The velocities of ultrasonic waves of frequency 4 MHz in the reciprocal mixture K,Tl/BrN03 have been measured by a pulse method. In the miscibility zone the ultrasound velocity may be predicted using the equation of state of Buehler. It is concluded that the reciprocal mixture is far from ideality for high concentrations in KNO3. In the immiscibility zone the ultrasound velocity is well calculated assuming a mixture of two phases. Finally the isothermal compressibility may be predicted on the basis of cellular theory if the mixture is not too far from ideality.

1. INTRODUCTION

Since the first measurements of ultrasound speeds in molten salts of Bockris and Richards (1) numerous studies were carried out but it seems that no study has been published, to our knowledge, concerning the reciprocal mixtures involving a polyatomic anion and an halide ion until the recent paper on (NaK/BrN03) by our group (2). Contrary to liquids like silicates, molten salts such as nitrates, sulfates, halides of metals do not exhibit a strong tendency to immiscibility: some miscibility gaps have been reported in a few binary mixtures with BeF2. However numerous reciprocal systems of molten salts exhibit a miscibility gap between two liquids, although subsidiary binaries are miscible at any concentration. Generally the components are halides, nitrates or sulfates. Therefore, we thought it might be of interest to conclude our study on nitrates, together with their binary, ternary, quaternary and reciprocal mixtures (without a miscibility gap) by a study of the reciprocal mixture (KTl/BrN03) with such a gap. The latter was chosen because the experimental investigation of the miscibility zone is precise and complete (3). The stable diagonal we studied is KNO3-TlBr. The temperature of monotectic and upper consolute point are respectively 444°C and 543°C. The width of the gap at 444°C goes from 15.5 to 92.5 TlBr mole per cent, the molar fraction corresponding to upper consolute point is 0.57.

For an extended bibliography see ref.(2).
2. EXPERIMENTAL

The apparatus used was described in detail previously (4). Some minor modifications were made of the furnace. The vapour pressure of TlBr is important (71mmHg at 630°C) and our method prohibits the use of a closed vessel. Therefore, in order to reduce vaporization out of the cell the oven was constructed with no temperature gradients. In this case the vaporization remains slight during the experiment.

A pulse method was used. The ultrasonic waves of 4MHz passed through the melt and silica rods. The velocity was measured directly from the transit time of the wave through a known thickness of molten salt.

The salts used were pure grade as supplied by Prolabo (RP) or Merck. After a stay of several days in a drying oven, they were set into the measuring cell and heated for several hours under an overpressured and dry argon atmosphere.

The temperature zone studied (above 444°C) was above the melting temperature of KNO₃ (337°C) and even more above that of TlNO₃ (206°C). In order to avoid a strong decomposition of the nitrates, we had to limit ourselves to comparatively low temperatures: a few tenth of degrees around the demixing zone.

3. RESULTS

The ultrasonic velocities in KNO₃ and KBr were determined previously (5). Those of TlNO₃, TlBr and (KNO₃+TlBr) are shown respectively on fig.1,2,3 and well represented by a linear polynomial as a function of temperature \( v = a - bt \) (table I) as well in the miscibility zone as in the immiscibility gap, for the mixture.

| TABLE I - TEMPERATURE VARIATION OF ULTRASONIC SPEED IN FUSED SALTS KNO₃ + TlBr |
|-----------------|-----------------|-----------------|-----------------|
|                 |                 |                 |                 |
|                 | miscibility zone |                 | immiscibility zone |
| Xₖ             | a m.s⁻¹°C       | b m.s⁻¹°C       | a m.s⁻¹°C       | b m.s⁻¹°C       |
| 0.09            | 1380            | 0.653           | 1380            | 0.65            |
| 0.15            | 1502            | 0.908           | 2059            | 2.02            |
| 0.30            | 1475            | 0.764           | 1662            | 1.21            |
| 0.43            | 2076            | 1.710           | 2186            | 1.89            |
| 0.76            | 2035            | 1.295           | 2096            | 1.34            |
| 0.82            | 2128            | 1.320           | 2147            | 1.36            |
| TlNO₃          | 1808.7          | 0.718           |                 |                 |
| TlBr           | 1367.0          | 0.627           |                 |                 |

