Self-Diffusion Coefficients in Molten $AgNO_3$-$NaNO_3$ and $AgNO_3$-KNO_3 Mixtures

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The self-diffusion coefficients of the constituent cations in the systems (Ag-Na)NO_3 and (Ag-K)NO_3 have been investigated by the "diffusion-into-the capillary" method at three concentrations (x_{AgNO_3} = 0.25; 0.50; 0.75) and at temperatures ranging from 250 to 400°. A temperature dependence given by the Arrhenius equation and an almost linear variation with composition were observed. The correlation existing between the ionic size of diffusing cations and the diffusion coefficients in these melts is discussed.

Self-diffusion coefficients in binary molten salt systems have been very little investigated so far. Several data refer to the binary alkali nitrate systems [1–3], the other binary molten salt mixtures having been scarcely investigated [4–7]. This lack of data is largely due to the experimental difficulties met with the self-diffusion coefficient measuerments. As a part of the program for studying the transport properties of binary molten nitrate systems [8–11], we started a systematic investagation of self-diffusion coefficients in silver nitrate – alkali nitrate systems for which no data are available in the literature. With this investigations we aim not only at supplying the data which are missing but hope to examine how ionic parameters of the diffusing species such as size and polarizability, affect the diffusion coefficient in these mixtures.

Presently we report the results concerning the self-diffusion coefficients of the constituent cations in (Ag-Na)NO_3 and (Ag-K)NO_3 mixtures, as a function of concentration and temperature.

Experimental and Results

The "diffusion-into-the capillary" method was used for self-diffusion coefficient measurements. The experimental set up and details concerning the operation were described elsewhere [11]. The alkali nitrates and silver nitrate were the same reagent grade quality as the salts used in our earlier work [11]. The same radioactive isotopes, i. e. $^{24}Na^+$, $^{42}K^+$ and $^{110}Ag^+$ were used as tracers.

The obtained results for the (Ag-Na)NO_3 and (Ag-K)NO_3 mixtures are listed in Tables 1. and 2.

Table 1.
Self-difusison coefficients of Ag^+ and Na+ in molten (Ag-Na)NO_3.

mole % $AgNO_3$	T °C	$D_{Ag^+} \cdot 10^5$ $cm^2 sec^{-1}$	T °C	$D_{Na^+} \cdot 10^5$ $cm^2 sec^{-1}$
75	303	1.84 ± 0.01	316	2.04 ± 0.04
	329	2.14 ± 0.02	338	2.32 ± 0.03
	337	2.32 ± 0.02	347	2.44 ± 0.04
	339	2.33 ± 0.04	353	2.44 ± 0.05
	360	2.57 ± 0.05	362	2.49 ± 0.03
50	309	1.94 ± 0.06	294	1.69 ± 0.01
	327	2.12 ± 0.04	299	1.85 ± 0.01
	346	2.31 ± 0.08	330	2.26 ± 0.04
	363	2.50 ± 0.07	342	2.34 ± 0.04
	378	2.79 ± 0.10	362	2.60 ± 0.01
25	309	1.98 ± 0.03	326	2.09 ± 0.06
	336	2.16 ± 0.04	319	2.01 ± 0.03
	346	2.25 ± 0.07	342	2.21 ± 0.04
	356	2.37 ± 0.05	355	2.42 ± 0.02
	376	2.77 ± 0.06	371	2.66 ± 0.09

The temperature dependence of self-diffusion coefficients in all studied mixtures is well decribed by the simple Arrhenius equation

$$D_+ = D_0 \exp\{-E_{D^+}/RT\}.$$

The experimental data have been fitted to the linear dependence of log D_+ vs. $1/T$ by means of the least

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squares calculation. Any small nonlinear dependence, if present, could not be distinguished due to the experimental errors. The obtained pre-exponental factors, D_0, and activation energies of diffusion E_{D^+}, as functions of composition are given in Table 3 along with the standard deviations. The data for single $AgNO_3$, $NaNO_3$ and KNO_3 in Table 3 were taken from our previous paper on self-diffusion coefficients in molten nitrates [11]. As far as we know, a systematic investigation of cationic self-diffusion coefficients in silver nitrate-alkali nitrate systems has not been published elsewhere. The only available data refer to the self-diffusion coefficients of Ag^+ in $(Ag\text{-}K)NO_3$ measured by the porous frit technique [12] over the composition range 50–75 mole % $AgNO_3$, between 180–240°.

Table 2. Self-difussion coefficients of Ag^+ and K^+ in molten $(Ag\text{-}K)NO_3$.

