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# ELECTRICAL CONDUCTIVITY, ION MOBILITIES AND TRACER-DIFFUSION COEFFICIENTS IN MOLTEN NITRATES BINARY MIXTURES

by

S. FORCHERI, V. WAGNER and E. BERRA

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Electrical conductivity, ion mobilities and cation tracer diffusion coefficients have been measured in molten nitrate binary mixtures $(Na-Tl)NO_3$, $(Na-Rb)NO_3$ and $(Tl-Rb)NO_3$. In some cases density and viscosity measurements were as well carried out.
The following characteristic points have been found to be valid for the nitrate binary mixtures :

— The equivalent conductivity excesses depend on the difference in cationic size. The equivalent conductivity of systems the cations of which have the same radius, or the components of which have about the same molar volumes, depends linearly on the composition.
— Fluidity presents small positive deviations from linearity in the systems with cations of different sizes.
— The internal ion mobility of the smaller cation varies rapidly with composition in the region near by the component with the smaller cation. The mobility of the larger cation is rather insensible to the change in composition. The mobility of both cations is nearly equal at the side of the larger cation. No significant crosses of mobility seem to exist.
— The cation diffusion coefficients, if corrected for the variation of the fluidity, vary nearly linearly with composition. The diffusion of traces in pure salts is enhanced (hindered) if the diffusing particle is larger (smaller) than the proper cation of the melt.

All these experimental evidences point out that the polarization of the common anion in these mixtures is the main factor determining the transport behaviour.

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# SUMMARY

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# KEYWORDS

## Electrical Conductivity, Ion Mobilities and Tracer-Diffusion Coefficients in Molten Nitrates Binary Mixtures. (*)

Equilibrium properties of molten binary mixtures with a common anion have been successfully correlated to the anion polarization effect [1] [2] [3].

To obtain detailed information on the factors affecting transport properties, conductivity, electrical and diffusional ion mobility must be determined.

This paper presents some results relative to the nitrate binary mixtures.

## EXPERIMENTAL METHODS AND PRELIMINARY RESULTS

The experimental set up and methods will not be described here. Only few information on the method for determining electrical and diffusional mobilities is given.

These quantities have been measured by means of a zone radio-tracer electrophoresis and diffusion technique on thin layers of ceramic oxides [4] [5] [6]. The thin layers, which adhere to sintered aluminia or zirconia strips, are of two different types :

- powder and then the preparation is performed according the usual thin layers chromatographic techniques, or

- fritted porous material (aluminia, zirconia or magnesia) and then the layer is obtained with a flame spraying technique by exposing the sintered strip to a flux of molten ceramic particles.

The impregnation with the salt of these thin layers is achieved by capillary action by connecting the strip to two reservoirs containing the melt, via quartz fiber or small ceramic strip bridges.

The mobility of both cations of the mixture are determined simultaneously at each composition by measuring the velocity of displacement of several-labelled zones when a potential drop is applied to the ends of the strip.

The ionic mobility of a cation is proportional to its zone mobility $u_z$:

$$u_w = K u_z \quad (K > 1)$$

where $u_z$ is the rate of the displacement of the labelled zone in unit apparent electrical field, and the factor K accounts for the obstruction

of the particles of the porous support to the ionic migration.

If this correction factor is defined as the inverse of the obstruction factor defined by Crawford and Edward [7] for paper electrophoresis, $i_d$ est, as the ratio of the calculated conductivity of the melt without the non conducting particles, and the measured conductivity of the strip :

$$K = \frac{c}{c_p} = \frac{R_p \, X. p}{d} \tag{1}$$

where $R_p$ is the resistance of the strip per unit length, X = the specific conductivity of the melt, d the density, and p the salt weight per unit length, then the following formula for $u_w$ can be used :

$$u_w = \frac{X}{d} \frac{p.1}{q} \tag{2}$$

where 1 = measured displacement of the labelled zone, q = ionic charge passed through the strip.

According this formula $u_w$ can be determined without any knowledge of the K factor. On the contrary to measure diffusion coefficients from the Gaussian activity distribution on the strip, these parameters must be determined by means of a measurement of $R_p$. The formula used is :

$$D = - \frac{1}{2.3} \frac{K}{4 \, St} \tag{3}$$

where S is the slope of the plots log activity vs the squared distance from the Gaussian centre and t is the diffusion time.

In Fig. 1 the assembly used in the diffusion experiments is shown. The strip is in reverse position in respect of the usual one for measuring $R_p$ with the knife-type electrodes placed in contact with the porous layer.

Fig. 2 presents the diffusion profiles of Tl-204 in $TlNO_3$ determined at two different times . According to the diffusion equation, the slopes of the straight lines reported in the lower part of the figure are inversely proportional to the respective diffusion times.

To make sure that there are no selective interactions between the porous support and the various salts, a series of determinations of the obstructive factor was carried out by measuring the conductivity of porous thin layers impregnated with various molten nitrates.

In Fig. 3 $K = \frac{1}{\beta}$ ( $\beta$ = obstruction factor) is plotted vs the section of the electrolyte for a number of aluminia porous fritted layers impregnated with various molten nitrates: in all the cases the K factor is independent from the salt on the support. In Fig. 4 the same factor is plotted vs the fraction of the bed filled with the salt (the porosity

of the bed), for a series of aluminia powder strips. The solid line represents the function :

$$K = ( 1 - 0.61 \ \theta ) \ ( 1 - \theta ) \ \frac{(1 + \theta)}{(1 - \theta \ 2/3)} \qquad (4)$$

in which $\theta$ is the fraction of the bed filled with the non-conducting particles.

This equation, derived by Boyack and Giddings accounts for the obstruction in zone electrophoresis with any simple grain geometry. It has been obtained starting from the consideration that the obstruction to the migration in systems of this type is a consequence of two factors : the tortuosity of the channels of the support and of the variation of the cross section of the electrolyte along the migration patways ($i_d$ est, it involves a tortuosity and a constriction factor).

To make sure that the ionic mobility values are not influenced by selective interactions between unlike charged ions and the support, an internal reference frame is chosen by referring the cationic mobilities to the $NO_3^-$ ion [8] [9].

## RESULTS

### Electrical conductivity

In Fig. 5 the specific and equivalent conductivity isotherms of the three systems are reported. The Na-Rb and Na-Tl systems were also investigated by De Noojer [10] and Protsenko [11].

The equivalent conductivities were calculated by using molar volume data available in literature for Na-Rb [12] [13]; the results of our determinations for Na-Tl [14] and a linear extrapolation for Tl-Rb.

Na-Tl and Na-Rb isotherms exibit usual negative deviations from linearity [15] whereas that of Tl-Rb is linear with composition.

The calculated excesses of apparent activation energy for the equivalent conductivity for the binary systems Na-alkaly nitrates, Tl-alkali nitrates and Rb-alkali nitrates are always positive; the larger the difference between the cationic radii the larger is this effect [14]. For the Tl-Rb system the activation energy is additive.

### Internal mobilities

Fig. 6 presents the cationic internal mobilities of the three systems. The following observations can be drawn :

- On the side of the smaller cation the mobility of this latter varies rapidly with the composition.

- The mobility of the larger cation is less influenced by the changes in composition.

- No significant crosses of mobility exist.

- For the (Tl-Rb) system, the cations of which have the same size (or the components of which have nearly equal molar volumes) the mobilities are equal and vary linearly with composition.

This behaviour, except for the crosses of mobility is similar to that of (Li-K)Cl [9], investigation by Laity, of (Li-K)SO$_4$ of Kvist [16] and, if internal quantities are considered, to that of (Li-K)NO$_3$ of Lantelme and Chemla [17] [18].

Fig. 7 presents the fluidity isotherms of the three systems.

Data relative to Na-Tl are Friz's unpublished results Data relative to Na-Rb are of Murgulescu and Zuca [19].

The few data relative to Rb-Tl are of ours preliminary results.

Now, if the polarization of the common anion, as suggested by Laity, is the main factor determining the transport behaviour of mixtures, two conditions must be verified.

- First : the negative excesses of equivalent conductivity of binary mixtures must be related to the polarization energy term; according Lumsden [3] :

$$\left[ \frac{1}{r_I^2} - \frac{1}{r_{II}^2} \right]^2 \qquad (5)$$

or better :

$$\left[ \frac{1}{V_I^{2/3}} - \frac{1}{V_{II}^{2/3}} \right]^2 \qquad (6)$$

where $V_I$ and $V_{II}$ are the molar volumes of the two salts.

The plots of the excesses of equivalent conductivity vs this polarization term is linear : the first point is fairly well verified.

- Second : the trend of mobilities in a binary system passing from a pure component to the mixture must be related to the probability of formation of polarized anion with composition.

If these solutions are considered as regular ones, i$_d$ est, if the ions are randomly distributed [20], we can define the function :

$$p = \frac{P_{Nax}}{P_{0.5}} = \frac{X_{Na}(1-X_{Na})}{0.25} \qquad (7)$$

where $X_{Na}$ = molar fraction of NaNO$_3$, as the ratio between the chance of finding an ion triplet Na-NO$_3$-Me ( Me=Tl or Rb) at composition $X_{Na}$, and the chance of finding it at the equimolecular mixture.

