Miscibility Gaps in Fused Salts. Note I.
Binary Systems Tl (Cl, Br, J) + (Na, K, Rb, Cs) NO_3 *

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Binary molten systems of TlCl, TlBr and TlJ mixed with alkali nitrates have been studied. The existence of miscibility gaps in the liquid state for the seven different systems $NaNO_3+Tl(Br, J)$, $KNO_3+Tl(Br, J)$, $RbNO_3+Tl(Br, J)$ and $CsNO_3+TlJ$ has been pointed out. The ability to demixing according to some characteristics of the couples of cations in each system has been discussed.

Till now the known cases of molten salt systems splitting into two liquid phases are not numerous: sometimes, however, it is possible to find groups of systems constituted by salts possessing similar characteristics, which show a more or less extensive immiscibility in the liquid state.

In particular, Rostkovskii [1] as early as 1929 had found a miscibility gap in the $TlBr+KNO_3$ system, the study of which, about 25 years later, was resumed by Semenchenko et al. [2].

It was our purpose to investigate the occurrence and extent of immiscibility in systems of type $TlX+MeNO_3$, where X is a halogen and Me an alkali metal. In the present paper we report about the twelve binary systems of thallous chloride, bromide and iodide with sodium, potassium, rubidium and cesium nitrate.

Apparatus and Materials

The apparatus (Fig. 1) consists of a furnace, A, (the temperature of which could be measured by means of a chromel-alumel thermocouple, and controlled by means of a Leeds & Northrup 3-action CAT control unit), with quartz windows, B, for direct inspection of the Pyrex test-vessel, C. A second chromel-alumel thermocouple (calibrated by comparison with a NBS certified Pt—Pt, Rh thermocouple) was introduced into the tubing, D, and connected with a Leeds & Northrup potentiometer Type K-3. The test-vessel, after filling, was sealed at E and hung at a Chemap Vibro-Mixer, F, allowing a strong shaking of the melt.

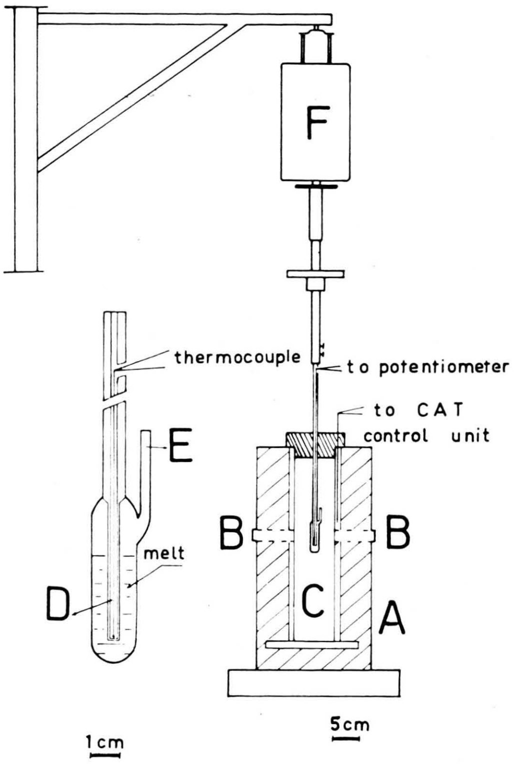

Fig. 1. Apparatus.

Each sample was heated till it gave a homogeneous melt and then cooled very slowly, in order to identify demixing or crystallizing, both instrumentally and visually, as well as possible: the measurements were repeated at least twice on each sample.

The materials used were: C. Erba RP $NaNO_3$ and KNO_3; 99.9% pure L. Light & Co. $RbNO_3$ and $CsNO_3$; TlCl, TlBr and TlJ obtained through precipitation from an aqueous solution of C. Erba RP $TlNO_3$ (l. c. [3]). All the salts used were carefully dried before use.

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[1] A. P. Rostkovskii, J. Russ. Phys. Chem. Soc. **61**, 89 [1929].

[2] V. K. Semenchenko and T. I. Shashkina, Zh. Fiz. Khim. **28**, 735 [1954].

[3] Gmelins Handbuch der anorganischen Chemie, 8. Ed. 1940.

Thallous halides at the experimental temperatures possess considerable vapour pressure. The use of a sealed test-vessel and vigorous shaking of the melt allowed to overcome this inconvenience.

Results and Discussion

The results are shown in Fig. 2 – 4, where the circles represent the experimental points. The curves, which limit the fields of existence of the different phases, could sometimes be drawn without any difficulty (continuous curves), and sometimes they could not (dashed curves). Moreover, in certain regions of the diagrams it was not possible to take reliable measurements owing to different reasons, e. g., thermal decomposition, formation of solids not perfectly crystallized, etc. The detailed study of the solid phases will be the object of a later research.

