Cationic Self-Diffusion in Molten (Tl-Na)NO_3 and (Tl-Rb)NO_3 Systems

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The cationic self-diffusion coefficients in molten $(Tl-Na)NO_3$ and $(Tl-Rb)NO_3$ systems were investigated as a function of temperature and concentration. The obtained data were examined from the viewpoint of polarization and ionic size effects.

Within our study of cationic diffusion coefficients in binary molten nitrates[1], a systematic investigation of the $(Tl-Alk)NO_3$ series was undertaken in order to provide additional information on the nature of the ionic interactions in these mixtures. We report here the results obtained in $(Tl-Na)NO_3$ and $(Tl-Rb)NO_3$.

The experimental set up was similar to the one previously employed[2]. Reagent grade $NaNO_3$ and $RbNO_3$, recrystallized several times from distilled water and dried for 24 h at 140°, were used. Special precautions were taken in preparing and melting $TlNO_3$[3]. The mixtures were made up by weight from previously melted components. ^{24}Na, ^{86}Rb, and ^{204}Tl isotopes were used as tracers.

Table 1. Cationic self-diffusion coefficients in molten $(Tl-Na)NO_3$ mixtures.

x_{TlNO_3}	$t°$	$D_{Tl^+} \cdot 10^5$ $cm^2 \cdot sec^{-1}$	x_{NaNO_3}	$t°$	$D_{Na^+} \cdot 10^5$ $cm^2 \cdot sec^{-1}$
0.70	266	1.12 ± 0.01	0.75	319	1.72 ± 0.01
	276	1.21 ± 0.01		347	2.00 ± 0.02
	282	1.30 ± 0.02		359	2.10 ± 0.01
	287	1.33 ± 0.02		389	2.75 ± 0.02
	300	1.45 ± 0.01			
0.50	263	1.08 ± 0.03	0.50	263	0.96 ± 0.03
	276	1.16 ± 0.01		285	1.17 ± 0.04
	280	1.17 ± 0.01		291	1.19 ± 0.01
	299	1.43 ± 0.02		304	1.31 ± 0.01
	317	1.58 ± 0.03		325	1.53 ± 0.04
	323	1.93 ± 0.05			
0.30	290	1.17 ± 0.01	0.25	271	1.15 ± 0.01
	292	1.14 ± 0.03		293	1.35 ± 0.04
	312	1.38 ± 0.01		309	1.53 ± 0.02
	318	1.48 ± 0.01		321	1.66 ± 0.03
	328	1.66 ± 0.04		324	1.69 ± 0.02
0.10	315	1.38 ± 0.04	0.05	257	1.12 ± 0.01
	326	1.43 ± 0.05		272	1.24 ± 0.01
	335	1.62 ± 0.02		279	1.32 ± 0.01
	360	1.83 ± 0.02		290	1.46 ± 0.01
	368	1.91 ± 0.02		305	1.66 ± 0.02

Table 2. Cationic self-diffusion coefficients in molten $(Tl-Rb)NO_3$ mixtures.

x_{TlNO_3}	$t°$	$D_{Tl^+} \cdot 10^5$ $cm^2 \cdot sec^{-1}$	x_{RbNO_3}	$t°$	$D_{Rb^+} \cdot 10^5$ $cm^2 \cdot sec^{-1}$
0.75	251	0.86 ± 0.01	0.75	325	1.47 ± 0.05
	263	0.94 ± 0.02		335	1.59 ± 0.05
	274	1.09 ± 0.02		355	1.87 ± 0.03
	285	1.24 ± 0.01			
	347	2.00 ± 0.05			
0.50	266	0.91 ± 0.01	0.50	288	1.17 ± 0.05
	290	1.18 ± 0.02		295	1.27 ± 0.02
	296	1.24 ± 0.01		313	1.45 ± 0.04
	332	1.69 ± 0.01		340	1.79 ± 0.01
	355	1.93 ± 0.02		350	1.95 ± 0.05
0.25	282	0.93 ± 0.02	0.25	270	1.22 ± 0.02
	290	1.07 ± 0.03		321	1.68 ± 0.03
	317	1.37 ± 0.01		380	2.38 ± 0.02
	344	1.63 ± 0.04			
	358	1.87 ± 0.03			
0.05	319	1.23 ± 0.04	0.05	263	1.30 ± 0.02
	327	1.30 ± 0.02		309	1.69 ± 0.01
	346	1.56 ± 0.01		325	1.91 ± 0.02
	374	1.91 ± 0.04		344	2.15 ± 0.02
	378	1.98 ± 0.04			

For each system, the self-diffusion coefficients of both cations were measured as a function of temperature in the whole concentration range from pure $TlNO_3$ to pure alkali nitrate. The results obtained are summarized in Tables 1 and 2. Figures 1 and 2 show the diffusion isotherms at 320° for $(Tl-Na)NO_3$ and $(Tl-Rb)NO_3$, respectively. The values of the self-diffusion coefficients of the Na^+, Rb^+ and Tl^+ ions in the corresponding pure nitrates were taken from our previous papers[2, 3].

