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$AgNO_3$-$LiNO_3$-$RbNO_3$ Phase Diagram

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The ternary system of silver, lithium, and rubidium nitrates has been studied. Five vertical sections were established: $AgNO_3$-$Li_{0.5}Rb_{0.5}NO_3$; $Li_{0.5}Rb_{0.5}NO_3$-$Ag_{0.5}Rb_{0.5}NO_3$; 20 mol% $AgNO_3$; 80 mol% $AgNO_3$; and the section 5 mol% $LiNO_3$. Ten invariant points were found. A schematic representation of ternary equilibria is given. The three binary systems are also reported.

1. Introduction

The molten salt systems are used in the storage and transfer of thermal energy produced from solar radiation. The determination of phase diagrams for such salt systems is important for a better exploitation of solar energy. The present article deals with the ternary system $AgNO_3$-$LiNO_3$-$RbNO_3$. This system has been previously studied by Protsenko and Kiparenko,[1] who found four invariant points, three of them being eutectic points and the fourth a quasi-peritectic point.

2. Experimental

Differential thermal analysis and differential scanning calorimetry were used to investigate the phase diagrams of binary and ternary systems. X-ray diffraction was used for the identification of phases.

3. Results

3.1 Binary Systems

3.1.1 $AgNO_3$-$LiNO_3$. The present investigation found this binary system to be a simple eutectic system with the eutectic liquid point at 25 mol% $LiNO_3$ and 445 K; there is also a polymorphic transition in $AgNO_3$ at 434 K. The solubility of each component in the other seems to be nil or negligible[2] (Fig. 1). These results agree with the data of Sinistri and Franzosini,[3] Lobbia and Cingolani,[4] Vallet,[5] and Palkin.[6]

3.1.2 $AgNO_3$-$RbNO_3$. The present investigation found this binary system to exhibit a congruently melting compound $Ag_{0.5}Rb_{0.5}NO_3$ (melting point = 411 K) and an incongruently melting compound $Ag_{0.33}Rb_{0.67}NO_3$ with two polymorphic forms. The latter compound appears at 404 K and decomposes at 414 K. The $AgNO_3$-$RbNO_3$ system also contains three metatectic reactions at 437, 495, and 555 K, which are the result of the phase transitions of $RbNO_3$, and a peritectic reaction, which is the result of the phase transition of $AgNO_3$ at 437 K, beside two eutectic points at 36 mol% $RbNO_3$ (at 401 K) and 60 mol% $RbNO_3$ (at 407 K). A very narrow domain of miscibility exists in the region of $RbNO_3$, which becomes large in the $AgNO_3$ region[7] (Fig. 2). These results complete those of Palkin[6] and Protsenko and Kiparenko.[1] These earlier investigations mentioned two eutectics, the congruently melting compound and the incongruently melting compound, with the latter appearing at room temperature and not having a high-temperature polymorph. Neither study gives any indication of the formation of solid solutions.

3.1.3 $LiNO_3$-$RbNO_3$. The components of this system give rise to an intermediate chemical compound,