The decrease of the sodium mobility, or of the ratio between the mobility and fluidity, in the range $0.5 < X_{Na} < 1$, may be related to the increase of this function by means of a relation of this type :

$$U_x = U_1 - (U_1 - U_{0.5})P \qquad (8)$$

where $U_1$ is the ratio between the mobility and fluidity in pure sodium nitrate and $U_{0.5}$ the same quantity in the equimolecular mixture. In Fig. 8 this quantity is plotted vs the composition (for Na-Tl and Na-Rb); the crosses represent the calculated points.

### Effect of traces of foreign cations on the mobility of the proper ion of the melt

This point of view is also supported by the results of a series of conductivity determinations in $NaNO_3$ containing small quantities of other univalent nitrates.

The determination of the electrical conductivity in systems of this type represents a simple tool to investigate the effect of a foreign cation on the mobility of the proper cation of the melt : infact the slope of the curve conductivity vs concentration of the added impurity, at concentration zero of the added impurity, represents the tendency to lowering or to increasing of the internal mobility of the proper cation of the melt, caused by the adding of the foreign ion.

In Fig. 9 the decrease of the conductivity of $NaNO_3$ vs the concentration of the added salts is reported. In the right part of the figure the slopes of the straight-lines are plotted vs the polarization parameter.

In Fig. 10 the above plots are compared with an analogous one relative to the system $Li_2SO_4$-alkali $SO_4$; data on sulphates are of Kvist. The slope of the sulphates is larger of that of nitrates (as the polarizability of the anions).

### Diffusion

In Fig. 11 the cation tracer diffusion coefficients relative to the systems $(Na-Tl)NO_3$ [6] $(Na-Rb)NO_3$ and some preliminary results on $(Tl-Rb)NO_3$ are presented.

There are small positive deviations from linearity (as in the case of the fluidity); a similar trend has been also observed in $(Li-K)NO_3$ by Lantelme and Chomla [18] and in $(Li-Na)CO_3$ by Spedding and Mills [21].

In the case of the Na-Tl the apparent activation energies for diffusion of both cations are equal one to another at all compositions.

A similar behaviour has been observed by Francini and Martini, [22] [23] by means of polarographic measurements, relatively to a large number of cations and anions in nitrate eutectics.

Fig. 12 presents the plots of $\frac{D}{\phi}$ for the three systems. This function is nearly constant with composition in the case of Tl-Rb and it decreases linearly in the Na-Tl and Na-Rb. This behaviour indicates that the larger the size of the proper cation of the melt, the larger is the hinder to the diffusion of both cations.

If we consider the diffusion of the traces in pure nitrates and if we attempt to apply the Stokes (Sutherland)- Einstein relationship in the classical form :

$$D = \frac{K}{\underline{a}} \qquad \frac{\phi T}{r_{Me'}} \qquad (9)$$

we can see from the Fig. 13 that this relationship accounts fairly well for the diffusion of traces of the proper ion of the salts, if an $\underline{a}$ value of about 4.6 $\pi$ is chosen.

The diffusion coefficients of foreign ions smaller (larger) than the proper ions are below (above), the straight line in Fig. 13 ($\underline{a}$ value of about 7 $\pi$ for Na in $TlNO_3$ and Li in $KNO_3$; a values of about 3.5 $\pi$ for Tl in $NaNO_3$ and K in $LiNO_3$). Na in $TlNO_3$ is more actracted by the nitrate as in pure $NaNO_3$, Tl in $NaNO_3$ less actracted by the nitrate as in $TlNO_3$.

Fig. 14 presents the ratio between the $\underline{a}$ value for the diffusion of the foreign ion and the $\underline{a}$ value for the proper ion of the melt for a series of diffusions of traces in molten $NaNO_3$ and $CsNO_3$ vs the polarization parameter; diffusion data in $CsNO_3$ have been taken from a Ketelaar's [24] recent reference.

When the radius of the diffusing ion is larger than that of the proper ion of the melt this ratio decreases; and viceversa when the radius of diffusing particles is smaller.

From Raman spectroscopy evidences, in pure molten univalent nitrates, Janz [25] pointed out that the metal ion-nitrate interaction, may cause "the time of residence of the cation near the anion to be long compared with the time of the molecular vibration". It can be expected that in mixtures this effect for a given cation would be enhanced or hindered according the polarization direction. The stand of a cation near the anion will cause a sort of "cooperative act" [21] during the diffusion, which may be related or explain the approximate constance of the diffusion activation energy for all the ions in the same melt, irrespective of the different a values.

Finally one can observe that the transport behaviour of the $(Na-Tl)NO_3$ system is rather similar to that of the alkali-nitrate binary systems. It seems that the variation of the London dispersion forces between the cations in mixture, which have some influence on the equilibrium properties of this system [26] are not very significant as regards the irreversible processes.