The temperatures at which demixing takes place (by cooling and shaking), are reported in Tab. 1 for

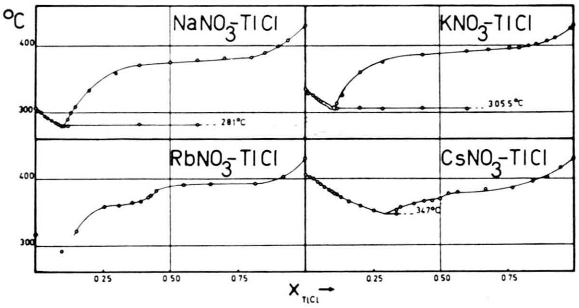

Fig. 2. Systems $TlCl + (Na, K, Rb, Cs) NO_3$.

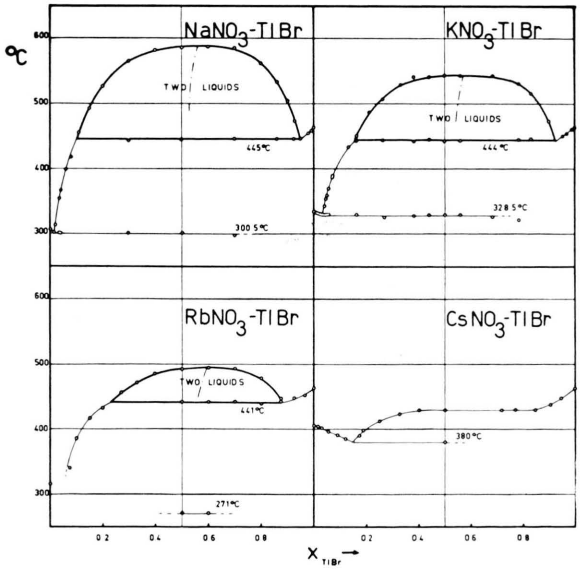

Fig. 3. Systems $TlBr + (Na, K, Rb, Cs) NO_3$.

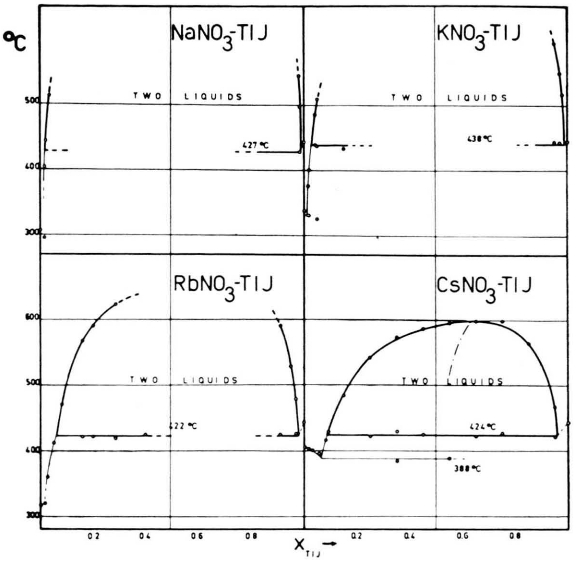

Fig. 4. Systems $TlJ + (Na, K, Rb, Cs) NO_3$.

System	x_{TlBr}	t (°C)
$TlBr + NaNO_3$	0,109	455
	0,150	492,$_5$
	0,200	526
	0,300	565
	0,400	582
	0,502	586
	0,600	587,$_5$
	0,700	585,$_5$
	0,802	561,$_5$
	0,860	533
	0,900	504,$_5$
	0,926	473
$TlBr + KNO_3$	0,161	451
	0,209	486
	0,262	506,$_5$
	0,330	528
	0,380	541
	0,439	541
	0,500	543,$_5$
	0,562	542
	0,684	542
	0,784	530
	0,830	517
	0,899	473
$TlBr + RbNO_3$	0,277	457
	0,330	471
	0,400	485
	0,500	492
	0,600	494,$_5$
	0,700	493
	0,801	478
	0,875	447
$TlBr + CsNO_3$	—	—

System	x_{TlJ}	t (°C)
$TlJ + NaNO_3$	0,019	444
	0,035	513
	...	...
	0,980	543,$_5$
	0,985	496
$TlJ + KNO_3$	0,043	485
	0,051	509
	...	...
	0,951	594
	0,971	548
	0,978	515
$TlJ + RbNO_3$	0,079	471
	0,158	567
	0,200	590
	0,287	624
	...	...
	0,911	590
	0,950	528
	0,968	478
$TlJ + CsNO_3$	0,091	429
	0,150	484
	0,249	542
	0,350	573
	0,451	586
	0,550	595
	0,650	598
	0,750	598
	0,851	564
	0,949	467