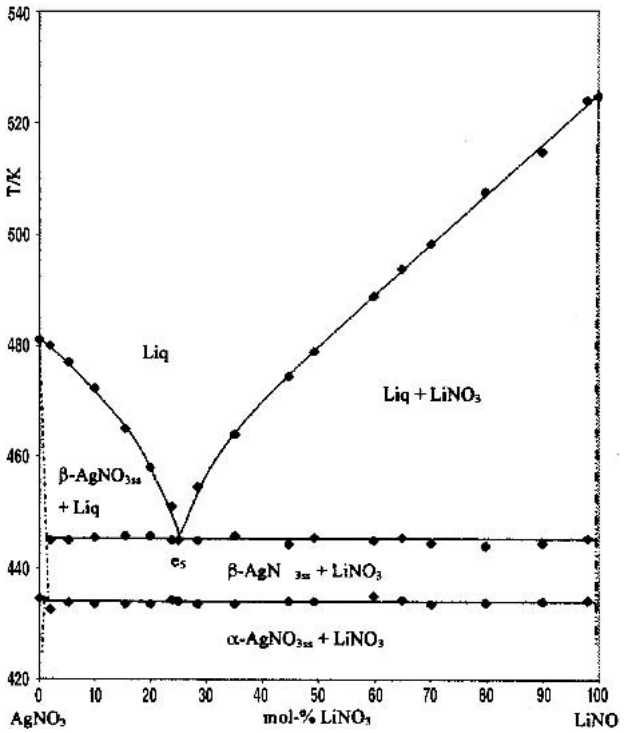

Fig. 1 Phase diagram of the binary system $AgNO_3$-$LiNO_3$

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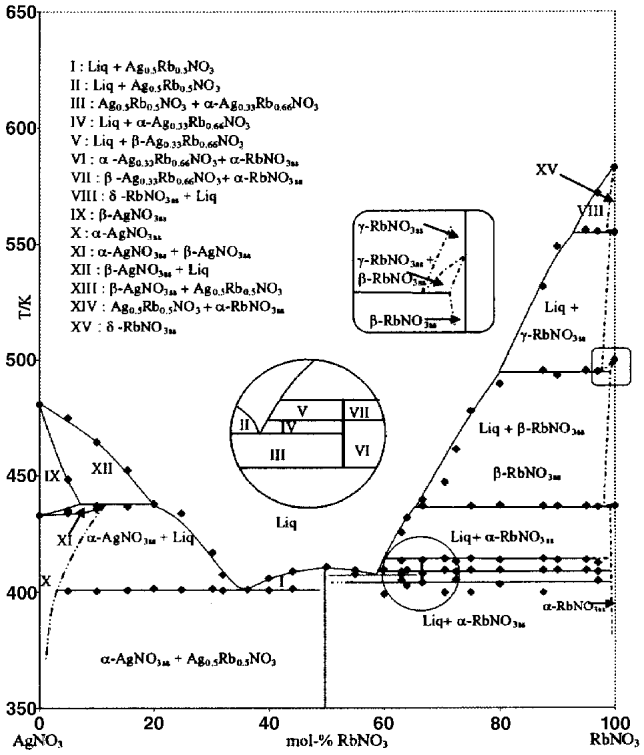