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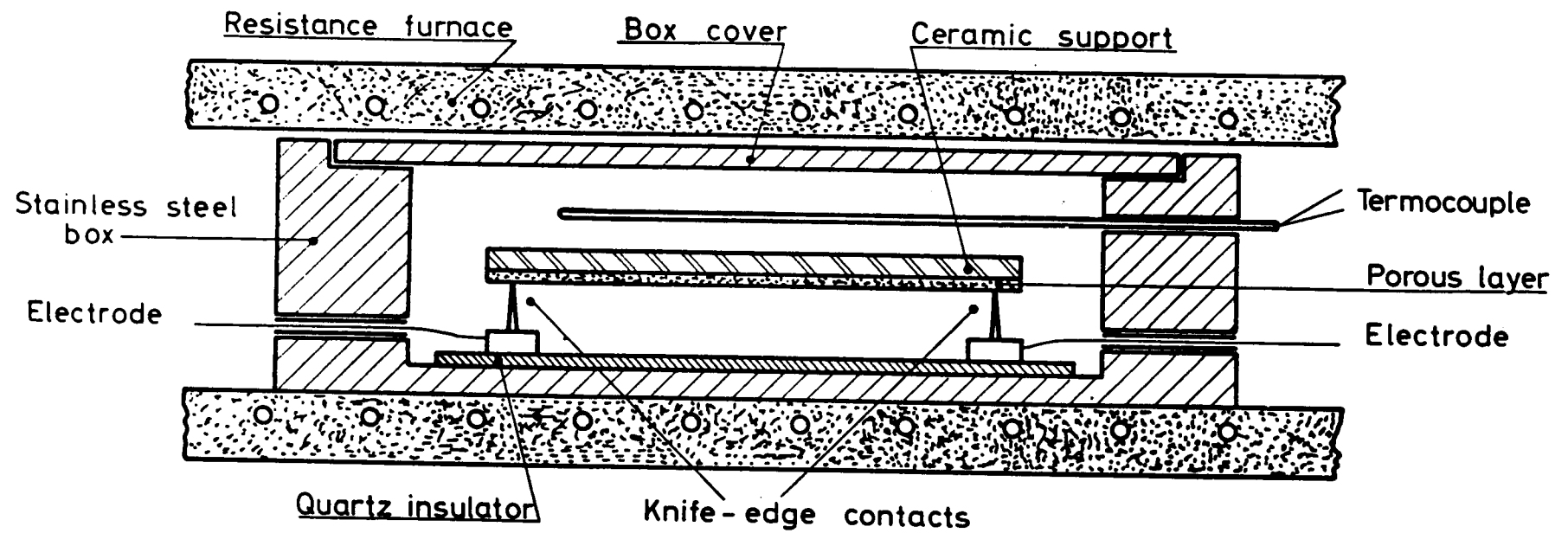
FIG. 1: Assembly for tracer-diffusion experiments
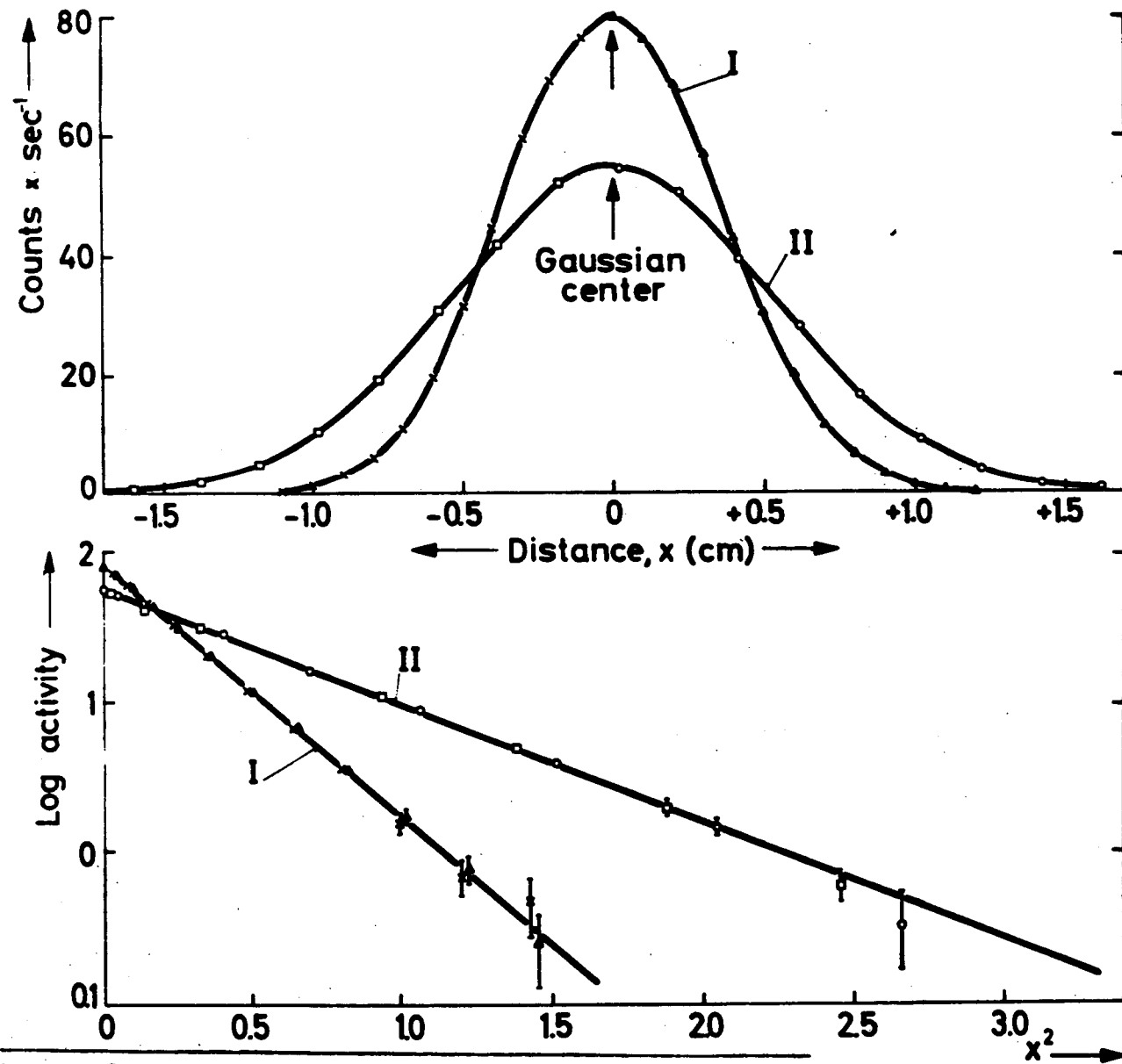
FIG. 2: Diffusion profiles of Tl-204 in TlNO3 determined at two
different times. In the lower part: plots of log activity
vs the squared distance from the Gaussian centre
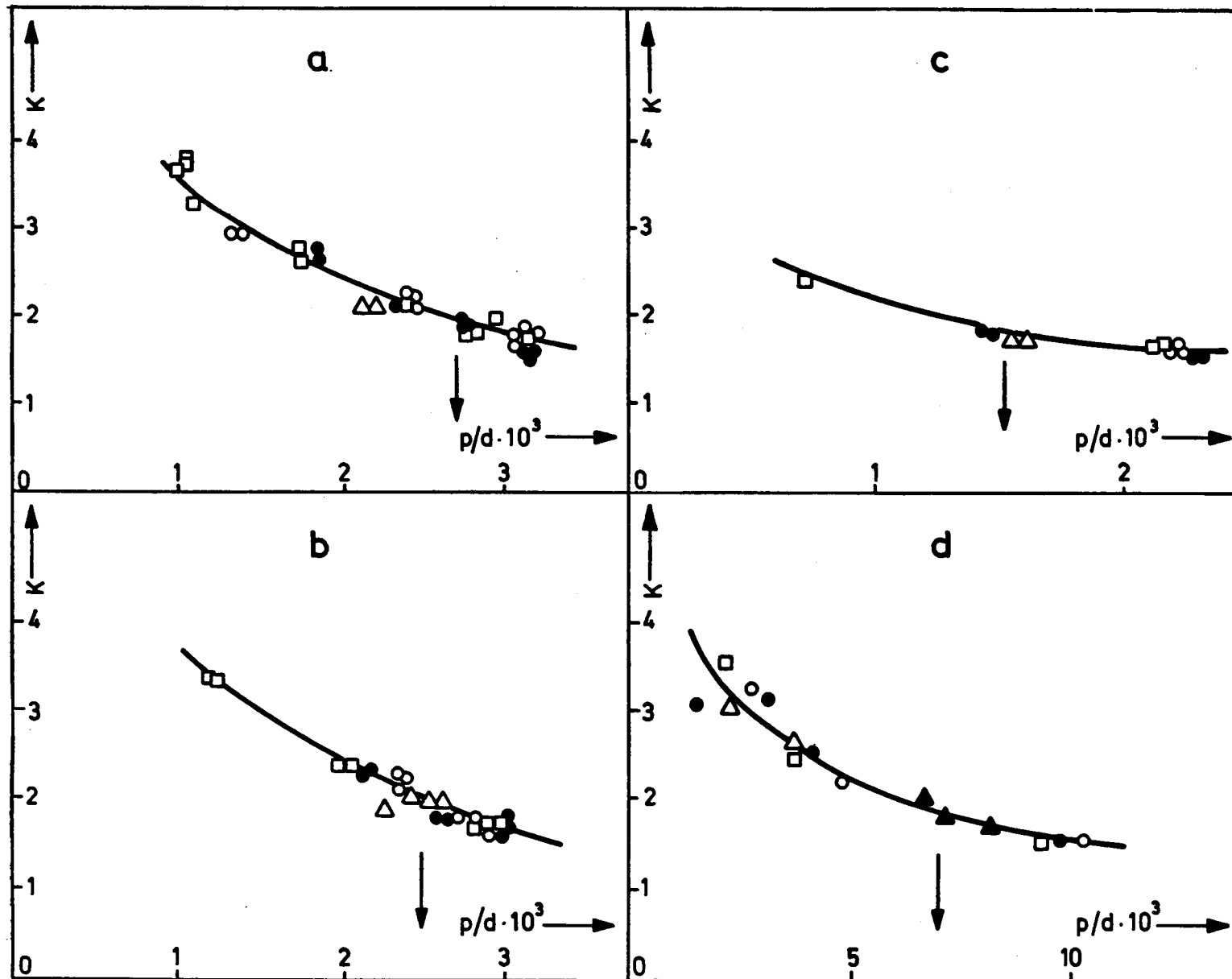
FIG. 3: K vs the section of the electrolyte for a number of impregnated fritted layers
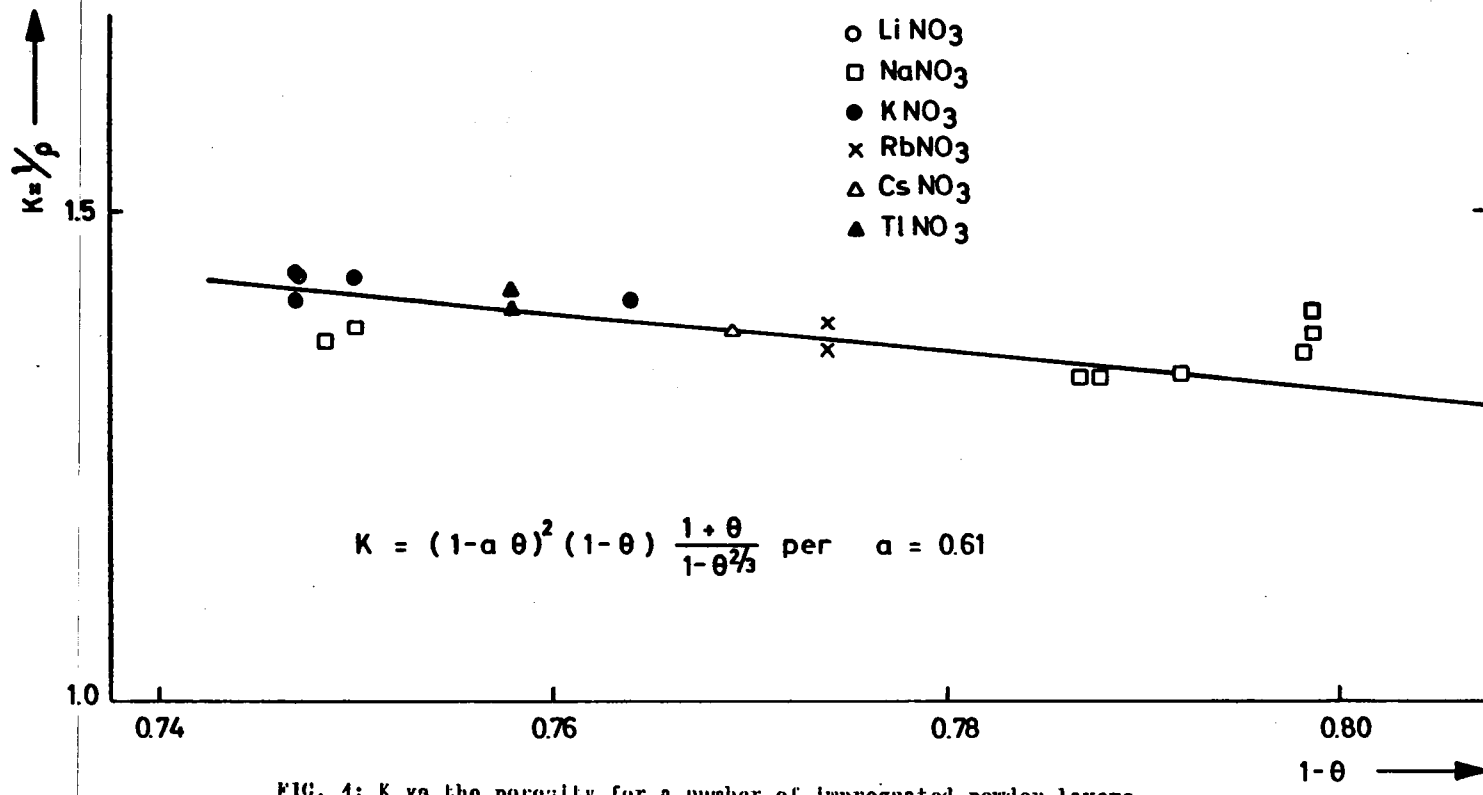
FIG. 4: K vs the porosity for a number of impregnated powder layers

