# Self-Diffusion Coefficients in the Molten $AgNO_3$-$AlkNO_3$ Systems

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The cationic self-diffusion coefficients in the fused (Ag-Li) $NO_3$, (Ag-Rb) $NO_3$ and (Ag-Cs) $NO_3$ systems have been investigated as a function of composition and temperature. The deviation from linearity of the $D_+$ vs. composition isotherms in the (Ag-Alk) $NO_3$ series is discussed in terms of ionic interactions. Quantitative relationships between $D_+$ and ionic size and mass have been established.

Our preliminary results [1] on the cationic self-diffusion coefficients in (Ag-Alk) $NO_3$ systems have proved their dependence on the ionic parameters which characterize the diffusing species. In order to establish the relation which expresses quantitatively this dependence, in addition to the previously studied (Ag-Na) $NO_3$ and (Ag-K) $NO_3$ mixtures [1] the remaining systems of the series, for which no data are available in literature: (Ag-Li) $NO_3$, (Ag-Rb) $NO_3$ and (Ag-Cs) $NO_3$ have been investigated. The results concerning the self-diffusion coefficients of both cations (except $D_{\mathrm{Li}^+}$ whose isotope can not be identified by the technique presently used) as a function of composition and temperature are reported in the following.

## Experimental Results

The "diffusion into the capillary" method previously described [1, 2] has been used for the measurements. The nitrates were the same reagent grade quality as those used in our earlier works [1, 2]. $^{110}Ag^+$ $^{86}Rb^+$ and $^{134}Cs^+$ were used as tracers. For each system the self-diffusion coefficients of both cations were measured over the entire concentration range from pure $AgNO_3$ to pure alkali nitrate at temperatures ranging from 240 to 400°. The experimental results are listed in Table 1 – 3.

In Table 4 are given the Arrhenius equation parameters ($D_0$ and $E_{\mathrm{D}^+}$) for the self-diffusion coefficients as determined by the least squares method. The data for single $AgNO_3$, $RbNO_3$, and $CsNO_3$ in Table 4 are taken from our previous paper on pure nitrates [2]. The diffusion coefficients of silver in the (Ag-Li) $NO_3$ system can, within experimental errors ($\pm 4\%$), equally well be represented by a linear temperature dependence as by an Arrhenius equation.

Table 1. Self-diffusion coefficient of $Ag^+$ in molten (Ag-Li) $NO_3$ system.

| $x_{\mathrm{AgNO_3}}$ | $T$ °C | $D_{\mathrm{Ag}^+} \cdot 10^5$, $\mathrm{cm}^2 \cdot \mathrm{sec}^{-1}$ |
|---|---|---|
| 0.75 | 232 | $1.12 \pm 0.03$ |
| | 266 | $1.39 \pm 0.01$ |
| | 307 | $1.70 \pm 0.05$ |
| | 330 | $1.88 \pm 0.03$ |
| | 343 | $1.99 \pm 0.02$ |
| 0.50 | 288 | $1.18 \pm 0.01$ |
| | 301 | $1.32 \pm 0.01$ |
| | 315 | $1.44 \pm 0.03$ |
| | 323 | $1.50 \pm 0.02$ |
| 0.25 | 288 | $1.42 \pm 0.04$ |
| | 302 | $1.58 \pm 0.05$ |
| | 328 | $1.92 \pm 0.05$ |
| | 336 | $2.05 \pm 0.04$ |
| | 350 | $2.21 \pm 0.02$ |

Table 2. Self-diffusion coefficients of $Ag^+$ and $Rb^+$ in molten (Ag-Rb) $NO_3$ system.

