ANOMALOUS BEHAVIOR OF AG(I) AND TL(I) IONS IN MOBILITIES OF MOLTEN NITRATES

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The data on internal cation mobilities, \( u \), in the molten binary nitrate systems (M, Ag)NO\(_3\) and (M, Tl)NO\(_3\) (M=alkali metal ion) determined by Klemm's countercurrent electromigration method are reexamined. In binary alkali nitrates \( u \) is well expressed by an empirical equation

\[
u = \frac{A}{(V_m - V_0)} \exp\left(-\frac{E}{RT}\right),
\]

where \( V_m \) is the molar volume; \( A \), \( V_0 \) and \( E \) are constants nearly independent of coexisting cations. If Ag\(^+\) is contained, the \( u \) of coexisting cations M negatively deviates from such an equation, and, on the contrary, if Tl\(^+\) is contained, the \( u \) positively deviates. Thus, Ag\(^+\) and Tl\(^+\) having relatively high polarizabilities have the opposite effects on \( u \), that is tranquilization effect and agitation effect, respectively. The reason has been interpreted in terms of the high polarizabilities and the difference in the sizes of Ag\(^+\) and Tl\(^+\).

INTRODUCTION

Since molten alkali nitrates have relatively low melting points, these are suitable media for experiments for a better understanding of the mechanism of ionic conductance in molten salts. As for the mechanism of ionic mobility, binary systems with a common anion supply us with more information than pure salts do, because mobilities of two cations can be compared under the same conditions.

We have so far measured the internal mobilities, \( u \), in molten binary alkali nitrates by countercurrent electromigration, and found that \( u \) of cations M1 such as Li, Na and K are well expressed by an empirical equation (1):

\[
u_{M1} = \frac{A}{(V_m - V_0)} \exp\left(-\frac{E}{RT}\right),
\]

where \( V_m \) is the molar volume of the mixture, and \( A \), \( V_0 \) and \( E \) are constants characteristic of M1 and nearly independent of coexisting cations.

More than 30 years ago Blander(2) proposed to compare the differences in the properties of Ag\(^+\) and Tl\(^+\) ions from those of Na\(^+\) and Rb\(^+\) for separating the physical properties in molten salts related to the relatively high polarizabilities. However, the role of polarizabilities for transport phenomena such as mobilities and diffusion coefficients has not explicitly been clarified yet. Thus, in the present work we have systematically reexamined the feature of cation internal mobilities in molten binary nitrate mixtures when Ag\(^+\) or Tl\(^+\) having high polarizabilities is contained as one of the binary cations.
EXPERIMENTAL

In molten binary nitrates (M1, M2)NO3 [M1=alkali metal ion, M2=Ag or Tl] countercurrent electromigration presented by Klemm (3) was performed to obtain the relative differences in internal mobilities of M1 and M2

$$\varepsilon = \frac{u_{M1} - u_{M2}}{x_{M1}u_{M1} + x_{M2}u_{M2}}$$  \hspace{1cm} [2]

where $x_i$ is the mole fraction of i. The experimental details were previously described (4).

From the $\varepsilon$ values and the data available on densities and electric conductivities, the internal mobilities were calculated by

$$u_{M1} = \frac{\kappa V_m / F}{1 + x_{M2} \varepsilon}$$  \hspace{1cm} [3]

$$u_{M2} = \frac{\kappa V_m / F}{1 - x_{M1} \varepsilon}$$  \hspace{1cm} [4]

where $\kappa$ is the electric conductivity, $V_m$ the molar volume, and $F$ the Faraday constant.

RESULTS

Detailed results on the internal mobilities in the binary systems (Ag, M)NO3 and (Tl, M)NO3 (M=alkali metal ion) measured by Klemm's countercurrent electromigration method have been given elsewhere (see Table 1).

Table 1. References where the internal mobilities in (M1, M2)NO3 are given.

| M1 | Li | Na | K | Rb | Cs |
|----|----|----|---|----|----|
| Ag | (5) | (4) | (5) | (6) | (6) |
| Tl | (7) | (8) | (9) | (7) | (9) |

Internal mobilities in the molten system (Ag, Tl)NO3 have also been measured (10).

The isotherms of internal cation mobilities in (Ag, M)NO3 and (Tl, M)NO3 are shown in Figs. 1 and 2, respectively.

DISCUSSION

In Table 2 some fundamental properties of alkali metal, Ag(I) and Tl(I) ions and their nitrate melts are given.