Table 1.

system	monotectic temperature t_m (°C)	upper consolute temperature t_c (°C)	$t_c - t_m$	at t_m °C the gap extends between: $x_{TlX,1}$	and $x_{TlX,2}$	$(x_{TlX,2}) - (x_{TlX,1})$	abscissa corresponding to t_c °C
$TlBr + NaNO_3$	445	588	143	0.10	0.95	0.85	0.56
$TlBr + KNO_3$	444	543	99	$.15_5$	$.92_5$	.77	.57
$TlBr + RbNO_3$	441	494	53	.23	.88	.65	.59
$TlBr + CsNO_3$	—	—	0	—	—	0	—
$TlJ + NaNO_3$	(427)	—	—	$.01_5$	.99	$.97_5$	—
$TlJ + KNO_3$	(438)	—	—	.03	$.98_5$	$.95_5$	—
$TlJ + RbNO_3$	422	—	—	.06	.98	.92	—
$TlJ + CsNO_3$	424	599	175	$.08_5$	.96	$.87_5$	.63

Table 2. The monotectic temperatures reported in the table are mean values of those measured on samples of different composition for a certain system. The maximum abscissa was singled out by applying the CAILLETET–MATHIAS's rule.

the systems showing a miscibility gap, together with the corresponding molecular fractions x.

In Tab. 2 further information about the fields of coexistence of two liquid layers are summarized.

None of the four systems containing thallous chloride shows a miscibility gap. However, the branches rich in TlCl of the liquidus curves are always "S" shaped, which proves a "tendency to split in the liquid phase" [4].

Among the systems $TlBr + (Na, K, Rb, Cs) NO_3$ only $TlBr + CsNO_3$ shows an "S" shaped branch, while the others demix. The tendency to split in the liquid phase is more pronounced in the $TlBr + CsNO_3$ system, than in those containing TlCl, inasmuch as the "S" shaped branch of the former shows a wide, almost isothermal interval.

On the contrary, when thallous bromide is mixed with $RbNO_3$, a miscibility gap is formed, having a basis about .65 x units wide, and a maximum about 53 °C above the monotectic temperature (441 °C). If rubidium nitrate is successively replaced with potassium and sodium nitrate, both the basis and maximum height of the gap progressively increase (see Tab. 2). Qualitative experiences carried out on the $TlBr + LiNO_3$ system seem to show that in this case the miscibility gap is particulary wide, but unfortunately this gap could not be investigated even in part, owing to the thermal instability of lithium nitrate at the demixing temperatures.

As pointed out in the first section, ROSTKOVSKII [1] had already studied the miscibility gap in $TlBr + KNO_3$. He had found a monotectic temperature 435 °C and an upper consolute temperature 535 °C, both being by 8 – 9° lower than those reported in Tab. 2. According to the measurements of this author, at the monotectic temperature the gap extends from $x_{TlBr} = .14$ to .925, in full agreement with our data. Also the eutectic line found by ROSTKOVSKII at 330 °C satisfactorily agrees with our finding ($328._5$ °C).

The progressive variation of the above mentioned demixing phenomena may be reasonably related to the differences between the radii, r, of the cations present, or also with the differences between the polarizing powers, P, of the same cations [4], as shown in Tab. 3. It may be inferred that the ability to demix in the $TlBr + MeNO_3$ systems progressively decreases with increasing ionic radius or with decreasing polarizing power of the alkali metal.

Me in the systems $TlBr + MeNO_3$	$(r_{Tl^+}) - (r_{Me^+})$ in Å	$(P_{Tl^+}) - (P_{Me^+})$	ability of demixing
lithium	+.89	−1.55	very strong (presum.)
sodium	+.54	− .55	strong
potassium	+.16	− .30	mean
rubidium	+.01	− .22	weak
cesium	−.20	− .14	very weak

Table 3. The ionic radii, r, and the polarizing powers, P, of the different ions are those reported by WAIT et al. [5].

Now, let us consider the systems including TlJ (see Fig. 3): though only the gap shown by $TlJ + CsNO_3$ could be thoroughly measured, it seems quite possible to draw a picture similar to that illustrated in Tab. 3, inasmuch as the area occupied by the miscibility gap is evidently extending by passing from cesium to rubidium, potassium and sodium nitrate.

In conclusion, it may be observed that, in the systems of type $TlX + MeNO_3$, the ability of demixing is increasing when Cs, Rb, K, Na, Li are successively taken as Me, and when, Me being the same, Cl, Br, J are taken as X.

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[4] Molten Salt Chemistry, Ed. M. BLANDER, Interscience Publ. Inc., New York 1964, p. 326–339.

[5] S. C. WAIT and G. J. JANZ, Quart. Rev., London **17**, 225 [1963].