| $x_{\mathrm{AgNO_3}}$ | $T$ °C | $D_{\mathrm{Ag}^+} \cdot 10^5$, $\mathrm{cm}^2 \cdot \mathrm{sec}^{-1}$ | $T$ °C | $D_{\mathrm{Rb}^+} \cdot 10^5$, $\mathrm{cm}^2 \cdot \mathrm{sec}^{-1}$ |
|---|---|---|---|---|
| 0.75 | 270 | $1.33 \pm 0.05$ | 292 | $1.42 \pm 0.01$ |
| | 294 | $1.62 \pm 0.02$ | 293 | $1.43 \pm 0.02$ |
| | 300 | $1.65 \pm 0.01$ | 328 | $1.77 \pm 0.07$ |
| | 305 | $1.78 \pm 0.04$ | 343 | $2.06 \pm 0.03$ |
| | 328 | $1.88 \pm 0.03$ | 384 | $2.64 \pm 0.02$ |
| 0.50 | 313 | $1.37 \pm 0.02$ | 277 | $1.04 \pm 0.03$ |
| | 324 | $1.48 \pm 0.03$ | 304 | $1.39 \pm 0.02$ |
| | 331 | $1.57 \pm 0.04$ | 309 | $1.34 \pm 0.03$ |
| | 355 | $1.82 \pm 0.02$ | 342 | $1.70 \pm 0.01$ |
| 0.25 | 304 | $1.18 \pm 0.01$ | 304 | $0.99 \pm 0.01$ |
| | 331 | $1.41 \pm 0.01$ | 313 | $1.14 \pm 0.01$ |
| | 341 | $1.50 \pm 0.01$ | 334 | $1.29 \pm 0.03$ |
| | 349 | $1.64 \pm 0.04$ | 345 | $1.45 \pm 0.02$ |
| | | | 362 | $1.57 \pm 0.03$ |

## Discussion

When the dependence of self-diffusion coefficients on composition is studied, some regularities are evident.

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Table 3. Self-diffusion coefficients of $Ag^+$ and $Cs^+$ in molten $(Ag\text{-}Cs)NO_3$ system.

| $x_{AgNO_3}$ | $T$ °C | $D_{Ag^+} \cdot 10^5$, $cm^2 \cdot sec^{-1}$ | $T$ °C | $D_{Cs^+} \cdot 10^5$, $cm^2 \cdot sec^{-1}$ |
|---|---|---|---|---|
| 0.75 | 223 | 0.80 ± 0.02 | 261 | 0.87 ± 0.03 |
| | 257 | 1.04 ± 0.05 | 294 | 1.29 ± 0.05 |
| | 292 | 1.48 ± 0.01 | 309 | 1.46 ± 0.06 |
| | 317 | 1.53 ± 0.05 | 322 | 1.61 ± 0.02 |
| | 330 | 1.83 ± 0.04 | 352 | 2.19 ± 0.04 |
| 0.50 | 282 | 1.02 ± 0.04 | 237 | 0.44 ± 0 |
| | 288 | 1.10 ± 0.04 | 268 | 0.74 ± 0.06 |
| | 320 | 1.38 ± 0.03 | 288 | 0.85 ± 0.03 |
| | 350 | 1.73 ± 0.04 | 305 | 0.96 ± 0.02 |
| | | | 340 | 1.38 ± 0.02 |
| 0.25 | 343 | 1.28 ± 0.02 | 341 | 1.37 ± 0.03 |
| | 370 | 1.64 ± 0.03 | 360 | 1.62 ± 0.04 |
| | 385 | 1.84 ± 0.02 | 375 | 1.76 ± 0.02 |
| | 410 | 2.19 ± 0.01 | 392 | 2.01 ± 0.03 |