$$K = (1 - a \, \theta)^2 (1 - \theta) \, \frac{1 + \theta}{1 - \theta^{2/3}} \quad \text{per} \quad a = 0.61$$
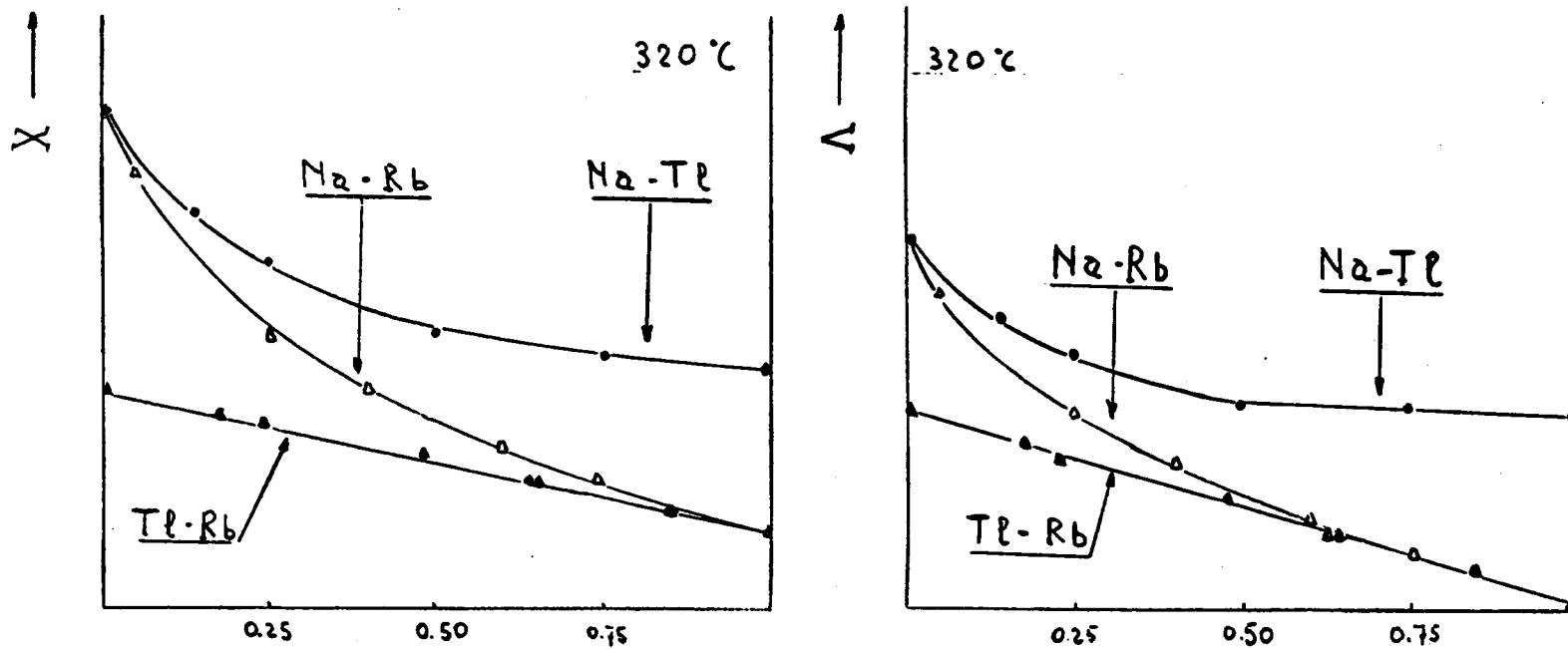
FIG. 6: Internal mobility isotherms
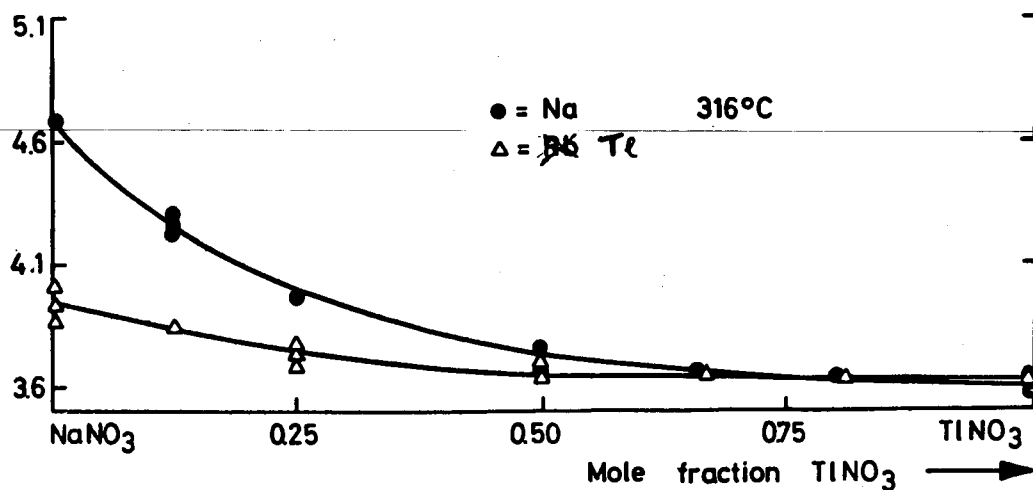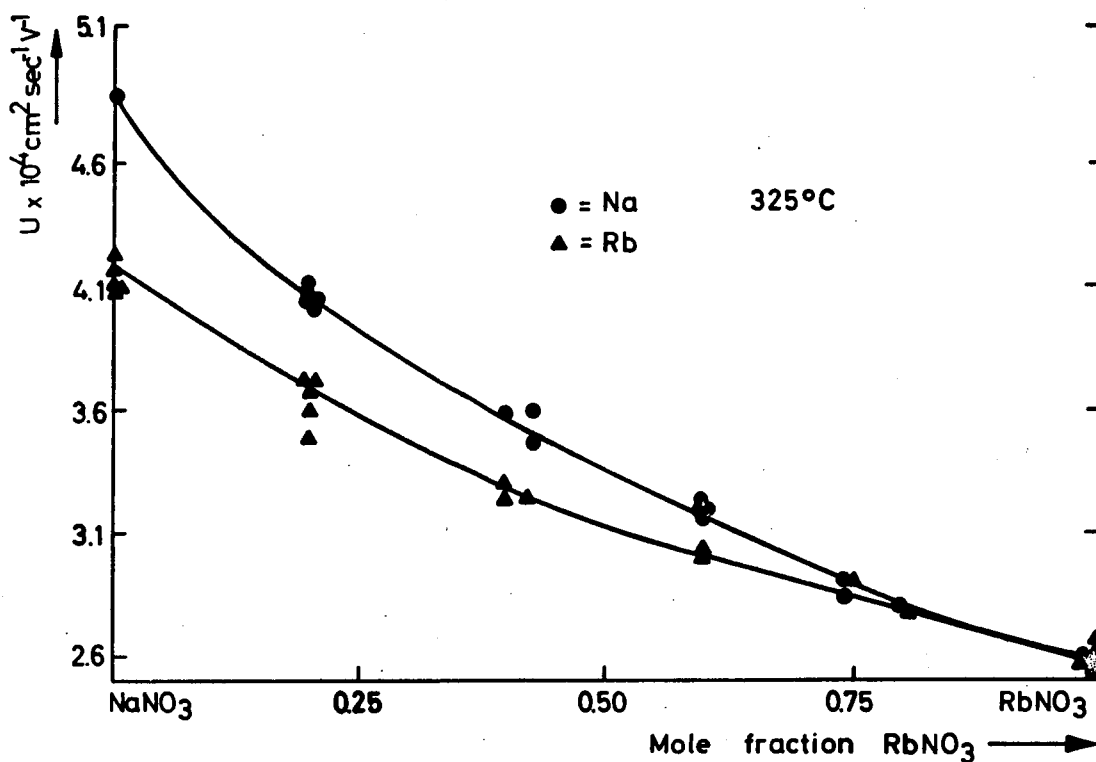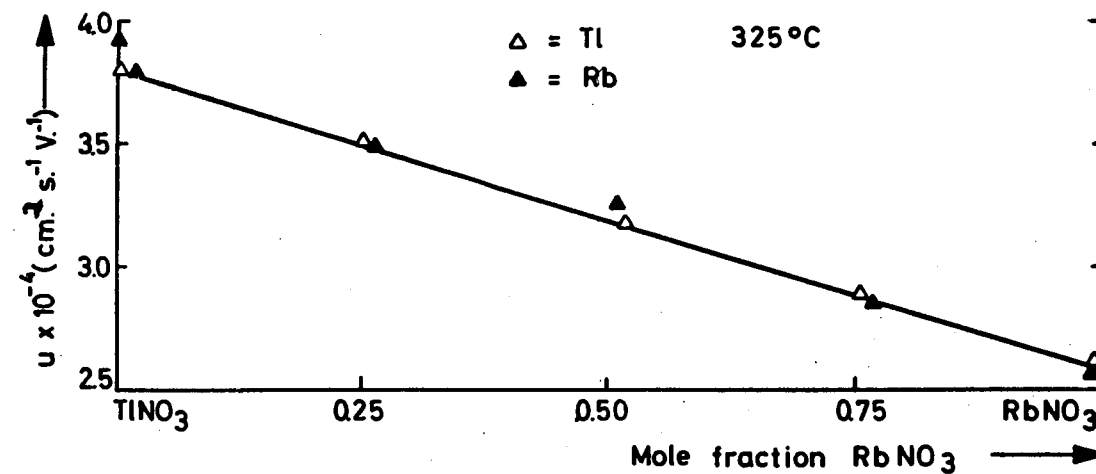
FIG. 7: Fluidity isotherms