Mole % $AgNO_3$	T °C	$D_{Ag^+} \cdot 10^5$ cm²sec⁻¹	T °C	$D_{K^+} \cdot 10^5$ cm²sec⁻¹
75	292	1.64 ± 0.04	315	1.66 ± 0.01
	320	1.91 ± 0.03	321	1.82 ± 0.03
	338	2.13 ± 0.07	336	1.98 ± 0.03
	342	2.27 ± 0.01	342	2.03 ± 0.02
	358	2.57 ± 0.07	373	2.52 ± 0.05
50	283	1.17 ± 0.02	291	1.17 ± 0.05
	310	1.59 ± 0.03	313	1.44 ± 0.03
	322	1.54 ± 0.04	334	1.67 ± 0.04
	349	1.88 ± 0.05	356	1.90 ± 0.07
	362	2.27 ± 0.05	365	2.12 ± 0.05
	379	2.62 ± 0.08		
25	323	1.31 ± 0.06	315	1.29 ± 0.02
	330	1.38 ± 0.02	328	1.45 ± 0.03
	346	1.61 ± 0.03	341	1.56 ± 0.01
	361	1.81 ± 0.05	348	1.70 ± 0.02
	369	1.90 ± 0.08	364	1.90 ± 0.01

A comparison with Sjöblom's data [12] was made at the compositions $x_{AgNO_3} = 0.5$ and 0.75 at the two temperatures this author has worked at, namely 180° and 230°. For this purpose we used the data in Table 3, assuming their validity beyond our experimental temperature range. In view of the uncertainty of this extrapolation the obtained data are informative only. They were in both mixtures, lower than those given by Sjöblom. The agreement is better at 180° where the difference is about 10 %, but it exceeds 50 % at 230°. This large dicrepancy may be attributed to a slight decomposition of molten $AgNO_3$. We observed in our experiments that any decomposition of $AgNO_3$ strongly influences the obtained diffusion coefficient, leading to higher values for it. Therefore. some precautions were taken in preparing and melting pure $AgNO_3$ and its mixtures with alkali nitrates, in order to avoid any decomposition.

Discussions

The self-diffusion coefficients of the cations at 350° calculated by means of the data in Table 3, are plotted versus composition in Figure 1.

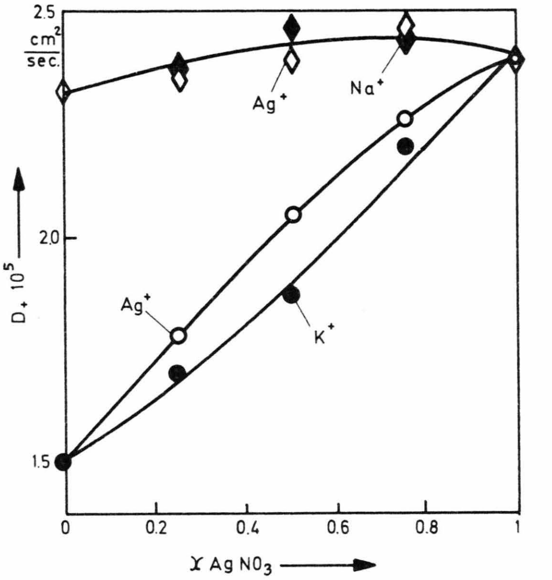

Fig. 1. Self-diffusion coefficients of the cations as a function of composition in $(Ag\text{-}Na)NO_3$ and $(Ag\text{-}K)NO_3$ at 350 °C.

Table 3. Pre-exponential factor and activation energy of diffusion coefficients in $(Ag\text{-}Na)NO_3$ and $(Ag\text{-}K)NO_3$.

mole % $AgNO_3$	$(Ag-Na)NO_3$				$(Ag-K)NO_3$			
	$D_0^{Ag^+} \cdot 10^3$ cm²sec⁻¹	$E_D^{Ag^+}$ cal/mol	$D_0^{Na^+} \cdot 10^3$ cm²sec⁻¹	$E_D^{Na^+}$ cal/mol	$D_0^{Ag^+} \cdot 10^3$ cm²sec⁻¹	$E_D^{Ag^+}$ cal/mol	$D_0^{K^+} \cdot 10^3$ cm²sec⁻¹	$E_D^{K^+}$ cal/mol
100	0.47 ± 0.02	3680 ± 80	—	—	0.47 ± 0.02	3680 ± 80	—	—
75	0.84 ± 0.14	4374 ± 180	0.52 ± 0.02	3793 ± 189	1.11 ± 0.04	4757 ± 390	1.44 ± 0.46	4795 ± 440
50	0.64 ± 0.12	4097 ± 185	0.82 ± 0.20	4234 ± 269	1.99 ± 0.09	5660 ± 460	1.55 ± 0.42	5465 ± 375
25	0.44 ± 0.20	3824 ± 255	0.62 ± 0.10	4048 ± 184	2.72 ± 0.33	6324 ± 140	1.98 ± 0.36	5885 ± 205
0	—	—	1.129 ± 0.04	4347 ± 223	—	—	1.48 ± 0.19	5674 ± 178

