485
	.601	488
	.700	488
	.800	481
	.890	446
$(Rb,Cs)NO_3$ 1 : 1 $t_{max} = 460$	0.360	442
	.450	457
	.549	459
	.650	460
	.750	458
	.825	444

Table 1.

Systems TlBr +		$-\Delta t$(°C)
(Na, K)NO_3	1:1	8.5
(Na, Rb)NO_3	1:1	13
(Na, Cs)NO_3	1:1	20
(K, Rb)NO_3	1:1	1
(K, Cs)NO_3	1:1	3.5
(Rb, Cs)NO_3	1:1	0 (estimated)

Table 2.

nitrate), a satisfactorily linear dependence is found (Fig. 6) [5].

The correctness of the above considerations is proved by the agreement which is obtained in predicting the t_{max} for the $TlBr + LiNO_3$ system by using the data concerning either the $TlBr + NaNO_3$ and $TlBr + (Li, Na)NO_3$ (1:1), or the $TlBr + KNO_3$ and $TlBr + (Li, K)NO_3$ (1:1) mixtures. From Fig. 6 are obtained

$$\Delta t = -11\ ^\circ C$$

for the $TlBr + (Li, Na)NO_3$ (1:1) system, and

$$\Delta t = -37\ ^\circ C$$

[5] As regards cationic radii and the radius of ion NO_3^-, we have referred respectively to Note I [1] and to the paper by KLEPPA and HERSH [2].

for the TlBr + (Li, K)NO_3 (1:1) system. It follows that for the TlBr + $LiNO_3$ system t_{max} is evaluated as 640 °C in the first case, and as 643 °C in the second: the mean value is reported in Fig. 5.

b) Mixtures of two thallous halides with $NaNO_3$

The experimental data regarding LL equilibria in the title systems are summarized in Table 3. In Fig. 7 SL and LL curves for a number of systems Tl(Cl, Br) + $NaNO_3$ are reported. The TlCl + $NaNO_3$ system [1] does not present any LL equilibria, but an SL curve with an "S"-shaped branch. Progressively increasing TlBr quantities produce the "emersion" of a miscibility gap, the extent of which gradually increases and becomes the largest in the TlBr + $NaNO_3$ system [1]. In the latter the demixing curve shows no inflection and the primary crystallization from one of the two liquid phases takes place at a constant temperature. On the contrary, in the systems containing both Tl-halides the LL curves show an inflection at $0.50 < x_{TlX} < 0.60$ and the temperatures of primary crystallization in each system are increasing as x_{NaNO_3} increases: these temperatures, however, cannot be measured with a great accuracy, and so in Fig. 7 the curves limiting the inferior parts of the gaps are dashed.

System $NaNO_3$ +	x_{TlX}	t (°C)
Tl(Cl, Br) 5.25 : 1 $t_{max} = 410$	0.340	398
	.390	405
	.425	404.5
	.475	412
	.535	405.5
	.585	399
	.650	396
	.700	388.5
Tl(Cl, Br) 3 : 1 $t_{max} = 431$	0.230	407
	.300	422
	.380	430
	.450	431
	.500	427
	.550	424
	.625	422
	.722	412
	.800	396.5
Tl(Cl, Br) 1 : 1 $t_{max} = 497$	0.175	443
	.230	465
	.310	488
	.400	496
	.450	497
	.550	491
	.650	485
	.750	472
	.825	449
	.850	439
Tl(Cl, Br) 1 : 3 $t_{max} = 546$	0.140	464
	.227	507
	.300	531
	.370	543
	.450	546
	.525	543
	.600	542
	.700	534
	.800	514.5
	.875	478
	.910	451

System $NaNO_3$ +	x_{TlX}	t (°C)
Tl(Cl, J) 3 : 1 $t_{max} = 612$	0.065	492
	.100	552
	.200	602
	.300	611.5
	.400	601
	.475	586
	.550	562
	.650	531
	.750	501
	.850	449
	.900	406.5
Tl(Cl, J) 5.25 : 1 $t_{max} = 547$	0.060	467
	.089	505
	.147	535.5
	.250	546
	.350	545
	.450	525
	.550	495
	.650	466
	.750	441
	.824	413
Tl(Cl, J) 9 : 1 $t_{max} = 492$	0.100	439
	.115	452.5
	.150	468.5
	.225	492
	.300	490
	.400	477
	.520	448
	.600	428.5
	.690	412
	.750	400
Tl(Cl, J) 19 : 1 $t_{max} = 424$	0.100	386
	.150	405
	.200	418.5
	.300	421
	.400	411
	.475	401
	.550	390.5
	.650	379
	.725	378

Table 3.