FIG. 8: Function U - $\frac{u}{\theta}$ vs composition; the crosses represent the calculated points according formula (8)

(Na - Rb)NO₃     325°C

Mole fraction RbNO₃

(Na - Tl)NO₃     316°C

Mole fraction Tl NO₃
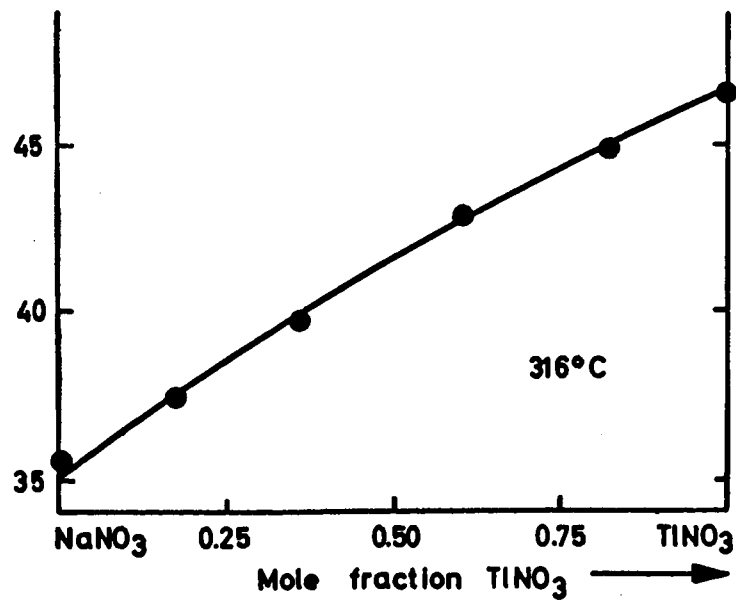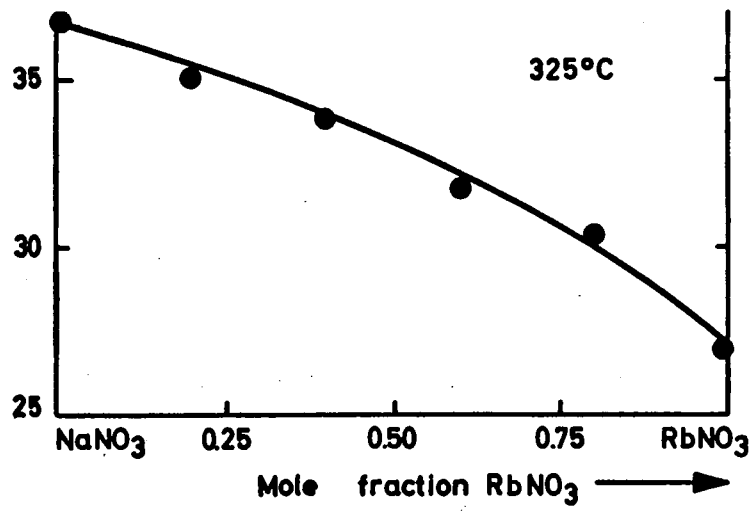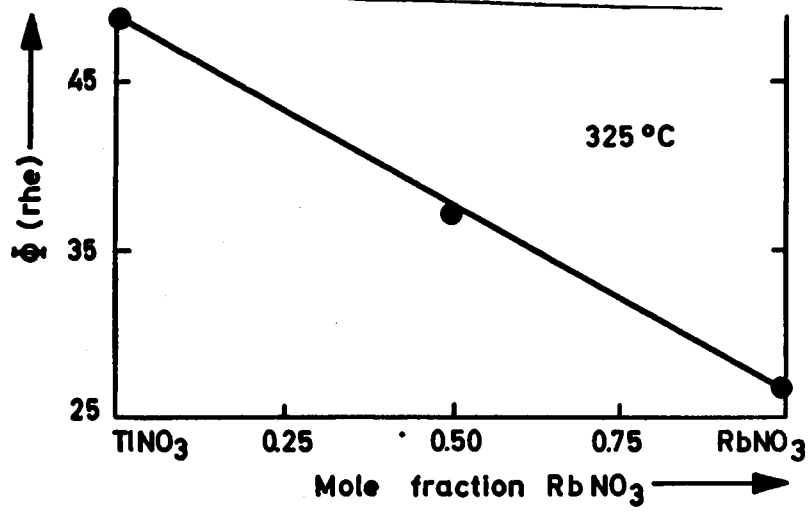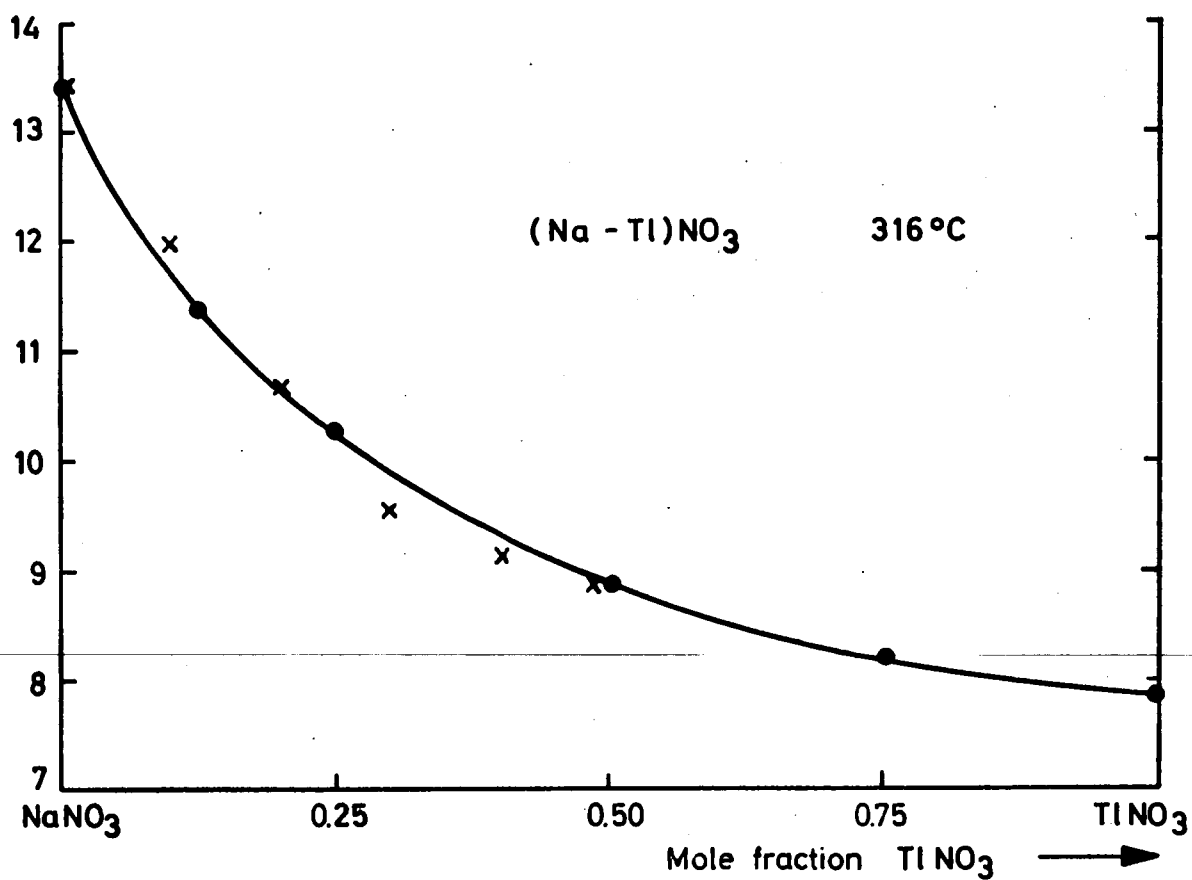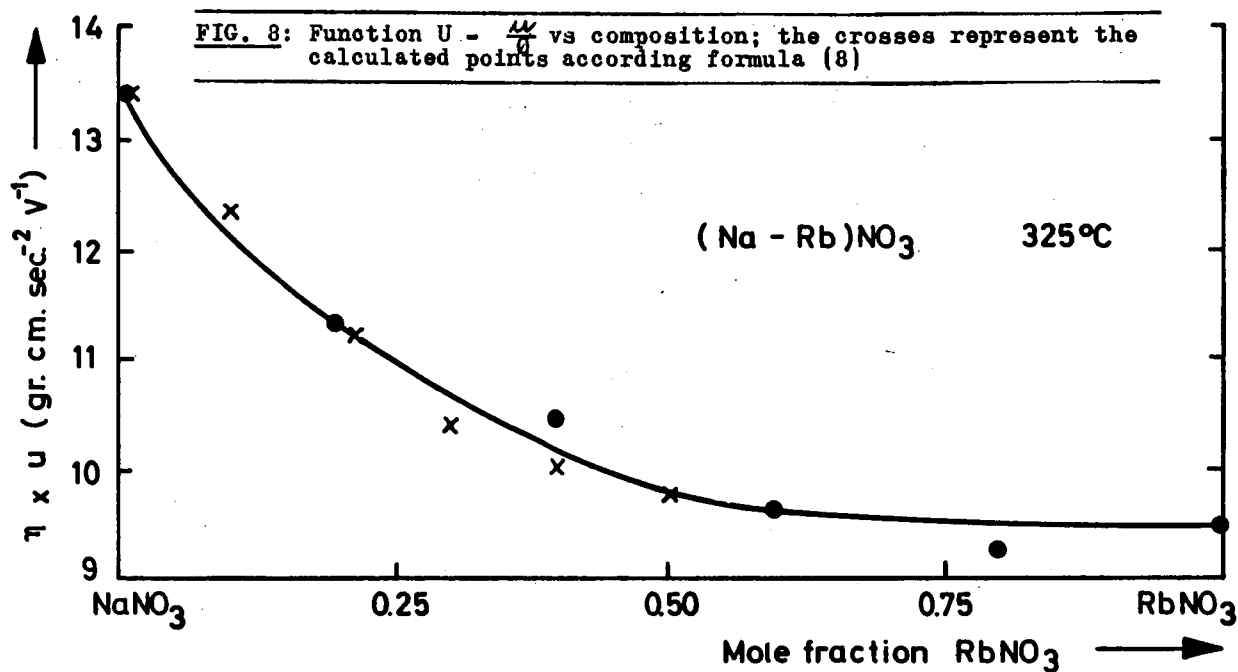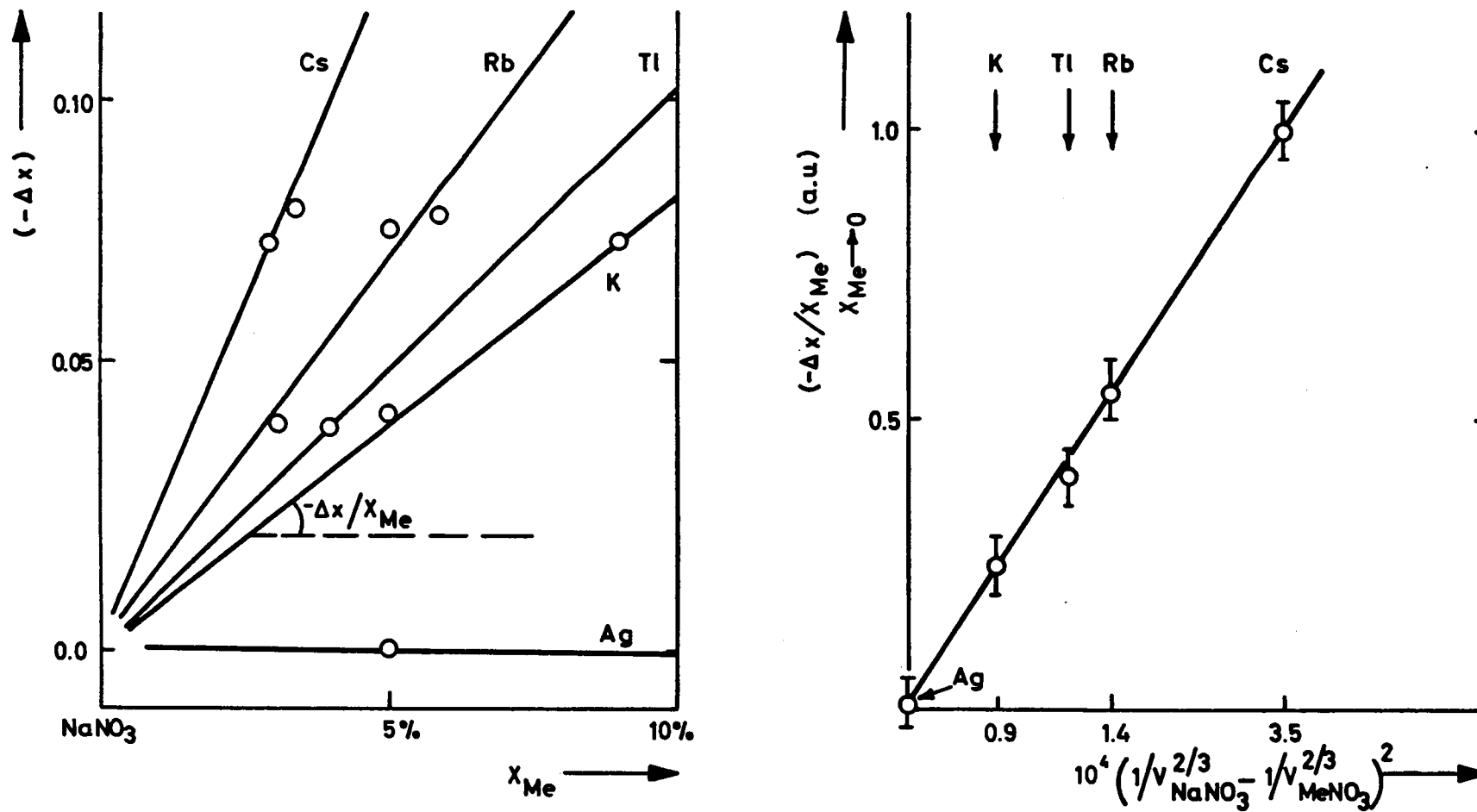