In Table 3 a comparison of $u_{M1}$ and $u_{M2}$ in (M1, M2)NO3 is given, which is seen from Figs. 1 and 2.
Table 2. Some fundamental properties of alkali metal, Ag(I) and Tl(I) ions and their nitrate melts.

| Cation   | LiNO₃ | NaNO₃ | KNO₃ | RbNO₃ | CsNO₃ | AgNO₃ | TINO₃ |
|----------|-------|-------|------|-------|-------|-------|-------|
| Ionic radius * (11) (pm) | 59(IV) | 102(VI) | 138(VI) | 152(VI) | 167(VI) | 115(VI) | 150(VI) |
| Ionic mass (g mol⁻¹) | 6.941 | 22.98 | 39.09 | 85.46 | 132.9 | 107.8 | 204.3 |
| Polarizability (2) (10⁻³⁰ m³) | 0.030 | 0.182 | 0.844 | 1.42 | 2.45 | 1.72 | 3.50 |
| Polarizability/ionic radius³ | 0.146 | 0.172 | 0.321 | 0.404 | 0.526 | 1.13 | 1.04 |
| Nitrate melting point (°C) | 261 | 308 | 333 | 316 | 414 | 212 | 206 |
| Molar volume at 350 °C (10⁻⁶ m³ mol⁻¹) | 39.64 | 44.95 | 54.24 | 59.34 | 67.48** | 44.49 | 57.28 |

* The roman numerals in the parentheses indicate coordination numbers for which the ionic radii are given here.
** The value under the melting point is the extrapolated value with respect to temperature.

Table 3. A comparison of $u_{M1}$ and $u_{M2}$ in (M1, M2)NO₃.

| M1 | Li | Na | K | Rb | Cs |
|----|----|----|---|----|----|
| Ag | u_Ag > u_M1 | Chemla effect | Chemla effect | u_Tl > u_K | u_Tl > u_Rb | u_Tl > u_Cs |
| Tl | | | | | |

Table 4. An effect on $u_{M1}$ caused by M2 in (M1, M2)NO₃ melts.

| M1 | Li | Na | K | Rb | Cs |
|----|----|----|---|----|----|
| Ag | no effect | | | tranquillization effect | |
| Tl | | agituation effect | |

(M1, Ag)NO₃ mixtures
Internal mobility of Ag⁺, $u_{Ag⁺}$ In (M1, Ag)NO₃, $u_{Ag⁺}$ is greater than $u_{M₁}$ under all the experimental conditions.

We have previously found that internal mobilities are strongly related with separating motion of neighboring cation and anion called the self-exchange velocity (SEV) (12), which can be calculated by molecular dynamics simulation (MD). For molten AgNO₃ MD has not been performed yet. However, the SEV may be
considered in terms of the potential profiles. The separating motion of a cation of interest (Ag; C in Fig. 3) from the referenced anion (NO₃; A in Fig. 3) may be classified in three stages as shown in Fig. 3:

1. another anion (NO₃; B) reaches the cation,
2. the cation(C) moves away from the referenced anion(A) toward the anion (B), as the potential barrier becomes low enough compared with the kinetic energy, and
3. the cation(C) moves away together with the other anion (B) from the referenced anion(A).

As the potentials for AgNO₃ are not available, Ag-Cl potentials (13) are used here, which may be sufficient for the present qualitative discussion. The potential profiles are considered for ions arranged, for simplicity, in one dimension. In Fig. 4 the potential felt by Ag⁺ collinearly located between two Cl⁻ is shown. This is obtained by superposition of the two pair potentials. The shape of the potential depends also on the distance between the two anions. The potential without the dispersion term is also shown here, which resembles that for Na⁺ to some extent. When the dispersion term, which is caused by the polarizability, is included, the flat region of the potential well becomes wider, and therefore the SEV of Ag⁺ will become large. The flat region for Ag⁺ on varying the distance between the two anions may be wider than that for other cations such as Li⁺, Na⁺ and K⁺. This may be the reason why the internal mobility of Ag⁺ is greater than that of any other cations.

The internal mobilities of Ag⁺ in (Ag, M₂)NO₃ as a function of molar volume are shown in Fig. 5. Figure 5 reveals that $u_{Ag⁺}$ is well expressed by such an equation as Eq. (1) with the parameters: $A=7.01\times10^{-11} m^5 V^{-1} s^{-1}$, $V_0=-(49.05-0.048(r/K))\times10^{-6} m^3 mol^{-1}$ and $E=19.86$ kJ mol⁻¹. Thus, $u_{Ag⁺}$ is not affected by the kind of M₁ except for Li⁺ and Tl⁺. The former is due to the free space effect, and the latter is attributed to the agitation effect, which will be discussed later.

