

Self-Diffusion of Tl⁺ in Molten Thallium Nitrate

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The self-diffusion coefficient of Tl⁺ in molten TlNO₃ in a temperature range of about 100° above the melting point was measured by the “diffusion-into-the capillary” method. The obtained results are discussed in terms of ionic interactions occurring in TlNO₃ melt.

Fused TlNO₃ is expected to show strong ionic interactions, given the d¹⁰s² structure of the Tl⁺ ion. To elucidate the nature of this interaction, a study of the diffusion coefficient has been undertaken.

The “diffusion-into-the capillary” method¹ was employed. The TlNO₃ used in the experiments was p. a. reagent grade quality (Schuchard, Fisher Scientific Co.), carefully dried and recrystallized twice from fuming nitric acid. A decomposition of the salt was avoided by melting in NO₂ atmosphere. ²⁰⁴Tl radioactive isotope was used as tracer.

The experimental results, obtained in a temperature range of about 100° above the melting point, are listed in Table 1 and displayed in Fig. 1, together with the values quoted in the literature^{2,3}. Only in the 245–290° temperature range there is good agreement between the two sets of data (departure of 5%), while at the lower and higher temperatures the differences reach 10–15%.

Several mathematical functions were tested in order to express the experimental D_{Tl^+} values as a function of temperature. As illustrated in Fig. 2, there is a nonlinear behaviour on both the $\log D_{Tl^+}$ vs. $1/T$ and the $\log D_{Tl^+}$ vs. $1/(T - T_0)$ plot, which proves that neither Arrhenius nor the free volume theory⁴ are acceptable. According to the “*f*” test, the D_{Tl^+} values are best fitted (a standard error of $\pm 0.65 \cdot 10^{-2}$) to the following polynomial equation:

$$D_{Tl^+} = 2.8524 \cdot 10^{-4} - 1.1053 \cdot 10^{-6} T + 1.1099 \cdot 10^{-6} T^2.$$

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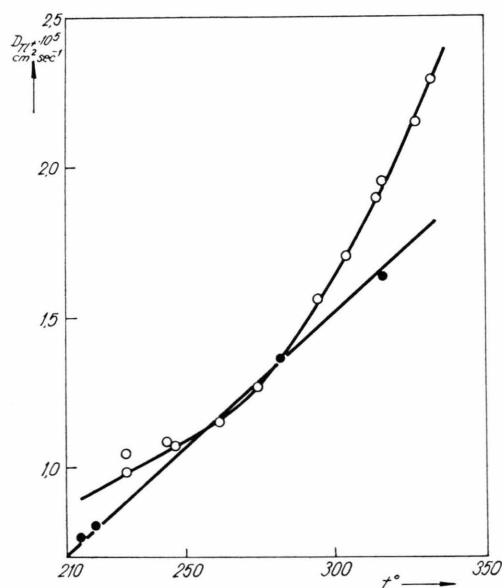


Fig. 1. Self-diffusion coefficient of Tl⁺ in molten TlNO₃. ○ present data; ● literature data^{2,3}.

Qualitatively, the non-Arrhenius behaviour shown in Fig. 2 may be explained in terms of the partially covalent character of the anion-cation bond in fused TlNO₃, already confirmed by spectroscopic data. According to Raman studies^{5–7}, the high values of the relative intensities of the ν_1 mode obtained for TlNO₃ ($I_M^{TlNO_3} = 285$ compared to $I_M^{RbNO_3} = 110$, even if the two nitrates have a similar ionization potential) are due to an anion-cation covalent type interaction involving the “back donation of electrons” from the d orbital of Tl⁺ into the π system of the NO₃[–] ions. Additional support for a π -inter-

Table 1. Self-diffusion coefficients of Tl⁺ in molten TlNO₃.

<i>t</i> °	230	230	244	246	261	274	294	297	304	316	327	332
$D_{Tl^+} \cdot 10^5 \text{ cm}^2 \cdot \text{sec}^{-1}$	1.04	0.98	1.08	1.07	1.15	1.27	1.56	1.53	1.70	1.95	2.15	2.29



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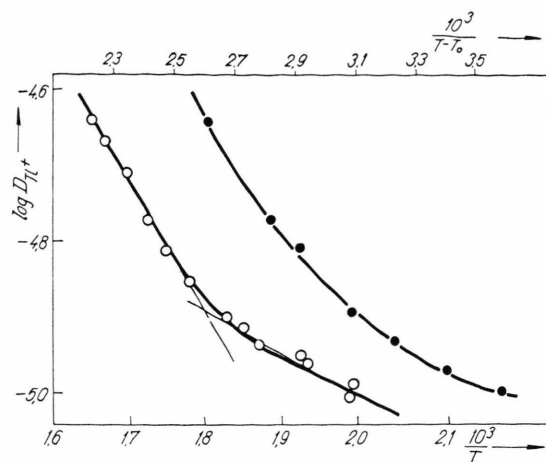


Fig. 2. $\log D_{\text{Tl}^+}$ vs. temperature in molten TlNO_3 .
○ Arrhenius plot; ● $\log D_{\text{Tl}^+}$ vs. $1/(T - T_0)$.

action model of $\text{Tl}^+ \cdot \text{NO}_3^-$ ion pairs is provided by the recent Raman spectra⁸ of TlNO_3 in liquid ammonia. We have calculated the London interaction parameters^{9, 10}:

$$c_{ij} = \frac{3}{2} \frac{\alpha_i \alpha_j I_i I_j}{I_i + I_j}$$

for various monovalent cations, and found out the same differences among TlNO_3 and AlkNO_3 melts ($c_{\text{Tl}-\text{Tl}} = 275.6 \cdot 10^{-60} \text{ erg cm}^6/\text{mol}$ compared to $c_{\text{Rb}-\text{Rb}} = 49.9 \cdot 10^{-60} \text{ erg cm}^6/\text{mol}$). Obviously, in

molten TlNO_3 there is a stronger ion-pair interaction and a more pronounced covalency.

Most probably, with increasing temperature the increase of thermal vibration would make such ionic association less stable. Their dissociation, with the consequent changes, is suggested by the noticeable change of slope observed around 280° on the Arrhenius diffusion plot (Figure 2). It may prove a change in size of the diffusion governing unit on cooling through this temperature. The same is indicated by the interdiffusion coefficient of Tl^+ obtained in molten LiNO_3 ¹¹; it gets closer to that of Rb^+ as the temperature rises, indicating a reduction of the London dispersion interaction contributions with rising temperature.

It is worth mentioning that the Nernst-Einstein (N.E.) equation holds in TlNO_3 melts at higher temperatures, which confirms the ionic character of the melt in the temperature range in question. Thus, if use is made of experimental values of ionic mobilities³: $u_{\text{Tl}^+}^{316} = 3.5 \cdot 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$ and $u_{\text{Tl}^+}^{325} = 3.75 \cdot 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$, in calculating diffusion coefficients, the following values are found: $D_{\text{Tl}^+}^{316} = 1.77 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ and $D_{\text{Tl}^+}^{325} = 1.93 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. They differ by less than 10% from the corresponding experimental values. Unfortunately, no data in the lower temperature range are available, so that nothing can be said, as yet, on the validity of the N.E. equation in that region.

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