FIG. 9: Left side: function $-\dfrac{\Delta x}{X_{Me}}$ vs $X_{Me}$ in molten $NaNO_3$.
Right side: slopes of the above plots vs the polarization parameter
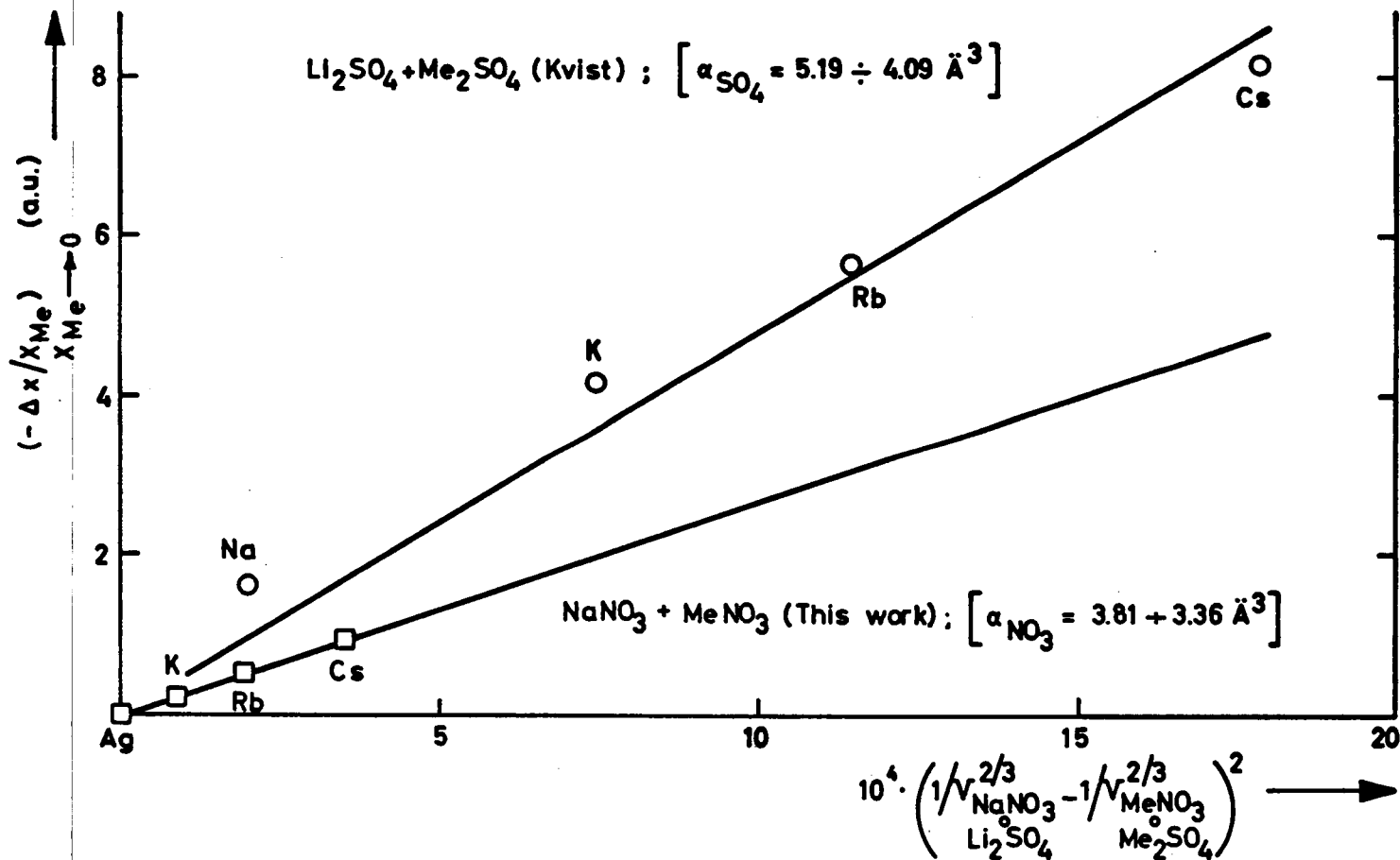
FIG. 10: Function $\left[-\dfrac{\Delta x}{x_{Me}}\right]_{x_{Me}\to 0}$ vs the polarization parameter in molten $NaNO_3$ and in molten $Li_2SO_4$
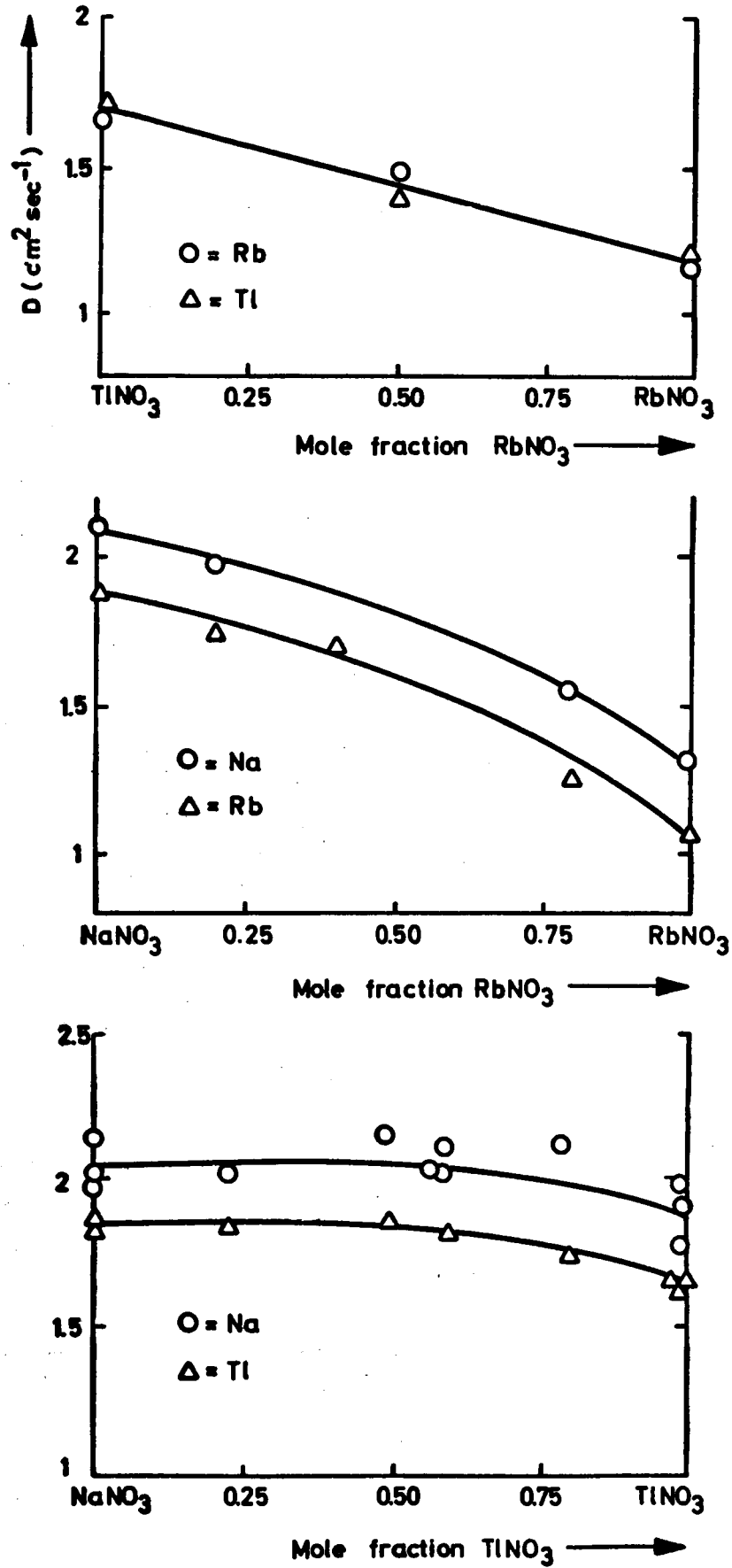
**FIG. 11:** Cation diffusion coefficients isotherms
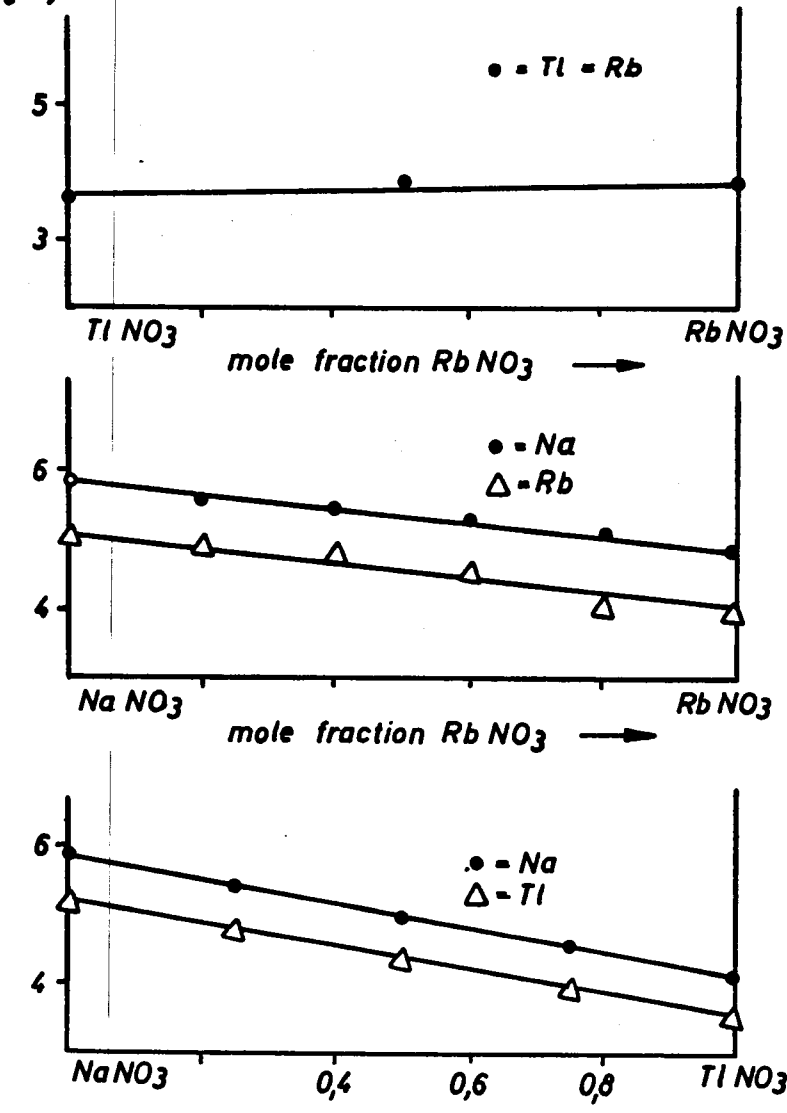