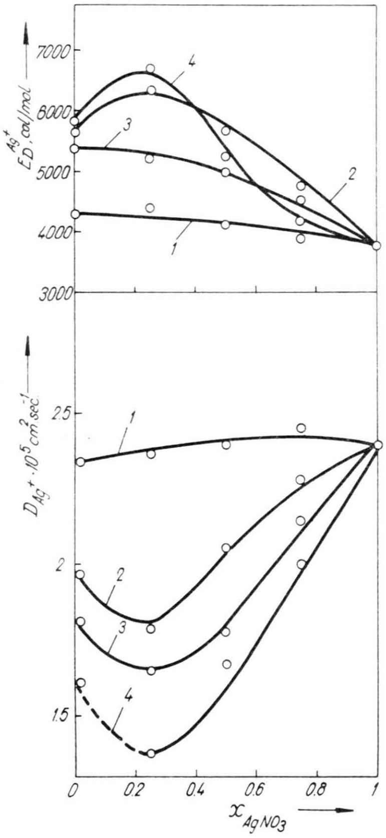

Fig. 1. Diffusion coefficient of $Ag^+$ and activation energy vs. composition in $(Ag\text{-}Alk)NO_3$ systems at 350°.
1) $(Ag\text{-}Na)NO_3$; 2) $(Ag\text{-}K)NO_3$; 3) $(Ag\text{-}Rb)NO_3$; 4) $(Ag\text{-}Cs)NO_3$.

As can be seen in Figure 1, where $D_{Ag^+}$ is plotted against composition, the deviation from additivity increases as the difference in size of the two cations

Table 4. Pre-exponential factor and activation energy of diffusion coefficients in $(Ag\text{-}Alk)NO_3$ systems (Alk = Li, Rb, Cs).

| | $(Ag\text{-}Li)NO_3$ | | $(Ag\text{-}Rb)NO_3$ | | | | $(Ag\text{-}Cs)NO_3$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $x_{AgNO_3}$ | $D_0^{Ag^+} \cdot 10^3$ $cm^2/sec$ | $E_D^{Ag^+}$ cal/mol | $D_0^{Ag^+} \cdot 10^3$ $cm^2/sec$ | $E_D^{Ag^+}$ cal/mol | $D_0^{Rb^+} \cdot 10^3$ $cm^2/sec$ | $E_D^{Rb^+}$ cal/mol | $D_0^{Ag^+} \cdot 10^3$ $cm^2/sec$ | $E_D^{Ag^+}$ cal/mol | $D_0^{Cs^+} \cdot 10^3$ $cm^2/sec$ | $E_D^{Cl+}$ cal/mol |
| 1 | 0.47 ± 0.02 | 3680 ± 80 | 0.47 ± 0.02 | 3680 ± 80 | — | — | 0.47 ± 0.02 | 3680 ± 80 | — | — |
| 0.75 | 0.27 ± 0.006 | 3177 ± 26 | 0.62 ± 0.24 | 4132 ± 491 | 1.22 ± 0.24 | 5012 ± 219 | 0.74 ± 0.22 | 4461 ± 394 | 4.38 ± 0.73 | 6595 ± 83 |
| 0.50 | 0.72 ± 0.04 | 4572 ± 57 | 0.98 ± 0.9 | 4977 ± 123 | 1.05 ± 0.62 | 5023 ± 531 | 1.17 ± 0.25 | 5220 ± 225 | 3.23 ± 1.88 | 6639 ± 508 |
| 0.25 | 1.33 ± 0.006 | 5066 ± 81 | 1.17 ± 0.6 | 5281 ± 498 | 1.40 ± 0.47 | 5643 ± 491 | 3.12 ± 0.32 | 6720 ± 125 | 1.83 ± 0.38 | 5962 ± 271 |
| 0 | — | — | — | — | 1.16 ± 0.10 | 5480 ± 125 | — | — | 1.32 ± 0.03 | 5810 ± 320 |

becomes larger. The hindrance occuring in the silver ion diffusion (Fig.1) when $AgNO_3$ is added to an alkali nitrate melt, becomes more marked as the radius of the alkali cation increases, thus indicating an increase of ionic interaction in the K, Rb, Cs, sequence. The same is suggested by the maximum observed on the $E_D^{Ag^+}$ vs. composition curves (Figure 1). In Fig. 1, at the mol fraction $x_{AgNO_3} \approx 0$, we have used the interdiffusion coefficient data given by Sternberg and Herdlicka[3, 4]. The value $D_{Ag^+}^{\text{inter}}$ in $CsNO_3$ at 350° was calculated by extrapolating the experimental results beyond their temperature range. For completeness, our earlier data[1] for (Ag-Na)$NO_3$ and (Ag-K)$NO_3$ are also given in Figure 1.