Fig. 2 Phase diagram of the binary system $RbNO_3$-$LiNO_3$

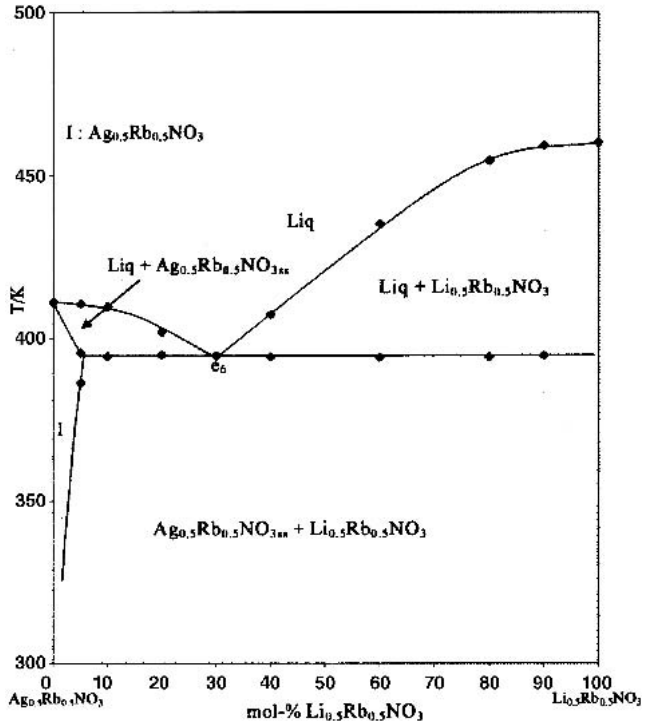


Fig. 4 Section $Ag_{0.5}Rb_{0.5}No_3$-$Li_{0.5}Rb_{0.5}NO_3$

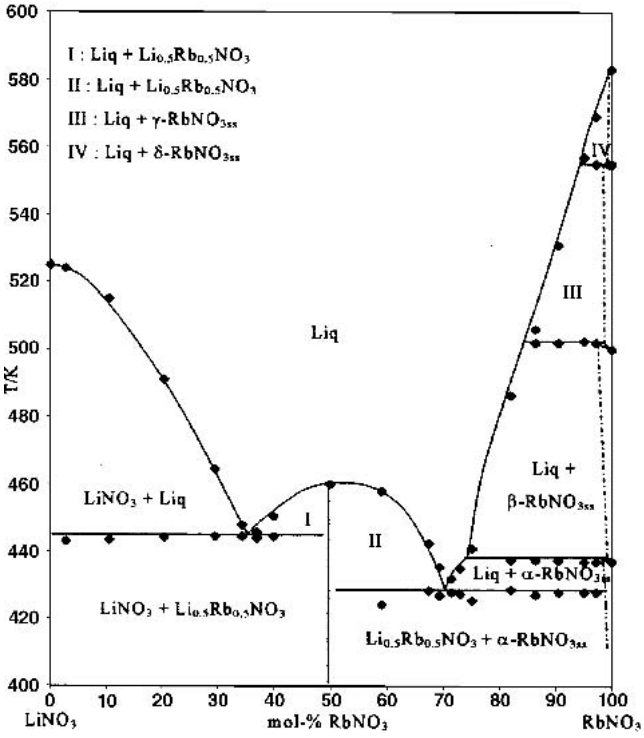


Fig. 3 Phase diagram of the binary system $LiNO_3$-$RbNO_3$

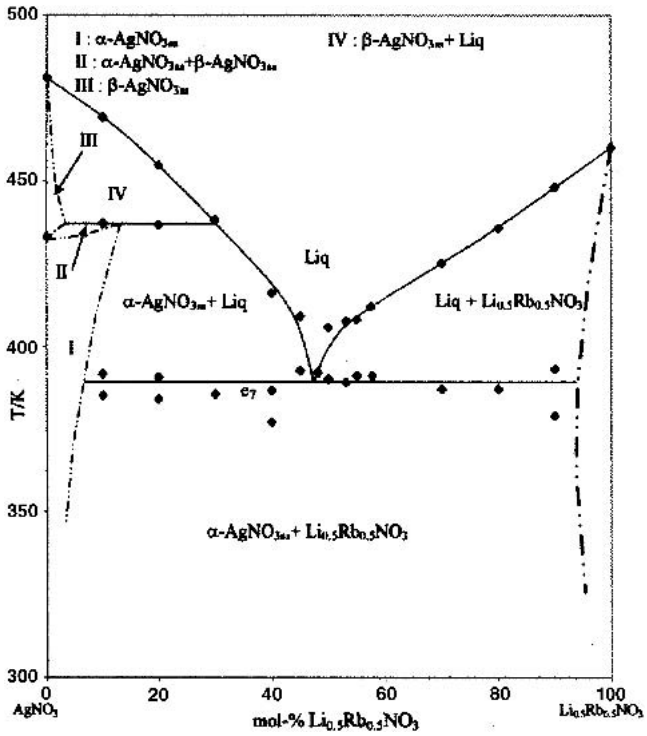


Fig. 5 Section $AgNo_3$-$Li_{0.5}Rb_{0.5}NO_3$

$Li_{0.5}Rb_{0.5}NO_3$, which melts without decomposition at 460 K. The system presents two eutectics at 36 mol% $RbNO_3$ (at 444 K) and 71 mol% $RbNO_3$ (at 427 K). The compound exhibits three peritectic reactions that are induced by the three phase transitions of $RbNO_3$. The corresponding invariants are at 437, 502, and 555 K. Finally, a slight solid