FIG. 12: Function $\frac{D}{\varnothing}$ vs composition
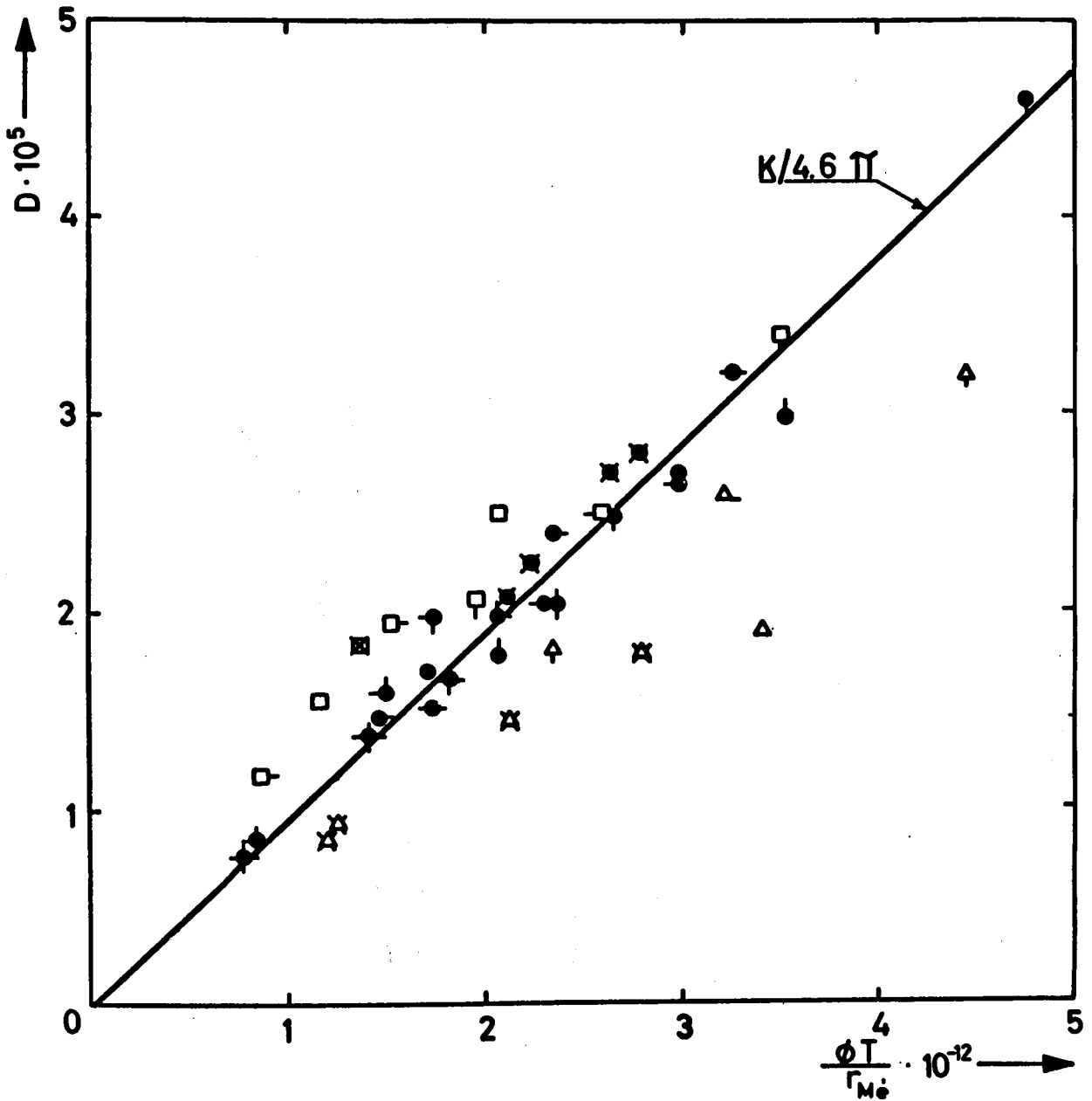
FIG. 13: D vs $\dfrac{\emptyset T}{r_{Me'}}$ (eq.9). Circular full points:
size of the diffusing ion - size of the proper ion of the melt - Square open points: size of the d.i.> size of the p.i. of the melt - Triangular open points: size of the d.i.< size of the p.i. of the melt.
For detailed references relative diffusion and viscosity data see (6).