Internal mobility of M₁, $u_{M⁺}$ As seen from Table 2, the molar volume of AgNO₃ is slightly smaller than that of NaN₂O₃, whereas the ionic radius of Ag⁺ is considerably greater than that of Na⁺. This suggests that the distances of Ag⁺-NO₃⁻ and Ag⁺-Ag⁺ become smaller owing to the high polarizability.

In Figs. 6, 7 and 8, $u_{Li⁺}$, $u_{Na⁺}$ and $u_{K⁺}$ as a function of the molar volume are shown, respectively. The $u_{Na⁺}$ and $u_{K⁺}$ in the mixtures with AgNO₃ slightly but appreciably deviate negatively. The $u_{ab}$ and $u_{Ca}$ also show a similar tendency. These are ascribed to the tranquilization effect caused by Ag⁺. If a cation (C,) shown by a dotted circule in Fig. 3 strongly interacts with anion B, the motion of anion B will be retarded, which will tranquilize the SEV of cation C from anion A. This tranquilization effect is caused by the strong interaction of Ag⁺-NO₃⁻ due to the high polarizability of Ag⁺. On the other hand, as shown in the inset of Fig. 6, $u_{Li⁺}$ in the mixture system (Li⁺, Ag⁺)NO₃ lies on the empirical equation at higher molar volume, that is at high concentration of Ag⁺, but deviates negatively at low molar volume.

The reason that Ag⁺ does not play the role of a tranquilizer for $u_{Li⁺}$ in (Li⁺, Ag⁺)NO₃ is explained as follows: the potential profile felt by anion B from cation C and cation C, is shown in Fig. 9 for the case B as Cl⁻, C as Li⁺ and C as Ag⁺. Here, the potential of Cl⁻ is adopted for anion B instead of NO₃⁻; for Li⁺-Cl⁻ pair potential, the one presented by Tosi and Fumi (14) is used. Since the interaction of Li⁺-anion is stronger than that of Ag⁺-anion, Ag⁺ does not play a role of a
tranquilizer for $u_{Li}$.

Incidentally, the negative deviation at high concentration of Li$^+$ may be attributed to the free space effect caused by the restricted rotational motion of NO$_3^-$ due to the small free space. The fact that, while $u_{Li}$ in pure LiCl is considerably greater than $u_{Na}$ in pure NaCl, $u_{Li}$ in pure LiNO$_3$ is nearly equal to $u_{Na}$ in pure NaN$_3$ will support this assumption; $u_{Li}$ and $u_{Na}$ in pure LiNO$_3$ and NaN$_3$ are 5.414x10$^{-8}$ m$^2$V$^{-1}$s$^{-1}$ and 5.427x10$^{-8}$ m$^2$V$^{-1}$s$^{-1}$ respectively, at 623 K. $u_{Li}$ and $u_{Na}$ in pure LiCl and NaCl are 20.53x10$^{-8}$ m$^2$V$^{-1}$s$^{-1}$ and 14.15x10$^{-8}$ m$^2$V$^{-1}$s$^{-1}$, respectively, at 1083 K.

(M1, Ti$^+$)NO$_3$ Mixtures

Internal mobility of Ti$^+$, $u_{Ti}$. In (Li, Ti)NO$_3$ and (Na, Ti)NO$_3$ the Chemla effect (1) occurs, that is the isotherms of the mobilities of the two cations have a crossing point.

It is interesting to note that in (K, Ti)NO$_3$, $u_{Ti}$ is greater than $u_{K}$, whereas the ionic radius of Ti$^+$ is greater than K$^+$. This may be accounted for on the assumption that due to the high polarizability of Ti$^+$ the accessible distance of Ti$^+$-Ti$^+$ is shorter than that of K$^+$-K$^+$, even if the distance between nuclei is slightly greater for the former than for the latter. This feature is schematically shown in Fig. 10. The Ti$^+$-NO$_3^-$ distance is also considered to become shorter owing to the high polarizability than that in a hypothetical case of its lower polarizability. The NO$_3^-$ neighboring to Ti$^+$ more favorably moves away than that neighboring to K$^+$ does. Thus, internal mobility of Ti$^+$ is greater than that of K$^+$. In Fig. 11 the radial distribution functions (15) for molten KNO$_3$ and TiNO$_3$ obtained by X-ray diffraction are shown. Although the peak around 460 pm assignable to Ti$^+$-Ti$^+$ correlation seems to be slightly more distant than that assignable to the sum of K$^+$-K$^+$ and O$^-$-O$^-$ interactions, the former is tailed toward shorter distance than the latter. Further, the assumption that the motion of NO$_3^-$ is vigorous in the systems containing Ti$^+$ may be also supported by the finding that the external transport number of NO$_3^-$ in pure TiNO$_3$ is relatively large (0.69 at 220°C (16)).