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In Figure 2, the dependence of the self-diffusion of Ag^+ on composition is completed by adding, at the mole fraction $x_{AgNO_3} \simeq 0$, the interdiffusion coefficient as quoted in the literature [13, 14]. Figure 2 clearly shows that with increasing concentration of silver nitrate no changes occur in $(Ag\text{-}Na)NO_3$ mixtures, while in $(Ag\text{-}K)NO_3$ mixtures D_{Ag^+} first sharply decreases up to 25 mole % $AgNO_3$, and than increases upon further addition of $AgNO_3$. It is further noteworthy that the E_{D^+} vs. x plot in this system indicates (Figure 3) that there might be a maximum in the region where the minimum is observed on the D_{Ag^+} vs. x curve. Both these facts suggest a certain hindrance of the diffusion of the Ag^+ ions occuring when $AgNO_3$ is added to a KNO_3 melt. According to the current view [15], due to the different size and (induced) polarizability of the two cations in the melts, some changes in the cation-anion energy take place, on mixing.

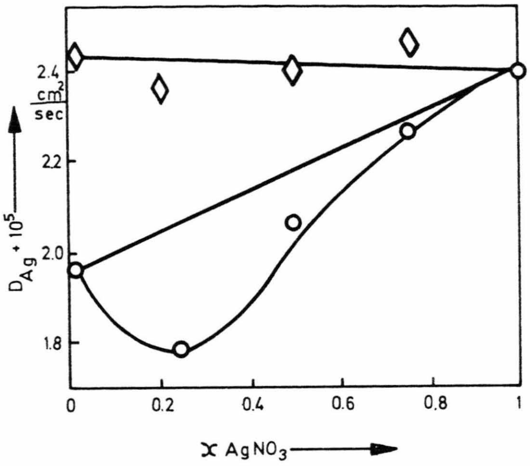

Fig. 2. Diffusion coefficient of Ag^+ vs. composition at 350 °C. ◇ $(Ag\text{-}Na)NO_3$; ○ $(Ag\text{-}K)NO_3$

As far as the $(Ag\text{-}Na)NO_3$ system is concerned, the E_{D^+} values vary practically linearly with the composition (Figure 3). We consider that the data in Figs. 1, 2 and 3 fully illustrate the marked resemblence of Ag^+ and Na^+ ions with respect to their diffusion coefficients. As for the electrical conductivity [16–18], viscosity [9] and thermodynamic properties [19], additivity is fulfilled for the tracer diffusion isotherms. For transport numbers also Duke *et al.* [20] found a linear dependence on the mole fraction, but more recently Richter and Amkreutz [21] have claimed, on the basis of their transport number by EMF measurements that the $(Ag\text{-}Na)NO_3$ system does not meet the requirements of an idealized melt and that the linearity of λ is only a consequence of a compensation effect. Our data on diffusion support rather the ideal behaviour of the $(Ag\text{-}Na)NO_3$ system.

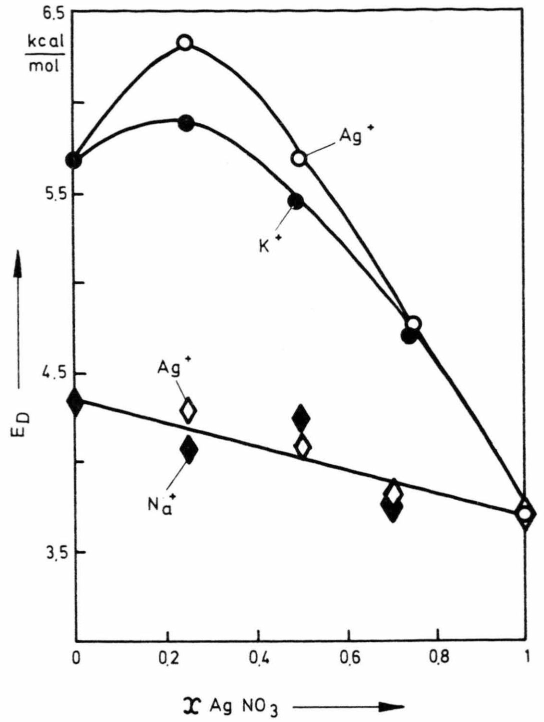

Fig. 3. Activation energy of diffusion coefficients in $(Ag\text{-}Na)NO_3$ and $(Ag\text{-}K)NO_3$ systems.