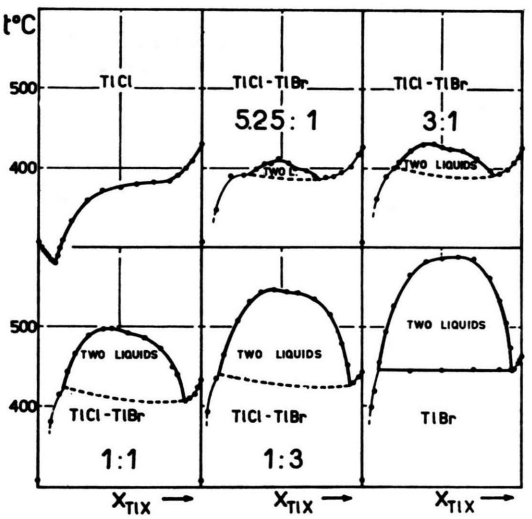


Fig. 7. Systems: Tl(Cl, Br) + $NaNO_3$.

In the Tl(Cl, J) + $NaNO_3$ systems (see Fig. 8) the miscibility gaps, at the same concentrations of the second halide, are much larger than in the Tl(Cl, Br) + $NaNO_3$ systems. Besides, we have to point out that in the systems containing Tl(Cl, J) the SL curves may also present a minimum on the TlX richer side.

In a plot of the quantities T^3_{max} for the systems which contain Tl(Cl, Br) *vs* x'_{TlCl} (molecular fraction of TlCl in the mixtures of the two Tl-halides), by extrapolating to $x'_{TlCl} = 1$, a value $t_{max} = 357$ °C can be calculated for the "submerged" gap in the TlCl + $NaNO_3$ mixture. In a similar way, for the systems containing Tl(Cl, J), a value of t_{max} can be calculated, which is in good agreement with the previous one (see Fig. 9).

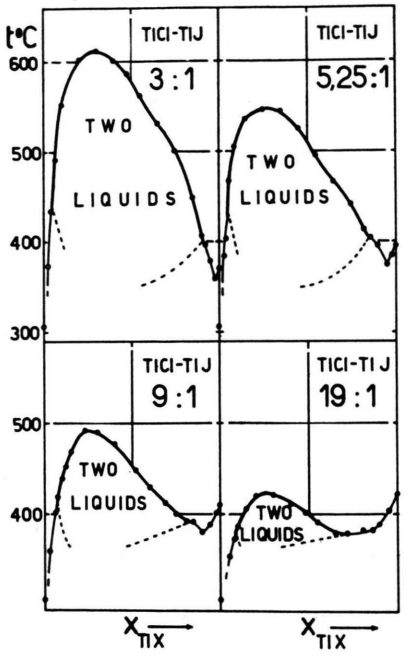


Fig. 8. Systems: $Tl(Cl, J) + NaNO_3$.

For the same system $TlCl + NaNO_3$ it is reasonable to suppose that the "submerged" gap has its maximum at $x_{TlCl} = 0.6 \pm 0.1$, that is within an interval where the SL equilibrium temperatures vary from 376° to 382 °C. Therefore, the miscibility gap in this system appears to be more deeply "submerged" than for $TlBr + CsNO_3$. This is in conformity with the fact that, in the latter system, the "S"-shaped branch of the SL curve shows an isothermal portion, while this does not appear for $TlCl + NaNO_3$.

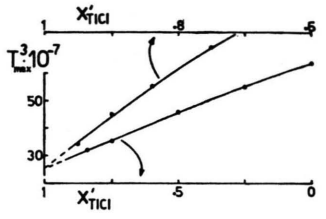


Fig. 9. T^3_{max} as a function of x'_{TlCl} for the systems: $Tl(Cl, Br) + NaNO_3$ (lower scale), and $Tl(Cl, J) + NaNO_3$ (upper scale).

Acknowledgment

The authors wish to thank Dr. Giorgio Flor for having carried out the measurements on the $Tl(Cl, J) + NaNO_3$ systems.