A comparison with literature data is possible for the $(Tl-Na)NO_3$ system whose cationic tracer diffusion coefficients were reported[4] for the whole concentration range at 316° and for the range $0 \leqq x_{NaNO_3} \leqq 0.3$ at 219°. Whereas the present data show systematic negative deviations from linearity with minima at $x_{TlNO_3} = 0.5$ of the D_{Na^+} iso-

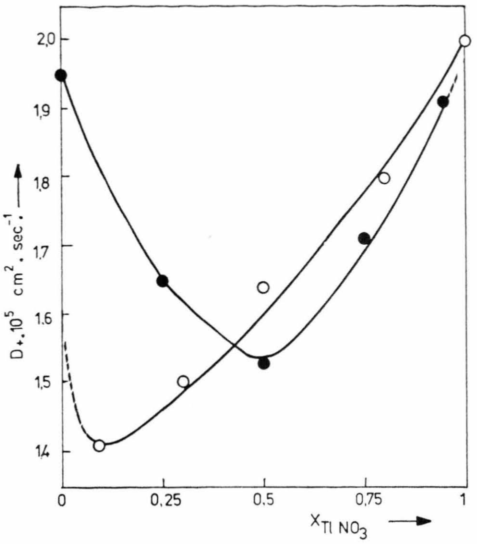

Fig. 1. Cationic diffusion isotherms in (Tl—Na) NO_3 system at 320°. ○ D_{Tl^+}; ● D_{Na^+}.

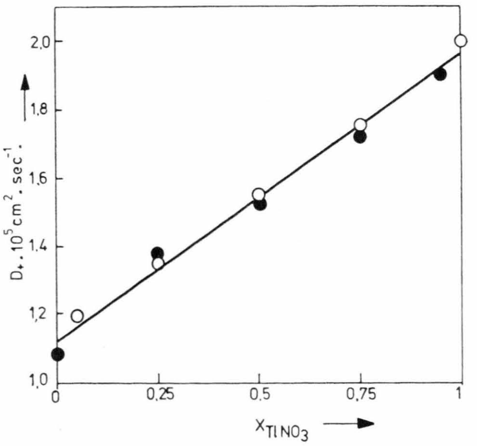

Fig. 2. Cationic diffusion isotherms in (Tl—Rb) NO_3 system at 320°. ○ D_{Tl^+}; ● D_{Rb^+}.

therm, and at $x_{TlNO_3}=0.1$ of the D_{Tl^+} isotherm (Fig. 1), a smooth dependence on concentration with both cationic tracer diffusion coefficient isotherms showing small positive deviations from linearity is indicated by Forcheri and Wagner[4]. The percentage differences between the two series of data are very high, reaching ~30% for D_{Na^+} and ~20% for D_{Tl^+}. We find it difficult to explain these discrepancies, more so as at the temperature in question (316°) both self-diffusion coefficients in the pure nitrates are in reasonable agreement (~5%). The present data should be more reliable since, as will be shown in the following, they agree better with other data on the transport properties of (Tl — Na) NO_3 mixtures.

In the (Tl — Rb) NO_3 system (cf. Fig. 2) the additivity is fulfilled within the experimental errors for both cations.

Lumsden's model of anionic polarization[5] offers a satisfactory explanation for the different behaviour of the two systems: In the (Tl — Rb) NO_3 system the polarizing strengths of the two cations (Z/r^2) are similar due to their similar size (the Pauling radii are respectively $r_{Tl^+}=1.40$ Å and $r_{Rb^+}=1.48$ Å). Correspondingly, the mixtures behave quasi-ideally, as do the electrical conductance isotherms[6]. Moreover, the Tl^+ and Rb^+ ions have practically equal ionic mobilities in aqueous solutions at infinite dilution[7] and the lattice energy of the corresponding solid nitrates differs only by 5%[8]. The size of the Na^+ ion, however, is very different from that of Tl^+ ($r_{Na^+}=0.95$ Å), and consequently a polarization of the common anion occurs in the (Tl — Na) NO_3 system, causing an increased hindrance of relative anion-cation motion, which explains the negative deviations from linearity shown in Figure 1. Moreover, according to Raman spectra evidence[9—11] in molten $TlNO_3$ the "back-donation of electrons from cation into the π system of the NO_3^- ions, results in a N — O bond of lower bond order, more easily distorted while the π nature of electrons makes them easily polarized". Given the high polarizing strength of the Na^+ ion, by adding $NaNO_3$ into the $TlNO_3$ melt, one may assume the formation of some ionic agglomerates with Na^+ lying in the second coordination sphere, which accounts for the similar values, within experimental errors, of D_{Tl^+} and D_{Na^+} in the $TlNO_3$ rich melt (up to $x_{TlNO_3}=0.5$ as seen in Figure 1). On further addition of $NaNO_3$, the above phenomenon is evidently reduced, which promotes the freedom of the Na^+ ions and the observed increase of D_{Na^+}, rising from the equimolecular mixture to the pure $NaNO_3$ melt.

Additional support for the hypothesis advanced is provided by electrical conductance and ionic mobility data[4]. Thus, within the range $1 \geqq x_{TlNO_3} \geqq 0.5$, the u_{Tl^+} and u_{Na^+} values are equal and electrical conductance does not differ from the value observed in the pure $TlNO_3$ melt. In the $NaNO_3$ rich region, both the electrical conductance and u_{Na^+} increase in a manner which is similar to that of the diffusion coefficient.

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