In concluding, it seems of interest to recall some interdependence between D_{Ag^+} and the size of the cations in the melt.

In order to get a more general picture we shall also refer in the following to the data regarding D_{Ag^+} in $(Ag\text{-}Rb)NO_3$ and $(Ag\text{-}Cs)NO_3$ for wich we are presently measuring the self-diffusion coefficients of both cations as a function of temperature and composition. For the moment references are made to the equimolecular mixtures only.

We have ascertained that

a) within experimental error, a linear correlation can be established between D_{Ag^+} and the difference of the cationic radii in the $(Ag\text{-}Alk)NO_3$

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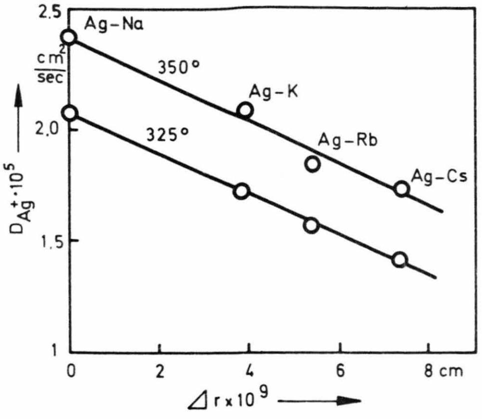

Fig. 4. Dependence of the self-diffusion coefficient of Ag^+ on the (r_1-r_2) difference.

mixtures. Figure 4 illustrates the data for equimolecular mixtures at two different temperatures;

b) the $D_{Ag^+} \cdot \eta/T$ parameter (where η is the viscosity of the mixture [9]) varies linearly with the reciprocal of the alkali cation radius. The same is true for the $D_{Ag^+}\, r_{Ag^+}/T$ parameter, as can be seen in Figure 5.

It is obvious from Figs. 4 and 5 that the length parameter is reflected in the diffusion coefficients in the (Ag-Alk)NO_3 systems. As already stated, work on these systems is in progress and a quantitative correlation will be attempted as soon as more experimental data are available.

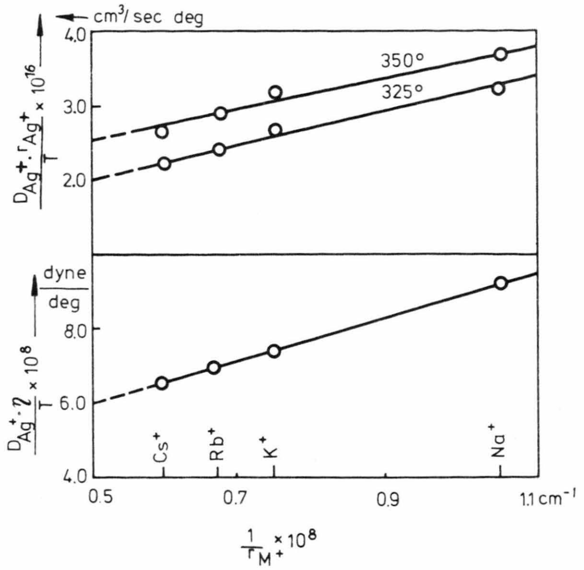

Fig. 5. Dependence of $D_{Ag^+} \cdot \eta/T$ and $D_{Ag^+}\, r_{Ag^+}/T$ on $1/r_{M^+}$ in molten equimolecular silver nitratealkali nitrate mixtures.

Adsorptionswärmen und Mischadsorptionswärmen von Stickstoff und Wasserstoff an einem Ammoniakkatalysator

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Heats of adsorption and heats of simultaneous adsorption of N_2 and H_2 on a ammonia catalyst

Heats of adsorption of H_2 and some H_2-N_2 mixtures have been determined on a reduced industrial iron catalyst in the range from 0,1 to 350 Torr at 35 °C by use of a Microcalorimeter "Calvet".

It is found that the heats of adsorption of the mixtures are 2–4 kcal/Mol higher than those of H_2 and it is concluded that the formation of surface complexes is responsible for this result.

Einleitung

Bei der Betrachtung der Adsorptionsmechanismen der Ammoniaksynthese gewinnt die Bildung von Adsorptionskomplexen unter Beteiligung von molekularem Stickstoff in den letzten Jahren ständig an Bedeutung.

Shvachko und Mitarb. [1] kamen durch Sekundär-

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