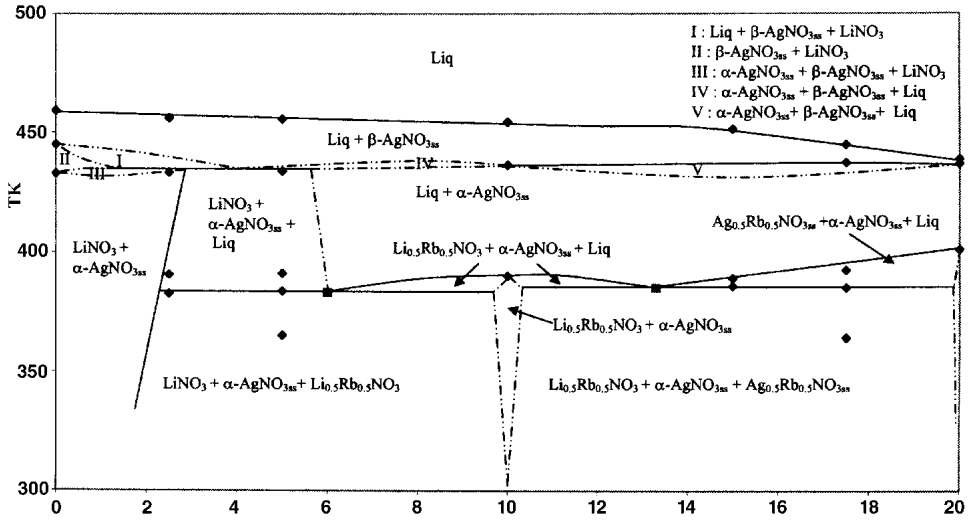


Fig. 6 The 80 mol% $AgNO_3$ section

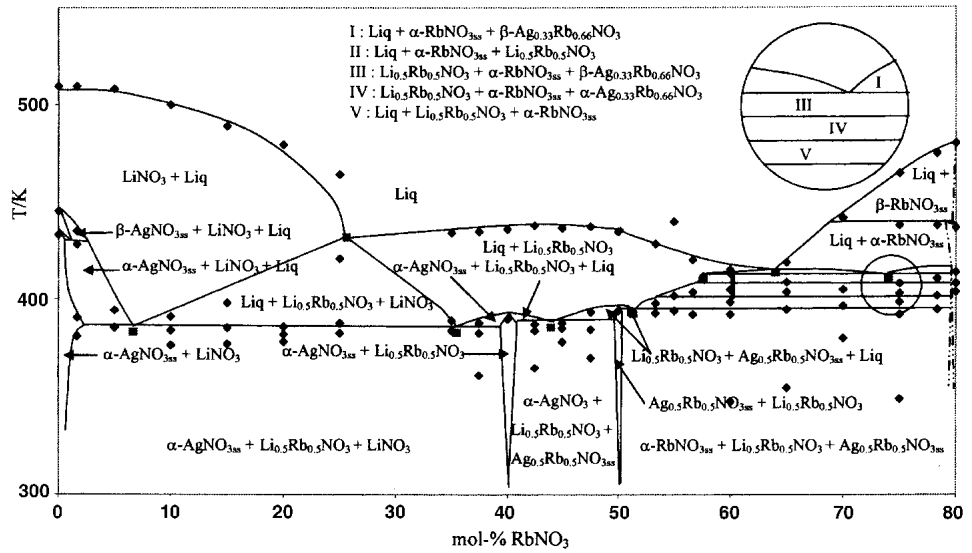