Since the ionic radii of Rb$^+$ and Cs$^+$ are greater than that of K$^+$, $u_{Ti}$ is naturally expected to be greater than $u_{Rb}$ or $u_{Cs}$.

In Fig. 12 $u_{Ti}$ as a function of molar volume is shown, as compared with $u_{Rb}$. The $u_{Ti}$ cannot be expressed by such an equation as Eq. (1). The $u_{Ti}$ most positively deviates from $u_{Rb}$ at pure TiNO$_3$. This means that $u_{Ti}$ is a function not only of the molar volume but also of the concentration of Ti$^+$. Figure 10 suggests that NO$_3^-$ neighboring to Ti$^+$ favorably moves away toward another NO$_3^-$.

Internal mobility of M1, $u_{M1}$. As partly shown in Figs. 6, 7 and 8, the internal mobilities of all alkali metal ions and Ag$^+$ deviate positively in the presence of Ti$^+$. In general, upward deviations may be explained in terms of the agitation effect (1). This means that Ti$^+$ has an agitation effect on the internal mobilities of these cations. The reason why Ti$^+$ having a large mass and a relatively large ionic radius has an agitation effect is explained as follows. As explained above by using Fig. 10, the motion of NO$_3^-$ becomes more vigorous, and therefore $u_{M1}$ also becomes large.

Comparison of the behavior of Ag$^+$ and Ti$^+$

It is noteworthy that, while Ag$^+$ and Ti$^+$ have high polarizabilities, these ions have the opposite effects on the internal mobilities of coexisting cations. As
mentioned above, Ag⁺ has a tranquilization effect except for the case of (Li, Ag)NO₃, whereas Tl⁺ has an agitation effect. The ionic radius of Ag⁺ is smaller than that of Tl⁺, and therefore the coulombic interaction of Ag⁺ with NO₃⁻ is considerably stronger than that of Tl⁺ with NO₃⁻. Thus, the motion of NO₃⁻ is restricted, which causes the tranquilization effect on the mobilities of coexisting cations. Whether the restriction involves the rotational motion of NO₃⁻ or not could be examined by comparing the behavior with that in chloride systems.

CONCLUSION

Although Ag⁺ and Tl⁺ have large polarizabilities, these ions have the opposite effects on the internal mobilities of coexisting alkali ions; that is, the tranquilization effect caused by Ag⁺ and the agitation effect by Tl⁺. The tranquilization effect may be caused by the strong attraction of Ag⁺-NO₃⁻ and the agitation effect by the small repulsion of Tl⁺-Tl⁺ and approach of Tl⁺-NO₃⁻ and hence the more active motion of NO₃⁻.

The high polarizabilities of Ag⁺ and Tl⁺ make the internal mobilities of these ions themselves larger than expected for a hypothetical case of lower polarizabilities. However, the mechanism for enhancing uAg and uTl seems to be different in these two cases owing to the difference in the ionic sizes. The high polarizabilities have quite different effects on the internal mobilities of coexisting cations. This difference is also caused by the ionic radii of these ions.

The present explanation needs to be substantiated by molecular dynamics simulation.

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REFERENCES

1. M.Chemla and I.Okada, Electrochim. Acta, 35, 1761(1990).
2. M.Blander, in Molten Salt Chemistry, M.Blander, p. 127, Interscience Pub., New York(1964).
3. A. Klemm, H. Hintenberger and P.Hoernes, Z. Naturforsch., 2a, 245 (1947).
4. K.Klemm, I.Okada and A. Klemm, Z.Naturforsch., 44a, 747(1989).
5. I.Okada and K.Klemm, Z.Naturforsch., 47a, 781(1992).
6. P.Chou, H.Matsura, I.Okada and C.Yang, Z. Naturforsch., 48a, 1207(1993).
7. K.Kawamura, I. Okada and O.Odawara, Z. Naturforsch., 30a, 69 (1975).
8. S.Baluja, J. Habsaki and I.Okada, Z.Naturforsch., 42a, 377 (1987).
9. P.Chou and I.Okada, Z. Naturforsch., in press.
10. P. Chou and I.Okada, Z. Naturforsch., 51a, 197 (1996).
11. R.D.Shannon, Acta Cryst., A32, 751(1976).
12. I. Okada, R. Takagi and K. Kawamura, Z. Naturforsch., 35a, 493(1980).
13. C.Marghentus and C. Sinistri, Z. Naturforsch., 43a, 751(1988).
14. M.P.Tosi and F.G.Fumi, J.Phys.Chem.Solids, 25, 45(1964).
15. H.Öhno, K.Igarashi, N. Umesaki and K. Fujikawa, X-Ray Diffraction Analysis of Ionic Liquids, Trans. Tech. Pub., 1994.
16. I.G.Murgulescu and D. Topor, Z.Physik.Chem.(Leipzig), 221, 39(1962).
Fig. 1. Internal cation mobilities in the molten binary systems (M1, Ag)/NO3. The mole fraction of the nitrate having larger molar volume is taken as the abscissa. It is assumed here that the molar volume of NaNO3 is greater than that of AgNO3.
Fig. 2. Internal cation mobilities in the molten binary systems (Na, Ti)NO₃ at 623 K.
Fig. 3. Three stages for leaving of cation C from the referenced anion A. B is the anion of the same kind with A; C, is a tranquilizer ion.