For the alkali cations, a smooth dependence of $D_{Me^+}$ on composition is observed (Fig. 2) and a systematical increase of the self-diffusion coefficient takes place as the composition of the melt is changing from pure $MeNO_3$ to pure $AgNO_3$.

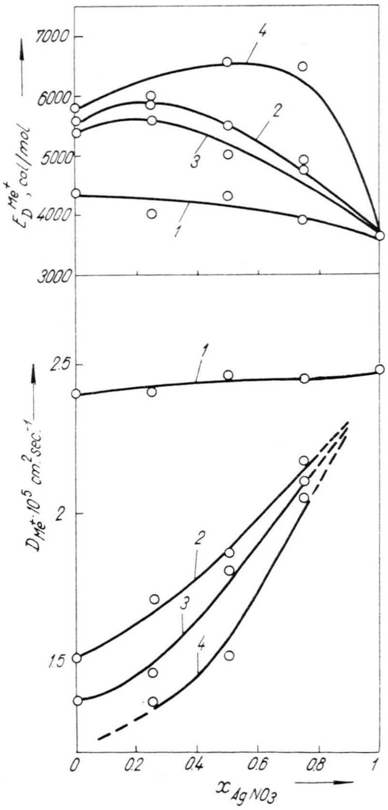

Fig. 2. Diffusion coefficient of alkali cation ($Me^+$) and activation energy vs. composition in (Ag-Alk)$NO_3$ at 350°
1) (Ag-Na)$NO_3$; 2) (Ag-K)$NO_3$; 3) (Ag-Rb)$NO_3$;
4) (Ag-Cs)$NO_3$.

The diffusion coefficient of $Na^+$ in pure $AgNO_3$ in Fig. 2 is the value of Sjöblom et al.[5]. For the other alkali ions there are no similar data in literature but, from the shape of the isotherms in Fig. 2 it appears that when $x_{AgNO_3} \rightarrow 1$, $D_{Me^+}^{\text{inter}}$ becomes the same for all the alkali ions. From the interdiffusion data in alkali nitrates in literature[6,7] we have ascertained that this trend is not accidental but a rule which is convincingly proved by the data in Table 5.

Table 5. Interdiffusion coefficients of alkali cations in fused alkali nitrates.

| Solvent | 450° $D_{Me^+}^{\text{inter}} \cdot 10^5$, cm$^2$·sec$^{-1}$ | | Literature |
|---|---|---|---|
| $NaNO_3$ | $D_{K^+}$ | 3.39 | Honig[7] |
| | $D_{Rb^+}$ | 3.28 | Honig[7] |
| | $D_{Cs^+}$ | 3.13 | Kwak[6] |
| $KNO_3$ | $D_{Na^+}$ | 2.75 | Honig[7] |
| | $D_{Rb^+}$ | 2.83 | Honig[7] |
| | $D_{Cs^+}$ | 2.66 | Honig[7] |
| $RbNO_3$ | $D_{Na^+}$ | 1.87 | Honig[7] |
| | $D_{K^+}$ | 2.13 | Honig[7] |
| | $D_{Cs^+}$ | 2.26 | Kwak[6] |
| $CsNO_3$ | $D_{Na^+}$ | 2.41 | Kwak[6] |
| | $D_{K^+}$ | 2.44 | Kwak[6] |
| | $D_{Rb^+}$ | 2.32 | Kwak[6] |

The special position of the (Ag-Na)$NO_3$ system in the (Ag-Alk)$NO_3$ series was already discussed[1]. We mention here that a similar linear dependence on concentration was observed for the interdiffusion coefficient measured by a gravimetric method[5] in the entire concentration range. Surprisingly, the more recent data on the interdiffusion coefficient obtained by the diaphragme cell method[8] show a minimum on the $D^{\text{inter}}$ vs. composition curve, that we think is difficult to explain.