Fig. 7 The 20 mol% $AgNO_3$ section

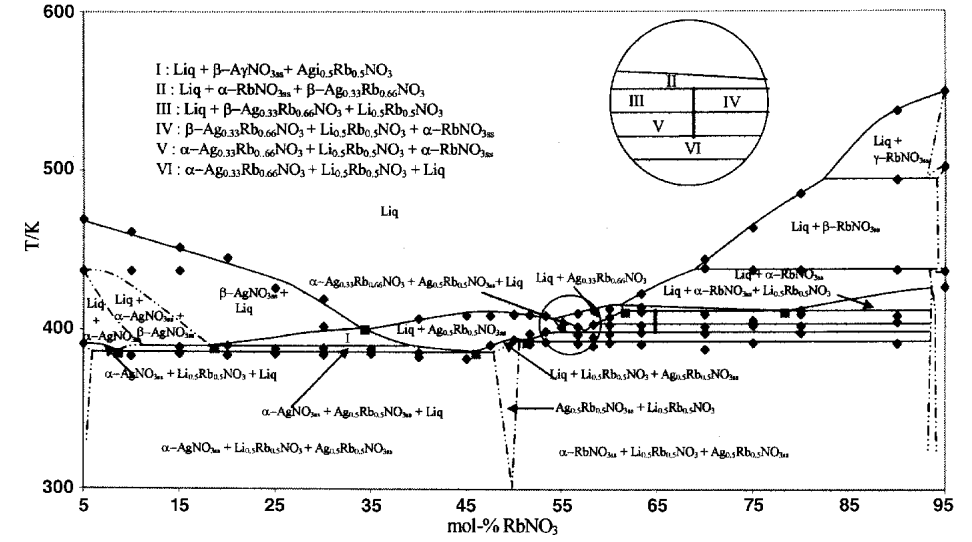
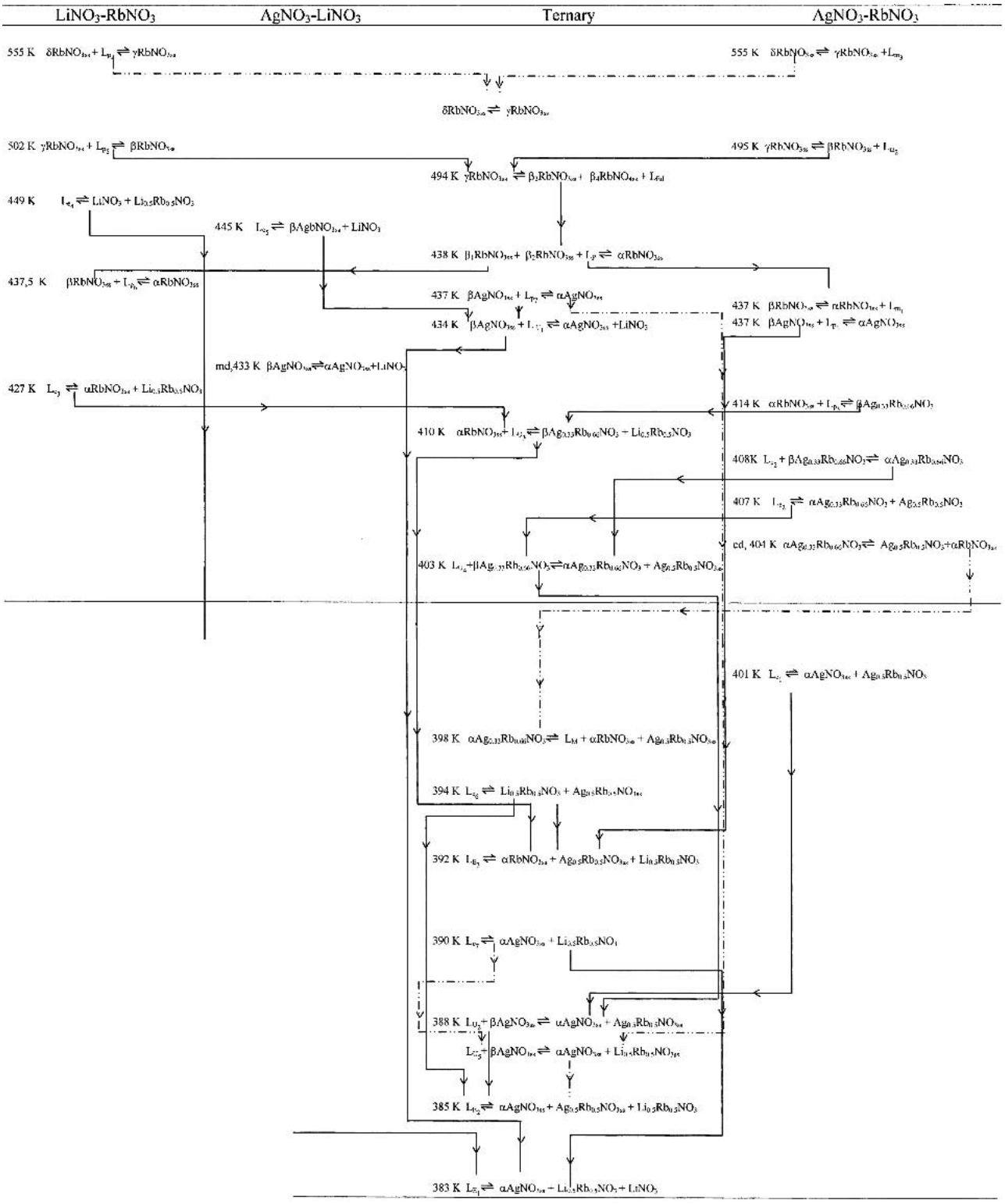