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4. Calculation of Ultrasound Velocities

The first goal of this work is to calculate the ultrasound velocity in order to reduce the number of experiments and to know if the mixture is close to ideality.

a. Miscibility zone

Starting from the Buehler equation:

\[ PV(1-\phi) = RT \]

with \( \phi = \left( \frac{V^*}{V} \right)^{1/3} \) where \( V^* \) and \( V \) are respectively the molar covolume and volume it was shown (6) that the ultrasound speed is given by:

\[ u = \left( 1 - \phi \right)^{1/2} \frac{aM}{R} - \frac{M\alpha^2}{C_P} \]  

(3.1)

\( \alpha \) is the expansion coefficient, \( C_p \) the molar heat capacity, \( M \) the molar mass. If the mixture is ideal, \( M, V, V^* \) and \( \alpha \) are easily calculable from the data of the four pure components from such expression

\[ M = \sum_{i} x_i M_i \]  

etc... (3.2)

The data \( V^* \) were calculated from (3.1) and ref.(5) ; \( V, C_p \) are extracted from Jânz's book (7). All these values, which are valid to about a hundred degrees above the melting point, were extrapolated to the studied range (for the nitrates it is higher than the melting point, for the bromides it is lower). The variation of \( u \) as a function of temperature is presented in fig.3 and as a function of mole fraction in fig.4. The deviation from experimental values is at most 7% and is generally smaller (near high concentrations of Ti). In the reciprocal mixture (NaK//NO_3Br) it is only 0.5%. So we can conclude that the reciprocal system (KTl//NO_3Br) is not ideal (at least as far as \( V, V^*, \alpha \) and \( u \) are concerned) even if a part of the 7% must be attributed to the numerous more or less justified extrapolations. But it is close to ideality. The excess volume of KBrNO_3 was estimated as a few thousandths (2), that one of KTlNO_3 is \( 3\% \) (8).

Noticing that the excess volumes of mixtures (alkali nitrate + thallous nitrate) are larger than those of alkali nitrates only (8) and that replacing one \( Br^- \) ion by an \( NO_3^- \) ion leads to very small volume variation in (NaK//BrNO_3)(2), the non ideal behavior can be attributed to the presence of \( Ti^+ \) and its partially covalent character. This fact is confirmed when we compare the constant velocity curves for (KNa//BrNO_3)(fig.5a) and for (KTl//BrNO_3)(fig.5b) as calculated from equation (3.1) at a given temperature. For the first mixture the velocity changes chiefly with the anion concentration and the difference is about 140m/s, for the second mixture the velocity is governed by the cation concentration and the difference is four times more important, about 550m/s.

In conclusion, the excess volumes of mixtures with \( Ti^+ \) (ie KTiBr, TlBrNO_3) which are unknown, are larger than a few thousandths, as

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those of the alkali ions.

b. Immiscibility zone

Let us label all the quantities for the first phase with a prime and for the second phase with a double prime. We get two obvious relations:

$$t = t' + t'' \quad (3.3)$$

$$ut = u't' + u''t'' \quad (3.4)$$

and a third one

$$\frac{u't'}{u''t''} = \frac{x'V'}{x''V''} \quad (3.5)$$

whereby the ultrasonic waves go through lengths proportional to the volume of each phase ($V'$ and $V''$ are molar volumes of each phase, $x'$ and $x''=1-x'$ give the number of moles in the two phases).

Let $x$ be the molar fraction of $Tl$Br in the quasi binary $(TlBr+KNO_3)$, and $x'$, $x''$ the mole fraction of $Tl$Br in the two phases, hence:

$$\frac{x''}{x'} = \frac{x-X}{x'-x} \quad (3.6)$$

and, combining (3.3), (3.4), and (3.5):

$$u = \frac{u'(1 + \frac{x''V''}{x'V'})}{1 + \frac{u'}{u''} \frac{x''V''}{x'V'}} \quad (3.7)$$