Since it is generally accepted[2, 3, 9–11] that $Na^+$ and $Ag^+$ in their molten nitrates ase of similar ionic size, it is evident that in the (Ag-K, Rb, Cs)$NO_3$ mixtures, the smaller cation is the $Ag^+$ ion. Accordingly, from Figs.1 and 2, the following regularities become evident: on mixing, the self-diffusion coefficient of the smaller cation decreases as compared with its pure salt, while it increases for the larger cation. This recalls the similar concentration dependence of cationic mobilities[6, 7, 12, 13]. Due to the approximate relationship existing between the two transport parameters, $D_i = k\,T\,u_i$, the above behaviour can be assigned to the same reasons. As for the ionic mobilities[13], Lumsden's anion polarisation model[14] provides a satisfactory explanation. According to this model, due to the different size and induced polarizability of the two cations in the melt, some changes in cation-anion bond energy take place on mixing:

- a strengthening of the attractive force between the smaller cation and the common anion causing a decrease in the diffusion coefficient of the smaller ion;
- a weakening of the larger cation-common/anion bond energy, allowing some slight increase in diffusion coefficient of the larger ion.

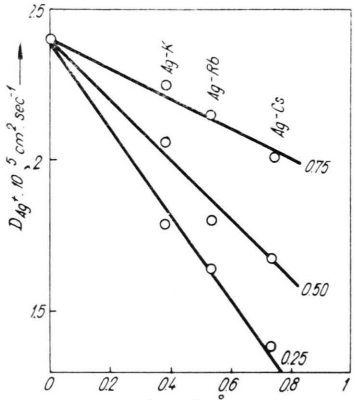

Fig. 3. Dependence of self-diffusion coefficient of $Ag^+$ on the $(r_1-r_2)$ difference.

Our preliminary results[1] have shown that a definite relationship exists between the diffusion coefficient and the crystal radii of ions in the melt. As seen in Fig. 3 for each mol fraction there is a linear dependence of $D_{Ag^+}$ on the difference of cationic radii. The equation of the straight lines ion Fig. 3, calculated by the least squares method is:

$$D_{Ag^+} = D^0_{Ag^+} - (1.946 \pm 0.243) \cdot 10^3\ (r_1 - r_2) \cdot (1 - x_{AgNO_3}) \tag{1}$$

where $D^0_{Ag^+}$ stands for the self-diffusion coefficient of $Ag^+$ in fused $AgNO_3$ at the considered temperature and $r_1$ and $r_2$ are the cationic radii in cm.

A similar linear relationship also holds for $D_{Me^+}$:

$$D_{Me^+} = a - (1.964 \pm 0.335) \cdot 10^3\ (r_1 - r_2)\, x_{MeNO_3}\,. \tag{2}$$

If we take in (2) $x_{MeNO_3} \cong 0$ the self-diffusion coefficient of the alkali cation represents just its interdiffusion coefficient in fused $AgNO_3$ and we have:

$$D_{Me^+} = D^{\text{inter}}_{Me^+} = a\,.$$

When $x_{MeNO_3} = 1$, $D_{Me^+}$ expresses the self-diffusion coefficient of the $Me^+$ cation in fused $MeNO_3$ so that:

$$D_{Me^+} = D^0_{Me^+} = a - (1.964 \pm 0.335) \cdot 10^3\ (r_1 - r_2)$$

and consequently, we may also write instead of (2) the following equation:

$$D_{Me^+} = D^0_{Me^+} + (1.964 \pm 0.335) \cdot 10^3\ (r_1 - r_2) \cdot (1 - x_{MeNO_3}) \tag{3}$$

which has a similar form with (1).