Fig. 8 The 5 mol% $LiNO_3$ section

Table 1 Reactions in the ternary system $AgNO_3$-$LiNO_3$-$RbNO_3$



solution exists in the $RbNO_3$ region (Fig. 3). According to Puschin and Radonicic,[8] and Diogenov and Sarapulova,[9] the system $LiNO_3$-$RbNO_3$ forms the compound $Li_{0.5}Rb_{0.5}NO_3$ and two eutectics. The temperatures and the compositions of the invariant points given in the literature differ from our data.

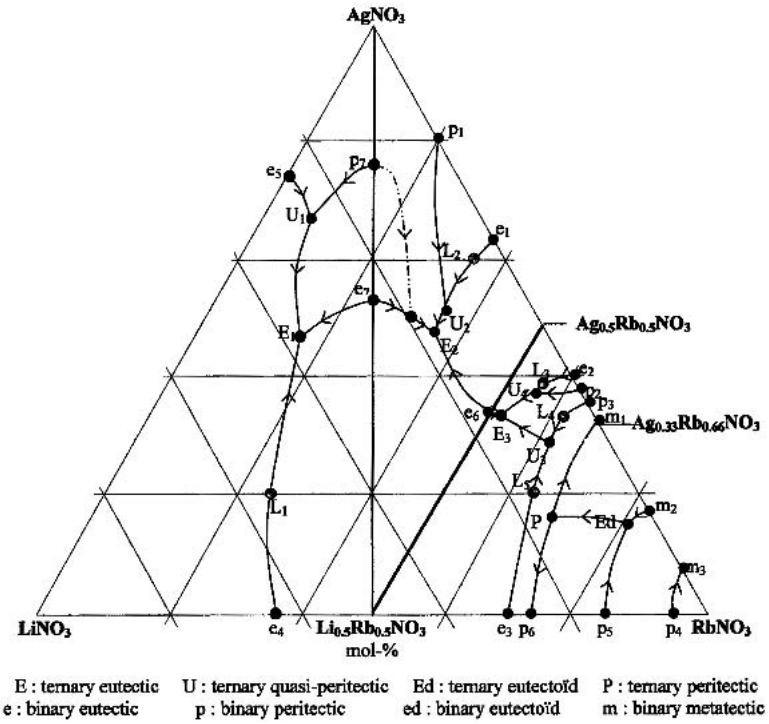


Fig. 9 Projection on the concentration triangle of the ternary system $AgNO_3$-$LiNO_3$-$RbNO_3$