$x'$ and $x''$ are given by the data in ref.(3), $V'$ and $V''$ can be calculated from the molar volume of the reciprocal system (2) which may be expressed as

$$V = \sum_{i=1}^{2} \sum_{k=3}^{4} x_i x_k V_{i,k} + \sum_{i=1}^{4} \sum_{j=1}^{4} \sum_{h=1}^{4} x_i x_j x_h V_{i,j,h}$$

where 1 and 2 stand for cations, 3 and 4 for anions, $V_{i,j}$ is the molar volume of pure salt (ij), and $V_{i,j,k}$ the excess molar volume for an equimolar binary mixture (ijk). The value of excess volume of $(KTN0_3)$ was given by Cleaver (8). For the three other binaries, we ascribed the values 4.10$^{-2}$, 5.10$^{-3}$, 7.10$^{-2}$ respectively for TlONo3Br, KNO3Br and KtBr. The values of $u'$ and $u''$ are the limiting values of speed in a miscible mixture at the demixing temperature. The variations of $u'$, $u''$ and $u$ with temperature are shown on fig.3. The difference between experimental and calculated values is at most 8%. The discrepancies may be ascribed chiefly to a possible decomposition of salts, to extrapolations, to estimations of $u'$ and $u''$ and above all of $V'$ and $V''$ and not to the physical state of mixture (drops or two superposed liquids).
5. COMPRESSIBILITY

The isothermal compressibility was obtained by using the classical equation:

\[ \beta_T = \left( \frac{V}{M\mu^2} \right)^2 \left[ 1 + \left( \frac{MT_{\text{tot}}}{C_p} \right)^2 / C_p \right] \]  

(4.1)

Where all the symbols have their usual significance. Similarly the compressibility of ideal mixtures, as defined by

\[ \beta_{\text{Ti}} = \frac{1}{V} \sum_{j=1}^{2} \sum_{k=3}^{4} x_j x_k V_{0,jk} \beta_{ik} \]  

(4.2)

was calculated. Both are shown in fig.6. It must be noticed that some "experimental" points are, in fact, extrapolated, but it seems it can be concluded, in spite of uncertainties, that the liquid is quasi ideal for TlxBr rich mixtures, and it departs from ideality when x_{KNO_3} increases (the discrepancy was 8%).

In previous works (2)(9) we proposed a model to calculate the isothermal compressibility. The agreement between experimental and calculated values was surprisingly good for associated mixtures (binaries, quaternaries, etc...) and for the reciprocal system (NaK/NO_3Br). But to take into account the "S shape" of \( \beta_m \) (fig.6) it is necessary to get a negative and dissymmetric excess volume. This needs an experimental verification before asserting that our model is valuable for a reciprocal mixture far from ideality.

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FIGURE 1. Ultrasonic speed in TNO₃

FIGURE 2. Ultrasonic speed in TBr

FIGURE 3. Ultrasonic speed in TBr+KNO₃ at constant molar fraction in KNO₃:

- 0.09 • 0.43
- 0.835 X 0.15
- 0.76 O 0.30
- 0.82

The full lines represent the calculated ultrasonic speed from Eq. (3.1)

FIGURE 4. Calculated and experimental ultrasonic speed at 545°C as a function of molar fraction in KNO₃. 

1. Extrapolated point
2. Measured point

(1) calculated from (3.1),
(2) experimental
FIGURE 5. Ultrasonic constant speeds calculated from equation (3.1)
a) \((K\text{Br}///\text{NO}_3\text{Br})\) experimental speeds (m.s\(^{-1}\)) \(\times 1024\) \(\nabla 1059\) \(\bullet 1144\)
\(\bullet 1436\) \(\Delta 1409\) \(\Delta 1329\)
b) \((\text{KNa}///\text{NO}_3\text{Br})\) experimental speeds (m.s\(^{-1}\)) \(\nabla 1688\) \(\times 1680\)
\(\Delta 1674\) \(\nabla 1660\) \(\bullet 1630\) \(\circ 1600\) \(\times 1658\) \(\Delta 1652\)
\(\Box 1648\) \(\nabla 1636\) \(\blacksquare 1615\) \(\bullet 1585\)

FIGURE 6. Isothermal compressibility at 545°C
(1) ideal from (4.2) \(\times\) extrapolated point \(\circ\) measured point