Fig. 4. The potential felt by Ag⁺ collinearly located between two Cl⁻ ions separated by 600 pm. The dotted line is for a hypothetical case without the dispersion term. The magnitude of the kinetic energy (1/2)kT at T=1000 K is shown for comparison.
Fig. 5. Internal mobilities of $\text{Ag}^+$ in $(\text{Ag, M}_2)\text{NO}_3$ at 623 K as a function of the molar volume. In the inset, $u_{\text{Li}}$'s in $(\text{Li, Ag})\text{NO}_3$ at 603 K are shown, as the data at 623 K are not available. The dashed and solid lines are drawn according to Eq. (1) with the parameters: $A=2.84\times10^{-11}\text{m}^3\text{V}^{-1}\text{s}^{-1}\text{mol}^{-1}$, $V_0=24.7\times10^{-4}\text{m}^3\text{mol}^{-1}$ and $E=17.80\text{ kJ mol}^{-1}$.

Fig. 6. Internal mobilities of $\text{Li}^+$ in $(\text{Li, M}_2)\text{NO}_3$ at 623 K as a function of the molar volume. In the inset, $u_{\text{Li}}$'s in $(\text{Li, Ag})\text{NO}_3$ at 603 K are shown, as the data at 623 K are not available. The dashed and solid lines are drawn according to Eq. (1) with the parameters: $A=2.84\times10^{-11}\text{m}^3\text{V}^{-1}\text{s}^{-1}\text{mol}^{-1}$, $V_0=24.7\times10^{-4}\text{m}^3\text{mol}^{-1}$ and $E=17.80\text{ kJ mol}^{-1}$.
Fig. 7. Internal mobilities of Na\(^+\) in \((\text{Na}, \text{M}_2)\text{NO}_3\) at 623 K as a function of the molar volume. The dashed line is drawn according to Eq. (1) with the parameters: \(A=6.60 \times 10^{-11} \text{m}^2 \text{V}^{-1} \text{s}^{-1} \text{mol}^{-1}\), \(V_s=(43.21-0.028(T/\text{K})) \times 10^{-4} \text{m}^3 \text{mol}^{-1}\), and \(E=21.31 \text{ kJ mol}^{-1}\). (1).

Fig. 8. Internal mobilities of K\(^+\) in \((\text{K}, \text{M}_2)\text{NO}_3\) at 623 K as a function of the molar volume. The dashed line is drawn according to Eq. (1) with the parameters: \(A=3.95 \times 10^{-11} \text{m}^2 \text{V}^{-1} \text{s}^{-1} \text{mol}^{-1}\), \(V_s=22.1 \times 10^{-4} \text{m}^3 \text{mol}^{-1}\), and \(E=18.00 \text{ kJ mol}^{-1}\). (1).
Fig. 9. Potential profile felt by Cl collinearly located between two different cations Li' and Ag'.

![Graph showing potential profile](image)

The shortest accessible distance between two cations:

\[
\text{Tl}^+ - \text{Tl}^+ < \text{K}^+ - \text{Tl}^+ < \text{K}^+ - \text{K}^+
\]

Fig. 10. Schematic representation of separating motion of NO₃⁻ from the referenced Tl' or K' ion.

![Schematic diagram](image)
Fig. 11. X-ray weighted radial distribution functions of KNO$_3$ at 653 K and TINO$_3$ at 503 K (15).

Fig. 12. Internal mobilities of Tl$^+$ in (M, Tl)NO$_3$ as a function of the molar volume as compared with those of Rb$^+$. 

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