Table 2 Composition of E_1, E_2, E_3, and U_3 points

Variables	E_1	E_2	E_3	U_3
T,K	383	385	392	410
mol%($LiNO_3$)	37.7	17	14	9
mol%($AgNO_3$)	47	47	34	29

3.2 Triangulation

After the optimization of the data of the binary systems with the logicial THERMOCALC, Feutelais[10] calculated the sections $Ag_{0.25}Li_{0.75}NO_3$-$RbNO_3$, $Ag_{0.5}Li_{0.5}NO_3$-$RbNO_3$, and $Ag_{0.75}Li_{0.25}NO_3$-$RbNO_3$. The compositions of the vertical lines show that the isopleths $AgNO_3$-$Li_{0.5}Rb_{0.5}NO_3$ and $Li_{0.5}Rb_{0.5}NO_3$-$Ag_{0.5}Rb_{0.5}NO_3$ are quasi-binary systems.

We have confirmed experimentally these results (Fig. 4, 5). The section $Li_{0.5}Rb_{0.5}NO_3$-$Ag_{0.5}Rb_{0.5}NO_3$ shows a quasi-binary eutectic at 394 K and a gap of miscibility in the $Ag_{0.5}Rb_{0.5}NO_3$ region. The phase diagram of the section $AgNO_3$-$Li_{0.5}Rb_{0.5}NO_3$ exhibits a quasi-binary eutectic at 390 K and a plateau induced by the phase transition of $AgNO_3$ at 437 K. A solid solution exists in the $AgNO_3$ region.

Consequently, three subtriangles ought to be expected in the system $AgNO_3$-$LiNO_3$-$RbNO_3$: $AgNO_3$-$LiNO_3$-$Li_{0.5}Rb_{0.5}NO_3$; $Li_{0.5}Rb_{0.5}NO_3$-$Ag_{0.5}Rb_{0.5}NO_3$-$AgNO_3$; and $Ag_{0.5}Rb_{0.5}NO_3$-$Li_{0.5}Rb_{0.5}NO_3$-$RbNO_3$. X-ray investigations confirmed this triangulation.

3.3 Invariant Points

Three sections were selected to seek invariant points in the $AgNO_3$-$LiNO_3$-$RbNO_3$ system. We considered the isopleths 20 and 80 mol% $AgNO_3$ and the section 5 mol% $LiNO_3$. The plots of these sections are shown in Fig. 6, 7, and 8. The temperatures of the ternary invariant reactions are 494, 438, 434, 411, 403, 398, 392, 388, 385, and 383 K. A schematic representation of the ternary equilibria is given in Table 1.

Figure 9 gives a projection of the ternary system $AgNO_3$-$LiNO_3$-$RbNO_3$ on the concentration triangle. So, the system contains three ternary eutectic points [E_1 (at 383 K), E_2 (at 385 K), and E_3 (at 392 K)], four ternary quasi-peritectic points [U_1 (at 434 K), U_2 (at 388 K), U_3 (at 410 K), U_4 (at 403 K)], a ternary eutectoid point [Ed (at 494 K)], and a ternary peritectic point [P (at 438 K)].

The compositions of the eutectic points and the quasi-peritectic point U_3 are given in Table 2.

The $AgNO_3$-$LiNO_3$-$RbNO_3$ system should show another invariant, U_5, on the subtriangle $AgNO_3$-$Li_{0.5}Rb_{0.5}NO_3$-$Ag_{0.5}Rb_{0.5}NO_3$, but it has not been detected. The reaction corresponding to this invariant is a quasi-peritectic one. The invariant point U_5 should be at a temperature between those of E_2 and E_7.

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