An alternative correlation could be established if we think that a mass effect should be observed in diffusion. Recently McDonald and Davis[15] have expressed some excess transport properties, i. e. viscosity and thermal conductivity, in terms of the mass differences of the two cations, using the rigid elastic sphere model[16].

Similarly, on the basis of the mass dependence of the diffusion coefficient from the kinetic theory of diffusion[17], we have assumed a linear dependence of $D_{Ag^+}$ on $\left(\frac{m_1 + m_2}{m_1 m_2}\right)^{1/2}$. As a consequence the self-

Table 6. Calculated and experimental self-diffusion coefficients in fused (Ag-Alk)$NO_3$ systems, at 350°.

| System | $x_{AgNO_3}$ | $D_{Ag^+} \cdot 10^5$, $cm^2 \cdot sec^{-1}$ $D_{exp}$ | $D_c$ Eq. (1) | $D_c$ Eq. (4) | $D_c$ Eq. (5) | $D_{Me^+} \cdot 10^5$, $cm^2 \cdot sec^{-1}$ $D_{exp}$ | $D_c$ Eq. (3) |
|---|---|---|---|---|---|---|---|
| (Ag-K)$NO_3$ | 0.75 | 2.25 | 2.21 | 2.17 | 2.21 | 2.22 | 2.17 |
| | 0.50 | 2.06 | 2.03 | 1.88 | 2.04 | 1.87 | 1.88 |
| | 0.25 | 1.79 | 1.85 | 1.60 | 1.87 | 1.72 | 1.70 |
| (Ag-Rb)$NO_3$ | 0.75 | 2.15 | 2.14 | 2.16 | 2.13 | 2.12 | 2.15 |
| | 0.50 | 1.80 | 1.88 | 1.86 | 1.88 | 1.82 | 1.89 |
| | 0.25 | 1.64 | 1.63 | 1.56 | 1.63 | 1.47 | 1.53 |
| (Ag-Cs)$NO_3$ | 0.75 | 2.01 | 2.04 | 2.15 | 2.02 | 2.05 | — |
| | 0.50 | 1.68 | 1.68 | 1.84 | 1.67 | 1.52 | — |
| | 0.25 | 1.37 | 1.32 | 1.54 | 1.31 | 1.38 | — |

diffusion coefficients could be expressed as:

$$D_{Ag^+} = D^0_{Ag^+} - (1.405 \pm 0.454) \cdot \left[1 - \left(\frac{m_{Ag} + m_{Me}}{m_{Ag}\, m_{Me}}\right)^{1/2}\right] (1 - x_{AgNO_3}) \,. \tag{4}$$

From (1) and (4) it follows that $D_{Ag^+}$ can also be written as:

$$D_{Ag^+} = D^0_{Ag^+} - (2.204 \pm 0.28) \cdot 10^3 \cdot \left[1 - \left(\frac{m_{Ag} + m_{Me}}{m_{Ag}\, m_{Me}}\right)^{1/2}\right] (r_1 - r_2)(1 - x_{AgNO_3}) \,. \tag{5}$$

The ability of (1), (3), (4) and (5) to predict the experimental results is given in Table 6. All in all, the data in Table 6 suggest that the cationic masses are probably as important as the differences in cationic radii in determining the diffusion coefficient. However the best fit with experimental results is given by Equation (1).

An attempt has been made to apply the above relationships to other data available in literature. It has been found that the experimental results are always given within experimental error by an equation of the form (1) when the smaller cation in the mixture is concerned and (3) for the larger one. The numerical value of the slope in (1) and (3) varies with the considered solvent. Table 7 illustrates the results for the $(Na\text{-}K)NO_3$ and $(Na\text{-}Cs)NO_3$ systems. The experimnetal results in Table 7 are those given by Lantelme[12] for $(Na\text{-}K)NO_3$ and by Kwak[6] for $(Na\text{-}Cs)NO_3$. It is worthnoting that the $D_c$ data for the $Na^+$ ion were calculated by (1) without changing the numerical values of intersection and slope. The good agreement with the experimental results in both systems indicates, once more, the similarity of the ionic sizes of $Ag^+$ and $Na^+$ ions in their molten nitrates.