**FIG. 14:** Ratio between the <u>a</u> value for the diffusion of the foreign ions and the <u>a</u> value for the diffusion of the proper ion for a series of diffusion of traces in molten $NaNO_3$ and $Cs NO_3$ vs the polarization parameter.
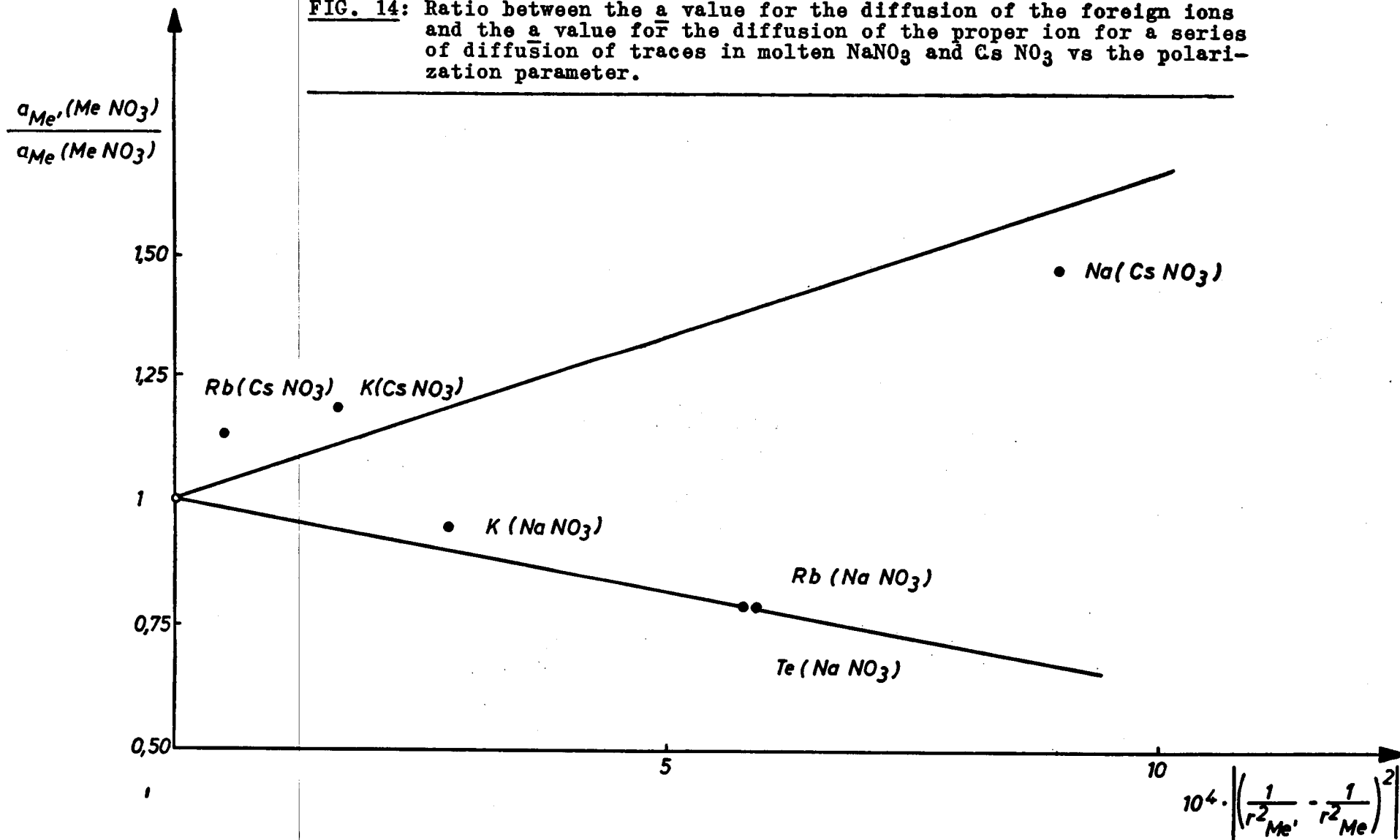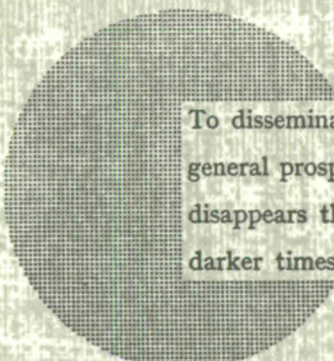
To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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