Table 7. Calculated and experimental self-diffusion coefficients in fused $(Na\text{-}K)NO_3$ and $(Na\text{-}Cs)NO_3$ systems.

| System | $x_{NaNO_3}$ | $D_{Na^+} \cdot 10^5$, $cm^2 \cdot sec^{-1}$ | | $D_{Me^+} \cdot 10^5$, $cm^2 \cdot sec^{-1}$ | | $T$ °C |
|---|---|---|---|---|---|---|
| | | $D_{exp}$ | $D_c$ | $D_{exp}$ | $D_c$ | |
| | 0.75 | 2.14 | 2.21 | 1.82 | 1.79 | |
| $(Na\text{-}K)NO_3$ | 0.50 | 2.06 | 2.03 | 1.75 | 1.69 | 350 |
| | 0.25 | 1.95 | 1.84 | 1.64 | 1.59 | |
| | 0.75 | 3.50 | 3.37 | 2.80 | 2.82 | |
| $(Na\text{-}Cs)NO_3$ | 0.50 | 3.18 | 3.04 | 2.57 | 2.64 | 450 |
| | 0.25 | 2.95 | 2.91 | 2.35 | 2.45 | |

None of the above mentioned regularities fit the $(Ag\text{-}Li)NO_3$ mixtures. As seen in Fig. 4, the $D_{Ag^+}$ vs. composition curves show a peculiar behaviour in comparison with the other systems of the series: significant deviations from additivity with a very pronounced minimum at equimolecular composition.

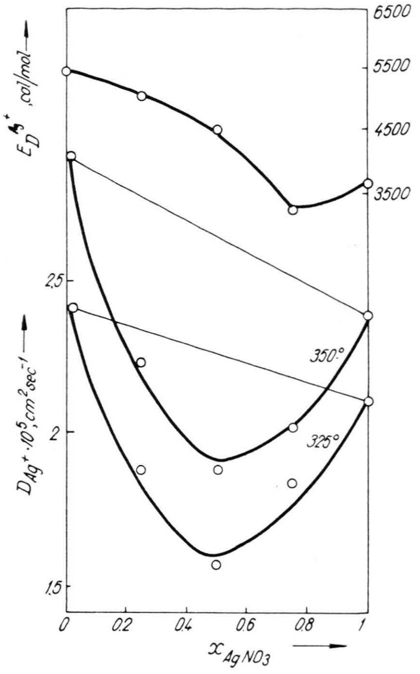

Fig. 4. Diffusion coefficients isotherms of $Ag^+$ ion and activation energy vs. composition in $(Ag\text{-}Li)NO_3$ system.

A similar dependence on composition is also shown by interdiffusion coefficients[8]. The peculiarity of this system is also evident from the minimum shown on the $E_D^{Ag^+}$ vs. composition plot, never observed for the other systems of the series. In Fig. 4 the literature data[3, 18] were used for $D^{inter}_{Ag^+}$ in $LiNO_3$ and $E_D^{Li^+}$ respectively. The magnitude of the deviations in Fig. 4 are too large to be caused by simple competitive interionic atractions. The observed effect may be due to some other factors such as closer packing or eutectic formation (as indicated by phase diagram[19, 20]) caused by the strong polarization exerted by the $Li^+$ ion.

Surprisingly, the recent Raman Spectra[21] indicate that, apart from changes in intensity, the librational bands are essentially unaffected in the $(Ag\text{-}Li)NO_3$ system, which implies no essential structural changes on mixing. This is not confirmed by the diffusion data.

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